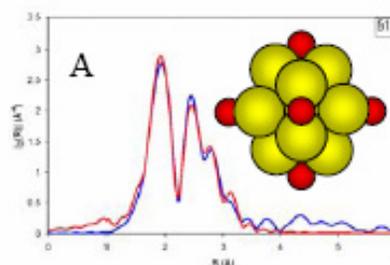
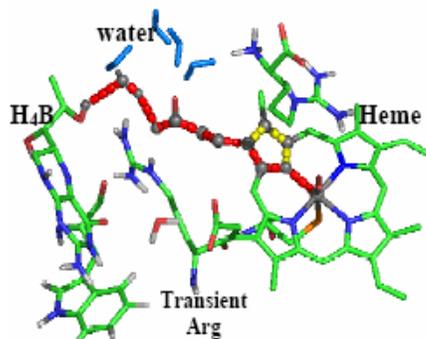
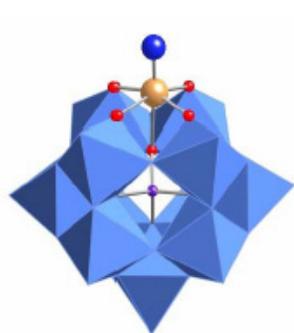
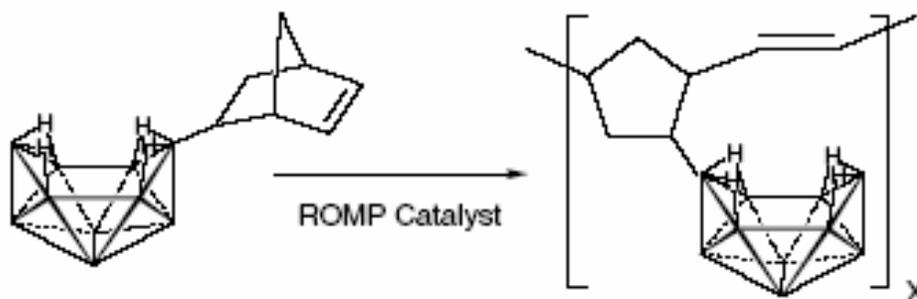
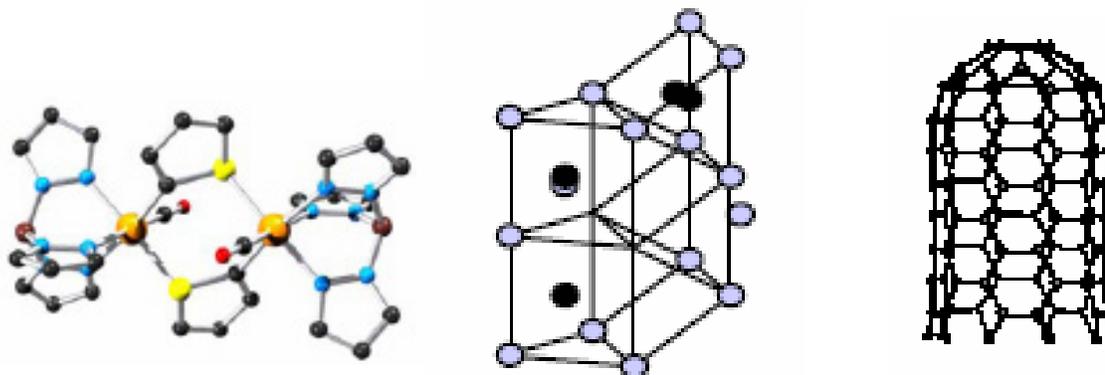


Frontiers in
CATALYSIS SCIENCE



Meeting of the Catalysis and Chemical Transformations Program
Chemical Sciences, Geosciences and Biosciences Division
Office of Basic Energy Sciences, U.S. Department of Energy
Rockville, MD **May 23-26, 2004**

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FOREWORD

This meeting of the Catalysis and Chemical Transformations Program is sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (OBES), U.S. Department of Energy. It is being held on May 23-26, 2004, at the Doubletree Hotel, Rockville, MD.

The purposes of this meeting are three-fold:

- to give participants an appreciation of the broad range of research topics currently supported by our program under the umbrella of catalysis and related sciences;
- to foster exchange of ideas and cooperation among participants;
- to discuss the exciting new opportunities for catalysis science, both at its core and at its interfaces with other disciplines, including materials science, biosciences, theory and simulation, instrumentation and analytical science.

Catalysis activities within OBES emphasize fundamental research aimed at understanding and controlling the chemical reactivity of fluid and condensed matter. The long-term goal of this research is to discover the natural laws and generalizations that enable the prediction of structure-reactivity relations. Such knowledge, together with our ability to synthesize complex structures, will help us to guide chemical reactions along desired pathways. Ultimately, these fundamental concepts will help promote efficient conversion of natural and synthetic resources, with minimum impact to our environment.

Special thanks go to our guest keynote speakers, who will expose us to recent advances in fields that lie both at the core of catalysis and at its boundaries with other multidisciplinary fields. The poster sessions have been designed to allow everyone to present their recent scientific outcomes, and to share ideas and opinions. The breakout sessions will permit participants to discuss the future prospects for these lively sciences.

The breakout aspect of this meeting was kindly organized by Drs. Bob Bergman, John Bercaw, Tom Rauchfuss, Dave Dixon, Eric McFarland, Daniel Resasco, Juergen Eckert and Miquel Salmeron, and we deeply appreciate their tremendous effort. We also thank the Oak Ridge Institute of Science and Education staff, Ms. Julie Malicoat in particular, for the logistical support and the compilation of this volume. We are indebted to the program participants, as you have worked hard to produce oral and poster presentations; to the session moderators, and to the rest of attendees, for their contributions.

Have a productive, highly interactive, and stimulating meeting.

John Gordon and Raul Miranda
Chemical Sciences, Geosciences and Biosciences Division
U.S. DOE – BES

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Meeting Agenda

2004 Catalysis Contractors' Workshop

Rockville, MD
May 23-26, 2004
(by invitation only)

Tentative Agenda

Day 1: May 23, 2004

5:00 p.m. Regency Room open and available for poster setup

Approximately

6:00 p.m. Dinner

Session A. **Posters I** (numbers 1-60)

8:00-10:00 p.m. **Poster Opening Session**

Day 2: May 24, 2004

8:00 a.m. COFFEE

8:30 **Workshop Overview**

Session B. **Focus on Materials**

Moderator: **Tom Rauchfuss**

9:00-10:00 **Invited Speaker- FRAZER STODDART (UCLA)**

10:00-10:20 COFFEE

10:20-10:40 **Larry Sita** (U. Maryland, College Park)

10:40-11:00 **Jeff Long** (UC Berkeley)

11:00-11:20 **Jeff Brinker** (Sandia N.L. – U. New Mexico)

11:20-11:40 **Larry Scott** (Boston College)

11:40-12:00 Discussion

12:00 LUNCH
CCT Performance

Session C. **Focus on Heterogeneous Catalysis and Surface Chemistry**

Moderator: **Jan Hrbek**

1:30-2:30 **INVITED Speaker- ROBERT SCHLÖGL (Fritz-Haber Institut)**
*The Impact of In-situ Analysis of Heterogeneous Catalysts for the
Improvement of Their Function*

2:30 -2:50 COFFEE

2:50-3:10 **Jim Dumesic** (Wisconsin)

3:10-3:30 **Eric Altman** (Yale)

3:30-3:50 **Jose Rodriguez** (BNL)

3:50-4:10 **Chris Jones** (Georgia Tech)

4:10-4:30 Discussion

4:30-6:00 Poster exchange: take down numbers 1-60; put up numbers 61-120

6:00 Dinner

**INVITED Speaker – MICHELLE BUCHANAN (Oak Ridge
National Laboratory)**

*The Hydrogen Economy: Opportunities for Fundamental Research to
Address some Grand Challenges*

8:00-10:00 p.m. Session A. **Posters II** (numbers 61-120)

Day 3: May 25, 2004

8:00 a.m. COFFEE

Session D. **Focus on Homogeneous Catalysis**

Moderator: **John Bercaw**

8:30-9:30 **INVITED Speaker- GEOFF COATES (Cornell University)**
*Discovery, Development, and Application of Catalysts for the
Synthesis of Defined Polymer Architectures*

9:30-9:50 **Ged Parkin** (Columbia)

9:50-10:10 **John Hartwig** (Yale)

10:10-10:30 **Susannah Scott** (UC Santa Barbara)

10:30-10:50 Discussion

10:50-11:00 COFFEE

Session E. **Focus on Biocatalysis**

Moderator : **Ged Parkin**

11:00-11:20 **Matt Kanan and David Liu (Harvard) – Invited Short Presentation**
A New Approach to the Discovery of Bond Forming Chemical Reactions

11:20-11:40 **Larry Que** (Minnesota)

11:40-12:00 Discussion

12:00-12:50 LUNCH

12:50-1:50 **INVITED Speaker- HOWARD TURNER (SYMYX)**

2:00-5:30 Breakout Sessions

Moderators: **Bob Bergman, John Bercaw, Dave Dixon, Dan Resasco, Eric McFarland, Tom Rauchfuss, Miguel Salmeron, Juergen Eckert**

6:00 Posters down

6:30 DINNER

INVITED Speaker – RICHARD CATLOW (University College London)
Computer Modelling as a Tool in Catalytic Science

8:00 Evening free to general participants. Moderators write up conclusions and recommendations.

Day 4: May 26, 2004

8:00 a.m. COFFEE

Session F. **Focus on Instrumentation, Theory and Simulation**

Moderator: **Dave Dixon**

8:30-8:50 **Mike Deem** (Rice University)

8:50-9:10 **Manos Mavrikakis** (U. Wisconsin)

9:10-9:30 **Miquel Salmeron** (L. Berkeley National Lab.)

9:30-9:50 **Ralph Nuzzo** (U. Illinois)

9:50-10:10 Discussion

10:10-10:30 COFFEE

10:30 Summary and Discussion from Breakouts A-D

12:00 Working Lunch

Conclusions

Recommendations for Future Workshops

2:00 End of Meeting

Invited Presentation Abstracts

The Impact of In-situ Analysis of Heterogeneous Catalysts for the Improvement of Their Function

Robert Schlögl

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Department of Inorganic Chemistry
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The in-situ analysis of working heterogeneous catalysts has been requested since a long time in the catalysis literature and appears on all strategy planning. It is the inherent complexity of the experiment and the resource-intensive operation of in-situ experiments that still limits the broad application of in-situ techniques both in academia and in industry. A key requirement for efficient operation would be a suitable access to synchrotron radiation facilities with dedicated experiments that form a group of experiments most useful for a large number of catalytic systems.

The contribution will use case studies of molybdate- and vanadate-based catalysts to elucidate the usefulness of in situ studies. This usefulness first is grounded in the access to an understanding of the material science and nanochemistry of such working systems. From there we derive lead ideas for reducing the chemical complexity of novel systems. We identify bottlenecks in our current synthesis strategy for oxide catalysts that are inadequate to obtain the optimal function from materials with a given chemical composition.

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The Hydrogen Economy: Opportunities for Fundamental Research to Address some Grand Challenges

Michelle V. Buchanan
Chemical Sciences Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Abstract

One of the Grand Challenges of the 21st Century is to achieve a sustainable energy supply. The 20th Century has seen remarkable advances in science and technology, resulting in expectations for a higher standard of living. This has required large increases in per capita energy. Projections of per capita energy needs for the 21st Century indicate that new technologies for sustainable energy production, storage, and use will need to be developed in the next 50 years. The so-called hydrogen economy is one such proposal that is presently being considered worldwide and was highlighted in President Bush's 2003 State of the Union Address. In this presentation the requirements of a hydrogen economy will be discussed in the context of the recent DOE report on "Basic Research Needs for the Hydrogen Economy". Hydrogen production, storage and utilization will be discussed with emphasis given to the large gap between present science/technology know-how and the requirements in efficiency/cost for a sustainable hydrogen economy. Opportunities for fundamental research in chemistry and materials to narrow this gap will be discussed.

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DISCOVERY, DEVELOPMENT, AND APPLICATION OF CATALYSTS FOR THE SYNTHESIS OF DEFINED POLYMER ARCHITECTURES, Geoffrey W. Coates, Department of Chemistry and Chemical Biology, Cornell University, Baker Laboratory, Ithaca, New York 14853, gc39@cornell.edu

Single-site polymerization catalysts are molecular complexes with the general formula L_nMR , where L_n is an organic ligand set that remains bound to and thus modifies the reactivity of the active metal center (M) during the entire chemical reaction, and R is an initiating group. By tailoring the coordination environment of the metal center, single-site catalysts are now available that can control the molecular weight, molecular weight distribution, comonomer incorporation, and both the relative and absolute stereochemistry of a polymer in a way that is often not possible using conventional heterogeneous catalysts. The discovery, optimization, and application of several single-site catalysts for the synthesis of polyesters, polyolefins, and polycarbonates will be presented.

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COMPUTER MODELLING AS A TOOL IN CATALYTIC SCIENCE

Richard Catlow

*Davy Faraday Laboratory of The Royal Institution, 21 Albemarle Street,
London, W1S 4BS, UK
Chemistry Department, University College London, WC1E 6BT, UK*

Computer modelling techniques are now well established in the study of catalysis at the molecular level, where they are able to provide increasingly accurate and reliable information on active site structures, reaction mechanisms and on the transport of reactants and products to and from the active site. This talk will attempt to review some recent developments in the field by focussing on a number of topical applications, concerning:

- i) The mechanisms of epoxidation in metal substituted microporous catalysts, where we will show how joint computational / experimental studies have developed detailed models for active site structures and epoxidation mechanisms.
- ii) The mechanisms of methanol synthesis on the surface of ZnO, where we concentrate on the identification of intermediates in this key reaction.
- iii) Reactions of small molecules on metal surfaces, where the focus is the identification of transition states of elementary reactions.

The lecture will consider some of the likely future directions in the field.

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Presentation and Poster Abstracts

Metal Segregated Cluster Complexes: Organometallic Models for Bimetallic Synergism and Interface Reactivity

Postdoc: Burjor Captain

Students: Jack Smith, Jr., Wei Fu, Lei Zhu

Department of Chemistry and Biochemistry, University of South Carolina
Columbia, SC 29208

Email: Adams@mail.chem.sc.edu

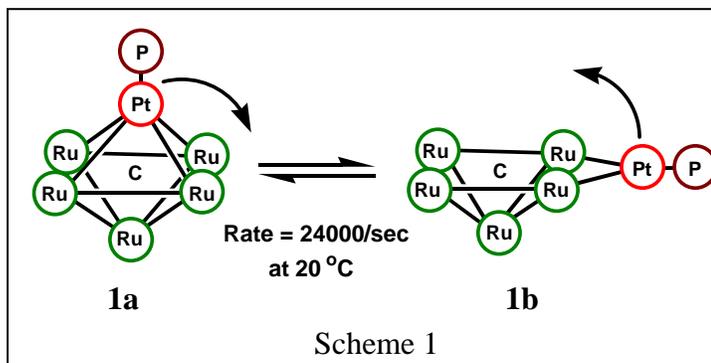
Goals

To investigate the synthesis and physical and chemical properties of bimetallic cluster complexes containing palladium and platinum. To study their catalytic properties under homogeneous conditions and to determine the mechanisms of the catalysis in order to identify the factors that produce that synergistic effects in catalysis that arise because of cooperativity involving the different types of metal atoms.

Significant Recent Achievements and Results

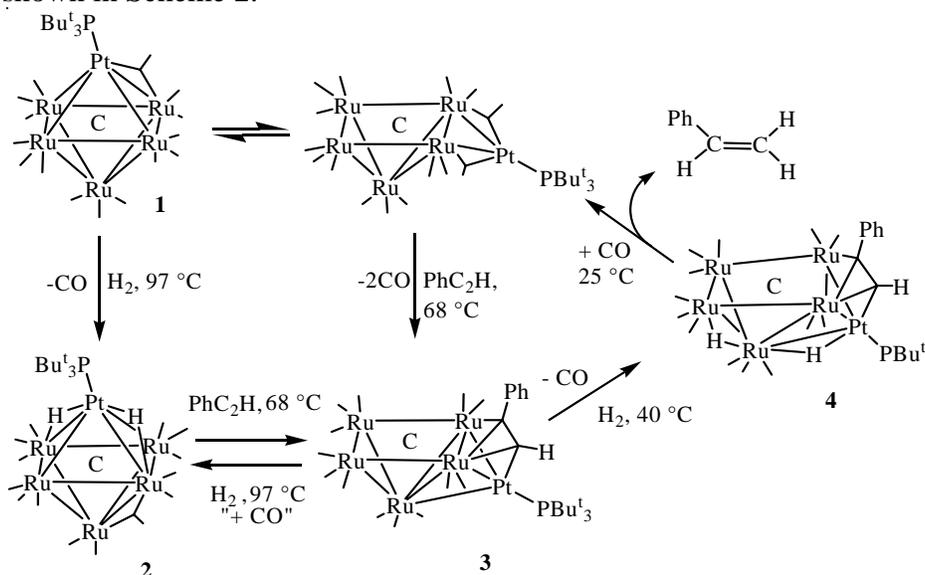
The new hexanuclear cluster compound $\text{PtRu}_5(\text{CO})_{15}(\text{PtBu}_3)(\text{C})$, **1** was obtained from the reaction of $\text{Pt}(\text{P}^t\text{Bu}_3)_2$ with $\text{Ru}_5(\text{CO})_{15}$. Compound **1** crystallizes in two isomeric forms. In one form the cluster consists of a square pyramidal arrangement of five ruthenium atoms with the one platinum atom spanning the square base **1a**. In the second form, **1b** the platinum atom has moved off the square base to an edge of the cluster of ruthenium atoms. The ^{31}P NMR spectrum of **1** at -40°C shows that both isomers exist in equilibrium in solution. Most interestingly, as the temperature is raised above -40°C , the resonances broaden, coalesce and average into a single resonance, $\delta = 103.9$, with appropriate coupling to platinum at 40°C , $\Delta H^\ddagger = 8.8(5) \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -8.4 \text{ cal mol}^{-1}\text{K}^{-1}$. The mechanism of the interconversion involves a reversible breaking and making of two Pt – Ru bonds with a shift of the platinum - phosphine group back and forth between the four-fold Ru_4 site and the two-fold edge-bridging Ru_2 site. It occurs at a rate of 24,000 per second at 20°C , see scheme. The great facility of the transformation can be explained by the participation of two CO ligands that help to stabilize the open cluster through bridging coordination to the platinum atom.

Compound **1** reacts with hydrogen in a hexane solution at reflux to yield the new dihydrido complex $\text{PtRu}_5(\text{CO})_{14}(\text{PBU}^t_3)(\mu_6\text{-C})(\mu\text{-H})_2$, **2**. Compound **2** consists of an octahedral cluster of six metal atoms, PtRu_5 , with a carbido ligand in the center and a PBU^t_3 ligand coordinated to the platinum atom. There are two hydrido ligands that bridge two of the Pt-Ru bonds.



The reaction of **1** with PhC_2H in a CH_2Cl_2 solution at reflux yielded the new alkyne complex $\text{PtRu}_5(\text{CO})_{14}(\text{PBU}^t_3)(\mu_6\text{-C})(\mu_3\text{-PhC}_2\text{H})$, **3**. Compound **3** consists of a platinum capped square pyramid pentaruthenium cluster with a carbido ligand in the center of the Ru_5 cluster. A PBU^t_3 ligand is coordinated to the platinum atom and a triply bridging PhC_2H ligand bridges one of the PtRu_2 triangles.

When **3** was treated with hydrogen in the presence of an 50-fold excess PhC_2H at 80°C , styrene was obtained catalytically at a rate of 20(2) turnovers/h. From these solutions we have isolated the new platinum-ruthenium cluster complex, $\text{PtRu}_5(\text{CO})_{12}(\mu_5\text{-C})(\text{PBU}^t_3)(\text{PhC}_2\text{H})(\mu\text{-H})_2$, **4**.⁸ Compound **4** contains a platinum-capped Ru_3 triangle of a Ru_5 cluster. One of the Ru-Ru bonds in the Ru_5 cluster was cleaved. Two CO ligands were eliminated in going from **3** to **4** and one equivalent of H_2 was added. The two hydrido ligands bridge a Pt-Ru bond and Ru-Ru bonds. Compound **4** also contains one PhC_2H ligand that bridges a PtRu_2 triangle. When treated with CO at room temperature, the hydrido ligands and the PhC_2H ligand were eliminated from **4** in the form of styrene and compound **1** was formed. Solutions of **4** and PhC_2H under hydrogen produce styrene catalytically at a rate of 21(2) turnovers/h at 80°C . A summary of these reactions is shown in Scheme 2.



Scheme 2

Interest to DOE Catalysis:

Bimetallic cluster catalysts of platinum mixed with rhenium, iridium or tin are widely and routinely used by the petroleum industry in the process of petroleum reforming. Platinum-rhodium catalysts are used in automotive catalytic converters to reduce toxic emissions. Supported bimetallic clusters of platinum and ruthenium are among the most active catalysts for the oxidation of methanol at the anode of the direct methanol fuel cell. Recent studies have shown that bimetallic cluster complexes are good precursors to bimetallic nanoparticles and supported catalysts, and highly dispersed nanoclusters on supports have been shown to exhibit very high catalytic activities for hydrogenation of a variety of unsaturated hydrocarbons.

Extended Impact on Science, Technology and Society:

It has been found that in certain cases combinations of two different metal catalysts perform reactions better than the sum of their components. The effect is called synergism. It can result from one metal enhancing the activity of the other, such as a promoter, or alternatively, the two metals can cooperate in chemical transformations by performing key reaction steps separately and sequentially or together simultaneously. Our studies of heterometallic reactivity will help to create a better understanding of these different forms of bimetallic cooperativity and synergism in the function of bimetallic homo- and heterogeneous catalysts. This is important for production of clean and efficient-burning fossil fuels, and should help to provide greater national energy self-sufficiency and a cleaner environment.

Future Plans:

It is planned to continue investigations of the reactions of the sterically crowded, unsaturated platinum and palladium phosphine complexes $M(\text{P}^t\text{Bu}_3)_2$, $M = \text{Pd}$ and Pt with various metal carbonyl cluster complexes in order to synthesize new bimetallic cluster complexes. Studies will be focused both the structures and physical properties of the bimetallic center and its chemical reactivity toward hydrogen activation and transformations of unsaturated hydrocarbons with fuel-related importance.

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Structure-Reactivity Relationships in Multi-Component Transition Metal Oxide Catalysts

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Goal

Understand how interactions between different transition metal cations in oxide catalysts can affect reactivity and selectivity in partial oxidation reactions and the selective catalytic reduction of NO.

Recent Progress

Our work has been focusing primarily on the oxides of the early transition metals Ti, V, and W. Oxides of these three metals are used together for the selective catalytic reduction (SCR) of NO emitted from power plants by NH₃. In addition, TiO₂ supports enhance the reactivity and selectivity of vanadia monolayers for partial oxidation reactions while WO₃ is used in gas sensing as well as catalysis. In addition to these materials, we have begun a collaboration with Jose Rodriguez of Brookhaven National Laboratory on Ni-doped MgO as a de-SO_x catalyst.

We use surface science techniques to associate the geometric and electronic structure of the surface with reactivity and selectivity. Because catalytically interesting oxides are often not available in single crystal form suitable for surface science studies, model catalysts are created by *in situ* epitaxial growth using molecular beam epitaxy (MBE). The MBE technique also allows doped and layered structures to be grown that can be used to study matrix and support effects. The reactivity of the film surfaces have been characterized using temperature programmed desorption (TPD) while the surface structure has been characterized on a macroscopic level using reflection high-energy and low energy electron diffraction (RHEED and LEED) and on a local level using atomic force and scanning tunneling microscopy (AFM and STM); photoelectron spectroscopy is used to characterize the electronic structure of the films.

Effect of reduction on the structure and reactivity of WO₃(100) thin films. We found that epitaxial WO₃(100) films grown on LaAlO₃(100) undergo a series of reversible surface reconstructions when they are oxidized and reduced. These include a set of $p(n \times 2)$ structures where n goes from 5 to 4 to 3 as the oxide is reduced. In STM images such as Fig. 1(a), these surfaces are made up of identical strands whose separation decreases as n decreases. When the $p(3 \times 2)$ surface is reduced the strands merge into (1 x 1) terraces with all the exposed W ions reduced to 5+. Based on this observation, we developed a model of the reconstructed surfaces constructed from narrow (1 x 1) terraces. The effect of these reconstructions on the reactivity of WO₃ was studied by characterizing 1-propanol adsorption and reaction using STM and TPD and comparing the results with those we previously obtained for a $c(2 \times 2)$ WO₃(001) single crystal. The molecules were found to adsorb on top of the strands at positions consistent with the locations of the W ions in our model as shown in Fig. 1(b) and 1(c). The TPD data showed that similar to the $c(2 \times 2)$ WO₃(001) surface, 1-propanol adsorbed at these sites dehydrates to

propylene; however, it does so at much lower temperatures indicating that the reconstructions affect the kinetics but not the favored pathway.

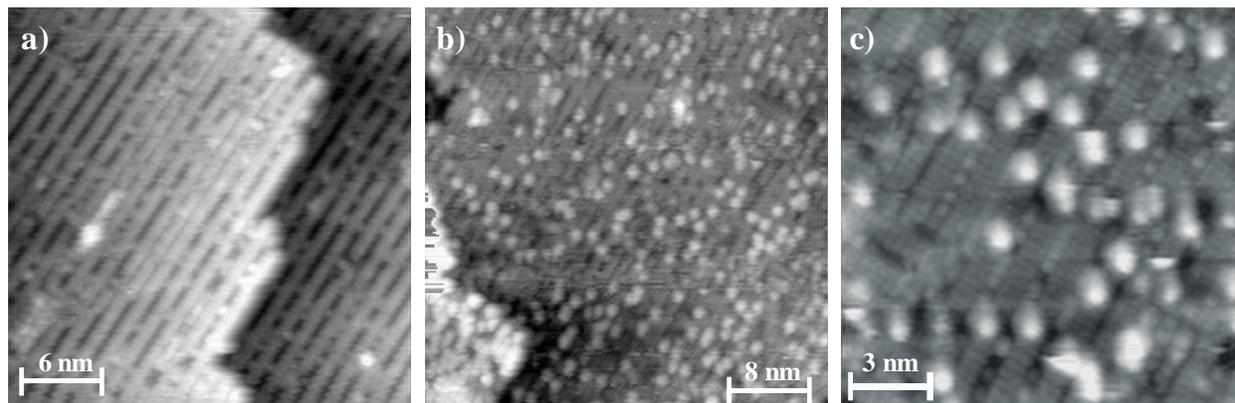


Figure 1. (a) STM image of the $p(n \times 2)$ $\text{WO}_3(100)$ reconstructed surface. In this image, the strand spacing, n , is predominantly $4x$ though a local $3x$ spacing can be seen in several places. (b) After exposing this surface to ~ 200 L 1-propanol at 300 K, white dots decorate the tops of the strands. (c) High-resolution image showing atomic resolution on the strands and the positions of the white dots associated with 1-propanol adsorption centered above the positions of the atomic scale features.

Growth and structure of vanadium oxides on anatase(001). It has long been known that vanadia monolayers supported on anatase are uniquely active and selective catalysts for several reactions, however, the structure of the vanadia monolayer has proved elusive. We have found that the vanadia monolayer lifts the anatase (4×1) reconstruction creating (1×1) LEED and RHEED patterns consistent with pseudomorphic growth of an unreconstructed vanadia layer. The V in the epitaxial monolayer is in the $5+$ oxidation state, however, if V^{5+} is maintained beyond 1 ML structural order is rapidly lost. On the other hand, at higher growth temperatures where V^{4+} predominates, RHEED and LEED indicate that epitaxy can be maintained in at least part of the film for tens of nanometers. In this case, LEED shows a $c(2 \times 2)$ termination attributed to half a monolayer of adsorbed oxygen oxidizing the surface V ions to V^{5+} . Thus a vanadia monolayer in the anatase structure can attain the V_2O_5 stoichiometry through oxygen adsorption, while the bulk anatase structure cannot accommodate this stoichiometry and so V_2O_5 does not grow epitaxially beyond 1 ML.

Growth and characterization of anatase(101) thin films. The (101) surface is the lowest energy anatase surface and thus at equilibrium accounts for most of the surface area exposed by anatase particles. Therefore, to draw a connection between surface science studies on low surface area samples with practical catalysts it is important to study this surface. Unlike the $[001]$ orientation, there are no readily available substrates lattice matched to anatase (101) . To get around this problem we have used vicinal $\text{LaAlO}_3(110)$ substrates where the lattice match is good along the substrate $[001]$ direction but poor in the orthogonal direction. The step spacing was chosen so that an integer number of anatase (101) unit cells fit between the steps so that mismatch strain is relieved at the interface rather than in the bulk of the film. RHEED patterns recorded during growth show the expected evolution from a stepped to a smooth surface as the TiO_2 film grows. Following growth, both RHEED and LEED show the surface diffraction patterns expected for anatase (101) .

Growth of vanadia monolayers on anatase(101). Vanadia in the monolayer range was found to behave very similarly on anatase (101) and anatase (001) . Both RHEED and LEED showed

(1x1) diffraction patterns consistent with a pseudomorphic monolayer. Photoelectron spectroscopy indicated that the V in the monolayer was predominantly in the 5+ oxidation state which can again be explained by oxygen adsorption atop a vanadia monolayer in the anatase structure. The results show how the anatase substrate can stabilize vanadia structures not found in bulk samples.

DOE Interest

Transition metal oxide catalysts are used to remove nitrogen oxides and sulfur oxides emitted from power plants and thus basic understanding of these catalysts that helps guide future improvements is important to clean, low-cost power generation. These same materials are also used as partial oxidation catalysts to upgrade hydrocarbon feedstocks to more valuable oxygenates. Improvements in reactivity and selectivity would make better use of scarce resources while reducing waste.

Future Plans

- 1) Comparison of the structure and reactivity of vanadia monolayers on anatase (001) and $\text{WO}_3(100)$. These WO_3 and anatase surfaces are isostructural and so comparing these systems will reveal how W–O–V bonds versus Ti–O–V bonds affect reactivity.
- 2) Comparison of vanadia monolayers on anatase with V-doped anatase surfaces. Doping changes the number of Ti–O–V bonds and the adjacency of V–O–V bonds, both of which are considered to strongly affect reactivity of the V cations but have not been characterized.
- 3) Growth and characterization of pure and W-doped V_2O_5 thin films. Rather than looking at how a support or surrounding matrix affects the activity of vanadia cations, in this part of the project we aim to understand how dopants, in this case W, affects vanadia cations on the surface of bulk V_2O_5

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New Heterogeneous Catalysts for the Selective Reduction of NO_x under Lean Conditions

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Goal

The original goal of this program was the identification and design of new noble-metal-based catalysts for the selective catalytic reduction of nitric oxide by hydrocarbons under excess oxygen (i.e., “lean”) conditions (HC-SCR). Eventually, the bulk of our efforts has been shifted to the use of organometallic cluster precursors for the synthesis of novel bimetallic catalysts. During this process we have continued to maintain an interest in NO_x abatement, but have redirected our efforts from the HC-SCR process to the more promising from a commercial standpoint, NO_x Storage Reduction (NSR) approach.

Recent Progress

A substantial amount of our efforts has been focused on the synthesis and characterization of supported bimetallic Pt-Au catalysts prepared from organometallic cluster precursors. Earlier synthetic and characterization efforts (i.e., kinetic and FTIR measurements) have shown that the use of a [Pt₂Au₄(C≡CBu^t)₈] cluster precursor leads to the formation of bimetallic Pt-Au particles on silica. More recently, we have extended this work to additional supports. In particular, through the use of the same cluster, we have also successfully synthesized bimetallic Pt-Au nanoparticles on alumina and titania. In all of these cases we have observed CO chemisorption on Au, which suggests that Au nanocrystallites capable of uptaking CO have been stabilized on all these supports. While small Au crystallites have been previously obtained by groups utilizing different synthetic techniques on certain supports (i.e., titanium or iron oxides), it is generally considered a challenge to stabilize such Au nanocrystallites on widely-used supports such as alumina and silica.

We have also investigated in detail the ligand removal process through the use of *in-situ* FTIR spectroscopy. So far, we have examined the behavior of the [Pt₂Au₄(C≡CBu^t)₈] cluster supported on Al₂O₃ and TiO₂, and have conducted treatments in various atmospheres and temperatures, monitoring the process continuously via *in-situ* FTIR spectroscopy. CO was also used as a probe to examine the availability of adsorption sites. The results suggest that substantial additional control over particle size may be exercised by the careful choice of ligand removal (i.e., “activation”) conditions.

Our success in synthesizing these Au nanocrystallites on different supports, allowed us to explore some mechanistic issues for the low temperature oxidation of CO. The kinetic results obtained for this reaction are in agreement with the work of Haruta and co-workers regarding the activity of Au nanocrystallites supported on titania (i.e., lightoff at temperatures near room temperature), although a completely different synthetic approach was used. Our results further support Haruta's thesis regarding the role of oxygen supplied by the support. This can be clearly demonstrated with the silica-supported Pt-Au cluster-derived system. Although in this case the catalyst has Au nanocrystallites capable of chemisorbing CO, it does not show any low temperature activity for the oxidation of CO. We also observed differences in the effect of water between the bimetallic Pt-Au cluster-derived catalysts and the monometallic Au catalysts (as reported by Haruta) suggesting that some mechanistic differences may exist.

We have also synthesized alumina- and magnesia-supported Pt-Ru catalysts from a $[\text{Pt}_2\text{Ru}_4(\text{CO})_{18}]$ cluster precursor. These materials have been imaged with the help of Dr. Penycook at ORNL through the use of HRSTEM. Atomic resolution images obtained clearly show the formation of 20-30 atom agglomerates even after very mild treatments. Individual metal atoms were also observed. The agglomeration process appears to proceed at a smaller scale on magnesia, in which case some intact clusters can be observed. Based on these results, we have initiated a comprehensive characterization program and we are in the process of obtaining images after a series of systematic treatments.

The catalytic properties of alumina-supported Pt-Ru catalysts were probed by the selective oxidation of CO in the presence of hydrogen. The kinetic results indicate no difference in the initial activities of cluster-derived and conventionally prepared Pt-Ru catalysts when a reduction treatment is applied prior to exposure to reaction conditions. However, the cluster-derived catalyst is stable, while a slow deactivation is observed with the conventionally prepared sample. In contrast, when the samples were oxidized prior to exposure to reaction conditions, the cluster-derived catalyst exhibits much higher activity than either the conventionally prepared one or the corresponding monometallic materials. Our working hypothesis is that bimetallic interactions between Pt and Ru in the cluster-derived samples stabilize Ru in a highly dispersed state and prevent sintering.

DOE Interest

These new catalysts appear to have unique structural properties and may find applications in a wide range of different reactions catalyzed by noble metals.

Future Plans

A renewal request is currently going through the peer review process. In this request a collaborative effort has been proposed between Professors Amiridis and Adams at USC and Dr. Penycook at ORNL. Our plan is to combine what we have learned from our previous work in the area of cluster-derived supported bimetallic catalysts, as well as, from homogeneous kinetic studies conducted by Professor Adams, in an attempt to design improved bimetallic catalysts for a number of different applications described below. It is expected that this work

will lead to a better understanding of: the “anchoring” of metal clusters on different supports (including issues related to their stability and/or agglomeration upon impregnation); the ligand removal process and the resulting changes of the structure of the metal clusters (i.e., induced metal segregation and/or agglomeration); the catalytic activity of the resulting nanoparticles for reactions of interest (i.e., selective hydrogenation/hydrogenolysis of functionalized olefins, selective oxidation of CO, and storage and reduction of NO_x under lean conditions); and the relationships between the nanoparticles’ structure and composition and their catalytic behavior.

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Transition Metal Complexes of Buckybowls: η^6 -Coordination of One and Two Cp^*Ru^+ Units to Corannulene ($\text{C}_{20}\text{H}_{10}$)

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Goal

The goal of this project is to explore the effects of transition metal coordination to curved-surface fragments of buckminsterfullerene (C_{60}) on their structures and reactivities. In other projects, we are designing new types of heterogeneous catalysts that contain tethered transition metal complexes.

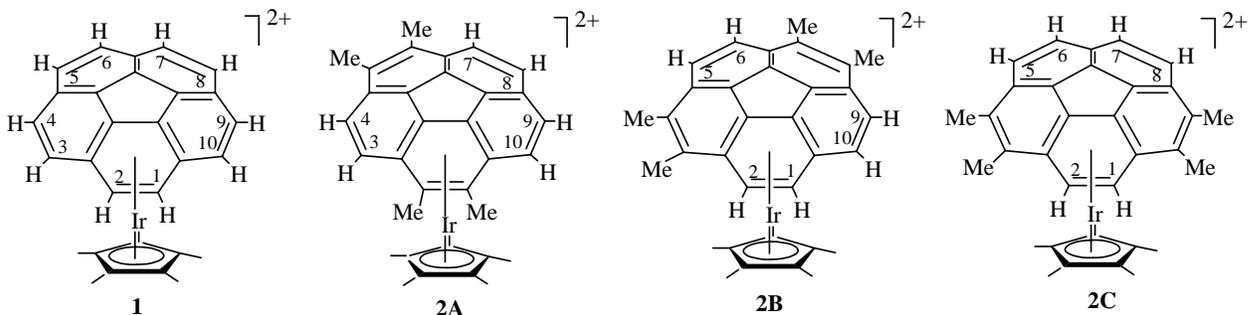
Recent Progress

Although many transition metal complexes bind to buckminsterfullerene (C_{60}), curved-surface fragments of C_{60} have a much lower tendency to coordinate to transition metal units. One of the simplest fragments is corannulene ($\text{C}_{20}\text{H}_{10}$). Its only complex that has been characterized by X-ray crystallography is prepared by the vapor-phase co-condensation of corannulene with $\text{Rh}_2(\text{CF}_3\text{CO}_2)_4$; the resulting extended-array compounds consist of corannulene units that are η^2 -coordinated to two or three Rh centers. Prior to our studies, the only other reported corannulene complex was $\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})^+$, which was only characterized by NMR spectroscopy in solution.

In collaboration with Peter Rabideau and Andrzej Sygula at the Ames Laboratory, we began investigations of corannulene binding to a variety of transition metal complexes. We found that the acetone complex $\text{Cp}^*\text{Ir}(\text{OCMe}_2)_3^{2+}$, where $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, reacts with corannulene at room temperature in CD_3NO_2 solvent to give quantitatively $\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})^{2+}$ (**1**), which was characterized by its ^1H , ^{13}C , COSY, and NOESY NMR spectra. Although it has not been possible to isolate the pure $\text{Cp}^*\text{Ir}(\eta^6\text{-corannulene})^{2+}$ complex or obtain X-ray quality crystals, the spectral data are fully consistent with structure **1** (Chart 1). The reaction of 1,2,5,6-tetramethylcorannulene ($\text{C}_{20}\text{H}_6\text{Me}_4$) under the same conditions gives initially all three possible isomers of $\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)^{2+}$ (**2**) (see Chart 1). However, over the course of 24 h, the $\text{Cp}^*\text{Ir}^{2+}$ unit in the major isomer **2B** migrates from a non-methylated ring to one of the methylated rings to give **2A**. The final reaction mixture contains 88% **2A** and 12% **2C**. It is not

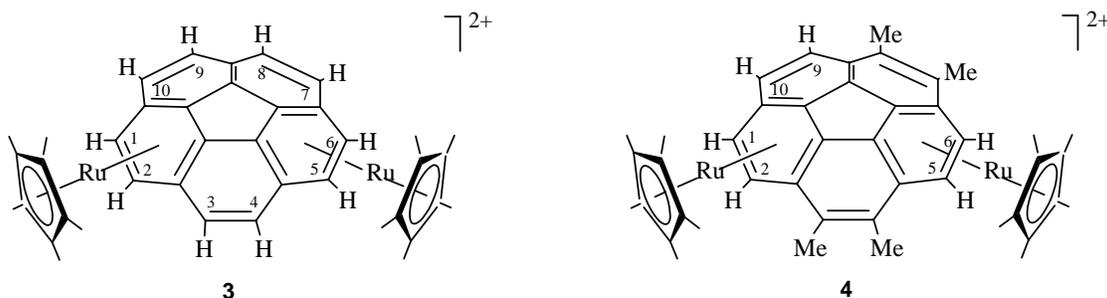
clear whether the migration of the $\text{Cp}^*\text{Ir}^{2+}$ occurs while remaining attached to the surface or by dissociation and re-association.

Chart 1



We have also found that $[\text{Cp}^*\text{RuCl}]_4$ reacts with AgBF_4 and $\text{C}_{20}\text{H}_{10}$ in CD_3NO_2 to give $(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_{10})^{2+}$ (**3**). NMR studies of **3** (Chart 2) show that the two Cp^*Ru^+ units are coordinated to non-adjacent arene rings. Very recently, we have obtained single crystals of **3** and determined its structure by X-ray crystallography. This structural result shows that the two Cp^*Ru^+ units are on opposite sides of the bowl and that the bowl is much less curved than free corannulene. Tetramethyl corannulene also reacts with two Cp^*Ru^+ units and gives only one isomer $(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_6\text{Me}_4)^{2+}$ (**4**) in which the Cp^*Ru^+ units are on non-adjacent, non-methylated arene rings.

Chart 2



From these studies, it appears that the Cp^*Ru^+ unit prefers non-methylated rings while $\text{Cp}^*\text{Ir}^{2+}$ prefers methylated rings. On the basis of our limited studies, electropositive (cationic) metal complexes coordinate more strongly than neutral fragments, e.g., $\text{Cr}(\text{CO})_3$, to corannulenes. Also, the observed η^6 and rim η^2 -coordination of corannulenes is very different from the η^2 -coordination of buckminsterfullerene (**1**) which suggests that these closely related types of molecules have different preferred coordination modes.

DOE Interest

Curved carbon surfaces are of fundamental interest because of their unusual structures, reactivities, physical strengths, and conducting properties. The modification

of these materials by transition metal attachments offers the opportunity to modulate these characteristics of curved-surface carbon.

Future Plans

A variety of curved-surface buckybowls will be examined in their reactions with transition metal fragments in order to explore features of both the bowls and the metal fragments that promote binding. Also we plan to investigate the effect of this coordination on activating the bowls to react in ways that lead to novel functionalized bowls. Catalytic studies, not discussed in this presentation, will also be continued.

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1. M. A. Reynolds, I. A. Guzei and R. J. Angelici, "Re₂(CO)₁₀-Promoted S-Binding, C-S Bond Cleavage and Hydrogenation of Benzothiophenes: Organometallic Models for the Hydrodesulfurization (HDS) of Thiophenes", *J. Am. Chem. Soc.*, **124**, 1689-1697 (2002).
2. J. Chen and R. J. Angelici, "Unusual Thiophene Complexes from Reactions of Cp*Ir(2,5-dimethylthiophene) with Sources of W(CO)₅, Cr(CO)₄, Mo(CO)₄, and Fe(CO)₃", *Inorg. Chim. Acta*, **334**, 204-212 (2002).
3. J. Chen, V. G. Young, Jr., and R. J. Angelici, "Syntheses, Structures and Reactions of η⁶-Complexes of Iridathiabenzene with Chromium, Molybdenum and Tungsten Carbonyls", *Organometallics*, **21**, 5951-5961 (2002).
4. K. J. Stanger, J. W. Wiench, M. Pruski and R. J. Angelici, "³¹P NMR and IR Characterization of Enantioselective Olefin and Arene Hydrogenation Catalysts Containing a Rhodium-Chiral Phosphine Complex Tethered on Silica", *J. Mol. Cat. A: Chemical*, **195**, 63-82 (2003).
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7. K. J. Stanger, Y. Tang, J. Anderegg and R. J. Angelici, "Arene Hydrogenation Using Supported Rhodium Metal Catalysts Prepared from [Rh(COD)H]₄, [Rh(COD)₂]⁺BF₄⁻, and [Rh(COD)Cl]₂ Adsorbed on SiO₂ and Pd-SiO₂," *J. Mol. Cat. A: Chemical*, **202**, 147-161 (2003).
8. M. A. Reynolds, I. A. Guzei and R. J. Angelici, "Hydrogenation and Carbon-Sulfur Bond Hydrogenolysis of Benzothiophene Promoted by Re₂(CO)₁₀ and H₄Re₄(CO)₁₂," *Inorg. Chem.*, **42**, 2191-2193 (2003).
9. K. J. Stanger and R. J. Angelici, "Hydrodefluorination of Fluorobenzene Catalyzed by Rhodium Metal Prepared from [Rh(COD)₂]⁺BF₄⁻ and Supported on SiO₂ and Pd-SiO₂," *J. Mol. Cat. A: Chemical*, **207**, 59-68 (2004).

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Radical and Non-Radical Reactions of Transition Metal-Activated Oxygen

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Collaborators: A. Ellern

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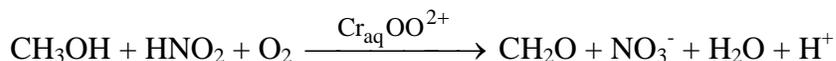
Goal

Develop mechanistic understanding of oxygen activation by transition metal complexes in thermal and photochemical reactions.

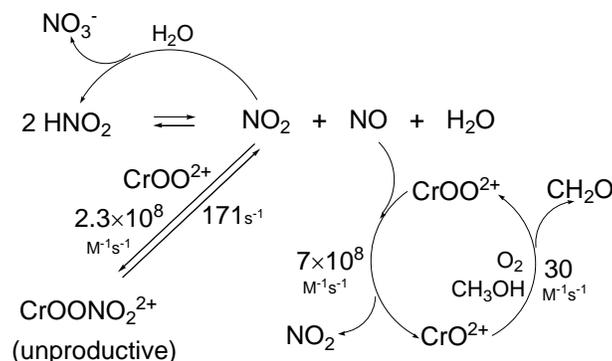
Recent progress:

Superoxometal-Catalyzed Co-oxidation of Alcohols and Nitrous Acid with Molecular Oxygen

A superoxochromium(III) ion, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, catalyzes the title reaction according to the stoichiometry:



The kinetics are second order in $[\text{HNO}_2]$ and independent of the concentration of the superoxochromium catalyst, substrate, and O_2 . The proposed mechanism features the disproportionation of HNO_2 to NO and NO_2 , both of which react readily with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{NO}$ reaction generates another equivalent of NO_2 and a mole of $\text{Cr}_{\text{aq}}\text{O}^{2+}$, the active oxidant. The two-electron oxidation of the alcohol by $\text{Cr}_{\text{aq}}\text{O}^{2+}$ produces $\text{Cr}_{\text{aq}}^{2+}$, which reacts with O_2 to regenerate the catalyst, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The $\text{NO}_2/\text{Cr}_{\text{aq}}\text{OO}^{2+}$ reaction yields the peroxyxynitrate complex, $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$, in a dead-end equilibrium process that has no effect on the catalytic reaction. The disproportionation of NO_2 yields the final nitrogen-containing product, NO_3^- , and regenerates an equivalent of HNO_2 . Under a fixed set of conditions, the relative catalytic efficiency of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ decreases with its concentration owing to the competition between O_2 and $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ for the intermediate $\text{Cr}_{\text{aq}}^{2+}$.

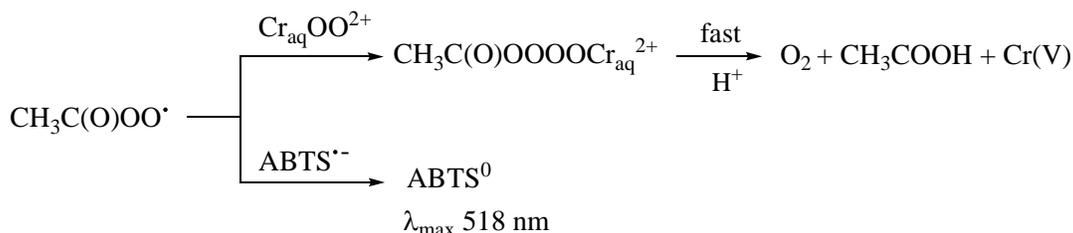


Rapid Cross-Disproportionation of Superoxometal Ions and Acylperoxyl Radicals

The rates of hydrogen atom abstraction by a superoxochromium complex, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, are comparable to the rates of hydrogen abstraction by alkylperoxyl radicals, ROO^\bullet . On the other

hand, the lifetimes of the two kinds of species in the absence of added substrates are very different, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ being much longer-lived than ROO^\bullet , such that dilute aqueous solutions of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ can survive for hours at room temperature. We have now found that a cross reaction between $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and acetylperoxyl radicals, $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$, has rates comparable to those for the coupling of organic peroxyl radicals.

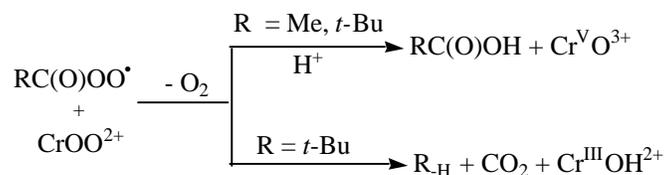
Laser flash photolysis of an organocobalt precursor in the presence of O_2 , $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, and a kinetic probe $\text{ABTS}^{\bullet-}$, yielded the rate constant for cross coupling $k_{\text{cross}} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. After the initial coupling step, the evidence points to the elimination of O_2 and formation of acetate ions and $\text{Cr}^{\text{V}}_{\text{aq}}$. The latter disproportionates and ultimately yields $\text{Cr}_{\text{aq}}^{3+}$ and HCrO_4^- . No CO_2 was detected. To the best of our knowledge, this is the first published example of such a cross coupling reaction.



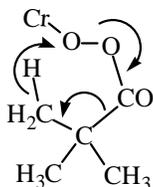
Reactions of Superoxo and Oxo Metal Complexes with Aldehydes

The aquachromyl(IV) ion, $\text{Cr}_{\text{aq}}\text{O}^{2+}$, reacts with acetaldehyde (CH_3CHO) and pivaldehyde ($\text{C}(\text{CH}_3)_3\text{CHO}$) by hydrogen atom abstraction and, in the presence of O_2 , produces acylperoxyl radicals, $\text{RC}(\text{O})\text{OO}^\bullet$. In the next step, the radicals react with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, a species accompanying $\text{Cr}_{\text{aq}}\text{O}^{2+}$ in our preparations. The reaction with $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ takes place as described above, and yields chromate and acetate.

The $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{C}(\text{CH}_3)_3\text{C}(\text{O})\text{OO}^\bullet$ reaction yielded isobutene, CO_2 and $\text{Cr}_{\text{aq}}^{3+}$, in addition to chromate. In the suggested mechanism, the transient $\text{Cr}_{\text{aq}}\text{OOOO}(\text{O})\text{CC}(\text{CH}_3)_3^{2+}$ branches into two sets of products. The path leading to chromate resembles the $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ reaction.



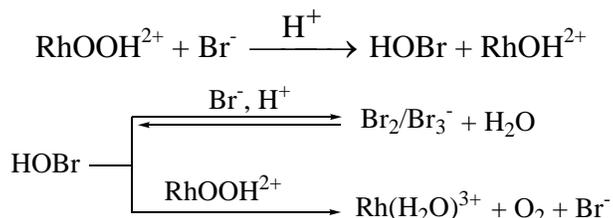
The other products arise from an unprecedented intramolecular hydrogen transfer from *tert*-butyl group to CrO entity, and elimination of CO_2 and O_2 .



A portion of $\text{C}(\text{CH}_3)_3\text{C}(\text{O})\text{OO}^\bullet$ was captured by $(\text{CH}_3)_3\text{COO}^\bullet$, which was in turn generated by decarbonylation of acyl radicals and oxygenation of *tert*-butyl radicals so formed.

Reduction and Oxidation of Hydroperoxo Rhodium(III) Complexes by Halides and Hypobromous Acid

Oxygen atom transfer from *trans*-(NH₃)₄(H₂O)RhOOH²⁺ to iodide takes place according to the rate law, $-d[(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}]/dt = k_1 [(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}][\text{I}^-][\text{H}^+]$. At 0.10 M ionic strength and 25° C, the rate constant k_1 has values $8.8 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$. The final products are (NH₃)₄Rh(H₂O)₂³⁺ and I₂/I₃⁻. The (NH₃)₄(H₂O)RhOOH²⁺/Br⁻ reaction also exhibits mixed third order kinetics with $k_{\text{Br}} = 1.8 \text{ M}^{-2} \text{ s}^{-1}$ at high concentrations of acid and bromide. Under these conditions, Br₂/Br₃⁻ is produced in stoichiometric amounts. As the concentrations of acid and bromide decrease, the reaction begins to generate O₂ at the expense of Br₂, until in the limit [H⁺] ≤ 0.1 M and [Br⁻] ≤ 0.01 M, Br₂/Br₃⁻ is no longer observed and O₂ is produced quantitatively. In this limit, the loss of (NH₃)₄(H₂O)RhOOH²⁺ is by a factor of ~2 faster than at the high [H⁺] and [Br⁻] extreme, and the stoichiometry is $2 (\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+} \rightarrow 2 (\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOH}^{2+} + \text{O}_2$, i. e. the reaction has turned into the bromide catalyzed disproportionation of coordinated hydroperoxide. In the proposed mechanism, the hydrolysis of the initially formed Br₂ produces HOBr, the active oxidant for the second equivalent of (NH₃)₄(H₂O)RhOOH²⁺. The rate constant k_{HOBr} for the HOBr/(NH₃)₄(H₂O)RhOOH²⁺ reaction is $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.



Interest to DOE

Understanding the mechanistic chemistry of oxygen activation by transition metal complexes is a prerequisite for the design of catalytic systems for oxidations by dioxygen, an area of potentially enormous environmental and energy-saving impact.

Future plans

Detailed mechanistic studies of the superoxometal-alkylperoxyl cross-reactions. Search for experimental proof for unusual intramolecular hydrogen abstraction reactions by a combination of specific isotope labeling and calculations.

Development of novel methods of preparation and reactivity studies of the active transients in oxygen activation reactions, including hydroperoxo, alkylperoxo, and high-valent metal oxo species.

Construction of catalytic systems that utilize molecular oxygen as active oxidant for organic materials.

Publications (2002-2003)

1. Pestovsky, O.; Bakac, A. "Generation and Reactivity of Rhodium(IV) Complexes in Aqueous Solutions" *Inorg. Chem.* **2002**, 41, 3975-3982
2. Bakac, A. "Kinetics of the Reaction of NO₂ with a Macrocyclic Nickel Complex" *Int. J. Chem. Kin.* **2002**, 34, 278-281
3. Bakac, A. "Rapid Cross-Disproportionation Between Superoxometal Ions and Acylperoxyl Radicals" *J. Am. Chem. Soc.* **2002**, 124, 3816-3817

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8. Lemma, K.; Bakac, A. "Reduction and Oxidation of Hydroperoxo Rhodium(III) Complexes by Halides and Hypobromous Acid" Inorg. Chem. **2004**, submitted

Nanostructured Metal Oxide Catalysts via Building Block Syntheses

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Period of Execution: September 1, 2001 – April 1, 2004

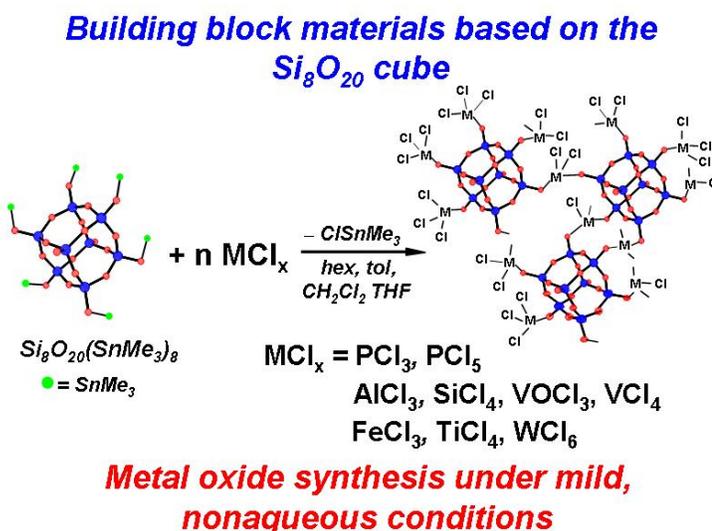
Goal

The primary goal of this research project is to initiate the development of a general methodology with which to prepare nanostructured mixed metal oxide catalysts in which the composition and surface structure in the immediate environment of the active sites may be tailored to enhance their activity. Ultimately, we seek to develop a three way correlation between the synthesis of these mixed metal oxides, their precise structure and the important properties they exhibit as catalysts (activity, selectivity and stability).

Recent Progress

1. *Building block syntheses:* We have succeeded in optimizing the syntheses of two analogues of the Si_8O_{20} building block (trimethyl and tri-*n*-butyl tin cubes). Both can be prepared pure in research sized samples. The synthesis of the tri-*n*-butyl tin cube can scaled up to produce larger sizes (100g and larger) using commercially available tri-*n*-butyltin ether. A manuscript describing the Si_8O_{20} core structures of the trimethyltin and octakis titanocene cubes is in preparation.

2. *The linking reaction:* We have made considerable progress in understanding the linking reactions used to prepare our building block solids. Work has focused primarily on silicon based liners (chlorosilanes) and linking groups derived from vanadyl chloride (VOCl_3). The vanadyl work is in press (*Chem. Comm.*). Two manuscripts describing the dependence of linking group distributions on dosing and addition



sequence strategies are in preparation. Our work is now expanding in two directions. First, to incorporate a broader range of catalytically active metals into these solids such as Ti, Mo, W and Zr. Second, to begin double building block studies with polyoxometallates and Keggin type clusters.

3. *Characterization of Microstructures:* Our strategy in approaching this objective has been dictated primarily by the techniques available to us which give information on the microstructures of these building block solids. The primary technique that we have employed has been solid state NMR investigations for the detection and identification of linkers (^{29}Si , ^{31}P , ^{119}Sn , ^{51}V , ^{27}Al) cage silicon atoms. From these studies, a strong case has been made for the survival of the cube in the formation of the cross linked matrix. Because NMR data can give only indirect evidence for structure in these cases, we have also initiated a long range project to learn how to collect and analyze X-ray and neutron scattering data on these amorphous samples. Our initial objective in these efforts is to detect and characterize the structure of the Si_8O_{20} cube within these matrices. These techniques are, however, broadly applicable to the determination of structure in partially ordered and disordered phases and specifically to metal oxide based materials. We have collected and processed data on an initial round of four samples and are currently beginning quantitative analysis of the radial distribution functions.
4. *Evaluation of Catalytic Activity:* We have just begun to test the activity of the vanadyl linked building block catalysts. More time and effort must be spent on this objective before conclusions can be drawn.

DOE Interest

We hope the building block approach to preparing nanostructured catalysts will become a new paradigm in the area of heterogeneous catalysis. As such, it could greatly impact the efficiency of a significant number of industrially important processes to the Nation (epoxidation and aluminosilicate based solid acids are two that are dealt with currently) but many more examples involving multiple metals can be envisioned). Because of the importance of catalysis to both the material and energy wealth of the country, the development of a broadly applicable, simple strategy of making single site, nanostructured supported catalyst would positively impact the use of the resources that our society depends on.

Future Plans

1. Publish our work based on 1) dosing, addition sequence and stoichiometry strategies using silicon linkers; 2) neutron and high energy X-ray diffuse scattering studies on the structure of amorphous building block solids; 3) a full

paper describing studies using VOCl_3 and VCl_4 as linkers and 4) a full paper describing the structures of Si_8O_{20} and $\text{Si}_{10}\text{O}_{25}$ spherosilicates.

2. My students and I will take samples to Argonne (IPNS) and conduct a second round of measurements with optimized sample configurations (larger samples and reduced hydrogen backgrounds) to obtain final scattering data on both samples measured previously (establish reproducibility) and new samples.
3. In collaboration with Dr. Overbury's group we will continue our initial survey of the catalytic activity of our building block catalysts for total oxidation reactions. Additionally, we will continue catalytic epoxidation studies with Ti, V linked solids.
4. Begin testing aluminum based solid acid catalysts for activity as alkylation and H/D exchange catalysts in hydrocarbons.

Publications:

One paper based completely on the support of the DOE is currently in press:

Building block syntheses of site-isolated vanadyl group in silicate oxides, Narendra N. Ghosh, Jason C. Clark, Geoffrey T. Eldridge and Craig E. Barnes, *Chem. Comm.* **2004**, 856.

Four manuscripts based on the support of the DOE are in preparation. Their titles are:

The Synthesis and Characterization by EXAFS and Solid State NMR of Nanostructured Silicate Building Block Solids containing Vanadium

Synthesis and Structures of Stannylated Spherosilicate Building Block Molecules for Materials Synthesis

The reaction of the $\text{Si}_8\text{O}_{12}(\text{OSnR}_3)_8$ Building Block with Silyl chlorides: Methodologies for Preparing Nanostructured Heterogeneous Catalysts by Design

A Diffuse Neutron Scattering Study of the Order within Amorphous Silicates Composed of Linked Silicate Building Blocks

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DE-FG02-03ER15471
DE-FG02-03ER15469

Mark A. Barteau (U. Of Delaware)
Richard M. Crooks (TAMU)
Manos Mavrikakis (U. Of Wisconsin)

CATALYSIS SCIENCE INITIATIVE: From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity

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Post-docs: Robert W. J. Scott (TAMU)

Students: Adrienne Lukaski, Orest Skoplyak, Amit Goda, Michael Gifford, Wei Huang, Soumitra Deshmukh (Delaware); Orla Wilson (TAMU); George Huber, Jeff Greeley, Shampa Kandoi (Wisconsin).

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Goals:

The goal of this project is to demonstrate a new paradigm for design for catalyst selectivity. Our approach is to enhance selectivity by design via the integration of four research components: Theory and Modeling; Surface Science; Materials Synthesis, Characterization and Scale-up; and Catalyst and Reactor Dynamics and Optimization. This integrative approach is being applied to three important catalytic reactions: selective hydrogenation, selective olefin oxidation and selective reforming of carbohydrates to produce alkanes. We focus on bimetallic catalysts as our principal design targets.

DOE Interest:

“Catalysis by design” has been a dream for decades. To specify the composition and structure of matter to effect a desired catalytic transformation with desired and predicted rate and selectivity remains a monumental challenge, especially in heterogeneous catalysis. Our research thrusts have been chosen not only for their practical and scientific relevance, e.g. for more efficient and sustainable chemicals and fuels production, but also because they provide a foundation for developing and exploring broadly applicable principles and strategies for catalyst design.

Research Plan:

We aim specifically to develop selective catalysts that can achieve high selectivity in the three important classes of reactions above. In all cases modeling at the atomic scale, surface science, materials synthesis, characterization and testing, and optimization (via multiscale modeling and through high-throughput experimentation) are carefully integrated to reach the selectivity objectives.

Catalytic hydrogenations are probably the most ubiquitous catalytic processes, yet there remain important scientific and practical challenges in carrying out selective hydrogenations that make this an exciting target for catalysis design. Two important challenges are the design of catalysts to preferentially hydrogenate specific functional groups, and the design of catalysts that are able to selectively hydrogenate a specific group of molecules in a complex stream, for example, the hydrogenation of aromatics in the presence of olefins refinery streams. We are leveraging a recently discovered low-temperature (~245 K) hydrogenation bimetallic Ni-Pt catalyst by the Chen group to develop two classes of selective catalysts: one for the selective hydrogenation of aromatic molecules in the presence of alkenes, and another for the preferential hydrogenation of specific functional groups. Low-temperature Pt-Ni catalysts particles formed inside zeolite supports selective for the adsorption of aromatic molecules are being explored for competitive hydrogenations of olefins and aromatics (Lobo). Very uniform

bimetallic particles of identical composition are being prepared using dendrimers (Crooks) and will be deposited on inert supports to investigate their preferential hydrogenation activity properties. High throughput experiments (Lauterbach) will speed up the development of the most selective samples. In parallel, Vlachos' group is developing a multiscale framework that can assist in the optimal design of high-throughput experiments. The objective here is the identification of conditions that maximize information content so that proper model training is realized that in turn can lead to model-based catalyst design.

We have chosen the epoxidation of olefins to develop and demonstrate design principles of selective oxidation catalysts. We have made significant progress with respect to ethylene epoxidation by silver-based bimetallic catalysts, and this work builds on this success by tackling more reactive olefins such as propylene and isoprene. The fundamental challenge is to design catalyst that control C-H bond activation, C-O bond formation and other relevant reaction steps to achieve high selectivity to the desired product. We have proven that selectivity of oxametallacycle reactions can be manipulated by surface modification by alloying and by surface promotion. DFT calculations in combination with surface science experiments are used to examine the formation of surface oxametallacycles by ring opening of propylene oxide on single-crystals silver surfaces. DFT calculations also predict oxametallacycle ring closure selectivity, the thermodynamics of transition states and the influence of surface modifications. Steady-state propylene oxidation experiments will determine if our understanding of ethylene epoxidation is applicable to propylene. High throughput methods will take the leads from these experiments to rapidly explore a large catalyst composition space.

The aqueous-phase reforming of carbohydrates for the generation of hydrogen and hydrocarbons is very new and could potentially revolutionize the structure of the energy market in the nation. It also has the potential to make a major contribution to reducing green house gases by displacement of fossil fuels in a wide range of applications. The aqueous-phase, low-temperature process, its simple reactor requirements and the use of carbohydrate feedstocks are all novel and advantageous characteristics that demand further scrutiny and improvement. As in the previous two applications, the crucial issue is selectivity. We aim at identifying how the structure of the catalyst can be altered to achieve high catalytic activity and controlled catalytic selectivity to alkanes. We also aim at identifying how the performance of the catalyst is controlled by the structure of the oxygenated hydrocarbon reactant. To that effect, the specific components of the research are high-throughput screening of diverse catalytic materials (with emphasis in bimetallics on various supports), detailed kinetic evaluation of promising catalyst systems, spectroscopic characterization of the promising materials and their surface intermediates, an theoretical studies with DFT to determine how to control bond-breaking and bond-making processes on idealized surfaces.

Recent Progress:

Considerable progress has been made with dendrimer-supported bimetallics of potential relevance to both selective hydrogenation and selective oxidation. The Crooks group has examined the synthesis, characterization and catalytic properties of bimetallic Pd/Au dendrimer-encapsulated nanoparticles (DENs) formed using sixth-generation polyamidoamine (PAMAM) dendrimers. The stable, water-soluble bimetallic Pd/Au DENs are fairly monodisperse with sizes on the order of 1-3 nm depending on the total metal loading. The catalytic hydrogenation of allyl alcohol was probed using the Pd/Au DEC in aqueous solution; results indicate that the hydrogenation of allyl alcohol is significantly enhanced for Pd/Au DEC compared to monometallic Pd or Au DENs. Characterization of these materials by NEXAFS and TEM in collaboration with the Chen and Buttrey groups is underway. The Crooks group has also explored the synthesis, characterization and optical properties of bimetallic Au/Ag dendrimer-encapsulated nanoparticles (DENs). Two synthetic routes were utilized – co-complexation of the respective metal salts leading to AuAg alloy DENs, and sequential loading of one metal salt to a seed nanoparticle of the other resulting in core-shell DENs. Chemical determination of the core-shell architecture was demonstrated via differential extraction of the particles from the dendrimer template. This provides us with a chemical method of differentiating between the two shell compositions, and allows for the chemical separation of metallic and bimetallic nanoparticles.

The Mavrikakis and Barteau groups have investigated, using DFT, the structures and vibrational spectra of possible oxametallacycle structures on Pd and Rh surfaces. The objective is to determine whether evidence for stable oxametallacycles can be found on surfaces of Group VIII metals. If so, this may suggest that the oxametallacycle is also a key intermediate in gas-solid (water-free) Wacker chemistry, and would have significant implications for metal-catalyzed olefin oxidations, the nature of the surface oxygen that participates in these, and the design of materials to achieve selectivity to different oxygenate products.

The Mavrikakis and Dumesic groups have initiated a systematic theoretical analysis for bond-breaking in EtOH over Ru and Pt surfaces. Both thermochemistry and activation energy barriers for C-C, C-O, C-H, and O-H in EtOH are calculated from first-principles. The tentative goal is to derive simple correlations between the kinetics and the thermochemistry of individual elementary steps, so that we can estimate catalytic properties of metals and bimetallic alloys for their carbohydrate reforming potential, based on thermochemistry alone. The Mavrikakis group has recently completed the development of the detailed Potential Energy Surface characterizing MeOH decomposition on Pt surfaces, providing the basis for further understanding of selectivity trends in alcohol decomposition/reforming on late transition metals. The UW team recently published a comprehensive study on the preferential oxidation of CO in the presence of H₂ on Pt, Au, and Cu surfaces, using a combination of DFT and microkinetic modeling. The main conclusion is that Au and Cu are more efficient PROX catalysts than Pt at low temperatures, mainly because CO binds more weakly on these surfaces and because the barrier to CO oxidation is considerably lower than the corresponding barrier for OH formation on Au and Cu. PROX is an important catalytic reaction which can be used to clean up reformat fuels from CO impurities, and thus is directly relevant to the carbohydrate reforming project.

The Dumesic group has made significant progress with the aqueous phase reforming of sorbitol. They have shown that this process can be tailored to selectively produce a clean stream of heavier alkanes consisting primarily of butane, pentane and hexane. This process takes place by a bi-functional pathway involving first the formation of hydrogen and CO₂ on the appropriate metal catalyst and the dehydration of sorbitol on a solid acid catalyst or a mineral acid. These initial steps are followed by hydrogenation of the dehydrated reaction intermediates on the metal catalyst. When these steps are balanced properly, the hydrogen produced in the first step is fully consumed by hydrogenation of dehydrated reaction intermediates, leading to the overall conversion of sorbitol to alkanes plus CO₂ and water. The selectivities for production of alkanes can be varied by changing the catalyst composition, the pH of the feed, the reaction conditions, and modifying the reactor design.

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2. Wilson, O. M.; Scott, R. W. J.; Garcia-Martinez, J.; Crooks, R. M.; "Synthesis, Characterization and Structure-Selective Extraction of AuAg Bimetallic Nanoparticles", *J. Am. Chem. Soc.*, **2004**, in preparation.
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4. Kandoi S., Gokhale A. A., Grabow L. C., Dumesic J. A., Mavrikakis M., "Why Au and Cu are more selective than Pt for preferential oxidation of CO at low temperature", *Catalysis Letters* **93**, 93 (2004).
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6. Huber G. W., Cortright R. D., Dumesic J. A., "Renewable Alkanes by Aqueous Phase Reforming of Biomass-Derived Oxygenates", *Angewandte Chemie International Edition* **43**, 1549 (2004).

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Experimental and Theoretical Studies of Surface Oxametallacycles: Connections to Heterogeneous Olefin Epoxidation

Students: Suljo Linic (Ph.D. 2003), Jerome Jankowiak (Ph.D. expected 2004), Michael Enever (Ph.D. expected 2005)

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Goals: The goals of this research are to determine, by both experiment and theory, the effects of surface structure and composition on the formation, stability and reaction selectivity of the novel oxametallacycle intermediates that we have discovered in olefin epoxidation, and to demonstrate new approaches to catalyst design from first principles.

Recent Progress: Oxametallacycles are key intermediates in the chemistry of olefin epoxidation by silver. We have successfully demonstrated the existence of surface oxametallacycles, their spectroscopic signatures, and their role in the selective epoxidations of ethylene and butadiene with silver catalysts. This work has culminated in the development of a complete reaction coordinate, shown in Figure 1, and a microkinetic model for the epoxidation of ethylene to ethylene oxide with silver. These account for the kinetics of ethylene epoxidation with unpromoted catalysts, and demonstrate that the kinetically significant steps in the reaction sequence are oxygen dissociation and oxygen atom addition to ethylene to form the oxametallacycle. We have recently shown that oxametallacycle reactions control the selectivity of ethylene epoxidation catalysts at low conversions, and have predicted (using DFT) and verified bimetallic combinations that improve ethylene epoxidation selectivity.

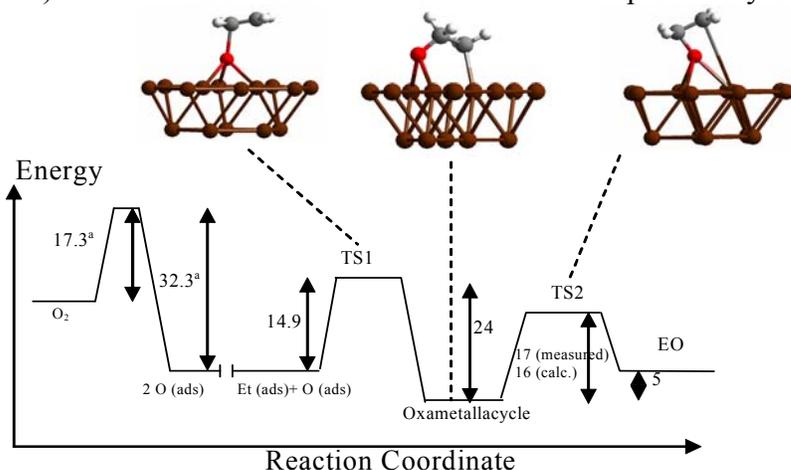


Figure 1. Reaction coordinate for ethylene epoxidation combining results from DFT calculations and surface science experiments.

We have used DFT to search for an energetically feasible, first order transition state that would lead from the oxametallacycle intermediate to acetaldehyde. Acetaldehyde is easily oxidized on silver to form surface acetates that are readily oxidized to form CO₂. The difference in Gibbs free energies of activation between the two reactions in Figure 2 is calculated to be 0.3 kcal/mol in favor of the formation of acetaldehyde vs. EO from the surface oxametallacycle. This indicates that the maximum selectivity to EO on unpromoted Ag is expected to be ~42% at 500 K, in agreement with the typical selectivities reported on unpromoted Ag.

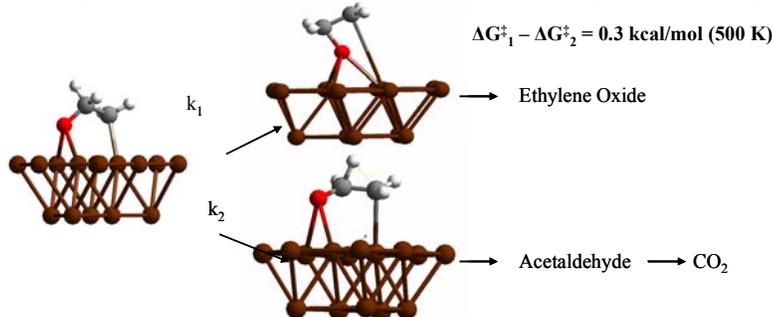


Figure 2. Competing oxametallacycle reaction channels.

We have examined quantitatively the kinetic isotope effect in the context of the mechanism in Figure 2. From the difference in activation barriers for oxametallacycle isomerization to acetaldehyde, we calculate the ratio k_{2H}/k_{2D} to be 2.7 at $T=420$ K. This suggests that the epoxide selectivity should increase from 49% to 73-74% at $T=420$ K when the reactant is switched from C₂H₄ to C₂D₄, using the reported selectivity of 49% for C₂H₄ epoxidation. This is in excellent agreement with the experimentally measured selectivity increase to 73% at 420 K.

Our goal has been the design of a stable catalyst that is capable of selectively converting ethylene and oxygen into ethylene oxide. The optimum catalyst should accentuate the difference between the activation barrier for production of acetaldehyde and the activation barrier for production of ethylene oxide. We have investigated bimetallics for this purpose using both computational and experimental tools. We predicted that a Cu/Ag alloy should be able to achieve selectivity for ethylene epoxidation that is greater than the selectivity of a pure Ag catalyst. To test the proposed hypothesis we synthesized high surface area Cu/Ag catalysts. These catalysts supported on porous α -Al₂O₃ monoliths. The Cu was deposited on the Ag catalyst via sequential impregnation and drying. Both catalysts were prepared following identical preparation procedures. We consistently observe approximately a 50% selectivity increase for the bimetallic catalysts compared to pure silver, as predicted from first principles. This example shows that first principles studies can be extremely valuable in the design of catalytic materials. This is, to our knowledge, the first example where the quantitative results of first principle approaches have been implemented to specify an alloy catalyst that is more selective than corresponding monometallic catalyst.

DOE Interest: The direct epoxidation of olefins remains one of the most challenging problems in heterogeneous catalysis. Although the epoxidation of ethylene by silver catalysts to form ethylene oxide (EO) has been practiced for decades, it is striking how little progress has been made in expanding this chemistry to other products and processes that would offer

higher efficiencies than current technologies. Our elucidation of the central role of the oxametallacycle in olefin epoxidation provides a platform, not only for understanding catalyst performance, but also for exploring the influence of catalyst promoters at the molecular level, and ultimately for rational catalyst design for new or improved processes.

Future Plans

1. Experimental and theoretical studies of promoter effects on oxametallacycle stability.
2. Surface science and DFT studies of oxametallacycle formation from other olefin epoxides.
3. Short contact time reactor studies of promoted bimetallic catalysts.

Publications (2002-present)

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2. S. Linic and M. A. Barteau, "Formation of a stable surface oxametallacycle that produces ethylene oxide," *Journal of the American Chemical Society*, **124**, 310 (2002).
3. M. A. Barteau, "New Perspectives on Direct Heterogeneous Olefin Epoxidation," *Topics in Catalysis*, **22**, 1 (2003).
4. S. Linic, J. W. Medlin and M.A. Barteau, "Synthesis of oxametallacycles from 2-iodoethanol on Ag(111) and the structure dependence of their reactivity," *Langmuir*, **18**, 5197 (2002).
5. S. Linic and M. A. Barteau, "Construction of a Reaction Coordinate and a Microkinetic Model for Ethylene Epoxidation on Silver from DFT Calculations and Surface Science Experiments," *Journal of Catalysis*, **214**, 200 (2003).
6. S. Linic and M. A. Barteau, "Control of Ethylene Epoxidation Selectivity by Surface Oxametallacycles," *Journal of the American Chemical Society*, **125**, 4034 (2003).
7. H. Piao, K. Adib, Z. Chang, J. Hrbek, M. Enever, M. A. Barteau and D. Mullins, "Multi-step reaction processes in epoxide formation from 1-chloro-2-methyl-2-propanol on Ag(110) revealed by TPXPS and TPD experiments," *Journal of Physical Chemistry B*, **107**, 13976 (2003).
8. S. Linic, J. Jankowiak and M. A. Barteau, "Selectivity driven design of bimetallic ethylene epoxidation catalysts from first principles," *Journal of Catalysis* (in press).
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11. M. Enever, S. Linic, K. Uffalussy, J.M. Vohs and M. A. Barteau, "Synthesis, Structure and Reactions of Stable Oxametallacycles from Styrene Oxide on Ag(111)," *Journal of Physical Chemistry B* (submitted).

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UC Riverside Portion of: Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes Through Tailored Nanostructures.

Postdoc: B. V. Rao

Students: R. Perry, E. Ulin-Avila, J. Zhang

Collaborators: Adzic, Feibelman, Heinz, Murray, S. O'Brien, T.S. Rahman

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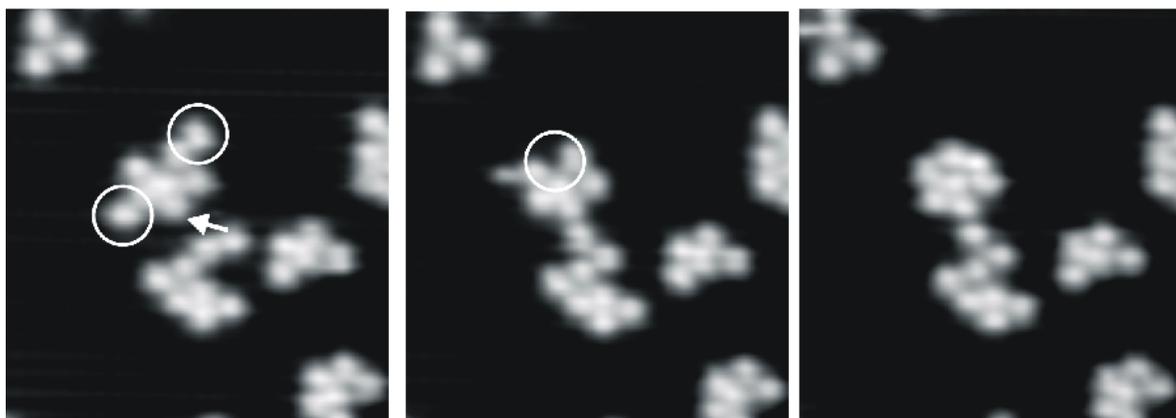
Goal

We perform fundamental studies of surface dynamic behavior in order to devise methods that enhance catalytic activity of supported nanoparticles by controlling surface diffusion behavior.

Progress During the First 6 Month of the Funding Period:

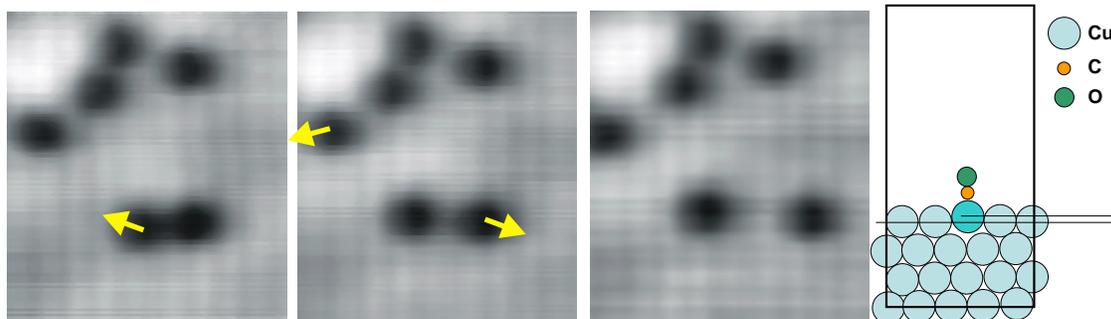
During the first six month of the project, experimental work focused mainly on equipment development and installation, as well as on software development for data analysis as anticipated in the original proposal. In addition, we performed diffusion measurements addressing CO and Thiophenol molecules on a flat Cu(111) surface. This data is required for reference in future experiments of photoexcited diffusion and in theoretical investigations by Feibelman and Rahman.

Thermal Thiophenol Diffusion: The behavior of sulfur containing compounds on metal catalyst particles is important for the hydrodesulfurization of gasoline. We investigated the diffusion behavior of thiophenol on Cu(111) in preparation for anticipated measurements of similar process on nanoparticles and under high excitation levels. Currently, the Rahman group performs calculation of the diffusion barriers in this system.



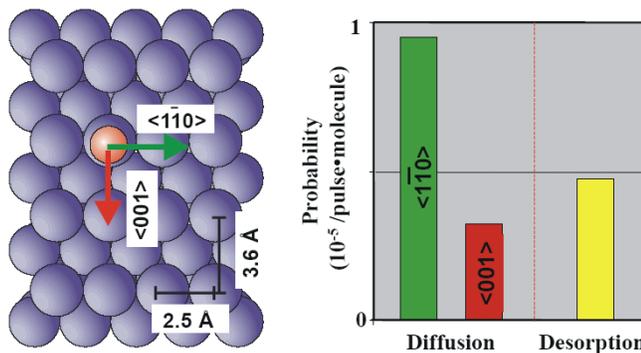
Diffusion and Cluster Formation of Thiophenol on Cu(111) at 90 K (-2V, 0.2 nA, 75x75Å)

Thermal CO Diffusion: We use CO molecules to investigate the effects of adsorbate-adsorbate interactions on the diffusive behavior. For this purpose, we follow a distribution of CO molecules on Cu(111) over time and determine their place exchange vector and frequency in correlation to their nearest neighbors. We anticipate to learn from these experiments how nearest neighbors can steer molecular dynamics on surfaces. Currently, the Rahman group performs calculations addressing the impact of neighbor interactions on CO diffusion barriers.



Diffusion of CO on Cu(111) at 30 K (-200mV, 0.1 nA, 45x40 Å) and relaxation of supporting Cu-atom as calculated by the Rahman group.

Excited CO Diffusion: In collaboration with the Heinz Lab, we followed the movement of CO molecules on Cu(110) after optical excitation of the substrate. Such measurements offer atomic resolution regarding the molecular adsites while reaching excitation levels comparable to high-temperature heterogeneous catalysis. Correspondingly, we find that low and high energy surface processes, such as diffusion along the atomic rows of Cu(110) and desorption from Cu(110) occur almost with the same likelihood, quite different from the low-temperature thermal case.



DOE Interest

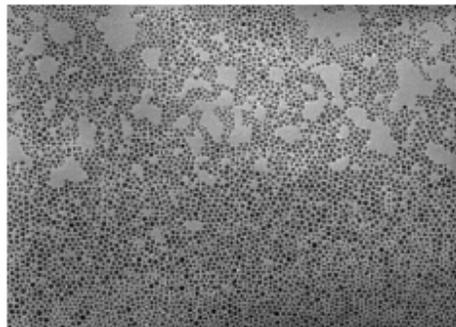
Catalytic reactions have great importance for a broad range of industrial and environmental processes ranging from catalytic CO oxidation in exhaust systems to catalytic hydro-desulfurization of gasoline. This project aims at understanding catalytic processes on the atomic scale by development and applications of methods that can follow molecular dynamics at high excitation level.

Future Plans

Optical Excitation of Surface Diffusion: Since December 2003 we are working on the installation of an upgrade of our laser system. This cavity dumper has passed initial tests and

will soon be utilized to excite molecular diffusion. These experiments will allow us atomic scale access to molecular reactions that require excitation levels comparable to several hundred Kelvin.

Cluster Deposition: At a recent meeting of the project participants in NY, we received samples of metal and semiconductor nanoclusters from the O'Brien group. Currently we work on the deposition of these samples. For this purpose, we develop an inkjet printer based system for the injection of nanoscopic volumes of chloroformic suspensions into UHV. Initial tests addressed sample degradation as a consequence of exposure to large quantities of chloroform: Exposure of Cu(111) at ambient temperatures to several ML (MegaLangmuir) of chloroform appears not to degrade the quality of the sample significantly and high-resolution scanning is still possible.



CuO₂ cluster sample prepared by the O'Brien group

Adsorbate Cluster Interaction: We anticipate the investigation of the transfer of adsorbates from a support to a deposited cluster both by thermal excitation of the adsorbates and by optical excitation of the sample surface. These investigations will provide atomically-resolved data on the support/catalyst interaction in an excitation regime comparable to realistic catalytic reactions.

Publications (2003-4)

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Electron transfer, Oxygen activation, and Nitric Oxide biosynthesis in NOS enzymes: Fundamental Understanding of Biocatalysis through the NOS reaction

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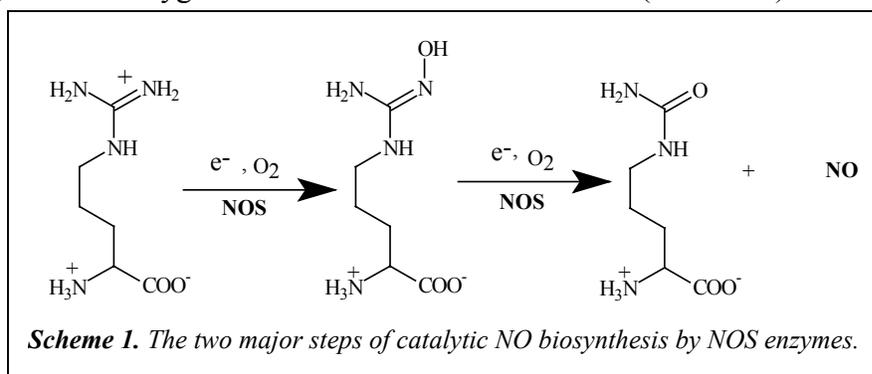
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Goal

To develop fundamental understanding of synergistic structural and kinetic control of the nitric oxide synthase overall biocatalysis, with particular emphasis on molecular mechanisms involved in electron transport and oxygen activation.

Recent Progress

The biological catalysis leading to the synthesis of Nitric oxide (NO) continues to be the focus of intense mechanistic and kinetic investigations. The biocatalytic synthesis of NO takes place on impressive molecular machineries, called nitric oxide synthases (NOSs), through a five-electron oxidation process of substrate L-arginine. The reaction, which takes place on an Fe-heme active center, proceeds in two steps via an N^ω-hydroxy-L-arginine intermediate, and uses oxygen as a co-substrate in the reaction (Scheme 1).



Our project uses an integrative approach using spectro-electrochemistry, site-directed mutagenesis/molecular biology and computational chemistry to develop molecular-level understanding of the NOS biocatalysis, and particularly how the long-range structural control and tunable redox activity affect kinetics of critical steps of this catalysis. In the present work we explore the role of the cofactor tetrahydrobiopterin (H₄B) in potential electron transfers during critical steps of oxygen activation.

Cofactor-Assisted Tunable Redox Activity: Direct electrochemistry carried on the heme domain of NOS (NOSoxy) shows that the redox potential of the electron transfer to the heme-Fe^{III} is modulated by the H₄B cofactor.¹ The binding of H₄B shifts the formal potential of the heme in NOSoxy towards more positive potentials, and seems to indicate that the dissociation constant of H₄B from the Fe^{II}-NOS domain is *ca.* 50-fold smaller than from the Fe^{III}-resting state (Figure 1). This is fundamentally very interesting in regards to long-range structural control; the mere binding of H₄B cofactor serves to tune redox properties of the heme for the first electron transfer to proceed, which in turn more likely triggers some structural change leading to tight binding of the cofactor away from the heme.

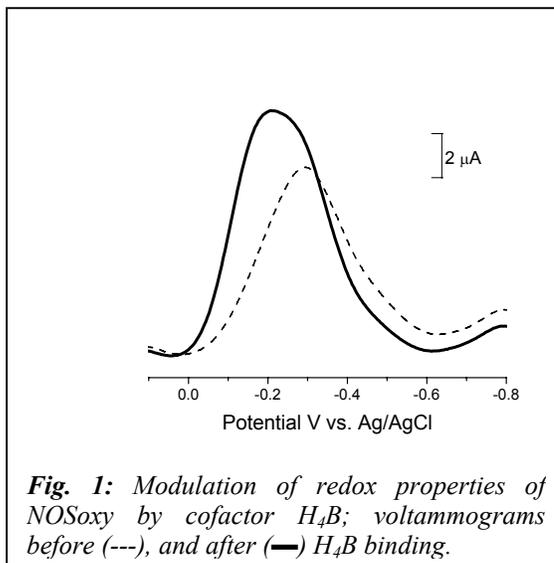
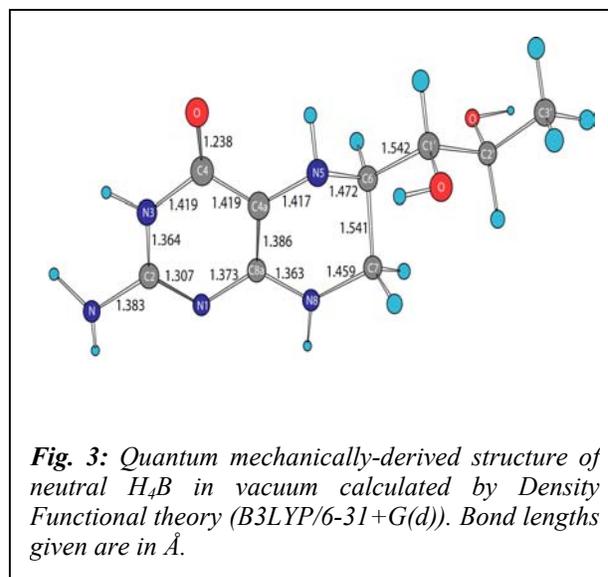
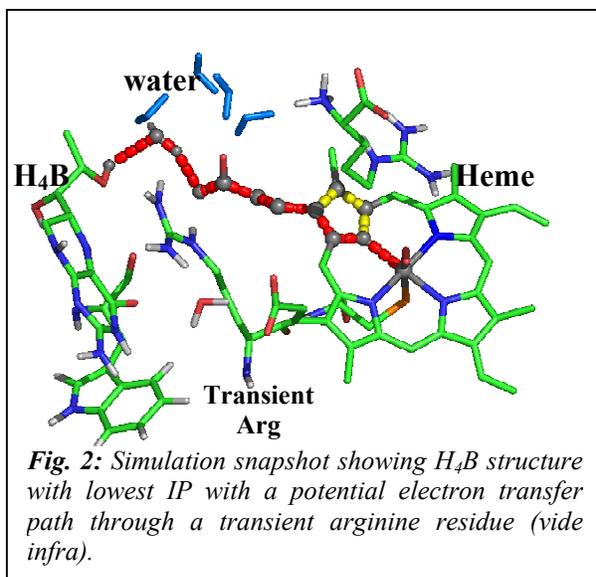


Fig. 1: Modulation of redox properties of NOSoxy by cofactor H₄B; voltammograms before (---), and after (—) H₄B binding.

H₄B and potential electron transfer in the oxygen activation process: A fast electrocatalytic process takes place on NOSoxy-modified electrodes in the presence of oxygen at the level of Fe^{III}/Fe^{II}-NOSoxy redox couple. Our fast-scan electrochemical experiments in these conditions point to a transient intermediate, possibly the ferrous-dioxy complex, whose lifetime depends on the presence of cofactor H₄B. These electrochemical results come in parallel with increasing evidence that the H₄B cofactor is involved in a crucial electron transfer (the second electron) in the oxygen activation process. Whether this crucial electron transfer from the H₄B cofactor to the heme moiety is governed by kinetic or thermodynamic constraints is yet to be fully addressed. This first requires independent study of redox properties of H₄B as a free entity and in protein environment.

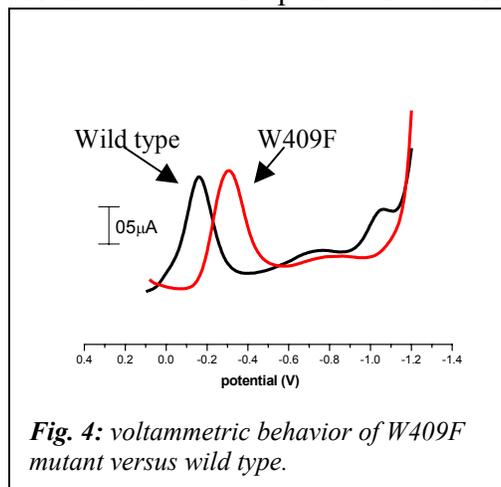
Two or one electron transfers on the ms time scale?; thermodynamic midpotential of H₄B/H₄B⁺⁺: One key aspect in investigating the redox behavior of the biopterin cofactor is the ability to measure the absolute number of electrons involved on the time scale of voltammetry (ms); this provides insights on the mechanism of its oxidation and on whether one can use the potentials measured outside the protein environment to draw conclusions on its involvement in the NOS reaction. Our measurements using chronoamperometry coupled to steady-state currents collected on ultramicroelectrodes indicate that the irreversible electro-oxidation of H₄B cofactor in pH 7 buffer actually involves 2-electron transfers per molecule, possibly invoking homogenous bimolecular disproportionation. The latter cannot happen in NOS and therefore the measured potential for free H₄B cannot be used to draw thermodynamic conclusions for the NOS reaction. Our initial attempts to measure the thermodynamic formal potential for the monoelectronic oxidation of H₄B point to fairly high oxidation potential (*ca.* 0.6 V/NHE), which suggests that the biopterin oxidation in the NOS reaction, if any, is highly modulated by the protein environment. In fact molecular dynamic simulation carried on NOS heme domain shows that the H₄B structure likely involved in electron transfer to the heme during the NOS reaction (with a very low ionization potential) is entirely different from the structure observed in the crystal structure (Figure 2).



Quantum mechanics-derived structure of H_4B : We performed quantum mechanical calculations on neutral H_4B in vacuum with Hartree-Fock using Density Functional Theory (B3LYP) Hamiltonians and 6-31+G(d) basis set. The quantum mechanical-derived structure (with bond lengths, bond angles and dihedral angles) is shown in figure 3. Subsequently, the structure of H_4B was extracted from the crystal structure of inducible NOS (iNOS, pdb id: 1NSI), hydrogen atoms were added and the all-atom H_4B structure was geometry optimized using the GROMACS program.⁴ We compared the geometry of H_4B obtained from quantum mechanical calculations (Figure 3) with both the molecular mechanics structure and the geometry of H_4B in the crystal structure (i.e. when bound to iNOS). Comparison of standard deviation between internal coordinates (bond lengths, bond angles, dihedral angles) of the crystal and molecular mechanics structures, on the one hand, and the quantum mechanical structure on the other hand shows that the crystal structure of BH_4 is very similar to the one calculated by quantum mechanics, which suggests that in the crystal structure of iNOS the H_4B cofactor is bound to in a relaxed state. This computational insight, together with our experimental electrochemical measurements on relaxed H_4B reinforces the idea that the structure involved in electron transfer to the heme must be a kinetic intermediate/transition state with an arrangement leading to favorable electron transfer.

OPLS parameters for further molecular dynamics: The OPLS force field gives more accurate electrostatic description of molecules and solvent because the partial atomic charges used in this force field are obtained from quantum mechanical calculations (with CHelpG method⁵). The quantum mechanics-derived structure of the biopterin cofactor (bond lengths, bond angles and dihedral angles) was used to derive OPLS parameters for neutral H_4B (i.e. partial atomic charges, bond stretching, angle bending constants, Ryckaert-Bellmans coefficients for the dihedral potential function, and Lennard-Jones parameters). Further investigations will focus on the derivation of an OPLS force field for the heme with the cysteine-thiolate coordination. This will allow extensive molecular dynamics simulation to accurately analyze the effect of protein dynamics and especially H_4B -neighboring aminoacids on the ionization potential of this cofactor with regards to the electron transfer to the heme moiety during the activation of molecular oxygen.

Investigating long-range structural and electronic control with site-directed mutagenesis: Site-directed mutagenesis is an important tool that we use to respond to feedback from spectro-electrochemical measurements and computational exploration. We use this approach to develop our molecular-level understanding of long-range structural and electronic control in the NOS reaction. Mutants questioning the role of particular residues (for instance the arginine that is potentially involved in electron transfer to the heme, see figure 2) can be prepared, purified, and tested experimentally. An example illustrating both the importance of this approach and the sensitivity of electrochemical measurements is given here (figure 4). It was hypothesized that a conserved proximal tryptophane (Trp 409 in) imparts unique electronic properties of Fe-heme in NOSoxy, which exhibits a distinctive electrochemical response compared to other P450s. This work shows that the W409F mutation, which apparently abolishes a vital hydrogen bonding to proximal cysteinate, has a drastic impact on the redox behavior of the heme in NOSoxy and can be easily detected by direct electrochemical measurements.



DOE Interest

Developing a molecular-level understanding of the functioning of nature's best optimized catalysts (enzymes), their structural flexibility, and long-range tight control of reactivity and selectivity, is a pre-requisite to meet the challenge for developing grounds for predictive catalysis, and to integrate these important concepts in the molecular design of next generation of catalysts.

Future Plans

Detailed study of tunable redox properties of heme in NOSoxys and study of enzyme turnover: We need to study very carefully detailed molecular/structural parameters governing the electronic properties of NOS active site and how these are used in various steps of the catalysis. Detailed study of enzyme turnover on modified electrodes is also underway.

Molecular dynamics simulations with OPLS parameters and QM/MM calculations: We are conducting further molecular dynamics simulations and QM/MM calculations to investigate critical steps in this complex catalysis. Insights from these studies will be fed into molecular biology efforts and site directed mutagenesis to construct a molecular-level understanding of crucial steps of the catalysis

Preparation and experimental measurements on specific mutants: Mutants addressing the molecular role of specific residues, including the transient arginine suspected to have a role in electron transport, or conserved tryptophane residues near the heme will be prepared for experimental investigation.

Publications (2004-)

“Direct Electron Transfer to Oxygenase Domain of Neuronal Nitric Oxide Synthase (NOS): A new Gate to Explore Unique Redox Properties of NOS Enzymes” Bayachou, M.; Boutros, J.A. *J. Am. Chem. Soc.* **2004**, *under peer-review*.

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Catalysts for Selective Olefin Oligomerization and Polymerization

Students: Wasilke, J., Diamanti, S.

Postdoctoral Fellows: Fang, X.; Chen, Y.

Collaborators: Kramer, E. (UCSB), Fredrickson, G. (UCSB), Baker, R. T. (LANL)

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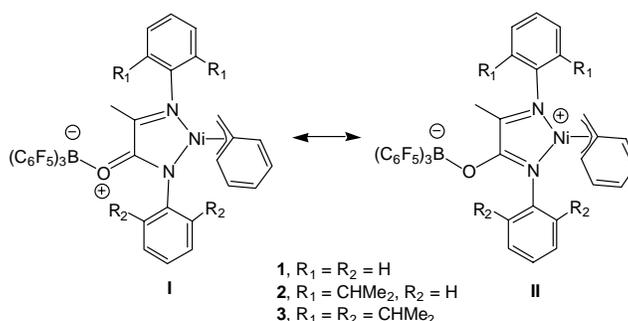
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Goals

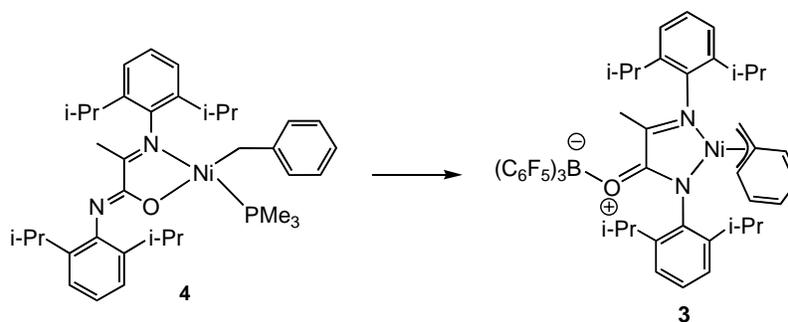
Provide homogeneous organometallic complexes that enable novel olefin polymerization reactions including concurrent tandem catalysis and living polymerization of ethylene with functionalized co-monomers.

Recent Progress

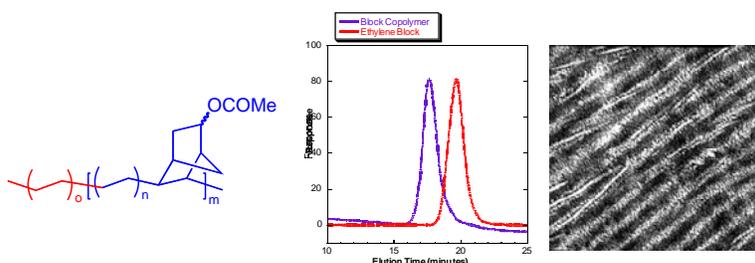
We recently reported the activation of nickel olefin polymerization initiators by attachment of a Lewis acid on the carbonyl functionality at a site removed from the monomer trajectory. Compounds **1-3** were recently prepared in our labs and exemplify our strategy. Resonance structures **I** and **II** illustrate the loss of electron density at nickel upon coordination to $B(C_6F_5)_3$.



α -Iminocarboxamide ligands were chosen because they can be readily prepared and because the size of the nitrogen aryl groups can be varied to modulate steric effects. Of interest to us was to control the size of the substituents on the pseudo axial sites, since blocking these sites in other nickel catalysts reduces chain transfer to monomer. Incorporation of the η^3 -benzyl fragment was selected, instead of the more frequently used methallyl, because it displays faster rates of initiation. Compound **3** is generated by addition of two equivalents of $B(C_6F_5)_3$ to compound **4**, as shown below. The reaction produces an equivalent of $Me_3P-B(C_6F_5)_3$, which precipitates out of solution. Compound **2** was used in the design of a triple component concurrent tandem catalysis method of preparing various types of branched polyethylene from ethylene alone. Much of this work has been published previously.



A substantial fraction of our recent work has been focused on the reactivity of compound **4** in the presence of phosphine acceptors, such as Ni(COD)₂. We found that the resulting solutions provided active initiators for the *quasi*-living homopolymerization of ethylene and, more significantly, the *quasi*-living co-polymerization of ethylene with 5-norbornen-2-yl acetate. These materials show microphase separation into functionality-rich domains and polyethylene-rich domains. Furthermore, they have been shown to be excellent compatibilizers for polyolefins with more polar materials, such as polycarbonates.



Efforts to identify a neutral, catalytically significant species were not successful. When mixtures of **4** and Ni(COD)₂ are mixed in C₆D₆ at room temperature and the solution is monitored by ¹H NMR spectroscopy, one observes no reaction before Ni(COD)₂ decomposition begins to occur in *ca.* 1.5 hours. We propose a similar argument to that given by Gibson for the activation of [P,O]Ni catalysts by Ni(COD)₂, where ethylene displaces a COD ligand. Once this step takes place, the resulting nickel species reacts with **1** to generate the active site. If COD displacement is slow, one would expect a slower initiation step relative to the propagation rate.

DOE Interest

New catalysts have been demonstrated for the polymerization of ethylene with monomers bearing polar functionalities. Furthermore, the controlled reactivity of these polymerization sites allows for the elaboration of more complex polymer structures, such as block copolymers with unique bulk properties. More efficient manufacturing methods and use of commodity plastics translates to a better management of petrochemical resources.

Future Plans

Our immediate goals are to improve the synthesis of complexes such as **4** and to probe the possibility that neutral species are responsible for the copolymerization reactions. The latter will be achieved by targeting the synthesis of the supposed catalytic

complexes and by examination of the resulting reactivity. We also recognize that the controlled reactivity afforded by compound **4**/Ni(COD)₂ may provide for unique methods of block copolymer synthesis. For example, it may be interesting to investigate how changes in ethylene pressure can be used to control the fraction of the polar monomer in the polymer chain. If these changes can be done within the timescale of the propagation sequence, we may be able to access block-copolymer structures simply by raising ethylene pressure.

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Catalysts for the Selective Synthesis of Fuels and Chemicals

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Goal

Structure-performance relationships are difficult to determine for most heterogeneous catalysts because such catalysts often contain a broad distribution of active sites. To overcome this limitation, we have been investigating catalysts with well-defined active sites. The goal of this project is to develop and apply both experimental and theoretical methods for obtaining a fundamental understanding of how the local composition and structure of a site affect its catalytic activity and selectivity.

Recent Progress

High-Activity Catalysts for Methanol Synthesis: The conversion of synthesis gas to methanol is limited by thermodynamics. Since the reaction is exothermic, higher per pass conversions are attainable at lower temperatures, but this requires catalysts that are more active than those currently available. We have shown that Cu/ZrO₂ catalysts can be made which exhibit high activity even at temperatures as low as 200°C.^{2,6} *In situ* infrared studies reveal that such catalysts are bifunctional. The zirconia serves to adsorb CO and all carbon-containing intermediates, whereas Cu serves primarily as a source of atomic hydrogen, which spills over on to the surface of the zirconia where the hydrogenation of CO occurs. The activity of Cu/ZrO₂ catalysts is intimately tied to the nature of the hydroxyl groups present on the zirconia surface. OH groups in which the O atom is coordinated to three Zr atoms are particularly effective for the adsorption of CO to form formate species. The proportion of such species is significantly higher on the surface of monoclinic zirconia than on the surface of tetragonal zirconia. Correspondingly, the activity of Cu/m-ZrO₂ is fourfold higher than that of Cu/t-ZrO₂. The substitution of Ce into the lattice of t-ZrO₂ results in a further increase in activity. Thus, Cu/t-Ce_{0.3}Zr_{0.7}O₂ is more than six fold more active than Cu/t-ZrO₂.

Catalytic Properties of Isolated Vanadyl Groups: Isolated vanadyl groups supported on metal oxides are active for a variety of oxidation reactions. We have prepared and characterized vanadyl groups supported on SBA-15. The occurrence of isolated VO₄ units was confirmed by Raman and UV-Visible spectroscopy, and by EXAFS. By varying the surface density of vanadia from 0.1 to 0.75 V/nm², it is possible

to vary the average distance between VO_4 units from 3.3 to 0.8 nm. The apparent activation energy for methanol oxidation to formaldehyde decreased with increasing VO_4 density. This trend is consistent with quantum chemical calculations, which show that the transition state for forming formaldehyde from an adsorbed methoxide species is strained when the reaction occurs on a completely isolated VO_4 , but becomes more relaxed when the transition state is achieved via the interaction of two VO_4 units proximate to each other.⁷

Olefin Epoxidation by Fe-Porphyrins: Iron porphyrins are effective catalysts for the epoxidation of olefins, but considerable controversy still exists as to the reaction mechanism and the effects of reaction conditions. We have initiated detailed studies of the oxidation of cyclooctene by H_2O_2 using FeTPFPFCl as the catalyst. The concentration of cyclooctene oxide is followed by GC, whereas the concentration of H_2O_2 is followed by ^1H NMR. The dynamics of Fe(III) porphyrin transformation to Fe(IV) porphyrin are followed by in situ UV-Visible spectroscopy. Extensive work on different parts of the mechanism suggests that epoxidation occurs via the scheme shown below:

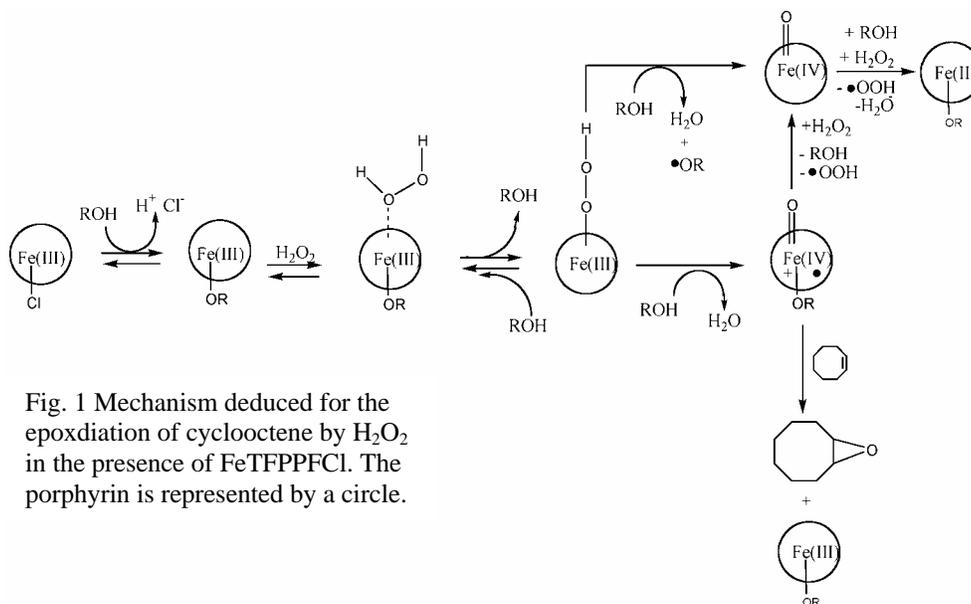


Fig. 1 Mechanism deduced for the epoxidation of cyclooctene by H_2O_2 in the presence of FeTPFPFCl . The porphyrin is represented by a circle.

Quantum Chemical Investigations of Reaction Pathways: In collaboration with Prof. Martin Head-Gordon, we have initiated quantum chemical studies aimed at elucidating reaction pathways occurring on single-site catalysts. We are also working on the development of novel approaches for conducting high-level, *ab initio*, quantum chemical calculations on active centers that are embedded in a surrounding medium that is treated at a lower level of theory. Methods have also been developed for the rapid determination of first and second derivative of the potential surface on which a reaction occurs.^{5,9} This advance accelerates search for transition states. As a target for the applications of methodological advances, we have focused on understanding the interactions of H_2O_2 with a vanadyl pyrazinic acid complex. A review has been written

defining the challenges for the application of quantum chemical calculations to problems in the field of catalysis.¹⁰

DOE Interest

The preparation and characterization of well-defined catalytically active sites is vital to the development of a fundamental understanding of the effects of local composition and structure on the activity and selectivity of such sites. Isolated-site catalysts are also well suited for theoretical investigations, which can explain how changes in the local environment of a site affect its catalytic performance. The knowledge gained from such studies will contribute to the development of active and highly selective catalysts.

Future Plans

High-Activity Catalysts for Methanol Synthesis: Work on the effects of metal cations substituted into the lattice of ZrO_2 will be continued with the aim of understanding the influence of the added elements on the Lewis and Brønsted acid/base properties of the oxide. Carefully prepared samples of ZrO_2 containing Ce, La, and Ti will be characterized to establish the extent of dispersion of the added metal into the framework. This will be probed by examining changes in the lattice parameters of the host oxide, and by use of EXAFS to determine the coordination number and bond distances of the added metal. IR spectra of H_2 and CH_4 adsorbed at liquid nitrogen temperature will be used to probe the strength and concentration of Lewis acid centers, since the chemical shifts in the spectra of these molecules have recently been shown to be a very sensitive probe of Lewis acidity. CO and CO_2 will also be used as probe molecules. In collaboration with Martin Head-Gordon, we will carry out quantum chemical calculations to determine the causes for the observed effects. Of particular interest will be to establish how small changes in the lattice parameter and the distribution of local charge affect site acidity and basicity.

Catalytic Properties of Isolated Metal-Oxo Groups: We will continue our investigations of isolated-site catalysts.⁸ We will extend our efforts on VO_x sites to include other metal oxo structures, such as MoO_x , ZnO_x , NbO_x , and SbO_x . All of the latter oxides have been shown to be catalytically active. A variety of molecular precursors will be used to prepare dispersed oxo structures, which will then be characterized by Raman and UV-visible spectroscopy, and by EXAFS. The interpretation of EXAFS spectra will be aided by carrying out quantum chemical calculations of the structures believed to be present in our samples and then simulating the X-ray scattering function for these structures.

Olefin Epoxidation by Fe-Porphyrins: Our studies of oxidation of hydrocarbons using Fe-porphyrins will be continued with an aim of establishing the effects of porphyrin composition on the rate parameters of individual elementary processes. Substitution of Fe for Co or Mn will also be explored to determine the effect of metal composition. Efforts will also be initiated to identify encapsulation strategies that might be used to trap individual metal-porphyrin complexes. Such site isolation could be used

to determine whether stereospecificity might be induced by using encapsulation methods which allow access of a reactant by only one channel. In this connection, comparisons will be made with studies of single Fe centers bonded to silica, in order to establish the effects of the atoms to which Fe is bound on its catalytic properties.

Quantum Chemical Investigations of Reaction Pathways: We will continue our collaboration with Martin Head-Gordon on the development of novel cluster embedding approaches. We plan to use the local space approximation (LSA), since this method provides an improvement over all other embedding techniques by fully accounting for self-consistent charge transfer between the local region and its environment. We plan to use exponentially formulated unitary transformations as well as tensor formulation of curvy-step-based energy minimization to radically improve the LSA method and convert it to a standard tool for quantum mechanical calculations on large systems of interest for a broad range of problems in catalysis.

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Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds

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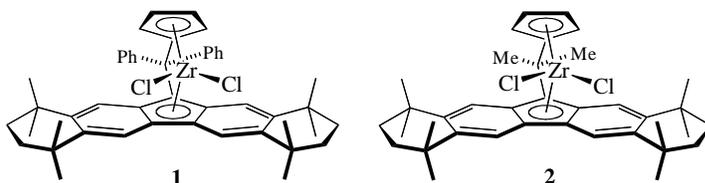
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Goal

Provide understanding of ligand effects on polyolefin stereochemistry and elementary rates for olefin polymerization with well-defined catalysts in order to guide development of superior catalyst systems

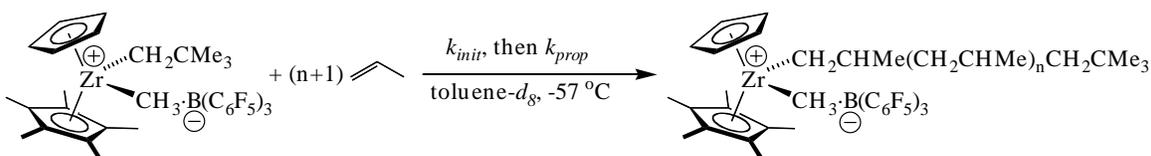
Recent Progress

Modern single-site metallocene catalysts for propene polymerization have provided new polymer microstructures and the opportunity to elucidate important aspects of catalyst stereocontrol. Highly stereoregular syndiotactic polypropylene is obtained with the catalyst systems $\text{Ph}_2\text{C}(\text{Oct})(\text{C}_5\text{H}_4)\text{ZrCl}_2/\text{MAO}$ (**1**/MAO) (Oct = octamethyloctahydrodibenzofluorenyl; MAO = methylaluminoxane) and $\text{Me}_2\text{C}(\text{Oct})(\text{C}_5\text{H}_4)\text{ZrCl}_2/\text{MAO}$ (**2**/MAO).



The syndiotactic polypropylenes obtained are largely devoid of stereoerrors by ^{13}C NMR analysis ($[r] > 98\%$) and melting temperatures as high as 153°C or 154°C (from **1** and **2**, respectively) are found for the thermally quenched polymers (without annealing). A related hafnium catalytic system, $\text{Ph}_2\text{C}(\text{Tet})(\text{C}_5\text{H}_4)\text{HfCl}_2/\text{MAO}$ (**3**) (Tet = tetramethyltetrahydrobenzofluorenyl) was found to be the most syndioselective of the hafnocenes tested ($T_m = 141^\circ\text{C}$). These metallocene dichloride precatalysts represent the first examples of transition metal complexes containing the Oct or Tet ligands. The solid state crystal structures of **1**, the diprotio ligand precursor of **1** ($\text{Ph}_2\text{C}(\text{OctH})(\text{C}_5\text{H}_5)$), and the zirconium analog of **3**, $\text{Ph}_2\text{C}(\text{Tet})(\text{C}_5\text{H}_4)\text{ZrCl}_2$, have been established by X-ray methods. Distal ligand influences are thus demonstrated to have an unexpectedly large effect on polymer stereochemistry.

To date, much of the information about the rates of initiation, propagation and chain transfer has been obtained from indirect studies, based on MW and productivity data. These phenomena do not address the likely highly variable (and likely low percentage) active site concentrations from system to system. Accordingly, a series of alkyl zirconocenium cations has been developed to model the propagating catalyst species in metallocenium-catalyzed α -olefin polymerization. These catalysts have allowed details of the mechanism of propene polymerization to be examined using direct NMR methods. The $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}(\text{CH}_2\text{CMe}_3)]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ catalyst is a suitable initiator for propene polymerization and for use in kinetic studies. Because the neopentyl group resembles the growing polymer chain, initiation is comparable in rate to propagation, and thus all zirconium centers soon participate enter the propagation cycle. These experiments represent some of the first direct mechanistic studies on functioning zirconocene catalysts for propene polymerization, where the $[\text{Zr}_{\text{active}}]$ is established. The study of propagation kinetics by this catalyst has been conducted. A second-order elementary rate constant for propagation, k_{prop} , is directly determined for zirconocenium-catalyzed propene polymerization. Kinetics of insertion into the $\{\text{Zr}\}\text{-R}$ (where $\text{R} = \text{CH}_2\text{CMe}_3$ or polymeryl) bond has been studied for other linear and branched α -olefins. These techniques are applied to exploring temperature, solvent, and ion effects on propagation kinetics for these catalyst systems.



DOE Interest

This new information on catalyst design and performance may lead to new types of polymers and/or new chemical transformations between hydrocarbons and transition metal centers, ultimately contributing to the development of catalytic reactions for the production of fuels, commodity and polymeric materials.

Future Plans

Now that suitably clean systems have been developed, we plan to measure the initiation, propagation and chain transfer rates for propylene and other olefins (butene, isobutene, branched α -olefins, etc.) as the cyclopentadienyl ligands, solvents, counter-anions (and their concentrations) are varied.

We are also examining the possibility that kinetic resolutions of chiral α -olefins (*e.g.* 3-methyl-1-pentene) might be effected by enantiopure, nonmetallocene catalyst systems. To this end we are currently preparing tetradentate, monoanionic phenolate ligands for use with group 3 metals that may be elaborated to include chiral versions.

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Strategic Design of Novel Catalysts for the Selective Synthesis of Fuels and Chemicals

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Goals

This program focuses on the design and understanding of novel homogeneous catalysts. Of particular interest are molecular systems capable of converting alkanes to metal complexes, and ultimately to alkenes and other functionalized organic products, with applications of these reactions to the atom-economical synthesis of commodity and fine chemicals. To achieve these goals a molecular understanding of catalytically active centers and fundamental organometallic reaction steps, of the type frequently encountered in catalytic cycles, is sought, together with the synthesis of potentially active metal centers in unusual chemical and physical environments. Significant parts of this work have been carried out in collaboration with other investigators at LBNL, the University of California, Berkeley, the University of North Carolina, Chapel Hill, and the Pharmacia/Pfizer Company.

Recent Progress

C-H Activation by Transition Metal Complexes (collaborative project with T. D. Tilley). During the past year we have explored further catalytic applications of our cationic Ir(III) complexes that catalyze efficient exchange of deuterium into organic molecules. Our most important finding was that this reaction can be carried out in polar solvents without immediately destroying the catalysts, and even labeled water (D₂O), the least expensive source of deuterium, can be used as a source of isotope label. Several new chelating ligands were explored to enhance the efficiency and stability of the catalyst system.

Catalytic Deuterium and Tritium Labeling of Molecules Relevant to Medicinal Chemistry Using Cationic Iridium Complexes (collaboration with M. Skaddan, Pfizer Global Research and Development). Our cationic iridium complexes of general formula Cp*(PMe₃)IrR⁺ have been used to introduce deuterium stoichiometrically into substituted naphthalene and benzene templates and several "drug-like" entities. We have found that efficient exchange occurs with several organic molecules using the cationic trihydride complex [Cp*(PMe₃)Ir(H)₃]⁺ as the catalyst precursor and deuterated water or acetone as solvent and deuterium sources. The exchange process is tolerant of a wide range of functional groups. Labeling of the anti-coagulant warfarin using subatmospheric pressures of tritium gas led to specific activities rivaling more conventional labeling methods. This work has generated strong interest from both Pfizer and Merck, and we have signed material transfer agreements to give both companies access to the catalysts for further exploratory studies.

Catalytic reactions of New Pincer Ligand Complexes (collaborative project with T. D. Tilley). The properties of a series of complexes whose synthesis was worked out

last year, bearing ligands in which two chelating arms are bound to the *meta* position of an aromatic ring (so-called “pincer” ligands), have been investigated. These studies have led to the isolation and full characterization of two novel paramagnetic Rh(II) complexes. This class of complexes has been used to carry out catalytic formation of aziridines (three-membered nitrogen-containing ring compounds) from imines and organic diazo compounds, and enantioselective synthesis of cyclopropanes from alkenes and diazo compounds.

Carbon-Carbon Bond Activation by Transition Metal Complexes (collaboration with M. S. Brookhart, University of North Carolina, Chapel Hill). C-C bond activation reactions are more rare than C-H bond activation processes, so we have continued our studies of the metal-mediated process that cleaves C-C bonds in organic nitriles that we reported last year. This has resulted in a substantially improved understanding of the mechanism of the reaction.

Generation of Carbanions by Direct Thermolysis of Acyliridium Complexes. We have found that heating acyl hydride complexes of general structure $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{COR})$, bearing certain types of R groups, undergo elimination of RH rather than aldehyde (RCHO). To our knowledge, this is a new type of primary organometallic transformation. We have obtained preliminary evidence that the reaction proceeds via iridium cation/carbanion ion pairs $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{CO})]^+\text{R}^-$.

Application of Catalytic C-H Activation Reactions to the Synthesis of Physiologically Active Organic Molecules (collaboration with J. A. Ellman, University of California, Berkeley). We have found several different types of catalytic reactions in which C-H activation can be used to form transient intermediate metal complexes starting with aromatic organic compounds, which then react with other organic substrates to give more complex organic products having new carbon-carbon bonds. These reactions have been carried out in both inter- and intramolecular fashion; they are quite general and are tolerant of a wide range of functional groups. We applied this chemistry to the synthesis of several important potentially physiologically active molecules. We have also discovered that performing these reactions under microwave irradiation leads to dramatically shortened reaction times and higher yields of products.

Future Plans

Catalytic Reactions Using Cationic Iridium Complexes. The cationic iridium catalysts $\text{Cp}^*(\text{PMe}_3)\text{IrR}^+$ used for exchanging deuterium and tritium into organic compounds are reasonably robust, but at the elevated temperatures (135 °C) needed for many exchange reactions, they undergo slow decomposition. Additional catalyst recovery/characterization and mechanistic studies are needed to elucidate the pathways for decomposition, with the goal of ultimately improving the catalyst lifetime. We also plan to explore modified ligands designed to increase the rate of C-H activation or prevent catalyst decomposition. We plan to examine the mechanism of this reaction to determine whether it constitutes a substantial improvement over our present exchange protocols, with an eye toward detecting and isolating potential intermediates, such as ketone- and alkoxide-metal complexes.

Catalytic Deuterium and Tritium Labeling of Molecules Relevant to Medicinal Chemistry Using Cationic Iridium Complexes (collaboration with M. Skaddan, Pfizer Global Research and Development). Our collaborative project with Pfizer will continue, with the goal of examining exchange of deuterium and tritium into actual drugs and drug metabolites, and using these labeled materials to track metabolic processes in living organisms.

Ultra-reactive cationic iridium complexes. With the goal of increasing both the charge and coordinative unsaturation of reactive iridium species, we have begun to look for methods that can be used to generate solvates of the doubly-charged metal cation $[\text{Cp}^*\text{Ir}(\text{PMe}_3)]^{2+}$. In an intriguing preliminary result, we have found that treatment of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{OTf})_2$ (OTf = trifluoromethanesulfonate or “triflate”) with salts of fluorinated tetraarylborate anions in the presence of 1,3,5-trimethylbenzene results in overall abstraction of the triflate ligands from the metal center and cleavage of one of the methyl-carbon bonds of the solvent. This is another rare example (see technical progress section) of a carbon-carbon bond activation reaction. Future studies will be directed at testing these hypotheses.

Application of Catalytic C-H Activation Reactions to the Synthesis of Physiologically Active Organic Molecules (collaboration with J. A. Ellman, University of California, Berkeley). A primary goal of future work on this sub-project will be the application of our directed catalytic aromatic C-H activation reactions to a wider range of organic substrates. We have obtained preliminary results which indicate that the carbon-carbon bond forming reactions we have seen with imidazoles can be extended to other heterocycles, such as oxazoles and thiazoles, and we plan to explore the scope and utility of these reactions. Another high priority will be to determine whether the C-H activation reactions with alkenes that generate products bearing new stereocenters can be carried out with effective levels of enantioselectivity. Finally, we have discovered that Lewis acid additives enhance the reactivity of several of our C-H activated coupling reactions. We plan to explore the scope of these reactions and determine how the presence of the Lewis acid modifies the mechanism of the transformation.

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Development of Highly Selective Catalysts in Supramolecular Nanoscale Reaction Vessels

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Goals

This is a new project whose goal is to apply recent advances in nanoscopic molecular recognition to problems in homogeneous catalysis. The approach involves incorporating catalytically active organometallic complexes into the cavities of well-characterized, self-assembled nanovessel “container”-type clusters (many of them chiral), and then determining if selective binding and reactivity of substrates can be induced to take place in these specifically designed cavities. There are parallels with nature’s most highly selective catalysts, enzymes. Thus we are combining generation of selective chemical environment and conceptual insights from organometallic chemistry and homogeneous catalysis to develop a method for designing a new generation of highly selective catalysts.

The clusters have polar ionic exteriors but the cavities are hydrophobic. Use of these reaction “nanovessels” should permit catalytic transformations that have been developed and optimized in non-aqueous media to be carried out in aqueous solution. Stereoselectivity may be achieved by utilizing the chirality imposed by the nanovessel environment, avoiding the necessity of working with conventional chiral catalysts.

Recent Progress

Several of our initial goals have been achieved during the past year. We have (a)

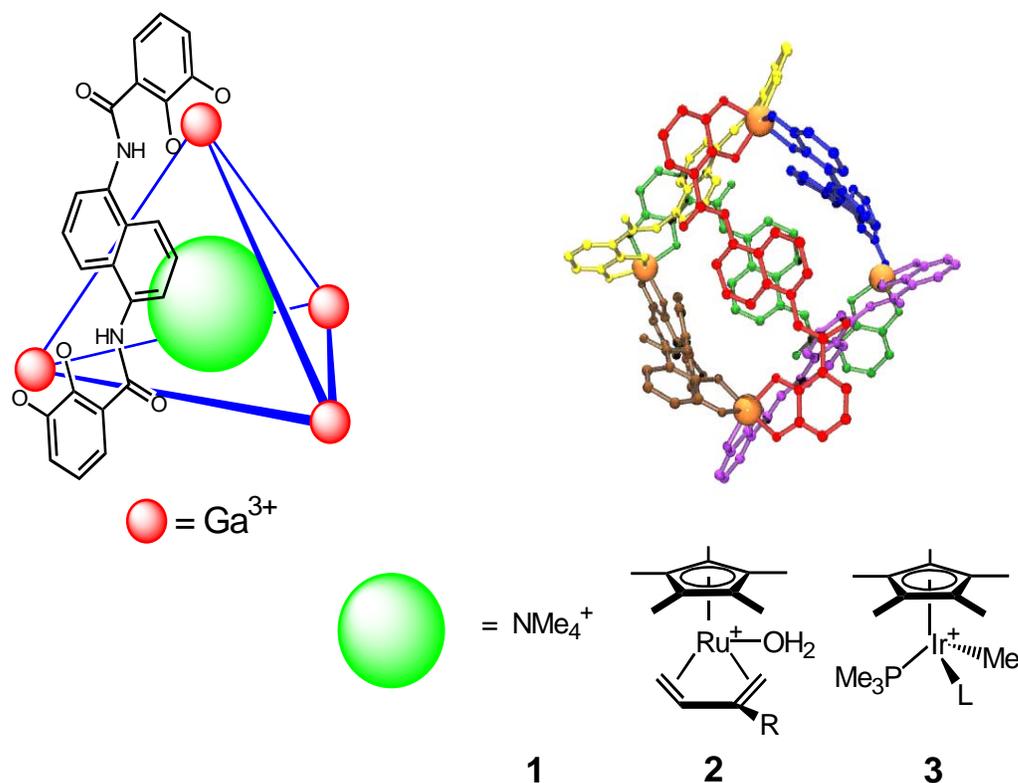


Figure 1. The M_4L_6 assembly illustrated (left) with structure of L and included guest G , and (right) as a molecular model of the full cluster without the encapsulated transition metal guest.

demonstrated that a wide range of organometallic complexes can be encapsulated into chiral nanovessels of the type shown in Fig. 1; (b) demonstrated that encapsulation of chiral guests occurs with promising diastereoselectivity, and (c) observed carbon-hydrogen bond activation reactions within the cavities of the nanovessels.

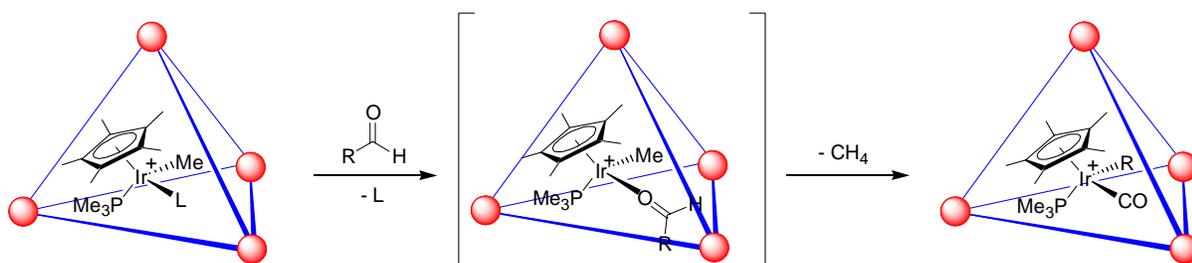
Use of chiral nanovessels in kinetic resolution of planar chiral ruthenium complexes.

The Raymond group has successfully prepared the nanovessels illustrated in Fig. 1. In the first phase of work on the present joint project, encapsulation of cationic organometallic complexes into the nanovessels was explored. Several monocationic organometallic complexes have now been prepared and successfully encapsulated into the cavity of the $[\text{Ga}_4\text{L}_6]^{12-}$ tetrahedral assembly (Figure 1). NMR spectroscopy allows for convenient and diagnostic evidence for formation of the host-guest complexes. The chiral environment of the cavity has a large impact on the encapsulated guest. For example, racemic mixtures of planar chiral complexes having general formula $[\text{Cp}^*\text{Ru}(\text{diene})(\text{H}_2\text{O})]^+$ (diene = isoprene, 2-ethylbutadiene, 2-propylbutadiene, 2-isopropylbutadiene) have been encapsulated into the chiral assembly. Analysis by NMR spectrometry shows that encapsulation of these complexes produces two diastereomeric inclusion complexes with diastereomeric excesses of up to 70%.

Similar findings result from encapsulation of iridium complexes of the general formula $[(\text{Cp}^*)(\text{PMe}_3)\text{Ir}(\text{CH}_3)(\text{L})]^+$ (**1**). We have shown that various iridium complexes can be encapsulated (L = substituted olefins, NCR). By changing the nature of L, the encapsulation of iridium complexes of various sizes and shapes can be investigated. When L = NCR, changing the alkyl substituent allows for a highly specific probe into the size and shape of the internal cavity of the nanovessel. For example, the iridium complex with benzonitrile (PhCN) is not encapsulated by the host, while the iridium benzyl cyanide (PhCH₂CN) complex is encapsulated with high diastereoselectivity. This illustrates that chiral recognition by the host cavity occurs when a close “fit” of the complex and cavity is achieved. In addition, the resolved assembly was successfully exploited for a dynamic resolution of one of the ruthenium complexes.

Intravessel Carbon-Hydrogen Bond Activation Reactions. The iridium guest complexes are analogous to the $(\text{Cp}^*)(\text{PMe}_3)\text{Ir}(\text{CH}_3)(\text{OTf})$ system that the Bergman Group has previously shown to activate C-H bonds in a variety of organic substrates at low temperatures. Dissociation of either L or OTf from the iridium center results in a highly reactive 16 e⁻ species. By changing the nature of L, the rate of dissociation and reactivity can be tuned.

In one of our most important results, we have found that the encapsulated iridium complexes react with aldehydes in aqueous solution, leading to activation of the aldehyde C-H bond at the iridium center followed by overall decarbonylation of the aldehydes. Our initial observations showed that with L = ethene, the reaction proceeded at a moderate rate at 75 °C. During the past year we have explored several other complexes with larger L ligands. These have proven to be substantially more labile, and the reaction can now be run at much lower temperatures. For example, when L = cis-2-butene, the intravessel C-H activation reaction goes to completion in 30 minutes at room temperature. Reaction of aldehydes with the “free” iridium



complexes in the absence of the nanovessel cluster also occurs in water, but reactions with different aldehydes proceed at very similar rates. In contrast, the encapsulated complex reacts rapidly with some aldehydes (e.g., acetaldehyde), but it is inert toward larger ones such as benzaldehyde and valeraldehyde. This demonstrates a significant type of “chemoselectivity” that has not been achieved with other methods.

Our ability to carry out these reactions at more moderate temperatures has allowed us to extend our intravessel C-H bond activation reactions beyond the aldehyde class of substrates. In preliminary results, we have found recently that the host-guest complex reacts with cyclopropane to form a new guest, $[(\text{Cp}^*)(\text{PMe}_3)\text{Ir}(\eta^3\text{-allyl})]^+$. The activation of ethereal substrates has also been investigated. For example, the host-guest complex reacts with dimethyl ether to form an encapsulated iridium Fisher carbene species.

There are many studies in the literature in which binding of various guests inside the cavities of synthetic nanovessels has been studied. However, systems in which chemical reactions have been observed to take place inside these cavities—especially self-assembled systems, such as ours—are rare. Therefore, the observation of C-H activation and other reactions in these systems is an important step forward, and raises many interesting questions concerning the scope, mechanism and eventual utility of these systems.

Future plans

Our first goal will be to focus on the intravessel C-H activation reactions, and try to understand the factors that allow the reactions to take place within the vessel cavity. Critical to this observation is the assumption that the complexes do not “leak out” of the vessel once they are encapsulated, and we intend to confirm this by using exchange experiments to study the rates at which the complexes move in and out of the nanovessel cavities. This will be followed by kinetic studies that will probe the sequence of primary binding and reaction events that occur during the C-H activation process. Our second important finding is the unusual shape selectivity observed in the reactions of aldehydes with the encapsulated iridium complexes. Studies of an expanded range of aldehydes will be carried out, with the goal of “mapping” the shape constraints that allow some aldehydes to react, but other very similar aldehydes to remain completely inert.

We will also follow up our initial results aimed at using the chiral nanovessels to carry out kinetic resolution of chiral organic and organometallic compounds. We have obtained preliminary results which indicate that we have been able to carry out a dynamic kinetic resolution of a complex that racemizes rapidly. We now need to confirm the utility of the chiral recognition properties of the nanovessels by resolving complexes that are stereochemically stable, so that we can isolate the resolved, optically active compounds after the resolution experiment.

Finally, our ultimate goal is to carry out catalytic chemistry within the nanovessel cavities. Our first indication that this might be possible comes from an extension of the reactions that we have observed in nanovessels to organic rearrangements. In this area, we have obtained preliminary results that cationic 3-aza-1,5-hexadienes can undergo carbon-carbon bond forming “aza-Cope” rearrangements both in water solution and inside nanovessel cavities. The rates of the intracavity rearrangements appear to be accelerated relative to the rates of the unencapsulated complexes in pure water, raising the possibility that the nanovessel reactions will act as true catalysts for these reactions. This possibility will be directly explored in the coming year. In addition, we plan to examine the catalytic reactions of several of the cationic organometallic complexes whose structures were outlined in the proposal submitted to obtain funding for this project.

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"Interactions of Neutral Vanadium Oxide and Titanium Oxide Clusters with Sulfur Dioxide, Nitrogen Oxides, and Water"

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GOAL

Determine which neutral metal oxide nanoparticles/clusters can enhance reaction rates for small molecule gas phase reactions. Specific systems presently under investigation are as follows:

1. CO/NO to CO₂/N₂ by Fe_xO_y and Cu_xO_y neutral clusters.
2. SO₂ to SO₃ by V_xO_y neutral clusters.

RECENT PROGRESS

Neutral cluster distribution for a number of metal oxide systems (generated by laser ablation) are determined by time-of-flight mass spectroscopy (TOFMS). 118 nm laser radiation (10.5 eV) is employed to ionize the neutral clusters without fragmentation. Mass spectral feature linewidths, RRKM calculations, density functional theory calculations, known ionization energies, and observed clusters all demonstrate that a single photon of 10.5 eV energy is enough energy to ionize these neutrals and not enough to fragment them in the time window appropriate for a time-of-flight mass spectrometer. The thermodynamically stable neutral clusters for each system under oxygen saturated growth conditions are as follows:

1. Fe_mO_m, Fe_mO_{m+1}, Fe_mO_{m+2};
2. Cu_mO_m, Cu_mO_{m-1};
3. (VO₂)_x(V₂O₅)_y for high O₂ concentrations and V_mO_{m+1,2,3} and V_mO_{2m} at low O₂ concentrations.
4. Zr_mO_{2m,2m+1};
5. Ti_mO_{2m,2m+1}.

Neutral metal oxides can fragment upon multiphoton ionization (193 nm and 355 nm laser radiation). In these instances, the neutral cluster fragmentation mechanism can be identified as loss of oxygen atoms; that is, M_xO_y + nhv → M_xO_{y-1,2,3}⁺ + (1, 2, 3) O.

Linewidths for the mass peaks can be as small as 1.7 ns for individual, nonfragmented ion features. These widths are the electron transit times for the microchannel plate ion detectors. RRKM calculations, experimental and calculated ionization energies, and linewidths present a consistent picture of the neutral cluster distributions and fragmentation behavior.

Fe_mO_n clusters are passed through a reaction cell containing various concentrations of CO and NO. The iron oxide clusters that appear to interact/react with this gas preferentially are Fe₂O₁, Fe₂O₂, and Fe₃O₃. In each instance, product species are observed: for NO, the products N, N₂, O are detected; and for CO, the products C, O, CO₂ are detected.

V_mO_n clusters are passed through a reaction cell containing various concentrations of SO₂. The clusters VO₂ and V₄O_n (4 ≤ n ≤ 8) are observed to be especially active/inactive for this gas. We are presently in the process of detecting the SO₃ product of this reaction enhancement by small, neutral vanadium oxide clusters.

Oxygen deficient V_8O_nCO , V_9O_nCO , and $V_{10}O_nCO$ ($2 \leq n \leq 4$) clusters have also been observed as the neutral cluster distribution of oxygen deficient vanadium oxide clusters (low O_2 concentration in the expansion/cluster generation gas) passes through a cell containing CO. In this case, CO complexes with specific V_mO_n clusters and no additional product species or loss of cluster intensity can be detected. While the complex formation is specific to the species indicated, the interaction between V_8O_n , V_9O_n , $V_{10}O_n$ ($2 \leq n \leq 4$) is too strong to release product (CO_2) even upon ionization of the complex.

This identification of active/reactive clusters of iron oxide and vanadium oxide mandates an effort to obtain cluster geometric and electronic structure and reaction/interaction potential energy surfaces for the cluster complexes and observed chemistry. We have begun this effort and will be continuing it in order to generate a microscopic, quantum mechanical mechanism for the conversions and complexes observed. We have begun this effort employing density functional theory at the BPW91/TZVP and BPW91/LANL2DZ levels. Starting structures for these high-level calculations are obtained from HF/STO-3G calculations and literature calculations with other approaches. We have thus far generated ground state structures for VO_2 , V_2O_4 , V_2O_5 , V_3O_4 , V_2O_6 and V_3O_7 at the BPW91/TZVP level and for V_2O_7 and V_4O_9 at the HF/STO-3G level. A number of isomers are identified for each cluster stoichiometry. For V_2O_5 , we have identified excited triplet states at ~ 1.5 eV and ~ 2.5 eV for different isomers. We are presently finishing the calculations for the V_2O_n system of clusters and will then begin reactivity/complex calculations with the two basis sets TZVP and LANL2DZ(V)/D95(O). These latter calculations will employ analytic second derivatives to distinguish transition states and generate a reaction potential energy surface for the clusters of interest, as determined from experiments.

DOE INTEREST

A fundamental, microscopic, mechanistic understanding of heterogeneous catalytic behavior is not presently available for any specific reaction system. We will generate this understanding for reaction rate enhancement by neutral gas phase metal oxide clusters and small molecules through experiment and theory. With this knowledge, we will model condensed phase surface and bulk catalysis and try to improve its efficiency and selectivity.

FUTURE PLANS

We will expand these studies to include more metal oxides and more reactions. Additionally, we will carry out calculations of the reaction/interaction potential energy surface for the cluster/reactant system that can generate the appropriate product.

The other metal oxide/reaction systems will include:

1. CO/NO converted to CO_2/N_2 by neutral copper oxide clusters;
2. decomposition of H_2O to generate H_2 and O_2 with reaction enhancement by neutral titanium oxide clusters and possibly ultraviolet light; and
3. generation of CH_3OH from CO/ H_2 (water gas) in the presence of neutral copper oxide, zinc oxide clusters, and mixed neutral copper zinc oxide clusters.

These new systems, which are somewhat more complicated than the two we are presently studying, will be explored based on the results from our current experimental and theoretical efforts.

A major focus of our future work will be to bridge the gap between cluster results and condensed phase catalysis through modeling of surface and bulk defects by cluster electronic and geometric structures.

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Novel Transport Behaviors of Porous and Composite Nanostructures

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Goal

Design, synthesis, and understanding of materials whose nanocomposite architecture allows tailoring of the motion of molecules, ions, electrons, and electronic excitations.

Recent Progress

Our NSET research focuses on two general classes of materials:

- natural (nanoporous-supported) membrane-bound ion channels or synthetic analogues that exhibit ionic or molecular selectivities
- nanocomposite systems that exhibit novel mass, charge and energy transport characteristics through controlled nanostructuring and nano-confinement effects.

For both classes of materials, our NSET research has provided well-defined and adjustable nanostructures, essentially model systems, important for establishing nanostructure/property relationships and for future modeling of transport behavior.

Robust Quantum Dots Array: We developed a general self-assembly procedure to prepare robust 3D nanocrystal (NC) arrays. Synthesis of water-soluble NC-micelles followed by surfactant mediated self-assembly with hydrophilic silicate precursors resulted in a nanocrystal mesophase composed of a FCC arrangement of NCs within silica. The robust, 3-D NC mesophase solids are of interest for development of collective optical and electronic phenomena, and, importantly, for the integration of nanocrystal arrays into device architectures. Initial experiments on a metal-insulator-metal capacitor fabricated with an ordered 3D gold nanocrystal/silica array as the 'insulator' demonstrated collective Coulomb blockade behavior below 100K and provided the first measure of current-voltage scaling for a well-defined 3D NC array.

Optically Swichable Nanocomposite: Using an evaporation induced self-assembly procedure, we prepared photo-responsive nanoporous films composed of monosized pores modified with azobenzene ligands that exhibited reversible *trans-cis* photo-

isomerization upon irradiation with visible and UV light. Confined within nanopores, optical switching resulted in extension (*trans*) and retraction (*cis*) of the ligands altering the pore size and dipole moment. By depositing these switchable films as membranes on a working ITO electrode, we developed a chronoamperometry experiment to monitor how optical switching of the pore size influenced mass transport of ferrocene dimethanol, a redox molecular probe. Under the experimental conditions, ferrocene dimethanol oxidized at the electrode surface, thus the oxidative current provided a measure of transport of the probe to the electrode surface. By measuring the temporal change in oxidative current during alternating exposures to UV and visible light, we confirmed that *trans-cis* isomerization upon UV exposure increased the diffusion rate while visible light exposure had the reverse effect. Corresponding UV/visible spectroscopy showed that temporal changes in oxidative current correlated exactly with temporal changes in the populations of *cis* and *trans* isomers, confirming our ability to optically adjust pore size and transport on the nanoscale.

Conjugated Polymer Silica Nanocomposites: Using an evaporation-induced self-assembly procedure, we incorporated PPV precursors into silica/surfactant mesophases. PPV/silica nanocomposites with a hexagonally ordered mesostructure were fabricated by pyrolysis of the PPV precursor. By controlling the temperature and atmosphere during pyrolysis, we can control the PPV conversion rate and conjugation length as indicated by their absorption and emission spectra. Nanostructuring should enable control of charge and energy transfer in conjugated polymer devices.

DOE Interest

Materials with controlled transport properties are needed in diverse areas of emerging technologies of interest to DOE, including membrane-based separations and sensing, drug delivery, fuel cells, artificial photosynthesis, and molecular electronics.

Future Plans

Robust Quantum Dots Array: Future work will extend initial work from Au to semi-conductor and magnetic NCs where we expect to control charge transport and spin-dependent tunneling; we will also explore catalytic behaviors of the NC arrays.

Optically Swichable Nanocomposite: We plan to extend our studies of optically mediated transport to several other classes of molecules in which we would expect to control transport based on size and/or polarity, such as hydrogel/silica nanocomposites in which transport is influenced by temperature and/or pH.

Conjugated Polymer Silica Nanocomposites: Optimize the synthesis conditions. Investigate the charge and energy transport behavior.

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Chemistry of Complex Organic Energy Resources

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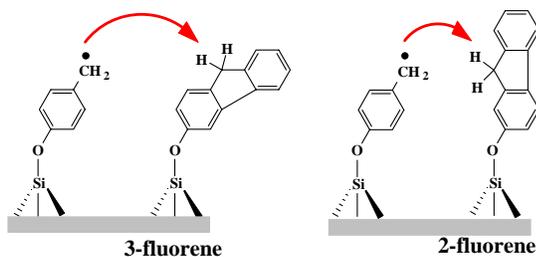
Goal

Study model systems (compounds, polymers, organic-inorganic hybrid materials) that reveal new molecular level knowledge of the chemical transformations of complex organic energy resources typified by biomass and fossil fuels.

Recent Progress

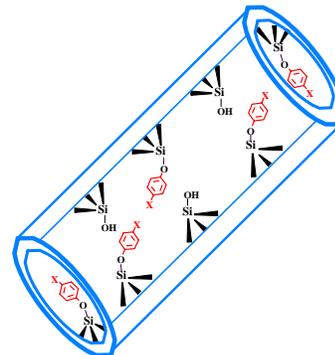
Research focused primarily on two theme areas. First, chemical transformations on surfaces were examined to investigate the impact of restricted mass transport on reaction rates and product selectivities, which can be important in the thermal and catalytic conversion of macromolecular energy resources. Organic molecules attached to the surface of silica nanoparticles or in the pores of mesoporous silicas were probed to understand the impacts of pore size and molecular orientation on high temperature, free-radical reactions. Solid-state C-13 NMR, transient optical spectroscopy, and computational modeling were used to probe the effect of surface confinement on molecular dynamics. In the second theme, molecular transformations of heteroatom-containing (e.g. O,N,S) functional groups in energy resources were examined because of their significance in environmental and processing issues. Emphasis was on elucidating thermal degradation mechanisms of oxygen-containing structures in lignin, and cross-linking mechanisms for aromatic carboxylic acids, salts, and esters in fossil fuels.

Molecular Orientation Effects in Surface Reactions. Thermolysis studies revealed that orientation effects on hydrogen transfer steps in free-radical reactions on surfaces, imposed by restrictions on diffusion, can significantly alter the kinetics of these reactions even at high temperatures.¹ This was established by examination of the kinetics of the free-radical decomposition of 1,3-diphenylpropane, covalently immobilized on nonporous silica nanoparticles, at 375°C in the presence of isomeric (by point of attachment) hydrogen donors. Reaction rates, which are controlled by hydrogen transfer to intermediate benzylic radicals, were found to be ca. three times faster for *meta*-linked hydroaromatic donor molecules as illustrated in the figure for the 2-fluorene relative to the 3-fluorene hydrogen donor. Molecular



modeling confirmed that the *meta*-linkage associated with the immobilized 2-fluorene affords the more favorable separation and geometry for the crucial hydrogen transfer step.

Effects of Pore Confinement. Hexagonal mesoporous silicas, MCM-41 and SBA-15, were found to be readily derivatized with aromatic phenols. Thermolysis studies of pore-confined 1,3-diphenylpropane revealed that both the reaction rate and product selectivity increased with decreasing pore size (5.6 – 1.7 nm), apparently a consequence of increasing pore surface curvature.² This could lead to improved control over chemical transformations occurring in porous solids, e.g. in catalytic processes.



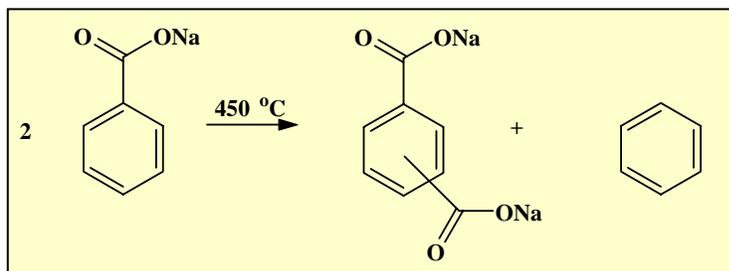
Spectroscopic Studies of Surface-Confined Aromatics. Surprisingly large (megahertz) rotational diffusion rates have been measured for silica-attached 1-pyrene and silica-attached benzene by time dependent fluorescence anisotropy and ¹³C NMR spectroscopy, respectively.³ A remarkable outcome of these findings is the ability to measure high resolution C-13 NMR spectra on these solid samples using the standard NMR techniques normally employed for liquid samples. Molecular mechanics calculations on the motion of benzene attached to a model crystalline silica surface yielded small rotational barriers consistent with the spectroscopic conclusions.

Pyrolysis Studies of Amino Acids. Studies on the formation of nitrogen-containing polycyclic aromatic compounds (N-PACs) and polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of the amino acid proline revealed that co-pyrolysis with carbohydrates, such as glucose, significantly enhanced the formation of N-PACs and PAHs compared to the pyrolysis of the amino acid alone. It was proposed that products derived from the Maillard reaction, such as the Amadori compound, are responsible for the enhanced product yield. These studies are important to understanding the mechanisms for potential PAH formation during pyrolysis of biomass.

Pyrolysis Studies of Thiophenes. In collaboration with Professor Jan Yperman at Limburgs University (Belgium), the removal of sulfur from thiophene structures in fuels was examined using atmospheric pressure, temperature programmed reduction with mass spectrometric detection (AP-TPR-MS) and silica-immobilized model compounds.⁵ The pathways resulting in low efficiencies for reduction of thiophenes to H₂S under the AP-TPR-MS conditions were deduced, which will improve interpretation of results obtained from studies on coals and other fuels.

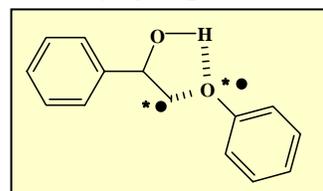
Pyrolysis Studies of Aromatic Carboxylic Acid Esters and Salts. In our efforts to understand cross-linking reactions in low-rank coal, the fundamental reaction pathways for the formation and decomposition of aryl esters were resolved by the study of the pyrolysis of phenyl benzoate.⁹ Aryl esters readily form from the condensation of aromatic carboxylic acids and phenols, which are prevalent in low-rank coal, and can act as low temperature cross-links. Although aryl esters should be thermally stable at 400°C, they readily hydrolyze to form aromatic carboxylic acids and phenols. From previous studies, we showed that aromatic carboxylic acids can lead to additional cross-linked products by dimerization to form anhydrides, followed by radical induced decomposition to produce aryl radicals.

Pyrolysis studies of sodium, potassium, and calcium benzoate were performed to determine the reaction products and mechanisms for mono and divalent carboxylic acid salts that are important structures in low rank coals.¹⁰ Detailed product studies indicated that sodium benzoate degradation proceeds slowly at 450°C to produce benzene and sodium phthalate as the major products. Mechanistic studies indicated that the major decomposition products form by an anionic pathway. Potassium benzoate reacted similarly but at a significantly faster rate. Interestingly, calcium benzoate was found to be stable at 450°C, and it decomposed very slowly at 500°C to generate a different



product distribution from the sodium and potassium cases. Benzophenone and benzene were the major products, while the minor products include triphenylmethane, 9-phenylfluorene, diphenylmethane, and biphenyl. The mechanistic origin of this different product distribution is currently being probed.

Computational Studies of Lignin Models. Computational studies on the impact of hydrogen bonding on C-O bond homolysis for lignin model compounds (β -O-4 aryl ethers) were conducted. Surprisingly, DFT calculations at the 6-31G* level had difficulty determining the transition state of the reaction. MP2 calculations at the 6-31G* level gave an optimized transition state for homolysis of $C_6H_5CH(OH)CH_2-OC_6H_5$ that showed hydrogen bonding between the hydroxyl group and the phenoxy radical. This hydrogen bonding lowers the transition state energy ca. 2 kcal/mol compared to $C_6H_5CH_2CH_2-OC_6H_5$, which does not contain the hydroxyl substituent. These computation results support our experimental thermolysis studies, which showed an accelerated rate for C-O homolysis in the model compound containing the hydroxyl group.



DOE Interest

The fundamental knowledge gained from this research contributes to the scientific foundation required for the development of new environmentally responsible, energy efficient processes for the utilization of organic energy resources.

Future Plans

Studies of chemical transformations on surfaces will examine pore confinement effects on ether-containing molecules that decay by a different free-radical mechanism than diphenylpropane. Studies will also be initiated on photochemical reactions of surface-bound molecules to see if control over the local molecular environment can be used to control the chemo- and regioselectivity. ^{13}C -NMR investigations of motional dynamics for surface-bound organics will examine the role of temperature, surface coverage, and molecular flexibility.

Investigations of the reaction mechanisms of oxygen-containing functional groups will focus on completion of studies on the pyrolysis of aryl ethers (lignin models) with an emphasis on understanding substituent effects and the impact of hydrogen bonding. Research on the pyrolysis mechanisms of “simple” carboxylic acid salts and esters will be completed with an emphasis on understanding the difference between divalent and monovalent salts. ^{17}O -NMR experiments will be performed on a series of homogeneous carboxylic acid polymers that are models for low rank coals and biomass materials. The studies will use synthesized and ^{17}O -labeled polyxylene and/or polystyrene polymers with varying carboxylic acid loadings. Initial studies will focus on whether anhydrides form during thermal processing of the polymers as found previously for simpler molecules.

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Metal Hydrides in Homogeneous Catalysis

Postdoc: Vladimir K. Dioumaev (2001-2004)

Collaborators: David Szalda (Baruch College), Jim Franz (Pacific Northwest National Lab), Jon Hanson (Brookhaven National Laboratory)

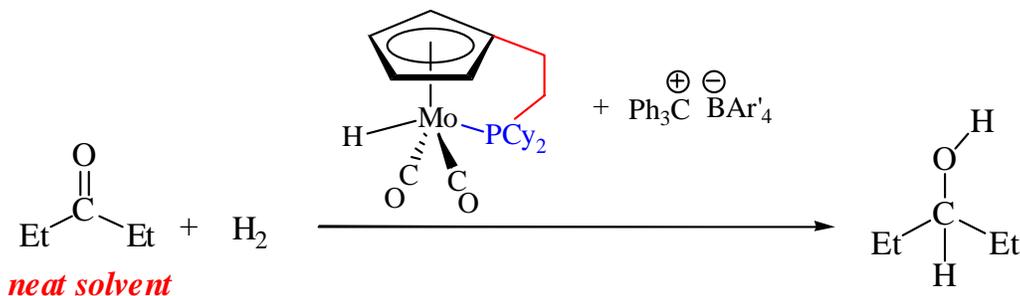
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Goal

Improve our understanding of the reactivity of transition metal hydrides in organometallic reactions, especially reactions where the M-H bond rupture occurs as a proton (H^+), a hydrogen atom (H^\bullet) or a hydride (H^-). We seek to use kinetic and mechanistic information to develop new homogeneous catalysts, particularly those that use cheap metals rather than precious metals, as well as catalytic reactions that are environmentally friendly, through use of readily recycled catalysts, solvent-free processes, or alternative renewable feedstocks.

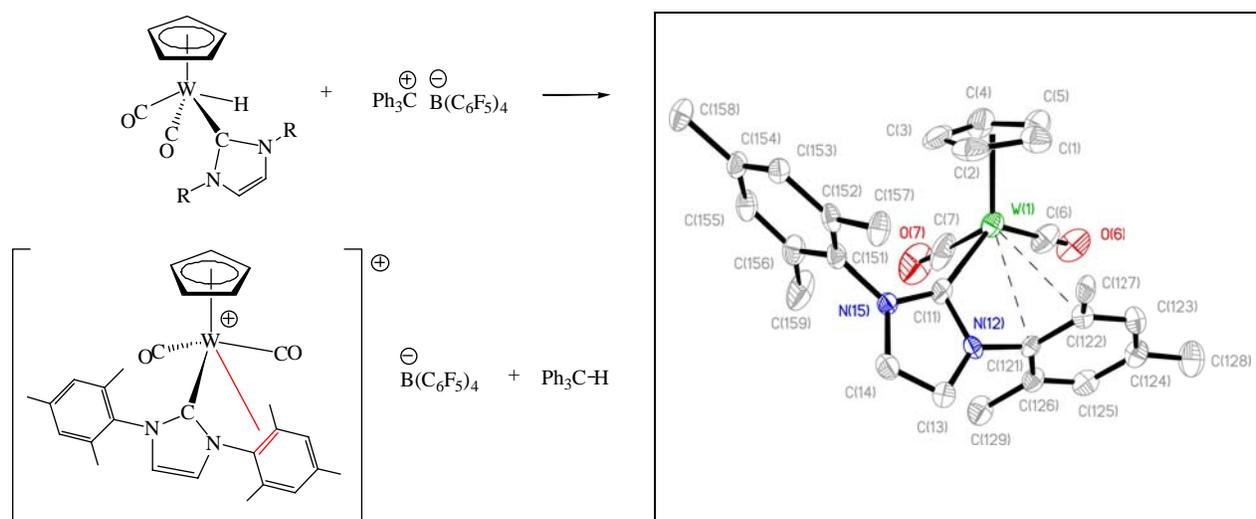
Recent Progress

Ionic hydrogenation catalysts based on the inexpensive metals molybdenum and tungsten have been developed based on mechanistic understanding of the individual steps required in the catalytic reaction. These hydrogenations proceed by H^+ transfer from a cationic dihydride, followed by H^- transfer from a neutral metal hydride. In contrast to traditional catalysts, these ionic hydrogenations do not require insertion reactions in which the ketone inserts into a M-H bond. A series of Mo and W complexes of formula $[Cp(CO)_2(PR_3)M(O=C(Et)_2)]^+$ were shown to serve as catalyst precursors for the ionic hydrogenation of ketones. The stability of these Mo and W catalysts is limited by dissociation of a phosphine, which is protonated to give HPR_3^+ under the reaction conditions. Suppression of phosphine dissociation was sought by using a two-carbon bridge to chelate the phosphine to the cyclopentadienyl ligand. Improved performance was found using catalysts obtained by reaction of $HMo(CO)_2[\eta^5:\eta^1-C_5H_4(CH_2)_2PR_2]$ ($R = Ph, Cy, tBu$) with $Ph_3C^+BAr'_4^-$. Advantages found with these new complexes include low catalyst

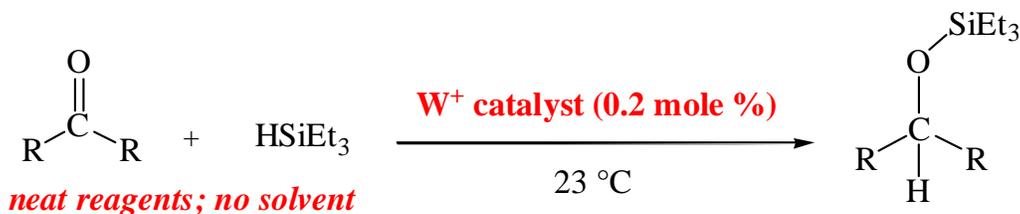


loadings (< 0.4 mole %), higher thermal stability, substantially longer lifetimes (hundreds of turnovers), and hydrogenation of liquid ketones under solvent-free conditions.

Recent efforts have focused on N-heterocyclic carbene ligands rather than phosphines. The tungsten complex $\text{CpW}(\text{CO})_2(\text{IMes})\text{H}$ (IMes = the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) was prepared by substitution of the phosphine ligand in $\text{CpW}(\text{CO})_2(\text{PMe}_3)\text{H}$ by IMes. Hydride abstraction from $\text{CpW}(\text{CO})_2(\text{IMes})\text{H}$ produces $\text{CpW}(\text{CO})_2(\text{IMes})^+$. The crystals of this complex were too small for conventional x-ray crystallography, but an x-ray crystal structure carried out at the National Synchrotron Light Source indicated a weak bonding interaction between the tungsten and one of the C=C bonds of a mesityl ring. Density functional computations (by Jim Franz; Pacific Northwest National Laboratory) provided additional evidence for this unusual bonding. The weak bond stabilizes the tungsten cation but is readily displaced by other ligands, such as THF or ketones. This cationic



complex is a catalyst precursor for hydrogenation and hydrosilylation of ketones. An unusual property is observed in the hydrosilylation of aliphatic substrates – the catalyst precipitates from solution at the end of the reaction, so that the liquid product can be separated from the catalyst by pouring off the liquid. The recovered catalyst can then be readily recycled and used again. These hydrosilylations are carried out in neat ketone/ HSiEt_3 , so that no solvent is used in either the reaction or the catalyst recycling.



DOE Interest

This research is aligned with the DOE goals of obtaining a more comprehensive understanding of the molecular details of homogeneous catalysts, seeking mechanistic information that will guide the design of improved catalysts. We also seek to contribute to the realization of the goal that catalytic processes be developed to be more environmentally benign.

Future Plans

Future experiments will involve synthetic attempts to prepare new complexes that have carbene ligands or partially fluorinated phosphines, with the goal being to design catalysts that have faster rates and improved lifetimes. A challenge for future development is to tailor catalysts and hydrosilanes with the aim of engaging a broader scope of substrates into solvent-free reactions with catalyst self-separation. This will require a better fundamental understanding of the factors governing miscibility of these complexes and their phase behavior. Of particular interest is the behavior of liquid clathrates, which are thought to be important in providing the desired physical properties of the recyclable catalysts studied thus far. Characterization of the liquid clathrates is worthwhile for us to understand their composition, and we will seek synthetic methods that exploit their properties as applied to recyclable catalysts.

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**Oxide-Supported Metal Catalysts:
Energetics, Particle Size and Chemisorption / Catalytic Properties**

Staff Scientist: Dr. Qiuming Yu (~10% of time).

Postdocs: Michael Gottfried (from Germany), Maria Smedh (from Sweden), Junfa Zhu.

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Collaborators: Prof. Sam Fain (Physics), Prof. Hajo Freund and Dr. Joerg Libuda (FHI Berlin), Drs. Bruce Kay and Zhdenek Dohnalek (PNNL), Dr. Noah Shamir (visiting scientist at Univ. of Washington, on leave of absence from his home institution in Isreal), Prof. Per Stoltze (Denmark). Undergraduate students: David Sunderland.

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Goal

To understand: (1) how metal particle size affects catalyst activity and selectivity, (2) how to maintain catalysts at their optimum size for extended periods while running chemical reactions, and (3) how to predict from short-term measurements whether new catalysts will resist sintering for long enough (on the order of one year) to be industrially useful.

Recent Progress

Recent results in this lab and others show that the chemical reactivity of oxide-supported transition metal particles can be tuned by varying their size below 10 nanometer, in some cases resulting in marked increases in catalytic activity or selectivity. Model catalysts involving well-defined metal nanoparticles on crystalline oxide supports were studied here using a variety of state-of-the-art experimental techniques, together with theory. We have studied model surfaces that mimic the sites on oxide-supported metal catalysts to clarify the interplay between the metal particles size and the chemical / catalytic reactivity of metal-on-oxide catalysts. We find that this interplay is dictated by the surface energetics involved. Recent results show correlations amongst: (1) the size of metal nanoparticles, (2) their energy, (3) their reactivity, and (4) their propensity to deactivate by sintering. We aim to: (1) predict sintering ratea, and (2) design new catalyst nanostructures which are sinter-resistant. Nanoparticle palladium catalysts supported on α -Al₂O₃(0001) were studied with atomic force microscopy (nc-AFM) to reveal how the size and number of Pd particles varies with time, and how their energy changes with particle size. These catalysts are active for methane combustion and substantially reduce NO_x emissions, but remain underutilized due to sintering problems. The effects of platinum nanoparticle size on reactivity toward hydrocarbon dehydrogenation were studied to better understand this important class of dehydrogenation catalyst.

Single Crystal Adsorption Microcalorimetry

The strength of bonding at the interface between the metal and its support dictate the metal nanoparticle size distribution, morphology and resistance to sintering, which in turn control catalytic activity. We have performed calorimetric measurements of metal adsorption energies and adhesion energies on well-defined surfaces, also directly probing the energies of metal atoms in supported metal nanoparticles. As the metal coverage increases, the particles grow, revealing the dependence of this energy on particle size, which we found to be much stronger than predicted with the usual Gibbs-Thompson relation. We found that accurate knowledge of metal energy versus particle size is crucial to accurately model long-term sintering rates of metal nanoparticles in catalysts. With this knowledge, we have developed a microkinetic model for sintering which, for the first time, is both accurate at simulating data and mechanistically-correct (see below).

Metal binding to carbide surfaces is important in metal-promoted carbide catalysts and in metal / carbide interfaces. We measured the adsorption energy of Pb (1×1) Mo₂C thin films on Mo(100).

We built and tested a new single crystal adsorption microcalorimeter system with a combination of DOE and NSF support. It has additional capabilities for XPS/AES, ISS and LEED. It has now proven capable of measuring adsorption and reaction energies of *molecules and molecular fragments* on single crystals. This system will be used to directly measure the energetics of catalytic intermediates well-defined metal particles.

The PI spent two two months in 2003 in Berlin working in the research group of Hajo Freund at the Fritz Haper Institute of the Max Planck Society. He constructed a third single crystal adsorption calorimeter and mounted it on Freund's molecular beam / surface scattering apparatus. That group, in collaboration with the PI, is currently measuring the effect of Pd particle size on the adsorption energy of small molecules (O₂, CO, NO) using this calorimeter. The support is a highly-ordered alumina thin film.

Sintering Kinetics of Well-Defined Metal Particles on Oxides

We have improved the microkinetic model for catalyst nanoparticle sintering in a way that we believe will have a very big impact on catalyst sintering studies in general, and improve methods for rapidly screening new catalysts. We proved that, to get a good model, one must include the very large change in the energy of metal particles with cluster size, which we measured by calorimetry. We showed that metal surface energy increases strongly as particle radius decreases below 6 nm.

We are continuing this work with a study of sintering of Pd particles on α -Al₂O₃(0001) using nc-AFM and TP-LEIS (see below).

Pd on Al₂O₃(0001) and MgO(100) Model Catalysts

Catalysts consisting of Pd nanoparticles on alumina are used for low-temperature methane combustion to minimize NO_x emissions in electric generator turbines and other applications. Long-term sintering is a real problem with commercializing these. We have used nc-AFM, XPS, TPD, LEIS, temperature-programmed LEIS and molecular beams to study the sintering and reactions of model catalysts prepared by vapor deposition of Pd onto α -Al₂O₃(0001) and an ordered MgO(100) thin film. The measurements of sintering

revealed that 2D particles of Pd cannot be seen by nc-AFM, even when the system is proven capable of atomic resolution on other samples. We found a size dependence in the chemical reactivity of Pd nanoparticles in the 1-4 nm range for dissociative methane.

Pt / ZnO(0001)-O and -Zn Model Catalysts

The dehydrogenation of benzene and cyclohexane on Pt / ZnO(0001)-O model catalysts was studied with temperature programmed desorption (TPD), low-energy ion scattering spectroscopy (LEIS), and X-ray photoelectron spectroscopy (XPS). Vapor-deposited Pt grows on this O-terminated ZnO face as 2-dimensional (2D) islands at low coverage, and later as 3D particles. The reactivity of these Pt nanoparticles toward H₂, benzene-d₆ and c-C₆D₁₂ was studied versus Pt coverage, which controls their lateral dimension and then their thickness.

In collaboration with Geoff Thornton's group in England, we studied benzene, phenol and C₁-C₃ oxygenates on ZnO(0001)-Zn using synchrotron techniques.

Au on TiO₂(110) Model Catalysts

Highly dispersed gold-on-titania catalysts have been the subject of extensive research due to their potential use in low-temperature CO oxidation in automotive applications, in selective propene epoxidation, and in other catalytic and photocatalytic oxidations mainly for selective oxidation or environmental cleanup. The size of the Au nanoparticles is crucial. We have addressed fundamental aspects of their sintering and mechanism of selective propene oxidation using Au / TiO₂(110) model catalysts.

Microkinetic Modeling of Catalytic Reactions

The PI also collaborated with the group of Per Stoltze (in Denmark) in developing a new microkinetic model for selective ethylene oxidation to ethylene epoxide over silver catalysts that successfully fits the rate measurements on both single crystal model catalysts and catalysts similar to those used industrially.

DOE Interests

Catalysts improve the efficiency of fuel utilization and reduce pollution during chemical processing, and thus promise to play a dominant role in future progress toward cleaner and more efficient chemical and automotive industries. Controlling nanoparticle size provides an important potential method for catalyst improvement, which we are exploring here. Learning how to maintain that particle size without sintering, which we also explore, will be necessary for industrial applications.

Future Plans

Calorimetry

We will continue our calorimetric measurements of metal adsorption on oxide supports with studies of the adsorption of Cu, Ni, Pd and K adsorption on a variety of thin-film oxide surfaces (ordered Al₂O₃, SiO₂, CeO₂(111), TiO₂(110), ZnO(0001)), for

comparison to our previous results with Cu, Ag and Pb on MgO(100) and ordered MoO_x thin films on Mo(100). This will reveal how the nature of the metal and oxide influences the heat of oxide adsorption and the metal / oxide adhesion energy. We will use our new calorimetry system to directly measure the energetics of catalytic intermediates on oxide-supported metal particles as a function of particles size. Specifically, we will investigate how the energetics of intermediates in the dehydrogenation of cyclohexane depend on particle size.

Sintering Kinetics

We will continue to study sintering kinetics of the systems mentioned above for which we measure metal adsorption energetics, to further test our conclusion above that the dramatic dependence of these energetics on particle size is essential to model sintering. Specifically, we want to provide direct measurements in catalytically-important systems of all of these three important properties so they can be correlated: (1) sintering rates, (2) particle sizes and number densities, and (3) metal adsorption energies.

Catalytic Reactivity / Chemisorption

We will continue to study the effects of particle size on the chemisorption reactivity and catalytic activity of the systems mentioned above for which we measure metal adsorption energetics. Specifically, we want to provide direct measurements in catalytically-important systems of all three of the important properties so they can be correlated: (1) catalytic reaction rates (or rates of elementary steps in the catalytic reaction), (2) particle sizes and number densities, and (3) metal adsorption energies.

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Fundamental Studies of the Design of Nanoporous Silicate Catalysts

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Goal

The goals of this program are to probe the mechanism of formation of clay catalysts via NMR, in situ time-resolved small angle X-ray scattering (SAXS), and microscopy; to elucidate the role of silica sol starting material on the morphology of mesostructured synthetic clays using NMR, XRD and TEM; to add catalytically active metal clusters to the synthetic clays either during sol-gel synthesis or on prepared clays, and characterize them using in situ and anomalous SAXS techniques to draw correlations between catalytic activity and structure; pursue organo-grafted clays using organosilanes in clay synthesis with the goals of compatibility with polymers, biocatalytic molecules and encapsulated metal nanoclusters.

Recent Progress

Several new mesostructured synthetic clay (MSC) materials were prepared and evaluated for their potential use as catalysts. Textural porosity was determined as a vital parameter to understand for catalytic as well as for polyelectrolyte applications. Synthetic hectorites derived from silica sol contain mesoporosity, which is useful for catalytic applications, whereas silane-derived clays, which are more like typical clays with microporous platelet morphology, do not. It was found previously that using a silica sol creates a MSC with high surface area morphological features (textural porosity), whereas use of other silicon sources creates a more traditional layered clay catalyst that is not as active. After extensive characterization, it was determined that the unique features of the MSCs, including especially their thermally stable mesoporosity, would lend themselves to selective catalysis. One example is the efficient hydrodesulfurization (HDS) of low-quality hydrocarbon feedstocks. In order to make strides towards this goal, we have begun with model compound studies.

New MSCs were prepared as a function of the size, pH, and counterion (and therefore the surface chemistry) of various silica sol precursors. Several techniques were applied to characterize the new materials, including XRD, TGA, N₂ porosimetry, and TEM. XRD showed slight differences in crystallinity, surface areas ranged from 195-293 m²/g with either H₂ or H₃ hysteresis loops, pore volumes varied from 0.31-0.49 cc/g, and TEM showed sol particle sizes slightly different in some cases from values provided by the manufacturer. For HDS, the conversion of dibenzothiophene (DBT) to biphenyl was examined using Co/Mo/S-loaded mesostructured clay supports. In this system, the metals are introduced sequentially as salts, then heated in air to create the oxide forms, and finally sulfided with H₂S in H₂ to create Co_xMo_yS_z particles.

Commercial HDS catalysts contain significant amounts of macroporosity whereas the MSC's are designed for the mesoporous range. This factor affects the selectivity of

the catalysts under actual processing conditions, for it is well known that the macroporous aluminas are not as selective. Therefore, it is expected that the designed mesoporous clays will be superior when selectivity is taken into account for converting the large sulfur-containing molecules present in an actual feed. A model compound HDS reaction was done first, with DBT, in collaboration with C. Marshall (CMT-ANL). The most active clay was derived from silica sol AS30. This sol has a particle diameter of 22 nm and it yields the highest observed synthetic clay pore volume at 0.49 cc/g, which may be related to the high activity.

Features such as porosity and active metal characteristics are especially important for deep HDS, where both hydrogenolysis and hydrogenation pathways occur. This is in contrast to HDS, which is dominated by hydrogenolysis. The conversion of 4,6-dimethyldibenzothiophene (DMDBT) was tested in collaboration with C. Song at Pennsylvania State University. The Co/Mo/S mesostructured clay catalysts were significantly more active than Co/Mo/S clay catalysts of typical platelet morphology. This clearly indicates that the unique morphology of the mesostructured clays is important. Whether it is the porous network, the nature of the Co/Mo/S particles, or a combination of both, which is the most important variable remains to be determined. The most active clays display an H3 N₂ isotherm hysteresis loop, whereas all of the rest have H2 loops. The importance of this textural porosity feature to catalytic activity will be examined in future studies. Furthermore, the most active MSC catalysts have the highest hydrogenation-to-hydrogenolysis ratios. This is critical because hydrogenation of DMDBT makes it easier to remove the sulfur atoms than for direct hydrogenolysis. The unique factors in the Co/Mo/S-MSCs causing this activity warrant further study as well.

It was also very interesting that the sol of smallest particle size (7 nm) showed poor catalytic activity results, for it was expected that the smaller size would allow more dissolution and perhaps more incorporation into the matrix. Upon close examination of the XRD results, it appears that the most crystalline clays yield catalysts that are the most active. In other words, the silicas that foster the sharpest and most intense clay diffraction peaks show the best catalytic results. The next section will detail plans to address which differences in the various silica sols promote this affect, and how best to exploit this feature. The materials were also provided to G. Sandi for testing as polymer-clay nanocomposite membranes for lithium ion transport in secondary batteries.

DOE Interests

The chemistry of synthetic clays is being studied to understand how a particular heterogeneous nanoporous catalyst is formed, and to exploit this knowledge for tailoring the characteristics of the catalytic material. Catalysts of high selectivity are always more desirable for their enhanced efficiencies. Metal nanoclusters of controllable size will be added to impart additional catalytic activity. The synthesis of the clay supports and of the metal loadings in terms of size and disposition are probed by a variety of techniques, including pioneering application of in situ SAXS for this purpose.

Future Plans

We have had enormous success in the past exploiting solid-state ²⁹Si and ¹³C NMR to examine formation of the synthetic clay catalysts. We will again make use of these methods to probe the crystallinity of the various silica sol samples made for HDS, and to compare the results with those from XRD. The issue to determine is why certain silica sols foster greater crystallinity in the clay catalysts, and we will explore factors such as particle size, pH, and counterions in these terms. Overall, it is quite important to determine the role of sol particles that are not fully reacted to the final clay. We will probe how these particles, as well as the metal nanoparticles described below, disrupt the clay layers. The parameters that control final particle size are also of interest. We have

demonstrated that we can tune the particle size to some extent, but have not determined the critical synthetic variables important to making this a highly reliable and sensitive (in terms of tunability) tool. Thus far, it appears that the role of sol particles is also critical here.

Another important question to address is whether the absence of silica impurity hastens or otherwise affects the clay crystallization mechanism and subsequent porosity and catalytic behavior. A complete understanding of such mechanisms leads to better catalyst design. A thorough analysis has been done to elucidate a crystallization mechanism for the hectorites derived from silica sol. For hectorites made from silanes the picture is not quite as complete. *In situ* SAXS experiments using a new flow cell design will be undertaken in order to aid in this understanding.

Of further interest as well is the disposition of the Co/Mo/S metal clusters that are deposited on the support surface, and TEM and XRD measurements will be taken for this analysis. Future HDS tests will use the larger sulfur-containing molecules that are more prevalent in actual feedstocks than the model DBT and DMDBT molecules. This will provide a better probe of the selectivity of the meso- vs. macroporous catalysts. Furthermore, hydrogenolysis vs. hydrogenation pathways for deep HDS will be compared to derive information about how morphological features can affect the mechanism.

We will exploit our prior knowledge gained from mechanistic determinations to synthetic clays that contain a catalytically active metal component. Bifunctional catalysts contain both an acidic component (typically for hydrocarbon cracking) and a metal component. We will probe the mechanism of formation of metal-containing clay catalysts via NMR, *in situ* time-resolved small angle X-ray scattering (SAXS), anomalous SAXS (ASAXS), microscopy, and other techniques. The catalytically active metal ions or metal clusters will be added by adsorption of metal precursor species followed by chemical reduction and by adsorption of colloids, either during sol-gel synthesis or on prepared clays. It is expected that the differing textural porosities will have an effect on cluster size and shape. Furthermore, it is expected that, if the clusters are small enough (1-2 nm), they will reside within individual interlayers. Larger particles will reside on the surfaces. The size, shape and disposition of such metal-containing clusters will be monitored by the ASAXS technique. *In situ* SAXS experiments will also be performed. A comparison of the clay catalysts after a catalytic reaction will then be made in order to assist in understanding the role of the metal nanoclusters in the particular catalytic reaction.

Organosilanes are of special interest because of their now demonstrated ability to be incorporated into the framework of clay as it is crystallizing. One natural extension of this process for us to study is the simultaneous incorporation of templating molecules such as polymers, and their effect on porosity or network structures. We will also compare and contrast the mechanism of formation of organo-grafted clays with silane-derived hectorite and silica sol-derived hectorite, using the techniques described above (NMR, TEM, SAXS, etc.).

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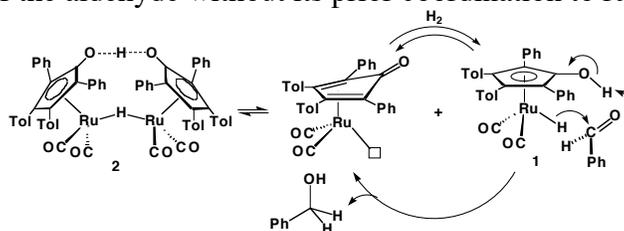
Mechanistic Studies at the Interface Between Organometallic Chemistry and Homogeneous Catalysis

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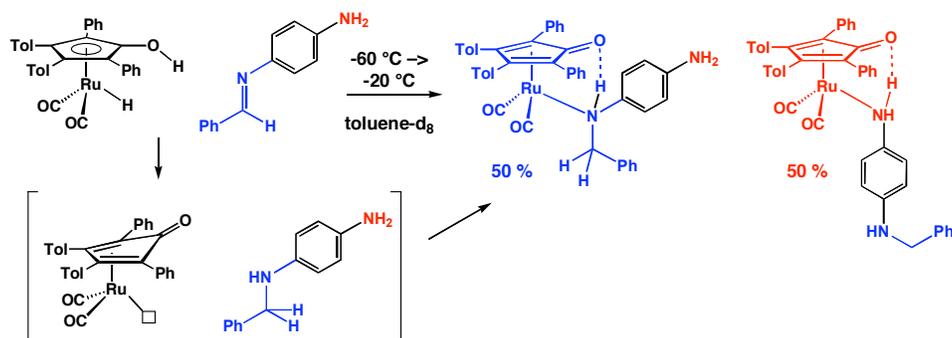
Graduate Students: Susie C. Martins, Jeffrey B. Johnson, Galina Bikzhanova, Sharon Beetner,
 Undergraduate Student: David Priebe

Research Goals and Specific Objectives. Our goal is to learn the intimate mechanistic details of reactions involved in homogeneous catalysis and to use the insight we gain to develop new and improved catalysts. Our work centers on the hydrogenation of polar functional groups such as aldehydes and ketones and on hydroformylation. Specifically, we are concentrating on catalysts capable of simultaneously transferring hydride from a metal center and a proton from an acidic oxygen or nitrogen center to an aldehyde or ketone; reaction of the organometallic product with hydrogen regenerates the active reducing agent. Selective and mild catalytic hydrogenation of ketones and aldehydes is a modern green alternative to stoichiometric reductions by LiAlH_4 and NaBH_4 which require extensive work-up procedures. In the case of hydroformylation, we are probing the underlying reasons for the enantioselectivity of catalysts and are searching for regioselective catalysts for production of branched aldehydes rather than the normally preferred straight chain aldehydes. This added selectivity would enable industrial use of hydroformylation for production of branched aldehydes.

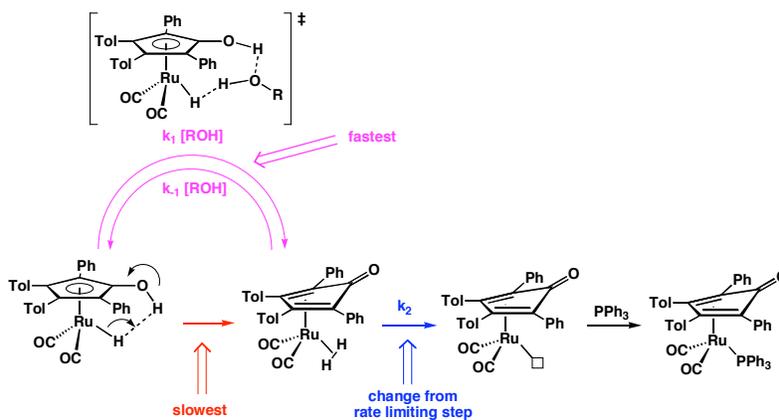
Recent Progress with $(\text{C}_5\text{R}_4\text{OH})\text{Ru}(\text{CO})_2\text{H}$ Hydrogenation Catalysts. Youval Shvo described a remarkable catalytic system in which the key intermediate $(\text{C}_5\text{R}_4\text{OH})\text{Ru}(\text{CO})_2\text{H}$ has an electronically coupled acidic OH unit and a hydridic RuH unit. Our efforts have centered on understanding and improving upon this important catalyst for reduction of aldehydes and ketones. Our mechanistic studies have established that the reduction of aldehydes by $(\text{C}_5\text{R}_4\text{OH})\text{Ru}(\text{CO})_2\text{H}$ to produce alcohols and a diruthenium bridging hydride species occurs much more rapidly than regeneration of the ruthenium hydride from the diruthenium bridging hydride species. Our mechanistic studies require simultaneous transfer of hydride from ruthenium to the aldehyde carbon and of a proton from the CpOH unit to the aldehyde oxygen and support reduction of the aldehyde without its prior coordination to ruthenium.



An alternative mechanism for aldehyde and imine reduction involves ring slippage and coordination of the substrate to Ru prior to hydrogen transfer. This ring slip mechanism has alcohol or amine “born in the coordination sphere of the metal” while transfer of hydrogen without prior coordination would give a trappable coordinatively unsaturated intermediate. Since we have shown that alcohol complexes are too kinetically labile to observe, we turned to imine reduction to resolve the issue since the resulting amine complexes are kinetically robust. While attempts to *intermolecularly* trap the coordinatively unsaturated intermediate with a second amine led only to formation of an amine complex derived from the imine, *intramolecular* trapping was successful. This provides evidence for concerted hydrogen transfer outside the coordination sphere of the amine to give a coordinatively unsaturated intermediate and amine inside the same solvent cage, followed by more rapid coordination of the amine than diffusion from the cage.

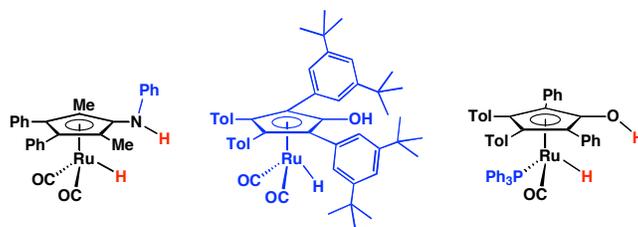


Another important step in the catalysis is the regeneration of **1** from reaction of H₂ with the diruthenium complex **2**. Preliminary studies of the microscopic reverse of this process (hydrogen evolution from **1** which occurs at 80 °C) in the presence of alcohol (the product of aldehyde hydrogenation) have shown that a dihydrogen complex is formed reversibly at a rate much faster than hydrogen evolution. Kinetic and theoretical studies in collaboration with Professor Qiang Cui of Wisconsin indicate an important role for alcohol in mediating transfer of hydrogen to ruthenium.



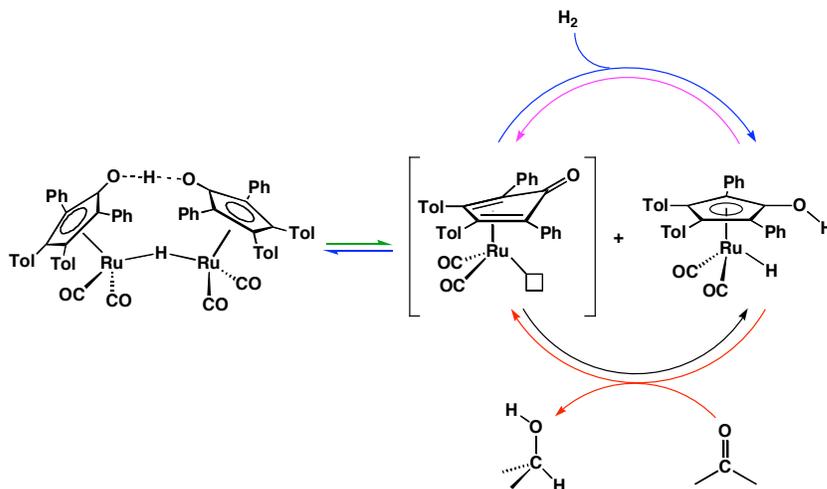
One key to developing more active catalysts is to destabilize the bridging hydride intermediate to prevent its formation or to speed its conversion to a reactive monohydride by reaction with H₂. We have found three successful ways to sterically destabilize the bridging

hydride and to obtain more active catalysts. First, replacing the CpOH group by a sterically more crowded CpNHPH group successfully prevented formation of a bridging hydride. Catalysis of aldehyde reduction at room temperature by these CpNHPH catalysts is accomplished in the presence of acid. Second, the large *t*-butyl groups on the aryl rings of the (C₅R₄OH) groups destabilized the diruthenium bridging hydride and produced a catalyst for aldehyde and ketone reduction at room temperature. Third, addition of sterically large phosphines on the ruthenium complexes prevented formation of a diruthenium bridging hydride. These phosphine substituted complexes reduce aldehydes rapidly at room temperature.



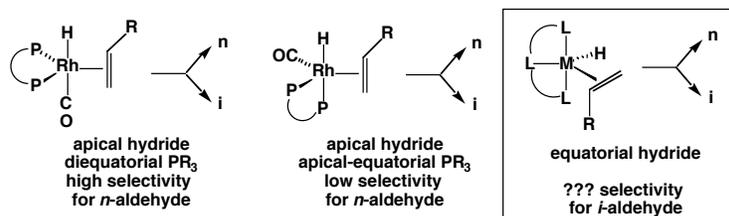
Future Plans

Our mechanistic studies of hydrogenation catalysts related to **1** will now concentrate on kinetically modeling the entire catalytic system. We will check our model by predicting and then observing the major species present during catalysis. If successful this will confirm our picture of the reaction mechanism and provide a firm basis on which to design better catalysts. We already have measured the kinetics of aldehyde reduction and decomposition of the ruthenium hydride monomer. Measurement of the rate of dissociation of the bridging hydride dimer and the equilibrium constant for conversion of the dimer to hydride monomer, should allow complete kinetic modeling.



While highly regioselective catalysts for hydroformylation of linear alkenes to *n*-aldehydes have been developed, catalysts for selective conversion of linear alkenes to *i*-aldehydes have been elusive. Rhodium hydroformylation catalysts are trigonal bipyramidal compounds with axial hydride ligands. The formation of Rh alkyls occurs by addition of the apical hydride to an equatorial alkene ligand. The selectivity of this process consistently favors

n-alkyl formation. In an effort to find an *i*-selective catalyst, we will attempt to constrain the hydride ligand to an equatorial position; the addition of an equatorial hydride to an equatorial alkene should have different selectivity rules and we hope that the change may favor *i*-alkyls. Tridentate ligands with natural bite angles around 80-90° should complex to an equatorial and both apical sites in a trigonal bipyramid and thus force a hydride ligand to an equatorial position.



Impact on Science of Relevance to DOE. Better understanding of fundamental organometallic reactions and catalytic processes will aid and enable design of energy and material efficient chemical processes. Our work is contributing to the development of catalysts for the selective and mild hydrogenation of ketones and aldehydes; this will provide a modern green alternative to reductions by LiAlH₄ and NaBH₄ which require extensive work-up procedures and produce waste streams. The development of regioselective hydroformylation catalysts for conversion of alkenes to *i*-aldehydes will provide a new route to these important intermediates in organic synthesis. Discovery of enantioselective routes to *i*-aldehydes would enhance the value of the procedures.

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HIGH PRESSURE CATALYSIS IN A UHV ENVIRONMENT: INTERACTION OF HYDROGEN WITH AND HYDROGENATION CHEMISTRY ON Ni ALLOYS

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The aim of this project is to carry out high-pressure, heterogeneous catalytic hydrogenation reactions in a low-pressure, ultrahigh vacuum environment. Results to date show that bulk hydrogen is the reactive species in the high pressure hydrogenation of ethylene adsorbed on Ni(111) to ethane and the hydrogenation of acetylene adsorbed on Ni to ethylene. Surface bound hydrogen is found to be unreactive for hydrogenation of the carbon-carbon multiple bond. The present work extends this investigation into the interaction of hydrogen with a Ni alloy. The Ni alloy serves as a more suitable model for the commercial hydrogenation catalyst, Raney Ni, than the Ni(111) surface. These investigations are carried out under the single collision conditions of an ultrahigh vacuum environment. The model catalyst is a Au-Ni surface alloy, which hints at the formation of bulk H upon interaction with H₂ at low pressures. This interaction is an unusual one in an ultrahigh vacuum environment and suggests that the hydrogenation reactions of unsaturated hydrocarbons will be equally intriguing. This investigation also probes the possibility that additional kinds of hydrogen are present on the models of the commercial catalyst that are not present on Ni(111). Investigations of hydrogenation reactions, which are high pressure heterogeneous catalytic reactions, in a low pressure, ultrahigh vacuum environment have now become possible because of the culmination of many studies in our laboratory. These studies have resulted in the development of new physical processes and techniques: collision induced absorption, collision induced recombinative desorption, bulk vibrational spectroscopy and the synthesis of adsorbed reactive intermediates by translational and collision induced activation. These new processes allow the simulation of a high pressure environment while maintaining the single collision conditions in which microscopic steps and intermediates can be elucidated and detected by molecular beam scattering coupled with high resolution electron energy loss spectroscopy. These investigations have already revealed a new kind of reactant, bulk H, with a chemistry of its own and will continue to provide critical tests of the mechanisms for heterogeneous catalytic reactions.

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Structure-Property Relationship in Metal Carbides and Bimetallic Alloys

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Research Goals:

It is well known that the electronic and catalytic properties of transition metals can be modified by alloying with carbon or with another metal. The resulting metal carbide or bimetallic alloy often demonstrates properties that are distinctively different from those of the parent metal. The objective of the project is to use selected carbides and bimetallic alloys as model systems to unravel the relationship between the electronic/geometric structures and the chemical/catalytic properties.

Research Approaches:

The current research project involves three parallel approaches: (1) Fundamental surface science investigations of the reaction mechanisms of several carefully-chosen hydrogenation and dehydrogenation probe reactions on carbide and bimetallic surfaces. (2) Correlation of chemical activities of these surfaces with their electronic properties using a combination of experimental measurements and DFT modeling. (3) Synthesis and evaluation of relevant carbide and bimetallic powder catalysts to bridge the “materials gap” and “pressure gap” between model surface science studies and heterogeneous catalysis.

Recent Progress:

In the past year we have made significant progress in correlating the structure-property relationship by modifying transition metals either with carbon atoms to make carbides, or with metal adlayers to make monolayer bimetallic surfaces (see attached publication list). In the area of transition metal carbides, our focus has been to modify the electronic and chemical properties of Groups 4-6 early transition metals by the formation of carbides. In addition, we have directly compared the chemical activities of carbide-modified surfaces with those of Pt-group metals using several probe reactions involving the hydrogenation and dehydrogenation of hydrocarbons. Overall, our results indicate that the activities of the carbide surfaces depend on both the location of the parent metal in the Periodic Table and the structure of the metal substrate. We have also investigated the reaction mechanisms of hydrogen and methanol on several carbide surfaces, which demonstrated the possibility of utilizing tungsten carbides (WC) and Pt-modified WC as potential alternative electrocatalysts for hydrogen and methanol fuel cells.

Similar to alloying metal with carbon to produce metal carbides, alloying with another metal provides a different way to tune the electronic and therefore chemical properties of transition metals. It is well known that bimetallic surfaces, prepared by depositing one metal onto another, often demonstrate novel physical and chemical properties that are not seen in either pure metal alone. We have discovered a novel low-temperature hydrogenation pathway in the Ni/Pt(111) and Pt/Ni(111) bimetallic system. We have utilized Density Functional Theory (DFT) modeling to determine a near linear correlation between the center of the d-band and the hydrogen binding energy on these bimetallic surfaces, revealing the critical role of weakly bonded hydrogen in the low-temperature hydrogenation. The utilization of DFT modeling enabled us to predict many other bimetallic systems with a wide range of hydrogen binding energy. We are currently performing experimental studies on selective bimetallic systems to determine whether the weakly-bonded hydrogen will lead to the selective hydrogenation pathways, such as the selective hydrogenation of the C=O bond in acrolein (CH₂=CH-CH=O).

Future Plans:

In the next year we will investigate the hydrogenation mechanisms of acrolein and cyclohexene on carbide-modified molybdenum (Mo) and tungsten (W) surfaces, and on Pt/Mo and Pt/W bimetallic surfaces. The reason for choosing the C/Mo, C/W, Pt/Mo and Pt/W surfaces is to directly compare the modification effect of alloying Mo (and W) with carbon and with Pt. The chemical activities of these surfaces will then be correlated with the electronic properties, which will be determined both experimentally and by DFT modeling. Furthermore, C/Mo, C/W, Pt/Mo and Pt/W powder catalysts will be synthesized and evaluated to correlate model single crystal surfaces and supported catalysts.

DOE Interest:

The overall goal of the current research is to demonstrate the possibility to predict and design materials with desirable catalytic properties. We believe that carbides and bimetallics are excellent model systems to directly correlate the relationship between electronic/geometric structures and chemical/catalytic properties. Such structure-property relationship, to be determined using a combination of surface science experiments, DFT modeling, and catalytic studies, should help in predicting and controlling the catalytic properties of transition metals in general and carbide/bimetallic catalysts in particular.

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2. M.B. Zellner and J.G. Chen, "Surface Science and Electrochemical Studies of WC and W₂C PVD Films as Electrocatalysts", Catalysis Today, submitted.
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5. H.H. Hwu, M.B. Zellner, and J.G. Chen, "The Effect of Oxygen Modification on the Electronic and Chemical Properties of C/Mo(110)", *Journal of Catalysis*, submitted.
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**New Generation Polymers from Inexpensive Renewable Sources
by Well-Defined Metal Alkoxide Catalysts: Polyethers, Polyesters, and Polycarbonates**

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Goal

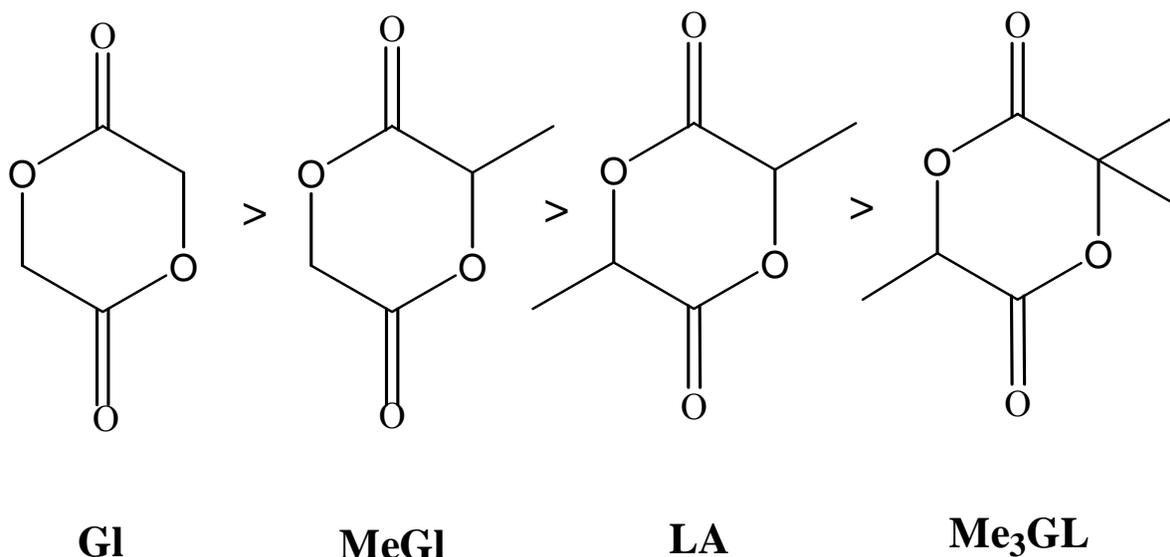
To develop environmentally benign routes to polyoxygenates such as polyesters and polycarbonates by the ring-opening polymerization of cyclic esters derived from renewable resources and the copolymerization of epoxides/oxiranes and carbon dioxide to replace condensation polymerizations involving phosgene.

Introduction

Current demand for polymers based on petroleum-derived chemicals continues to rise at an amazing rate [*Chem. Eng. News* June 2nd, 2003, pp 24-27]. This sets the stage for (i) the need to develop polymers that can replace existing petroleum-based ones by polymers derived from readily available and renewable resources; (ii) the development of biodegradable and biocompatible polymers for packaging, control release and biomedical applications (sutures, tissue matrices); and (iii) the development of environmentally benign chemical processes for the production of new generation polymers. This work targets the production of polyesters and their blends by ring-opening polymerization of cyclic esters derived from renewable sources, e.g. the production of polylactides, PLAs, from Lactides (D, L and *rac*) derived from corn and the formation of polycarbonates by ring opening copolymerization of epoxides/oxiranes and carbon dioxide as an alternative to current procedures involving the condensation polymerization of diols with phosgene or its equivalent. Our work involves three key aspects of the polymerization process. 1) We are establishing a fundamental understanding of the key reaction steps in the polymerization process: an elucidation of mechanism for the desired reaction pathway together, with an understanding of how to control/limit deleterious side reactions. 2) The development of new single-site metal catalysts that may afford an increase in the rate of polymerization and better control of polymer microstructure and molecular weight distribution. 3) The development of new polymer blends derived from alternate molecular precursors and the knowledge gained from 1) and 2) above.

Recent Results

Organotin(IV) Catalysts: Aryltin(IV) compounds Ar_3SnX and Ar_2SnX_2 where X = an alkoxide or NMe_2 and $\text{Ar} = p\text{-YC}_6\text{H}_4$ have been prepared and employed to study the ring-opening polymerization of L-lactide in hydrocarbon solvents. These catalysts are relatively slow and allow an examination of the rate of initiation, the ring-opening event: $\text{X} = \text{NMe}_2 > \text{OMe} > \text{OPr}^i > \text{OBu}^t > \text{OPh}$ and $\text{Y} = \text{CF}_3 > \text{F} > \text{H} > \text{Me}$.¹ This order establishes the importance of (i) the electrophilicity of the metal center and (ii) the basicity of the X ligand, together with the importance of steric factors. The latter is also seen in a comparison of the rates of ring opening of glycolide, methyl glycolide, lactide and trimethylglycolide as shown below.²



For the reaction involving $\text{Ph}_3\text{SnOPr}^i$ and L-LA, the activation parameters for the initial ring opening event were determined to be $\Delta H^\ddagger = 14(1) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = +44(4) \text{ eu}$.¹ For the ring-opening polymerization by $\text{Ph}_2\text{Sn}(\text{OPr}^i)_2$ as an initiator, the activation parameters $\Delta H^\ddagger = 12(1) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = +44(4) \text{ eu}$ were determined.² A comparison of the GPC and MS data for the polymerization of L-LA by Ph_2SnX_2 initiators, revealed a remarkable dependence on polymer microstructure and molecular weight distribution as a function of $\text{X} = \text{OPr}^i$ vs NMe_2 . Whereas the former produced long chains, the latter favored the formation of cyclic-PLA.² The formation of cyclic-PLA was traced to the preference for intrachain *trans*-esterification when $\text{X} = \text{NMe}_2$ due to the stability of the tin(IV) chelate complex $\text{Ph}_2\text{Sn}(\text{OCHMeC}(\text{O})\text{NMe}_2)_2$, which is the favored resting state of the catalyst.³ The relatively slow rates of ring opening of LA and ϵ' -caprolactone have allowed the study of the competing side reactions in these systems. It was found that chain transfer is faster than ring opening, which, in turn, is faster than *trans*-esterification.³

Single-Site Zinc, Magnesium and Calcium Catalysts: A detailed comparison of the chemistry of β -diiminate metal-amide/alkoxide catalyst precursors of the form LMX and $[\text{LMX}]_2$ where $\text{L} = \text{CH}(\text{CMeNC}_6\text{H}_3\text{-2,6-Pr}_2^i)_2$ and $\text{X} = \text{NSi}_2\text{Me}_6, \text{NPr}_2^i, \text{OBu}^t$ and OPr^i was made.⁴

Quantitative measurements revealed the greater electrophilicity of the magnesium complexes and their tendency to associate in non-polar solvents and/or bind additional ligands such as THF. In polymerization of lactide, the rates were in the order $Mg \gg Zn$ but zinc was found to be more tolerant and showed greater stereoselectivity in producing heterotactic PLA from *rac*-LA. The magnesium catalyst which is more aggressive in polymerization kinetics shows less stereoselectivity and also leads to higher PDI values due to competing *trans*-esterification reactions which become significant as the concentration of [LA] decreases with time.

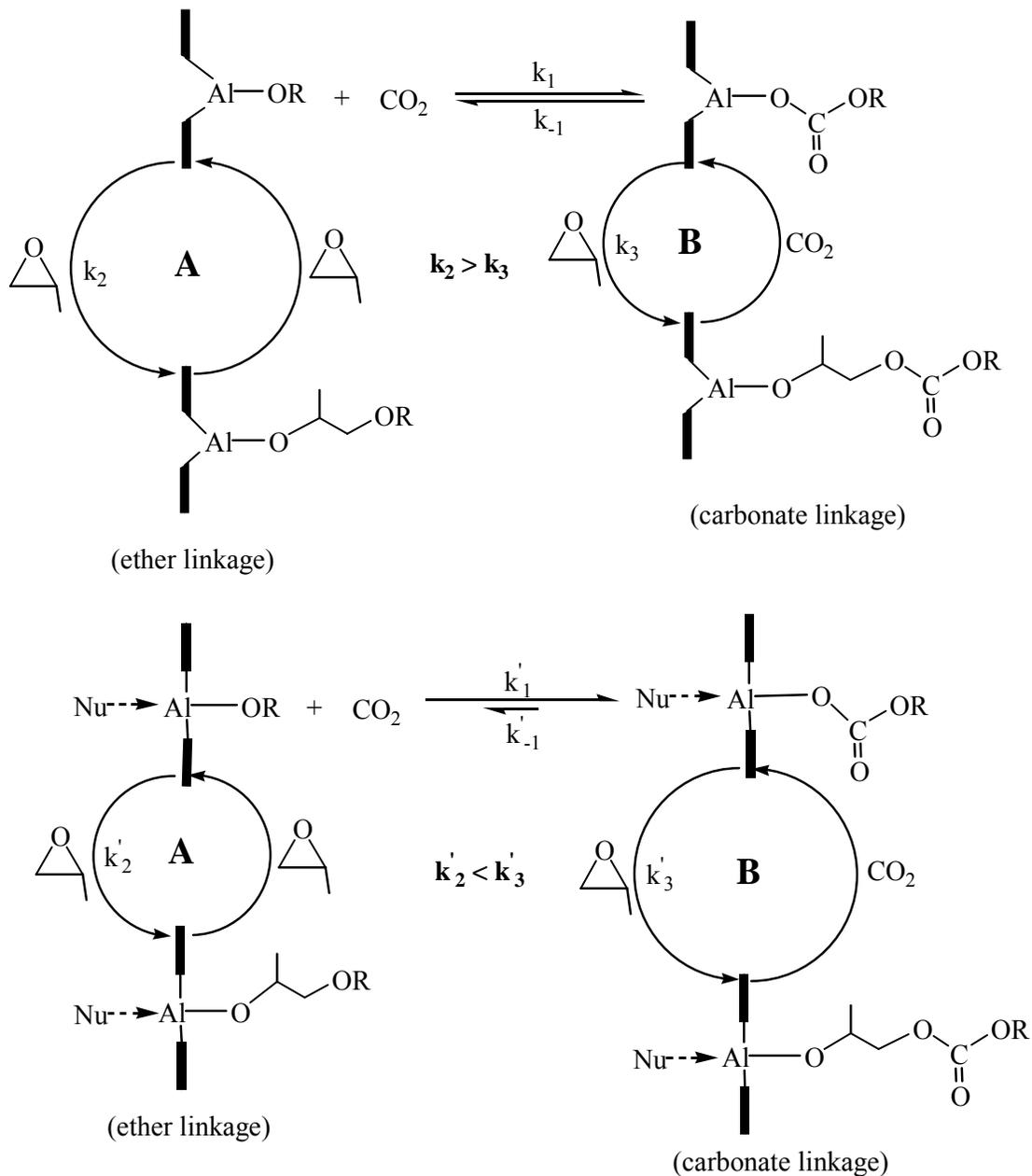
A new series of calcium initiators has been prepared.⁵ The use of the β -diiminate ligand is inappropriate as ligand scrambling can occur to give CaL_2 complexes and loss of single-site control. The use of the bulky *tris*-pyrazolyl borate with ^tBu substituents, $HB(pz^{Bu^t})_3$ prevents this and in competition experiments, the $HB(pz^{Bu^t})_3 CaX$ precursors where $X = NPr_2^i$ or OAr are the fastest catalyst reported to date: $Ca > Mg > Zn$. There is also significant stereoselectivity in the ring-opening polymerization of *rac*-LA by these calcium initiators. In CH_2Cl_2 , 200 equiv *rac*-LA give >80% heterotactic PLA in >95% yield in less than 1 min at 25°C! Rather interestingly, these magnesium and calcium alkoxide complexes will not react with propylene oxide or cyclohexeneoxide to give polyethers, PPO or PCHO. In the case of magnesium, ring opening is observed by allylic proton abstraction to give an ene-oxide ligand.⁴ Whereas, in the case of calcium, a PO adduct can be trapped, isolated and structurally characterized.⁶ This is particularly interesting since calcium is one of the industrially-important catalysts employed in the production of PEO and PPO by the Union Carbide process.

Co-Polymerization of PO and CO₂ by Porphyrin and Salen Metal Complexes:

Considerable attention has been given to the elucidation of the stereochemistry of polypropyleneoxide, PPO,⁷ and polypropylenecarbonate, PPC,⁸ by various heterogeneous and homogeneous catalyst systems. New assignments of regio- and stereo-sequences have been made. Based on these new assignments, we have been able to interrogate the mechanism of polymerization of PO and the co-polymerization of PO/CO₂ by porphyrin and salen metal catalysts LMX where $M = Al$ and Cr .⁹ The influence of the promoter dimethylaminopyridine, DMAP, has also been investigated.⁹

The reaction sequence is summarized in Scheme 1. In the absence of added DMAP, ring opening of PO occurs either once ($M = Al$, $L = salen$, $X = Cl$) or PPO is formed to the exclusion of PPC ($M = Al$, Cr , $L = porphyrin$, $X = Cl$ or OR). DMAP promotes 1) insertion of CO₂ into the $M-OR$ bond and 2) labilizes PO ring opening by X in the order $O_2CR > O_2COR \gg OR$. The stereochemistry of the ring opening of PO has also been studied and been shown to occur by competitive attack at the methylene and methine carbon. Attack at the methine carbon leads to ring opening by both retention and inversion of stereochemistry. Collectively, these results indicate that the reaction pathway leading to PO ring opening occurs by an associative interchange mechanism wherein DMAP coordination labilizes the *trans* $M-OC(O)OR$ bond to heterolytic cleavage and PO coordination to the electrophilic metal center.

Scheme 1. Proposed mechanism for PO/CO₂ copolymerization by (TPP)AlX systems.



DOE Interest

This work holds promise for the development of new environmentally friendly/green catalysis for polyoxygenates from renewable sources and the replacement of petroleum-based or noxious chemicals, e.g. *bis*-phenol-A and phosgene.

Future Plans

1. Work is underway to prepare new calcium catalysts LCaX that will be highly active to ring-opening polymerization of cyclic esters but resistant to hydrolysis and ligand scrambling.

2. A route to cyclic-PLA is being explored by anchoring an active metal-amide unit to a solid support. In this way, the growing PLA is attached to an immobilized active single site and intra-chain esterification releases the PLA to the solution medium.

3. Further studies of the copolymerization of oxiranes and CO₂ in the presence of promoters and cocatalysts and chain transfer agents are underway in an attempt to prepare new polymer blends of polyether polycarbonates and polyether-polyester copolymers.

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Competitive Transport through Zeolitic Membranes

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Goal

Develop an understanding of adsorption and competitive transport through zeolite membranes.

Recent Progress

Considerable progress has been made in the synthesis of zeolitic membranes for use in separations and catalysis. Many studies have characterized the permeation of single components or mixtures where the relative fluxes are measured; however, little is known about their detailed operation through the nanoporous network, i.e., within and between the zeolite crystals that comprise the membranes. We have employed in situ spectroscopy and frequency response analyses coupled with simulation studies to elucidate the molecular transport processes.

In Situ Infrared (variable angle ATR) to follow transport: It is crucial to determine the relative concentration of competing species within the membrane as a function of distance to understand the competitive transport through the membrane. Infrared spectroscopy is able to distinguish between different species within a network. Attenuated total reflectance is able to probe within a media in contact with an infrared transparent crystal. If the angle of incidence is varied, the depth of penetration within the media varies up to $\sim 5\text{-}10\mu$. A schematic for the experiment is depicted in figure 1 left. A Harrick Sci. Seagull was modified to pass a gas over a membrane pressed against a ZnSe hemispherical crystal. A motor drive varies the angle of incidence from $20\text{-}80^\circ$ from the normal. This corresponds to from 5μ to less than 1μ penetration.

The peaks corresponding to benzene at 3046cm^{-1} and isopropanol at 2883cm^{-1} as a function of time and the angle are shown in figure 2 following the introduction of a pulse containing a 50:50 mixture of benzene and isopropanol. The angle is expressed from the surface normal such that 31° corresponds to a larger depth of penetration and, thus, probes closer to the surface from which the pulse was introduced on one side of a silicalite membrane. The benzene is the first to penetrate into the membrane followed by the isopropanol. However, the relative concentrations invert during desorption as the isopropanol is apparently more strongly bound within the membrane. The differences in concentration with position indicate the relative rates of diffusion while the persistence in time reflects the relative energetics of

competitive adsorption. While this gives a good *in situ* picture of competitive diffusion through the bed, it is also necessary to understand and characterize the competitive diffusion within the zeolite crystals which comprise the membrane.

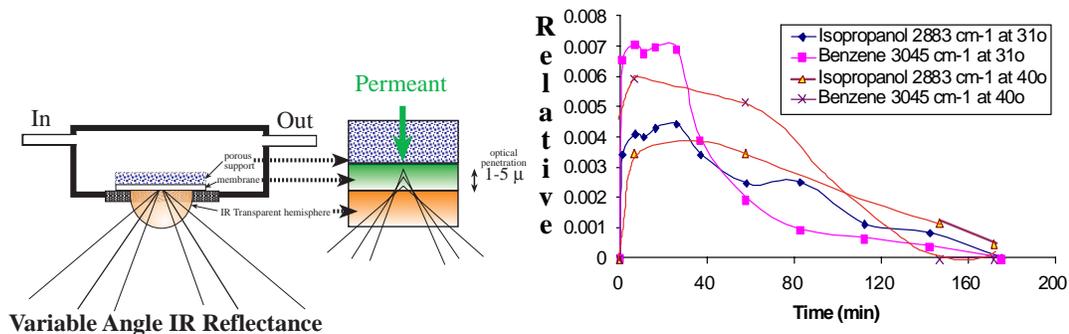


Figure 1 (left): Schematic of variable angle ATR optical path (left) wherein a zeolite membrane is pressed against a ZnSe hemispherical crystal. A pulse of sorbing gas mixture is introduced into the He stream and the composition within the membrane is monitored at different depths by varying the angle of incidence.

Figure 2 (right): Results for a pulse of a 50:50 mixture of benzene and isopropanol detected in time at different incident angles at 25°C. The 31° angle senses the diffusing species nearer to its source above the membrane than the 40° angle. A He carrier gas eventually removes the sorbing species.

Competitive Sorption within the Zeolite by Frequency Response: Zeolite crystals sorb diffusing species in often complex ways. The network can be multidimensional and anisotropic such that a single species might exhibit more than one effective diffusion rate. As an example, benzene diffuses with two rates within the straight or zig-zag channels of ZSM-5/silicalite. As a consequence there would be four effective rates for the diffusion within the pore network structure of silicalite for p-xylene and benzene. Similarly, o-xylene and p-xylene exhibit three different diffusivities as o-xylene only diffuses within the straight channels while p-xylene has access to both. Frequency response can quantify each of these diffusion processes within the crystals and, more importantly, determine the influence of one species on the individual diffusivities of another species. This is the only technique that provides this direct measurement of individual diffusivities in mixtures of competing species.

As an example, we have measured the influence of ortho-xylene and benzene on the transport of para-xylene within the zig-zag or straight pores of silicalite. The results are summarized in figure 3.

Figure 3: The influence of o-xylene (left) or benzene (right) on the individual diffusivities for p-xylene within the straight and the zigzag channels in silicalite. These have each been normalized to the pure p-xylene diffusivities¹.

¹ Note that the diffusivity of p-xylene in the straight channels is almost an order of magnitude faster than in the zigzag channels of silicalite.

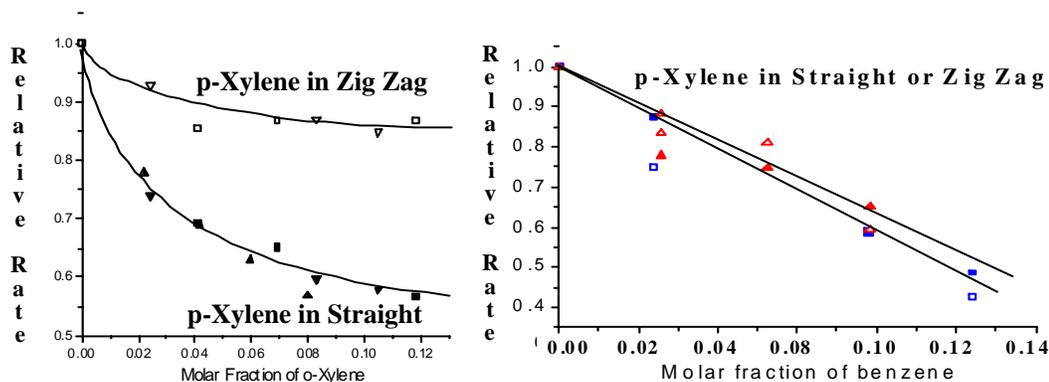


Figure 3 shows that *o*-Xylene has a different effect than Benzene on the two *p*-Xylene diffusion processes, shown on the left. *o*-Xylene impedes the diffusion of *p*-Xylene in the straight channels much more than the diffusion of *p*-Xylene in sinusoidal channels. On the other hand Benzene impedes the diffusion of *p*-Xylene in each pore system equally, seen on the right. These studies demonstrate that there are several forms of traffic control for diffusion within a pore network, in this case anisotropic traffic control. While it is commonly believed that *o*-xylene resides at the intersections of the two pore systems, it does not block the transport within the zig-zag channels as much as within the straight channels.

Completing Prior Work: Papers on our parallel studies of adsorption in mesoporous solids and the adsorption of nitrogen within zeolites as studied by $^{15}\text{N}_2$ NMR are completed and several papers are in press on these subjects. The studies described herein have not yet been published but are being submitted spring 2004.

DOE Interest

Zeolites and other nanoporous solids are employed throughout industry for selective catalysis and separations. The diffusion of pure fluids through nanoporous solids is not of practical significance; rather, it is mixture transport that must be understood. These studies have developed techniques to quantify and to understand sorption and transport of mixtures within membranes and also within single zeolite crystals. These will be further developed and applied to mixed porous systems in our future studies.

Future Plans

The focus of our future studies is the development and application of experiment and simulation to understand how mixtures of guests and mixtures of pore sizes conspire to produce observable transport properties.

Experimental Characterization of Sorption Transport in Pore Networks: We will develop techniques to characterize multidimensional pore network structures and transport of competing species within these. The systems studied include inorganic membranes (including zeolites) and the new meso-micro-porous solids, e.g., SBA-15. Most importantly, these experimental techniques will become the basis for the

development of theoretical approaches for the simulation of transport in these real networks.

Theoretical Analyses and Modeling; The combination of experimental studies of competing diffusion in membranes is central to our future studies in collaboration with Scott Auerbach in Chemistry. He has already developed molecular dynamics and grand canonical Monte Carlo for the simulation of single components within single crystals and through membranes.

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Hydrocarbon Dehydrogenation and Oxidation over Model Metal Oxide Surfaces

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Goal

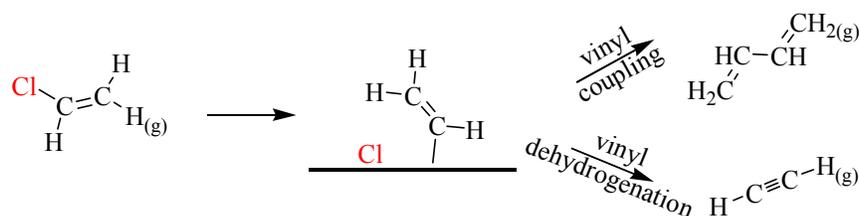
Develop a fundamental understanding of the factors controlling the selectivity of alkane dehydrogenation reactions over metal oxides surfaces.

Recent Progress

The current focus of our work is on the reactivity of C₂ hydrocarbon fragments over the model α -Cr₂O₃ (10 $\bar{1}2$) surfaces. Halogenated hydrocarbons are used as precursors to surface hydrocarbon fragments since C-X (X=halogen) bonds are more readily broken than C-H bonds in alkane and alkene reactants. Reactions of C₂ alkyl and alkenyl species are under study experimentally and computationally as a basis for understanding the origins of the overall reaction selectivity observed for ethane dehydrogenation over chromia based catalysts.

The ideal stoichiometric α -Cr₂O₃ (10 $\bar{1}2$) surface exposes cations with a single coordination vacancy, but these cation sites can be capped with terminal chromyl oxygen (Cr=O) species via dissociative O₂ adsorption. Oxygenated reaction products are only observed in the presence of terminal oxygen. Our work is currently focused on the reactions of fragments to non-oxygenated products over the stoichiometric surface.

Reactions of Alkenyl Fragments: Vinyl chloride (CH₂=CHCl) has been used as a precursor for the preparation of surface vinyl groups. Synchrotron based XPS measurements indicate that the C-Cl bonds in vinyl chloride are broken by 200 K, prior to the evolution of the gas phase products. NEXAFS of the C 1s edge indicates the persistence of a $\pi^*_{C=C}$ resonance after C-Cl bond cleavage, indicative of the expected vinyl reaction intermediate. Thermal desorption experiments give 1,3 butadiene (CH₂=CH-CH=CH₂), acetylene (HC≡CH), ethylene (CH₂=CH₂) and dihydrogen (H₂) as gas phase reaction products above room temperature. Vinyl coupling to butadiene and dehydrogenation to acetylene are competing reactions with a branching ratio that depends on the coverage of surface Cl adatoms. Higher Cl coverages favor acetylene formation, presumably by inhibiting the surface diffusion and subsequent coupling of vinyl fragments. Chlorine adatoms also stabilize the surface vinyl fragments, and increase the barrier to dehydrogenation. The rate limiting step for the production of ethylene and H₂ is vinyl dehydrogenation to release surface H.



1-chloro-1-fluoroethene ($\text{CH}_2=\text{CFCl}$) and 1,1-dichloroethene ($\text{CH}_2=\text{CCl}_2$) have been used as precursors to vinylidene surface intermediates. Work with the chlorofluorocarbon suggests a mechanism that proceeds via initial C-Cl bond cleavage followed by α -fluorine elimination to vinylidene. The only gas phase reaction product is acetylene produced from vinylidene isomerization. Thermal desorption studies show that the reaction limited evolution of acetylene occurs with the same activation barrier for the chlorofluorocarbon and dichlorovinylidene reactants, indicating that vinylidene isomerization is the likely rate limiting step since the barrier to α -Cl elimination should be less than α -F elimination. This conclusion is born out by synchrotron based XPS measurements for dichlorovinylidene that indicate both C-Cl bonds are broken prior to the evolution of gas phase reaction products.



Reactions of Alkyl Fragments: Ethyl iodide ($\text{CH}_3\text{CH}_2\text{I}$) has been used as a precursor for the preparation of surface ethyl fragments. Thermal desorption experiments give ethylene ($\text{CH}_2=\text{CH}_2$), ethane (CH_3CH_3) and dihydrogen as gas phase products. β -H elimination is the rate limiting step for the formation of all the products.

Coke Forming Surface Intermediates: Reactions of the C_2 surface intermediates investigated to date (vinyl, vinylidene, ethyl) all occur cleanly with little surface carbon deposition and no evidence of complete dehydrogenation or C-C bond breaking.

Computational Studies: Density functional theory is being used to compliment our experimental studies of the reaction of hydrocarbon fragments on $\alpha\text{-Cr}_2\text{O}_3$ ($10\bar{1}2$). To date, calculations have been completed for bulk and ($10\bar{1}2$)surface geometric and electronic structure, along with an investigation of O (terminal $\text{Cr}=\text{O}$) and Cl adatoms. Work is currently in progress on the adsorption geometry of vinyl chloride for comparison to our NEXAFS results.

Work also continues on our examination of the electronic structure of various bulk oxide minerals, primarily silicates and aluminosilicates. We are investigating the relationship between the electron localization function, binding sites of H atoms in bulk and minerals and on surfaces, and identification of site for electrophilic and nucleophilic attack.

DOE Interest

The reaction pathways of hydrocarbon surface intermediates control the selectivity of alkane activation/dehydrogenation catalysts. The development of efficient and selective alkane activation catalysts will allow the use of cheaper feedstocks for chemical synthesis.

Future Plans

NEXAFS and synchrotron based XPS will be used to investigate vinylidene precursors and intermediates. Density functional theory will be used to examine the bonding geometry of vinyl and vinylidene surface intermediates for comparison to NEXAFS data. Preliminary thermal desorption work with cis-1,2-dichloroethene shows the desorption limited evolution of acetylene. Future work will also investigate the reaction of trans-1,2-dichloroethene to determine if the reaction kinetics are sensitive to the structure of the reactant.

The reactions of other surface intermediates (acetylide, ethylidene, ethylidyne) will also be investigated. Special attention will be paid to those intermediates that show potential as coke formers.

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Abnormal Carbene Binding: Homogeneous Catalytic Processes in Complexes with Non-Phosphine Ligands

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Goal

Develop catalytic chemistry with nontraditional C-donors as spectator ligands.
Document and try to understand properties of new ligands such as abnormal C5 bound NHCs.

Recent Progress

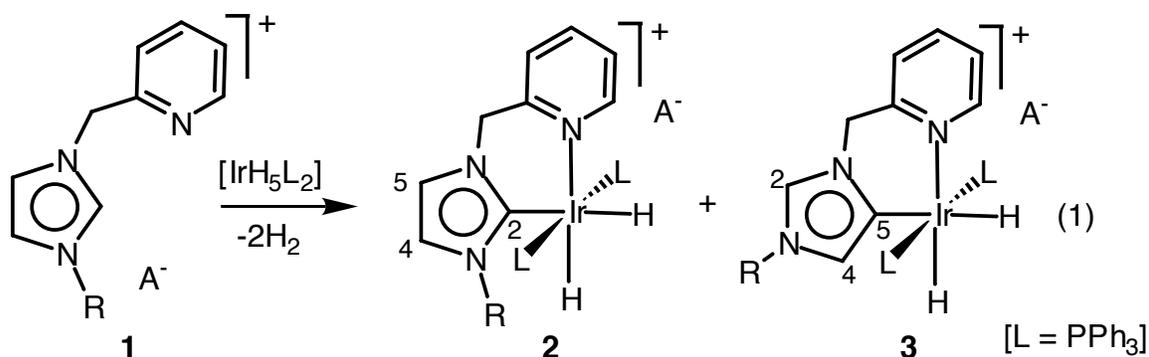
Rising interest in NHCs is suggested by the sharply increasing number of documents found by *Web of Science* under 'NHC or imidazol-2-ylidene': 1998, 17; 1999, 38; 2000, 42; 2001, 55; 2002, 61; 2003, 92. This may be associated with the useful properties often found for such catalysts: air stability, unusual selectivity and high rates. Beyond catalysis, we have also found some abnormal binding modes for NHCs and have begun to document their electronic and steric properties. Normal NHCs are more donor than any PR_3 ligands and abnormal (C5 bound) NHCs prove to be even more so. Strong donor ligands are often associated with useful catalytic properties.

Aldehyde Reduction Catalysis: Hydrogen transfer reduction of aldehydes fails with phosphine complexes probably because aldehyde decarbonylation deactivates the catalyst. Using a stereoelectronic strategy, described below, that favors Ir(III) over Ir(I), we designed¹² some chelate NHC catalysts that prove to have high activity and resist decarbonylation. By moving to alkali carbonates as bases, we were even able to reduce aldehydes that give only aldol products under conventional conditions. In this case it is the high activity of the catalyst that contributes to avoidance of byproducts.

Chelate NHCs for Control of Oxidation State: Chelating NHCs having $-(\text{CH}_2)_n-$ linkers show oxidation state preferences in Rh and Ir that are linker length dependent.¹⁴ We have traced this property to the anisotropy of the NHCs and the tendency of the linkers to fix the rings in different orientations depending on linker length. Square planar M(I) is preferred when the NHC rings are aligned with the out-of-plane z axis, unoccupied in square planar M(I). Such an alignment occurs for $n = 3$ and 4. In contrast, for $n = 1$ and 2, the NHC rings are aligned between the z axis and the xy plane in such a way that M(III) is preferred, possibly for electronic reasons, the NHCs being such strong donors.

Abnormal Carbenes: We have developed ways of deliberately synthesizing abnormal (C4-bound) NHCs from imidazolium salts substitutionally blocked at C2. The Ir(I) species [(cod)IrCl(NHC)] can readily be synthesized by transmetalation from the Ag complex, formed from the imidazolium salt with Ag₂O. Ir(III) species can readily be synthesized by direct metallation with IrH₅(PPh₃)₂. In the Ir(I) case, we prepared [(CO)₂IrCl(NHC)] derivatives of analogous normal and abnormal NHCs and, after comparison with a [(CO)₂IrCl(PR₃)] series, find the abnormal carbene has a Tolman electronic parameter a full 11 cm⁻¹ lower, indicating the abnormal NHC is a far more donor ligand.

Ion Pairing: We saw in last year's report that the abnormal/normal ratio 2/3 in the metallation shown is strongly dependent on the nature of the counter-ion, A⁻. We now have a working model for the mechanism in which the imidazolium C2-H bond is engaged in tight ion pairing/hydrogen bonding with the counterion, A: C-H...A. In the TS for C2-H oxidative addition, we expect the CH proton to be acidified relative to the ground state, as in a sigma complex, so anions like Br⁻ that ion pair more strongly stabilize this TS and more of the normal (C2-bound) NHC is formed versus the C5-H ion-independent pathway.



In other work, a full paper² on the influence of ion pairing on the heterolysis of H₂ by an Ir(III) system with an internal basic site has been published. Here, bulky ligands cause ion pairing at a site distant from the metal, which results in the heterolysis of a bound H₂ so that the proton so formed can maintain contact with the counterion. Small ligands allow ion pairing with the bound H₂ so no heterolysis occurs.

Pincer Complexes: Two papers^{5,7} deal with pincer NHC complexes of Pd and Ru. In the first, fluxionality between two chiral conformations is accelerated by the transient coordination of an outer sphere anion. In the second, a new Ru(II) complex is tested for various catalytic reactions without success.

Skeletal Rearrangement of Norbornadiene: The reaction of a methylene-bis-triazolium ligand precursor with [(nbd)RhCl]₂ leads to an unusual rearrangement of the norbornadiene to a metal-bound nortricycyl group.⁴

Carbon-carbon coupling: A rare η^2 -butadienyl complex was formed from an alkyne double insertion in Ir(III) with each alkyne undergoing a vinylidene rearrangement, as verified by isotope labeling.⁶ Catalytic versions were sought without success.

Alkyne Hydrosilylation Mechanism: An η^2 -vinyl pathway was proposed⁸ to explain net trans alkyne hydrosilylation to vinylsilane via transition metal catalysis even in cyclic cases where an alternative pathway was suggested.

Agostic C-C Bonds: A set of criteria, proposed¹⁰ for distinguishing between an agostic C-C bond and a close metal-ligand contact, was used to rule out an agostic C-C bond in $[(C_5H_4MeEt)Ir(PPh_3)_2]^+$, a case in which it had previously been suggested.

Reviews: A number of invited reviews^{1,3,9,13} have appeared on the DOE work. In the last, we consider how NHC catalysis may allow molecular recognition elements to be introduced into homogeneous catalysis.

DOE Interest

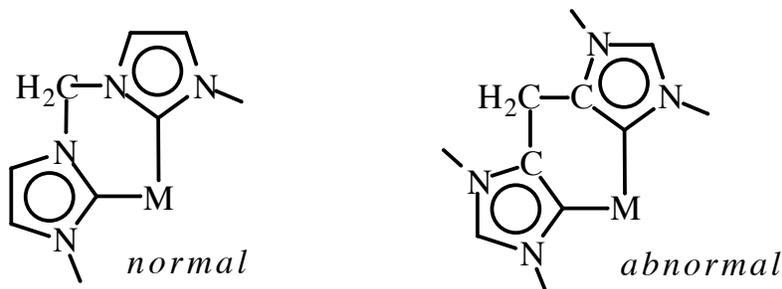
These new catalysts appear to be much more stable to air and thermally than traditional phosphine-stabilized ones and are not easily poisoned by substrate impurities. This could make homogeneous catalysis easier to apply and hence more accessible to a wider user group. NHCs, specially abnormal NHCs have exceptional donor power, a property that has been associated in the past with useful catalytic properties.

Future Plans

Chelate NHCs for Control of Oxidation State: One unresolved point in this area is whether the kinetic linker length dependence seen above¹⁴ implies a thermodynamic dependence. We need to find a suitable equilibrium to test this proposal. If so, catalytic applications are possible by using the linker length to adjust the relative energies of M(I) vs. M(III); many catalytic pathways involve M(I) and (III) states.

Hydrogen Transfer Catalysis: Extension of the work in ref. 12 shows the catalysts have activity for imines, with the possibility of selective reduction of imines in the presence of aldehydes.

Abnormal Carbenes: The possibility of constructing chelates with stable C-C links rather than the potentially labile N-C links that are alone possible for normal carbenes, abnormal carbenes have strong possibilities for useful development as ligands in catalysis. We hope to apply our compounds to challenging catalytic reactions such as alkane dehydrogenation and functionalization, halocarbon dehalogenation, hydrocarbon coupling and related reactions. The oxidation resistance of the carbene ligands gives the opportunity to carry out oxidation reactions with these and related catalysts. Reactions of green chemistry interest such as dehalogenation also seem appropriate.



Double CH Activation We are in the final stages of completing our mechanistic work on this system. One interesting result is the demonstration that alpha-elimination requires orthogonality between the newly forming carbene plane and the M-H bond of the H that is transferred. In one case, the reverse alpha-elimination path only occurs if the stereoelectronic situation is favorable.

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From First Principles Design to Realization of Bimetallic Catalysts for Ultrahigh Selectivity

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Goal

Synthesize and characterize bimetallic structurally well-defined catalysts.

Recent Progress

Pd/Au bimetallic catalysts

We have examined the synthesis, characterization and catalytic properties of bimetallic Pd/Au dendrimer-encapsulated nanoparticles (DENS) formed using sixth-generation polyamidoamine (PAMAM) dendrimers. Bimetallic Pd/Au DENS were synthesized by the co-complexation method as well as the sequential loading method using Au and Pd DEC seeds. The resulting stable, water-soluble bimetallic Pd/Au DENS are fairly monodisperse with sizes on the order of 1-3 nm depending on the total metal loading. UV-visible spectroscopy was used to follow the loading and reduction of the metal salts within the dendrimers by both methods; significant differences were seen comparing Au/Pd DENS formed by co-complexation and sequential loading, suggesting the nanoparticle architectures formed by the two methods were quite different. Single particle x-ray energy dispersive spectroscopy (EDS) indicates that all the individual particles are bimetallic with percentage compositions near the percentage composition of the original metal salts incorporated into the dendrimer. Finally, the catalytic hydrogenation of allyl alcohol was probed using the Pd/Au DEC in aqueous solution; results indicate that the hydrogenation of allyl alcohol is significantly enhanced for Pd/Au DEC compared to monometallic Pd or Au DENS.

Ag/Au bimetallic catalysts

We have explored the synthesis, characterization and optical properties of bimetallic Au/Ag dendrimer-encapsulated nanoparticles (DENS). Two synthetic routes were utilized – co-complexation of the respective metal salts leading to AuAg alloy DENS, and sequential loading of one metal salt to a seed nanoparticle of the other resulting in core-

shell DENs. Physical characterization of the particles was carried out using UV-vis absorption spectroscopy, TEM and single-particle EDS. Chemical determination of the core-shell architecture was demonstrated via differential extraction of the particles from the dendrimer template. $\text{Au}_x\text{Ag}_{1-x}$ random alloys ($0.5 \leq x \leq 1.0$) and core-shell DENs were extracted from the dendrimer template with *n*-alkanethiol molecules in the presence of excess reducing agent. Particles with an Ag shell can also be extracted with *n*-alkanoic acids, while neither pure Au nor core-shell bimetallic DENs with an Au shell can be extracted in this way. This provides us with a chemical method of differentiating between the two shell compositions, and allows for the chemical separation of metallic and bimetallic nanoparticles.

DOE Interest

The dendrimer templating approach is a very good route to the synthesis of chemically and structurally well-defined catalytic nanoparticles. The partnership with the University of Delaware group will allow us to guide future development of highly selective bimetallic catalysts according to theoretical models and study their catalytic properties in depth.

Future Plans

We intend to investigate the effect of the metal composition in an AuAg bimetallic DEN on the catalytic rate of the reduction of 4-nitrophenol. Ag nanoparticles are known to catalyze this reaction which should enable us to study the affect of a second metal using UV-vis spectroscopy. Pt and Pd nanoparticles are also known to catalyze this reaction and so we envisage using different combinations of metal to study catalytic effects.

We are also investigating the formation of heterogeneous catalysts via deposition of DENs onto solid oxide supports as well as the incorporation of DENs into sol-gel syntheses of metal oxides, followed by calcination to remove the dendrimer templates. TEM results have indicated that the dendrimers can be removed with minimal aggregation of the metallic or bimetallic nanoparticles. In addition, single particle EDS results have shown that bimetallic compositions in the resulting materials can be quite carefully controlled. These materials can be more conveniently examined by methods such as extended x-ray absorption fine-structure spectroscopy (EXAFS) to yield structural information for the bimetallic nanoparticles. In addition, metallic and bimetallic nanoparticles on titania supports after dendrimer removal are currently being studied as catalysts for gas-phase reactions such as CO oxidation.

In both current and future projects we are collaborating with the Delaware group.

Publications (2003-2004)

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Improved Modeling of Transition Metals: Applications to Catalysis and Technetium Chemistry

- Collaborators: Prof. T. Brent Gunnoe (NC State U.); Dr. David P. White (AaiPharma)
- Graduate Research Assistants: Tom Klinckman; Yong Zhao; K. A. Pittard
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Goals:

Develop and test *de novo* design and analysis protocol for transition metal complexes. Integrate our research with leading experimental groups on problems of importance to the DOE research mission. Investigate important catalytic materials and transformations.

Recent Progress:

i. Regioselective C-H activation of Heterocycles

Selective and catalytic transition metal mediated C-H functionalization of simple aromatic feedstocks (*i.e.*, substrates that lack pendant functionality) are notably scant. $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ (Tp = hydridotris(pyrazolyl)borate) reacts at 90 °C with furan or pyrrole to yield the corresponding products from *selective* C-H activation at the 2-position of the heteroaromatic. Gunnoe and coworkers also obtained catalytic formation of 2-ethyl-furan from ethylene and furan; interestingly, no products are obtained with pyrrole as the substrate, Figure 1.

In collaboration with Gunnoe (NC State U.), we investigated regioselective C-H activation of furan and pyrrole by $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$. Our primary objective was the determination of the mechanism for C-H activation. Comparison of oxidative addition and σ -bond metathesis pathways indicates the latter to be favored, Figure 1. Furthermore, the selectivity for C-H

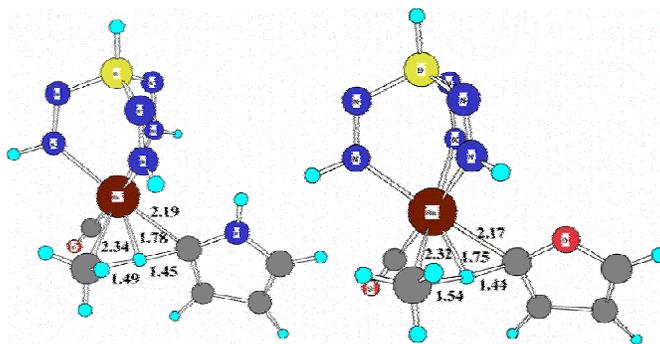


Figure 1. Calculated geometries for C-H activation of furan and pyrrole indicate σ -metathesis transition states.

activation the 2-position of the substrate is not thermodynamic but kinetic, due to both steric factors (repulsion between the pyrazolyl borate ligand and substrate) and electronic (disruption of conjugation in the heteroaromatic substrate). The inability to experimentally observe catalysis reactivity with 2-pyrrole is still unclear, and remains an area of active research for the future.

ii. Catalytic Hydrophenylation

Alkyl benzenes such as ethyl benzene are important industrial products. Traditionally, these have been made through Friedel-Crafts catalysis involving carbocationic intermediates. Products with linear alkyl chains cannot be easily accessed in high yields with traditional catalytic methods. These and other approaches also require the formation of organo-halides, whose manufacture often require multi-step syntheses. It is desirable to effect the transformations directly from hydrocarbons, and with systems that may afford linear products.

Gunnoe has identified $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ as a catalyst for hydrophenylation of olefins. We are currently engaged in a collaboration to study the mechanism of this transformation (“Catalyzed Addition of Arene C-H Bonds to Olefins;” M. Lail, C. M. Bell, T. R. Cundari, D. Conner, T. B. Gunnoe *J. Am. Chem. Soc.* – to be submitted.). Our computational research has focused on the mechanism of the prototypical transformation: ethylene + benzene \rightarrow ethylbenzene. The proposed mechanism involves C-H activation of benzene, followed by insertion of ethylene in the Ru-Ph bond to yield the β -phenethyl complex, $\text{L}_n\text{Ru}-\text{CH}_2-\text{CH}_2-\text{Ph}$. Subsequently, C-H activation of a second equivalent of benzene regenerates the $\text{L}_n\text{Ru}-\text{Ph}$ intermediate, Figure 2.

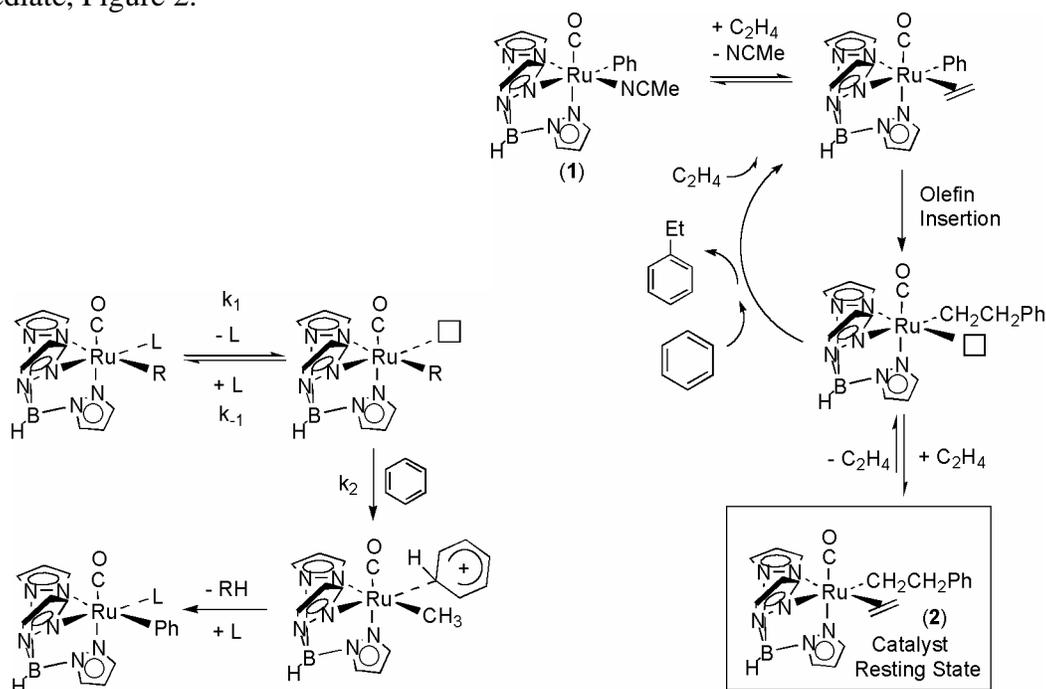


Figure 2. Catalytic cycle for Addition of Arene C-H Bonds to Olefins.

As with furan and pyrrole, we first sought to identify the pathway for the initial C-H activation of benzene by $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$, Figure 2 (left hand side). A variety of mechanistic possibilities were evaluated. Our calculations indicate that after initial displacement of

acetonitrile by benzene (η^2 - π -coordinated), σ -bond metathesis is the preferred route for C-H activation; the transition state (TS) structure for benzene C-H activation is analogous to that shown in Figure 1 for furan and pyrrole.

Subsequent to formation of the L_nM -Ph as the catalytic intermediate, Figure 2 (right hand side), olefin insertion into the Ru-Ph bond proceeds with a barrier of 19 kcal/mol to give a β -phenethyl complex, which our calculations indicate is stabilized by a π -interaction between Ru and the ipso and ortho carbons of the pendant phenyl group. This intermediate is >2 kcal/mol more stable than the isomeric L_nRu -CH₂-CH₂-Ph conformation that involves an agostic Ru...H β -C β interaction. The agostic intermediate precedes β -H elimination. Hence, the greater stability of the π complex may explain why β -H elimination reaction (an unwanted side reaction) is minimized in this complex, and also suggests how to further thwart this reaction in future generation catalysts. Calculations are also consistent with the proposed resting state of the catalyst as an olefin complex of L_nRu -CH₂-CH₂-Ph, Figure 2.

Future collaboration in this area is ongoing with the Gunnoe group. Of prime interest is the identification of new and improved catalysts. To this end, simple (*i.e.*, replacement of the CO in TpRu(CO)(Me)(NCMe) with PR₃) and more drastic (e.g., Ru^{II}-pincer complexes, or iron derivatives of the Tp complex) modifications will be looked at. Of particular interest is the role of metal/ligand modification on the linear/branched product ratio. Bulkier PR₃ and the smaller, hence more sterically congested, iron complex may be expected to enhance formation of linear products. These hypotheses will be evaluated computationally by our group in the search for improved experimental catalysts. Additionally, a comparison of the kinetics and thermodynamics of the desired hydrophenylation versus the undesired β -H elimination pathways for other metal and ligand combinations will be a subject of considerable attention.

iii. De Novo Design of Transition Metal Complexes

Two fundamental issues that have arose in our applications-oriented catalysis research projects involved coordination isomerism (*e.g.*, coordination to either the axial or equatorial binding site of a trigonal bipyramidal complex) and structural isomerism (*e.g.*, trigonal bipyramid versus square pyramid for a five-coordinate complex). These forms of isomerism are particularly significant to catalysis studies as five-coordinate species are prevalent in catalytic pathways, often being generated *in situ* as active species by ligand dissociation from stable six-coordinate catalyst precursors. Hence, we pursued the issues of coordination and structural isomerism in the past year.

A study of coordination isomerism was performed on ML₅ complexes (“Evaluation of Coordination Isomerism in Transition Metal Complexes;” T. R. Cundari, C. Buda, A. A. Flores – manuscript in preparation). Trigonal bipyramidal complexes from the Cambridge Structural Database were chosen for study as there are a vast number of experimental examples involving diverse metal/ligand combinations available for the testing of the computational methods.

One hundred seven (107) different trigonal bipyramidal, transition metal complexes incorporating metals from the entire transition series and a diverse assortment of ligands (hard/soft donors, π acceptors/donors, single/multiple/dative metal-ligand bonds, *etc.*) were investigated using semi-empirical quantum mechanics (specifically the PM3(tm) Hamiltonian) and density functional theory (pure and hybrid functions were both assessed). On average each complex studied had four possible coordination isomers differing in coordination to the ligands in either an axial or equatorial site (see Figure 3 for the simple example of an MA₃B₂ complex,

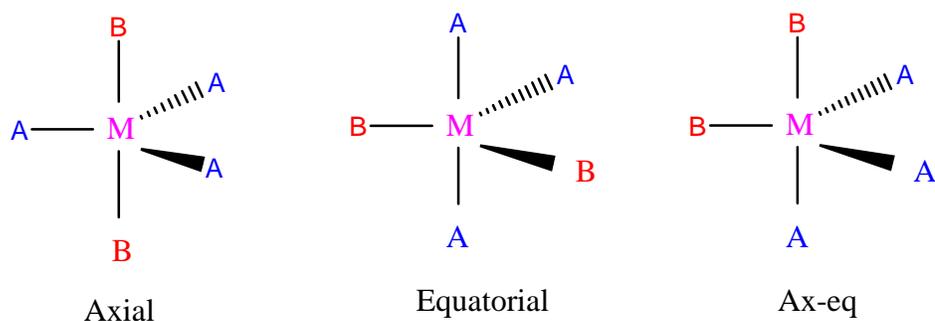


Figure 3. Possible coordination isomers for a trigonal bipyramidal MA_3B_2 complex.

i.e., two different ligand types). The different possible coordination isomers were often very close in energy, typically much less than 5 kcal/mol. Hence, we observed that prediction of the correct ground state coordination isomer was quite challenging and very sensitive to the level of theory employed. Lower-level, semi-empirical methods could more often than not identify the experimentally determined lowest-energy conformational isomer, but not at the success level (>90%) seen in our previous studies of other types of transition metal isomerism. Hence, it appears that in those cases where coordination isomerism is possible that semi-empirical quantum mechanics may be used with caution as a rough screen to obviate obviously high-energy conformers, but that for the most accurate work higher order (density functional theory) methods are needed. Despite the challenges inherent in the analysis of coordination isomerism, another research project indicated that semi-empirical quantum methods could predict with high confidence (>80%) the correct ground state geometries isomer of transition metal complexes. Future work will focus on linkage isomerism in *de novo* structural prediction of metal complexes.

iv. Catalysts for Carbon-Carbon and Carbon-Element Bond Formation

We undertook to apply the *de novo* design protocol that has been a major emphasis of this DOE-sponsored research to the catalytic active species in palladium-catalyzed bond couplings (“ONIOM Study of the Active Species in Pd-phosphine Catalyzed Coupling Reactions;” Cundari, T. R.; Deng, J.; Zhao, Y. J. *Mol. Struct. (THEOCHEM)*, **2003**, 732, 121-129). As alluded to in section A, carbon-carbon and carbon-element bond coupling reactions are very important in the elaboration of simple petrochemical feedstocks to higher-valued products. In this regard, palladium-phosphine catalysts have received considerable experimental interest. Phosphine (PR_3) co-ligands afford the ability to methodically alter the steric and electronic profile of their resulting complexes. Recent interest has emphasized bulky phosphines with the Pd(bulky aryl)₂(biaryl) motif, which result in very active catalysts. The active species in these reactions are unclear, due to their high reactivity, thus making them ideal candidates for computational research. Proposals have focused on mono- and bis-phosphine complexes of Pd⁰ as the active species in bond coupling by palladium catalysts. Our calculations suggest the active species is a mono-phosphine. Severe steric repulsion between the pendant groups on the aryl substituent weakens the Pd-P bonds, and pushes the equilibrium $Pd(PR_3)_2 \leftrightarrow Pd(PR_3) + PR_3$ towards the right. Additionally, there is also an electronic stabilization between the π -ring on the arene pendant group, and the Pd atom, Figure 4 (next page). The nature of this interaction is

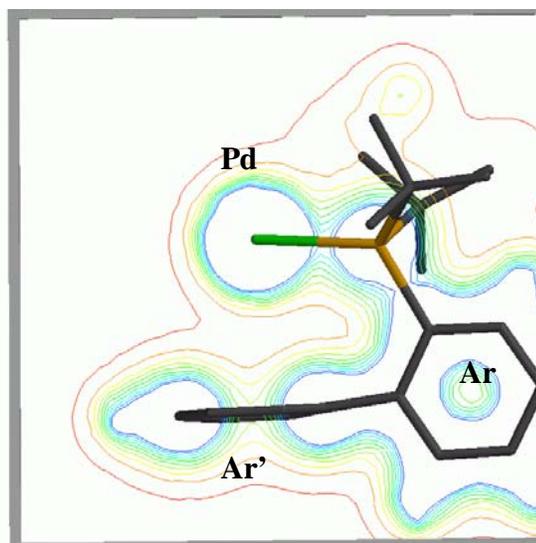


Figure 5. Pd- π -arene interactions in palladium-catalyzed C-C bond coupling.

consistent with experimental observations that complexes with saturated pendant groups have poorer reactivity than those with arene pendant groups. Furthermore, this Pd- π -arene interaction is not seen in the bis-phosphine models. The results suggest that the nature of the Pd- π -arene interaction is crucial in the catalyst performance, *i.e.*, if it is too strong it will quench the reactivity of the Pd and lead to a less active catalyst. Alternatively, if the Pd- π -arene interaction is too weak, the active species will be too “hot” and thus too unselective. Hence, identification of appropriate pendant groups that have Pd- π -arene interactions in an intermediate regime is key.

DOE Interest:

The ability to rationally design and analyze novel materials is crucial to the economical development of new catalysts for the efficient utilization of petrochemical feedstocks. Development of reliable and rapid computational chemistry techniques for modeling transition metal catalysts is central to this effort. The research to this point has made significant strides towards the goal of computer-aided design and analysis of transition metal catalysts.

Future:

In addition to continuing to exploit the *de novo* structural prediction protocol we have developed for transition metals, and to pursue the collaborations outlined above, the upcoming year promises to be particularly exciting as we tackle a new area of research, *i.e.*, the development, testing, and application of accurate computational methods for transition metal thermochemistry. This research will proceed on several fronts: (1) identification of a suitable computational test bed for which experimental heats of formation are accurately known, (2) assessment of standard computational chemistry methods for the compounds identified in section (1), and (3) development of improved and efficient methods for transition metal thermochemistry that can achieve chemical (*ca.* ± 2 kcal/mol) accuracy.

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Structure and Function of Supported Base Catalysts

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Goal

Understand how atomic structure and composition affect the reactivity of surface oxygen atoms on supported basic compounds and transition metals.

Recent Progress

Structure and Reactivity of Cesium Oxide

1. *Quantum chemical study of cesium oxide, peroxide and superoxide*

In collaboration with Professor Matthew Neurock, gradient-corrected periodic density functional theory was used to examine the bulk and low index surfaces of several cesium oxides (Cs_2O , Cs_2O_2 , and CsO_2). The Cs_2O {010} surface exposing both Cs and O atoms adsorbed CO_2 with a strength of -284 kJ mol^{-1} . The adsorption of CO_2 in the bidentate configuration on the {001} and {100} surfaces of Cs_2O_2 exhibited adsorption strengths of -101 kJ mol^{-1} and -186 kJ mol^{-1} , respectively. The oxygen-rich CsO_2 surface failed to adsorb CO_2 . Mulliken charge analysis and CO_2 adsorption strengths provided a consistent ranking of base strength: $\text{Cs}_2\text{O} > \text{Cs}_2\text{O}_2 > \text{CsO}_2$.

2. *Structure and reactivity of zeolite-supported cesium oxide*

Earlier work in our lab demonstrated that cesium oxide supported inside the supercage of a zeolite catalyzes a variety of reactions such as alkylation of toluene with methanol, cyclo-addition of carbon dioxide to ethylene oxide, and double bond isomerization of 1-butene. Although all of the reactions exploit the basic properties of the catalyst, each one requires a different level of base strength. For example, double bond isomerization in olefins requires a strong base that is readily poisoned by adsorption of carbon dioxide, whereas ethylene oxide easily reacts with carbon dioxide to make ethylene carbonate over a weak base. Strong base sites capable of olefin isomerization are only a small fraction of total base sites on zeolite-supported cesium oxide, as titrated by CO_2 adsorption. In-situ Raman spectroscopy of a Cs-zeolite catalyst revealed a feature at 1036 cm^{-1} , which is in the carbonate region of the spectrum. The feature is substantially shifted from bulk cesium carbonate (1051 cm^{-1}) and is perturbed greatly by adsorption of gas phase CO_2 . No evidence for cesium peroxide or superoxide was found in the Raman spectrum. These results suggest that a cesium "oxycarbonate" is the species responsible for the basic properties in the zeolite.

Although CO₂ poisons the strong base sites of zeolite-supported cesium oxide, the behavior of O₂ on the catalysts is less clear. Exposure of a catalyst to O₂ lowered activity for 1-butene double bond isomerization at 373 K, but a He purge at that temperature after O₂ treatment was sufficient to prevent deactivation. Interestingly, co-feeding O₂ with 1-butene at 373 K completely deactivated the catalyst, which cannot be recovered by a simple He purge. In-situ IR spectroscopy revealed that CO₂ is formed at 373 K when the olefin and O₂ are co-fed to the reactor. Apparently, adsorbed CO₂ poisons the catalyst. These results are evidence for a low temperature combustion reaction.

Since most of the basic sites on Cs-zeolites are not very strong, we began exploring the catalytic conversion of propionic acid and formaldehyde to methacrylic acid. The reactor system is functioning well and has been tested with a CsBi-SiO₂ catalyst that has been described in the literature. The basic zeolites produced in our lab are selective for the reaction at low conversion, but are not quite as active as the silica-derived catalyst.

Base Promotion of Ru Catalysts

In addition to catalysis by solid bases, we have been investigating the mechanisms of base promotion of Ru catalysts for ammonia synthesis. The kinetics of ammonia synthesis over unpromoted and Cs, Ba, and La promoted Ru/MgO were studied and modeled. Although Cs promotion of Ru lowered the activation barrier for N₂ dissociation, the enthalpy of dihydrogen adsorption and therefore the H atom surface coverage increased. Thus promotion of Ru catalysts with bases cannot be attributed solely to an effect on dinitrogen dissociation, which is the rate-determining step. Base promotion is a trade off between lowering the activation barrier for N₂ dissociation and increasing the competitive adsorption of H₂. The coverages of nitrogen-containing species determined by an optimized kinetic model matched well those determined experimentally by isotopic transient analysis over the same catalysts.

DOE Interest

The work performed in this program elucidates fundamental principles important in the design of basic and base-promoted catalysts. Solid bases are environmentally benign alternatives to liquid bases.

Future Plans

Low Temperature Oxidation. Work with oxygen poisoning of strong base catalysis during 1-butene isomerization revealed formation of CO₂ at 373 K. Thus, future work will be aimed at understanding the oxidation reaction, with a goal of designing oxidation functionality into new materials.

Effect of Water on MAA Synthesis. Preliminary work with base catalysts for methacrylic acid synthesis revealed strong inhibition by water, which is a product of the reaction. As we continue to explore the concept of shape selective base catalysts, we plan to modify the materials with hydrophobic coatings to improve their water tolerance.

Publications 2003-2004

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- S.E. Siporin, R.J. Davis, "Use of Kinetic Models to Explore the Role of Base Promoters on Ru/MgO Ammonia Synthesis Catalysts," *J. Catal.* under review.
- S.E. Siporin and R.J. Davis "Isotopic Transient Analysis of Ammonia Synthesis over Ru/MgO Catalysts Promoted by Cesium, Barium or Lanthanum," *J. Catal.* in press.
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Towards Rational, Nanoscale Control of Catalysis: A Fundamental Study of Zeolite Nucleation Kinetics

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Goal

Develop the theoretical and simulation technology to predict barriers to zeolite nucleation in the presence of structure directing agents.

Recent Progress

Monte Carlo Simulation of Nucleation: An atomic-scale model for silicate solutions was introduced for investigation of the nucleation process during zeolite synthesis in the absence of a structure directing agent. Monte Carlo schemes were developed to determine the equilibrium distribution of silicate cluster sizes within the context of this model. How the nucleation barrier and critical cluster size change with Si monomer concentration is discussed. Distance and angle histograms as well as ring size distributions are calculated and compared with known zeolite structures. The free energies of critical clusters are compared with those for small clusters of alpha-quartz.

We surveyed the size and flatness of rings that occur in known zeolites and also in a set of hypothetical structures. The results suggest that 16-membered rings, while rarely observed in zeolites, are not unique and should be thermodynamically accessible. Conversely, the results also show that rings of a given flatness, or planarity, become exponentially less likely as ring size increases. We compared the geometry of rings in known zeolites with the geometry of unconstrained rings as determined from Monte Carlo simulation. The rings that occur in zeolites are flatter than unconstrained rings due to the constraints imposed by the crystal. The thermodynamic factors that determine the flatness of rings in crystals is investigated by using a reverse umbrella sampling technique. Interestingly, the energy required to bring rings from an unconstrained state to the crystalline flat state is roughly 5 kJ/mol-Si, which is similar to the range of stabilities observed for zeolites and also to the range of interaction energies between zeolites and structure directing agents.

Some interesting predictions, such as that the nucleus is amorphous, that the cross-over length scale is in the range of 3-5 nm, and that there should be more 16-ring zeolites, seem to have been borne out by recent experiments.

Zeolite Structure Solution: The synthesis, structure solution, and characterization of the high-silica zeolite SSZ-55 was described. SSZ-55 was synthesized at hydrothermal conditions using a [(1-(3-fluorophenyl)cyclopentyl)methyl]trimethyl ammonium cation as the structure-directing agent. The framework topology and symmetry of SSZ-55 were determined by the Monte Carlo method ZEFSAII. Rietveld refinement of the X-ray powder diffraction data confirms the space group assignment of $Cmc2_1$. Transmission electron microscopy confirms the unit cell parameters and the topology of the structure. SSZ-55 contains one-dimensional pores circumscribed by 12 T-atom rings. The topology of SSZ-55 is that of the ATS framework, previously described for AIPO-based molecular sieves.

Simulation Technology: The optimal allocation of replicas to a homogeneous or heterogeneous set of processors was derived for parallel tempering simulations on multi-processor machines. In the general case, it is possible without substantially increasing wall clock time to achieve nearly perfect utilization of CPU time. Random fluctuations in the execution times of each of the replicas do not significantly degrade the performance of the scheduler.

DOE Interest

Understanding zeolite nucleation is important not only scientifically for the discovery and synthesis of new materials, but also in an engineering sense for improving the performance of existing materials that are not performing as well as they could due to poor "crystallinity." Considerations include catalysts with improved catalytic properties for improving refining economics and for reducing environmentally-unfriendly by-products, design of better, smarter, and more energy-efficient separation processes, and design of zeolites that are more effective for radioactive waste cleanup and stewardship purposes. Parallel tempering is a general materials simulation method now in use.

Future Plans

Monte Carlo Theory of Structure Directing Agents: Develop the open-ensemble nucleation theory to accommodate the presence of a variable number of structure directing agents.

Quantification of Templating Effects: By how much do structure directing agents lower the nucleation barrier? How do they discriminate among possible zeolite structures? Do the templates go towards the middle of the critical clusters or the surface? At what size does the cluster start to become crystalline rather than amorphous?

Comparison with Experiment: Compare with NMR results. Compare with nucleation rates, when available. Possibly compare with osmotic pressure/preferential interaction parameters.

Zeolite-Related Publications (2002-2003)

- 1) D. J. Earl and M. W. Deem, "Optimal Allocation of Replicas to Processors in Parallel Tempering Simulations," Hans C. Andersen Festschrift, *J. Phys. Chem. B*, to appear.
- 2) R. A. Curtis and M. W. Deem, "A Statistical Mechanics Study of Ring Size, Ring Shape, and the Relation to Pores Found in Zeolites," *J. Phys. Chem. B* **107** (2003) 8612-8620.
- 3) M. W. Deem, "The Monte Carlo Approach to Library Design and Redesign," invited chapter, in *Experimental Design for Combinatorial and High Throughput Materials Development*, John Wiley & Sons, 2003, pp. 239-276.
- 4) Others and M. W. Deem, "Future Directions in Solid State Chemistry: Report of the NSF-Sponsored Workshop," *Prog. Solid State Chem.* **30** (2002) 1-101.
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Catalyst Design by Discovery Informatics

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Goal

Develop and apply an informatics-intensive model-based approach that extracts knowledge from high throughput data for the design of catalysts, focusing on aromatics production from light alkanes, single-site aryloxide catalysts for polyolefin production, hydrogen production from the water gas shift reaction, and development of parallel mass spectrometry for high throughput analysis of catalysts.

Recent Progress

Aromatization: An elementary step model involving 37 reaction families and 22 parameters has been fit to our data on propane aromatization over ZSM-5 with a Si/Al=16 using our reaction modeling suite (RMS) of software tools. The good agreement between the experimental results and model predictions, as well as the excellent match between optimized model parameters and literature values, suggests that we have a robust microkinetic model for this system that can quantify the activity of Brønsted acid sites in HZSM-5. Building on previous DFT work [*J.Phys.Chem.B*, **2004**, *108*, 971], we are also conducting a mechanistic analysis of C6-C9 diene cyclization over Brønsted acid sites in an embedded-cluster (QM/MM) model of H-ZSM-5. These DFT runs are being used to determine relative activation energies for C6, C7, and C8 cyclization, which provide a direct test of the optimized model parameters. DFT work on propane activation involves pathway analysis of propane dehydrogenation over both Brønsted sites and GaH₂ substituted sites. Our initial findings show that embedded-cluster type calculations, compared to bare-cluster calculations, appear to give both qualitative and significant quantitative differences in transition state results for this system. In an attempt to provide descriptors that can be computed directly and quickly, we are employing an electronegativity equalization method (EEM) to yield partial charges and sensitivity parameters. Specifically, the effects of topology and next nearest neighbor on the framework electronegativity, hardness, and local softness are of interest, and we have developed a Mathematica code to do the EEM. When generalized, this facile computational tool will be used to: (1) to screen potential frameworks and compositions for synthesis experiments and more detailed computation studies and (2) to obtain descriptors for each catalyst tested and

characterized. In preparation for a move to Ga-modified ZSM-5, we have been studying toluene disproportionation to benzene and xylene on these materials. Surprisingly, we find that the rate of reaction is enhanced by Ga exchange. Preliminary studies suggesting a synergy between Ga and the Brønsted sites are guiding continuing work. While the data used were obtained on a single plug flow reactor, our 8 barrel reactor is nearly ready for use. We have also begun to synthesize ZSM-5 and are setting up a new small angle x-ray scattering instrument that can monitor crystallite size *in situ*.

Olefin Polymerization: We are making excellent progress on the synthesis of new catalysts, DFT calculations of catalyst structure and bonding, and visualization of the quantum chemical results. The final cost-sharing for the GPC equipment will be available in July, but we have preliminary data on borrowed instrument time that confirm our ability to determine chain propagation and termination rate constants from GPC of the polymer product. In addition, we have a new analysis that allows us to extract the number of different operative catalytic sites during the polymerization and, thus, to confirm that the catalysts operate in a true single-site fashion. A more efficient route to synthesis of the Ti dimethyl catalyst precursors along with details of the activation process and direct NMR observation of ligand-specific deactivation processes is in press (1). The DFT work has shown that the geometry of the active compounds is well represented though B3LYP level of theory, based on comparisons to existing crystal structure data of representative aryl oxides. The current emphasis is on modeling the active compound interactions with its complementary counter-ion, which we deem will significantly impact the reaction chemistry.

The Water Gas Shift Reaction: We have measured the rates and reaction orders on Pt catalysts modified by CeO₂, BaO and MgO. BaO enhances the rate by a factor of 3 while MgO had no promoting effect. Both BaO and MgO suppress the methanation rate. Ceria, at a factor of 20, has the strongest promotion effect of the additives studied so far but is subject to deactivation, perhaps due to carbonate formation. All three promoters lead to a power rate law $R = k \cdot [\text{CO}]^0 \cdot [\text{H}_2\text{O}]^{0.5} \cdot [\text{CO}_2]^{-0.4} \cdot [\text{H}_2]^{-0.5}$. Addition of the WGS reaction chemistry to the RMS compiler is nearly complete. It will be used to speed the kinetic modeling. A four-reactor system to obtain kinetic data has been designed.

Parallel Mass Spectrometry: A four-channel rectilinear ion trap (RIT) mass spectrometer is being designed and constructed for high-throughput characterization of four parallel gas streams flowing from separate catalyst beds. The instrument will consist of multiplexed arrays of identical sample introduction capillaries, glow discharge sources, multipole ion transfer optics, RIT mass analyzers, and detectors. However, the parallel channels will be assembled in a single manifold and have common vacuum pumps and control electronics. Careful analysis of a number of ionization options led to the choice of a glow discharge (GD) system. Occurring at 0.1-1 Torr, this method can be tuned to resemble electron impact or chemical ionization. A test of a hydrogen, oxygen, propylene mixture in He in a commercial triple quad showed the absence of complicating ion molecule reactions at conditions expected for the GD system. The physical layout and pumping calculations have also been completed and show that pumping requirements can be kept within reasonable bounds.

Informatics Infrastructure: First, we are engaged in high-throughput quantum chemistry simulation for each of the three application areas. In this first year of the project we will simulate several thousand different chemical structures. In order to handle this large flow of data, a job sequencing program has been developed for the automatic submission, retrieval and archival of this data. The sequencer makes the most efficient use of a variety of local and

national computational resources. *Second*, significant progress has been made in developing a unique visualization environment to begin to extract knowledge from high throughput experimental and computational data. Specific progress includes (i) the development of rendering algorithms that allow for semi-transparent visualization of molecular orbitals, where the underlying atomic centers and connecting bonds can still be seen and (ii) the beginning design of a graphics environment, where the experimental, theoretical and quantum chemical attributes of complex data are linked together. *Third*, we have begun the first steps toward design of a database by addressing the need for a platform independent language that can be used internally, nationally and internationally. We have critically examined the chemistry extension to XML called Chemical Mark-up Language, CML. CML has a number of features that are useful in representing chemical structure; however, CML does not currently have a rich enough vocabulary for quantum chemistry. We are currently working on developing the appropriate extensions to CML for quantum chemistry and are making contact with the standards organization. *Finally*, we are extending the RMS chemistry compiler that is able to translate reaction mechanisms written in near English language to the relevant set of differential equations. Debugging, fixing memory leaks, and other modifications of the compiler now allow generation of about 1500 reactions. Refinements have also been made to the differential-algebraic equation solver to allow equilibrium constraints. Sensitivity analysis to determine the robustness of the estimated parameters and analysis of the degree of rate control have also been added.

DOE Interest

Validation of this new design concept has the potential to change the catalysis research landscape by dramatically shortening hypothesis testing and new discovery cycles for virtually any catalyst system. A particular value of the approach is that knowledge archived in the model retains its value for new problems. Over time, overlapping knowledge bases from a variety of problems will accelerate discovery cycles even more. Sharing that knowledge and the resources to tune it to particular systems through a National Database can enable broad access to these benefits.

Future Plans

All phases of this multidisciplinary project are off to a good start and are on the track outlined in the proposal. The aromatization study will focus on Ga-promoted ZSM-5, the olefin polymerization work will increase the kinetic data rate and begin building models guided by the DFT calculations. The water gas shift study will also analyze a wide variety of catalysts and use that data, along with fundamental studies of ceria promoted Pt, to drive the modeling process. Machine drawings and construction will be followed by modification of the control electronics and LabVIEW programming in the parallel mass spec project. The informatics group is aiming for a demonstration of the use of visualization of linked archived data to aid model building at the Catalysis Database Workshop scheduled for September 14, 2004 at Purdue.

Publications

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3. Katare, S., Caruthers, J. M., Delgass, W. N., Venkatasubramanian, V., "Hybrid Genetic Algorithm-based Parameter Estimation Framework", *Comp. and Chem. Engg.* submitted.
4. Venkatasubramanian, V., Patkar, P., Katare, K., Hsu, S.-H., Bhan, A., Caruthers, J. M., Delgass, W. N., and Thomson, K. T., "Discovery informatics: a model-based integrated framework for product engineering", to appear in the proceedings of the international conference on the Foundations of Computer-Aided Product Design, FOCAPD 2004, Princeton, NJ, July 2004.

Understanding Propylene Epoxidation of Gold/Titania Catalysts

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Goal

Understand the fundamental roles of gold, titanium, and hydrogen in the epoxidation of propylene by $H_2 + O_2$ over Au/Ti catalysts.

Recent Progress

The initial conclusions of this work showing that isolated tetrahedral Ti minimizes propylene oxide (PO) degradation has led us to focus on TS-1 supports. In addition to providing completely isolated Ti, the nanoporous nature of these materials provides two distinct potential gold environments: small clusters (<0.55 nm) in the pores and larger particles on the exterior. Experimental efforts have been directed at isolating these environments to probe the nature of the Au sites, while a DFT theory approach shows the viability of Au clusters as catalytic sites for production of HOOH.

Coated Materials: One approach we have tried to accentuate interior sites is to grow S-1 (silicalite) on the external surface of TS-1. Since S-1 has no Ti, the external surface should not be active even if gold resides there. We have successfully coated the TS-1 particles, but XPS showed that even though the Ti content of the surface had been decreased by an order of magnitude, some measureable external Ti remained, and the activity of the catalyst was similar to that made on the uncoated support. To avoid the leaching of Ti by the strongly basic solution of the synthesis, we siliated TS-1 using a solution of tetraethyl orthosilicate in toluene under refluxing conditions. Since the siliation coating is thin, we were not able to measure the surface Ti content, but the siliated catalyst showed much slower activation, indicative of Si or, more likely, Au migration to create active sites (see Figure 1). The final activity was similar to that of the standard, unsiliated catalyst. While these results could be interpreted to support activity within the volume of the TS-1 particles, a small number of highly active sites on the external surface cannot be ruled out. An

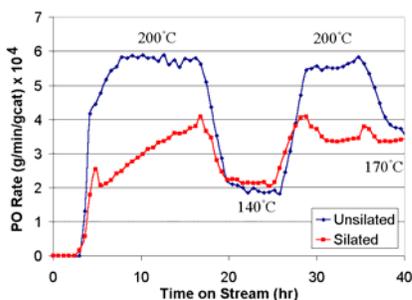


Figure 1: Steady state kinetics for a siliated and unsiliated catalyst showing the difference in activation behavior.

While these results could be interpreted to support activity within the volume of the TS-1 particles, a small number of highly active sites on the external surface cannot be ruled out. An

attempt to invert the process by growing a TS-1 coating on S-1 was not successful because homogeneous nucleation of TS-1 produced separate small TS-1 particles and some anatase. Interestingly, a catalyst made on this support was one of the most active materials we have produced; making 12% PO at 200 °C and a space velocity of 7000 cm³/h/g_{cat} and 87% selectivity. Addition of Ti to the surface of an uncalcined S-1 material and calcining should have added some Ti to the surface layer, but catalysts made from this support made mostly CO₂. The coated catalysts produced the same apparent activation energy as we have found for the uncoated materials, indicating no change in the rate limiting step.

Au Placement: Attempts to force gold to the outer surface by working with supports with the template left in, and to force gold inside by first doing insipient wetness impregnation of the vacuum-dried support, redrying and then doing incipient wetness contacting of the Na₂CO₃ solution both produced active catalysts. The former confirms that the outer surface can support activity, but does not differentiate the active Au phase by size. The latter did not show a dramatic increase in activity as might be expected if the Au activity were inside and the amount of Au residing there were increased. Attempts to selectively leach the ca. 2 nm Au particles on the exterior surface of the TS-1 with a 2% NaCN solution lowered the gold content by an order of magnitude and lowered the activity by about a factor of 4. The leaching was not found to be exclusive to the large particles on these supports, however, so the experiment only confirmed that the activity is not linear in Au content.

Enhanced Activity: Two promising leads to higher activity have been developed. The first involves highly defected TS-1 supports grown around carbon pearls. Surface defects and the extraframework titanium seen in DRUV may result in a less hydrophobic support and account for the ease in which these supports capture gold during deposition precipitation. A catalyst synthesized using carbon pearls with a titanium content of 2.77 wt % and a gold loading of 0.3 wt % Au had a conversion exceeding 11% at 200°C and a space velocity of 7000 cm³/hr/g_{cat}. Selectivity remained high, varying between 87 and 95 % depending on the reaction temperature. A second method of enhancing the useful Au content consists of exposure of a calcined TS-1 support to 1M NH₄NO₃ followed by vacuum drying. Deposition precipitation of gold on this support substantially increased the capture efficiency of Au and produced a catalyst with 8.5 % conversion of propylene with 85% selectivity at 200 °C at a gold loading that would normally produce large non-selective particles.

DFT Computations: In collaboration with Ken Thomson, we have studied the viability of Au₃-neutral-cluster-catalyzed production of hydrogen peroxide. The reaction path found has activation barriers less than 10 kcal/mol. The reactions proceed on the edges and one side of the triangular Au₃ cluster, which makes this mechanism viable for a cluster in contact with a support surface. The Au₃ cluster remains in a triangular geometry throughout the reaction but the electron population on the Au trimer during the catalytic cycle, as calculated with the Natural Bond Orbital method, varies from a charge of +0.304 (cationic) (Au₃O₂H₂) to -0.138 (anionic) (Au₃H₂). Au₃ in the reaction initiation intermediate, Au₃O₂, is also cationic in character with a charge of +0.390. It is interesting to note that the interaction of Au₃ with a model oxidic support, TS-1, was essentially neutral in character, the Au₃ charge population being -0.044. Formation of hydrogen peroxide does not involve breaking the O-O bond, but does break the H-H bond in a step

that is rate limiting at standard conditions. The highest energy barrier in the cycle is 8.6 kcal/mol for desorption of HOOH from Au₃H₂. Adsorption of HOOH on this site is unactivated. This route to formation of hydrogen peroxide, combined with existing mechanisms for epoxidation by HOOH over TS-1, gives a fully plausible, energetically favorable, closed cycle for epoxidation of propylene by H₂ and O₂ over Au/TS-1 catalysts. Thus, isolated molecular gold clusters can act as viable sites for this reaction.

DOE Interest

This system is a prime example catalytic nano-specificity. Only nano-size Au particles are active. Understanding the origins of that activity will have fundamental importance beyond the PO reaction. Likewise, the importance of partial oxidation reactions accentuates the impact of improvements in their efficiency. Evidence continues to mount that HOOH is the oxidant in the PO reaction. Understanding the *in situ*, generation of HOOH by gold could have application well beyond the production of PO.

Future Plans

XPS: A key issue to be resolved is experimental proof of whether small Au clusters have activity for the PO reaction. Quantitative XPS of Au/Si intensity ratios can indicate whether Au enters the interior volume of the TS-1 crystallites and also whether large amounts of gold, not in observable crystallites, exists on the TS-1 supports. This information will allow quantitative interpretation of rate data on catalysts prepared to emphasize small clusters versus larger Au particles. The XPS studies will be done at the University of Delaware.

Effects of Ammonium Ion: The recent discovery that ammonium pretreatment dramatically increases the capture of gold into useful sites will be explored vigorously. We would like to understand the origin of the effect, and use it to enhance activity. The increased site density in high activity catalysts enhances the opportunity to characterize those sites spectroscopically and, thus, to enhance understanding. For the same reason, we will continue to examine supports with manipulated external surface area, such as the materials grown around carbon pearls, and high surface area amorphous materials.

DFT Computations: Now that we have shown a viable route to PO through HOOH production on small Au clusters, we would like to know effects of cluster size, cluster charge, and interaction with the support surface. Such studies are underway.

Publications

1. Yap, Nora., Andres, Ronald P. and Delgass, W. Nicholas, Reactivity and Stability of Au in and on TS-1 for Epoxidation of Propylene with H₂ and O₂, J. Catal., submitted.
2. Wells, David H., Jr., Delgass, W. Nicholas, and Thomson, Kendall T., Formation of Hydrogen Peroxide From H₂ and O₂ over a Neutral Gold Trimer: a DFT Study, J. Catal., submitted.
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Molecular Level Control through Dual Site Participation

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Goal

The overall goal of this research program is to explore the hypothesis that it is possible to design a bimetallic surface such that each metal catalyzes different elementary reaction steps in an overall reaction pathway. A corollary to this hypothesis is that the different ensemble size requirements for an elementary reaction step can be used to force that step to occur on only one of the metals.

Recent Progress

Previously, we suggested that the hydrogen-assisted dechlorination of 1,2-dichloroethane catalyzed by supported Pt-Cu catalysts was selective toward ethylene formation when the C-Cl bonds of the chlorocarbon dissociated on the Cu sites. The dissociation of the C-Cl bonds of 1,2-dichloroethane on Pt results in the formation of ethane. It was proposed that the increase in selectivity toward ethylene at the expense of ethane that occurs when the with decreasing Pt to Cu atomic ratio was indicative of the size-demanding nature of 1,2-dichloroethane dissociation on Pt. Specifically, the dilution of Pt with Cu decreases the number of Pt ensembles large enough to dissociate the C-Cl bonds or to adsorb strongly ethylene and hence preventing its desorption without hydrogenation. Thus, the research was focused on identifying the sites for ethylene production and understanding the reasons why Pt in the ethylene selective Pt-Cu catalysts does not hydrogenate the olefin to paraffin. For this purpose, a combination of reaction kinetics, spectroscopic, and theoretical investigations have been conducted.

Chemical Kinetics Experiments: The reaction kinetics of 1,2-dichloroethane and H₂ or D₂ were measured as well as the H-D exchange kinetics of ethylene, ethane and 1,2-dichloroethane with D₂. Most noteworthy is the result that no deuterated ethylene formed in the CH₂Cl-CH₂Cl+D₂ reaction over Pt-Cu/SiO₂ catalysts with Pt/Cu atomic ratios of 1:3 and 1:6 at 473 K when the ethylene selectivity of the catalyst exceeded 90-95%. These results are consistent with the idea that dissociation of 1,2-dichloroethane on Cu produces ethylene because, as it is known from literature, Cu does not catalyze H-D exchange with hydrocarbons but Pt does. As well, no H-D exchange was observed for ethane and for 1,2-dichloroethane over the same catalysts at 473 K. However, the H-D

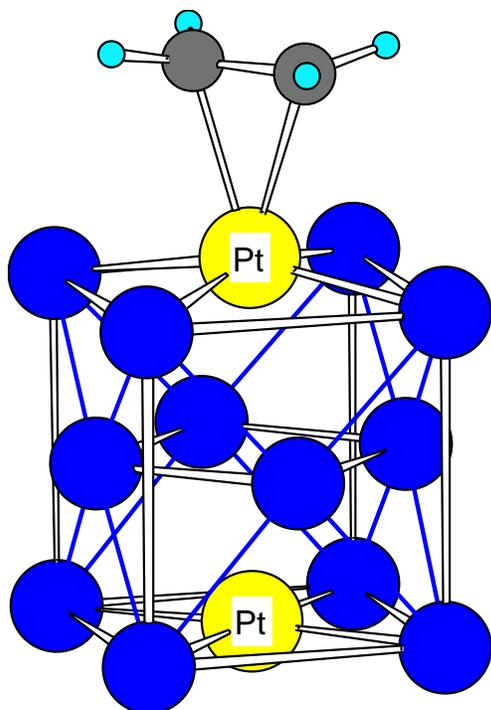


Figure 1. Optimized structure of ethylene adsorbed on a Cu₁₂Pt₂(100) cluster of D_{4h} symmetry.

dramatically increases ethylene selectivity for catalysts with a high Pt to Cu atomic ratio. The CO is not consumed in the reaction and its effect is reversible; elimination of CO from the reaction mixture restores the initial ethylene selectivity. These results are consistent with the hypothesis that for Pt-Cu surfaces Cu sites are responsible for ethylene production.

DFT Cluster Study: To elucidate the factors that control the high ethylene selectivity of Pt-Cu catalysts in the 1,2-dichloroethane dechlorination reaction, adsorption of ethylene was probed by DFT using a Cu₁₂Pt₂(100) cluster as a model of the Pt-Cu surface. For this investigation of ethylene adsorption, the whole C₂H₄/Cu₁₂Pt₂ structure was optimized, as shown in Figures 1. An analysis of the interaction of ethylene with the cluster allowed us to conclude that C₂H₄ adsorbs on the Pt atop site as a π -complex. The C-C bond length increases to 1.40 Å. (The length of the C-C double bond in gas phase C₂H₄ is 1.33 Å calculated within B3LYP/6-31G* set). According to the calculations, the formation of a di- σ -complex of C₂H₄ with the Cu₁₂Pt₂ cluster is highly energetically unfavorable. It is concluded that the low energy of C₂H₄ adsorption on the sites containing isolated Pt atoms may be responsible for the high ethylene selectivity of the catalysts with high Cu/Pt atomic ratio.

DOE Interest

One of the key challenges in catalysis is to develop the fundamental understanding necessary to synthesize catalysts that are 100% selective toward the desired product. This understanding is of great importance to the Department of Energy

exchange proceeded readily with ethylene and was accompanied by its hydrogenation to ethane. Readsorption of ethylene on Pt sites or dissociation of 1,2-dichloroethane thereon to form a surface di- σ -complex may result in deuterated ethylenes and/or ethanes, both of which likely form via ethylidyne species. However, di-deuterated ethane can also form by the deuteration of the surface di- σ -complex.

Infrared Spectroscopy Investigations:

The idea that ethylene in 1,2-dichloroethane dechlorination catalyzed by Pt-Cu catalysts forms on Cu sites is also supported by results obtained in FTIR investigation. It was shown that CO serves as an effective blocker of Pt sites in Pt-Cu/SiO₂ catalysts for 1,2-dichloroethane adsorption, and, hence, in the presence of CO 1,2-dichloroethane cannot compete for the Pt adsorption sites. The 1,2-dichloroethane does compete effectively with CO for the Cu sites. Thus, the addition of CO into a CH₂Cl-CH₂Cl+H₂ reaction mixture

to meet our long- term goals of energy self-sufficiency and minimal environmental impact of our advancing technology.

Future Plans

It is of paramount importance that a better understand is developed concerning the reactivity of different active sites on the Pt-Cu surfaces toward 1,2-dichloroethane. This insight is crucial for understanding the mechanisms of the classic dechlorination and hydrogen-assisted dechlorination reactions of multi-chlorinated hydrocarbons catalyzed by Pt-Cu surfaces. To this end, both experimental and theoretical approaches will be employed.

The interaction of 1,2-dichloroethane and ethylene, the product of 1,2-dichloroethane hydrogen-assisted dechlorination reaction, with Cu, Pt and Cu-Pt surface of different compositions will be probed by FTIR. Concomitantly, the potential energy surfaces for the 1,2-dichloroethane dissociation on different sites of Pt-Cu surfaces will be calculated. A DFT cluster study will be conducted with different Pt-Cu clusters of the general formula $\text{Cu}_{14-n}\text{Pt}_n$ ($n = 2, 4, 6, 10, 14$) which will serve as models of the active sites with different compositions. Both Langmuir-Hinshelwood mechanisms with bare metal surface and Eley-Rideal mechanisms with the surface covered with H will be considered.

Spectroscopic mechanistic investigations of chlorocarbon dechlorination reactions will be complemented by macroscopic kinetic studies with label molecules to establish the rate determining elementary step of the reaction and to link individual reaction steps with specific the certain active sites on the bimetallic surface.

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Thermodynamic Studies of Transition-Metal Hydride Bonds in Solution

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Purpose

The formation and cleavage of M-H bonds are important steps in many reactions catalyzed by homogeneous and heterogeneous catalysts as well as enzymes. The objectives of this research are to develop a quantitative understanding of M-H bond free energies in solution and to demonstrate the usefulness of this knowledge in catalyst design.

Recent Progress

Summary of progress prior to FY 2003. Three independent methods have been developed for measuring the thermodynamic hydride donor ability (hydricity) of transition-metal hydrides, an important thermodynamic property. Hydricity scales have been constructed for transition metal hydride complexes and transition metal formyl complexes. These scales permit the quantitative calculation of the driving forces for H⁺ transfer reactions. Free energy relationships have been developed that are capable of accurately predicting all three solution bond-dissociation free energies (SDBFEs), ΔG_{H^+} , ΔG_{H^\bullet} , and ΔG_{H^-} for five-coordinate Ni hydride complexes from easily measured half-wave potentials. The knowledge derived from these thermodynamic studies was used to design a system for stoichiometric reduction of coordinated CO to a formyl using H₂ and a base under ambient conditions.

Technical progress in FY 2003-FY2004. **[Ni(Et₂PCH₂NMeCH₂PEt₂)₂]²⁺: A Functional Model for Hydrogenases.** The complex [Ni(PNP)₂](BF₄)₂ (where Et₂PCH₂N(Me)CH₂PEt₂ is PNP) is a catalyst for hydrogen oxidation that incorporates both hydride and proton acceptor sites in a single metal complex. Comparison of [Ni(PNP)₂](BF₄)₂, Ni(PNP)₂, and [HNi(PNP)₂](PF₆) with analogous Ni complexes of depp in which the bridging N has been replaced with a methylene group has been used to confirm the important role of the pendant N base in hydrogen activation and proton transfer processes. Heterolytic activation of hydrogen by [Ni(PNP)₂](BF₄)₂ is observed with the formation of a NiH site ($\Delta G_{H^-} = 66$ kcal/mol) and a protonated N atom of the pendant base on one diphosphine ligand ($pK_a = 10.6$). The NH and NiH protons of this product, [HNi(PNP)(PNHP)]²⁺, undergo rapid intramolecular exchange ($\sim 10^4$ s⁻¹) with each other and intermolecular exchange with protonated bases in solution. The rapid proton transfer between Ni and N results in a 0.6 V decrease in the oxidation potential of [HNi(PNP)₂]⁺ compared to [HNi(depp)₂]⁺ and a much more reversible process. These results demonstrate that the catalytic cycle for hydrogen oxidation involves participation of the pendant base of the PNP ligand in two key proton transfer steps that are similar to steps proposed for the di(thiomethyl)amine ligand of the Fe-only hydrogenases.

Thermodynamic Hydride Donor Abilities of [HW(CO)₄L]⁻ Complexes (where L = CO, PR₃ or P(OR)₃) and Their Reactions with [C₅Me₅Re(PMe₃)(NO)(CO)]⁺.

The hydride-donor abilities of [HW(CO)₅]⁻, *cis*-[HW(CO)₄P(OMe)₃]⁻, and *cis*-[HW(CO)₄(PPh₃)]⁻ (36-40 kcal/mol) were measured in acetonitrile, and the reactions of these complexes with [Cp*Re(PMe₃)(NO)(CO)]⁺ were studied. The *cis*-[HW(CO)₄(L)]⁻ are some of the most powerful hydride donors reported to date for transition-metal hydrides, but it is interesting to note that the neutral HRh(dppb)₂ complex (where dppb is 1,2-bis(diphenylphosphino)benzene) with a hydride donor ability of 34 kcal/mol is even more hydridic than the anionic tungsten complexes.

Periodic Trends in Metal Hydride Donor Thermodynamics: Measurement and Comparison of the Hydride Donor Abilities of the Series [HM(PNP)₂]⁺ (M = Ni, Pd, Pt; PNP = Et₂PCH₂N(Me)CH₂PEt₂). The complexes M(PNP)₂²⁺ (M = Pd, Pt, Ni and PNP = Et₂PCH₂N(Me)CH₂PEt₂) were synthesized, and their thermodynamic properties were determined in acetonitrile. The ΔG_H⁻ values for [HPt(PNP)₂]⁺, [HPd(PNP)₂]⁺, and [HNi(PNP)₂]⁺ are 54.7, 53.8, and 66.7 kcal/mol, respectively. The pK_a values of [HPt(PNP)₂]⁺, [HPd(PNP)₂]⁺, and [HNi(PNP)₂]⁺ are 27.9, 22.8, and 22.2, respectively. The palladium hydride has an acidity equal to that of the analogous nickel hydride and a hydricity equal to that of its platinum analog. Compared to Ni and Pt, Pd is both a strong acid and a good hydride donor. This ability to act as both a hydride donor and a proton donor may contribute to the frequent observation that second row transition metals are better catalysts than either their first or third row counterparts.

Hydricities of BzNADH, C₅H₅Mo(PMe₃)(CO)₂H, and C₅Me₅Mo(PMe₃)(CO)₂H in Acetonitrile. The formal transfer of a hydride ion, H⁻, is a fundamental reaction in biological and chemical catalysis. In many biological hydride transfer reactions, organic cofactors such as NADH/NAD⁺, NADPH/NADP⁺, and FADH/FAD⁺ are involved. Similarly, the kinetic hydricities of a series of CpM(CO)₂(L)H and Cp*M(CO)₂(L)H complexes (where M = Mo or W, and L is CO or a monodentate phosphine ligand) have been studied in detail by Bullock and coworkers. Thermodynamic hydride donor abilities for a number of these same complexes have been reported by Sarker and Bruno. In the course of our studies, the thermodynamic hydride donor abilities previously reported for BzNADH and CpMo(CO)₂(PMe₃)H were found to be incorrect. For NADH analogs, our new results lead to a simple correction of previously reported hydride donor abilities by -13 kcal/mol. The previously reported ΔG_H⁻ value of 88.6 kcal/mol for CpMo(PMe₃)(CO)₂H has been found to be 58 ± 2 kcal/mol using a combination of equilibrium and calorimetric methods. As a result of these studies, the hydricities of [HM(diphosphine)₂]⁺ complexes (M = Ni, Pd, Pt), [HW(L)(CO)₄]⁻ complexes, transition-metal formyl complexes, NADH derivatives, CpMo(CO)₂(PMe₃)H, and Cp*Mo(CO)₂(PMe₃)H have been cross referenced and can now be placed on a common absolute scale.

Using Ligand Bite Angles to Control the Hydricity of Palladium Diphosphine Complexes. A series of [Pd(diphosphine)₂](BF₄)₂ and Pd(diphosphine)₂ complexes have been prepared for which the natural bite angle of the diphosphine ligand varies from 78° to 111°. Structural studies have been completed for seven of the ten new complexes described. These structural studies indicate that the dihedral angle between the two planes formed by the two phosphorus atoms of the diphosphine ligands and palladium increases by over 50° as the natural bite angle increases for the [Pd(diphosphine)₂](BF₄)₂

complexes. Linear free-energy relationships are observed between pK_a and the Pd(I/0) couple and between ΔG_{H^-} and the Pd(II/I) couple. The measured values for ΔG_{H^-} were all 57 kcal/mol, whereas the values of ΔG_{H^-} ranged from 43 kcal/mol for $[\text{HPd}(\text{depe})_2]^+$ (where depe is bis(diethylphosphino)ethane) to 70 kcal/mol for $[\text{HPd}(\text{EtXantphos})_2]^+$ (where EtXantphos is 9,9-dimethyl-4,5-bis(diethylphosphino)xanthene). It is estimated that the 33° change in the natural bite angle of the ligand contributes approximately 20 kcal/mol to the observed difference of 27 kcal/mol for ΔG_{H^-} .

Future Research

Studies of HRh(diphosphine)₂ complexes. Previous studies from our laboratories have demonstrated that HRh(dppb)₂ (where dppb is bis(diphenylphosphino)benzene) is a very good hydride donor with a ΔG_{H^-} value of 34 kcal/mol. This compound is the most hydridic compound that we have studied to date. It is anticipated that HRh(depe)₂ (where depe is bis(diethylphosphino)ethane) should be much more hydridic with a ΔG_{H^-} value of ≈ 25 kcal/mol. This and related HRh(diphosphine)₂ complexes will be prepared and the hydride donor abilities of these compounds will be measured. If these hydrides can be generated from hydrogen and a base, it may be possible to replace traditional stoichiometric hydride reagents such as NaBH₄ with hydrogen and a base. Rhodium dihydrides, $[\text{H}_2\text{Rh}(\text{diphosphine})_2]^+$, containing ligands with different natural bite angles will be studied using approaches similar to those used to determine the thermodynamic properties of the $[\text{H}_2\text{Co}(\text{dppe})_2]^+$ system. The objective is to demonstrate that the thermodynamic driving force for oxidative addition of H₂ to $[\text{Rh}(\text{diphosphine})_2]^+$ complexes is also controlled by natural bite angles.

At the opposite end of the hydride donor scale are transition metal hydrides that are poor hydride donors. Some examples from our previous work include $[\text{HPd}(\text{EtXantphos})_2]^+$ and $[\text{HPt}(\text{EtXantphos})_2]^+$ with ΔG_{H^-} values of 70 kcal/mol and 76 kcal/mol, respectively. These hydrides should be stable to acids with pK_a values as low as 4 and 0, respectively, in acetonitrile, or aqueous pK_a values of -3 and -7. The stability of these hydrides and selected new hydrides in solutions of various acids and in neat acidic solvents such as CF₃COOH will be studied. The ability of hydrides to form in these acidic solutions from H₂ gas will also be determined. Formation of stable hydrides from hydrogen under very acidic conditions will open up the possibility of carrying out a number of catalytic reactions in homogeneous solutions that are analogous to those performed with heterogeneous catalysts.

Model Development. Thermodynamic data can be invaluable in designing and understanding stoichiometric and catalytic reactions, independent of any underlying model or theory. However, a model that can be used to quantitatively predict all three bond-dissociation free energies for transition-metal hydrides in solution would be very useful. Current data indicates that a ligand additivity approach can be used to determine the effects of substituents in $[\text{HNi}(\text{diphosphine})_2]^+$ complexes. Detailed studies of chelate bite-size effects have also been carried out for $[\text{HPd}(\text{diphosphine})_2]^+$ complexes. Combining these results with the data we hope to obtain on the Pt and Rh complexes discussed above should enable us to develop a semi-empirical model that will account for the effects of metal, substituents, and chelate bite angles. Molecular orbital calculations will be used to supplement these experimental data. Using this combined approach a comprehensive model will be developed that is capable of predicting all three bond

dissociation free energies associated with the homolytic and heterolytic cleavage of the M-H bonds in five-coordinate transition-metal hydride complexes.

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Fundamental Studies of the Reforming of Oxygenated Compounds over Supported Metal Catalysts

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Goal

Understand surface chemistry for supported metals to control catalytic activity, selectivity and stability for production of clean fuels from biomass-derived oxygenated hydrocarbons

Recent Progress

We have recently reported a process to generate hydrogen by aqueous-phase reforming (APR) at temperatures near 500 K of oxygenated hydrocarbons derived from biomass, such as sorbitol, glycerol, and ethylene glycol. The APR process is greenhouse-gas neutral, because the CO₂ by-product that accompanies the H₂ is consumed by biomass growth. In addition to utilizing renewable feed-stocks, the APR process eliminates the need to vaporize water and the oxygenated hydrocarbon, which reduces the energy requirements for producing hydrogen. Importantly, we have demonstrated how the APR process can be operated to achieve very low levels of CO (100 ppm) in a single-step catalytic process, because the reforming of oxygenated hydrocarbons and the water-gas shift reaction are both thermodynamically favorable at the same low temperatures.

We have conducted detailed catalyst characterization studies and reaction kinetics measurements for aqueous-phase reforming over Pt, Ni, and NiSn-based catalysts. The results from these studies allow us to document the role of Sn in controlling the selectivity of Ni-based catalysts and to determine the reaction conditions under which NiSn-based catalysts perform as well or better than Pt catalysts for aqueous-phase reforming reactions. Aqueous-phase reforming of sorbitol, glycerol, and ethylene glycol solutions produces an effluent gas stream composed of 50-70 mol% H₂, 30-40 mol% CO₂, and 2-11 mol% alkanes (dry basis) at high conversion. Addition of Sn to Ni improves the selectivity for production of H₂ by ethylene glycol reforming from 35 to 51 % at a Ni:Sn ratio of 270:1, while the alkane selectivity is reduced from 44 to 33%. At a Ni:Sn ratio of 14:1, the hydrogen selectivity increases to 90 %, while alkane production is nearly eliminated. As the system pressure decreases to the bubble-point of the feed (25.1 bar at 498 K), production of alkanes decreases and the hydrogen selectivity increases accordingly. The addition of Sn to Ni significantly decreases the rate of methane formation from C-O bond cleavage, while maintaining sufficiently high rates of C-C bond cleavage required for hydrogen formation. Turnover frequencies for hydrogen

production at 498 K over Raney-Ni-based catalysts are several times lower than that over 3 wt% Pt/Al₂O₃ based on CO chemisorption. However, the high CO uptakes and high densities of Raney-Ni-based catalysts lead to comparable rates of hydrogen production per unit reactor volume as 3 wt% Pt/Al₂O₃ at 498 K. Results from XRD, SEM, and ¹¹⁹Sn Mössbauer spectroscopy suggest that Raney-NiSn catalysts are comprised of alumina and nickel particles surrounded by a Ni-Sn alloy. After exposure to reaction conditions, Sn is present primarily as Ni₃Sn alloy with small amounts of Sn(IV) associated with alumina.

We have shown how the selectivity for production of hydrogen can be increased for liquid-phase reforming of glucose. Glucose is a particularly important reactant for the generation of hydrogen from renewable resources, because this sugar makes up the major energy reserves in plants and animals. While the selectivity for hydrogen production is insensitive to the liquid-phase concentration of sugar-alcohols such as sorbitol, the hydrogen selectivity from reforming of glucose decreases as the liquid concentration increases from 1 to 10 wt% because of undesired hydrogen-consuming side reactions that occur in the liquid phase. This decrease in selectivity is an important limitation, because processing dilute aqueous solutions involves the processing of excessive amounts of water. We have found that high selectivities can be achieved for hydrogen production from high liquid-phase concentrations of glucose by combining a hydrogenation reactor with an APR reactor and employing hydrogen recycle between reactors.

We have shown how aqueous-phase reforming of sorbitol can be tailored to selectively produce a clean stream of heavier alkanes consisting primarily of butane, pentane and hexane. For example, the conversion of sorbitol to alkanes plus CO₂ and water is an exothermic process that retains approximately 95 % of the heating value and only 30 % of the mass of the biomass-derived reactant. Production of alkanes by aqueous-phase reforming of sorbitol takes place by a bi-functional reaction pathway involving first the formation of hydrogen and CO₂ on the appropriate metal catalyst (such as Pt) and the dehydration of sorbitol on a solid acid catalyst (such as silica-alumina). These initial steps are followed by hydrogenation of the dehydrated reaction intermediates on the metal catalyst. When these steps are balanced properly, the hydrogen produced in the first step is fully consumed by hydrogenation of dehydrated reaction intermediates, leading to the overall conversion of sorbitol to alkanes plus CO₂ and water. In general, the selectivities to heavier alkanes increase as more solid acid sites are added to a non-acidic Pt/alumina catalyst. The alkane distribution also shifts to heavier alkanes when the pH of the aqueous sorbitol feed is lowered by addition of mineral acid.

DOE Interest

New catalysts and new process conditions have been identified to produce hydrogen containing low levels of carbon monoxide from renewable biomass resources. This new aqueous-phase reforming process takes place in a single chemical reactor with a rate per reactor volume comparable to the rates currently achieved in the multi-reactor production of hydrogen from non-renewable fossil fuel resources. We have also developed catalysts and process conditions for the production of liquid alkanes from renewable biomass resources.

Future Plans

We hope to understand further the factors controlling the activity, selectivity, and stability of catalysts for aqueous-phase reforming of oxygenated hydrocarbons. In particular, our current supported platinum catalyst exhibits excellent selectivity and stability for production of hydrogen, but we wish to improve catalytic activity, especially at lower temperatures. Our current Raney-NiSn catalyst exhibits good activity and selectivity for production of hydrogen at pressures near the bubble point of the feed, but we wish to improve catalyst performance at higher pressures, and we wish to improve catalyst stability. Our future work will involve studies of new metal-alloy systems on new catalyst supports.

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Related Rhenium(V) Catalysts Adopt Different Mechanisms for Oxygen Atom Transfer

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Postdoctorals: A. O. Bouh, N. Koshino, G. Lente, M. Li, B. Saha

Collaborators: R. J. Angelici, A. Ellern, M. Pruski, T. B. Rauchfuss, W. Wang

Goal: Characterization of the mechanisms of oxygen atom transfer reactions

Recent Progress:

The same reactions catalyzed by three closely-related rhenium(V) compounds three adopt different mechanisms. This is evident from the kinetics and supporting information such as substituent effects, trapping of reaction intermediates, competition kinetics, etc. The three catalysts, **1**, **2**, and **3**, whose structural formulas are shown below, all catalyze oxygen atom transfer reactions that do not occur at all without a catalyst. With any one of these catalysts, however, the reactions occur with a clean 1:1 stoichiometry:



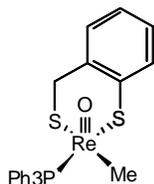
The rate equations for catalysts **1** and **2** are:

$$-\frac{d[\text{PyO}]}{dt} = k_1 \times \frac{[\mathbf{1}] \cdot [\text{PyO}]^2}{[\text{PPh}_3]} \quad (\Rightarrow \text{nucleophilic assistance for Py-O cleavage})$$

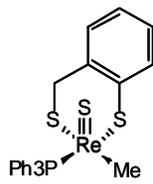
$$-\frac{d[\text{PyO}]}{dt} = k_{2a} \times [\mathbf{2}] \cdot [\text{PyO}]^{1/2} \quad (\Rightarrow \text{a chain mechanism})$$

The best-characterized reaction for **3** is $\text{RS(O)R}' + \text{PPh}_3 \rightarrow \text{RSR}' + \text{Ph}_3\text{PO}$, which proceeds according to

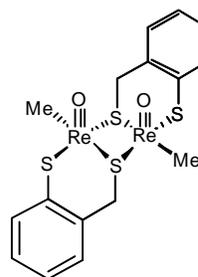
$$\frac{d[\text{RSR}']}{dt} = \left\{ \frac{k_0 + k_1 \cdot K \cdot [\text{PAR}_3]}{1 + K \cdot [\text{PAR}_3]} \right\} \times K_{3P} \cdot [\text{MeS(O)Ph}] \cdot [\mathbf{3}]_{T,t} \quad (\Rightarrow \text{parallel nucleophilic pathways})$$



MeReO(mtp)(PPh₃) **1**



MeReS(mtp)(PPh₃) **2**

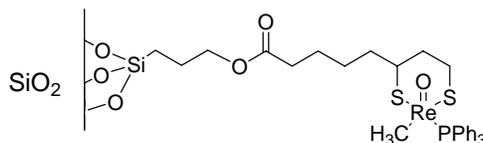


{MeReO(mtp)}₂ **3**

Future Plans (without bibliography)

I. Tethered Rhenium(V) Catalysts [with R. J. Angelici and M. Pruski]

This collaboration has resulted in the synthesis of the propanedithiolate (pdt) complex MeRe(O)(pdt)(PPh₃) tethered on amorphous silica (structure **A**).



A

Preliminary solid state ³¹P NMR studies of the solid show that the complex has the same structure on the silica surface as it had before tethering. Initial catalytic studies show that the activity of the tethered complex is very similar to that of the homogeneous complex for the t-BuOOH oxidation of sulfides including dibenzothiophenes to

their sulfoxides. Moreover, the tethered catalyst has been used in five successive reactions with up to 3,500 turnovers.

In light of the success realized by tethering to a silica surface an oxorhenium catalyst with a modified propanedithiolate ligand, continuation of this collaborative effort promises further rewarding results. The target reactions remain $R_2S/R_2SO + \textit{tert}\text{-BuOOH} \rightarrow R_2SO/R_2SO_2 + \textit{tert}\text{-BuOH}$ not only because they hold some potential for removal from diesel fuel of the most sterically-encumbered disulfides (*e.g.*, 4,6-dimethyldibenzothiophene, which cannot be treated by HDS processing) but also because they allow comparisons as further catalysts are studied.

Further studies of tethered dithiolate ligands may afford $\text{MeRe(S)(dithiolate)PPh}_3$ (analogous to **2**, see Accomplishments). Will a chain mechanism still operate with the tethered version of this catalyst as it does with **2**? (Actually, this seems somewhat dubious in light of the bimolecular chain initiation step, but the point needs testing.) Will the tethered version of $\{\text{MeRe(O)(mtp)}\}_2$, **3**, still be so much more reactive than $[\text{MeRe(O)(mtp)PPh}_3]$, **1**, as is the case in the homogeneous reactions?

Further, the tethered catalyst $\text{MeReO(dithiolate)Py}$ will be examined. We hypothesize that it will be an excellent catalyst whereas it fails as a homogeneous catalyst owing to what appears to be bimolecular decomposition of the dioxorhenium(VII) intermediate $\text{MeRe(O)}_2(\text{mtp})$, see Section IV. Because tethering precludes bimolecular steps, the pyridine tethered catalyst may be more successful than the PPh_3 derivative.

II. Alkyl and Aryl Rhenium Catalysts ($R \neq \text{Me}$)

No stable $R\text{-ReO}_3$ analogs of MeReO_3 have been isolated. Several such compounds have been prepared in solution, however, where they are reported to persist for some time. We propose to use them as solution reagents, in three studies. The most important reactions will be the attempted conversion to oxorhenium(V) dithiolates by either of these reactions:



As Re(V) derivatives, compounds with R groups other than Me can be expected to be more stable than in the Re(VII) forms, $R\text{-ReO}_3$. The Re(V) compounds will be tested as catalysts for OAT reactions, because the R group bound to rhenium has been a hitherto unavailable variable.

Because MeReO_3 activates hydrogen peroxide, the compounds $R\text{-ReO}_3$ will also be explored as peroxide-activating catalysts. How will the thermodynamics and kinetics of peroxide binding differ among various R groups as compared to $R = \text{Me}$? How will the reactivities of $R\text{-Re}^{\text{VII}}$ (peroxo) complexes compare to those of the Me-Re analogs?

The decomposition reported upon attempts to isolate pure solid compounds of $R\text{-ReO}_3$ suggests that the process may entail higher-order (second-order?) kinetics. The literature gives no guidance, neither on the kinetics of decomposition nor on the identities of the resulting organic products. This will comprise another aspect of the studies. We hypothesize that R -coupling products, R_2 and $\text{RH} + R_{\text{H}}$, will be found.

III. Compounds and Catalysts with PhS-Re Groups in lieu of Me-Re

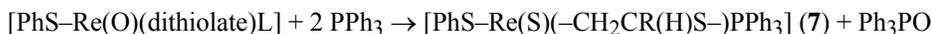
Dirhenium heptoxide, Re_2O_7 , can be used to prepare compounds that are similar to **1** and **3**, above, save that PhS-Re replaces Me-Re . Compounds already characterized crystallographically include the following:



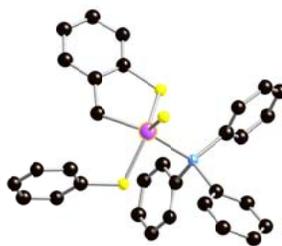
Others, including $[\text{PhS-Re(O)(mtp)(PPh}_3)]$, have been detected by NMR and electronic spectroscopy, and are still being characterized. This transformation will be studied, and compared with the Me-Re case.



Further reaction with PPh₃ affords compound **7**:



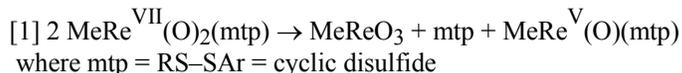
It is the first rhenium(V) compound of this series with a C–Re bond not arising from a methyl group coordinated to rhenium. Moreover, the chemistry by which it was realized will be investigated.



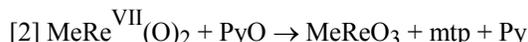
This is a remarkable transformation: a new Re–C bond has been created; a six-membered ring has been converted to a five-membered ring, a thiolate sulfur is now a thio-rhenium group, and the oxo group is now a phosphine oxide. Its mechanism will be studied by kinetics and other methods. The product has been isolated, and its x-ray structure was identified in the first part of exploring the novelty of this reaction.

IV. Dioxorhenium(VII) Compounds and Intermediates

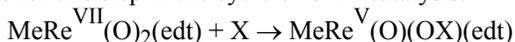
The dimer $\{\text{MeRe}(\text{O})(\text{mtp})\}_2$, **3**, is 150-fold more reactive as an OAT catalyst than the phosphine monomer **1**. We attribute the enhanced reactivity to the need for **1** to cycle repeatedly through a step entailing loss of the strongly coordinated PPh₃ ligand. Thus we reasoned that MeReO(mtp)Py, with a weaker Lewis base and a more labile Py ligand, would be superior. In fact, this catalyst decomposed at an early stage of the reaction, and only inactive MeReO₃ remained. A retrospective analysis suggests that a reactive catalyst will lead to a higher steady-state concentration of the dioxorhenium(VII) intermediate. Plausibly, but not proven, is that the intermediate rhenium(VII) species decomposes by *second-order* kinetics, making the overall situation worse for the most reactive catalyst. A reasonable but untested transition state is shown, which is in accord with the reactions written.



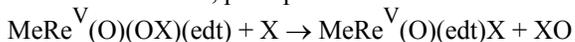
with this net result:



We plan to probe this hypothesis by warming the dioxorhenium compound detected by ¹H NMR at –40 °C in toluene to determine whether the decomposition follows second-order kinetics. We have also learned that the analogous species MeRe^{VII}(O)₂(edt) persists in solution at room temperature for many hours, consistent perhaps with the inability to form 1,2-dithiacyclobutane by reductive elimination. The compound MeRe(O)₂(edt) will be another candidate for study on a longer time scale; its persistence will also enable the direct evaluation of rate constants for this step in the cycle of OAT catalysis:



If the rate constants allow, perhaps data can also be obtained for the hitherto elusive step



V. Sulfonate-bound rhenium catalysts.

The compound MeRe(O)(hq–SO₃[–])₂, containing the sulfonated ligand 8-hydroxyquinolate, offers the prospect of supporting this rhenium catalyst on a silica surface. Recent reports demonstrate that metal complexes may be anchored to amorphous and mesoporous silicas by hydrogen bonding of a sulfonate (–SO₃[–]) group either in a ligand in the complex or in a triflate (CF₃SO₃[–]) counter-ion. This relatively simple method of immobilizing metal complex catalysts on solid supports would be used with MeRe(O)(hq–SO₃[–])₂(Na⁺)₂. This complex on amorphous silica would be used as an oxidation catalyst.

VI. Nucleophilic assistance of OAT reactions

The results presented for reactions catalyzed by **1**, **2**, and **3** gave kinetic evidence for YO cleavage requiring a nucleophile. In the cases explored, Py-O, R₂S-O, PPh₃, and a RS⁻ (from the dithiolate sulfur) performed this function.

Our plan is to explore this effect systematically, and to gain firmer evidence that the effect is indeed nucleophilic. Thus we will use a series of nucleophiles such as *m*- or *p*-R-C₅H₄N and *m*- or *p*-ArSMe, to determine whether the rate constants correlate with nucleophilic parameters in general. By making these studies quantitative through the application of the Hammett substituent constant approach, it will be possible to evaluate the extent to which the transition state benefits from this added interaction. Coupled with this, DFT calculations will be performed to find transition state energies, comparing values with and without the nucleophile incorporated.

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Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes

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Goal

The goal of this research is to advance the fundamental chemistry of yttrium and the lanthanide elements to optimize the use of their special properties in energy related areas.

Recent Progress

The project is currently focused on understanding and developing the catalytic chemistry available from lanthanide complexes in the presence of organometallic Group 13 compounds. Lanthanide salts react with organoaluminum reagents to form highly efficient and selective catalysts for the polymerization of isoprene to high cis-1,4-polyisoprene, the main component of natural rubber. Little is known about the catalyst or its reaction chemistry despite the fact that it has the potential to provide information not only on effective methods to polymerize dienes, but also on the unique features of the lanthanides in catalysis. Typical industrial catalysts for lanthanide-based diene polymerization are generated by reacting mixtures of neodymium carboxylates derived from industrially available carboxylic acids with an excess of ethylaluminum chloride reagent and then with an excess of an isobutylaluminum compound. The first step was thought to make LnCl_3 which subsequently gets alkylated to make an active "LnR" moiety. Initially, not even the composition of the components used to make the catalyst was known.

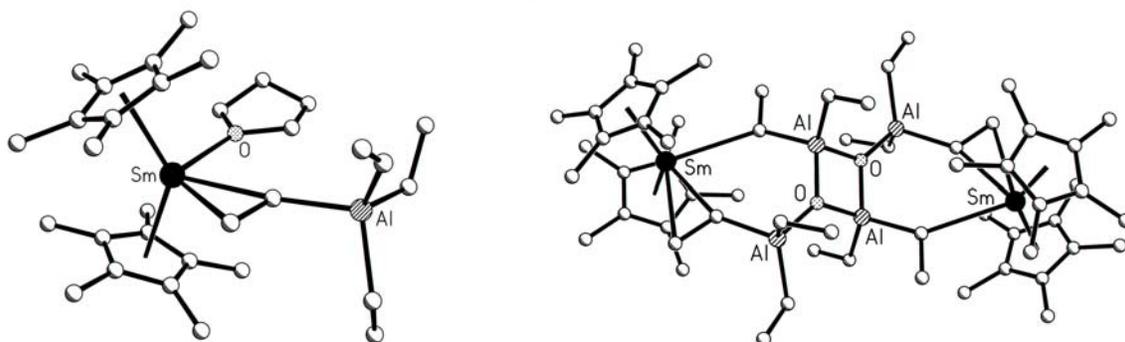
We have synthesized fully characterized lanthanide carboxylates and examined their sequential reaction chemistry with Et_2AlCl and Al^iBu_3 . These well-defined precursors generate catalytically active species that polymerize isoprene to high cis-1,4-polymer. The lanthanide carboxylate/ Et_2AlCl reaction products are not simply LnCl_3 as previously thought: Al and carboxylate and ethyl groups are still present. Since these products decompose in solvents polar enough to dissolve them, it has been difficult to study the next stage of catalyst formation involving Al^iBu_3 addition.

To obtain more information on the carboxylate to chloride to alkyl (to hydride? to allyl?) conversions presumably involved in catalyst preparation, the well defined coordination environment of soluble bis(cyclopentadienyl) complexes has been used. Several key classes of relevant complexes are already available, $[(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{O}_2\text{CR})]_n$, $[(\text{C}_5\text{Me}_5)_2\text{LnCl}]_n$, $[(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{AlR}_4)]_n$, $[(\text{C}_5\text{Me}_5)_2\text{LnH}]_n$, and $(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{allyl})$ for $\text{Ln} = \text{Sm}$ due to facile synthetic access via divalent samarium. Sm is similar in size and chemistry to Nd, the metal most commonly chosen for diene polymerization, and is less paramagnetic. Facile access to another class important in evaluating this chemistry, the unsolvated $[(\text{C}_5\text{Me}_5)_2\text{SmR}]_n$ complexes has just been discovered and, as discussed below, has provided independently interesting chemistry. In addition, the isoprene and

butadiene derived allyl complexes, $[(C_5Me_5)_2Sm]_2(C_5H_8)$ and $[(C_5Me_5)_2Sm]_2(C_8H_{12})$, are available.

Reactions of R_2AlCl and R_3Al ($R = Me, Et,$ and iBu) with metallocene carboxylates and chlorides have revealed both unexpected results and subtle differences as a function of aluminum reagent that may provide information on why particular reagents are commonly chosen for diene polymerization catalysis. The $[(C_5Me_5)_2Sm(O_2CPh)]_2$ carboxylate does not react with R_2AlCl simply to replace carboxylate with chloride, as presumed in the literature. Products containing 2Cl per Sm are isolated as Al adducts, $(C_5Me_5)_2Sm(\mu-Cl)_2AlR_2$, instead of $[(C_5Me_5)_2SmCl]_3$.

Other unexpected results have come from comparing $R = Et$ to Me and iBu . $AlEt_3$ reactions differ from $AlMe_3$ and Al^iBu_3 in giving the unusual $(\mu-\eta^2;\eta^1-Et)$ complexes, $(C_5Me_5)_2Sm(THF)(\mu-\eta^2;\eta^1-Et)AlEt_3$, shown on the left below, and the ethylaluminumoxane, $[(C_5Me_5)_2Sm]_2[(\mu-\eta^2;\eta^1-Et)AlEt_2OAlEt_2]_2$, below right, obtained from $[(C_5Me_5)_2Sm(O_2CPh)]_2$.



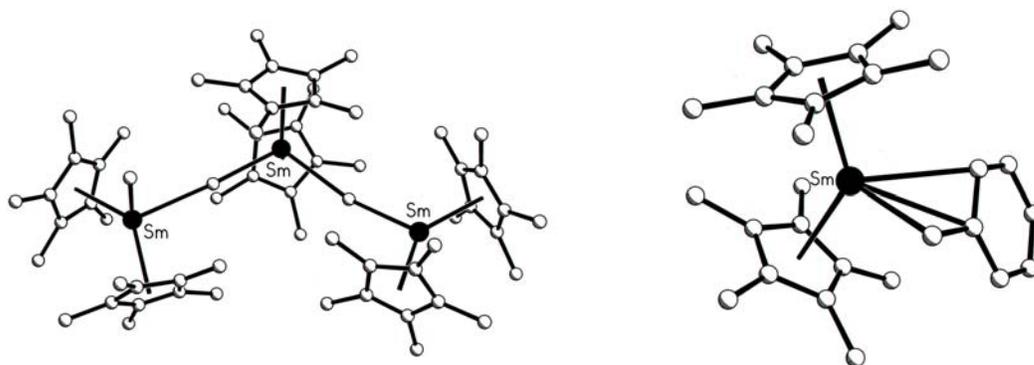
In each of these complexes, the ethylaluminum variation is providing extra coordination via side-on bonding in a coordination mode not identically available with Me and iBu analogs. Such a weak interaction could explain how the bimetallic ethyl-containing Al/Nd complexes isolated in the metal carboxylate/ Et_2AlCl reactions could fragment upon dissolution. Such a weak interaction could protect/stabilize the metal center during catalysis as the substrate insertion is occurring before another equivalent of monomer arrives. Similar scenarios are envisioned in olefin polymerization catalysis with agostic intermediates.

In addition to the modeling studies described above, efforts have been made to identify less complicated catalytically active isoprene polymerization systems. We now find that simple lanthanide diiodides including TmI_2 , DyI_2 , NdI_2 , and SmI_2 , can initiate polymerization to high-cis 1,4-product without activators. These precursors are directly available from the metal and iodide reagents and do not have the problem of an unknown number of coordinated carboxylic acid ligands that can be present in industrial lanthanide carboxylate precursors.

We have also found that catalytically active systems can be obtained directly from fully characterized lanthanide carboxylates, $Ln[O_2CCMe_2Et]_3$ and only AlR_3 initiators, i.e. chloride free. In this case, the polymer is a bimodal blend of cis- and trans-1,4-polyisoprene that may have some advantage over pure cis-1,4-polyisoprene in terms of processing for certain applications.

As described above, unsolvated samarium alkyl complexes, $[(C_5Me_5)_2SmR]_x$, were previously unavailable for modeling the carboxylate to chloride to alkyl catalyst

formation pathway. We now find that the unsolvated cations $[(C_5Me_5)_2Ln][(\mu-Ph)_2BPh_2]$ are good precursors to such complexes when treated with alkyl alkali metal reagents. $[(C_5Me_5)_2SmMe]_3$ was isolated for the first time in this way and found to have the unusual asymmetric non-cyclic structure shown below. This complex is a potent C-H activation reagent and reacts with benzene and toluene to form $(C_5Me_5)_2SmPh$ and $(C_5Me_5)_2Sm(CH_2Ph)$, which has the η^3 -structure shown below. These complexes and their Et and iBu analogs offer additional possibilities for modeling this system and developing new chemistry.



Future Plans

A thermal field flow fractionation system has been obtained and will be used to more fully characterize the polyisoprene obtained from the above systems. The reaction chemistry of the $(C_5Me_5)_2Sm(\mu-Cl_2)AlR_2$ intermediates with iBu_3Al will be examined to model that step in the catalyst preparation. Subsequent modeling will focus on hydride, alkyl, allyl, and diene-derived ligand reactivity. The synthesis of unsolvated $[(C_5Me_5)_2SmR]_x$ complexes with alkyls larger than methyl will be explored following preliminary evidence of unusual results along these lines. The diene polymerization activity of these metallocenes will be examined to evaluate the effect of the presence of the ancillary ligands. The binary catalyst systems will be pursued to define the best catalytic initiator for further study.

Potential Impact in Science and Technologies of Interest to DOE

Fundamental knowledge of lanthanide chemistry can be applicable to a variety of energy related topics involving the special properties of these metals. This project focuses on the catalytic formation of high quality synthetic rubber which is important in the manufacture of fuel efficient tires. This study may provide fundamental knowledge on the special features of lanthanide polymerization catalysis which can be utilized in catalytic reactions involving other strategic materials. This project also provides training to Ph.D. students in the chemistry of the f element heavy metals.

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Nanocluster Catalysts Formation and Stabilization Fundamental Studies

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Goals

The primary goals of our DOE-funded program are: to determine which stabilizers and other factors are best for the formation, stabilization and catalytic activity of transition-metal nanoclusters; to continue our mechanistic studies of the nucleation, growth and, now, agglomeration of transition-metal nanoclusters; and to exploit nanoclusters as catalysts.

Recent Progress

Our DOE-funded research continues to proceed very well, producing a number of fundamental contributions, as detailed below:

(1) Nanocluster Formation and Stabilization Fundamental Studies

In 2002 we reported the first methods to evaluate modern transition-metal nanocluster catalyst formation and stability.¹ Our new methods and results provide the first *anion series* of the relative ability of anions to promote the kinetically controlled formation, stabilization and desired catalytic properties of, for example, prototype Ir(0) nanoclusters: $P_2W_{15}Nb_3O_{62}^{9-} \sim [(P_2W_{15}Nb_3O_{61})_2O]^{16-} \sim SiW_9Nb_3O_{40}^{7-} \sim ([P_2W_{15}(TiOH)_3O_{59}]^n)_n$ ($n = 1, 2$) $> C_6H_5O_7^{3-} > [-CH_2-CH(CO_2^-)]_n^{n-} \sim OAc^- \sim P_3O_9^{3-} \sim Cl^- \sim OH^-$. The essence of this series, the first of its kind, is: *Bronsted basic polyoxoanions* $> citrate^{3-} > other common anions used in nanocluster syntheses$.^{1,2} Our results also reveal the need to scavenge the H^+ formed during nanocluster syntheses from metal salt, MX_n , reduction by H_2 .²

(2) Molecular Insights into How Preferred Oxoanions Bind to and Stabilize Transition-Metal Nanoclusters: A Tridentate, C_3 Symmetry, Lattice Size-Matching Binding Model.

Our ability to evaluate nanocluster stabilizers led, in turn, to a tridentate, C_3 symmetry lattice size-matching model for how preferred stabilizers bind to $\{111\}$ surfaces of transition-metal nanoclusters.³ This important result provides the first molecular insights into how preferred, tridentate stabilizers bind to transition-metal nanocluster catalysts.³ A prediction of the lattice-size-matching, that HPO_4^{2-} is a previously unappreciated, preferred stabilizer for transition-metal nanocluster catalysts, has also been verified.⁴

(3) Fundamental Studies of Nanocluster Agglomeration and Surface Active Sites.

Recently, we were able to measure all three rate processes relevant to nanocluster formation and stability: nucleation (rate constant k_1), growth (autocatalytic surface growth, k_2), and agglomeration (rate constant k_3).⁵ The ability to measure routinely nanocluster

agglomeration rate constants, k_3 , is important since it provides a quantitative measure of nanocluster stability.⁵

We also reported a CS₂ poisoning method that allows us to titrate the number of active sites atop a nanocluster's surface for the first time.⁶

(4) Synthetic Studies That Underpin Our Nanocluster Catalytic and Mechanistic Work.

Careful, reliable, and fully reported synthesis and characterization studies form the backbone on which reliable catalytic and mechanistic studies are built. Our studies under this heading this past period include a reliable synthesis of the P₂W₁₅O₅₆¹²⁻ polyoxoanion,⁷ a scaled-up synthesis of our prototype, 38 Å, Ir(0)_{~2000}•P₂W₁₅Nb₃O₅₆⁹⁻ nanoclusters,⁸ and the synthesis and characterization of the preferred precursor to HPO₄²⁻-stabilized nanoclusters, {[Bu₄N][(1,5-COD)Ir•HPO₄]}_n.⁹

(5) Nanocluster Catalysis Studies: The “Is It Homogeneous vs Heterogeneous Catalysis?” Question and Nanocluster Arene Hydrogenation Catalysis.

We published a review in 2003 that is the first comprehensive summary of the literature of the historically perplexing question of “Is it homogeneous or heterogeneous catalysis?”¹⁰ Thirty systems that are claimed to be single-metal homogeneous catalysis, but that are likely nanocluster catalysis, are identified in our review.

We then went on to show that benzene hydrogenations previously believed to be catalyzed by Ru(II)(η⁶-C₆Me₆)(OAc)₂, are in fact catalyzed by Ru(0) nanoclusters.¹¹ Our study is of further significance in revealing a *heterogeneous* nucleation and then autocatalytic surface-growth mechanisms for *thin-metal film* formation.¹¹ We also published a review on nanocluster arene hydrogenation.¹²

DOE Interest

Nanoclusters are metal particle catalysts closely analogous to the metal particles in the most commonly used commercial catalysts, heterogeneous catalysts. However, nanoclusters have the advantage of being soluble; *hence, they can be made and studied by powerful solution synthesis, spectroscopic characterization and kinetic methods*. Well-defined nanoparticle catalysts promise to be important in the development of the concepts and technical advances en route to achieving the “Holy Grail” of heterogeneous catalysis, namely single-site, high selectivity, and high activity metal-particle catalysts.

Future Plans

Our future plans are: to continue our studies of the factors and additives (solvents, polymers, dendrimers, cations, and ionic liquids) that best allow the formation and stabilization of catalytically active transition-metal nanoclusters; to complete for publication our work on the record activity, selectivity at higher conversions and catalytic lifetime nanocluster catalysis of acetone hydrogenation that we discovered; and to investigate the detailed mechanism of formation of Pt and Pd nanoclusters. These studies—all of a fundamental nature—promise to continue to make excellent use of our DOE grant support, funding for which we remain most grateful.

Publications (2002-2004)

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3. “Molecular Insights for How Preferred Oxoanions Bind to and Stabilize Transition-Metal Nanoclusters: A Tridentate, C₃ Symmetry, Lattice Size-Matching Binding Model”, Özkar, S.; Finke, R. G. *Coord. Chem. Rev.* **2004**, in press.
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12. “A review of soluble transition-metal nanoclusters as arene hydrogenation catalysts”, Widegren J. A.; Finke, R. G. *J. Mol. Catal. A: Chemical* **2003**, *191*(2), 187-207.

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Studies Relevant to Catalytic Activation of Small Molecules

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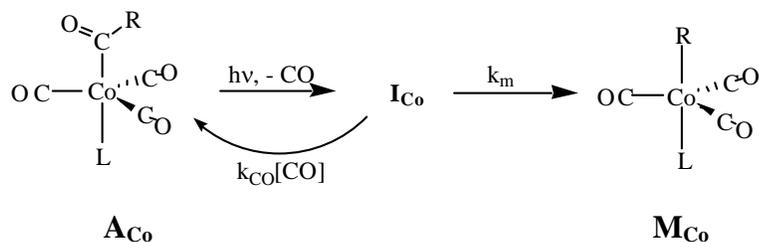
Goal

Application of quantitative kinetics techniques to elucidate fundamental mechanisms relevant to the catalytic activation of small molecules.

Recent Progress

Time-resolved infrared (TRIR) and optical (TRO) spectroscopic techniques were used for the preparation and interrogation of organometallic intermediates relevant to homogeneous catalytic mechanisms. Recent studies were concerned with the carbonylation mechanisms involving manganese and cobalt carbonyls and rhodium and iridium halide complexes. Of particular note was implementation of a high pressure variable temperature (HP/VT) IR flow cell for TRIR studies under conditions closer to operating catalysts.

The migratory insertion mechanism: Homogeneous phosphine modified cobalt-based hydroformylation catalysts are used for the commercial synthesis of alcohols from the heavier olefins, and have drawn renewed attention for specialized applications owing to lower sensitivity to certain feedstock impurities. In order to move the target of inquiry closer to proven carbonylation catalysts, we examined the TRIR spectra and temporal behavior of intermediates \mathbf{I}_{Co} generated as the parameters solvent, T, [CO], R-, L, etc were varied.



Studies by Dr. Steve Massick demonstrated that flash photolysis of $\text{Co}(\text{CO})_3(\text{L})(\text{C}(\text{O})\text{R})$ promptly gives \mathbf{I}_{Co} (*IC* 2003). The T and P_{CO} ranges accessible with the HP/VT flow system allows for accurate measurement of rate laws for \mathbf{I}_{Co} decay with respect to [CO] ($k_{\text{obs}} = k_m + k_{\text{CO}}[\text{CO}]$) and of activation parameters ΔH^\ddagger and ΔS^\ddagger for both pathways. DFT calculations suggest that the most stable among possible configurations of \mathbf{I}_{Co} would involve η^2 -acyl coordination. This appears borne out by the spectra and kinetic behavior

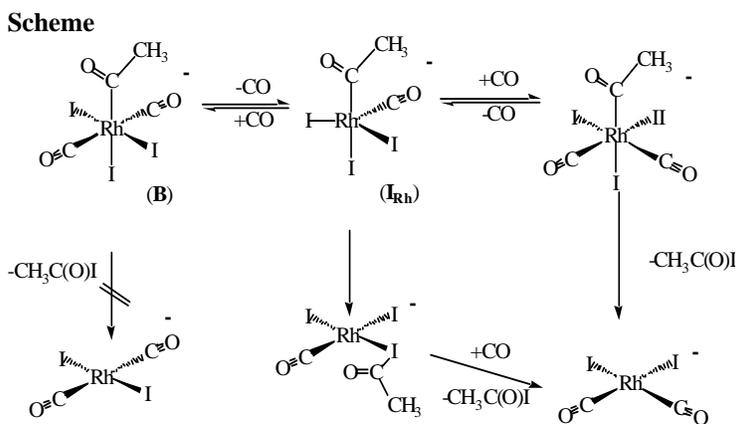
of reactive intermediates generated by flash photolysis of $\text{RC(O)Co(CO)}_3\text{L}$ ($\text{R} = \text{CH}_3, \text{CD}_3, \text{or Et}$; $\text{L} = \text{PPh}_3 \text{ or P}^n\text{Bu}_3$) in several solvents.

Graduate student Jon Marhenke investigated related intermediates generated from the phosphine substituted dimers $\text{Co}_2\text{L}_2(\text{CO})_6$ (**D**) that are precursors of cobalt hydroformylation catalysts (JM Ph.D. dissertation 2002). His goal was to map the essential reactivities of mononuclear radicals such as $\text{Co(CO)}_3\text{L}$ (**R**) as well as "unsaturated" $\text{Co}_2\text{L}_2(\text{CO})_5$ dinuclear complexes (**D_{CO}**) formed by CO labilization, both of which may be intermediates in the catalysis mixtures. **D_{CO}** was found to be reactive toward CO ($k_{\text{CO}} = 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in $25^\circ \text{ C}_6\text{D}_6$) and toward L ($k_{\text{L}} = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). Both rates proved relatively solvent independent, suggesting that the empty coordination site may be stabilized by a semi-bridging carbonyl. **R** could be trapped by chlorocarbons to give $\text{ClCo(CO)}_3\text{L}$ ($k \sim 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ with DCE), but in the absence of such traps, it undergoes facile ligand substitution with CO ($10^5 \text{ M}^{-1} \text{ s}^{-1}$) and with L ($10^6 \text{ M}^{-1} \text{ s}^{-1}$). Reaction of **R** with H_2 was not competitive; however, we plan to probe this under CO/ H_2 mixtures at pressures and T more closely approximating those for operating catalysts.

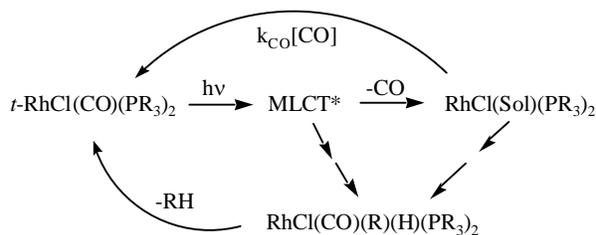
Visiting researcher Verena Mertens (U. Münster) carried out a similar investigation for the analogous reactions of $\text{Mn(CO)}_4(\text{C(O)R})$ intermediates (**I_{Mn}**) generated from flash photolysis of the manganese pentacarbonyl models $\text{Mn(CO)}_5(\text{C(O)R})$ ($\text{R} = \text{CH}_3 \text{ or } \text{CD}_3$) (IC 2002). As seen for the cobalt complexes, she found negligible isotope effect on the rate of MeMn(CO)_5 (**M_{Mn}**) formation, supporting an earlier conclusion that agostic intermediates have little impact on the reaction dynamics of **I_{Mn}**. The ΔH_m^\ddagger value for the **M_{Mn}** to **I_{Mn}** methyl migration reaction is higher (64 kJ mol^{-1}) in THF, where **I_{Mn}** was concluded to be the solvento complex $\text{Mn(CO)}_4(\text{THF})(\text{C(O)R})$, than in cyclohexane (35 kJ mol^{-1}), where the chelated species $\text{Mn(CO)}_4(\eta^2\text{-C(O)R})$ predominates.

Intermediates relevant to alcohol carbonylations by Rh and Ir complexes. Studies by Marhenke, undergraduate Veronica Reyes and visiting researcher Maurizio Volpe (U. Palermo) probed rhodium carbonyl iodide complexes and a related iridium system that are catalysts for methanol carbonylation to acetic acid. The crucial C-C bond formation step involves the migratory insertion of CO into a M-R bond to give metal acyls such as $\text{Rh(CO)(L)}_2\text{I}_2(\text{C(O)R})^-$ ($\text{L} = \text{solvent, CO or I}^-$), some of which have been characterized by NMR techniques. We used stopped flow mixing to prepare $[\text{Rh(CO)}_2\text{I}_2(\text{C(O)CH}_3)]^-$ (**B**) and TRIR techniques to

study the transient intermediates. The stopped-flow mixing method also provides the opportunity to study subsequent thermal reactions of the species generated. **B** underwent both thermal and photochemical elimination of $\text{CH}_3\text{C(O)I}$ to give *cis*- $\text{Rh(CO)}_2\text{I}_2^-$. These studies indicate that CO labilization to give the 5-coordinated species **I_{Rh}** is necessary before reductive elimination



Photocatalytic C-H activation by Rh(I) phosphine complexes: The Rh(I) complexes *trans*-RhCl(CO)L₂ (L = PPh₃ (**I**), P(*p*-tolyl)₃ (**II**) or PMe₃ (**III**)) are precursors in the photocatalytic activation of hydrocarbons. Ps and ns time-resolved TRO and ns TRIR spectral studies showed that photoexcitation leads to CO labilization to form the solvated complexes RhCl(Sol)L₂ (**A_i**). The ps studies demonstrate that an initial excited state is formed promptly (< 30 ps) and decays to **A_i** with lifetimes ranging from 40 - 560 ps depending upon L and the medium (*Inorg. Chem.* 2001, 40, 1466). Second order rate constants (k_{CO}) for reaction of the **A_i** with CO were determined and these depend on the nature of L and the solvent, the slowest rate being for **A_I** in tetrahydrofuran ($k_{\text{CO}} = 7.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$), the fastest being for **A_{III}** in dichloromethane ($1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Each **A_i** also undergoes competitive unimolecular reaction with solvent to form long lived transients with TRIR properties suggesting that these to be Rh(III) products. A fraction of the oxidative addition could not be quenched, so the short-lived MLCT state appears to participate directly in C-H activation.



DOE Interest

Elucidating the fundamental mechanisms of catalytic reactions allows for the design of selective chemical transformations that are more energy efficient and environmentally friendly.

Future Plans

We are directing our attention to three new projects concerned with mechanistic evaluation of other catalytic transformations of small molecule substrates.

Metal-based radical intermediates. The target is to generate certain metal-based organometallic radicals and to interrogate quantitative reactivities using time-resolved spectroscopy. Of particular interest are metal acyl radicals proposed as intermediates in a ethylene hydrocarboxylation catalyst based on molybdenum carbonyls with alkyl iodides as promoters.

Reactions of free and coordinated NO_x. Our goal is concerned with the quantitative reaction chemistry of NO_x species and the metal complexes LM-NO_x (L = polydentate ligand) with various substrates (**S**) (*JACS* 2002). Of particular interest are mechanisms by which the metal promotes oxygen atom transfer from coordinated NO_x to various reductants. We will couple this with NO autoxidation and probe the viability of atom-economic dioxygen activation toward selective oxidation mediated by iron porphyrins and other metal centers.

Halogen/oxide metathesis reactions This project is designed to probe reactions of halocarbons with simple MO_x models, to elucidate mechanisms defining the rates and efficiencies of the MO_x/halocarbon reactions. Characterizing such mechanisms may contribute to understanding the X/O metathesis chemistry used as a key step in approaches to hydrocarbon partial oxidation (Zhou et al *Chem. Commun.* 2003, 2294; Lorkovic' et al *Chem. Commun.*, 2004, in press) and analogous processes such as the metal oxide catalyzed halocarbon transformations of potential interest with regard to environmental remediation.

Recent Publications

Time Resolved Spectroscopic Studies Relevant to Reactive Intermediates in Homogeneous Catalysis. The Migratory Insertion Reaction, P. C. Ford, S. M. Massick *Coord. Chem. Rev.* 2002, 226, 39-49

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Reactions of Nitrogen Oxides with Heme Models. Characterization of $\text{Fe}(\text{TPP})(\text{NO}_2)$ as an Unstable Intermediate, Mark D. Lim, I. M. Lorkovic, K. Wedeking, A. W. Zanella, C. F. Works, S. M. Massick, P. C. Ford, *J. Amer. Chem. Soc.* 2002, 124, 9737-9743.

Activation parameters for reactive intermediates relevant to carbonylation catalysts based on phosphine modified cobalt carbonyls. S. M. Massick, T. Büttner, P. C. Ford *Inorg. Chem.* 2003, 42, 575-580.

Rhodium catalyzed reduction of nitroaromatic compounds under water gas shift conditions. M. M. Mdleleni, R. G. Rinker, P. C. Ford, (invited article) *J. Molecular Catalysis A, Chemical*, 2003, 204: 125-131

Activation parameters in flash photolysis studies of $\text{Mo}(\text{CO})_6$, C. Kayran, M. Richards, P. C. Ford, *Inorg. Chem. Acta* 2004, 357, 143-148

Free Radical Chemistry of Energy Utilization: Homolytic Properties of Reactive Intermediates in Catalyst Model Systems

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Students: Thomas A. Bowden

Collaborators: Thomas Bitterwolf, Wendy Shaw, Ed Rosenberg, Morris Bullock, Michel Dupuis, Donald M. Camaioni, M.S. Alnajjar, Jerome Birnbaum, John C. Linehan

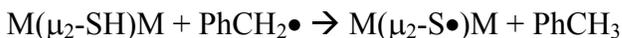
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Goal

Develop quantitative experimental and theoretical measures of homolytic bond strengths and free radical reactivity of active site models of HDS, hydrogenation and thermal hydrocarbon resource conversion pathways. Develop quantitative kinetic, thermochemical, and theoretical descriptions of catalytic organic/organometallic free radical transformations in conversion of hydrocarbon resources to fuels.

Recent Progress

Homolytic Properties of Activated S-H Groups. S-H bond strengths in $\text{CpMo}(\mu_2\text{-SH})_2(\mu_2\text{-S})_2\text{MoCp}$ (**1**) and $(\text{CO})_3\text{Fe}(\mu_2\text{-SH})\text{Fe}(\text{CO})_3$ (**2**) structures were calculated to be 73 and 72 kcal/mol, considerably weaker than conventional RS-H bonds, which vary from 91.2 kcal/mol (H_2S) to 2-mercaptanaphthalene (79 kcal/mol). The activated bonds have been demonstrated to be 100 to 1000-fold more reactive to carbon-centered free radicals than conventional thiols:



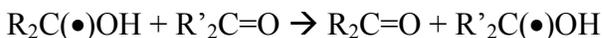
The radical $\text{CpMo}(\mu_2\text{-SH})_2(\mu_2\text{-S}\bullet)(\mu_2\text{-S})_2\text{MoCp}$, (**3**), exhibits the unique properties of a *persistent free radical*, undergoing slow self-reaction, and selectively forming cross-termination products in the presence of a *reactive* radical such as benzyl, to form the benzyl-**3** cross-product to the exclusion of self-reaction of **3**: the dimer of **3** forms a disulfide with an S-S bond strength of only 33 kcal/mol (cf. 47 kcal/mol PhS-SPh). Appending a CpCo group to **1** above to form $\text{CpMo}(\text{CoCp})(\mu_2\text{-SH})_2(\mu_2\text{-S})_2\text{MoCp}$ leads to the remarkable reduction in S-H bond strength to only 38 kcal/mol, thus defining the final (but not rate-determining) activation step in cleavage of strong C-S and S-H bonds, key to HDS and hydrogen activation.

Homolytic Properties of embedded $\mu_2\text{-H}$ in Os-H-Os structures (ref. 3) Kinetic studies of the free radical reactivity of Os-($\mu_2\text{-H}$)-Os HDN model systems in hydrogen abstraction by benzyl radical revealed that the embedded $\mu_2\text{-H}$ is reduced in reactivity by

only a factor of ca. 10 from terminal Os-H hydrides, e.g., the μ_2 -H hydrogen remains readily accessible.

Characterizing Weak π -interactions Between Aryl groups and W and Mo Cationic Centers of Hydrogenation Catalysts. (ref. 4). High level electronic structure calculations were used to characterize weak bonding interactions between aryl rings and W and Mo centers, leading to detectable rehybridization and structural modification of the complexing π -systems. (Collaboration with M. Bullock of BNL).

Theoretical and Kinetic ESR Studies of Catalysis of Electron transfer/proton transfer. New temperature-dependent ESR kinetics and high-level ab initio theoretical examination of H atom transfer from ketyl radicals to ketone acceptors, including theoretical treatment of solvation, have allowed the prediction of free energies of reaction of ketyl radicals leading to hydrogen transfer to acceptor molecules:



Extension of theoretical solvation models allows the overall prediction of the temperature dependence of the novel proton transfer/electron reaction, including the role of a preequilibrium formation of a solvated hydrogen bonded complex $R_2C(\bullet)OH \cdots OC_2R'$.

Theoretical Studies of C-H bond strengths in Complex Organic structures. (ref. 6) New C-H bond strengths were determined for an extended series of C-H bonds with complex aryl substituents were determined that quantitatively defined the combined steric and electronic effects of substituents in petroleum-related structures. Advanced electronic structure calculations were employed to validate experiment and theory for the complex systems.

Kinetics of new Single Step removal of S atom from Thiiranes by tributylstannyl radical. (ref. 2) New kinetics for removal of sulfur atom from thiiranes by $Bu_3Sn\bullet$ to form olefins were determined. The anchimeric effect of stabilization of a carbon radical center by the thiirane ring was explored, together with the theoretical potential surface for rearrangement of the thiiranylmethyl radical.

DOE Interest

DOE interest lies in the objective of defining the molecular basis for controlled modification of molecular catalyst properties in important processes such as clean fuels production through understanding of C-S bond cleavage, hydrogenation, hydrogen activation and related technologies.

Future Plans

Theoretical Efforts will continue to define electronic characteristics of bonding in clusters leading to activation of S-H, M-H, S-C and related bonds important in hydrogen activation and transfer in catalytic processes. The reactivity of MoS clusters, with reactive carbon centered free radicals will be carried out to define formation and cleavage

of C-S bonds. The S-H bond in catalyst systems will be characterized using solid state NMR approaches (^1H CRAMPS solid state NMR) and kinetic methods for measuring detailed S-H reactivity. Bond strengths in catalytic systems involving M-H, C-H, S-H will be determined to validate parallel theoretical bonding properties. Potential surfaces for H_2 activation and hydrogenation are being determined for MoS, MoH and WH systems. Accurate solvation energies by improved theoretical methods and application in H^+ transfer/ e^- transfer pathways.

Publications (2002-present)

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(2) Franz, J. A.; Shaw, W. J.; Lamb, C. N.; Autrey, T.; Kolwaite, D. S.; Camaioni, D. M.; Alnajjar, M. S.; "Absolute Rate Constants for Reactions of Tributylstannyl Radicals with Bromoalkanes, Episulfides, and ω -Halomethyl-Episulfides, -Cyclopropanes, and -Oxiranes: New Rate Expressions for Sulfur and Bromine Atom Abstraction" *J. Org. Chem.* **2004**; 69(4); 1020-1027.

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Combined TEM and XAFS analysis of 3D structure of small (<100 atom) gold nanoparticles

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Goal

To obtain local metal-metal and metal-ligand bonding geometry in monodisperse gold nanoparticles.

Recent progress

We focused on thiol-stabilized gold nanoparticles that have been predicted theoretically to adopt regular polyhedral shapes (cuboctahedral, icosahedral, or dodecahedral) depending on their size. In this size scale (<100 atoms) the particles still show discrete properties of molecular clusters (e.g., HOMO-LUMO band gap detectable by UV-visible light spectroscopy) and significant size effects (decrease in the bond length compared to the bulk metal gold and enhanced bond length disorder). This makes them an attractive object for XAFS investigation because XAFS is a local, short range order probe. Pair correlations between the absorbing atom and its nearest neighbors can be measured within ca. 8 Å distance range from the center. Therefore, small nanoparticle that have diameter of ca. 1nm are ideal for XAFS investigation. At the same time, these particles are large enough to be probed by the electron microscopy methods. Among the electron microscopy techniques that we applied are: scanning transmission electron microscopy (STEM), high-angle annular dark-field (HAADF), high resolution electron microscopy (HREM), electron microdiffraction. The combination of these methods allows us to probe short (using XAFS) and long range order (using electron microdiffraction) structures in clusters of a large variety of sizes and shapes. The description of our electron microscopy results can be found in our Abstract "Nanoscale Materials for Catalysis". Here we focus on the progress achieved in XAFS analysis of small metal clusters.

We developed analytical protocol that allows us to discriminate between the several polyhedral shapes (Fig. 1) of the clusters by comparing the first nearest neighbor coordination numbers characteristic for these shapes against the experimental, model-independent values.

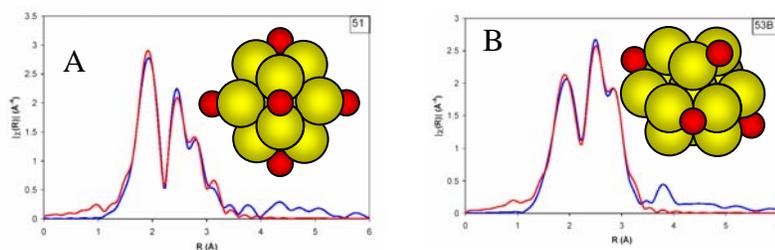


Figure 1. Icosahedral (top) and cuboctahedral (bottom) models of atomic packing in $\text{Au}_{13}[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_6$. Shown also are EXAFS data and FEFF fits for the sample A (with band gap) and B (without the band gap) that were best fit by using the 13-atom icosahedral and cuboctahedral models, respectively.

To compare coordination numbers measured experimentally v. theoretical predictions for different polyhedral shapes we generated atomic coordinates for various cluster shapes and morphologies (for supported clusters). Figure 2 shows the model behavior of 1NN Au-Au coordination number as a function of number of atoms in the cluster (for a cluster of a certain topology, the number of atoms follows a unique sequence of “magic numbers” as cluster size increases).

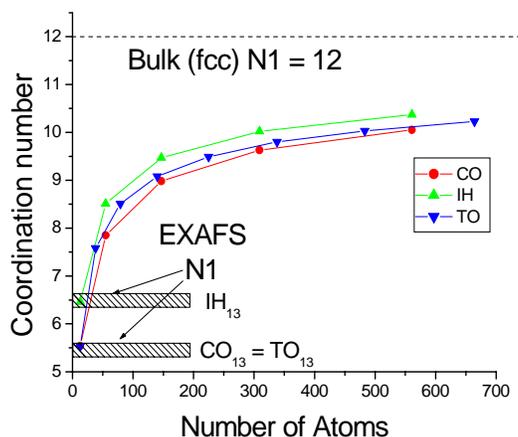


Figure 2. Simulated sequences of the first nearest neighbor Au-Au coordination numbers as functions of “magic numbers” corresponding to the cuboctahedral (CO), icosahedral (IH) and truncated octahedral (TO) models. Small particles show dramatic difference in

the coordination numbers between the IH and CO (or TO) models: 6.5 and 5.5, respectively.

By comparing experimental results for 1NN Au-Au coordination number with different model predictions (Fig. 2), we can make an accurate determination of both the cluster size and cluster shape (Table I). This method is particularly sensitive for small metal clusters, less than 200-300 atoms in size, because the curves (Fig. 2) level off for larger clusters.

EXAFS	Sample A	Theory (IH)	Sample B	Theory (CO)
N(Au-S)	0.94(9)	0.923	0.94(14)	0.923
N ₁ (Au-Au)	1.98(32)	1.846		
N ₂ (Au-Au)	4.48(47)	4.614		
N(Au-Au)	6.46(47)	6.46	5.90(50)	5.54

Table I. Experiment v. theory: Results for the 13 atom Au-thiol clusters obtained by XAFS. N1 and N2 describe the icosahedrally split coordination numbers in two 1NN subshells (Fig. 3).

Icosahedral and cuboctahedral clusters can also be distinguished by XAFS due to the marked bond length splitting due to icosahedral strain, that is absent in fcc clusters (cuboctahedral or truncated octahedral). This splitting is demonstrated in Fig. 3.

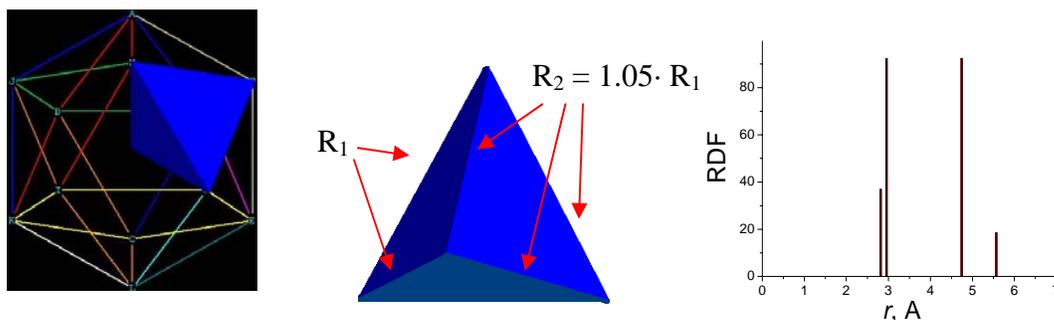


Figure 3. Schematic of the icosahedron that is made of 20 face sharing pyramids. Each pyramid is symmetrically distorted so that the distances R_2 are ca. 5% longer than R_1 . The plot in the right is the calculated radial distribution function for the icosahedral structure that demonstrates two subshells in the first nearest neighbor coordination shells.

Another unique advantage of analyzing small clusters by XAFS is in its enhanced sensitivity to the metal-ligand bonding geometry. Indeed, for systems with relatively large surface-to-volume ratio (e.g., in a 13 atom fcc cluster, this ratio is 92%, for 55 – 76%, for 147 – 63% etc.), the local environment of surface atoms can be analyzed with

unprecedented detail. The coordination numbers of Au-S (Table I) that we obtained by XAFS in the two types of clusters, icosahedral and cuboctahedral, were very similar to each other, within their uncertainties, and equal to ca. 0.94. Combined with the knowledge of the total number of S per cluster (6), this experimental result indicates that S atom is located above the edge connecting two Au atoms (therefore, the total number of Au-S bonds per 13 atom cluster is 12, and the model Au-S coordination number is $N_{\text{Au-S}} = 0.923$, in agreement with our XAFS result). The alternative models of Au-S bonding geometry consider S atom being bound to one or three Au atoms (Fig. 4). The coordination numbers in these cases are either 0.46 or 1.4, respectively, i.e., outside of the experimental error bars.

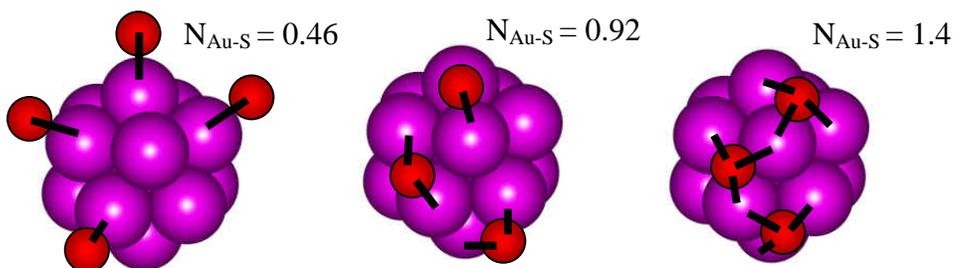


Figure 4. Different models for Au-S bonding geometry.

DOE interest

The model systems described above have the advantages of being both well-defined and easily characterizable by a variety of physical and spectroscopic techniques, while embedding many of the structural and electronic properties relevant to catalytic systems. Nanoscale catalysts, though, are generally used in complex supported forms and are, as a result, harder to characterize at the same level of detail. To address this deficiency we have begun to explore systems of nanoparticles of direct interest to energy technologies. Very small metal clusters can exhibit patterns of reactivity and catalytic activity that are dramatically distinct, and sometimes completely opposite, than behaviors seen with larger clusters. It therefore remains a significant need in research to fundamentally understand and predict the local structure and stability of catalytic materials that can be specifically tailored by design and optimized for an application in technology, goals that remain beyond the reach of our current understandings. Our studies will also provide critical experimental tests for theories developed to describe the nature of the structures and dynamical properties exhibited by mono- and hetero-metallic nanoscale assemblies and the chemical properties they embed.

Future plans

Our cluster analysis methods outlined here will be further tested and improved by applying them to larger clusters: thiol-protected gold clusters as well as those made of other metals (e.g., Pt, Ru, Ag, Pd), as well as nanoalloys). We will use the combination of electron microscopy and UV-visible light spectroscopy techniques to characterize size

distribution of the particles. We will integrate future TEM-XAFS data analysis with theoretical calculations to help interpret and accelerate identification of cluster bonding motifs, possible metastable structures, and determining electronic properties and reactivity of relevant clusters. Namely, we will calculate/simulate realistic nanometer-sized, metallic clusters (i.e., those equivalent to experiment) by electronic-structure and molecular-dynamic techniques to address the issues of complex geometries (cluster size and corresponding thermodynamically- or kinetically-stabilized shapes and atomic arrangement), of shape evolution (kinetics), as well as local bonding effects that determine reactivity. In the more distant future, we will investigate the effect of supports on the topology and structure (and thereby properties) of clusters, as well as a complete study of formation, stability, and dynamics of metallic clusters.

Representative publications

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Model Studies of Reactions in Environmental Catalysis on Nanophase Materials

Postdocs: †Biener, Juergen, †Chan, A.S.Y; Kang, Dae-Hyuk; †Kretschmar, Ilona

Graduate Students: Deng, Xingyi; Diener, L.J.; Quek, S.-Y

Collaborators: Fleming, Beate; Hoffmann, Roald; Kaxiras, E.; Nart, F.

†Partial DOE support only

Goal

To study elementary steps important in environmental catalysis on well-defined metal oxide nanostructures and thin films for the purposes of identifying of reaction sites for these important processes.

Recent Progress

In our recent work we have focused on two areas: (1) the synthesis and characterization of MoO_3 and TiO_2 nanostructures; and, (2) reactive studies of NO_x and possible intermediates in hydrocarbon-assisted NO_x reduction on oxide thin-films grown on $\text{Mo}(110)$. The metal oxide nanostructures will be used as model systems to study site-selective reactivity in NO_x reduction and hydrocarbon oxidation.

Synthesis of Metal Oxide Nanostructures. We have successfully developed methods for synthesizing nanocrystalline MoO_3 and TiO_2 using the $\text{Au}(111)$ -“herringbone” surface as a template (Figures 1). We have completed detailed studies of the MoO_3 nanostructures, thus far. Detailed investigations of the TiO_2 are currently underway.

The MoO_3 nanostructures are crystalline and one layer high as determined using both scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Furthermore, the MoO_3 forms a $c(4 \times 2)$ superlattice on the Au and lifts the herringbone reconstruction of the Au under the oxide nanocrystals. The Mo is ~94% Mo^{6+} , based on the Mo(3d) binding energies measured using X-ray photoelectron spectroscopy (XPS). The remaining Mo is in the +5 oxidation state.

We are able to thermally reduce the MoO_3 to a 1:1 mixture of Mo^{6+} : Mo^{5+} with no other oxidation states detected in XPS. Shear planes develop in order to accommodate the Mo^{5+} . We are currently in the process of studying the chemical behavior of these materials.



Figure 1: STM image of MoO_3 nanostructures grown on $\text{Au}(111)$.

We are also collaborating on with Prof. E. Kaxiras (Harvard, Physics) and his student, Ms. S.-Y. Quek, in order to understand the electronic properties of these metal oxide nanostructure using density functional theory (DFT). We are able to determine the atomic-scale structure of these oxides and to simulate our STM images using DFT.

Reactive Studies of NO_x Reduction. We have performed detailed studies of NO and NO₂ reduction and investigated possible intermediates important in hydrocarbon-assisted NO_x reduction on thin-film oxides and chemisorbed oxygen overlayers grown on Mo(110). Our work has shown that the low oxidation states present on these materials favors oxygen loss to the surface. Oxygen release from NO₂ and nitromethane, a postulated intermediate in hydrocarbon-assisted reduction of NO_x, is rapid on these materials, based on results of infrared and temperature programmed reaction spectroscopies.

DOE Interest

The reduction of NO_x and the oxidation of hydrocarbons are two of the most important catalytic processes for clean and efficient energy usage. Our work is significant in that we are able to study these reactions on a molecular level. Our recent synthesis of metal oxide nanostructures will enable us to image reactions that occur at specific types of reactive centers in order to better model catalytic processes for NO_x reduction and hydrocarbon oxidation.

Future Plans

Nanostructure synthesis and growth. We will devise methods for the synthesizing nanostructures of Mo and Ti oxides with specific oxidation states present. A combination of STM, XPS, and vibrational (infrared reflection and high resolution electron energy loss) spectroscopy will be used to fully characterize these materials.

Reactive studies. We plan to investigate elementary reactions important in NO_x reduction and hydrocarbon oxidation over the Mo_xO_y and Ti_xO_y nanostructures. Our goal will be to determine if there are specific types of sites that promote these elementary steps. STM will be used to image reactive centers and temperature programmed reaction will be used to measure product distributions.

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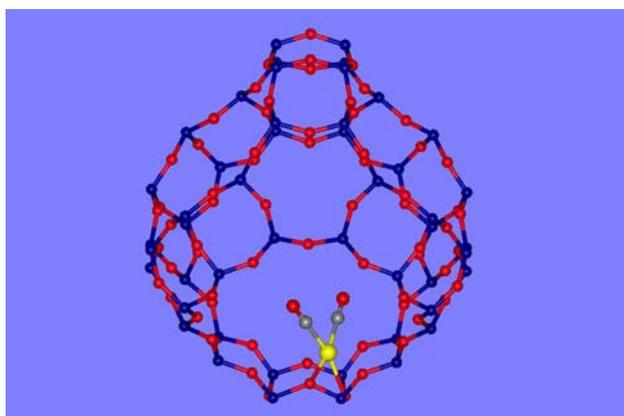
SPECTROSCOPY, THEORY, AND IMAGING OF NANOCATALYSTS ON CRYSTALLINE SUPPORTS: REPRESENTATION OF METAL-SUPPORT-ADSORBATE COMBINATIONS AS MOLECULAR ANALOGUES

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Our group investigated the synthesis and characterization of supported metal complexes and clusters with nearly uniform structures, elucidating the bonding of the metals to oxide and zeolite supports, understanding of supports and adsorbed intermediates in catalytic reactions as mutually interactive ligands, and developing in-situ methods for investigation of the effects of these ligands on working catalysts. The work is placing surface catalysis on a foundation that begins to rival that underlying molecular catalysis in solution.

Using precursor metal complexes with reactive ligands such as $\text{Au}(\text{CH}_3)_2(\text{acac})$, $\text{Rh}(\text{CO})_2(\text{acac})$, and $\text{HRe}(\text{CO})_5$, we have prepared structurally simple supported metal complexes and determined their structures in detail, exemplified by that of the following dealuminated Y zeolite-supported rhodium dicarbonyl, a square-planar cationic complex:

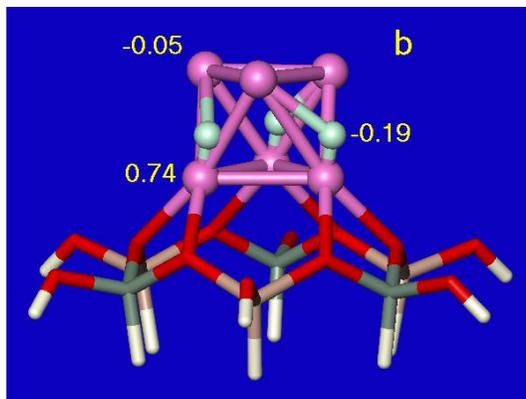


We characterized the complex by IR and EXAFS spectroscopies and density functional theory, with the results being in good agreement with each other and demonstrating the strong chemical bonding between the Rh atom and oxygen atoms of the support surface. The data identify crystallographically specific sites at which the complex is bonded; the Rh is bonded at cation sites (near Al ions) in the zeolite, and correspondingly the theory shows the charge on the Rh atom to be about +0.54 electronic charges, similar to values characterizing Rh atoms in analogous compounds and explaining the Rh–O EXAFS distance of about 2.1 Å, which essentially matches the crystallographic Rh–O distances in the analogous compounds. The supported complex is characterized by extremely sharp ν_{CO} IR bands, consistent with its nearly unique structure. We infer that almost all the rhodium dicarbonyls in the zeolite are present in crystallographically equivalent sites. Similarly, $\text{Re}(\text{CO})_3$ complexes have been formed in the zeolite; the specific bonding sites in the dealuminated Y zeolite have been inferred from IR and EXAFS data.

These two supported metal complexes are important in being perhaps the most uniform and best-defined structures incorporating metals on supports. They demonstrate and quantify the bonding of cationic metal complexes to the supports. They are representative of an important and growing class of catalyst, exemplified by the supported metallocenes used for commercial olefin polymerization.

Our group also worked to improve methods of preparation of nearly uniform metal clusters and to determine their structures and catalytic properties. Working with the TEM expert Larry Allard, we have obtained increasing strong evidence of the near uniformity of the clusters, illustrated in the figure below for Os_5C carbonyl clusters on MgO . The TEM results are important in demonstrating how ideally suited these samples are to exact structural characterization. Similar micrographs have been obtained for the decarbonylated Os_5C clusters.

Similarly, decarbonylation of precursor metal carbonyls on supports has given high yields of Ir₄, Ir₆, and Rh₆. EXAFS spectroscopy shows that the metal–support oxygen distances in these and essentially all oxide- and zeolite-supported group 8 metals are characterized by metal–oxygen distances of about 2.1 Å; this is a cation–oxygen bonding distance, now well confirmed by density functional theory for several of our supported metal complexes. The theory characterizing Rh₆ supported on zeolite X, shown below,



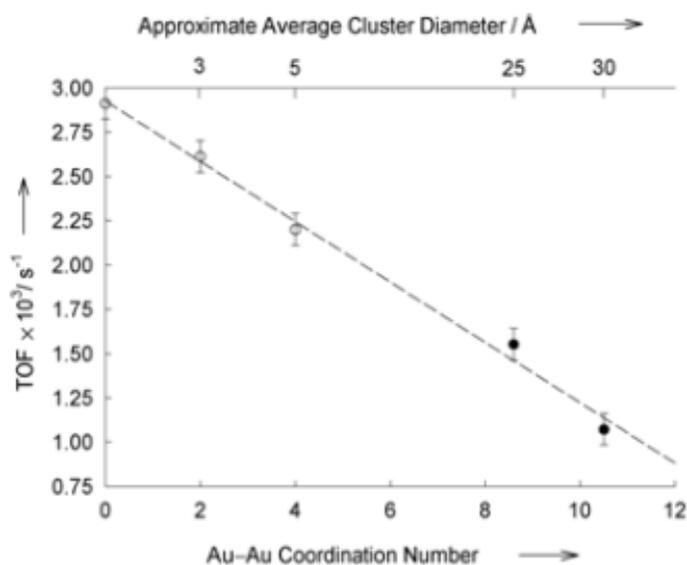
shows that the Rh atoms at the interface with the support are positively charged (with about +0.74 electronic charge per atom, although the Rh atoms farther removed from the support bear hardly any charge), which explains the metal–oxygen distance (the theoretical and experimental values agree, being about 2.1 Å) and shows that the metals in supported metal clusters are chemically bonded to the supports through cations at the interface. This result explains the relatively high stability of highly dispersed oxide-supported metals and raises some compelling questions: how does the reactivity of the charged cluster differ from that of an uncharged cluster (if it exists), and what are the properties of the structure that would exist if the top 3 Rh atoms were removed from the structure shown above; would it be a stable, cationic raft cluster?

The combination of theory and EXAFS spectroscopy characterizing supported metal clusters also shows that they are not ligand-free; rather, hydrogen (from support OH groups or water) oxidizes the clusters (this accounts for the positive charges on the interface atoms) and decorates them with hydride ligands, shown in the above figure. The charged cluster with hydride ligands is 370 kJ/(mol of Rh₆) more stable than the bare cluster on the hydroxylated zeolite. The hydride ligands expand the metal frame, extending the metal–metal distances by about 0.2 Å relative to those of the free clusters, accounting for the EXAFS data for a large family of supported metals. These results explain the chemistry of hydrogen spillover.

We have oxidized Rh₆ and Ir₆ clusters on a support, apparently making the first stable metal oxide clusters of these noble metals.

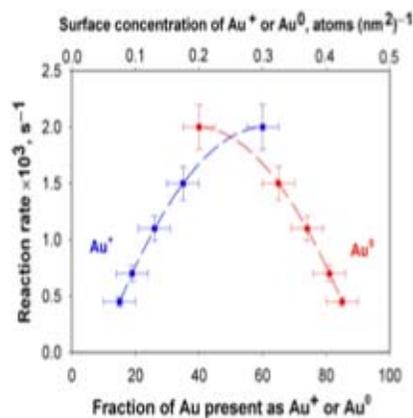
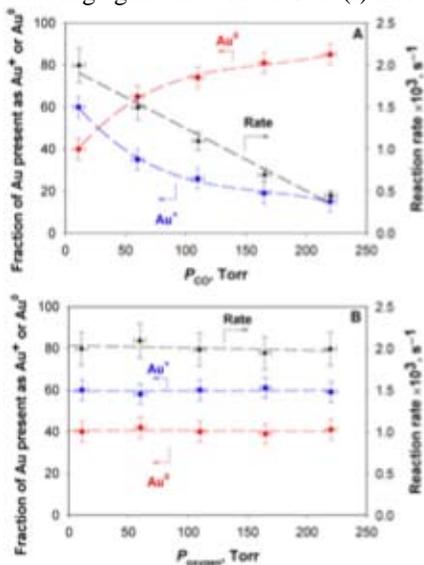
There has been a high level of excitement generated by recent discoveries of high activities of highly dispersed supported gold catalysts for reactions such as CO oxidation. We have emphasized work on these catalysts in our DOE project and plan more gold work in the proposed continuation. Most interpretations of the activity of gold have focused on effects of cluster size. However, we found physical evidence (from XANES of a working catalyst) for the presence of cationic gold (along with zerovalent gold) in a CO oxidation catalyst. We prepared a set of samples beginning with a mononuclear cationic dimethyl gold complex on MgO, which is well characterized by IR and EXAFS spectroscopies.

This and a family of samples formed from it by gentle reduction and sintering of the gold were used as catalysts for ethylene hydrogenation, with the results shown below:



The data (EXAFS, IR, and XANES of the working catalysts)¹⁷ identify site-isolated cationic gold complexes as the catalytically active species; there is no evidence for activity of the reduced gold clusters, in contrast to the published interpretations for this reaction catalyzed by supported gold. The results are confirmed by TPR/TPO data. The results raise a question: how general is the importance of cations in catalysis by gold and other noble metals?

Results demonstrating the relationship between the activity of MgO-supported gold catalyst and the amounts of cationic and zerovalent gold in it are shown below. Because the EXAFS data show that the average size of the gold clusters in each of these catalysts was essentially the same, any effect of this cluster size on the observed catalytic reaction rates was negligible, and the changes in catalytic activity were the result of changes in the oxidation state of gold. The data show that higher concentrations of cationic gold corresponding to lower partial pressures of CO in the reacting mixture lead to higher catalytic activity. Because CO must be adsorbed to react on the catalyst, increasing CO partial pressures would be expected to give higher CO surface coverages and thus higher rates of CO oxidation—but the effect is evidently more than offset by reduction of the gold by CO and removal of catalytic sites. The data show that both Au(I) and Au(0) are present in the working catalysts; that their relative amounts depend on the composition of the reacting atmosphere; and that the catalytic sites incorporate Au(I). CO plays a dual role as a reactant and a reducing agent that converts Au(I) into Au(0), thereby diminishing the catalytic activity.



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Carbon-Hydrogen Bond Functionalization Catalyzed by Transition Metal Systems

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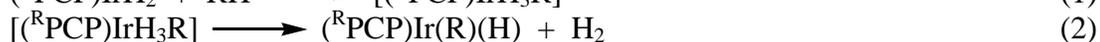
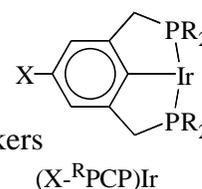
Goal

Development of new catalysts for the functionalization, particularly dehydrogenation, of alkanes and alkyl groups; elucidation of fundamental principles and factors controlling the catalytically relevant reactivity of transition metal complexes with small molecules.

Recent Progress

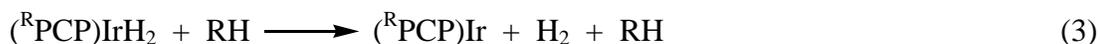
Recent work has focused on two major areas: (i) the dehydrogenation of alkanes and alkyl groups, including an elucidation of mechanism, the development of improved catalysts, and efforts to expand applications beyond alkanes; (ii) development of a fundamental understanding of the factors that govern the thermodynamics and kinetics of E-H bond activation by transition metal complexes.

*Acceptorless dehydrogenation catalyzed by "PCP" pincer-ligated iridium complexes.*¹⁻³ Under the auspices of this grant we previously developed the first system for the efficient solution-phase catalyzed dehydrogenation of alkanes that did not require the use of a sacrificial hydrogen-acceptor. The catalysts are based upon "PCP" pincer ligands. Theoretical (DFT) studies of this system by other workers led to the proposal that these catalysts operate via C-H addition to the dihydrides, i.e. via an associative mechanism (eqs 1-2), possibly involving Ir(V) intermediates.



associative (A or I_A) pathway, proceeding via Ir(V) (or non-classical transition states)

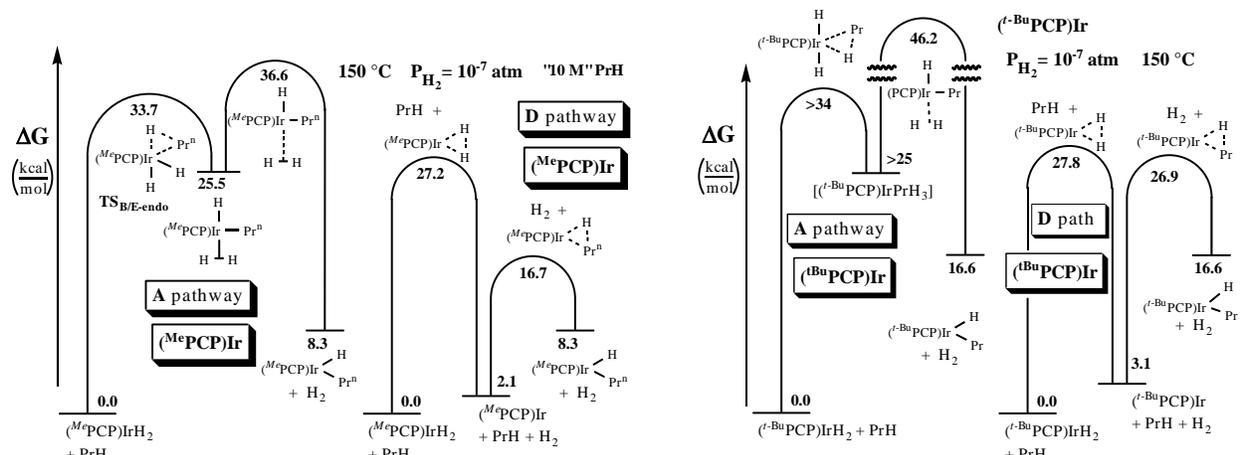
An alternative pathway (eqs 3-4), an Ir(I) mechanism, involves H₂ loss prior to C-H addition. Clearly these pathways are different at the most fundamental level; therefore distinguishing which one (or ones) is operative is critical to catalyst design.



dissociative (D) pathway, proceeding via an Ir(I)/Ir(III) couple

Our own DFT calculations confirm that the Ir(V) (**A**) pathway indeed has a lower energy barrier than the Ir(I) pathway. However it must be understood that acceptorless dehydrogenation is a highly endothermic process (ca. +24 – 32 kcal/mol). Therefore an equal (or greater) and ΔS term of opposite sign is required for the reaction to proceed. When this very large *entropic factor* is correctly incorporated into the catalytic cycle, mechanistic conclusions are strongly affected.

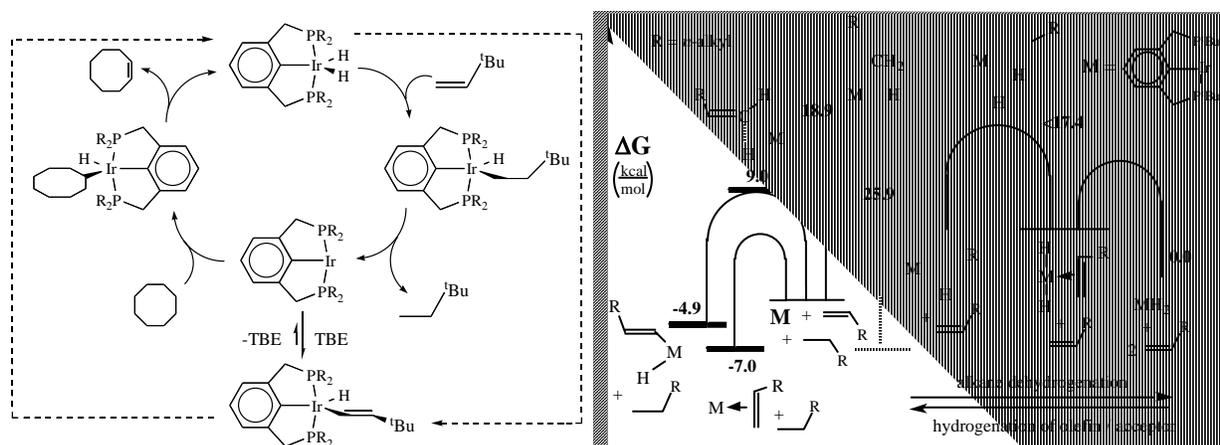
The Ir(V) (**A**) pathway requires a very unfavorable C-H addition (eq 1). This uphill step must be followed by loss of H_2 , which is also endothermic. The entropic “payback” is only realized after this full “free-energy-price” is paid in the course of the **A** pathway (Scheme 1). In contrast, the **D** path involves initial loss of H_2 , which requires a significant enthalpic price (calculated as ca. 28 kcal/mol for R = t-Bu). However, the entropic gain is then obtained and the following step, C-H addition to $(^R\text{PCP})\text{Ir}$, occurs with a lower barrier than the back reaction of H_2 under the reaction conditions. Accordingly calculations with the truncated $^{\text{Me}}\text{PCP}$ ligand reveal a significantly lower overall barrier for the **D** path (27.2 vs. 36.6 kcal/mol). When the full $^{\text{tBu}}\text{PCP}$ ligand is modeled, steric effects yield a *much* greater difference favoring the **D** path, (27.8 vs. ca. 46 kcal/mol). Experimental evidence in support of this conclusion derives from the fact that while $(^{\text{tBu}}\text{PCP})\text{IrH}_2$ undergoes facile H/D exchange with C_6D_6 , and slow exchange with *n*-octane, no H/D exchange is observed with C_6D_{12} even at 180 °C (i.e. the barrier to C-D addition is prohibitively high; but acceptorless dehydrogenation with cycloalkanes is permitted).



Scheme 1. Free-energy profiles for **D** and **A** pathways $R\text{-H} = \text{propane}$, 150 °C, $P(H_2) = 10^{-7} \text{ atm}$ and 10 mol/L alkane for the reaction of alkane with $(^{\text{Me}}\text{PCP})\text{IrH}_2$ (left) and $(^{\text{t-Bu}}\text{PCP})\text{IrH}_2$ (right).

Steps in the cycle subsequent to C-H addition are presumably the same as occur in the transfer-dehydrogenation system; these have been investigated within the context of that reaction.

Transfer-dehydrogenation.^{4,5} Our goal in the mechanistic study of transfer-dehydrogenation has been largely achieved: the elucidation of a quantitative energy profile for the entire catalytic cycle. Comparison with computational results will allow us to gauge the accuracy of individual reaction steps and calibrate for the purpose of comparison with proposed, structurally related catalysts. We have found that the resting states are the dihydride and the TBE vinyl C-H addition product for the COA/TBE system, and predominantly the π -bound α -olefin complex for the *n*-alkane/ α -olefin system.

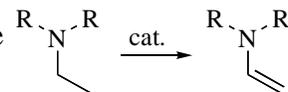


Scheme 2. Mechanism of COA/TBE transfer-dehydrogenation cycle (left); free-energy profile for *n*-alkane/ α -olefin couple (right), experimentally extrapolated from COA/TBE profile.

New catalysts. We have synthesized the electron-rich, *p*-methoxy substituted, analogues of the (R^{PCP})Ir catalyst, viz. (MeO-R^{PCP})IrH_n (R = *i*-Pr, *t*-Bu). These catalysts are more robust and generally more effective than the parent species. For example, acceptorless dehydrogenation of cyclodecane catalyzed by (MeO-^{*i*Pr}PCP)IrH_n has yielded 3000 turnovers – the highest value obtained to date for a solution phase dehydrogenation system.

Non-alkane substrates. The dehydrogenation of HCCH linkages of non-alkane substrates is being explored. We have had particular success so far with the following two substrates and, in particular, using the above-noted new catalyst, (MeO-^{*i*Pr}PCP)IrH_n :

(i) Dehydrogenation of tertiary amines.⁶ We have developed the first system for the conversion of tertiary amines to the corresponding enamines. Enamines are broadly useful organic synthons owing to their nucleophilic β -carbon. The pincer catalysts are especially effective in the dehydrogenation of aminoethyl groups, to give the unsubstituted vinyl amine; these are particularly reactive and difficult to synthesize via conventional routes. Accordingly we have made, in very good yield, several very fundamental enamines that have not been previously reported.



(ii) Dehydrogenation of (saturated) polyolefins.⁷ Introduction of double bonds into aliphatic polymers is an important reaction for the purposes of functionalization and cross-linking. Using (MeO-^{*i*Pr}PCP)IrH_n, we have achieved 11% “yield” (based on monomer units) and 100% yield based on NBE sacrificial acceptor, after 10 minutes at 150 °C.

Thermodynamic “selectivity” of C-H bond addition.⁸ Organometallic species hold great promise in the context of C-H bond activation in large part due to their extraordinary selectivity: a preference, in many cases, for activation of stronger C-H bonds.⁹ Computational studies have been conducted revealing that the origin of this selectivity is based on simple electronegativity factors.

N-H addition.¹⁰ In collaboration with the group of John Hartwig we have found that the (PCP)Ir unit is capable of adding N-H as well as C-H bonds. While N-H addition is of great importance in catalysis, this represents an unusual observable example of this apparently simple oxidative addition reaction. The PCP system allows comparison of the thermodynamics of N-H and C-H addition. Exchange with exogenous amine is facile, permitting substituent-effect studies and elucidation of the factors that govern thermodynamics and kinetics of this important reaction.

DOE Interest

The dehydrogenation of alkanes is a reaction of tremendous potential value in terms of economics and energy efficiency, opening potentially new routes to the synthesis of olefins ranging from high-value natural products to commodity chemicals produced on the largest scales. For example, α -olefins are produced in the order of 4×10^9 lb/year, currently via ethylene oligomerization – a process that is very circuitous, energy-inefficient, and unselective with respect to product chain-length.¹¹ Applications on an even larger scale than any currently practiced olefin syntheses can be envisaged. For example dehydrogenation of alkanes, followed by reactions such as dimerization or metathesis and then hydrogenation of the product, could be incorporated into cycles that, overall, effect the corresponding transformations of *alkanes* (e.g. dimerization or metathesis). Such reactions are of great interest in the context of petroleum reforming and the utilization of natural gas (which is currently converted indirectly into *n*-alkanes via Fischer-Tropsch chemistry).

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Toward an Understanding of Catalysis by Supported Metal Nanoclusters

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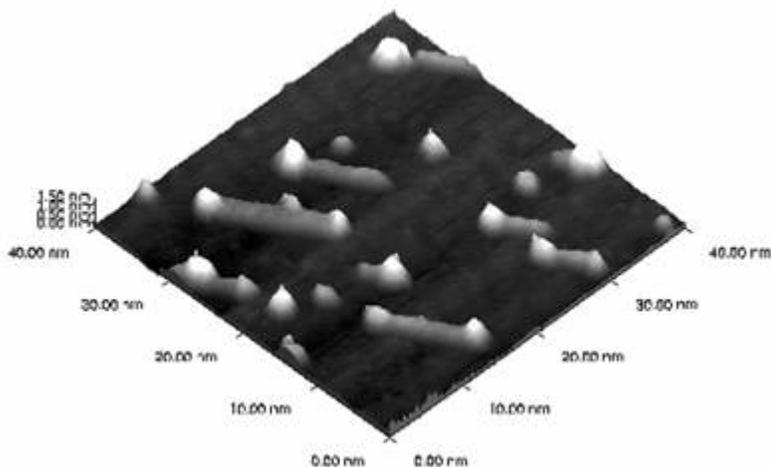
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Goal

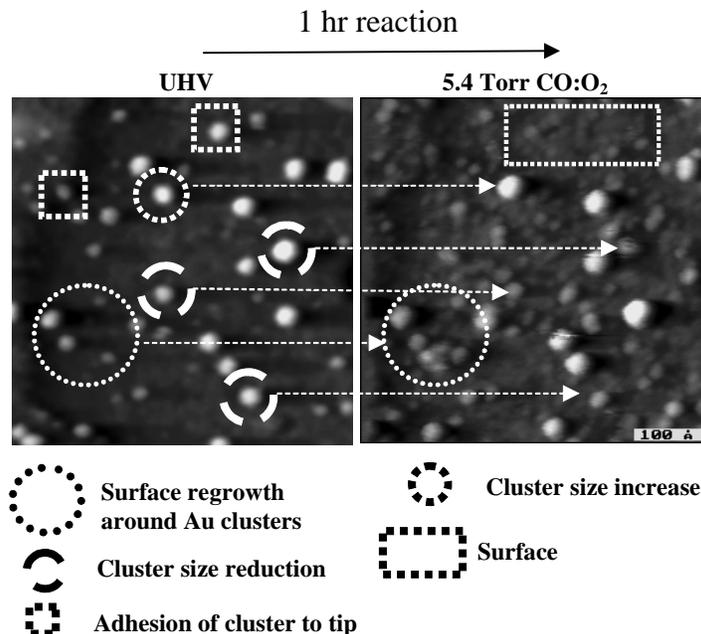
Develop an atomic-level understanding of catalysis by supported metal nanoclusters

Recent Progress

Synthesis of a Sinter Resistant Mixed Oxide Support for Au Nano-Clusters: In order to make highly active Au catalysts more stable, mixed oxide supports have been developed by substituting Ti atoms in a silica thin film network. Depending on the amount of Ti deposited, the titania-silica surface consists of either atomically implanted Ti atoms or TiO_x islands. After depositing Au onto these titania-silica surfaces (under both low and high Ti coverages), it is found that the Ti defects and TiO_x islands act as nucleation sites for Au cluster formation, leading to a marked increase in the cluster density compared to the Ti-free SiO₂ surface. Furthermore, the Au clusters stabilized by the TiO_x islands (figure below) do not sinter when exposed to reaction temperatures and pressures.



In Situ Characterization of Model Catalysts: Using scanning tunneling spectroscopy (STM) an experimental approach has been developed that allows a pre-selected area of the surface to be targeted and individual supported nanoparticles imaged over a reactive pressure range spanning twelve orders of magnitude (figure below). In conjunction with the STM studies, polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) has been used to study the CO + NO reaction over a Pd (111) single crystal surface as well as Pd clusters supported on a planar SiO₂ surface over the pressure range 10⁻⁶ – 240 mbar between 300 and 625 K. By combining in situ STM and PM-IRAS, the structural and spectroscopic details of supported metal clusters can be assessed under reaction conditions.



Identification of Defect Sites on Oxide Surfaces by Metastable Impact Electron Spectroscopy (MIES): Defect sites on SiO₂ and MgO have been identified and quantified using MIES and MIES of adsorbed Xe (MAX). Furthermore, it has been shown that CO and metal deposition are appropriate probes for estimating defect density on oxide surfaces.

Inelastic neutron scattering (INS) study of the surface species formed in situ on reacting propylene, H₂ and O₂ over Au/TiO₂: INS has been used to identify a hydro-peroxy species formed from reaction over a Au/TiO₂ catalyst at realistic conditions of: (i) H₂ with O₂; and (ii) propylene with H₂ and O₂. Identification of this species is a crucial step in detailing the reaction mechanism of these important selective oxidation reactions.

DOE Interest

New strategies for synthesizing sinter resistant catalysts by designing well-defined defect structures offer new possibilities for constructing nanostructured catalysts that are highly stable toward reaction conditions and thermal-induced sintering. This is a key step in the development of highly dispersed, size-limited catalysts for new catalytic applications. The development of in situ methods for characterizing the morphology of nanocatalysts and the

surface species formed during reaction are keys to the ultimate synthesis of practical commercial nanocatalysts.

Future Plans

The immediate objectives of this project are: (1) the mechanisms of nanocatalyst sintering and deactivation using in situ scanning tunneling microscopy, (2) the design of sinter-resistant supports for metal nanocatalysts; and (3) the surface intermediates formed during selective oxidation by noble metal nanocatalysts.

Mechanisms of Nanocatalyst Sintering and Deactivation: Future work will address the sintering kinetics of metal nanocatalysts using our custom designed in situ STM apparatus that allows imaging of planar model catalysts at pressures to 1 atm and temperatures to 1000K.

The Design of Sinter-Resistant Supports for Metal Nanocatalysts: Recent work using point defects of Ti in SiO₂ is being extended to Al defects in order to investigate the role of heteroatom point defects in stabilizing supported metal nanoclusters.

Surface Intermediates in Selective Oxidation by Noble Metal Nanocatalysts: PM-IRAS is currently being used to investigate vinyl acetate synthesis on mixed-metal Pd-Au clusters supported on silica. Ancillary experiments with HREELS, XPS, ISS, and UPS/MIES are addressing the nature of the active site for this important commercial selective oxidation reaction.

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Studies of Metal-Oxide and Oxide-Oxide Interactions in Ceria-Based Catalysts

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Goal

Understand the catalytic properties of ceria and ceria-supported metals for reactions important in automotive catalysis and energy-related problems.

Recent Progress

Ceria-supported metals have been shown to exhibit superior activities for the water-gas-shift (WGS) and other reactions related to fuel processing for the production of H₂. However, the effect of pretreatment conditions and the effect of adding oxide dopants to ceria are only poorly understood. These catalysts are also easily poisoned by sulfur.

Sulfur Poisoning of Pd/Ceria: A complex series of species formed upon exposure of Pd/ceria to SO₂, including a surface sulfite at room temperature that converts to a sulfate above 473 K. Ce(SO₄)₂ and Ce₂(SO₄)₃ decompose to SO₂ and O₂ at well defined features 1023 K and 1123 K respectively. The sulfates are easily reduced to Ce₂O₂S in CO or H₂ above ~750 K. The formation of CO₂ from the reduction of the sulfate occurs in the same temperature range as CO₂ production from reduction of Pd/ceria, except that more CO₂ is formed from the sulfur-poisoned catalyst.

Effect of Sulfur on WGS: The WGS reaction on Pd/ceria can be understood through a redox mechanism in which Pd/ceria is reduced by CO and reoxidized by H₂O. However, upon exposure to SO₂, the WGS rates on Pd/ceria dropped to a value close to that observed on Pd/alumina. This observation can be explained by the fact that, even though cerium sulfates can be readily reduced by CO and re-oxidized by O₂ at 723 K, the Ce₂O₂S formed by reduction of the sulfates cannot be re-oxidized by H₂O or CO₂.

Sulfur Poisoning of Ceria-Zirconia: Upon exposure to SO₂ above 473 K, bulk sulfates are formed on CeO₂ but only surface sulfates on ZrO₂. The sulfates on zirconia were found to be stable to somewhat higher temperatures than those on ceria. For the mixed oxides, the quantity of sulfates increased linearly with the Ce content and the decomposition features were similar to a linear sum of pure ceria and pure zirconia. The sulfates on both oxides could be reduced by CO above 750 K.

Fe additives for WGS: The addition of small amounts of Fe to Pd/ceria increased WGS rates by almost an order of magnitude but had no effect on Pt/ceria or Rh/ceria catalysts. The increased activity is shown to be due to Pd-Fe alloy formation. It appears that formation of the alloy provides the energetic driving force for reduction of the Fe, even though Fe would normally exist as Fe₃O₄ under WGS conditions.

Mo additives for WGS: Mo was shown to be a very effective poison for WGS reaction on Pd/ceria. Results suggest that the formation of a monolayer MoO_x species (1.8 Mo/nm²) is sufficient to suppress surface oxidation and reduction of ceria, thus poisoning the reaction.

Effect of Dopants on Hydrocarbon Oxidation Over Ceria: The addition of dopants like Sm₂O₃, Gd₂O₃ and La₂O₃, in the form of solid solutions, is often thought to enhance the activity of ceria for hydrocarbon oxidation. However, we found that rates for n-butane and propane oxidation decreased by more than 100 times upon the addition of these additives, while rates for methane and ethane were completely unaffected.

DOE Interest

Ceria-based catalysts find applications in automotive catalysis and have properties that make them potentially attractive for fuel processing and WGS catalysis.

Future Plans

- 1) We are developing the capability to characterize the oxidation and reduction of ceria-based oxides electrochemically, using what amounts to a solid-oxide fuel cell to pump oxygen to the sample and to probe the P(O₂) above the sample. We are interested in characterizing the nature of the oxygen in promoted ceria catalysts to understand why the dopants have a large effect on activity.
- 2) We are studying ceria overlayers on Y-doped ZrO₂ single crystals in order to characterize the dissolution of ceria under oxidizing and reducing conditions. These are being characterized by XPS and Rutherford Ion Backscattering.
- 3) We are beginning an investigation of NO_x traps, focusing in particular on issues involving sulfur poisoning and regeneration. Materials being developed for commercial application are similar to three-way catalysts but include BaO for trapping the NO as nitrates.

Publications (2002 - present)

- 1) "SO₂ Poisoning of Ceria-Supported, Metal Catalysts", R. J. Gorte, and T. Luo, in "Catalysis by Ceria and Related Materials", A. Trovarelli, editor, Imperial College Press (2002) pp 377 - 389.
- 2) "An Examination of Sulfur Poisoning on Pd/Ceria Catalysts", T. Luo, J. M. Vohs, and R. J. Gorte, *Journal of Catalysis*, 210 (2002) 397-404.
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- 6) "The Activity of Fe-Pd Alloys for the Water-Gas Shift Reaction", S. Zhao and R. J. Gorte, *Catalysis Letters*, 92 (2004) 75-80.
- 7) "Deactivation of the Water-Gas-Shift Activity of Pd/Ceria by Mo", S. Zhao, T. Luo, and R. J. Gorte, *Journal of Catalysis*, 221 (2004) 413-420.
- 8) "Characterization of SO₂-Poisoned Ceria-Zirconia Mixed Oxides", T. Luo and R. J. Gorte, submitted.
- 9) "A Study of the Effect of Sm Doping on Ceria in Hydrocarbon Oxidations", S. Zhao and R. J. Gorte, submitted.
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Joint NMR and Diffraction Studies of Catalyst Structure and Binding

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Goals

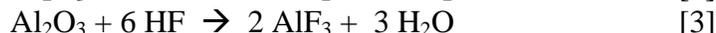
Research carried out under DOE support focuses on two areas. Our first goal is to develop and then use a combination of structural probes to characterize catalytic surfaces and how they change during the catalytic reaction. In the second project, we use novel NMR methods to characterize gas binding, sorption properties and acidity of a variety of molecular sieves and catalytic surfaces.

Recent Progress

Particularly, noteworthy achievements in this period include: (a) a study of the effect of the fluorinating agent on catalyst structure, (b) development of new pair distribution function analysis methods for studying catalyst structure in real time, (c) the design and testing of probes to measure distances between acidic sites and (d) molecular dynamics simulations of α -AlF₃ nanoparticles and their surfaces.

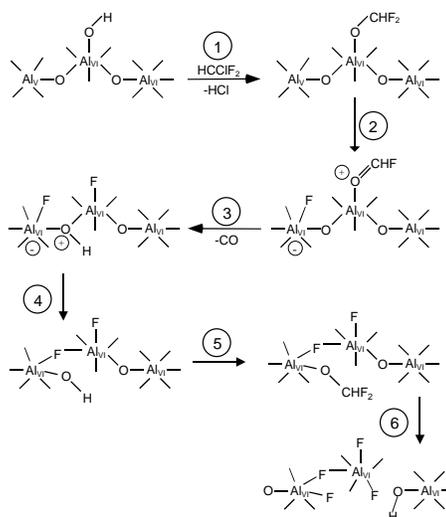
Study of the effect of the fluorinating agent on catalyst structure

We have investigated the structures of a series of pristine and Zn²⁺-impregnated aluminas following fluorination with HF and HCFC-22 (CF₂ClH), by using both solid state NMR and X-ray powder diffraction methods. Our work has shown that the acidity of the fluorination agent influences the structures formed on fluorination. The presence of protons in the fluorinating agent was proposed to favor the formation of Al-X-Al linkages with smaller bond angles, as found in the β -AlF₃ and pyrochlore phases. The pyrochlore phase is stabilized by zinc impregnation, presumably due to the vacant A site in this structure, which can accommodate Zn²⁺ ions more readily than the vacancies in the β phase. The pyrochlore is not favored with HCFC-22 reactions [1], in contrast to the HF reactions [2-3], where the stoichiometry AlF₂OH represents an obvious intermediate in the fluorination reaction.



The fluorination reaction of CHClF₂ on high surface area aluminas was studied in detail by NMR. The first stages of reaction lead to the formation of terminal F-Al groups. ²⁷Al NMR indicates that 5-coordinate Al sites are initially consumed, suggesting that the 5-coordinate aluminum species are predominately localized near the surface of the high surface area alumina particles. The sorption of the basic molecule dimethylphenyl

phosphine, coupled with ^{31}P NMR, showed that the untreated alumina samples do not initially contain Brønsted acid sites, but that these sites are formed on partial fluorination. In contrast, the Lewis acid sites, initially present on the untreated alumina, decrease in concentration on fluorination. Continued fluorination of the surface eventually leads to the destruction of the Brønsted acid sites, the Lewis acid sites remaining but in lower concentrations than on the initial untreated alumina. Based on the results of this NMR study we proposed a mechanism of fluorination of the surface of alumina using CHClF_2 (see scheme on the right).



Molecular Dynamics (MD), Diffraction and Pair Distribution Analysis (PDF) Studies of the Surfaces and Bulk Structure of Aluminum Fluorides

We have applied two new approaches to study the structure of catalytic materials. First, we developed a new method for collecting data suitable for PDF analysis in real time (with S. Billinge, Michigan State and coworkers at the APS (Peter Lee) and BNL (Jonathon Hanson)). This was made possible through the use of image plate area detectors and the new technique was termed rapid acquisition pair distribution function analysis (RA-PDF). Use of the image plate required that methods were developed to handle a series of data corrections for effects such as Compton scattering (which are not a problem when conventional solid state detectors are used). The approach was used to follow the phase transition of $\alpha\text{-AlF}_3$ at $\sim 470^\circ\text{C}$, from a distorted to cubic ReO_3 phase, and to monitor the Al-F bond lengths throughout the transition. The results were consistent with our M.D. simulations of this phase, which showed that the high, temperature “cubic phase” still comprises a distorted ReO_3 network, but that the AlF_6 octahedra rapidly convert between different tilting schemes so that they appear cubic, on average, even on the timescale of the MD simulations. MD simulations were used to explore the effect of size on the distortions found in $\alpha\text{-AlF}_3$, in order to examine why the catalytically-active phase of $\alpha\text{-AlF}_3$, that grows on $\gamma\text{-Al}_2\text{O}_3$ differs structurally from bulk $\alpha\text{-AlF}_3$. The simulations showed that nano-particles of $\alpha\text{-AlF}_3$ are more distorted than the bulk phase. Considerable rearrangements of the surfaces are observed, and the surfaces are extremely dynamic at the temperatures relevant to catalysis. At low temperatures, a lower number of coordinately unsaturated Al atoms are observed, some of the F ions bridging more than one surface Al site. At high temperatures, these sites become exposed, increasing the number of sites available for gas binding.

New Probe Molecules for Characterizing Acidity

Acidic faujasites are widely used as for example cracking catalysts in petroleum refinement. Many methods, including IR, temperature-programmed desorption, microcalorimetry and solid state NMR, have been applied to characterize acidity. While the acidity itself is one of the major concerns, the information of the distances,

interactions and synergy between adjacent different acid sites (i.e., Brønsted and/or Lewis acid sites) is required to develop an understanding of catalytic function, especially in bifunctional catalytic reactions that involve more than one active site. However, to date only probe molecules with single basic group have been used to measure acidity. We have used a new class of probe molecules, diphosphines, which have two basic sites, in combination with solid state ^{31}P NMR, to probe both the acidities and distances between Brønsted acid sites in HY zeolites.

DOE Interest

The design of optimized, new, tailor-made catalysts for different applications requires the development and application of new characterization methods to probe structures of the as-synthesized materials, and how they change during the catalytic reaction.

Future Plans

We propose to continue to evaluate our new probe molecules to explore proximity between acid sites in both molecular sieves and on surfaces, and the effect of this on catalysis. PDF methods will be exploited to explore the structures of a series of disordered and amorphous catalysts as a function of time-on-stream.

Publications (2002-4)

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8. "A Combined Solid State NMR and Diffraction Study of the Structure and Acidity of Fluorinated Aluminas: Implications for Catalysis," P. J. Chupas, D.R. Corbin, V. N. M. Rao, J. C. Hanson, C.P. Grey, *J. Phys. Chem. B.*, 107, 8327-8336 (2003).
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10. "Probing Local and Long Range Structure Simultaneously: An In-Situ Study of the High Temperature Phase Transition of $\alpha\text{-AlF}_3$," P. J. Chupas, S. Chaudhuri, J. C. Hanson, X. Qiu, P. L. Lee, S. D. Shastri, S. J. L. Billinge and C. P. Grey, *J. Am. Chem. Soc.*, in press (2004).
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Ruthenium Mediated C-H Activation and C-C Bond Formation Reactions

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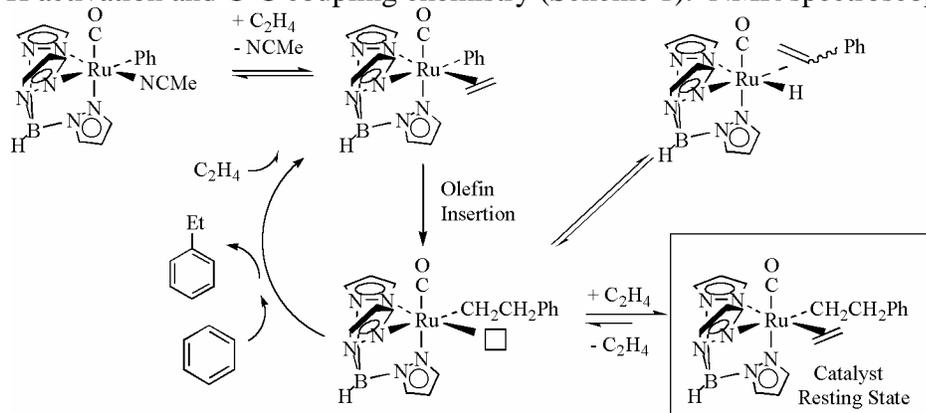
Goals

Develop metal-mediated C-H activation chemistry for catalytic hydroarylation of unsaturated organic compounds.

Recent Progress

Catalytic Hydroarylation: $\text{TpRu}(\text{CO})(\text{R})(\text{NCMe})$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_2\text{Ph}, \text{Ph}$ or 2-furyl; $\text{Tp} = \text{hydridotris}(\text{pyrazolyl})\text{borate}$) serve as catalyst precursors for the addition of aromatic C-H bonds across C=C bonds. For example, $\text{TpRu}(\text{CO})(\text{Ph})(\text{NCMe})$ catalyzes the addition of benzene C-H bonds across ethylene and α -olefin double bonds. The primary products of these reactions are alkyl benzenes, and the reactions that incorporate α -olefins are moderately selective for linear over branched products.

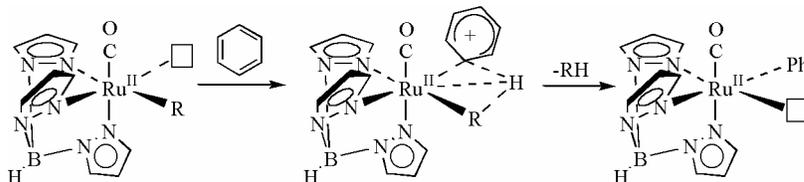
Mechanism of Hydrophenylation: The catalytic hydrophenylation reactions do not proceed *via* a traditional Friedel-Crafts mechanism. Rather, the Ru(II) metal center serves to mediate C-H activation and C-C coupling chemistry (Scheme 1). NMR spectroscopy indicates



Scheme 1. Proposed catalytic cycle.

that $\text{TpRu}(\text{CO})(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-H}_2\text{C}=\text{CH}_2)$ is the catalyst resting state, and the inverse dependence of the rate of catalysis on olefin concentration is consistent with this conclusion. The independent preparation and isolation of $\text{TpRu}(\text{CO})(\text{NCMe})(\text{CH}_2\text{CH}_2\text{Ph})$ has been achieved, and reactivity studies with this complex suggest that β -hydride elimination to form $\text{TpRu}(\text{CO})(\text{H})(\eta^2\text{-styrene})$ is facile. However, under reaction conditions the elimination sequence is reversible and does not disrupt catalysis. For α -olefins, analogous β -hydride elimination produces disubstituted olefins that undergo displacement more readily than styrene.

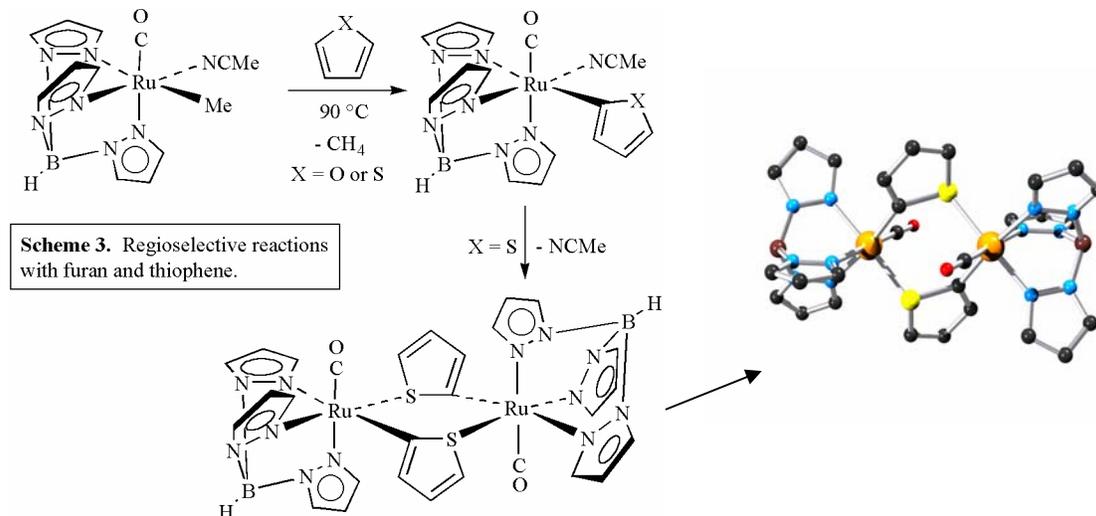
Consistent with the proposed metal-mediated C-H activation, the reaction of $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ with C_6D_6 produces CH_3D . In addition, catalytic reactions of C_2H_4 in C_6D_6 produce $\text{C}_6\text{D}_5\text{CH}_2\text{CH}_2\text{D}$, while catalysis in a 1:1 molar mixture of C_6H_6 and C_6D_6 reveals a kinetic isotope effect of 2.8(2). DFT calculations reveal that the C-H activation step does not proceed through a Ru(IV) oxidative addition intermediate. Rather, C-H bond breaking and forming occurs simultaneously. In the calculated transition state, the hydrogen atom of the activated C-H bond is 0.87 Å out of the aromatic plane indicating that the transformation is best considered as an electrophilic aromatic substitution (Scheme 2). This view of the C-H



Scheme 2. Proposed pathway for C-H activation.

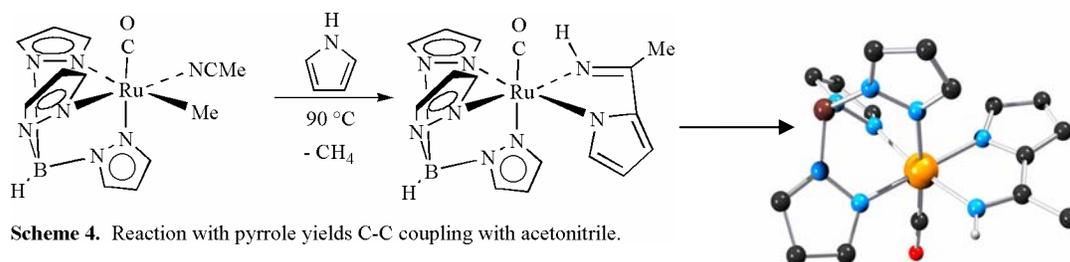
activation step is consistent with the regioselectivity of reactions with five-membered heterocycles (see below). In addition, calculated transition states reveal Ru-H interactions. Thus, the transition states exhibit "oxidative" character.

Heteroaromatic Substrates: The proposed electrophilic aromatic substitution pathway for C-H activation provides an opportunity for regioselective transformations. For example, stoichiometric reactions of $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ with furan or thiophene yields methane and 2-furyl or 2-thienyl products, respectively (Scheme 3). The addition of the 2-position C-H



Scheme 3. Regioselective reactions with furan and thiophene.

bond of furan to ethylene {using 1 mol% of $\text{TpRu}(\text{CO})(\text{NCMe})(2\text{-furyl})$ } to yield 2-ethylfuran demonstrates that catalytic transformations with heteroaromatic substrates is feasible. The reaction of $\text{TpRu}(\text{CO})(\text{NCMe})(\text{Me})$ with pyrrole yields the product from C-C coupling with the acetonitrile ligand (Scheme 4). Isotopic labeling studies are consistent with a reaction mechanism that involves initial C-H activation at the pyrrole 2-position.



Future Plans

C-H Activation: An electrophilic aromatic substitution pathway has been proposed for the C-H activation step. The rate of aromatic C-H activation of a series of 2-substituted 1,3-xylenes with $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ will be used to probe this conclusion. For an electrophilic substitution mechanism, a significant rate dependence on the donating ability of the substituents is anticipated. For a σ -bond metathesis mechanism, insignificant electronic influence is expected. Differentiating these two pathways is relevant to controlling the regioselectivity of C-H activation.

Future Generations of Catalysts: Second generation catalysts are being designed to probe the impact of ligand variation on regioselectivity as well as catalyst activity and longevity. Can altering the steric bulk of the ligand set allow control over the regioselectivity of olefin insertion or do electronic effects dictate the outcome of this discrete step? This question will be probed by synthesizing catalysts of the type $\text{TpRu}(\text{L})(\text{Ph})$ (L = phosphines) for which donating ability and steric profile can be systematically controlled. In addition, our early studies are consistent with the C-H activation step proceeding through an electrophilic aromatic substitution pathway suggest that increasing the donating ability of the ancillary ligands may suppress the rate of the C-H bond breaking step. However, DFT studies reveal "oxidative character" in this reaction step. The impact of electron density on catalyst activity will be experimentally probed through variation of phosphine identity.

Oxidation to $\text{TpRu}(\text{III})$ systems could enhance the metal electrophilicity as well as promote facile olefin insertion reactions. Unfortunately, single-electron oxidation of $\text{TpRu}(\text{CO})(\text{NCMe})(\text{R})$ (R = Me or Ph) results in production of ethane or biphenyl and $\text{TpRu}(\text{CO})(\text{NCMe})(\text{OTf})$. Preliminary evidence suggests that the reaction pathway from the desired Ru(III) systems [$\text{TpRu}(\text{CO})(\text{NCMe})(\text{R})$][OTf] to $\text{TpRu}(\text{CO})(\text{NCMe})(\text{OTf})$ involve CO migratory insertions. Thus, oxidation of $\text{TpRu}(\text{L})(\text{NCMe})(\text{R})$ (L = phosphine) should afford isolable Ru(III) systems.

Reactions with C=X Bonds ($X = \text{O}$ or N): The evidence of insertion of acetonitrile into a Ru-pyrrolyl bond suggests the possibility of catalytic C-C coupling reactions with other unsaturated substrates such as aldehydes, ketones, imines, isonitriles, carbon dioxide, ketenes, etc. Successful transformations could allow the facile and regioselective synthesis of functionalized systems from simple aromatic compounds. It is anticipated that electrophilic metal centers will afford regioselective C-H activation and that bond polarization ($\text{Ru}^{\delta+}-\text{C}^{\delta-}$ with $\text{C}^{\delta+}=\text{X}^{\delta-}$) will afford control over the regioselectivity of C=X insertion. Our preliminary studies will focus on the details of C=X insertion into Ru-aryl bonds.

DOE Interest

The chemistry proposed herein addresses several program targets by seeking to develop, understand and predict catalyst activity of systems that enable processing of reagents from fossil sources (hydrocarbons) into commercially important materials. The unreactive nature of hydrocarbons has historically necessitated harsh conditions for processing (even in the presence of heterogeneous catalysts), and consumption of significant energy is a result of both high reaction temperatures as well as the common requirement of elaborate purification steps due to poor catalyst selectivity. The current catalysts could provide the foundation for the development of useful systems that target synthetic cycles of relevance to both commodity and fine chemical markets.

Publications

Prior to DOE Funding

1. "Addition of Arenes to Ethylene and Propene Catalyzed by Ruthenium" Lail, M., Arrowood, B., Gunnoe, T. B.* *J. Am. Chem. Soc.* **2003**, *125*, 7506-7507.

In preparation

2. "Stoichiometric and Catalytic C-H Activation of Heteroaromatic Compounds by Ru(II): Experimental and Computational Studies" Pittard, K. A., Cundari, T. R., Gunnoe, T. B.*, Day, C. S., Petersen, J. L. Manuscript in preparation
3. "Experimental and Computational Studies of Ru(II) Catalyzed Addition of Aromatic C-H Bonds to Olefins" Lail, M., Bell, C. M., Conner, D., Cundari, T. R., Gunnoe, T. B.* Manuscript in preparation
4. "Oxidatively Induced Elimination of Alkyl and Aryl Ligands from Ruthenium" Lail, M., Gunnoe, T. B.* Manuscript in preparation

Nanoscale Pores for Heterogeneous Catalysis

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Goal

To investigate the radius of curvature effect of nanopore materials [Single Walled Nanotubes of carbon (SWNT) and mesoporous molecular sieves (MCM-41)] on adsorption and catalysis.

Recent Progress

Multivariate Correlation and Synthesis Prediction of V-MCM-41: The synthesis process for MCM-41 materials comprise many process variables, several of which interact. For example, the main independent variable of interest is the pore diameter which is varied by changing the chain length of the templating surfactant, but this also affects the degree of structural order (and in some cases the degree of incorporation of first-row transition metals). By using the designed experiment, statistical approach to synthesis, quantitative synthesis models have been developed for V-MCM-41 (and a preliminary model for Co-MCM-41) and tested. These can then be used to prepare series of samples with varying pore size but constant composition and a high degree of structural order.

Radius of Curvature Effects on the Air Oxidation of Methanol on V-MCM-41: Our initial investigation of methanol oxidation to formaldehyde on V-MCM-41 was performed on very low loading (about 0.4 wt %) vanadium catalysts because this assures isolated V sites and is less likely to disrupt the MCM-41 structure. The rate was observed to vary over about one order of magnitude and exhibited a maximum at the mid-range of pore sizes investigated. The activity for methanol oxidation also correlated with a shift in the energy of the V pre-edge X-ray absorption feature, which we interpreted as a change in the oxidation potential of V with change in pore size. Based on previous modeling of radius of curvature on the bond angle distribution of Si-O-Si units in MCM-41, we suggested that the molecular origin of the oxidation potential of V-MCM-41 (shift in the energy of the V pre-edge X-ray absorption feature) was likely a response of the V-O-Si bond angle and the resulting rehybridization of molecular orbitals caused the change in oxidation potential and perturbed the rates of reduction of V^{+5} and re-oxidation of V^{+4} . When both the reduction and re-oxidation were of equal rate, the over all catalytic rate would be optimum and explain the maximum in the catalytic oxidation rate of methanol. Using the multivariate synthesis approach, we have confirmed this observation on the improved materials and are now trying to understand why this radius of curvature effect only applies to V-MCM-41 of low loading.

Radius of Curvature Effect on Reduction Stability of Co-MCM-41: In an investigation of Co-MCM-41 initiated before the current grant period, we observed that Co in MCM-41 was unusually stable with regard to reduction at 773K by hydrogen, but have only recently discovered that reducibility varies with pore size. This is perhaps the most dramatic effect of

radius of curvature so far observed. The temperature-programmed reduction (TPR) of several samples of MCM-41 is shown in Figure 1 below. The pore size ranges from about 3.1 nm – 1.9 nm, labeled from C18 – C10, where the label indicates the template chain length used in the synthesis. The minor reduction peak just above 500°C is the result of Co^{3+} reduction. The amount of this species is less than 5% in the largest pore Co-MCM-41, and decreases linearly with pore size to zero in the smallest pores. Isomorphously substituted Co^{2+} in tetrahedral Si sites⁵ is the major species in Co-MCM-41 and this reduces at temperatures above 650°C with both the on-set of reduction and the peak rate of reduction increasing as the pore size decreases.

There is also a systematic change in the shape of the TPR curve being broad for the large pore Co-MCM-41 and narrow for the small pore material. The integrated area is constant which is consistent with the fact that the Co loading in all of these materials is constant at 1 wt %. There may be several contributions to this kinetic effect. First, as the redox stability increases, the initiation of reduction begins at higher temperature and the higher temperature would imply a higher rate (narrower reduction peak in the TPR). Second, the concentration of Co (in atoms per unit volume of MCM-41) increases with decrease in pore diameter if the wall thickness remains

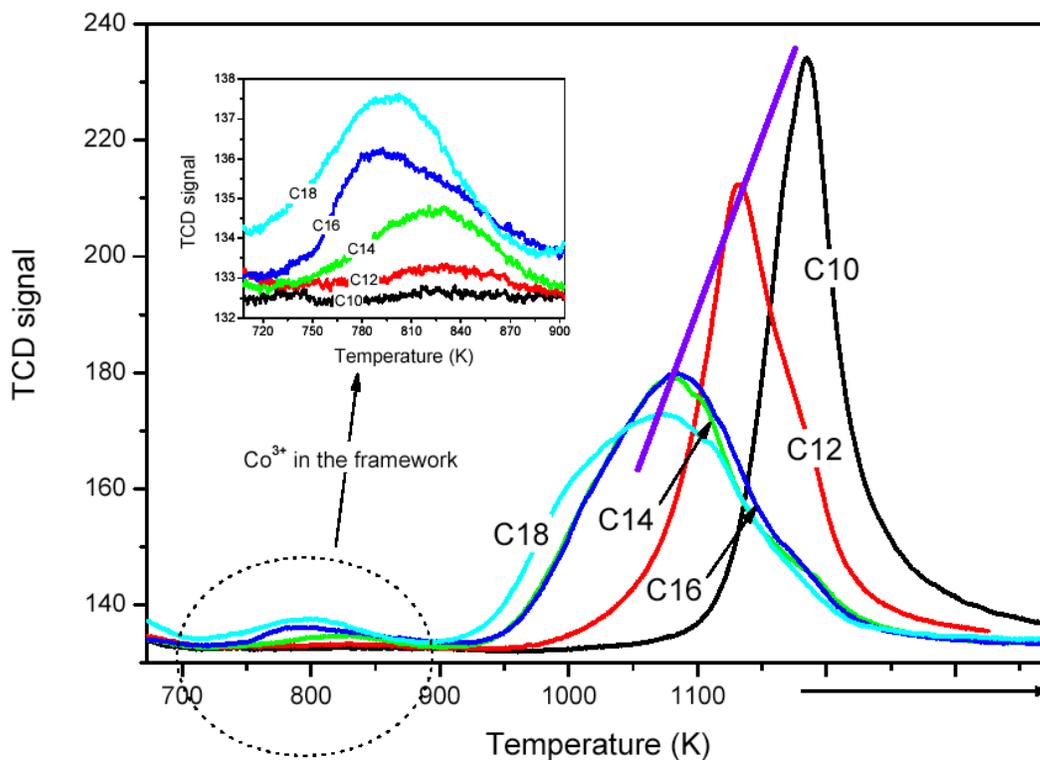


Figure 1

Radius of Curvature Effect on Co-MCM-41 Derived Catalysts for Synthesis of SWNT: Properties of SWNT depend on the tube diameter providing an incentive to find a catalyst that selectively produces a given size. Co-MCM-41 is a precursor to such a catalyst, produced by pre-reduction of Co-MCM-41 to form a narrow distribution of Co clusters, and provides good selectivity and the flexibility to vary the SWNT average diameter with a distribution of about ± 0.05 nm by catalyst design. We have synthesized SWNTs in four average diameter distributions in the range of 0.5 – 0.8 nm, which linearly correlate with the pore size of the Co-MCM-41 catalyst. The diameter of the SWNT has been

estimated from nitrogen adsorption isotherms and direct observation by TEM. The SWNT average diameter is determined by Co metal cluster size that is controlled by the pore size and Co loading of the Co-MCM-41 catalyst.

DOE Interest

Metal substituted MCM-41 can be used to prepare highly dispersed and stable supported first-row transition metals, e.g., Co, which are good catalysts for both traditional energy related reactions, e.g., Fischer-Tropsch synthesis, and emerging catalytic applications, e.g., synthesis of single walled nanotubes of carbon of narrow diameter distribution.

Future Plans

Our proposed research is a continuation of the investigation of radius of curvature effects on catalyst preparation, adsorption, and catalytic activity and selectivity. Our goals are to: a) build a quantitative model for the synthesis Co-MCM-41, similar to that developed for V-MCM-41, with the objective of generalizing it to other first-row metals, e.g., to Ni-MCM-41, b) to determine mechanism for the radius of curvature effect on methanol oxidation over V-MCM-41 with the objective of extending it to Co-MCM-41, c) to understand the mechanism of Co metal cluster formation from Co-MCM-41 on a molecular level with the objective of extending this to Ni-MCM-41, i.e., to prepare very high dispersions of Ni clusters in the MCM-41 matrix, comparable to that which has been achieved for Co, and d) to initiate a study of adsorption and catalysis reactions on SWNT to determine the magnitude of radius of curvature effects of pores of < 1 nm that can be synthesized in carbon tubes (catalytically using Co-MCM-41).

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***In situ* time-resolved X-ray diffraction (TR-XRD) as a tool for characterizing catalysts and active sites**

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11973

The development of techniques for characterizing the structural properties of catalysts under the high-pressure conditions of industrial processes is widely recognized as a top priority in the area of heterogeneous catalysis. At the NSLS beam line X7B, we have put together a facility capable of conducting *in situ*, sub-minute TR-XRD experiments under a wide variety of temperature and pressure conditions ($80\text{ K} < T < 1250\text{ K}$; $1\text{ Torr} < P < 150\text{ atm}$). [1] Current measurements also include control of gas flow and measurement of gas composition of the products with mass spectrometry. [2] This important advance results from combining the high intensity of synchrotron radiation with new parallel data-collection devices. Using TR-XRD, one can obtain information about structural details, phase composition, kinetics of transformation, intermediate phases and crystal characteristics. Examples of problems studied to date with TR-XRD include: (1) hydrothermal synthesis of zeolites [3] and mesoporous materials [4] and substrate binding of zeolites; [5] (2) reduction/oxidation of oxide catalysts; [2] (3) changes to the AlF_3 structure when it becomes an active catalyst; [6] and (4) the synthesis of metal phosphide catalysts. [7] Recently, we have applied these techniques to the hydrothermal synthesis of nano-crystalline MnO_2 and CVD deposition of nanocrystals on graphite and MgO .

In the last three years, we have developed a new cell that supports pressures up to 150 Atm. using a sapphire tube. Low-pressure EXAFS measurements can be made with this cell by using a kapton tube in place of the sapphire tube (Fig. 1). We have also been exploring new detectors that will allow for more rapid data acquisition. Specifically, we have tested a new detector built by the NSLS that can measure 5 powder patterns per second. This detector would allow for sampling rates 100 times faster than what we currently have.

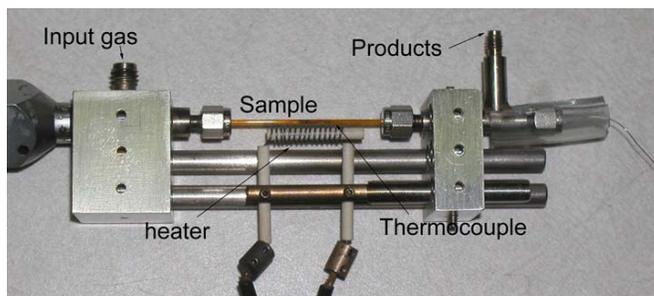


Fig. 1. Flow cell for *in situ* X-ray diffraction and EXAFS measurements.

In addition, we have helped to implement an identical *in situ* XRD setup at the Argonne National Laboratory Advanced Photon Source (APS) beam line ID1. This allows *in situ* measurements with high-energy X-rays (80keV to 127keV). At these energies, the absorption corrections are insignificant even for metal catalysts, and the data range goes to Q as high as 30\AA^{-1} . This enables significant improvements in the quality of powder profile refinement results. The high energy measurements also permit the determination of time-resolved changes of local structural information from amorphous and disordered materials. These results are obtained by

analyzing entire diffraction patterns measured to high Q using the PDF technique.[8] These time-resolved PDF diffraction experiments are possible when high-energy X-rays (>50 keV) are combined with area detectors.[9] With this approach, we are analyzing *in situ* measurements of: nanocrystalline α -MnO₂ synthesis, metal carbide formation by methane carburization of metal oxides, nanoparticle cubic ZrO₂ formation from amorphous ZrO₂, dehydrogenation of Ti sodium aluminate, bulk[10] and nano CuO reduction and nano ceria oxidation/reduction. This set of measurements was made at the APS, but could be carried out at high-energy beam lines at the NSLS.

C. Application to studies of the reduction/activation of oxides

In a project that also involves work with oxide single crystals and UHV photoemission (section 6.2.1.1.B), we have investigated with TR-XRD the mechanism for the reduction of several oxide powders (NiO, CuO, Cu₂O, MoO₃, CoMoO₄, NiMoO₄, CeO₂) under atmospheric pressures of hydrogen at elevated temperatures.[2, 11] Partial reduction in hydrogen is a method frequently used for the activation of oxide catalysts, and TR-XRD has proven to be useful for the identification of suboxides that have specific chemical properties. The results of the TR-XRD point to the existence of an induction time as a common phenomenon in the reduction of an oxide. The magnitude of the induction time depends on the amount of defects and O vacancies in the oxide lattice.

CuO is used as a catalyst or catalyst precursor in many important processes (methanol and higher alcohols synthesis, water-gas shift reaction, methanol steam reforming, CO oxidation) and there has been considerable controversy about the relative stability of Cu⁺¹/Cu⁰ species under reducing conditions. In order to solve this controversy, one needs *in situ* measurements under standard process conditions. We have used *in situ* TR-XRD to show that reduction with H₂ or CO usually does not produce significant amounts of Cu₂O (or Cu₄O₃) intermediates before metallic copper forms. However, if one limits the flow of the reductant gas (H₂ or CO), then a Cu₂O intermediate is formed (see Fig. 2). The Cu₂O phase formed under these conditions shows extra oxygen in the cavities of the lattice structure. We have also shown that a Cu₂O phase is required during the water shift reaction.

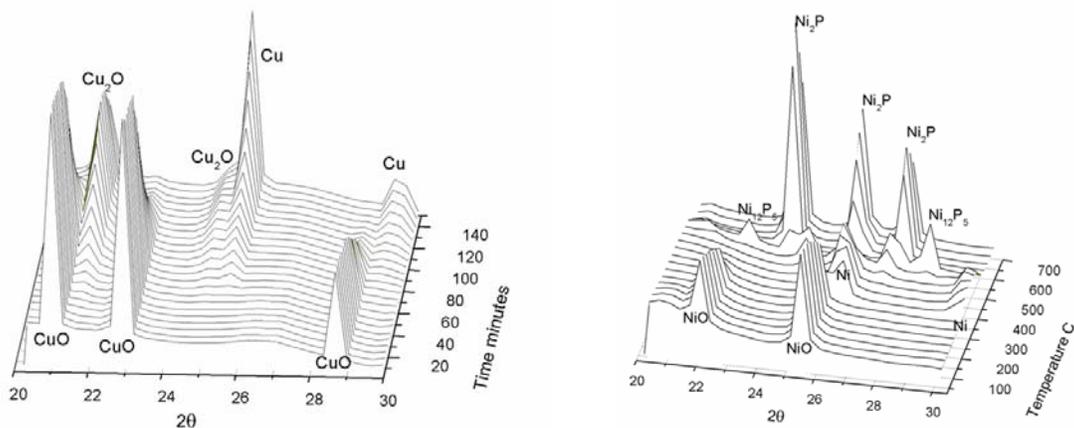


Fig. 2. *In situ* diffraction patterns during the reduction of CuO with limited CO flow (left); *in situ* diffraction patterns during the synthesis of HDS catalysts (right).

D. Application to the synthesis of phosphide and carbide catalysts

Our group has started several projects focused on studying the chemical and catalytic activity of phosphidenitride and carbide compounds. Silica-supported nickel phosphide ($\text{Ni}_2\text{P}/\text{SiO}_2$) has shown particular promise as a new generation of hydrodesulfurization (HDS) catalyst that leads to the ultimate goal of clean burning fuels. Our TR-XRD studies of its synthesis show the sequence of $\text{NiO} \rightarrow \text{Ni} \rightarrow \text{Ni}_2\text{P}_5 \rightarrow \text{Ni}_2\text{P}$ silica-stabilized phases (right panel of Fig. 2). The understanding of the catalytic properties of $\text{Ni}_2\text{P}/\text{SiO}_2$ has been facilitated by our new knowledge about the pathway for its formation and first principles density functional calculations. [7]

This work is supported through contract DE-AC02-98CH10086 with the US DOE Division of Chemical Sciences. The authors would like to acknowledge the contributions of Peter Chupas and Peter Lee at the Argonne National Laboratory.

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Chemistry of Complexes with Transition Metal-Heteroatom Bonds: Novel Insertion Chemistry and macromolecule Synthesis

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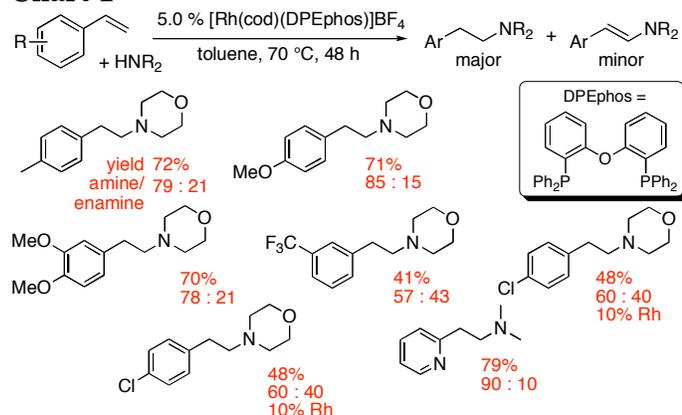
Goals

Major objectives of our current research under DOE support include the development of reactions needed to observe catalytic hydroamination, the discovery of new hydroamination systems that make use of these reactions, the development of new classes of insertion reactions that generate amido and alkoxo complexes, and the study of triarylamine materials.

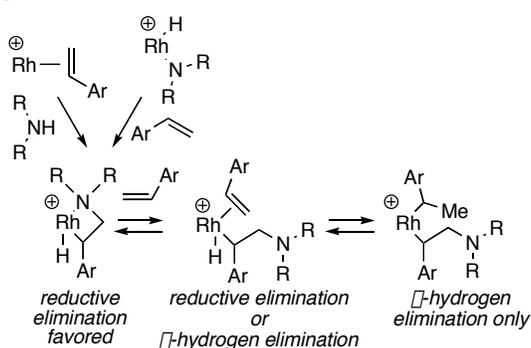
Recent Progress

1) *New catalytic hydroaminations.* We uncovered the first transition metal-catalyzed, anti-Markovnikov hydroamination of unactivated vinylarenes in high yields. This reaction occurred $[\text{Rh}(\text{COD})(\text{DPEphos})]^+$ as catalyst. Previous studies conducted by Beller generated enamine as the major product. Our rhodium-catalyzed reactions formed enamine in competition with amine, but amine was the major product in most cases. As shown in Chart 1, the reaction of electron-neutral or electron-rich vinylarenes with a variety of secondary amines in the presence of catalyst formed the products from anti-Markovnikov hydroamination in good to excellent yields.

Chart 1



Scheme 1.

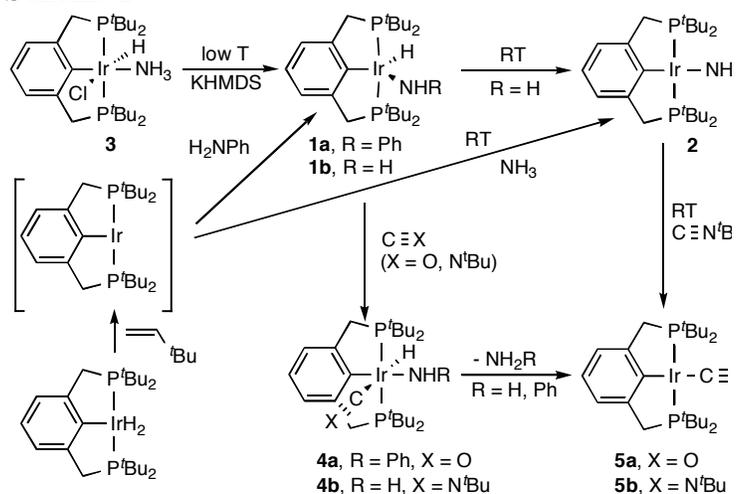


Reactions of morpholine, *N*-phenylpiperazine, *N*-Boc-piperazine, piperidine, 2,5-dimethylmorpholine, and perhydroisoquinoline reacted with styrene to form the amine product in 51-71% yield. Reactions of a variety of vinylarenes with morpholine generated amine as the major product. Reactions of morpholine with electron-poor vinylarenes gave lower ratios of amine to enamine than reactions of electron-rich vinylarenes at the same concentration of vinylarene, but conditions were developed with lower concentrations of electron-poor vinylarene to maintain formation of the amine as the major product. Reactions of dimethylamine with vinylarenes were fast and formed amine as the major product. Mechanistic studies on the hydroamination process showed that the ratio of amine to enamine was lower for reactions conducted with higher concentrations of vinylarene and that one vinylarene influences the

selectivity for reaction of another. A mechanism depicted in Scheme 1 proceeding through a metallacyclic intermediate that opens in the presence of a second vinylarene can account for these and other mechanistic observations.

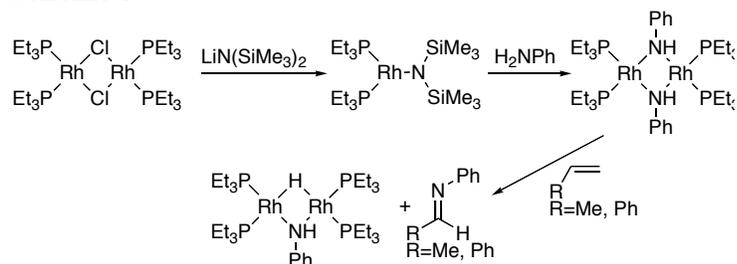
2) *Thermodynamics of Oxidative Addition and Reductive Elimination of Ammonia.* To help identify viable pathways for the hydroamination of olefins catalyzed by complexes of the cobalt triad, we studied oxidative additions and reductive eliminations of ammonia from (PCP)Ir fragment (PCP=1,3-di-*tert*-butylphosphinobenzene) complexes with PCP pincer ligands, in collaboration with Alan Goldman. Alan's student focused on the oxidative addition of aniline and the electronic effects that control the thermodynamics and structures of the iridium anilide complexes. In addition to addressing the feasibility of N-H addition as part of the mechanism for hydroamination, these studies revealed the relative reactivities and stabilities of amine and amido hydride complexes relative to C-H activation products. Our results are summarized in Scheme 1. Reaction of aniline with the (PCP)Ir unit generated from (PCP)IrH₂ and norbornene resulted in the N-H oxidative addition product [(PCP)Ir(PhNH)(H)] (**1a**). In contrast, reaction of this fragment with ammonia gave the ammonia complex [(PCP)Ir(NH₃)] (**2**). The amido hydride complex that would be formed by oxidative addition of ammonia, [(PCP)Ir(NH₂)(H)] (**1b**), was generated independently by deprotonation of the ammonia complex [(PCP)Ir(H)(Cl)(NH₃)] (**3**) with KN(SiMe₃)₂ at low temperature. This amido hydride complex underwent reductive elimination at room temperature to form the ammonia complex **2**. Addition of CO to anilide complex **1a** gave [(PCP)Ir(PhNH)(H)(CO)] (**4a**). Addition of CN^tBu to terminal amido complex **1b** formed [(PCP)Ir(NH₂)(H)(CN^tBu)] (**4b**), the first structurally characterized iridium amido hydride. Complexes **4a** and **4b** underwent reductive elimination of aniline and ammonia; parent amido complex **4b** reacted faster than anilide **4a**. These observations suggest distinct thermodynamics for the formation and cleavage of N-H bonds in aniline and ammonia. Complexes **1a**, **2**, **4a**, and **4b** were characterized by single-crystal X-ray diffraction methods.

Scheme 2



3. *Aminations of Olefins with Isolated Amido Complexes.* Transfer of alkyl and hydride groups from transition metal complexes to olefins, most often by insertion reactions, is a staple of homogeneous catalysis. The transfer of an amido group of a discrete isolated compound to an olefin is unknown. We

Scheme 3

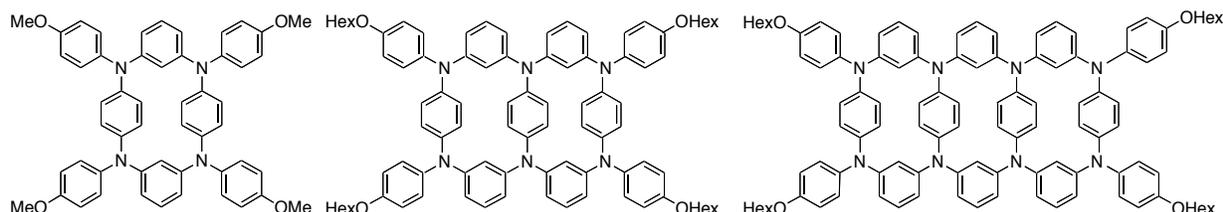


have found in unpublished work the first examples of such a transformation. As shown in Scheme 2, we prepared a dimeric rhodium anilide complex bound by trimethylphosphine. This complex reacted with styrene and alkenes, such as propylene to form the corresponding imine product from Markovnikov addition. Our mechanistic data are preliminary at this time. However, the reactions are clearly

first-order in olefin and appear to be half-order in rhodium dimer. These data suggest that the reaction of olefin occurs to a monomeric rhodium complex formed by cleavage of the dimer to form two 14-electron, monomeric rhodium complexes. Insertion of olefin into the rhodium-amido linkage to form a π -amino, π -arylalkyl and π -hydrogen elimination would account for the formation of product. Coordination of olefin to one monomer and attack of the amido group of a second monomer is inconsistent with the half-order behavior because both halves of the dimer would be a part of the final irreversible step.

4. *Applications of Triarylamines formed by Palladium-Catalyzed Amination in Materials Chemistry.* In addition to studies on new organometallic chemistry, we have been conducting work in collaboration with two groups on extensions of our studies on the preparation of electronically interesting triarylamines by the palladium-catalyzed amination of aryl halides. In one collaboration, we have prepared dendritic amines with pendant functional groups for studies on metal-organic dendritic frameworks with Omar Yagahi at Michigan. Crystalline materials have been more difficult to obtain by linking the larger dendrimers with metal ions, and we have no results to report on these materials at this time. We have also been conducting work with Ted Goodson at Wayne State on the photophysics of triarylamine cyclophanes shown in Chart 2. A full paper is currently being written on these studies. Comparisons of EPR, electrochemical, UV-vis, steady state fluorescence and time-resolved fluorescence studies have revealed that the ladder materials in Chart 2 give rise to radicals that are more delocalized than the square cyclophane, but that conformation of the contiguous aryl groups of the steps in these ladders affect the electronic properties.

Chart 2



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NMR and Computational Studies of Solid Acidity

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Goals and Objectives

This project has focused very strongly on the further elucidation of the mechanisms of methanol-to-hydrocarbon catalysis, both methanol-to-olefin (MTO) and methanol-to-gasoline (MTG). MTG is closely related to MTO, the difference being secondary reactions in the former that convert olefins to mixtures of alkanes and methylbenzenes. MTO is of great interest as part of integrated schemes for the conversion of natural gas to polyolefins. The mechanism of MTO/MTG has been a long-standing intellectual challenge for fundamental research in solid acid catalysis. We continue to be interested as well in other opportunities leading to improved mechanistic understanding in catalysis by microporous solids.

Significant Recent Achievements and Results

Twenty or more distinct mechanisms have been proposed to describe the formation of the “first” C-C bond in methanol conversion catalysis. These include mechanisms based on carbenes, free radicals, oxonium ylides, simple carbenium ions, and various other exotic intermediates. In a recent series of papers we have presented very strong evidence that hydrocarbon synthesis occurs by a “hydrocarbon pool” mechanism. The essential idea of the hydrocarbon pool is that the active site is not simply an acid site in an inorganic cage or channel, it also includes a large organic molecule that acts as a scaffold on which C-C bonds are made and broken while passing through comparatively stable structures.

Recently we have developed definitive tests of some of the other mechanisms of MTO chemistry, including the first ever studies of carbene chemistry in a microporous solid acid. Furthermore we have developed experimental procedures for testing a competing proposal that the initiation period in MTO catalysis is driven by framework methoxy groups as key intermediates. Those experiments clearly show that methoxy

groups are extraordinarily stable under MTO initiation conditions and have only trivial roles in the alkylation of existing olefins and methylbenzenes. Other lines of investigation include heteroatom-substituted hydrocarbon pool species. We continue to develop novel procedures related to the synthesis of novel catalysts with well-defined molecular sites.

Interest to DOE Catalysis:

Fundamental study of catalytic reaction mechanism and the discovery of new catalysts and processes are central to progress in catalysis. Recent progress in methanol conversion catalysis has provided a clearer, molecular-level understanding of zeolite (and zeotype) catalysis than has usually been possible in the past. In addition, the development and application of methodologies such as novel reactors, in situ spectroscopy, and theoretical study verified by experiment is useful in enabling other research.

Extended Impact on Science, Technology and Society:

Ethylene is one of the largest volume chemicals, and demand is rising much faster than it can be met through production as a by-product of cracking. Methanol-to-olefin catalysis is widely expected to become a major component of the chemical industry by the end of the decade. As such it is expected to become a highly successful route for methane utilization. Scientific interest in the mechanism of methanol conversion catalysis is clearly evidenced by published papers reporting the application of very diverse experimental and theoretical methodologies by researchers both inside and outside the mainstream of catalysis.

Recently we learned that our DOE funded work is closely followed by the pharmaceutical industry, and I have been invited to visit the laboratories of one of the top three drug companies to better inform them of this work. It turns out that hydrolysis of drug components in solid formulations is a major contributor to reduced shelf life. An active area of investigation is the use of solid acids and bases in formulations to control hydrolysis rates. For example, when aspirin is formulated with microcrystalline calcium carbonate its shelf life is extended. Our DOE work is being studied closely as a guide to the development of rational procedures for ranking the strengths of acids and bases used in pharmaceuticals and to develop novel formulations.

Future Plans:

As before, our work includes in situ NMR and computational chemistry. In the past year we have implemented Gaussian 03 on powerful desktop G5 computers, with the result that many of the graduate students run computations routinely before and after experiments. Many of our recent papers are primarily based on flow reactor studies, catalyst synthesis, and other types of experimentation that we did not commonly use several years ago. We are in the early stages of transitioning our program to include other mechanistic problems in catalysis. We are also positioning ourselves for work in the area of designing novel microporous catalysts with well-defined molecular sites.

Publications for the Years 2002 - 2003.

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Columbia University Contribution – Part 2 : “Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes through Tailored Nanostructures”

Students: Dan Quinn, Idan Mandelbaum

Collaborators: Stephen O’Brien, Ludwig Bartels, Talat Rahman, Radoslav Adzic, Peter Feibelman

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Goal

The overall goal of the project is to pursue the development of new catalysts that produce specific surface reactions by applying steric and entropic control using appropriately selected and developed nanostructures. The Heinz group will investigate the fundamental processes of energy transfer at surfaces that may be used to control these processes and to examine how nanostructured materials can serve to enhance catalytic activity and selectivity. Particular use will be made of ultrafast laser techniques that permit one to produce and probe non-equilibrium processes.

Progress during the first 6 Month of the Funding Period:

During the first six month of the project, our investigations have examined the nature and dynamics of surface processes occurring in the presence of high levels of electronic excitation. These excitation conditions are achieved, without significant overall sample heating, by the use of femtosecond laser pulses that can effectively decouple the electronic excitations in a metal substrate from those of the lattice. In this fashion, we learn about the fundamental energy transfer mechanisms between the substrate and adsorbed molecules that can occur in catalytic processes. Such detailed understanding of energy transfer process will aid in assessing the possibility of retaining energy released in one step of a catalytic process to assist another step, thus circumventing complete thermalization of excess energy and achieving a measure of entropic control. To this end, we have conducted experimental work along two related directions of study for this regime of high electronic excitation densities: one probing the effect of isotopic mass on desorption and one examining lateral motion of adsorbates, i.e., surface diffusion processes. For the former study, we chose the system of O₂/Pd(111), for which the conventional thermal and photochemistry have been well characterized. For the latter study, conducted in collaboration with Ludwig Bartels’ group (UC Riverside), we have investigated the CO/Cu(110), a well-characterized system that exhibits anisotropic diffusion under equilibrium conditions.

Isotope Effect in Electronically Induced Desorption: The isotope effect provides an excellent tool to investigate adsorbate dynamics and energy transfer at surfaces. While the isotopic mass has essentially no effect on the electronic potential energy surfaces or the strength of

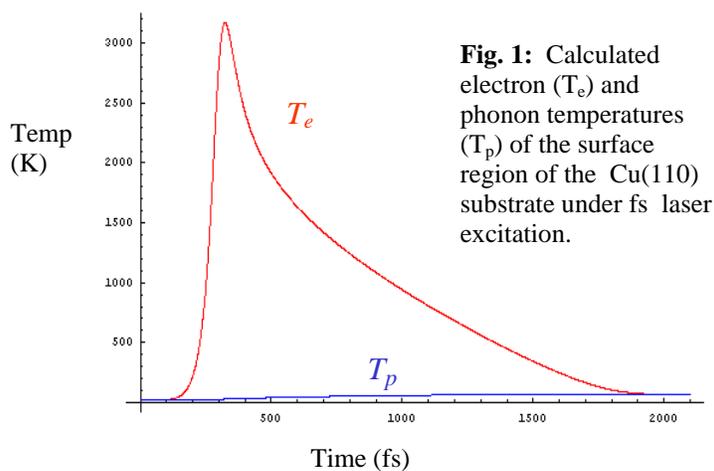
adsorbate/substrate electronic coupling, the isotopic mass of a molecule does determine its dynamics on a given potential energy surface, since its acceleration varies inversely with mass for the prescribed force.

For the O₂/Pd(111) system, the probability of laser-induced desorption under femtosecond laser excitation of the Pd substrate was examined for homonuclear molecules of the O¹⁶ and O¹⁸ isotopes. In this system, coupling of the nuclear motion of the adsorbed molecules to substrate electronic excitation is known to be strong, and desorption induced by femtosecond laser pulses occurs readily through energy transfer from substrate electronic excitations. Since the substrate electrons can be described to high accuracy by a thermalized energy distributions, it is natural to ask whether the coupling to the adsorbate nuclear degree of freedom is sufficiently strong that the electronically driven desorption process can be described simply as a transient thermal process occurring at the substrate *electronic* temperature.

Measurement of the isotope effect provides a direct answer to this basic issue in the description of the femtosecond laser-induced process. We have observed an isotope effect for the relative desorption yield of molecules with O¹⁶ compared with O¹⁸ of 1.8±0.3. Within the context of a quasi-thermal description of the process, such a large isotope effect cannot be understood. On the other hand, for nonequilibrium conditions very large isotope effects are known to occur. We have initiated work on a model of energy transfer to explain the observed isotope effect.

Surface Diffusion under Nonequilibrium Conditions:

The Heinz group in collaboration with the Bartels group has investigated the possibility of inducing lateral motion of adsorbates by means of high density of electronic excitation in a metal substrate. This experiment was conducted on a Cu(110) surface using adsorbed CO molecules. The system was chosen because the equilibrium diffusion properties have been extensively investigated by previous researchers. Also, a strong anisotropy in the diffusion rate parallel and perpendicular to the atomic rows of the Cu(110) surface was observed under conditions of thermal equilibrium.



To achieve the desired high density of electronic excitation, the Cu(110) substrate was irradiated with femtosecond laser pulses. The resulting substrate excitation exhibited a high density of electronic excitation at the surface. Following a coupled diffusion model, we have calculated the temporal evolution of the electronic and phononic temperatures in the substrate, as shown in Fig. 1.

The lateral motion of the adsorbed CO molecules induced by the electronic temperature transient was observed using scanning tunneling microscopy to characterize the atomic position of individual CO molecules before and after laser excitation. Because of the significant thermal expansion of the tip and sample (compared to the small tip-sample separation), the measurement required a novel experimental approach in which the tip was withdrawn from the sample during laser excitation. By careful implementation of the method, the same set of adsorbed molecules could be located after tunneling conditions were re-established.

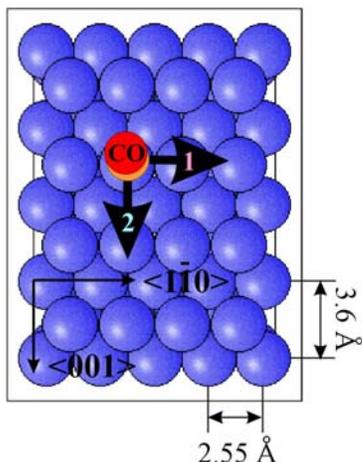


Fig. 2: Migration of CO molecules parallel (1) and perpendicular (2) to the atomic rows of the Cu(110) surface was observed by direct STM measurements.

In this fashion we have determined the absolute probability for motion of the CO parallel and perpendicular to the atomic rows of the Cu(110), indicated in Fig. 2. We found that electronically induced diffusion was possible. Moreover, the relative efficiency for motion in the two distinct directions differed sharply from that found for motion under conditions of thermal equilibrium.

These initial results demonstrate the possibility of inducing surface motion of adsorbates with electronic excitation and the distinct branching ratios that may occur in this regime compared with the usual thermal response. Modeling of these results is on-going in conjunction with Rahman's group at Kansas State.

DOE Interest

Catalytic reactions have great importance for a broad range of industrial and environmental processes. It is the aim of this project to explore new approaches that rely on recent developments in nanostructured materials and on advances in our fundamental understanding of molecule/surface interactions to produce catalysts with higher efficiency and greater selectivity, with the potential for impact on diverse and significant set of chemical processes.

Future Plans

Continuation of the above projects: The combined laser-STM experiments will be continued to gain an improved understanding of the role of non-equilibrium excitation conditions in inducing surface processes and reactions. Interest will focus on further studies of surface dynamics, as well as on the possibility of inducing and observing *biomolecular* surface reactions. Enhanced collaboration with Rahman's group and others will bring additional theoretical support for this project.

Investigations of nanostructured materials: In collaboration with Stephen O'Brien and Radoslav Adzik, we will examine the behavior of reactions, and particularly, photoinduced reactions on nanostructured materials. Both traditional surface science methods to study the behavior of the ensemble of molecules on surfaces and STM-based techniques capable of probing individual molecules will be explored. Material systems to be examined include metal oxide nanoparticles, as produced by O'Brien, and metallic nanostructures, as produced by Adzik.

Publications (2003-4)

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Controlling the Thermal and Non-Thermal Reactivities of Metal Oxide Structures Through Nanoscaling

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Goal

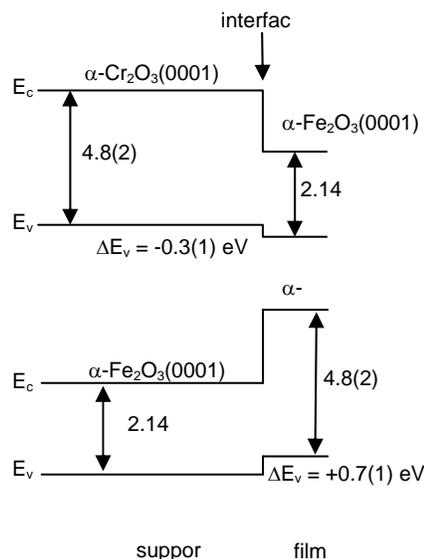
Explore the impact of nanoscaling the dimensions of a supported semiconducting metal oxide on its ability to promote photochemistry. Effective electron-hole pair separation can be achieved between a supported semiconducting metal oxide and its semiconducting host support when a band offset heterojunction is established. This project involves synthesis of model nanoscale oxide-oxide photocatalysts using molecular-beam epitaxy, characterization using a variety of atomic-level techniques, surface photochemistry and photodynamics studies, and theoretical modeling of structure and charge transfer.

DOE Interest

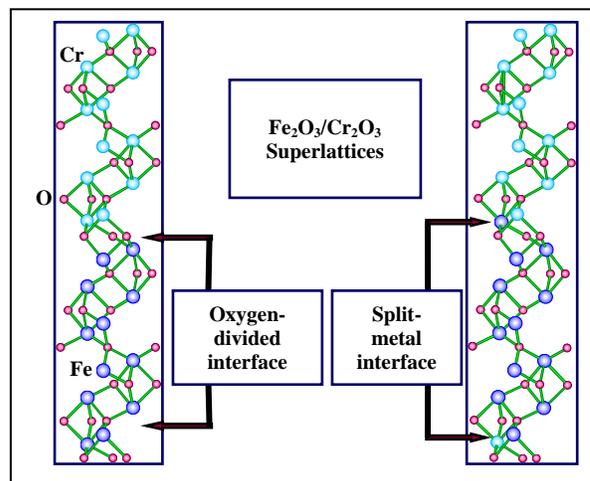
Advance basic understanding of heterogeneous photocatalysis with an emphasis on using nanotechnology to promote reactivity of supported oxide on oxide systems.

Recent Progress

- The α - $\text{Cr}_2\text{O}_3(0001)$ - α - $\text{Fe}_2\text{O}_3(0001)$ system provides a band offset interface in which the supported oxide forms an epitaxial film on the support. Layered film structures of these two materials maintain the in-plane lattice parameter of α - $\text{Fe}_2\text{O}_3(0001)$. Thus, the α - $\text{Cr}_2\text{O}_3(0001)$ layers are under a 2.4% tensile stress. A partial inward relaxation in α - $\text{Cr}_2\text{O}_3(0001)$ layers along the c axis is also observed, revealing the presence of artificially structured epilayers with a c/a ratio of 2.70, compared to 2.78 in bulk α - $\text{Cr}_2\text{O}_3(0001)$. The valence band offsets are -0.3 ± 0.1 eV and $+0.7 \pm 0.1$ eV when the top layer is Fe_2O_3 and Cr_2O_3 , respectively. The noncommutativity in band offset is not due to either anisotropic strain or quantum confinement, but rather appears to be due to a growth-sequence-dependent interface dipole. In either case, excitation of the α - Fe_2O_3 (band gap of ~ 2 eV) should result in a charge separation situation in which electrons (for α - Fe_2O_3 termination) or holes (for α - Cr_2O_3 termination) are available to react with adsorbed species.



- Using first-principles density functional theory, we have modeled the atomic, electronic and magnetic structure of epitaxial interfaces between α -Fe₂O₃(0001) and α -Cr₂O₃(0001). Our model was a superlattice with a period of about 27.5Å, corresponding to the shortest-period superlattice considered in a recent series of experiments (Chambers et al., Phys. Rev. B 61, 13223 (2000)). Two different epitaxial interface structures were studied: (i) an oxygen plane separating an Fe double layer from a Cr double layer, or (ii) a metal double layer split between Fe and Cr.



We found that these two structures are close

- in total energy but have distinct spin structure and different valence band offsets (chromia above hematite by 0.4 and 0.6 eV for (i) and (ii), respectively), possibly explaining the experimental non-commutative band offset seen in this system (0.3 ± 0.1 eV for hematite grown atop chromia, and 0.7 ± 0.1 eV for the reverse). We found that both the magnetic and electronic properties of the interfaces are further modified by the interfacial monolayer. For the split metal interface, which is favored through the growth pattern, the band offset can be changed from 0.62 eV (no interfacial) up to 0.90 eV with the Sc₂O₃ interfacial, and down to 0.37 eV with the Co₂O₃ interfacial. The band gap remains open for the interfacial monolayers based on Al, Ga, Sc, and Co, but it closes for Ti, V, and Mn. With iron ions coupled ferromagnetically in the (0001) plane and antiferromagnetically between neighboring layers, magnetic properties of thin films can be controlled through the number (even or odd) of iron layers.
- Identification of charge transfer and trapping sites on semiconducting oxide surfaces is of fundamental importance in furthering the field of heterogeneous photocatalysts. Using scanning tunneling microscopy, electron energy loss spectroscopy, and photodesorption, we observed both electron trapping and hole transfer events on the (110) surface of TiO₂ rutile. UV irradiation of a saturated monolayer of trimethyl acetate (TMA) on TiO₂(110) at room temperature resulted in hole transfer to the carboxylate group, followed by (CH₃)₃C-COO bond cleavage and desorption of CO₂ and isobutene/isobutane. Hole transfer to TMA proceeded in the absence of a gas-phase electron scavenger (which is typically O₂) because the accompanying photogenerated electrons could be trapped at the surface as Ti³⁺ cations bound to bridging OH groups. The extent of electron trapping, gauged by electron spectroscopy, correlated directly with the yields of photodesorption fragments resulting from the hole transfer channel. Charge at the Ti³⁺ sites was titrated in the dark via a reaction between O₂ and the Ti³⁺-OH groups.
- We have determined optimal parameters for formation of the single Cu₂O phase, crystalline nano-clusters on the SrTiO₃(100) substrate using oxygen plasma assisted MBE. The Cu₂O-SrTiO₃ system provides a band offset heterojunction in which holes should accumulate on the Cu₂O particles and excited electrons should transfer to the conduction band of the SrTiO₃ surface. Among a number of growth parameters, primarily substrate conditions (termination and defect density) have been found to control cluster shape and lateral distribution uniformity.

Future Plans

- Determine cross sections for photo-induced decomposition of a model organic (trimethyl acetic acid) on the α -Cr₂O₃(0001) / α -Fe₂O₃(0001) system as a function of α -Cr₂O₃(0001) film thickness to probe the effect of nanoscaling in 1-D on charge transfer across the oxide-oxide and oxide-adsorbate interfaces.
- Perfect the MBE growth of high-quality epitaxial films of SrTiO₃ on Si(001). Photon irradiation of this band offset system results in excited electron accumulation on the SrTiO₃ film. We are exploring several synthesis routes to achieve maximum film quality, while eliminating substrate oxidation. Subsequent, photochemical studies will be performed on the photodecomposition and photodesorption of methyl halides on this system.
- Perform femtosecond photo-reflectivity studies on model single and dual component photocatalysis to probe the impact of the oxide-oxide interface on lifetimes of electron/hole pairs.
- Model charge transfer across α -Cr₂O₃(0001) / α -Fe₂O₃(0001) interface including role of spin states and interfacial structure.
- Employing UHV based SPM for *in-situ* studies of surface photo- and thermal-chemistry of small molecules in the cluster-substrate systems. Main focus will be on getting information at atomic/molecular level (including for the non-conductive systems) and in the wide temperature range (~20-1000 K).

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Catalysis: Reactivity and Structure

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Collaborators: M.A. Barteau, J.M. White, C.H.F. Peden, D. A. Chen, C. P. Grey, A.I. Frenkel, A. Maiti, L. Gonzalez, J.-Y. Kim, M. Pérez, D.J. Szalda, M.E. Bussell, K. Nakamura, J. Gomes, J. Franz

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Goal

Provide an improved understanding of active sites on oxide, carbide, sulfide and phosphide catalysts. Modify the catalytic activity through the manipulation of the local electronic structure of the metal active site.

Synthetic and mechanistic understanding of reactivity of organometallic complexes related to catalysis.

Recent Progress

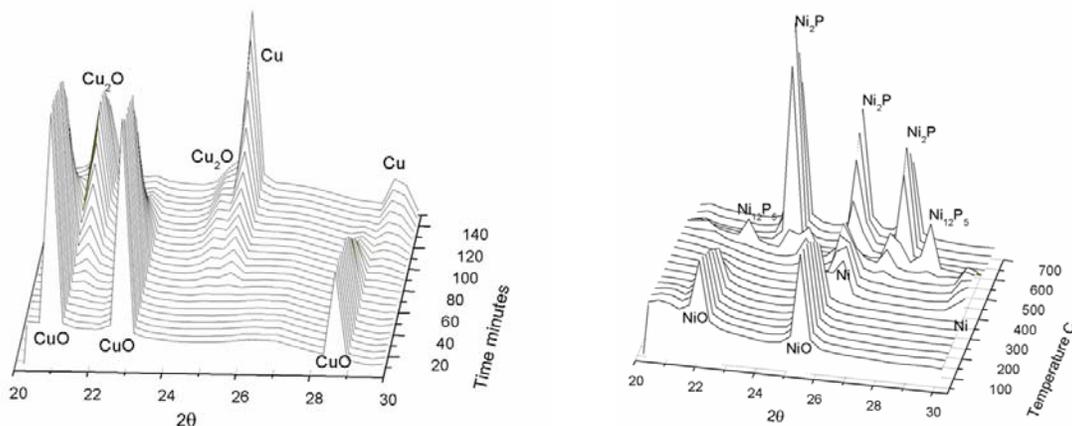
In the last three years our Catalysis group has been very actively investigating the generation of active sites on oxide surfaces through the creation of oxygen vacancies (TiO_2 , NiO , MgO , CeO_2) and metal doping ($\text{Cr}_x\text{Mg}_{1-x}\text{O}$, $\text{Zr}_x\text{Ce}_{1-x}\text{O}_2$). These active sites have been characterized and their properties studied, using synchrotron-based techniques such as photoemission and near-edge X-ray absorption spectroscopy in combination with density functional calculations. In this area, we have focused mainly on oxides that are involved in the destruction of air pollutants. Our studies illustrate the important role played by O vacancies in desulfurization reactions on titania, and the tremendous impact that metal doping can have on DeSO_x and DeNO_x reactions on MgO and CeO_2 . The cases of $\text{Cr}_x\text{Mg}_{1-x}\text{O}$ and $\text{Fe}_x\text{Mg}_{1-x}\text{O}$ are particularly interesting because the dopant element is “trapped” in a relatively low oxidation state. Cr_2O_3 and Fe_2O_3 (with the metal cations in a “+3” oxidation state) are the most common oxides of chromium and iron. But Cr^{2+} and Fe^{2+} can be expected from a charge balance in $\text{TM}_x\text{Mg}_{1-x}\text{O}$. Indeed, results of core-level photoemission and XANES indicate that the formal oxidation state of Cr and Fe atoms in $\text{TM}_x\text{Mg}_{1-x}\text{O}$ is close to “+2”. The behavior of $\text{Cr}_x\text{Mg}_{1-x}\text{O}$ and $\text{Fe}_x\text{Mg}_{1-x}\text{O}$ illustrates a fundamental property for designing chemically active mixed-metal oxides: the second metal or dopant agent is not fully oxidized (*i.e.*, not in a high oxidation state) and provides occupied electronic states with a low stability. This property makes possible effective interactions between the oxide surface and the LUMO of SO_2 , with subsequent S-O bond cleavage.

In conjunction with projects in the Catalysis on the Nanoscale program at BNL, we started a research program to investigate the behavior of surfaces of early transition metal carbides. Density functional theory was employed to study the stabilities and chemical

activities of several metal carbide surfaces: $\text{Mo}_2\text{C}(001)$, $\text{MoC}(001)$, $\text{TiC}(001)$, and $\text{VC}(001)$. Typically, pure early transition metals are very reactive elements that bond adsorbates too strongly to be useful as catalysts. In general these systems are not stable in a chemical environment. The inclusion of C into the lattice of an early transition metal produces a substantial gain in stability. Furthermore, in a metal carbide, the carbon atoms moderate the chemical reactivity through ensemble and ligand effects leading to a better catalyst according to Sabatier's principle.

Metal carbides can be very good catalysts for hydrodesulfurization processes and have the potential to replace metal sulfide catalysts in oil refineries. We investigated the interaction of sulfur and sulfur dioxide with $\text{TiC}(001)$ using photoemission and first-principles density-functional calculations. Contrary to common assumptions, our studies revealed the existence of strong $\text{S}\leftrightarrow\text{C}$ interactions. The carbon atoms are not simple spectators, and play an important role in the energetics for the dissociation of S-O bonds.

The development of techniques for characterizing the structural properties of catalysts under the high-pressure conditions of industrial processes is widely recognized as a top priority in the area of heterogeneous catalysis. At the NSLS beam line X7B, we have put together a facility capable of conducting *in situ*, sub-minute TR-XRD experiments under a wide variety of temperature and pressure conditions ($80\text{ K} < T < 1250\text{ K}$; $1\text{ Torr} < P < 150\text{ atm}$). Current measurements also include control of gas flow and measurement of gas composition of the products with mass spectrometry. This important advance results from combining the high intensity of synchrotron radiation with new parallel data-collection devices. Using TR-XRD, one can obtain information about structural details, phase composition, kinetics of transformation, intermediate phases and crystal characteristics. Examples of problems studied to date with TR-XRD include: (1) hydrothermal synthesis of zeolites and mesoporous materials and substrate binding of zeolites; (2) reduction/oxidation of oxide catalysts (see figure, left side); (3) changes to the AlF_3 structure when it becomes an active catalyst; and (4) the synthesis of metal phosphide catalysts (see figure, right panel).



In situ diffraction patterns during the reduction of CuO with limited CO flow (left); *in situ* diffraction patterns during the synthesis of HDS catalysts (right).

Ionic hydrogenation catalysts based on the inexpensive metals molybdenum and tungsten have been developed based on mechanistic understanding of the individual steps

required in the catalytic reaction. These hydrogenations proceed by H^+ transfer from a cationic dihydride followed by H^- transfer from a neutral metal hydride; insertion reactions required in traditional catalysts are not needed. A series of Mo and W complexes of formula $[Cp(CO)_2(PR_3)M(O=Ct_2)]^+$ were shown to serve as catalyst precursors for the ionic hydrogenation of ketones, but their stability is limited by dissociation of a phosphine, which is protonated to give HPR_3^+ under the reaction conditions. Suppression of phosphine dissociation was sought by using a two-carbon bridge to chelate the phosphine to the cyclopentadienyl ligand. Improved performance was found using catalysts obtained by reaction of $HMo(CO)_2[\eta^5:\eta^1-C_5H_4(CH_2)_2PR_2]$ ($R = Ph, Cy, ^tBu$) with $Ph_3C^+BAr'_4^-$. Advantages found with these new complexes include low catalyst loadings (< 0.4 mole %), higher thermal stability, substantially longer lifetimes (hundreds of turnovers), and hydrogenation of liquid ketones under solvent-free conditions. Recent efforts have focused on N-heterocyclic carbene ligands rather than phosphines. Hydride abstraction from $CpW(CO)_2(IMes)H$ ($IMes =$ the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) produces $CpW(CO)_2(IMes)^+$ which was shown to have a weak interaction between the metal and one $C=C$ bond of a mesityl ring. This cationic complex is a catalyst precursor for catalytic hydrosilylation of ketones. An unusual property is observed in the hydrosilylation of aliphatic substrates – the catalyst precipitates at the end of the reaction, facilitating recycle and reuse of the catalyst. These hydrosilylations are carried out in neat ketone/ $HSiEt_3$, so that no solvent is used in either the reaction or the catalyst recycling.

DOE Interest

Studies of more efficient and selective catalysts for energy conservation and transformation; understanding the performance of catalysts for hydrocarbon transformations and the control of environmental pollution.

Future Plans

The focus of this research program will be on understanding the active sites of catalysts based on carbides, sulfides, nitrides and phosphides of early-transition metals. These compounds can have low cost and very good performance as catalysts. The phenomena responsible for the catalytic properties of the early-transition metal compounds are not well understood. We are particularly interested in correlations between electronic properties and catalytic activity.

The experience and knowledge gained in our past studies will be very useful for our future work, where we will be working with oxides as supports, and investigating the chemistry of desulfurization, hydrocarbon transformations, $DeSO_x$ and $DeNO_x$ processes on bulk compounds or nanoparticles of carbides, sulfides, nitrides and phosphides.

Future experiments in homogeneous catalysis will seek improved catalysts, using carbene ligands and partially fluorinated phosphines. A challenge for future development is to tailor catalysts and hydrosilanes with the aim of engaging a broader scope of substrates into solvent-free reactions with catalyst self-separation. This will require a better fundamental understanding of the factors governing miscibility of these complexes and their phase behavior.

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Structure and Electronic and Catalytic Properties of Oxide Nanostructures with Controlled Domain Size and Connectivity

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Goals

This program addresses the design, synthesis, and structural and functional characterization of small oxide domains useful in oxidation and acid catalysis. One component of this program is a collaboration with Alexis T. Bell and it has focused on oxidative dehydrogenation of alkanes on MoO_x and VO_x oxides. This component includes efforts to synthesize materials with controlled Mo-O-V connectivity and to develop UV-visible, Raman, and infrared methods for the structural characterization of complex oxides. A parallel component aims to develop more effective acid and redox catalysts based on molecular polyoxometallate (POM) and noble metal oxide clusters. These latter efforts have led to mechanistic details of the bifunctional pathways required for the synthesis of complex oxygenates from methanol, which these oxide clusters catalyze with unprecedented rates and selectivities near ambient temperatures. They have also led to titration methods useful to determine the number of active sites and their catalytic chemistries and to the synthesis of hybrid organic-inorganic catalysts consisting of oxide clusters modified by organic bases for independent control of redox and acid functions. This latter component represents a spin-off from our previous studies in acid and oxidation catalysis.

Recent Progress

Oxidative Dehydrogenation (ODH) of Alkanes on Supported Oxide Domains (with Alexis T. Bell)

Kinetic and isotopic studies have led to a detailed mechanistic picture of ethane and propane ODH on VO_x and MoO_x catalysts. C_2H_6 - C_2D_6 - O_2 led to alkenes without concurrent formation of $\text{C}_2\text{H}_{6-x}\text{D}_x$ indicating that C-H bond activation is irreversible; kinetic isotope effects showed that C-H activation limits overall rates and occurs at methylene C-H bonds in propane. $^{16}\text{O}_2$ - $^{18}\text{O}_2$ - C_2H_6 reactions on V^{16}O_x domains led to ^{16}O in initial H_2O and CO_x products, consistent with the involvement of lattice oxygens in redox cycles. No $^{16}\text{O}^{18}\text{O}$ isotopomers formed from $^{16}\text{O}_2$ - $^{18}\text{O}_2$ - C_2H_6 mixtures, as expected from irreversible O_2 dissociation steps. This catalytic sequence accurately describes the kinetic dependence of ODH rates on C_2H_6 , O_2 , and H_2O and suggests that lattice oxygens, vacancies, and OH groups are the most abundant reactive intermediates. The reactivity of exposed MoO_x and VO_x species increased with MO_x surface density, as UV-visible and Raman spectroscopies detect a gradual evolution of structure from isolated MO_x species to oligomers and crystallites. Alkene yields and selectivities were highest on isolated MO_x species and increased with temperature. Homogeneous oxidation reactions prevalent above 800 K were controlled by O_2 staging strategies, which extended operation to temperatures causing homogeneous combustion in co-fed reactors.

A mechanistic connection between propane ODH and ligand-to-metal electronic transitions near the UV-visible absorption edge in dispersed metal oxides was established for VO_x , MoO_x , WO_x , and NbO_x domains of varying size on Al_2O_3 , ZrO_2 , and MgO . ODH turnover rates increased as absorption edge energies decreased. Electron transfer during both C-H bond

activation and ligand-to-metal transitions becomes more facile with increasing oxide domain size, leading to more stable activated complexes in C-H activation steps. Pre-edge features in UV-visible spectra were recently used to measure directly the number of reactive intermediates during steady-state and transient catalytic reactions and led to the first quantitative determination of the number of reduced centers prevalent during reaction and of rate constants for individual C-H bond activation and vacancy re-oxidation during alkane ODH. We find, consistent with our previous conclusions, that the extent of reduction during catalysis increases with VO_x domain size.

VO_x species dispersed on MoO_x oligomers coated on Al_2O_3 were used to probe the influence of Mo-O-V and interactions with supports on alkane ODH. Preliminary reaction and characterization data showed that atomic mixing occurs and that it leads to surface reactivities intermediate between the pure active oxides and to slight improvements in alkene selectivities and attainable yields.

Acid Catalysis on Supported WO_x Nanostructures

Supported and unsupported WO_x clusters prepared by anchoring of aqueous molecular and ionic complexes consist of well-defined domains detected by Raman, UV-visible, and X-ray absorption spectroscopic methods and by titration of Bronsted or Lewis acid sites using selective probes. Alcohol dehydration rates (per W-atom) occurs on Bronsted acid sites formed during catalysis and they reached maximum values on polytungstate domains prevalent at intermediate WO_x surface densities on Al_2O_3 , ZrO_2 , SiO_2 , and SnO_2 supports. Dehydration occurs on Bronsted acid sites, the number of which was measured during catalysis by titration with 2,6-di-tert-butylpyridine and by in situ UV-visible spectroscopy. The number of acid sites depends sensitively on the support, because of its marked effects on domain size and reducibility, but turnover rates (per Bronsted acid site) were essentially unaffected by the support.

Bifunctional Redox-Acid Catalysis on Polyoxometallate and Noble Metal Oxide Clusters

We have shown in a parallel program that V-Mo POM and RuO_x clusters catalyze oxidative reactions of methanol and dimethylether with unprecedented selectivities to complex oxygenates via previously unrecognized bifunctional redox-acid pathways. Rates, stability and selectivity significantly exceed those reported previously for one-step oxidative syntheses. These materials were incorporated into this project, which started during 2002, in an effort to understand and exploit the observed acid-redox pathways involved in methylal and methylformate synthesis and to extend the use of hybrid organic-inorganic catalysts to control relative contributions from acid and redox functions. More recently, we have shown that RuO_x and PdO_x clusters catalyze these bifunctional reactions near ambient temperatures with much higher rates and selectivities than supported POM clusters. This project addresses also the development of site titration and spectroscopic methods to measure the density of acid and redox sites and the local structure and electronic properties in multi-component dispersed oxides with well-defined domain size and atomic connectivity.

Dispersed oxide domains were prepared via anchoring of solvated precursors on oxyhydroxide colloids and by attaching organometallic precursors and Keggin POM structures with binary oxide shells on hydroxylated oxide support surfaces. Kinetic and mechanistic studies showed that reactions occur via initial HCHO formation on active oxide clusters in catalytic sequences limited by C-H activation in adsorbed methoxides, followed by acetalization and dehydrative condensation reactions leading to methylformate and methylal, in some cases with significant involvement of support surface sites. HCHO synthesis occurs via catalytic redox cycles similar to those proposed previously for methanol oxidation on Fe-Mo oxides, but at significantly lower temperatures, apparently because of the facile redox cycles available on reducible POM and noble metal oxide clusters. At relevant methanol concentrations, rates become limited by O_2 dissociation, a kinetic hurdle that we have recently overcome by exploiting

the higher oxygen chemisorption energies of Ru and Pd metal clusters relative to metal-oxygen bond energies in the corresponding oxides. This coupling of oxidative dehydrogenation and acid chemistries has not been rigorously exploited and opens up significant opportunities for the synthesis of complex oxygenates using in situ formed HCHO intermediates and methanol and dimethylether reactants produced in emerging large-scale deployments of natural gas conversion technologies.

Research Plans

Studies of the synthesis and characterization of well-defined monolayer supported oxide catalysts will continue with emphasis on concurrent development of techniques to determine the structure, density, and reactivity of active oxygen species and the atomic connectivity among metal centers in complex oxide clusters. Mechanistic studies of oxygen insertion and hydrogen abstraction steps will continue with increasing involvement of theoretical methods to probe the electronic and chemical properties of oxide nanostructures and their vibrational spectra. Synthesis methods will exploit sequential deposition of oxides monolayers as two-dimensional oligomers followed by the anchoring of another oxide in efforts to extend the type and composition of heterolinkages and to probe their local structure and their reactivity in C-H activation steps. These materials pose significant structural characterization challenges because of the catalytic relevance of local structure and heteroatom connectivity. Raman, UV-visible, and X-ray absorption probes of inorganic structures and infrared spectra of unreactive probes adsorbed at low temperatures (H_2 , N_2 , CO , CO_2), aided by theoretical models, will be used to develop a structural picture of these dispersed binary oxides. Methanol and alkane oxidation reactions will be used to probe the catalytic consequences of atomic connectivity among components. Also, our recent mechanistic insights into alkane oxidation pathways will be extended to higher alkanes, in which the presence of C-H bonds at primary, secondary, or tertiary carbon atoms introduce additional routes for H-abstraction and oxygen insertion steps. In situ UV-visible spectroscopic methods will be extended to these oxidation reactions and to catalysts based on POM and noble metal oxide clusters useful in methanol oxidation reactions to measure the number of reduced centers during selective oxidation of alkanes and alkanols. Specifically, the potential of these methods to obtain otherwise inaccessible rate parameters for elementary steps for realistic materials and conditions will be exploited by extending these methods to catalytic systems of greater organic and inorganic complexity.

Our on-going research also exploits and extends our recent findings about the remarkable activity and selectivity of small domains of noble metal oxides in oxidation reactions. Previously, these materials have been considered excellent combustion. As small domains and at much lower temperatures, however, their tendency to reduce more slowly than bulk crystallites, opens selective oxidation channels unavailable in bulk oxides at higher temperatures. The detailed pathways for bifunctional redox-acid pathways for methanol and dimethylether conversion to complex oxygenates will be probed on supported RuO_x and PdO_x clusters using kinetic and isotopic methods; exploratory reactivity studies will examine the behavior of other dispersed noble metal oxides. The structure and redox properties of these clusters will be determined by in situ Raman and UV-visible spectroscopies, using methods that we recently developed for assessing the electronic structure and the concentration of reduced centers during catalysis. The identity and reactivity of reactive intermediates and the oxidation state of bulk and surface metal atoms will be determined by combining infrared and X-ray absorption spectroscopies during catalysis. The number and role of Bronsted acid sites will be probed using titration with hindered organic bases during reaction. Specific effects of supports on the dispersion and reducibility of Ru and Pd oxide domains and on the rate and selectivity of secondary reactions will be explored by varying oxide dispersion through changes in surface density, synthetic protocols, and thermal treatments. Theoretical studies of redox potentials of noble metal oxides with varying cluster size

will be used to develop systematic protocols for choosing compositions and sizes most effective for specific reactions. Finally, we will start exploratory evaluations of these materials for oxidation reactions of alkanes and alkenes and for the coupling of HCHO intermediates formed in methanol and dimethylether oxidation reactions with support functions able to catalyze C-C formation reactions via aldol condensation and related pathways.

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New Tools for CO₂ Fixation by Homogeneous Catalysis

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Goal

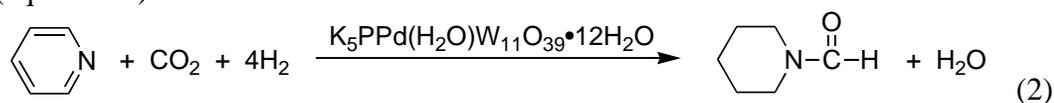
The development of new or more efficient methods for the conversion of CO₂ into useful organic products, via the design or discovery of new catalysts, ligands, solvents, and methods.

Recent Progress

New CO₂ hydrogenation catalysts: The application of homogeneous catalysis is hampered, at least partly, by over-reliance on complexes of the extremely expensive platinum-group metals. A study⁷ of the catalytic activity of combinations of phosphine and amine ligands with other transition metal salts as potential CO₂ hydrogenation catalysts (cf. equation 1) has revealed Ni- and Fe-containing catalysts that have up to three orders of magnitude greater than the activity of the only previously-known catalyst outside of the platinum group metals.



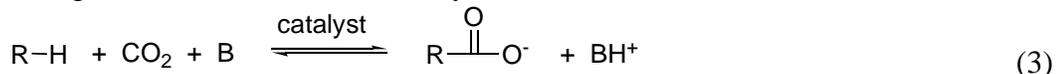
The co-hydrogenation of CO₂ and aromatic amines catalyzed by a Pd/W cluster was found to give alkylformamides via simultaneous hydrogenation of C=C, C=N and C=O double bonds (equation 2).



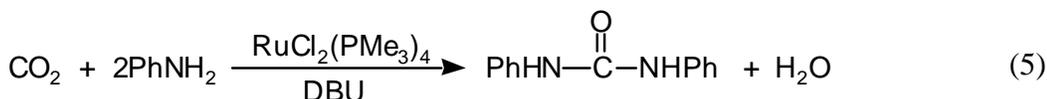
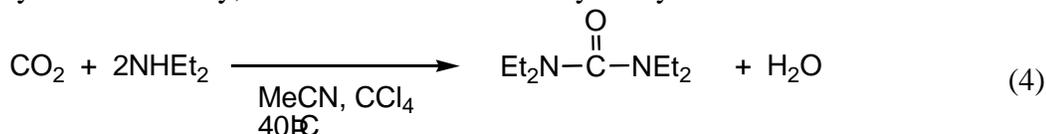
Spectroscopic and crystallographic studies of the catalysts for CO₂ hydrogenation: The group of Dr. John Linehan (PNNL) and the Jessop group together determined the structures of some of the complexes generated from the catalyst precursors RuCl(OAc)(PMe₃)₄ and RuCl₂(PMe₃)₄, identified most of the major species present during the catalysis, and found an explanation for the effect of various acidic promoters on the catalytic activity.² The same efforts led to strong evidence that the previously-accepted mechanism for CO₂ hydrogenation by Ru catalysts is incorrect. With the new mechanism in mind, a cationic catalyst precursor was prepared and found to be as active as RuCl(OAc)(PMe₃)₄ without any need for acidic promoters.

Catalytic carboxylation: While the use of an amidine base has been known to promote the insertion of CO₂ into particularly acidic C-H bonds such as those of fluorene, the method

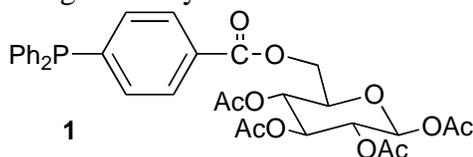
has not been reported for compounds containing significantly less acidic C-H bonds. We have used high-throughput screening methods to identify catalysts capable of promoting this reaction. Early screening has given us several promising hits, which we are now working to confirm using conventional-scale chemistry.



Synthesis of Substituted Ureas: Substituted ureas can be prepared catalytically from amines and CO₂, but at temperatures below 100°C the yields are extremely low. We have developed a catalyst-free method for this reaction, which gives tetraalkylurea in up to 71% isolated yield.¹ Similarly, we have found a Ru-catalyzed synthesis of carbanilide.⁴



Lewis basic bifunctional phosphines Utilization of CO₂ as a solvent for catalysis is also of interest but requires the identification of catalysts that are CO₂ soluble. In a search for an aromatic phosphine that is more CO₂-soluble than PPh₃, the Jessop group in collaboration with Dr. Eric Beckman at the University of Pittsburgh has found two phosphines, **1** and tris(2-furyl)phosphine, that are significantly more soluble in scCO₂ than is PPh₃.



Obedient Catalysts: An “obedient” catalyst would be one that reversibly changes its nature when it is commanded to do so by the operator; the command would take the form of some chemical or physical trigger. In collaboration with the Eckert group, we have found that expansion of an organic solvent by the application of gaseous (subcritical) CO₂ increases the fluorophilicity of the solvent to such an extent that the solvent is able to dissolve highly fluorinated complexes or catalysts: the complex precipitates and can be captured by fluorosilica when the CO₂ pressure is released. This can be used as a *new method for catalyst recovery*, in which the fluorosilica is omitted or replaced by fluorinated silica, the fluorosilica catalyst is induced to dissolve in the organic solvent by the presence of CO₂, and the recovery of the catalyst after the reaction is achieved by release of the CO₂ pressure.⁸ *The catalyst is homogeneous during the catalysis and heterogeneous during the separation.*

Utilization of CO₂ in combination with new solvents: In work partly funded by this grant, the group has discovered a new method for recovering and recycling homogeneous catalysts without the use of volatile or halogenated organic solvents. The combination of supercritical CO₂ and liquid polymer (poly(ethylene glycol)) gives a biphasic solvent system which is environmentally benign, nontoxic, extremely inexpensive in materials, and very efficient for catalyst recycling. Application of this method to hydrogenations, including the fixation of CO₂, has also been achieved.

DOE Interest

Development of new catalysts for hydrogenation and C-H insertion reactions of CO₂ could result in wider use of waste CO₂ as an inexpensive feedstock that does not rely on the availability of oil. The products of CO₂ insertion into C-H bonds already include aspirin, but given appropriate catalyst identification a much wider range of products could be prepared.

The discovery of the entirely nontoxic and benign solvent system of PEG and scCO₂ makes it possible to use, recover and recycle homogeneous catalysts without the use of volatile organic solvents and without significant heavy metal contamination of the product. The method has the potential to increase the usage of homogeneous catalysis in industry, not only for CO₂ fixation but for many reactions, by eliminating the usual weakness of homogeneous catalysts – the separation problem.

Future Plans

1. To develop and study catalysts and promoters for the synthesis of carboxylic acids (by insertion into C-H bonds).

2. To develop bifunctional ligands capable of secondary interactions with CO₂, and to demonstrate the effect of those interactions on rates or equilibrium constants of reactions and the efficiency of catalysis involving complexes of those ligands.

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Basic Principles that Govern the Interaction of Organometallic Catalysts with Supports – The Science of Immobilized Molecular Catalysts

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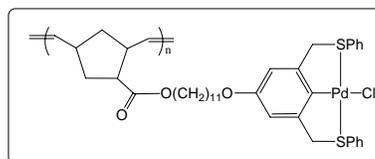
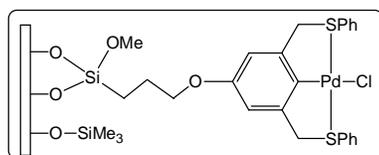
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Goal

To develop fundamental rules that guide the design of immobilized organometallic catalysts by conducting long-term, systematic studies utilizing an interdisciplinary approach that combines theory and computation with experiment.

Recent Progress and Work Underway

In this new project, metal complexes based on two established ligand systems (salen and pincer) are being explored on several different supports by a combination of experiment and theory/simulation. Initial investigations have focused on the Pd(II) SCS and PCP pincer system immobilized on both polymeric and silica supports. These complexes are at the center of a debate about the mechanism of Heck and Suzuki couplings catalyzed by palladacycle catalysts.

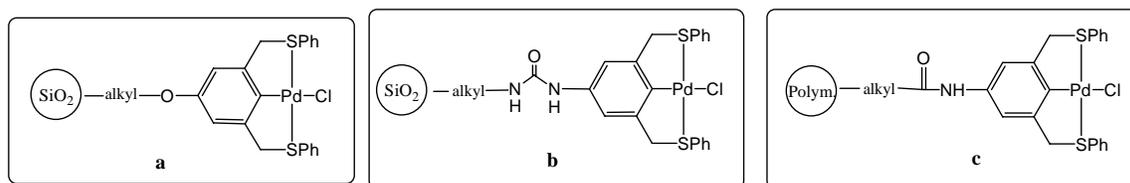


Heck Couplings with Pd-SCS pincer complexes: There are several reports in the literature that have identified Pd(II) pincer complexes as ideal catalysts for immobilization to allow for recoverable and reusable Heck catalysts. This idea stems from the observation that the complexes are stable at high temperatures in a variety of solvents and the fact that the reaction can be carried out under air. We have shown that the Pd-SCS complexes that we have prepared (see above) decompose under reaction conditions and that homogeneous palladium species are the true catalyst¹. Thus, these are not recoverable and recyclable catalysts.

Mechanism of Heck Coupling with Pd(II)-SCS pincer precatalysts: We have found that these complexes decompose under reaction conditions to form soluble Pd(0) catalytic species when using both polymeric or silica-supported precatalysts. These palladium species are likely present in the form of molecular Pd(0) moieties in equilibrium with Pd(0) colloids¹. Control

experiments indicate that molecular Pd(0) is the actual active species. These observations contradict the hypothetical mechanism that was postulated for these catalysts due to their stability under reaction conditions (reducing conditions) - a novel Pd(II)-Pd(IV) cycle. Indeed, this work indicates that a Pd(0)-Pd(II) cycle is more plausible¹, as suggested for the related half-pincer complexes and all other well-established Pd systems.

Role of Linker Structure on Catalytic Behavior: Subtle changes in the ligand/linker structure may drastically affect the catalyst stability and behavior. Previously, there have been reports that Pd(II)-SCS-pincer complexes tethered to soluble polymers via an alkyl chain with an amide linkage to the aromatic ring are stable, recyclable catalysts (complex C below). This is in contrast to our findings with polymer and silica-immobilized complexes with ether linkages to the surface tether, as described above and shown in complex A below. To probe these differences, we have prepared Pd(II)-SCS complexes immobilized on silica via a urea connection to the alkyl surface linkage (complex B below). The silica-immobilized catalyst behaves exactly like the systems with the ether tether. However, the homogeneous analogue displays some activity even in the presence of Hg(0), which should extinguish all activity associated with Pd(0) catalysts. Thus, it appears that there is a distinct difference between soluble (polymer and homogeneous) and insoluble (silica) systems with amide or urea linkages. With these systems, a Pd(II)-Pd(IV) catalytic cycle may still be a possibility. Investigations into these systems are ongoing.



Role of Ligand Structure on Catalyst Stability: Exploratory quantum calculations are being utilized to assess the influence of subtle ligand changes on complex stability. As the complexes with ether linkages have been shown via experiment to be less stable than those with amide or urea linkages, the subtle electronic influence of these groups on Pd-ligand bonds are being explored. Furthermore, complexes that give stronger ligand-metal interactions are being explored computationally [Pd(II)-PCP].

Influence of Polymer Backbone Structure on Catalyst Accessibility: A combined experimental and modeling study is underway aimed at elucidating the role of polymer backbone structure in solution on catalyst accessibility and thus, catalyst activity. A series of polynorbornene and polyoctene polymers with side chains containing simple acidic groups have been prepared. Catalytic productivity in simple test reactions will be correlated with polymer backbone structure (rigid rod vs. random coil) as determined by multidimensional NMR and molecular modeling.

DOE Interest

Fundamental rules that allow for the design of stable, recyclable immobilized organometallics is a “holy grail” of catalysis science. Such discoveries would enable lower cost, more selective and more environmentally benign catalytic transformations. In particular, a general methodology to allow for chiral heterogeneous catalysis would have tremendous impact. In addition, Pd-catalyzed carbon-carbon bond forming reactions are of tremendous commercial importance.

Future Plans

Elucidating the Catalytic Mechanism for PCP, NCN and SCS Pd(II) precatalysts: It is critical to determine if any of these catalysts are capable of promoting the Heck and Suzuki coupling reactions as stable complexes utilizing a Pd(II)-Pd(IV) cycle. If so, they are ideal catalysts for immobilization. This work will combine experimental investigations including *in-situ* spectroscopy and quantum computational studies.

Gold Nanoparticles as Solution Supports: Gold nanoparticles decorated with metal complexes attached via thiol-Au interactions will be prepared and evaluated alongside similar catalysts on polymeric and silica supports.

Mn, Co, Cr Salen Complexes: Chiral salen complexes of several transition metals will be prepared and evaluated as catalysts for a variety of reactions on polymeric and silica supports.

Publications (September 2003-present)

- 1) Yu, K.; Sommer, W.; Weck, M.; Jones, C. W.; Silica and Polymer-Tethered Pd-SCS-Pincer Complexes: Evidence for Precatalyst Decomposition to Form Homogeneous Catalytic Species in Mizoroki-Heck Chemistry, manuscript submitted, March 12 2004.

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Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds

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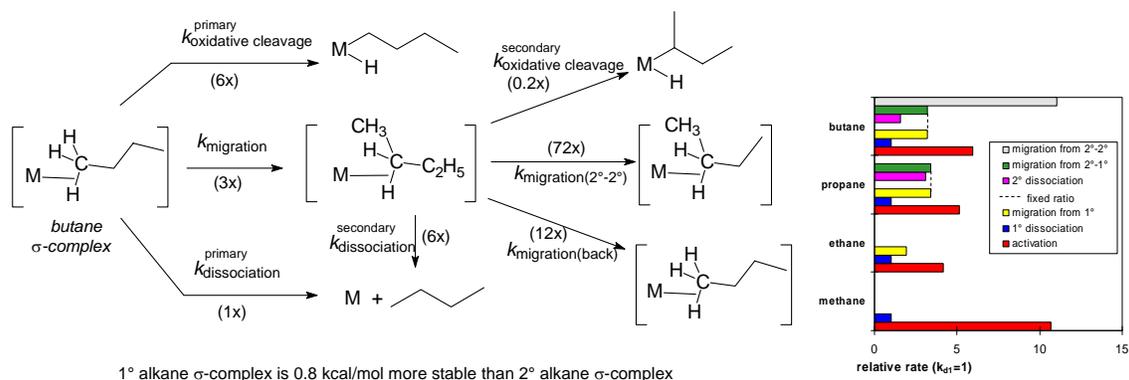
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Goals

Fundamental studies of the reactivity of metal complexes with C–H and C–C bonds in saturated and unsaturated hydrocarbons that include: (1) discovery of new carbon-carbon bond cleavage reactions, (2) fundamental studies of C-H bond cleavage reactions of trispyrazolyl-boraterhodium complexes, (3) catalytic C-H and C-C bond functionalization, and (4) carbon-fluorine bond activation.

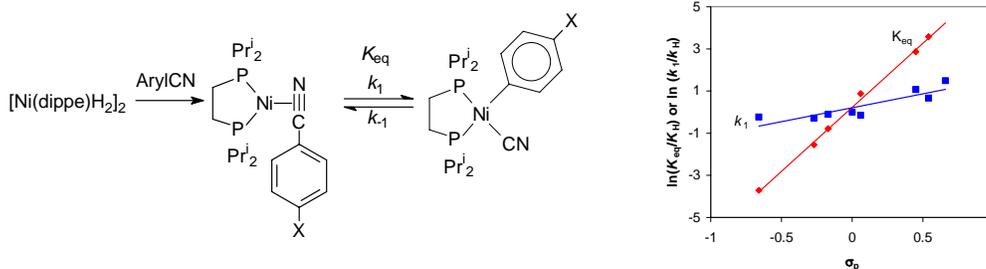
Recent Progress

Relative rates of processes in primary (1°) and secondary (2°) alkane complexes.
Our rhodium-trispyrazolylborate studies on hydrocarbon activation make use of the reactive 16-electron fragment [HB(3,5-dimethylpyrazolyl)₃]Rh(CNCH₂CMe₃), abbreviated herein as Tp⁺RhL. In the current project period, we established that (1) the Tp⁺RhL fragment coordinates to a linear alkane to give a σ -complex and that the coordination is favored at the methyl group over the methylene group by a ratio of 2.5:1. (2) a methyl group in pentane coordinates 1.9 times faster than the more hindered methyl group of isobutane. (3) the oxidative cleavage of a methyl C-H bond (primary C-H) occurs 28.5 times faster than the C-H bond in a methylene group (secondary C-H). These conclusions were made building upon our earlier studies of the relative rates of oxidative cleavage, migration, and dissociation indicated below. The relative rate of secondary activation can now be included in this scheme.

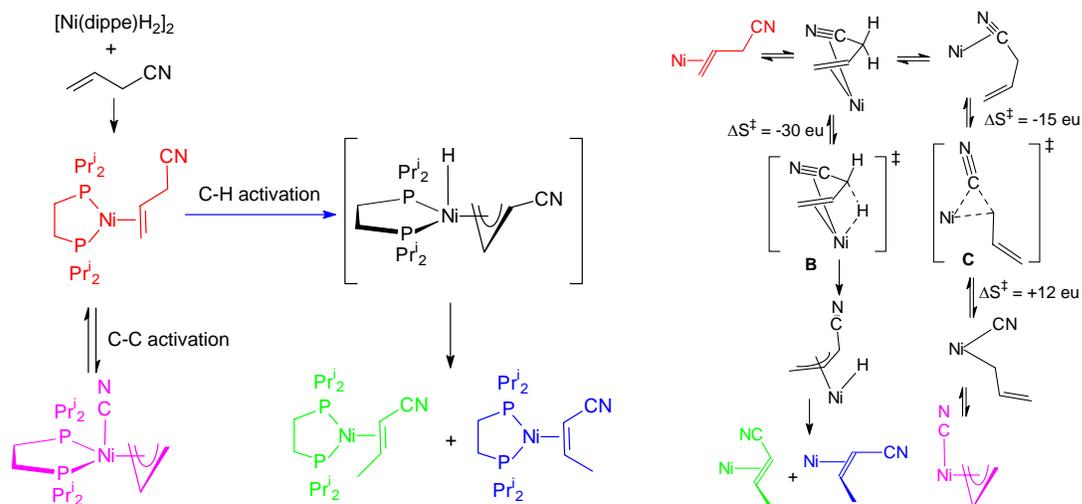


C-C Bond Cleavage Studies-C-CN cleavage in aryl nitriles. We have discovered that aryl nitriles undergo sp^2 - sp C-CN cleavage when reacted with NiL₂ fragments, and η^2 -nitrile adducts can be observed as reaction intermediates. The reaction is quite general, and can be controlled via the electronic demands of the aryl group as shown in

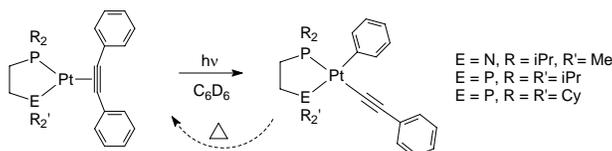
the equation below. K_{eq} was found to be strongly dependant ($\rho = +6.1$) on the electronics, whereas the rate of cleavage k_1 was found to be less dependant ($\rho = +1.3$).



C-C Bond Cleavage Studies-C-CN cleavage in allylnitriles. C-C cleavage of allylnitriles at a nickel metal center has been found to generate both a strong metal-cyanide bond and a π -allyl ligand, and has been found to be both facile and reversible. Indeed, this reaction forms the basis of DuPont's synthesis of adiponitrile for the production of nylon via addition of HCN to butadiene. As summarized below, the intermediate can be seen and the temperature dependent rates be used to establish the mechanism of reaction, in which key transition states **B** and **C** are differentiated by their widely different entropies of activation (ΔS^\ddagger) for formation from the olefin complex or the π -allyl cyanide complex.

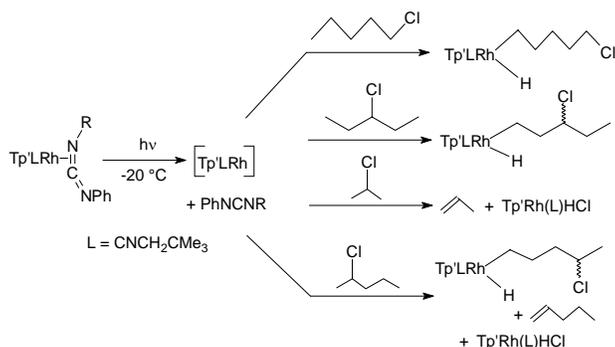


C-C Bond Cleavage Studies-C-CN cleavage in arylacetylenes. We have also discovered an important new type of C-C bond oxidative addition, cleavage of sp - sp^2 C-C bonds in aryl acetylenes. This is a *new class* of C-C bond cleavage, and offers many exciting possibilities. We have found that irradiation of either P-P or P-N chelate complexes of Pt-(diphenylacetylene) leads to the clean and quantitative formation of the oxidative addition product.

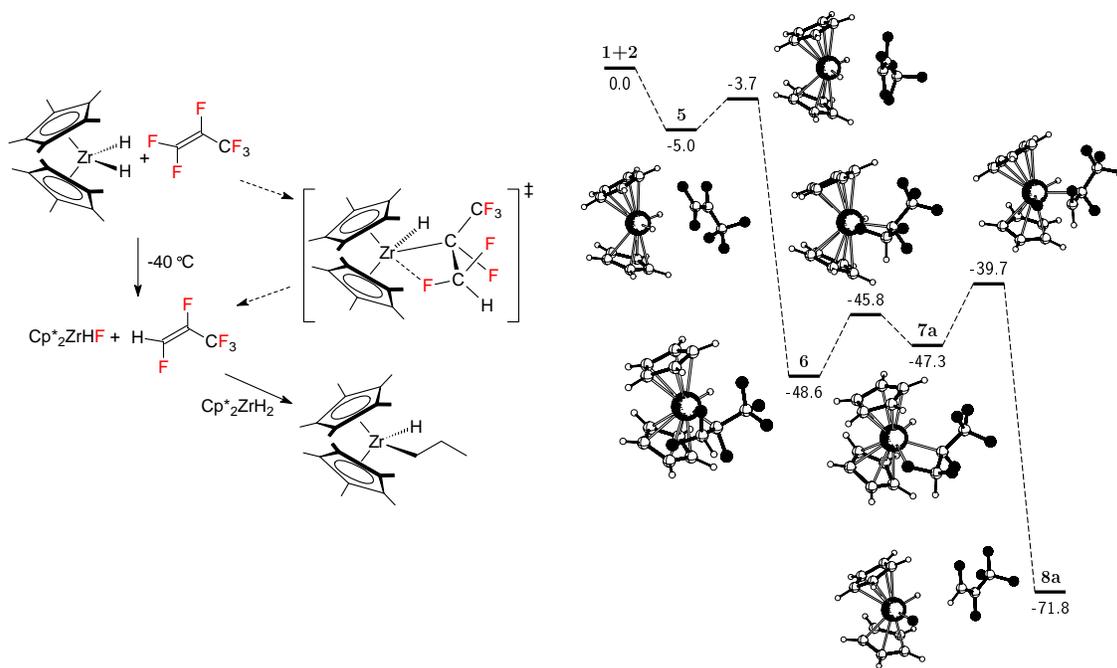


The reaction works for all complexes we have examined to date. Furthermore, the oxidative cleavage reaction is reversible, in that heating the Pt(II) complexes results in their reversion to the Pt(0)-alkyne complexes. Consequently, we now have methodology to break and make C-C≡C bonds, and further development of this reaction will be the subject of future studies.

C-H Activation Reactions in Functionalized Hydrocarbons. We have found surprisingly that the Tp*Rh(I) fragment reacts with chloroalkanes selectively via terminal C-H activation. No C-Cl cleavage is observed. The only exception is in β-chloroalkanes, but even here it is believed that terminal C-H activation occurs initially followed by rapid β-chloride elimination.



Activation of Strong C-F Bonds in Fluorocarbons. We have found that C-F cleavage in perfluoropropene gives first the selective formation of *E*-CHF=CF₂. Further reaction with zirconium hydride leads to complete defluorination with no further intermediates being seen. A collaborative joint theoretical/experimental investigation has revealed that the lowest energy mechanism proceeds via olefin insertion followed by β-fluoride elimination.



DOE Interest

This project demonstrates that alkane activation occurs preferentially at the terminal positions of the alkanes, where functionalization would produce the most desirable products. C–C cleavage chemistry will allow selective, low temperature reforming of the strongest C–C bonds, complementing existing capabilities. C–F bonds are the strongest of all single bonds, which accounts for the widespread inertness of fluorocarbons, and the ability to catalytically cleave and/or hydrogenate the C–F bonds in these special organic compounds could provide useful pathways for the conversion of CFC's into less harmful HFC's.

Future Plans

Our future research will focus on the items presented in our proposal where we have had success. These include: (1) carbon-carbon bond cleavage reactions with new classes of substrates, (2) studies of C-H bond cleavage reactions of functionalized hydrocarbons such as nitriles, ketones, and amines using trispyrazolylboraterhodium complexes, (3) reactions of hemilabile ligands, and (4) carbon-fluorine bond activation.

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19. Jones, W.D. Vetter, A.J. Wick, D.D. Northcutt, T.O., Alkane complexes as intermediates in C-H bond activation reactions,” *ACS Symposium Series*, in press.
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22. Clot, E. Megret, C. Kraft, B.M. Eisenstein, O. Jones, W.D., Defluorination of perfluoropropene using $\text{Cp}^*_2\text{ZrH}_2$ and Cp^*_2ZrHF : A mechanistic investigation from a joint experimental-theoretical perspective, *J. Am. Chem. Soc.*, in press.

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Electrophilic Metal Alkyl Chemistry in New Ligand Environments

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Goal

The current objective of this project is to characterize the reactions of olefin polymerization catalysts with polar monomers, to provide a basis for the development of strategies for the synthesis of functionalized polymers by insertion polymerization.

Recent Progress

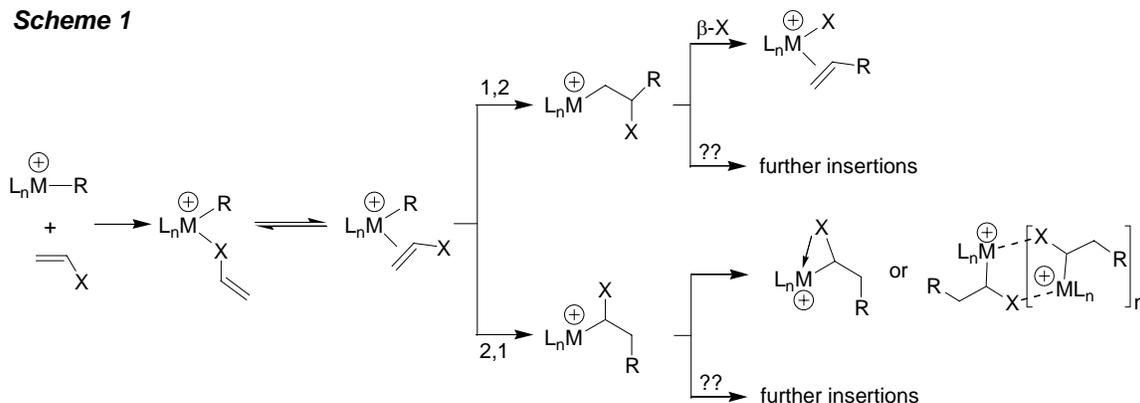
The polymerization of olefins by insertion chemistry using single-site metal catalysts provides a powerful approach to the synthesis of polyolefins with exquisite control of composition and structure. The development of metal catalysts that are capable of polymerizing or copolymerizing *functionalized olefins* by insertion mechanisms would significantly expand the scope of metal-catalyzed polymerization and enable the synthesis of new materials with enhanced properties. While limited success has been achieved in the copolymerization of acrylates and vinyl ketones with ethylene and propylene using Pd, Ni or Cu catalysts, general strategies for designing catalysts with functional group tolerance are lacking. The most important monomers are $\text{CH}_2=\text{CHX}$ compounds, such as vinyl chloride, vinyl acetate, acrylates, vinyl ethers, and acrylonitrile, in which the functional group is directly bonded to the olefin. These cheap commodity monomers can be polymerized by radical or ionic mechanisms, but control of polymer composition and structure in such reactions is limited compared to what is possible (in principle) through tuning of the catalyst structure in a metal-catalyzed insertion process. Important long term polymer targets include (i) new homopolymers with enhanced properties, such as stereoregular, defect-free PVC, (ii) linear ethylene/ $\text{CH}_2=\text{CHX}$ copolymers via direct synthesis from the monomers, and (iii) new copolymers such as vinyl chloride/ α -olefin copolymers (plasticizer-free, flexible PVC-type materials) or styrene/vinyl chloride copolymers (flame resistant polystyrene-type materials).

To pursue these goals it is necessary to develop new generations of olefin polymerization catalysts that are tolerant of functional groups. We are investigating the reactions of single-site catalysts with $\text{CH}_2=\text{CHX}$ monomers in order to identify and understand the chemical issues that underlie this challenge. We are using the results of these studies to define strategies for multiple $\text{CH}_2=\text{CHX}$ insertions and polymerization.

We investigated the reactions of representative early and late metal single-site catalysts with vinyl chloride, vinyl acetate, vinyl ethers, and acrylonitrile, as summarized generically in Scheme 1. In most cases, $\text{CH}_2=\text{CHX}$ monomers form $\text{C}=\text{C}$ π -complexes with $\text{L}_n\text{M}(\text{R})^+$ catalyst species. In the case of acrylonitrile, N-bound adducts are

observed for L_2PdMe^+ catalysts, but subsequent insertion chemistry implies that the $C=C$ π -complexes are accessible. In most cases, $L_nMR(CH_2=CHX)^+$ species undergo either 1,2 insertion to produce $L_nM(CH_2CHRX)^+$ species, or 2,1 insertion to produce $L_nM(CHXCH_2R)^+$ species. The β -X-substituted 1,2 insertion products are susceptible to β -X elimination. The α -X-substituted 2,1 insertion products have the potential to undergo further monomer insertions. However, in the systems studied to date, these species form chelated or aggregated species by $X \rightarrow M$ coordination, or are unreactive for further insertions due to the electronic effect of the α -X substituent.

Scheme 1



We studied the reactions of vinyl chloride with Ti, Zr, Fe, Co, Ni and Pd single-site catalysts. Two important reaction channels were observed. First, certain catalysts initiate radical polymerization of vinyl chloride through the action of radicals derived directly from the catalyst/activator or by autoxidation of metal alkyl species by trace oxygen. This mode was observed for Cp^*TiCl_3/MAO , $(C_5R_5)_2ZrR^+$ catalysts in the presence of trace O_2 , and some neutral Pd catalysts. Competing radical polymerization is not a long-term problem because it may be avoided by using non-redox active metals and anaerobic reaction conditions. The second general reaction observed is *net* 1,2 vinyl chloride insertion into L_nMR active species followed by fast β -Cl elimination. This process terminates chain growth after a single insertion. β -Cl elimination is fast for both early and late metal L_nMCH_2CHRCl species and is the main obstacle to insertion polymerization of vinyl chloride. Low temperature NMR studies of the $(Me_2bipy)PdMe^+$ system show that vinyl chloride coordinates more weakly than ethylene or propylene, but inserts much faster than these olefins. These differences result from the fact that vinyl chloride is a poorer donor than ethylene or propylene. We are investigating several strategies to direct 2,1 vinyl chloride insertions, which would produce $L_nMCHClCH_2R$ intermediates that cannot β -Cl eliminate without chain walking. As a first step in this direction, we studied $L_2Pd(CH_2Cl)^+$ chloromethyl species to probe how an α -Cl substituent would influence the reactivity of the Pd-R unit. Our results show that CO insertion is retarded by the electron-withdrawing power of the α -Cl, but is not completely inhibited. We also investigated vinyl chloride insertion into Pd and Zr acyl species and found that both steric and electronic factors influence the insertion regiochemistry.

We investigated the reactions of vinyl acetate with a set of cationic L_2PdMe^+ catalysts containing bis-imidazole, bis-pyridine or bis-imine ligands (L_2) with varying steric and electronic properties. We found that vinyl acetate forms $C=C$ π -complexes with $L_2Pd(Me)^+$ species, but coordinates more weakly than ethylene or propylene. The

$L_2Pd(Me)(\text{vinyl acetate})^+$ adducts undergo competitive 2,1 insertion, leading to stable *O*-chelated $L_2Pd\{CH_2Et(OAc)\}^+$ species, and 1,2 insertion, leading to transient $L_2Pd\{CH_2CHMe(OAc)\}^+$ species that undergo rapid β -OAc elimination to $L_2Pd(OAc)^+$ and propylene. Surprisingly, sterically crowded $L_2Pd(Me)(\text{vinyl acetate})^+$ species are more prone to 2,1 insertion than are sterically open $L_2Pd(Me)(\text{vinyl acetate})^+$ species. The insertion rates of $L_2Pd(Me)(\text{olefin})^+$ complexes vary in the order ethylene > propylene > vinyl acetate. The factors that control the regioselectivity and rate of vinyl acetate insertion are not yet fully understood, but it is clear that steric effects are very important. These studies show that the key challenges to achieving incorporation of vinyl acetate in an insertion polymerization include (i) to enhance vinyl acetate coordination and insertion, (ii) to control the regioselectivity of vinyl acetate insertion, and (iii) to sequester the β -acetate groups on the growing polymer chain generated by 1,2 insertion to prevent β -OAc elimination, and/or to labilize the $Pd\{CHR(OAc)\}$ chelates formed by 2,1 insertion to enable subsequent monomer coordination.

DOE Interest

The discovery of efficient and clean catalytic processes is of strategic importance to the US chemical industry and the US economy. The development of new catalysts that can polymerize functionalized olefins, particularly commodity $CH_2=CHX$ monomers such as vinyl chloride, would significantly expand the scope of olefin polymerization catalysis and provide new polymers with enhanced properties. This work is providing insights to the specific chemical challenges that must be met to achieve this goal.

Future Plans

The studies above are helping us to identify the specific chemical issues that must be understood and controlled to achieve the long term goal of insertion polymerization of $CH_2=CHX$ monomers. To address these issues we are pursuing the following studies:

(i) We will develop catalysts that are inherently more reactive than presently known catalysts so that insertion can be made more competitive with elimination processes and can be made to proceed even when an electron-withdrawing substituent is present in the α -position of the alkyl.

(ii) We are studying the reactions of L_nMR species with D-labeled vinyl chlorides to determine the detailed mechanisms of "net 1-2 insertion/ β -H elimination" reactions.

(iii) We will explore "multifunctional" catalysts that present flexible arrays of pendant (i.e. covalently attached to ancillary ligands) Lewis acids, Lewis bases, charged moieties, or hydrogen-bond donors and acceptors, in the second coordination sphere. These systems are being designed so that the pendant groups can sequester the X groups in the growing chain and labilize chelated/aggregated $L_nM(CHXCH_2R)^+$ species to prevent the termination processes identified above. A critical design feature is that the second sphere functionalities must be attached to the catalyst by flexible linkers to enable migratory insertion to proceed.

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A New Approach to the Discovery of Bond-Forming Chemical Reactions

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Current approaches to reaction discovery assay different reaction conditions to effect a specific transformation for one particular set of functional groups. An approach that simultaneously assays the reactivity of multiple combinations of functional groups in a single experiment in principle could enable a more thorough exploration of chemical reactivity. In this lecture, we will describe a new method for discovering chemical reactions wherein > 100 pairs of functional groups are assayed for covalent bond formation in a single one-pot experiment. Our method relies on Watson-Crick base pairing to organize a complex mixture of DNA-linked functional groups at nM absolute concentrations into discrete pairs of functional groups at mM effective molarity. Each pair of functional groups is encoded by a unique DNA sequence. In a reaction discovery experiment, sub-pmol quantities of the DNA-linked functional groups are incubated under a set of reaction conditions and a simple *in vitro* selection is used to separate sequences encoding bond-forming functional group combinations from sequences encoding non-reactive combinations. PCR amplification and microarray analysis of the selected sequences efficiently identifies the reactive combinations. We have used this method to discover a novel Pd-mediated reaction between a terminal olefin and a terminal alkyne to form an enone. The reaction proceeds under aqueous, room temperature conditions with a catalytic amount of Pd. Our results represent a new strategy for exploring chemical reactivity in a highly efficient manner (> 2,000 reactions per two-day experiment).

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CATALYTIC SYNTHESIS OF OXYGENATES: Mechanisms, Catalysts and Controlling Characteristics

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Objective

Design, synthesize, test, and characterize new acid catalysts for catalytic synthesis of ethers from alcohols derived from natural gas and renewable resources that link together research on oxygenates as environmentally compliant fuels, monomers, and high-value chemicals. We found that ethers with *primary* alkyl substituents, such as methylisobutyl ether (MIBE), preferentially are *cetane* boosters, and these ethers are also storage chemicals for olefins such as isobutene and have the potential for conversion to reformat hydrocarbon gasoline. The most efficient mechanism is a concerted, dual-site S_N2 pathway with chirality inversion in the alkyl group.

Recent Progress

Novel Active Zirconia-Based Dual-Site Catalyst. An (HO)₃ZrO₃SO-CH₂CH₂-OSO₃Zr(OH)₃-derived catalyst was synthesized and tested for the coupling of methanol (MeOH) with isobutanol (i-BuOH) to form MIBE. The catalyst was characterized by HR-XPS, NIR diffuse reflectance, ¹H NMR, and ¹³C MAS-NMR to determine its state during synthesis and the dominant factors for producing the high activity and selectivity [1]. The results verified the μ₂-CH₂CH₂- ligand abridging two -OSO₃⁻ groups in the glycol diester anchored precursor was completely removed upon calcination at 773K to yield proximal acid groups surface-grafted on zirconia. The catalyst exhibited higher activity and selectivity than traditional sulfated zirconia catalysts. The surface acidity corresponded to 7.2 μmol acid sites/m², which was about 50% higher than that of sulfated zirconia prepared by standard methods of sulfate impregnation.

Mesoporous Catalysts. A propylsulfonic acid-derivatized mesoporous SBA-15 catalyst was synthesized, characterized in terms of surface properties, and shown to have *high selectivities* for MeOH + i-BuOH coupling to form MIBE > DME, with no detectable formation of butenes at temperatures <400K [2]. This catalyst possessed uniform parallel pores ≈7.4 nm in diameter (shown in Fig. 1), surface area of 674 m²/g, acid exchange capacity 1.6 meq H⁺/g of SiO₂, and excellent thermal stability. At elevated temperatures, the selectivity toward MIBE and DME increased with alcohol pressure, while isobutene selectivity simultaneously decreased. This catalyst also showed higher catalytic activity for ether formation than other inorganic solid acid catalysts. Kinetic analysis was consistent with competitive adsorption of the two reactant alcohols onto Brønsted acid sites, with isobutanol being more strongly adsorbed than methanol. All experimental data were satisfactorily fitted using Langmuir-Hinshelwood kinetic laws.

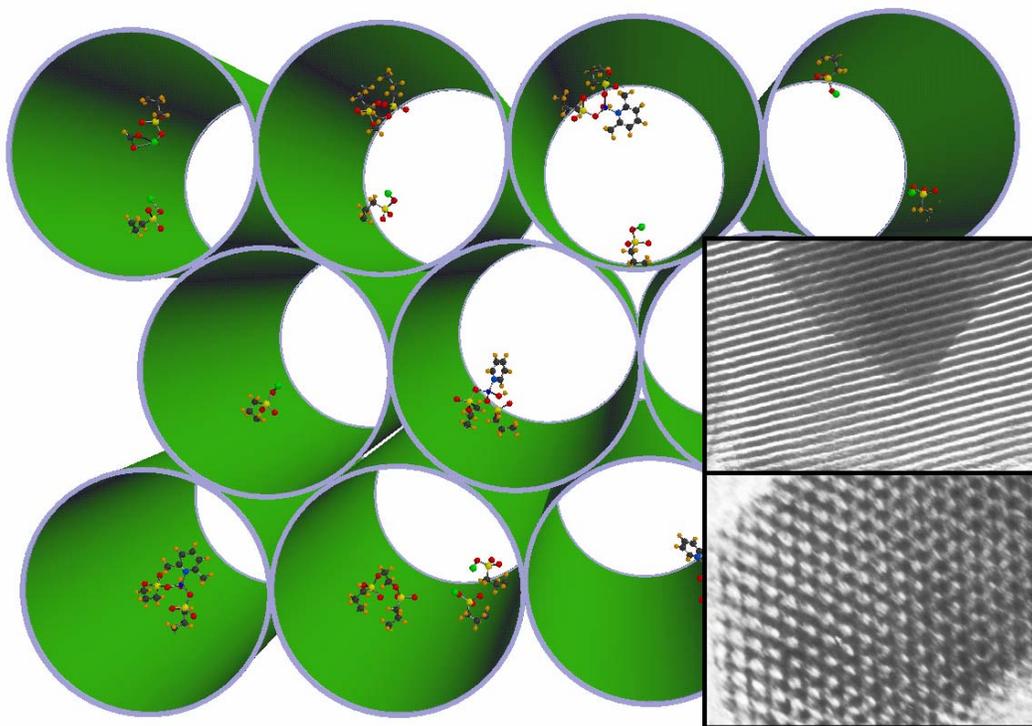


Fig. 1. Schematic of the mesoporous SBA-15 material with intrapore complexes formed at the wall-anchored propylsulfonic acid sites and TEM (inset with mag. = 50,000x) of the improved, highly ordered propylsulfonic acid-derivatized mesoporous SBA-15 catalyst was subsequently synthesized that contained one H^+ per 7.5 Si atoms on the pore walls [3].

Acid-Base Interactions and Ion Exchange by XPS. XPS showed that the precursor thiol were completely oxidized to $\equiv\text{Si}(\text{CH}_2)_3\text{SO}_3\text{H}$ functionalities. The properties of the Brønsted acid sites were investigated by HR-XPS before and after adsorption of pyridine (py) and ethylenediamine (en) [3], and after ion exchange of the $-\text{SO}_3\text{H}$ protons with K^+ , NH_4^+ , Co^{2+} , Ni^{2+} , and Cu^{2+} [4]. XPS core-level shifts (CLS) of S2p photoemission to lower binding energies (BEs) identified $-\text{SO}_3\text{H}$ groups as sites for donor hydrogen bonding to the adsorbed nitrogen bases that reflected the strength of the $-\text{H}\cdots\text{N}\equiv$ bond. The N1s CLS to higher BEs identified the N atom of py and one of the two N atoms of en as hydrogen bond acceptors. An all-electron, nonrelativistic DFT theory yielded an excellent correlation between the calculated core-level orbital energies with observed XPS CLS [4]. As a result of this combined study, the propylsulfonic groups of SBA-15 were identified as weaker acids than those of Nafion-H and SZ, albeit ones with high surface concentration and ion-exchange capacity.

Catalytic Properties at High Pressures and Kinetics. This SBA-15 catalyst was extensively tested for the dehydrocondensation of $\text{MeOH} + i\text{-BuOH}$ to form MIBE, DME, and isobutene (IB) [5]. The mesoporous structure with 7.7 nm diameter pores was maintained after >1600 h of testing at elevated temperatures and pressures, and the Brønsted acid sites (1 meq/g of catalyst) were stable under these reaction conditions. Again, kinetic studies demonstrated that the ethers were formed by surface-catalyzed $\text{S}_{\text{N}}2$ reactions that follow Langmuir-Hinshelwood kinetics involving competitive adsorption of the alcohols, while IB formation utilizes a vacant Brønsted acid site adjacent to the adsorbed $i\text{-BuOH}$ molecule [5]. As a function of the alcohol pressure,

the IB formation rate exhibited a distinct maximum (shown in Fig. 2), and this kinetic behavior is similar to that observed with Nafion-H and other acid catalysts. Because of the high apparent activation energy of isobutene synthesis compared with the much lower apparent activation energies of the ethers, lower reaction temperature along with higher reactant pressures favor the formation of ethers over olefins.

Theoretical Calculations of Transition States (TS). Kinetic analysis indicated that a precursor state in which both reacting alcohols are brought to proximity on the catalyst surface is effective in lowering the TS barrier. The TS of the reaction of MeOH + i-BuOH over Nafion-H was modeled using two fluorosulfonic acid functionalities ($\text{CF}_3\text{SO}_3\text{H}$) as the catalytic sites [6]. The results of extended model calculations for SBA show convincingly that dissociation-reassociation of the C-O bond in the adsorbed methanol subject to the “rear attack” onto its inverting methyl group is the dominant feature of the reaction pathway at the TS (shown in Fig. 2). *The overall barrier height and its connectivity with reactants and products is strongly influenced by the concerted motion of the “far away” atoms and the flexibility of the entire dual-site ensemble with the hydrogen-bonded adsorbates.* This dual-site $\text{S}_{\text{N}}2$ reaction is facilitated by a proton transfer between the neighboring sites that minimizes charge imbalance in the TS.

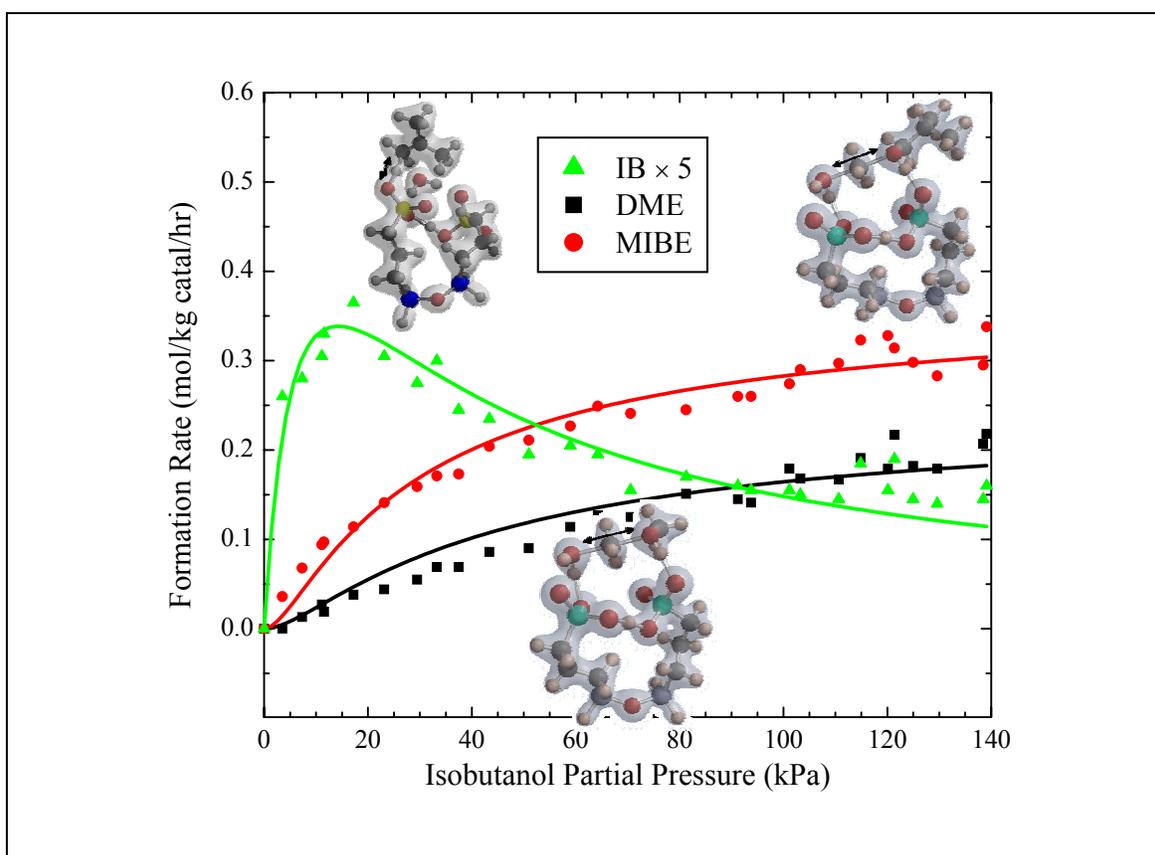


Fig. 2. Rates of MIBE, DME, and isobutene formation from MeOH/i-BuOH = 12.3/6.2 mol/kg catal/h at 404K in N_2 carrier gas as a function of i-BuOH partial pressure. Also shown are the computationally determined TS for the overall reaction pathways yielding MIBE, DME, and isobutene. The TS shows a planar configuration of the inverting CH_3 group in forming ethers.

In addition, the theory afforded energies and optimized geometries of sorption adducts, including that of partial hydrogen transfer between the surface acid and adsorbed nitrogen bases [3]. The theory also has a predictive value in that one can calculate models of structurally and chemically different pendant groups that enable the control of acid strength, properties of cation-exchanged transition metals for surface organometallic chemistry, and reaction pathways catalyzed by this mesoporous material. A correlation was established between core-level orbital energies calculated by DFT methods and observed experimental XPS BEs for nitrogen-containing polymers [3]. Examples were shown of calculated N1s core-level shifts upon hydrogen bonding of Brønsted acids with dry pyridine, a weak nitrogen base. These correlations were found to be useful for the XPS characterization of conjugate acid-base pairs on surfaces and interfaces of importance in polymer science and catalysis utilizing polymeric and inorganic materials [3]. Expanding the application of angle-resolved XPS and theory to surface sites and surface layers, it was demonstrated that copper phthalocyanine (CuPc) forms thin film on a reconstructed Au(001) surface, with one flat-lying CuPc molecule per unit cell [7]. Combined with theory, X-ray photoelectron diffraction in the valence band region permitted a full determination of the valence bond molecular orbital electronic structure [7].

Impact

Although we focus herein on a specific class of ether-forming reactions, we are contributing to the development of a systematic knowledge regarding the relation between composition, structure (including podality of the anchored acids), concentration (including molecular proximity), and function of solid acids with applications in oxygenate synthesis, hydrocarbon reforming, and amine synthesis. With the use of advanced computational methodology, the experiment receives a better interpretation than heretofore feasible, including spectroscopy, reactivity, and predictability of pathways.

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Fundamental Studies of Chemisorption and Catalysis on Alloy Surfaces

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Goal

Elucidate the chemical reactivity of well defined, ordered Pt-Sn alloy surfaces in order to develop the foundation for a molecular level understanding of the activity and selectivity of bimetallic Pt catalysts.

Recent Progress

We have investigated primarily Pt-Sn alloy surfaces, including detailed structural characterization, UHV studies of adsorption and reactions of hydrocarbons on these surfaces, and measurements of the rates of catalytic hydrocarbon conversion reactions at elevated pressures (up to 1 atm) over these model catalysts. We have made good progress toward our goals, producing discoveries and exciting new results that we believe will have a substantial impact on the field of catalysis. Evidence for this statement comes from the large number of citations to our work in the literature, the patent activity regarding catalysts that are related to the systems that we have investigated, and the reception given to presentations of our results at many conferences and technical venues.

Coking Resistance of Pt-Sn alloys Probed by Acetylene Chemisorption: Acetylene (C_2H_2) is a reactive molecule with a low C:H stoichiometry that can be used to evaluate aspects of the resistance of metal-based catalysts to the formation of carbonaceous residue (coking). While thermal decomposition of C_2H_2 under UHV conditions on Pt is irreversible with complete conversion of the chemisorbed monolayer into surface carbon, alloying with Sn strongly reduces the amount of carbon thus formed. This is consistent with observations of increased lifetimes for technical Pt-Sn bimetallic catalysts compared to Pt catalysts used for hydrocarbon conversion reactions.

Oxidation of Ordered Pt-Sn Surface Alloys by O_2 : We have studied the oxidation of two, ordered Pt-Sn surface alloys at 380-425 K using moderately high pressures of oxygen (O_2) at $P(O_2)=2\times 10^{-2}$ Torr. Two kinetic regions for oxygen uptake were distinguished and apparent activation energies determined. Overall, these results are

consistent with previous studies on bulk Pt-Sn alloys, but new information is obtained on the role of alloy surface structure in controlling the initial stages of oxidation kinetics.

Hydrogenation of Crotonaldehyde over Sn/Pt(111) Alloy Model Catalysts: Gas-phase hydrogenation of crotonaldehyde ($\text{CH}_3\text{CH}=\text{CHCHO}$) was studied over two Sn/Pt(111) surface alloys which were used as a model catalysts. The influence of the alloy structure, hydrogen pressure, and temperature on activity and selectivity toward 2-butenol ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$) formation was investigated. The hydrogenation activity was about two times higher for the bimetallic Pt-Sn catalysts compared to that for Pt(111), but little change in selectivity was observed. Butyraldehyde was formed as the main product in all cases. Therefore, alloy formation improves hydrogenation activity toward both of the C=C and C=O functional groups, and can not solely explain the improvement in selectivity toward formation of the unsaturated alcohol that has often been reported for supported Pt-Sn catalysts versus pure-Pt catalysts.

Probing the Chemistry of CH_3I on Pt-Sn Alloys: These results point to the importance of adjacent "pure Pt" three-fold hollow sites as reactive sites for CH_3I decomposition. We note that CH_3I , and presumably the other short-chain alkyl halides, are not reactive enough on Pt-Sn alloys to serve as convenient thermal precursors for preparing species small alkyl groups such as $\text{CH}_3(\text{a})$ for important basic studies of the reactivity and chemistry of alkyl groups on Pt-Sn alloys. Another approach is required.

Hydrogenation of Cyclohexanone on Pt-Sn Surface Alloys: The hydrogenation activity at low temperature (325 K) was substantially higher for both Pt-Sn alloy catalysts than that of the Pt(111) surface, with the activity proportional to the amount of Sn in the surface layer. However, the selectivity over the two Pt-Sn alloys was the same as for Pt(111).

Adsorption and Reaction of Acetaldehyde on Pt(111) and Sn/Pt(111) Surface Alloys: Acetaldehyde (CH_3CHO) is adsorbed more weakly and the chemical reactivity of CH_3CHO on these Sn/Pt alloys is decreased from that on the Pt(111) surface. Thus, the presence of Sn in the surface layer of these Pt-Sn alloys does not thermally activate acetaldehyde for reaction in UHV due to the thermodynamic driving force provided by the Sn-O interaction. We attribute this to be primarily because of kinetic barriers that arise from Pt-Sn bonding interactions in the alloy and acknowledge the important implications of this observation for the synthesis of organic molecules by selective oxidation over PtSn catalysts.

Alloy formation and CO adsorption on bimetallic Ca/Pd(111) surfaces: In a collaboration initiated by Prof. Roel Prins (Department of Chemistry, Swiss Federal Institute of Technology (ETH), Zurich, Switzerland), we have studied surface science aspects of Ca-modified, supported Pd catalysts for methanol synthesis. The presence of Ca at the Pd(111) surface increases the CO adsorption energy and causes a 110-K shift of the CO thermal desorption peak to higher temperature than from a clean Pd(111) surface. This Ca-Pd-CO interaction is so strong that it drives Ca out of a Ca-Pd alloyed layer to the overlayer upon CO adsorption, which is evident from the disappearance of the

characteristic LEED pattern of the alloy. This migration of Ca atoms occurs without oxidation of Ca. These observations are discussed with reference to possible active phases in Ca-modified, supported Pd catalysts for methanol synthesis and the special nature of Ca over alkali metal promoters for this catalysis.

DOE Interest

Well-defined alloy surfaces allow us to cleanly probe the role of alloy phases in bimetallic supported metal catalysts, and to directly connect to theoretical calculations of energetics and mechanisms of hydrocarbon catalysis over bimetallic surfaces. This improved understanding of reactions and catalysis at alloy surfaces aids efforts to design and develop new catalysts and catalytic processes.

Future Plans

Role of Adsorbed Hydrogen in the Reactivity at Pt-Sn Alloy Surfaces: We need to improve our understanding of how coadsorbed hydrogen influences adsorption energies and reaction barriers on alloy surfaces. We have preliminary data suggesting large effects on both quantities on Pt-Sn alloys compared to the much smaller effects on Pt.

Catalytic Reactions: We hope to extend our studies of catalytic reactions over well-defined surfaces to include the three ordered Sn-Pt(100) bimetallic surfaces. These have higher Sn concentrations than the Sn-Pt(111) alloys studied previously and novel chemistry. In addition, we plan to extend our studies of the thermal stability of Sn-oxide/Pt interfaces in vacuum to include studies in atm.-pressure H₂.

Activation Energies for Dehydrogenation on Pt-Sn Alloys: We need to better establish values, at least lower limits, for C-H bond cleavage and other elementary surface reactions on Pt-Sn alloys. We plan to utilize much larger hydrocarbons, including multi-ring systems, in order to extend the temperatures at which hydrocarbons are adsorbed on alloy surfaces and thus increase our ability to probe surface reactions.

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5. “Hydrogenation of Crotonaldehyde over Sn/Pt(111) Alloy Model Catalysts,” D. Jerdev, A. Olivas, and B. E. Koel, *J. Catal.*, **205**, 278-288 (2002).

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TRANSITION METAL-MEDIATED REACTIONS OF SMALL MOLECULES

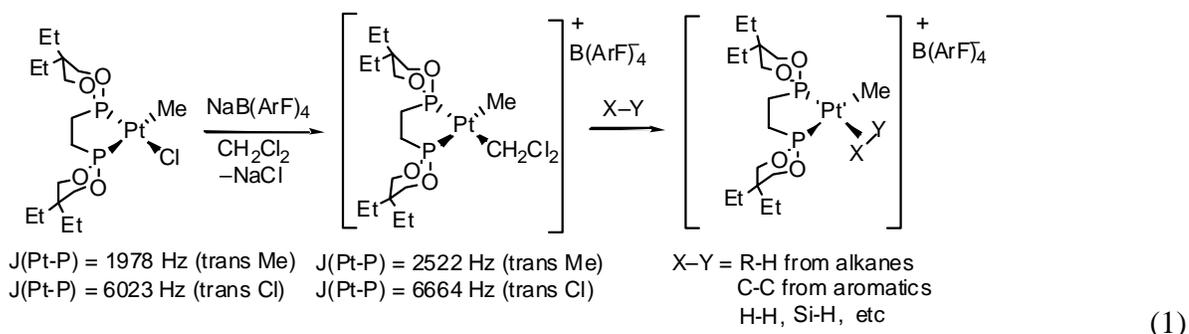
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Research Goals. The main goal is to study the binding and heterolytic cleavage of σ bonds on highly electrophilic cationic complexes to provide groundwork for applications ranging from hydrogen storage to the design of new catalysts to convert methane to liquid fuels. A key component is the design of new metal-ligand systems such as complexes containing diimines with hemilabile pendant groups that can stabilize unsaturated 16e complexes. Ligands that cannot form potentially competing intramolecular (agostic) C–H interactions such as tied-back (caged) phosphites and bidentate diphosphonites are ideally suited for binding weak ligands such as alkanes. Observation of a CH_4 or alkane complex by NMR at low T and/or high pressure and vibrational spectroscopic investigations of the reaction coordinate for H–H bond splitting are also important goals.

Recent Progress. *Electrophilic Complexes for σ Bond Activation.* We have developed an extensive array of very reactive unsaturated (or weakly solvent-coordinated) cationic complexes of Mn, Re, Ru, Pd, and Pt containing diimine or phosphite ligands. We have begun to study Pt(II)-diphosphonite ligand systems analogous to our previously studied cationic Pt-diphosphine complexes.



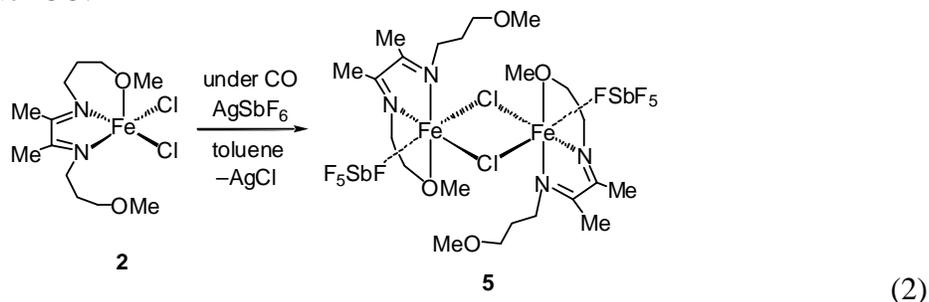
The extremely large NMR $J(\text{Pt-P})$ values for these complexes reveal that the Pt center is very electron poor, especially for the cation with bound dichloromethane. The latter is more electrophilic than $[(\text{depe})\text{PtMe}(\text{OEt}_2)]^+$ that gives C–H activation and C–C coupling of arenes (below) and should be an excellent precursor for studies of σ -bond complexes.

Mechanism of Activation of Arenes on Cationic Pt Complexes. We had found that $[(\text{depe})\text{PtMe}(\text{OEt}_2)]^+$ undergoes novel conversion in benzene to $\{[(\text{depe})\text{Pt}]_2(\mu\text{-biphenyl})\}^{2+}$ and recently formulated a reaction mechanism, culminating in a *JACS* publication.³ The first step is C–H activation of benzene with subsequent liberation of methane to generate a cationic Pt–Ph complex. The C–C coupling reaction is then proposed to occur via an η^1, η^2 -bridged phenyl dimer. After dissociation of one of the η^2 -benzene ligands, a migratory insertion of the η^2 -benzene ligand into the Pt–Ph bond occurs to form a complex that can be viewed as containing two η^1 -allyl interactions.

This complex then undergoes η^1 - η^3 -type allyl migration reactions on the arene ring to which the Pt fragments are attached to generate the μ -biphenyl complex.

Theoretical Studies of Bonding and Oxidative Addition of Germanes and Silanes to Mo(CO)(diphosphine)₂. We have been studying σ complexes of silanes and germanes, Mo(CO)(η^2 -Ph_nEH_{4-n})(diphosphine)₂ (E= Si, Ge; n= 0-2). Homolytic E-H cleavage to give the oxidative addition (OA) products MoH(Ph_nEH_{3-n})(CO)(diphosphine)₂ can occur and is very sensitive to both the nature of E and the phosphine. Theoretical calculations have been carried out in collaboration with Lledos and a “tour de force” paper on all of this work has recently been published.⁵ Mo(CO)(EH_{4-n}vin_n)(H₂PCH₂CH₂PH₂)₂ were used as model complexes and vinyl groups (vin) worked well to model the phenyl substituents. The reaction coordinate for activation of the E-H bond toward OA was analyzed in terms of bond energies. The ease of OA is related to the E-H and M-E bond energies: the process will be favored by a large M-E bond energy and a small E-H bond energy. The energy of the Mo-Si bond versus Mo-Ge is only slightly higher (2.8 kcal/mol), indicating that the term ruling the thermodynamics of the OA process for silanes and germanes might be the E-H bond energy. Thus the factor that makes the observed OA of the Ge-H bond easier than that for Si-H is the relative weakness of the Ge-H bond. The ease of OA of H₂ lies between that of germanes and silanes because although the Mo-H bond energy is much higher than the Mo-E energies, the H-H bond is also significantly stronger than the E-H. The OA of CH₄ is the most difficult because the loss of the high C-H energy is not as well compensated for since M-C bonds in alkyl complexes are much weaker than M-H.

Diimine Complexes of Iron(II). Hydrogenase metalloenzymes have highly organometallic-like dinuclear Fe-Fe or Fe-Ni active sites with a CO ligand trans to the site for H₂ activation/production. We desired to model a key step in the enzyme function, heterolytic cleavage of H₂, by synthesizing an Fe(II)-CO complex with H₂ trans to CO and having a basic ligand cis to H₂ to accept a proton. A dichloro complex with a diimine ligand with pendant side-arms seemed an ideal precursor for this synthesis, but this high-spin system unexpectedly rejected binding of CO on removal of chloride with silver under CO.



As further incentive for CO to bind to Fe, the 5-coordinate complex (2) was employed as the precursor. Astonishingly, a paramagnetic chloride-bridged complex, 5, resulted, wherein the irons are weakly interacting with the SbF₆ anions rather than binding the normally strong CO ligand. The apparent reason, confirmed by calculations, is that Fe is in a high-spin state for this system and did not undergo spin crossover to a low-spin state that appears to be necessary for stable CO binding. There are no reported examples of a high spin octahedral Fe(II) complex containing neutral ligands undergoing spin-crossover carbonylation to form the low spin Fe-CO complex, and our work reinforces this.

DOE Interest. The research is relevant to conversion of methane to liquid fuels and relates to new materials for catalysis and hydrogen storage, one of the major challenges to a hydrogen-based economy. The activation of H₂ on a metal is central to industrial and enzymatic catalysis of hydrogenation reactions that occur on massive scales.

Future Research. *Alkane Coordination and Activation.* A difficult obstacle for studying alkane activation has been the low solubility of cationic species, e.g. [Mn(CO)₃{P(OCH₂)₃CMe}₂(CH₂Cl₂)]⁺, in hydrocarbons. Placement of long hydrocarbon tails on the tied-back phosphites could overcome the solubility problem, and we have begun to synthesize such ligands. We will also carry out solid-state NMR studies of the Mn complex under high pressure of methane in collaboration with researchers at Pacific Northwest National Lab to determine if methane displaces the dichloromethane ligand in the solid. The *diphosphonite* complexes of platinum (eq 1) and other metals will be investigated.

Vibrational and Dynamic Studies of Dihydrogen Complexes. Very little research has been done on vibrational studies of H₂ complexes, particularly their remarkable dynamic behavior in elongated H₂ complexes that exist in the "gray area" where the H-H bond is nearly broken (H-H bond is elongated to 1-1.5 Å). It should be possible to study in stepwise fashion the entire reaction coordinate for H-H bond breaking by vibrational spectroscopy, which would be an unprecedented achievement in science. There is obvious relation to hydrogen storage and production, both of which involve H-H bond breaking/formation via intermediates with at least transiently bound H₂. We will use of state-of-the-art vibrational spectroscopy to characterize the coordination properties and dynamic behavior of dihydrogen complexes in collaboration with Brian Dyer, a Laboratory Fellow at LANL who is a leader in the field of time-resolved vibrational spectroscopy.

Chemistry of σ Complexes in Ionic Liquids. Ionic liquids are excellent media for carrying out transition metal based catalysis and are being widely investigated because of the promise of significant environmental benefits. We will pursue chemistry in ionic liquids as an integral part of the above investigations, particularly as media for generating novel hydrogen-rich materials such as [M(H₂)_n]⁺ and MH_x(H₂)_n for possible application in hydrogen storage. Removal of halides from metal salts such as FeCl₂ under H₂ will be initially studied using spectroscopic diagnostics to identify hydride and/or dihydrogen ligand formation. Known metal organo compounds such as FeR₂ (R = bulky alkyl or aryl group) should react with acids under H₂ to form similar hydrogen-rich species. Importantly, the highly electrophilic cationic complexes we plan to study are very soluble in ionic liquids whereas they are nearly insoluble in conventional hydrocarbon solvents. Variations in ionic liquid, metal, and gaseous reactant should lead to other novel chemistry, e.g. alkane activation and catalytic reactions.

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2. "A One-Pot Synthesis of (η^6 -Arene)bis(triphenylphosphine)(methyl)ruthenium(II) Cations. X-ray structures of [$(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Me})(\text{Ph}_3\text{P})_2[\text{AlCl}_2\text{Me}_2]$] and the η^5 -Thiophene Analogue," X. Fang, J. G. Watkin, B. L. Scott, K. D. John, and G. J. Kubas, *Organometallics*, 21, 2336-2339 (2002).
3. "C–H Activation and C–C Coupling of Arenes by Cationic Pt(II) Complexes." W. V. Konze, B. L. Scott, and G. J. Kubas, *J. Am. Chem. Soc.*, 124, 12550-12556 (2002).
4. "Synthesis and Structure of a Diphosphonite-Bridged Ruthenium Dication, $\{[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-1,2-di(2'2'-diethyl-1',3'-propanedioxy)phosphinoethane)}\}^{2+}$," X. Fang, C. N. Iverson, B. L. Scott, K. D. John, J. G. Watkin, and G. J. Kubas, *Organometallics*, 22, 605-608 (2003).
5. "Oxidative Addition of Thiols, and Thiol/Thiolate Exchange Reactions of Low Valent Molybdenum and Tungsten Complexes. Synthetic, Structural, and Calorimetric Study of Trigonal Prismatic $\text{W}(\text{CO})_2(1,10\text{-phenanthroline})(3,4\text{-toluenedithiolate})$," R. F. Lang, T. D. Ju, J. C. Bryan, G. J. Kubas, and C. D. Hoff, *Inorg. Chim. Acta.*, 348, 157-164 (2003).
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7. "Heterolytic Splitting of H–H, Si–H, and Other σ Bonds on Electrophilic Metal Centers," G. J. Kubas, *Adv. Inorg. Chem.*, in press (May/June, 2004). [invited review].
8. "Structure of the First Homoleptic Manganese-Phosphine Complex, $[\text{Mn}(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_3][\text{BF}_4]$ " A. Toupadakis, B. L. Scott, and G. J. Kubas, *J. Chem. Crystallogr.*, in press (April, 2004).

Synthesis Strategy for Novel Oxide Catalytic Materials

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Goal

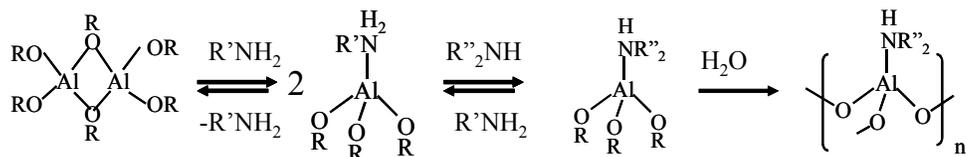
Develop synthetic concepts to control the surface chemical and catalytic properties of oxide by directing the chemistry during their preparation.

Recent Progress

We have investigated a synthesis method that can result in the formation of an aluminum oxide the surface of which has a high density of Lewis acid sites (coordinatively unsaturated Al ions) but free of hydroxyl groups without post-synthesis, high-temperature dehydroxylation. In addition, we showed that these sites are catalytically active. We have also begun to investigate a new, unit-by-unit approach to synthesize oxide-based catalysts. Progress in these directions has enabled us to begin research towards complete control of the structure, composition, arrangement of atoms, and morphology around a catalytic active site.

I. *Soft-chemical synthesis of aluminum oxide*

We have succeeded in bringing to practice our idea of protecting the coordinatively unsaturated site of the Al cation in the precursor using a neutral Lewis base (an amine) during preparation. With the Lewis acid site under protection, a rigid framework of Al oxide is formed by hydrolysis of the Al cations. Afterwards, the neutral Lewis base ligand is removed by displacement, thermal desorption, or oxidation as the final step to expose the coordinatively unsaturated Al cations. The following equation summarizes the steps involved.



Using a combination of ^1H and ^{13}C NMR, and ^{27}Al MAS NMR, we showed that Al alkoxide dimer precursor can be effectively dissociated by amines (first step), the bound amine can be exchanged with other amines that can serve better to protect the Al site (second step), and hydrolysis of the amine-Al alkoxide adduct can be carried out without dissociating the amine-Al bond (third step).

The resulting alumina has a rather high surface area of about 230 m²/g. Its surface properties were probed with FTIR of adsorbed amines. The adsorbed amine can be readily exchanged with other amines. By comparing the hydroxyl and the adsorbed amine IR band intensities, we concluded that the new alumina contained a much higher ratio of Lewis acid sites to hydroxyl groups than conventionally prepared alumina.

The catalytic properties were tested with the reaction of aminolysis of epoxide. On a surface area basis, the new alumina was about five times more active than a conventional alumina that had been pretreated by heating to 500°C (Fig. 1).

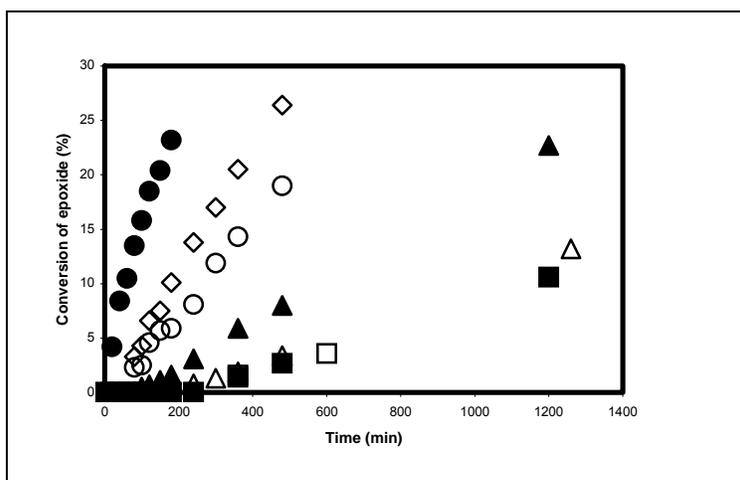


Figure 1: Conversion of cyclopentene oxide in reaction with piperidine catalyzed by various aluminas. ● PPD-Al₂O₃, ◇ SG-Al₂O₃-200, ○ SG-Al₂O₃-500-H₂O-200, ▲ SG-Al₂O₃-500-H₂O, △ PA-Al₂O₃-500-H₂O-200, ■ PA-Al₂O₃-500-H₂O, □ blank.

II. Unit-by-Unit Synthesis of Oxide

In order to achieve complete control of the structure and properties of a catalyst, we need to acquire synthesis know-how to build the catalyst. We began by developing a method to synthesize siloxane chains of a uniform but designated size that is analogous to peptide synthesis. Our method forms siloxane-siloxane bonds and can be repetitively applied to form a chain that offers precise control of its size and sequence. We illustrated the method by synthesizing various siloxane chains from disiloxane to pentasiloxane, by applying the following reactions alternately.



The formation of the desired products was confirmed using ¹H and ²⁹Si NMR. The results showed that pure compounds were obtained.

DOE Interest

We have made significant progress toward the goal of constructing catalysts with active sites in a cavity of a specified environment, which includes size of the opening (window) for access to the cavity, location of the active sites in the cavity, separation between active sites, and location of binding sites relative to the active site. Acquiring such capability would permit us to design catalysts that can achieve perfect selectivity of a chemical reaction, thereby reducing the energy and process requirements for separation and purification and conserve raw materials.

Future Plans

We will build upon the knowledge obtained to begin synthesis of a bicyclic siloxyalumoxane, which is a cage-like structure containing an AlO_4^- center as an active site. Successful synthesis of the structure would address two important aspects of design of the active site: its exact location within a cavity and the size of the access window. Different synthetic schemes will be explored, and some new synthetic steps will be developed. The synthetic schemes are formulated based on known chemistry of siloxanes and alumoxanes from the literature and from our own experience. Detailed characterization of each reaction step and the products is planned in order to enhance our understanding of the reactions and to develop our skill base to prepare for the next step towards our ultimate goal.

Publications

- (1) "A Soft-Chemical Method to Synthesize Lewis Acid Surfaces of Aluminum Oxide." Alexandr I. Kozlov, Mayfair C. Kung, Wen M. Xue, and Harold H. Kung, *Angewandte Chem. Int. Ed.*, 42 (2003) 2415.
- (2) "Catalytic Aminolysis of Epoxide by Alumina Prepared from Amine-Protected Al Precursor," W.M. Xue, M.C. Kung, A.I. Kozlov, K.E. Popp, and H.H. Kung, *Catal. Today*, 85(24) (2003) 219-224.
- (3) "Preparation and Characterization of Aluminum Oxide via Amine-Assisted Synthesis," Alexander I. Kozlov, Mayfair C. Kung*, Wen-Mei Xue, Harold H. Kung* and Shandong Yuan, submitted.
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- (5) "Stepwise synthesis of siloxane chains," Zhixiang Chang, Mayfair C. Kung, and Harold H. Kung, *Chem. Comm.* 2004, 206 - 207.
- (6) "Heterogeneous Catalysis: what lies ahead in nanotechnology," Harold H. Kung and Mayfair C. Kung, *Appl. Catal. A: General*, 246 (2003) 193.
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Mechanisms and Design in Homogeneous Catalysis

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Goal

Elucidation of fundamental reactivity patterns of transition metal alkyls in metallocene-catalyzed alkene polymerization and novel ligand development.

Recent Progress

Metallocene-catalyzed alkene polymerization is rapidly becoming the largest scale application of homogeneous catalysts in the world. Despite enormous investments in the development of new catalysts, ligand systems, and co-catalysts for alkene polymerizations, many fundamental aspects of catalytic polymerization remain unclear. In the last year of support, we have made significant progress in several areas: direct observation of polymerization events by NMR methods, identification of the mechanism by which polypropene isotacticity is lost during polymerization, and examination of the relative reactivities of various primary and secondary alkyls.

Direct Observation of Catalytic Events. Direct observation of polymer growth at the metallocene center enables “molecular level” characterization of catalyst structure and dynamics. We recently reported *the first example of the interception and characterization of the propagating species in a commercially-relevant metallocene-catalyzed polymerization reaction.* In this case, it is the propagating species for (EBI)ZrMe(MeB(C₆F₅)₃)-catalyzed polymerization of 1-hexene, propene, and ethene. Characterization of the propagating species using various labeled compounds (summarized in the adjacent graphic) is comprehensive and compelling. At temperatures < -40°C, the propagating species is stable for tens of hours and constitutes a living catalyst. By simultaneous monitoring of the consumption of alkene and conversion of the uninitiated catalyst to the propagating one, the rate laws and rate constants for initiation and propagation *are measured directly for the first time.* Importantly, for 1-hexene and (EBI)ZrMe(MeB(C₆F₅)₃) we find that *the rate constants and rate laws for initiation, propagation, and termination determined at low temperature by direct NMR observation correspond with those determined previously* over the temperature range of 0-50°C. Thus, we have found a rapid method for generating fundamental kinetic parameters for this important reaction.

Powerful mechanistic insights result from direct observation. One example is the nature of propagation: does the polymer grow continuously at a single center or is the growth, as suggested by Brintzinger, sporadic with stops and starts driven by ion-pair dissociation/association events? Careful labeling studies based on direct observation of the propagating species provide the answer: propagation is a continuous event.

Loss of Stereoregularity in Propene Polymerization. One of the more interesting and surprising proposals from the past decade of isotactic propene polymerization catalysis concerns loss of stereoregularity at low concentrations of propene. The proposal, chain-epimerization of the growing polymer, poses that low tacticity results primarily from epimerization of a correctly inserted monomer rather than insertion of the wrong enantioface. In effect, the catalyst first makes the correct decision and then changes its mind. Using direct-observation methods and extensive isotopic labeling, we have been able to “watch” chain-end epimerization events at metallocene-polymeryl intermediates for the first time. These studies confirm epimerization via tertiary alkyls and provide quantitative data for the overall rates of epimerization vs. termination. Importantly, extrapolation of these data to higher temperatures confirms that the *primary process for loss of stereoregularity in propene polymerization is chain-end epimerization* via a complex process with a high degree of nuclear motion.

Regioerrors, Catalyst Activity, and H₂ Responsivity. More recently we have examined the relative reactivity of secondary alkyls at metallocenes. Secondary alkyls result from 2,1-insertions of monosubstituted alkenes. Such regioerrors are thought by many to have dire consequences for catalysis according to the following logic: secondary alkyls are slow to insert monomers which leads to accumulation of catalyst in this dormant state. As a result, less of the catalyst lies in the active pool and the overall activity declines (estimates for the activity decrease are in the 10- to 100-fold range). The primary evidence for these hypotheses comes from hydrooligomerization and labeled ethene incorporation studies. In both types of studies, there is an over-representation of products from reaction of H₂ and/or C₂H₄ with secondary alkyls.

In contrast, our quench-label approaches to active site counting consistently demonstrate little accumulation of catalyst in the form of secondary alkyls. To resolve this important dilemma we have taken a direct approach: generate secondary alkyls in situ and directly measure their rates of isomerization, hydrogenolysis, and alkene insertion. Each direct measurement that we have made refutes the “conventional wisdom”. We find: (1) reaction of secondary alkyls with 1-hexene and propene at –80°C *not* slower than reaction of primary alkyls (such as Zr-polypropenyl or Zr-polyhexenyl cations) (2) *secondary alkyls are more reactive than primary alkyls toward H₂ and ethene by 1-3 orders of magnitude* (3) secondary alkyls are thermodynamically unstable with respect to primary alkyls and (4) secondary alkyls undergo β-H elimination with *significantly lower activation enthalpies* than primary alkyls. What does this mean? One clear implication is that secondary alkyls do not constitute “dormant” sites into which most of the catalyst is pooled. Equally importantly, the much higher reactivity of secondary alkyls toward H₂ means that *responsivity of a catalyst to H₂ as a chain transfer agent is critically dependent on the catalyst regioselectivity*. Less regioselective catalysts will be more responsive to H₂-based chain transfer.

Novel Ligands for Highly Selective Catalysis. Highly selective catalysts increase atom economy and energy efficiency while decreasing waste. Our goal is to develop new phosphorus chemistry that will enable broadened catalyst discovery via large phosphine ligand libraries. This project was seeded with DOE funding and so is briefly mentioned here.

We have shown that 3,4-diazaphospholanes provide a pathway to making enormous libraries of novel, chiral phosphine ligands. Recently we have demonstrated that monophosphine libraries of diazaphospholanes form highly effective ligands for Pd-catalyzed asymmetric allylic alkylation reactions. These studies have been extended to bead-based catalysts and demonstrate state-of-the-art selectivity while supported on beads. In the near future, we will report highly active, regio-, and enantio-selective alkene hydroformylation promoted by diazaphospholane ligands.

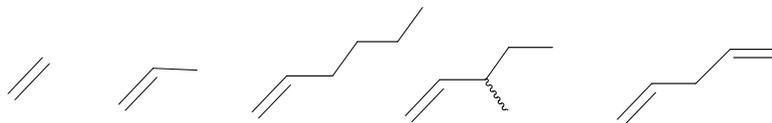
DOE Interest

Patterns in transition metal alkyl formation and reactivity control product selectivity in the largest worldwide catalytic transformations of organic feedstocks. This research program develops (1) a fundamental understanding of these patterns (2) specific, detailed mechanisms of actual (non-model) catalysts for the commodity-scale process of alkene polymerization and (3) novel techniques for studying catalytic transformations.

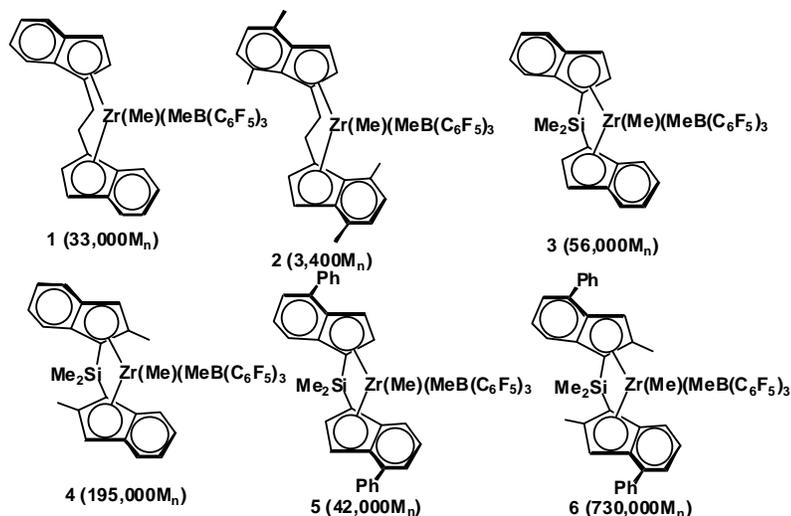
Future Plans

Quantitative Structure-Activity Relationships. Direct observation of polymer growth at the metallocene center enables “molecular level” characterization of catalyst structure and dynamics. We have previously demonstrated that one can intercept the propagating species for (EBI)ZrMe(MeB(C₆F₅)₃)-catalyzed polymerization of 1-hexene, propene, and ethene and *directly measure rates of initiation, propagation, and termination*. Furthermore, we have rigorously proven that the rates, rate laws, activation parameters, and rate constants obtained under low temperature conditions apply can be extrapolated to “real” polymerization conditions.

We now are accumulating quantitative data for insertion and termination rates as a function of alkene structure:



The second dimension of our study on structure-activity relationships concerns the influence of metallocene-ligand structure on the kinetics of elementary steps. The collection of ligands (along with polymer molecular weights obtained with these catalysts) under ongoing investigation is shown below.



The third dimension of our examination of structure-activity relationships concerns the influence of co-catalyst on polymerization rates. We are in the process of collecting data with non-coordinating anions (both $\text{B}(\text{C}_6\text{F}_5)_4^-$ and some of Warren Piers diboryl anions).

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6. 'Direct Observation of the Propagating Species in the $(\text{EBI})\text{Zr}(\text{Me})(\text{MeB}(\text{C}_6\text{F}_5)_3)$ -catalyzed Polymerization of 1-Hexene' Landis, C. R.; Rosaaen, K. A. *Polymer Material Science and Engineering*, **2002**, *43*, 301-302.
7. 'Heavy Atom Kinetic Isotope Effects, Cocatalysts, and the Propagation Transition State for Polymerization of 1-Hexene Using the $\text{rac}-(\text{C}_2\text{H}_4(1\text{-indenyl})_2)\text{ZrMe}_2$ Catalyst Precursor' Landis, C. R.; Rosaaen, K. A.; Uddin, J. *J. Am. Chem. Soc.*, **2002**, *124*, 12062-12063.
8. 'Direct Observation of Insertion Events at $(\text{EBI})\text{Zr}(\text{MeB}(\text{C}_6\text{F}_5)_3)$ -Polymeryl Intermediates: Distinction Between Continuous and Intermittent Propagation Modes' Clark R. Landis, Kimberly A. Rosaaen, Douglass R. Sillars *J. Am. Chem.*

- Soc.* **2003**, *125*, 1710-1711.
9. 'Catalytic Propene Polymerization: Determination of Propagation, Termination, and Epimerization Kinetics by Direct NMR Observation of the (MeB(C₆F₅)₃)propenyl Catalyst Species' Douglass R. Sillars and Clark R. Landis, *J. Am. Chem. Soc.* **2003**, *125*, 9894-9895.
 10. 'Resolved Chiral 3,4-Diazaphospholanes and Their Application to Catalytic Asymmetric Allylic Alkylation' Thomas P. Clark, Clark R. Landis, *J. Am. Chem. Soc.* **2003**, *125*, 11792-11793.
 11. 'Solid Phase Synthesis of Chiral 3,4-Diazaphospholanes and Their Application to Catalytic Asymmetric Allylic Alkylation' *Proc. Nat. Acad. Sci.* (in press).

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primary amine, secondary amine, urea, isocyanate, vinyl, and nitrile, with high reproducibility.^{2,3} We discovered that the particle morphology of the resulting materials could be directed to different particle shapes and sizes, such as spheres (**Figure 1a**), tubes, and rods (**Figure 1b**), simply by introducing different organoalkoxysilane precursors into our co-condensation reactions.^{2,3}

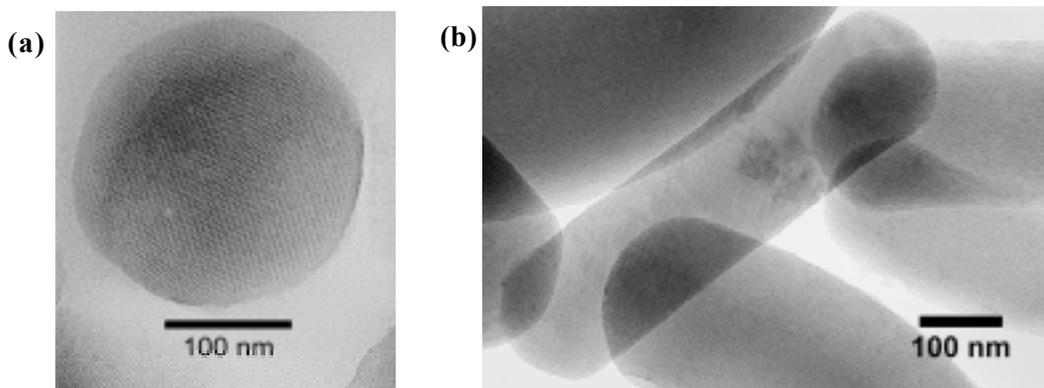


Figure 1. TEM micrographs of mercaptopropyl- and cyanopropyl-functionalized mesoporous silica materials (**a** and **b**, respectively).

Progress 3. Multi-functionalization: incorporation of multiple organic functional groups with precisely controlled relative concentrations

As previously described, the difference in “the hard/soft acid/base electrostatic matching” abilities of various organoalkoxysilane precursors with CTAB surfactant micelles can not only influence the loading of a particular functional group under our co-condensation condition, but also dictate the pore and particle morphology of the resulting mesoporous material. By introducing two organoalkoxysilanes with different structure-directing abilities as precursors of our co-condensation reaction, we can take advantage of such a difference between the two organoalkoxysilanes and utilize one precursor with *stronger structure-directing ability* to create the desired pore and particle morphology and employ the *other* for selective immobilization of catalysts. This strategy allows us to generate a series of multi-functionalized mesoporous silica materials with *control of both morphology and functionalization*.⁴

Progress 4. Tethering transition metal complex catalyst onto organically functionalized mesoporous silicas for formation-directing polymerization

To demonstrate the feasibility of using the morphologically defined silicas with precise control of the density and location of the organic functional groups as a support for *single-site heterogeneous catalysts*, we have used the aforementioned co-condensation method with *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine (AAPTMS), as the precursor.⁵ The AAPTMS groups then served as chelating ligands to bind with Cu^{2+} and form the catalytically active complexes. The resulting AAPTMS-functionalized particles (**Cu-MCM**) had a spherical shape with an average diameter of 500 nm and a BJH pore diameter of 25.6 Å.⁵ As depicted in **Figure 2**, the Cu-MCM served as a catalytic scaffold to direct and orient the conformation of the “molecular wire” formed through oxidative

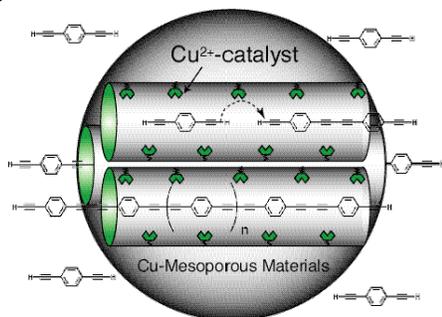


Figure 2. Schematic representation of Cu^{2+} -functionalized mesoporous silica (**Cu-MCM**) catalysts for oxidative polymerization of 1,4-diethynylbenzene into conjugated oligo(phenylene butadiynylene).

coupling reactions of 1,4-diethynylbenzene to a highly conjugated poly(phenylene butadiynylene) polymer (PPB). Fluorescence and ^{13}C solid state NMR provided spectroscopic evidence that isolated molecular wires with a high degree of alignment were formed within the parallel channels of our mesoporous catalyst.⁵ These results indicated that proper adjustment of the pore diameter and the distribution of catalytic groups are vital in order to prevent clogging of the pores with aggregated and/or cross-linked polymers.

Progress 5. Control of the selectivity of mesopore-tethered catalysts (Gatekeeping Effect)

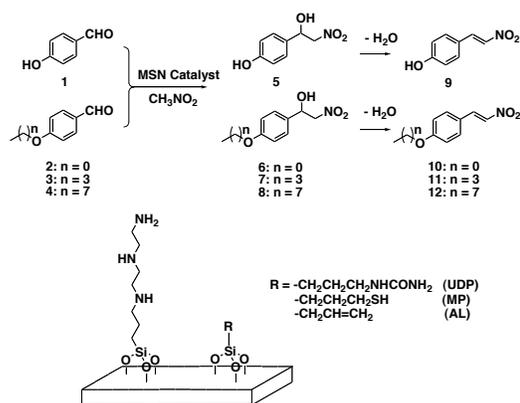


Figure 3. Bi-functionalized MSNs catalyzed competitive nitroaldol reaction.

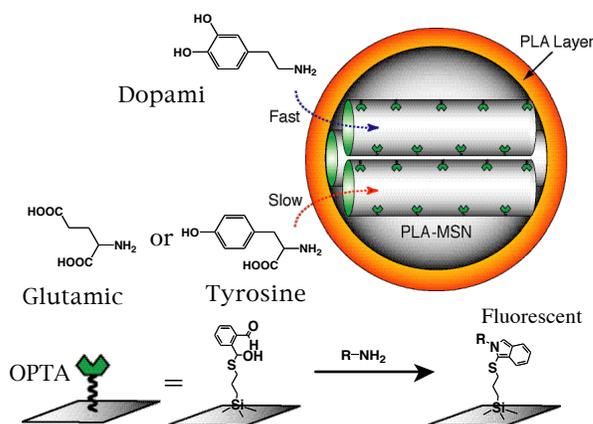


Figure 4. Schematic representation of the synthesis of PLA-coated MSN-based fluorescence sensor system for detection of amine-containing neurotransmitters, i.e., dopamine, glutamic acid, and tyrosine (R-NH₂).

highly efficient and selective catalysts. This research can also provide new fundamental knowledge about catalysis in general by deconvoluting the key factors that affect selectivity, reactivity and kinetics.

Future Plans

- *Control of the orientation and activity of tethered transition metal complex catalysts.* In order to understand the activity and selectivity of metal complex catalysts tethered on the walls of mesopores, we will characterize and control the location and the exact structure of the tethered catalysts on the surface.
- *Influence of the mesopore environment on catalyst selectivity and activity.* Our ability to anchor two types of groups on mesopore walls allows us to tether not only the catalyst but also other functional moieties. The influence of these auxiliary groups will be directed toward achieving various catalyst functions, such as enantioselectivity. These studies will use the concept of gatekeepers, which will be tested in the development of catalysts for the stereochemically controlled polymerization, selective hydrolysis, etc.

Publications (2002-present)

1. D. R. Radu, C.-Y. Lai, J. Huang, J. W. Wiench, M. Pruski, and V. S.-Y. Lin,* “Controlled Functionalization of MCM-41 Type of Mesoporous Silica with Anionic Organotrioxysilanes via Interfacial Electrostatic Designed Co-condensation” *Chem. Comm. (Cambridge, U.K.)*, **2004**, submitted.

We have demonstrated that the reaction selectivity of mesoporous catalysts can be controlled by using the novel concept of *gatekeepers*.^{6,7} Specifically, we prepared a series of bifunctionalized mesoporous silica nanosphere-based (MSN) catalysts for nitroaldol (Henry) reaction.⁶ In these catalysts (**Figure 3**), a common 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) primary group served as a catalyst, while three different secondary groups, ureidopropyl (UDP), mercaptopropyl (MP), and allyl (AL) functionalities, were incorporated as gatekeepers to control the reaction selectivity. We demonstrated that the selectivity of these bifunctionalized MSN catalysts could be systematically tuned simply by varying the polarity and hydrophobicity of the gatekeepers. In a separate study (**Figure 4**),⁷ we demonstrated a unique “sieving” effect of the poly(lactic acid) layer that was covalently attached to the exterior surface of mesoporous silica nanospheres. By utilizing this layer as a gatekeeper, we investigated the molecular recognition events between several structurally similar neurotransmitters, i.e., dopamine, tyrosine, and glutamic acid and a pore surface-anchored *o*-phthalic hemithioacetal (OPTA) group.⁷

DOE Interest

Developing catalytic systems that can coherently unite the best features of the homogeneous and heterogeneous areas of catalysis has been a key interest of DOE. By controlling the structure, reactivity and morphology of the mesoporous solid support and its interaction with the active sites, one can provide truly unique opportunities for the design of a new generation of

2. S. Huh, J. W. Wiench, J.-C. Yoo, M. Pruski, and V. S.-Y. Lin,* “Organic Functionalization and Morphology Control of Mesoporous Silica Materials via a Co-condensation Synthesis Method”, *Chem. Mater.* **2003**, *15*, 4247-4256.
3. C.-Y. Lai, D. M. Jeftinija, K. Jeftinija, S. Xu, S. Jeftinija, and Victor S.-Y. Lin,* “A Mesoporous Silica Nanosphere-Based Carrier System with Chemically Removable CdS Nanoparticle Caps for Stimuli Responsive Controlled Release of Neurotransmitters and Drug Molecules”, *J. Am. Chem. Soc.* **2003**, *125*, 4451-4459.
4. S. Huh, J. W. Wiench, B. G. Trewyn, S. Song, M. Pruski, and V. S.-Y. Lin,* “Tuning of Particle Morphology and Pore Properties in Mesoporous Silicas with Multiple Organic Functional Groups”, *Chem. Comm. (Cambridge, U.K.)*, **2003**, *18*, 2364-2365.
5. V. S.-Y. Lin,* D. R. Radu, M.-K. Han, W. Deng, S., Kuroki, D. R. Radu, B. H. Shanks, and M. Pruski, “Oxidative Polymerization of 1,4-Diethynylbenzene into Highly Conjugated Oligo(phenylene butadiynylene) Polymer Within the Channels of Surface-functionalized Mesoporous Silica and Alumina Materials” *J. Am. Chem. Soc.*, **2002**, *124*, 9040-9041
6. S. Huh, H.-T. Chen, J. W. Wiench, M. Pruski, and V. S.-Y. Lin,* “Controlling the Selectivity of Competitive Nitroaldol Condensation by Using a Bifunctionalized Mesoporous Silica Nanosphere-Based Catalytic System”, *J. Am. Chem. Soc.*, **2004**, *126*, 1010-1011.
7. D. R. Radu, C.-Y. Lai, J. W. Wiench, M. Pruski, and V. S.-Y. Lin,* “Gatekeeping Layer Effect: A Poly(lactic acid)-coated Mesoporous Silica Nanosphere-Based Fluorescence Sensor for Detection of Amino-Containing Neurotransmitters”, *J. Am. Chem. Soc.*, **2004**, *126*, 1640-1641.

Basic Investigations into the Reactivity of CO₂: New Methods of Activation of CO₂

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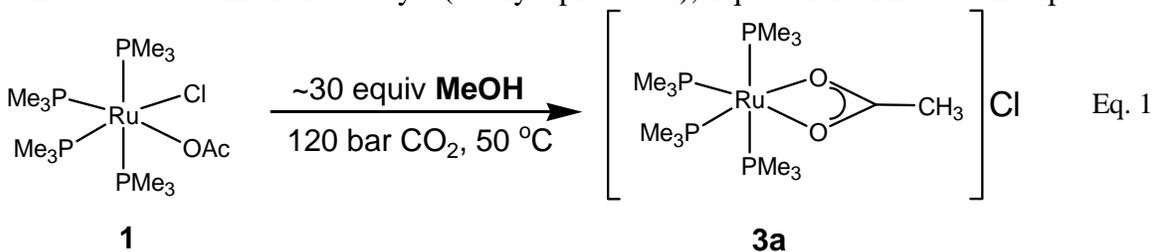
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Goal

Develop a fundamental understanding of the mechanisms of activation of relatively inert substrates.

Recent Progress

Ruthenium-based catalysts for CO₂ hydrogenation. Ruthenium-based catalysis of the hydrogenation of CO₂ to produce formic acid has been reported to be enhanced in the presence of protic co-catalysts, such as alcohols. We have used *in situ* high-pressure NMR spectroscopy to determine that the alcohol acts to produce cationic ruthenium complexes which appear to be a more active form of the catalyst (catalyst precursor), Equation 1. The cationic species **3**



gives the same high rates of CO₂ hydrogenation as does **1**, even in the absence of an alcohol additive.

In situ spectroscopy has also allowed us to interrogate the ruthenium complexes formed during catalysis. We have found little evidence for the involvement of a phosphine loss pathway for this series of catalysts. A proposed catalytic scheme based on our studies is shown in Figure 1. The chelated ruthenium formate cation **8** is only observed under H₂ and CO₂ pressure.

Reaction of CO₂ with alcohols. Alcohols and CO₂ have been found to be in equilibrium with the half-acid, R-O-C(O)-OH with the equilibrium far to the reactant side. In the presence of bases the half-acid salts can be observed using high-pressure NMR and IR spectroscopy. The equilibrium constant of this reaction is dependent upon the base, the alcohol, the CO₂ overpressure and the polarity of the solvent. The methyl carbonate DBU salt can be

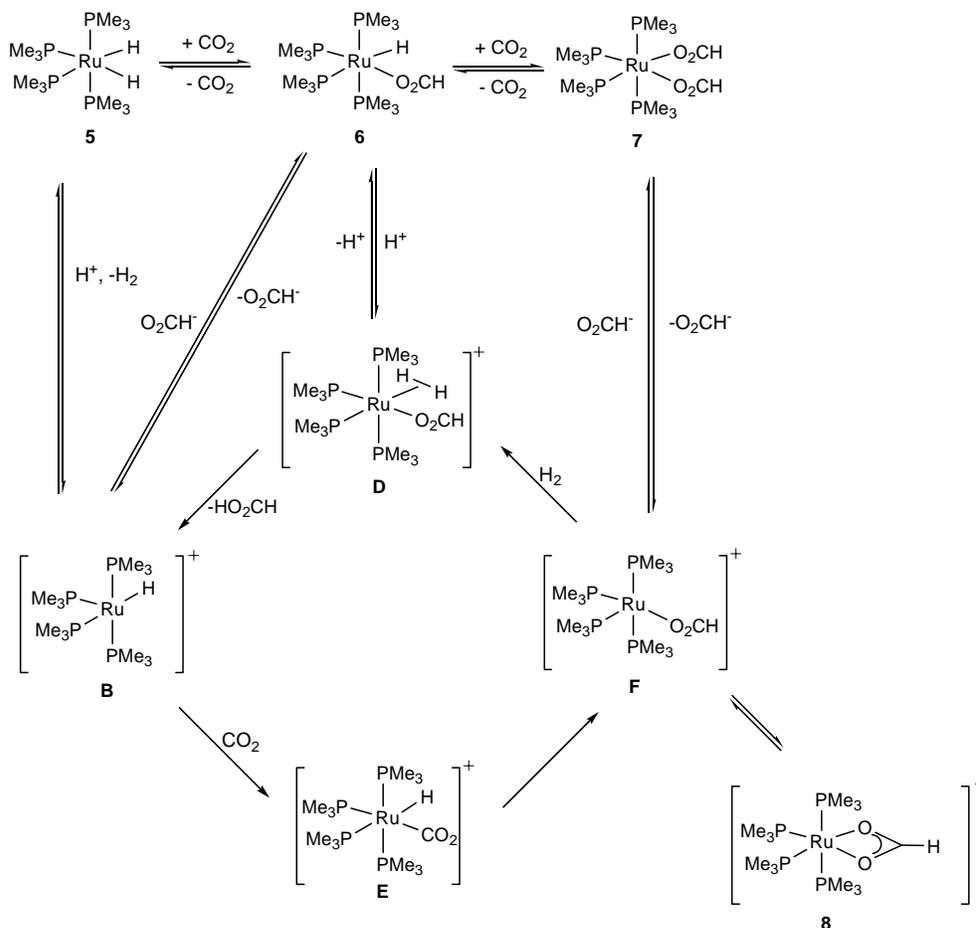
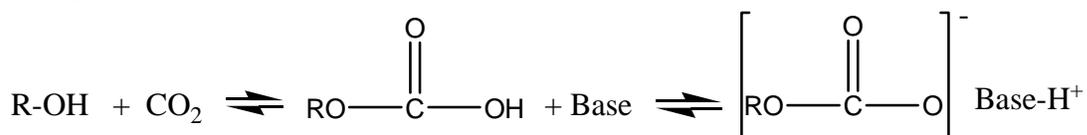


Figure 1.

quantitatively synthesized at low CO₂ pressures and used as a synthon for the production of dialkyl carbonates.



Activation of ethane toward hydroformylation. The photolysis of ethane in supercritical (SCF) CO₂ in the presence of *trans*-Rh(CO)(PMe₃)₂Cl was found to produce propionaldehyde, even in the absence of added hydrogen. The mechanism of this reaction was found to initiate with the photocatalytic dehydrogenation of ethane to form ethylene and hydrogen which then may proceed along a normal hydroformylation pathway. Step-scan FTIR spectroscopy of *trans*-Rh(CO)(PMe₃)₂Cl in SCF CO₂ shows new bands which are consistent for a CO₂ insertion product, a cyclic metal-anhydride, and *cis*-Rh(CO)(PMe₃)₂Cl which both decay back to the *trans* starting material.

Completing Prior Work. Papers describing the ruthenium catalyzed CO₂ hydrogenations and the hydroformylation of ethane have been published.

DOE Interest

The mechanisms of interactions of relatively inert substrates such as CO₂, ethane, methane, etc. are of fundamental interest for U.S. chemical and energy production. Fundamental understanding of reaction chemistry is necessary for efficient utilization of chemical feedstocks.

Future Plans

Interfacial catalysis. Initial studies into the complex reactions in multi-phase media are being conducted. While studies of homogeneous reaction systems still yield important fundamental information, the more complex multi-phase systems need to be better understood. These systems, which include liquid-liquid, gas-liquid, solid-liquid, solid-gas and more complex mixtures, may or may not follow similar reaction pathways to their homogeneous analogs. In a relatively simple case from our laboratory the addition of small amounts of hydrogen to a homogeneous supercritical solution of ethylene containing a manganese organometallic compound led to a separation into three phases, all of which contained at least some of each of the three reagents. In this and other multi-phase systems the paramount question is: Do the reagents behave as in a homogeneous system or are there other pathways for reaction? This question is being applied to both supercritical fluid systems and more mundane systems in which homo- and heterogeneous catalysis occurs. Time-resolved spectroscopy in combination with *in situ* high-pressure spectroscopy are being applied to this complex problem.

Publications

Munshi P, Main AD, Linehan JC, Tai CC, Jessop PG, "Hydrogenation of carbon dioxide catalyzed by ruthenium trimethylphosphine complexes: The accelerating effect of certain alcohols and amines", *J. Am. Chem. Soc.*, **2002**, *124* (27): 7963-7971.

Bitterwolf TE, Scallorn WB, Bays JT, Weiss CA, Linehan JC, Franz J, Poli R," Photochemical intermediates of trans-Rh(CO)L₂Cl where L = PMe₃, PBu₃, and i-Pr₂HN and cis-Rh(CO)(2)(i-Pr₂HN)Cl in frozen organic glasses", *J. Organomet. Chem.*, **2002**, *652* (1-2): 95-104.

Yonker CR, Linehan JC, " Investigation of the hydroformylation of ethylene in liquid carbon dioxide", *J. Organomet. Chem.* , **2002**, *650* (1-2): 249-257.

Tai CC, Pitts J, Linehan JC, Main AD, Munshi P, Jessop PG, "In situ formation of ruthenium catalysts for the homogeneous hydrogenation of carbon dioxide", *Inorg. Chem.*, **2002**, *41* (6): 1606-1614.

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Photocatalysis with Microporous ETS-10 Materials

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Goal

Develop the physical basis for understanding the photocatalytic properties of ETS-10 and related microporous titanosilicates containing wires of TiO₂ octahedra.

Background and Recent Progress

ETS-10 is a crystalline microporous semiconductor containing one-dimensional units of TiO₂ octahedra. These semiconducting wires act as photocatalysts and promote intermolecular reactions between adsorbed species. We are conducting a comprehensive investigation of photocatalysis in ETS-10 consisting of five interconnected research focuses. Firstly we are studying surface species formed in the micropores upon irradiation of ETS-10 with UV light. These studies will rely mostly on DRIFT spectroscopy, UV/Vis-diffuse-reflectance spectroscopy and EPR to characterize the species formed inside the pores. Second we will study the mechanisms of photooxidation of methanol and ethanol in the pores of ETS-10 (in its sodium and proton forms) and compare them to the well-understood mechanism of decomposition in TiO₂ anatase. Third, we will prepare new forms of ETS-10 containing other transition metals (Fe, V, Nb, etc.) with the objectives of reducing the bandgap, increasing the quantum yield, changing the nature of the excited species formed upon irradiation and changing the hydrophilic character of the pores (i.e. to make it more organophilic).

The interpretation of the experimental results and the selection of specific dopants will be closely tied to electronic structure calculations. We have recently begun first-principles calculations of dopant effects on the electronic structure of anatase and we are applying the same methods to understand the photochemistry of ETS-10. Modeling will be a proactive part of the research driving guiding the synthesis efforts of the research.

Our aims are that at the end of the funded period we will have a well-organized body of experimental data and modeling results that will let us make useful predictions about the photocatalytic properties of ETS-10 isostructural materials. The information should also help in the prediction of photocatalytically relevant steps in the oxidation of small molecules in the pores of different materials.

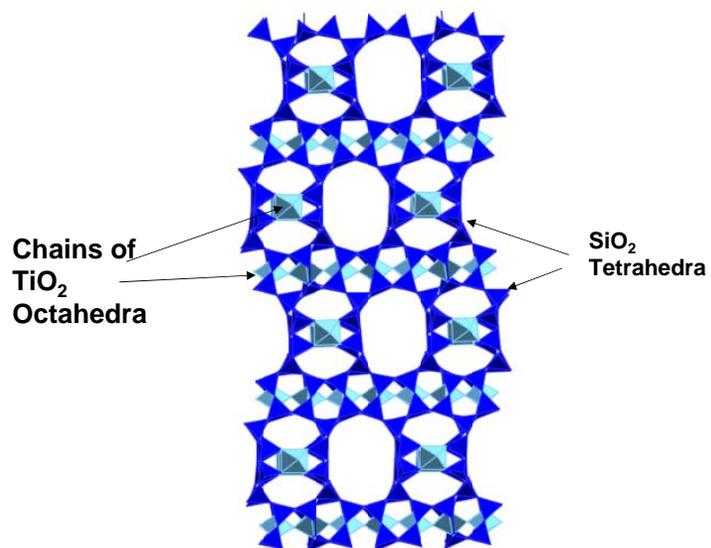


Figure 1: Framework structure of ETS-10.

**Cluster-Expanded Solids:
A Strategy for Assembling Functional Porous Materials**

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Goal

The intention of the research is to explore the use of molecular cluster precursors in the assembly of microporous coordination solids that function as sieves, sensors, or catalysts.

Recent Progress

Cyano-Bridged Frameworks Incorporating Mixed-Metal Clusters. Reactions of the face-capped octahedral clusters $[\text{Re}_5\text{OsSe}_8\text{Cl}_6]^{3-}$ and $[\text{Re}_4\text{Os}_2\text{Se}_8\text{Cl}_6]^{2-}$ with NaCN in a melt of NaNO₃ afford the cyano-terminated clusters $[\text{Re}_5\text{OsSe}_8(\text{CN})_6]^{3-}$ and $[\text{Re}_4\text{Os}_2\text{Se}_8(\text{CN})_6]^{2-}$. The former species reacts with $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution to yield the cluster-expanded Prussian blue analogue $\text{Ni}_3[\text{Re}_5\text{OsSe}_8(\text{CN})_6]_2 \cdot 33\text{H}_2\text{O}$. In addition, these clusters can be reduced by one electron to give the first 25-electron clusters of their type. As demonstrated with the synthesis and characterization of $\{\text{Re}_4\text{Os}_2\text{Se}_8[\text{CNCu}(\text{Me}_6\text{tren})]_6\}^{9+}$, the reduced diosmium cluster is capable of engaging in ferromagnetic exchange interactions, indicating its potential utility in the synthesis of a microporous magnet.

Cyano-Bridged Frameworks Incorporating $[\text{Zr}_6\text{BCl}_{12}]^{2+}$ Cluster Cores. The reaction between $[\text{Zr}_6\text{BCl}_{18}]^{4+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ in aqueous solution, leads to the immediate precipitation of the cluster-expanded Prussian blue analogue $(\text{Et}_4\text{N})[\text{Zr}_6\text{BCl}_{12}][\text{Cr}(\text{CN})_6] \cdot \text{Et}_4\text{NCl} \cdot 3\text{H}_2\text{O}$. The cubic Prussian blue type structure of this compound was confirmed via Rietveld profile analysis of X-ray powder diffraction data, and magnetization measurements reveal the onset of long-range magnetic ordering at 2 K.

Trigonal Prismatic Cluster Building Units. Simultaneous reduction of WCl_6 and CCl_4 with bismuth metal at 450 °C, leads, upon work-up, to the carbon-centered trigonal prismatic cluster $[\text{W}_6\text{CCl}_{18}]^{2-}$. Cyclic voltammetry experiments performed on solutions

containing this cluster show that it possesses five chemically-accessible redox states. Related reactions incorporating NaN_3 in place of CCl_4 led to the analogous nitrogen-centered cluster $[\text{W}_6\text{NCl}_{18}]^{2-}$.

New Metal-Chalcogen Cluster Building Units. Evaporation of binary transition metal chalcogenides and cocondensation of the vapor with PEt_3 has led to a range of new metal-chalcogen clusters. For example, evaporation of Cu_2Se enables isolation of $[\text{Cu}_{26}\text{Se}_{13}(\text{PEt}_3)_{14}]$ and $[\text{Cu}_{70}\text{Se}_{35}(\text{PEt}_3)_{21}]$, containing surface-ligated fragments of the original solid.

Prussian Blue Analogues Incorporating $[\text{Co}(\text{CN})_5]^{3-}$. The reaction between $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and the square pyramidal complex $[\text{Co}(\text{CN})_5]^{3-}$ in deoxygenated water yields the Prussian blue analogue $\text{Co}_3[\text{Co}(\text{CN})_5]_2 \cdot 8\text{H}_2\text{O}$, containing a high concentration of lattice vacancies. Upon dehydration, the compound retains crystallinity and exhibits a Type I dinitrogen sorption isotherm, characteristic of a microporous solid. Magnetic measurements showed it to behave as a ferrimagnet with an ordering temperature of 48 K, which is reduced to 38 K in the dehydrated solid. This is the first truly microporous material shown to exhibit magnetic hysteresis.

New Cyanomolybdate Building Units. Octahedral coordination of molybdenum(III) was achieved by limiting the amount of cyanide available upon complex formation. Reaction of $\text{Mo}(\text{CF}_3\text{SO}_3)_3$ with LiCN in DMF affords $\text{Li}_3[\text{Mo}(\text{CN})_6] \cdot 6\text{DMF}$, featuring the previously unknown octahedral complex $[\text{Mo}(\text{CN})_6]^{3-}$. Further restricting the available cyanide in a reaction between $\text{Mo}(\text{CF}_3\text{SO}_3)_3$ and $(\text{Et}_4\text{N})\text{CN}$ in DMF, followed by recrystallization from DMF/MeOH, yields $(\text{Et}_4\text{N})_5[\text{Mo}_2(\text{CN})_{11}] \cdot 2\text{DMF} \cdot 2\text{MeOH}$.

New Cyanorhenate Building Units. Reaction of $(\text{Bu}_4\text{N})\text{CN}$ with $[\text{ReCl}_6]^{2-}$ in acetonitrile affords yellow $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_7]$, featuring the pentagonal bipyramidal complex $[\text{Re}(\text{CN})_7]^{3-}$. In aqueous solution, this compound reacts with Mn^{2+} ions to generate the porous, and potentially photomagnetic, three-dimensional solid $[\text{fac-Mn}(\text{H}_2\text{O})_3][\text{cis-Mn}(\text{H}_2\text{O})_2][\text{Re}(\text{CN})_7] \cdot 3\text{H}_2\text{O}$. Addition of KIO_4 to the reaction solution, originally intended to prevent reduction of the rhenium during solid formation, instead yields white $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$, featuring the square antiprismatic complex $[\text{Re}(\text{CN})_8]^{3-}$.

Homoleptic Trimethylsilylacetylde Complexes. Reactions between simple transition metal salts and LiCCSiMe_3 have been shown to generate three new octahedral complexes: $[\text{Cr}(\text{CCSiMe}_3)_6]^{3-}$, $[\text{Fe}(\text{CCSiMe}_3)_6]^{4-}$, and $[\text{Co}(\text{CCSiMe}_3)_6]^{3-}$. Spectroscopic characterization of these molecules has enabled us to establish the ligand field strength of trimethylsilylacetylde as lying just below methyl in the spectrochemical series.

DOE Interest

The new microporous materials resulting from these studies may be of utility in a range of applications, including molecular sieving, detection of volatile organic compounds, ion exchange, and homogeneous catalysis.

Future Plans

Synthesis of a Microporous Magnet. Our efforts to produce molecular cluster building units capable of delivering strong magnetic coupling with surrounding metal ions will continue. The goal here is to generate solids with ordering temperatures at or above room temperature for use in performing magnetic separations (e.g., for the noncryogenic separation of dioxygen from dinitrogen). New targets of particular interest here include the clusters $[\text{Gd}_6\text{CCl}_{18}]^{9-}$, $[\text{Re}_{6-n}\text{M}_n\text{Q}_8\text{Cl}_6]^{(4+n)-}$ ($\text{M} = \text{Mo}, \text{W}$), $[\text{M}_6\text{Q}_8(\text{CN})_6]^{n-}$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}$), $[\text{W}_6\text{CCl}_{12}(\text{CN})_6]^{3-}$, and $[\text{B}_6(\text{CN})_6]^{1-}$. Relatedly, dioxygen-binding experiments will be carried out on porous phases incorporating $[\text{Co}(\text{CN})_5]^{3-}$.

Homogeneous Catalysis in Cluster-Expanded Prussian Blue Type Solids. Attempts will be made to exploit the coordinatively-unsaturated metal sites within dehydrated cluster-expanded Prussian blue solids for homogeneous catalysis.

Characterization of Photomagnetic Solids. The photomagnetic properties of porous solids incorporating $[\text{Re}(\text{CN})_7]^{3-}$ and $[\text{Re}(\text{CN})_8]^{3-}$ will be further characterized, with the intention of developing potential sensing applications.

Synthesis of Acetylenediide-Bridged Solids. The new trimethylsilylacetylide complexes obtained recently will be used in coupling reactions intended to produce unprecedented frameworks featuring acetylenediide bridges.

Publications (2002-2004)

1. "Cyanide-Limited Complexation of Molybdenum(III): Synthesis of Octahedral $[\text{Mo}(\text{CN})_6]^{3-}$ and Cyano-Bridged $[\text{Mo}_2(\text{CN})_{11}]^{5-}$ " Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2110-2111.
2. "Co₃[Co(CN)₅]₂: A Microporous Magnet with an Ordering Temperature of 38 K" Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 12096-12097.
3. "Cluster Synthesis via Ligand-Arrested Solid Growth: Triethylphosphine-Capped Fragments of Binary Metal Chalcogenides" Crawford, N. R. M.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 14842-14843.
4. "New Cyanometalate Building Units: Synthesis and Characterization of $[\text{Re}(\text{CN})_7]^{3-}$ and $[\text{Re}(\text{CN})_8]^{3-}$ " Bennett, M. V.; Long, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 2394-2395.
5. "New Routes to Transition Metal-Carbido Species: Synthesis and Characterization of the Carbon-Centered Trigonal Prismatic Clusters $[\text{W}_6\text{CCl}_{18}]^{n-}$ ($n = 1, 2, 3$)" Welch, E. J.; Crawford, N. R. M.; Bergman, R. G.; Long, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 11464-11465.
6. "Cluster-to-Metal Magnetic Coupling: Synthesis and Characterization of 25-Electron $[\text{Re}_{6-n}\text{Os}_n\text{Se}_8(\text{CN})_6]^{(5-n)-}$ ($n = 1, 2$) Clusters and $\{\text{Re}_6$

$\text{Os}_n\text{Se}_8[\text{CNCu}(\text{Me}_6\text{tren})]_6\}^{9+}$ ($n = 0, 1, 2$) Assemblies” Tulskey, E. G.; Crawford, N. R. M.; Baudron, S. A.; Batail, P.; Long, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 15543-15553.

7. “Atomlike Building Units of Adjustable Character: Solid State and Solution Routes to Manipulating Hexanuclear Transition Metal Chalcogenide Clusters” Welch, E. J.; Long, J. R. *Prog. Inorg. Chem.*, submitted.
8. “Determination of ^{77}Se - ^{77}Se and ^{77}Se - ^{13}C J -Coupling Parameters for the C_{4v} -Symmetry Selenocyanide Cluster $[\text{Re}_5\text{OsSe}_8(\text{CN})_6]^{3-}$ ” Ramaswamy, K.; Tulskey, E. G.; Kao, L.-F.; Long, J. R.; Hayes, S. E. *Inorg. Chem.*, submitted.
9. “Homoleptic Trimethylsilylacetylide Complexes of Chromium(III), Iron(II), and Cobalt(III): Syntheses, Structures, and Ligand Field Parameters” Berben, L. A.; Long, J. R. *J. Am. Chem. Soc.*, submitted.

New Vistas for Functionalized Polyoxometalates

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Goals

The development of rational methods for incorporating functionality into polyoxometalate (POM) systems and to employ the resulting species to catalytic advantage.

Recent Progress

Our principal recent efforts have focused on the synthesis and characterization of new classes of POM complexes incorporating nitrido ligands. Prototypical structures of these systems are shown below in Chart 1.

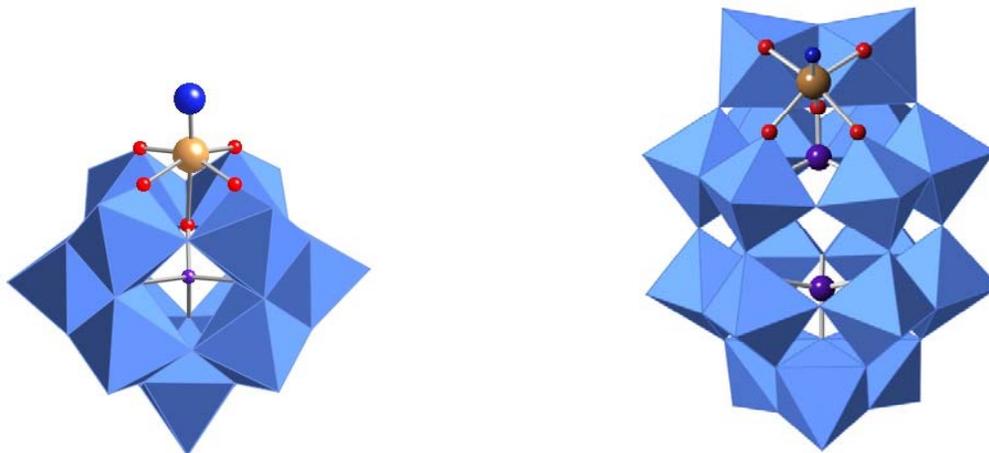


Chart 1. Nitrido-POM structures of the Keggin (left) and Dawson (right) families.

Osmium Nitrido-Keggin systems: Introduction of the $[\text{Os}^{\text{VI}}\equiv\text{N}]^{3+}$ unit into a Keggin POM framework has been accomplished in a straightforward reaction between $[\text{TBA}][\text{OsNCl}_4]$ and $[\text{TBA}]_4[\text{H}_3\text{PW}_{11}\text{O}_{39}]$ in acetonitrile in the presence of Et_3N . A single-crystal X-ray diffraction study of the product $[\text{TBA}]_4[(\text{Os}^{\text{VI}}\text{N})\text{PW}_{11}\text{O}_{39}]$ reveals, as expected, a twelve-fold orientational disorder in the solid state, but the identity and structure of the material has been established by a variety of techniques including electrospray MS and multinuclear (^{15}N , ^{31}P , ^{183}W) NMR studies.¹

Rhenium Nitrido-Keggin systems: Reaction of the classical Chatt nitride complex $[\text{Re}^{\text{V}}\text{NCl}_2(\text{PPh}_3)_2]$ with $[\text{TBA}]_4[\text{H}_3\text{PW}_{11}\text{O}_{39}]$ proceeds smoothly to yield the $[\text{Re}^{\text{VI}}\equiv\text{N}]^{3+}$ derivative $[\text{TBA}]_4[(\text{Re}^{\text{VI}}\text{N})\text{PW}_{11}\text{O}_{39}]$. A transient, extremely reactive $[(\text{Re}^{\text{V}}\text{N})\text{PW}_{11}\text{O}_{39}]^{5-}$ intermediate can be detected by ^{31}P NMR. The fully oxidized system $[\text{TBA}]_3[(\text{Re}^{\text{VII}}\text{N})\text{PW}_{11}\text{O}_{39}]$ has been isolated upon treatment of the Re^{VI} species with $[\text{TBA}][[\text{Br}_3]$. Cyclic voltammetry studies indicate that the corresponding $[\text{Re}^{\text{IV}}\equiv\text{N}]$ and $[\text{Re}^{\text{III}}\equiv\text{N}]$ derivatives can be generated upon electrochemical reduction.¹

Manganese Nitrido-Keggin and Nitrido-Dawson systems. Our most exciting recent result is the generation of the $[\text{Mn}^{\text{V}}\equiv\text{N}]^{2+}$ unit within both the Keggin and Dawson POM frameworks. Irradiation of the azido precursor $[(\text{Mn}^{\text{III}}\text{N}_3)\text{P}_2\text{W}_{17}\text{O}_{61}]^{8-}$ smoothly induces N_2 extrusion forming deep blue $[(\text{Mn}^{\text{V}}\text{N})\text{P}_2\text{W}_{17}\text{O}_{61}]^{8-}$. Isolation and purification of this material is difficult because of its high reactivity; we also suspect that it may be susceptible to photodegradation during its preparation. ^{31}P NMR spectra confirm the diamagnetism expected for $d^2 \text{Mn}^{\text{V}}$, and IR spectra reveal $\nu_{(\text{Mn}=\text{N})}$ at 1059 cm^{-1} . Photolysis of $[(\text{Mn}^{\text{III}}\text{N}_3)\text{PW}_{11}\text{O}_{39}]^{5-}$ similarly affords a deep blue material tentatively formulated as $[(\text{Mn}^{\text{V}}\text{N})\text{PW}_{11}\text{O}_{39}]^{5-}$.

Chromium Nitrido-Keggin system: We have recently prepared a Keggin-type POM incorporating the $[\text{Cr}^{\text{V}}\equiv\text{N}]^{2+}$ unit. The complex $[(\text{Cr}^{\text{V}}\text{N})\text{PW}_{11}\text{O}_{39}]^{5-}$ has been characterized by ESR and its electrochemistry indicates that the Cr^{VI} analogue should be easily accessible. Preliminary studies indicate that the nitrido ligand exhibits electrophilic character, reacting with PR_3 to generate the phosphorane iminato systems $[(\text{Cr}^{\text{III}}\text{N}=\text{PR}_3)\text{PW}_{11}\text{O}_{39}]^{5-}$.²

Nitrogenous Hexametalate Derivatives. We have reported the preparation, characterization and structure of a hexatungstate diazoalkane derivative namely, $[\text{TBA}]_2[\text{W}_6\text{O}_{18}(\text{NNC}(\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3)]$.³ This complex is the first diazoalkane derivative of a tungsten POM, and the second diazoalkane POM derivative of any type.

POMs as Polymer Pendants. We previously demonstrated that the POM-bound styrylimido ligand in the system $[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_4\text{CH}=\text{CH}_2)]^{2-}$ could serve as reactive entity allowing the preparation of various soluble styrenic co-polymers bearing POM units as backbone substituents. A patent application covering these materials has recently been allowed by the USPTO.⁴ We have extended these ideas to the preparation of other styrylimido systems including those of rhenium and gold.

DOE Interest

The POM framework is thermally and oxidatively robust, and can be tailored for solubility in aqueous or non-aqueous media by counteranion variation. As such, it presents an attractive and stable platform for metal-mediated catalytic transformations, provided that suitable functionality can be appended.

Future Plans

Reactivity of Nitrido-Polyoxometalates. The $[\text{Mn}^{\text{V}}\equiv\text{N}]$ -substituted Dawson and Keggin systems will be examined for olefin aziridination activity. Our initial approach will be to generate the species in the presence of trifluoroacetic anhydride and a suitable olefin, and then screen the reaction mixture for the desired trifluoroacyl aziridine product. Simple alkylations

will be also be pursued in an effort to access the long-sought organoimido-Keggin and -Dawson systems. Preliminary results on the $[(\text{Cr}^{\text{V}}\text{N})\text{PW}_{11}\text{O}_{39}]^{5-}$ species suggest that reactions of this complex with nucleophiles will be productive.

New Metal-nitrido POM systems. Keggin and Dawson POMs incorporating $[\text{W}^{\text{VI}}\equiv\text{N}]^{3+}$, $[\text{Mo}^{\text{VI}}\equiv\text{N}]^{3+}$, $[\text{V}^{\text{V}}\equiv\text{N}]^{2+}$, and $[\text{Fe}^{\text{V}}\equiv\text{N}]^{2+}$ units are current targets of exploratory synthesis in our laboratory.

Incorporating Remote Functionality into Organoimido-POMs. We are interested in creating multi-functional POM derivatives in which secondary metal centers can be tethered covalently to a POM anion through the intervention of an organoimido ligand bearing appropriate functionality. Our attention is now focused on incorporating bipyridyl-imido ligands into various POM frameworks.

Publications (2002-3)

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Nanoscale Phenomena in Surface Chemistry: Structure, Reactivity and Electronic Properties

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Goal

Identify the relations between nanometer-scale surface features (e.g., faceted structures and clusters) and heterogeneous chemistry.

Recent Progress

Our emphasis is on atomically-rough morphologically unstable surfaces [e.g., bcc W(111), fcc Ir (210), hcp Re (12-31)] that can undergo nanoscale faceting when covered by adsorbed gases or ultrathin films of metals (~1 monolayer thick), and annealed. Our objectives are:

(a) to identify the causes of faceting and other nanometer-scale growth phenomena on metallic surfaces, adsorbate-covered surfaces, and sulfided surfaces, and

(b) to correlate surface reactivity, surface structure, and surface electronic properties of surfaces with nanometer-scale features (facets, metallic clusters).

We use a surface science approach, including scanning tunneling microscopy (STM), low energy electron diffraction (LEED), temperature programmed desorption (TPD), and high resolution soft x-ray photoemission (HRSXPS), using synchrotron radiation at the National Synchrotron Light Source (NSLS). Details of recent results include:

Faceting of Ir and structure sensitive reactions: Ir (210) surfaces are unstable when covered with oxygen and heated to > 600K; nanometer scale pyramids having {311} and {110} facets cover the surface (identified by LEED and STM); see Figure 1. We have developed a novel chemical procedure to remove the oxygen and retain the atomically-clean, faceted Ir surface. By studying reactions over the clean *planar* surface and the clean *faceted* surface, several structure sensitive processes have been identified (see Figure 2), including the recombination and desorption of hydrogen, the thermal decomposition of acetylene, and the thermal decomposition of ammonia. In all cases, there are substantial differences in reaction kinetics over planar versus faceted surfaces.

Faceting of Re and structure sensitive reactions: The atomically-rough Re(12-31) surface, when covered with oxygen and heated to $T > 700\text{K}$, develops ridge-like nanoscale facets having $(01\bar{1}0)$ and $(11\bar{2}1)$ orientations. HRXPS is used to characterize the transition from an oxygen atom-covered surface to the onset of oxidation (ReO, Re₂O₃). Supported Re oxides have recently been shown to catalyze the oxidation of methanol to methylal (dimethoxymethane, CH₃OCH₂OCH₃). Using TPD, we have investigated the reaction of methanol over planar and faceted O-covered Re(12 $\bar{3}$ 1) to probe for structure sensitivity in this elementary step in methylal synthesis. We find that methanol reacts on O-covered Re(12 $\bar{3}$ 1) via two competing pathways: selective dehydrogenation to evolve gaseous CO and formaldehyde, and non-selective decomposition to deposit surface C, O and H. The data demonstrate clear evidence for structure

sensitivity associated with nanoscale facets, manifested by a substantially reduced activity of the faceted surface towards methanol dehydrogenation.

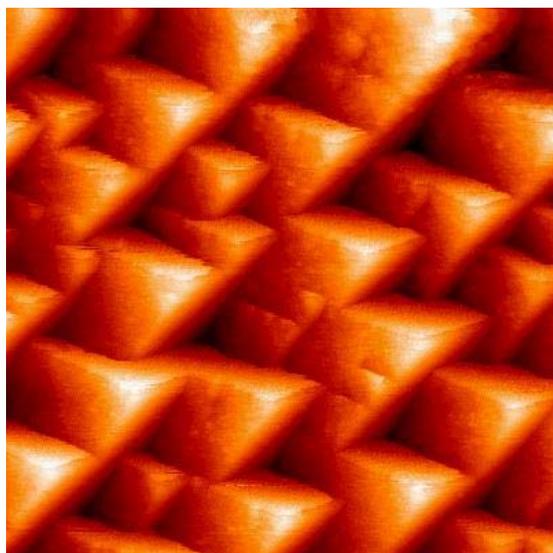


Figure 1. STM image of faceted Ir(210) surface, (100 nm x 100nm).{311} and {110} facets are formed by annealing the oxygen-covered surface to $T > 600\text{K}$.

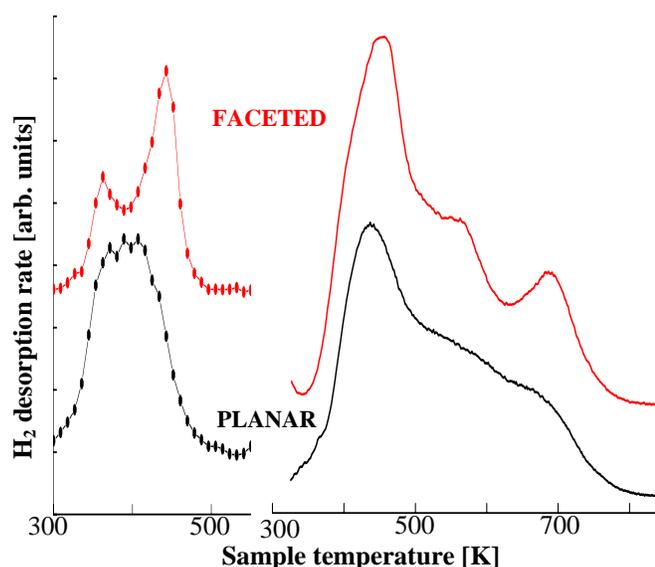


Figure 2: TPD spectra displaying structure sensitivity of planar and faceted Ir surfaces. Left, recombinative desorption of hydrogen; right, thermal decomposition of acetylene and desorption of hydrogen.

Bimetallic systems, from segregated monolayers to surface alloys: Monolayer metallic films that cause faceting of W(111) and Mo(111) are generally found to "float" on the outer surface, with little or no alloy formation. Multilayer films (Pt, Pd, Ir, Rh, ...) on W surfaces form alloys upon annealing. Theory and experiment have been combined to identify the conditions under which multilayers of Pt, Pd, Ru form surface alloys with unstable W surfaces, while monolayers remain segregated.

Growth of nanoscale metal clusters on sulfided surfaces: Both Cu and Ni atoms, when deposited onto the highly-textured sulfided S(4x4)/W(111) surface, form subnanometer-scale clusters at specific sites and exhibit self-limiting growth. Clear evidence for non-random nucleation is found, which may imply long-range interactions in nanocluster growth.

DOE Interest

These results provide new understanding of dynamic structural rearrangements at the surfaces of high area bimetallic and sulfide catalysts, and are clarifying the role of nanometer-scale size effects in energy-related surface reactions such as hydrogen generation, hydrocarbon reforming, and hydrodesulfurization.

Future Plans

Surface structure: We will use STM to determine the temperature-dependent shapes, orientations, size distributions and atomic structure of oxygen-induced facets on both Ir and Re surfaces. A new variable temperature STM system will allow us to determine the growth of facets and the relaxation of facets back to the planar surface, in real time. This has never been accomplished before! In a collaboration at U. of Illinois, LEEM (low energy electron microscopy) will be used to complement the STM studies: we will characterize nucleation and growth of faceted regions in real time over micrometer distance scales. These studies are important for determining the stability of nanometer-scale supported metal Ir and Re catalysts. A

longer-term prospect is the use of O-faceted surfaces as templates for growth of nanoscale metal clusters, including bimetallics.

Reactivity: Our reactivity studies will involve effects of facet size on acetylene chemistry and methanol oxidation over Ir and Re, respectively. A new direction is ammonia surface chemistry on planar and faceted Ir(210) (decomposition of ammonia will produce CO_x-free hydrogen, which has potential fuel cell applications). We are also developing Monte Carlo simulation methods to model reactions on nanoscale surface features.

Synchrotron radiation: Future work using synchrotron radiation will include the interaction of S overlayers on Re(12-31), the growth of Pt on both O-modified and S-modified Re surfaces, and a search for reaction intermediates in methanol chemistry over Re. Conditions for surface alloy formation on Re, Ir and W substrates will be established. We will collaborate with a group at the European Synchrotron Radiation Facility in France, in innovative studies of Grazing Incidence Small Angle X-Ray Scattering (GISAXS) to characterize faceted surfaces. This novel method can provide unprecedented insights into structure, dispersion, size distributions and orientation of nanoscale features on surfaces.

Publications (2003-2004)

1. "Adsorption and Decomposition of Acetylene on Planar and Faceted Ir(210)", W. Chen, I. Ermanoski, Q. Wu, T. E. Madey, H. Hwu, J. G. Chen, *J. Phys. Chem B* **107** (2003) 5231-5242.
2. "High Resolution Photoemission Study of Growth, Alloying, and Intermixing of Ultrathin Ruthenium Films on W(111) and W(211)", M. J. Gladys, G. Jackson, J. E. Rowe, and T. E. Madey, in press, *Surface Science* **544** (2003) 193-208.
3. "Ultrathin Pd and Pt Films on W(211)", J. Block, J. J. Kolodziej, J. E. Rowe, T. E. Madey, E. Schroder, *Thin Solid Films* **428** (2003) 47-51.
4. "Elucidation of the active surface and origin of the weak metal-hydrogen bond on Ni/Pt(111) bimetallic surfaces: A surface science and density functional theory study", J. R. Kitchin, N. A. Khan, M. A. Barteau, J. G. Chen, B. Yakshinskiy, T. E. Madey, *Surface Science* **544** (2003) 295-308.
5. "Oxygen induced nano-faceting of Ir(210)", I. Ermanoski, K. Pelhos, W. Chen, J. S. Quinton, T. E. Madey" *Surface Science* **549** (2004) 1-23.
6. "Pt-Induced faceting of tungsten field emitter tips " G. Antczak, R. Blaszczyzyn, T. E. Madey, in press, *Progress in Surface Science* **74** (2003) 81-95.
7. "Site Specific Nucleation of Ni Nanoclusters on S(4x4)/W(111)", Qifei Wu and Theodore E. Madey, *Surface Science* (2004), in press
8. "A High Resolution Photoemission Study of Surface Core-Level Shifts (SCLS) in Clean and Oxygen Covered Ir(210) Surfaces", M. J. Gladys, I. Ermanoski, G. Jackson, J. S. Quinton, J. E. Rowe, and T. E. Madey, *J. Electron Spectroscopy and Related Phenomena* (2004), in press.
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The Dynamics of Adsorption on Clean and Adsorbate-modified Transition Metal Surfaces

Postdocs: Xing-Cai Guo, Chia-ling Kao

Students: James Stinnet, Jason Weaver, Anders Carlsson, Chia-ling Kao

Goal

An understanding of molecular adsorption processes on surfaces is important for heterogeneous catalysis, thin film and crystal growth, and surface lubrication processes. Due to the industrial importance of reactions of alkanes on platinum catalysts, trapping of small molecules on the platinum group metals has been studied by the use of both molecular beam methods and stochastic molecular dynamic simulations in recent years. The goal of this work is to develop a methodology for predicting the adsorption probabilities of alkanes on metal surfaces.

Background and previous work

The trapping dynamics of small alkanes on Pt(111) and Pt(110)-(1×2) have been extensively investigated. To better understand the energy transfer process involved in adsorption, realistic molecular simulations of alkane adsorption were initially undertaken by Stinnett et al. for ethane trapping on Pt(111). By adjusting the parameters in the Morse potential used to represent the ethane-Pt interaction in the united atom approximation, good agreement between experiment and simulation was obtained. Subsequently, these potential parameters were used to successfully predict the trapping probabilities of ethane on Pt(110)-(1×2), Pt(111)-S, and Pt(111)-O. Stinnett et al. also extend their calculations to methane and propane on Pt(111) and Pt(110)-(1×2), finding excellent agreement between experiment and the predictions of theory over a wide range of incident energies and angles. Later, Weaver et al. extended the united-atom approximation to model the dynamics of n-butane, isobutane, and neopentane on Pt(111) using the same simulation methods. In the latter work the Morse potential was adjusted slightly to give a better fit of theory and experiment for all the alkanes, C₁ – C₅.

Recent results

More recently we began studies of the predictive capability of the theory to scale trapping probabilities for the alkanes from metal to metal. The first metal studied was palladium. Many physical properties of Pd(111) and Pt(111) are similar, such as the lattice parameter and the Debye temperature, the measure of the metal-metal force constants. Thus these two surfaces differ primarily in their atomic masses. In addition, the binding energies of alkanes to the two surfaces are nearly identical, so the interaction between small alkanes and the surfaces should be governed by nearly the same, if not identical, Morse potential parameters. We successfully predicted the trapping probabilities of several alkanes on Pd(111) to within 30% with *no* adjustment of the potential parameters obtained from Pt(111). The simulations clearly indicate that the excitation of lattice phonons plays a more important role in trapping than on Pt(111); this result appears to originate from the lower mass of the palladium atoms.

Although nickel is in the same group as platinum and palladium, the prediction of alkane trapping on Ni(111) offers a more stringent test of the scaling from one surface to another. First, the atomic mass of nickel is much lower (58.69 amu) than either platinum (195.05 amu) or palladium (106.4 amu). According to mass matching arguments, the trapping probability would be expected to be highest on Ni(111). However, the nickel surface is much stiffer than either Pt or Pd. Thus, the dynamical response of the surface to collisions of the incident gas should be affected appreciably. Furthermore, the alkanes bind less strongly to Ni(111) than to Pt(111) or Pd(111), suggesting that different Morse potential parameters may be necessary to describe the gas-surface collision.

For methane, ethane, propane, and n-butane at a fixed incident energy and angle, the trapping probability is highest on Pd(111), followed by Pt(111) and Ni(111), a result which deviates from the prediction of simple mass matching arguments. The lower binding energy of the alkanes and the higher lattice force constant for Ni(111) compared with Pt(111) and Pd(111) give rise to the lower trapping probability. Three dimensional stochastic trajectory simulations for alkane trapping on the three metals clearly indicate that incoming molecules lose considerable energy to Pd lattice vibrations, resulting in a high trapping probability. On the other hand, the stiffer Ni lattice prevents the excitation of surface phonons, consistent with experimental results.

Future work

Dissociative adsorption of alkanes on metals proceeds via both trapping-mediated and direct pathways. The above work relates directly to the trapping-mediated channel. In the direct process bond rearrangement should occur at a distance characterized by a bond length. This distance is significantly shorter than the distance at which the repulsion between the alkane and metal set in. Accordingly, one would expect there to be energy transfer from the translational energy of the incident molecule to the lattice. Since we know that energy transfer is sensitive to both the mass of the incident alkane and to the dynamical parameters of the metal, we expect there to be different energy “thresholds” for C-H bond breaking for different alkanes on each metal. However, preliminary evidence for both Pt(111) and Ir(110) indicate the opposite. We are engaged in a comprehensive study of this effect on surfaces with widely varying dynamical characteristics.

Selected Relevant Publications

1. J. F. Weaver, M.A. Krzuzowski, R.J. Madix, *Direct dissociative chemisorption of alkanes on Pt(111): influence of molecular complexity*, J. Chem. Phys. 112 (2000) 396
2. C.-L. Kao, A.F. Carlsson, R.J. Madix, *Molecular adsorption dynamics on oxygen covered Pt(111)*, Topics in Catalysis 14 (2001) 63 - 69.
3. C.-L. Kao, R.J. Madix, *The adsorption dynamics of molecular methane, propane, and neopentane on Pd(111): theory and experiment*, Journal of Physical Chemistry 106 (2002) 8248.
4. C.-L. Kao, J.F. Weaver, R.J. Madix, *The prediction of trapping probabilities for ethane by molecular dynamics simulations: scaling from Pt(111) to Pd(111)*, Surf. Sci. 505 (2002) 115-123
6. C.L. Kao, R.J. Madix, *The adsorption dynamics of small alkanes on (111) surfaces of platinum group metals*, Surf. Sci. *submitted*

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“Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis and Homogeneous Models”

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Graduate students: Christopher P. Nicholas, Nicholas Stahl, Hongbo Li, Neng Guo, Neraaj Saraiya, John Roberts

Collaborators: Peter Nickias (Dow Chemical Co.), Liong Tee (BP Chemicals), Ignazio Fragala (U. Catania), Alceo Macchioni (U. Perugia), Scott Collins (U. Akron), Moshe Kol (Tel Aviv U.), Jeremy Kropf (Argonne National Laboratory), Giuseppe Lanza (U. Potenza).

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Goals

The overall goals of this project are to understand, model, and exploit the pathways by which organometallic molecules undergo chemisorption and dramatic catalytic activity enhancements on the surfaces of metal oxides and halides. Such phenomena impinge directly on the efficiency, selectivity, and “greenness” of real-world, large-scale industrial catalytic processes and our ability to produce cleaner, more environmentally acceptable products. This research program combines organometallic synthesis, surface science and catalysis with *ab initio* quantum chemistry and involves significant collaboration with industrial scientists and researchers at National Labs. The specific objectives are to: 1) Understand early transition metal and f-element hydrocarbyl molecule chemisorption on “super Brønsted acid” and related high surface area supports, 2) Develop functional, homogeneous phase, crystallographically characterizable mono- and multimetallic models for the adsorbate species formed on oxide surfaces, 3) Characterize the thermochemistry, molecular structures, molecular dynamics, and catalytic properties of such species, 4) Understand in detail the reaction mechanisms these species undergo and use this understanding to create new, useful processes, 5) Computationally analyze the formation processes, electronic structures, bonding, and catalytic reactivity of such species. The properties investigated include new, more energy-efficient routes to environmentally acceptable polymeric materials.

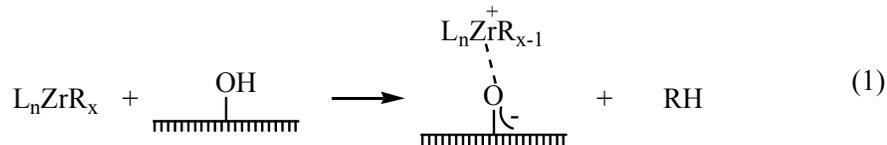
Recent Progress

In the past effort period, we focused on three primary areas: 1) Synthesis and characterization of the single-site organometallic species produced by chemisorption of early transition metal hydrocarbyls on highly Brønsted acidic metal oxides, 2) Understanding catalyst-cocatalyst structure and their interplay in single-site homogeneous polymerization catalyst function, 3) Using *ab initio* studies of single-site polymerization catalysts to understand the role of cocatalyst and solvation. A brief account of each activity is given below.

1. Metal Hydrocarbyl Chemisorption on Sulfated Metal Oxide Surfaces

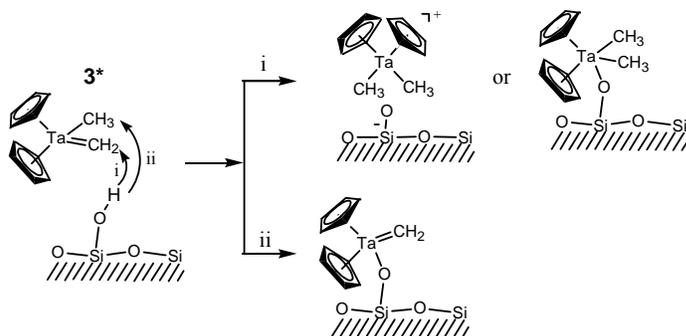
In the supported single-site catalyst area, structural studies including ^{13}C CPMAS NMR spectroscopy of the $^{13}\text{C}_\alpha$ - enriched model adsorbates, $\text{Cp}'_2\text{Th}(\text{}^{13}\text{CH}_3)_2$ (**1**^{*}), $\text{CpTi}(\text{}^{13}\text{CH}_3)_3$ (**2**^{*}) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Cp}' = \eta^5\text{-(CH}_3)_5\text{C}_5$), and organozirconium adsorbates, $\text{Cp}_2\text{Zr}(\text{}^{13}\text{CH}_3)_2$ (**3**^{*}), $\text{Cp}'\text{Zr}(\text{}^{13}\text{CH}_3)_3$ (**4**^{*}), and $\text{Zr}(\text{}^{13}\text{CH}_2\text{}^t\text{Bu})_4$ (**6**^{*}) chemisorbed on sulfated zirconia (ZrS) and alumina (AlS) reveal that all adsorbates undergo M-C σ -bond protonolytic cleavage at the very strong surface Brønsted acid sites to yield “cation-like” organometallic electrophiles (e.g., eq. 1). Kinetic and mechanistic studies of olefin and arene

hydrogenation and α -olefin homopolymerization mediated by the catalysts formed by chemisorption of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$, $\text{Cp}'\text{Zr}(\text{CH}_3)_3$, $\text{Zr}(\text{CH}_2\text{TMS})_4$, $\text{Zr}(\text{CH}_2^t\text{Bu})_4$, and $\text{Zr}(\text{CH}_2\text{Ph})_4$ onto ZrS or AIS follow the



order: **4/ZRS** \gg **5/ZRS** $>$ **6/ZRS** $>$ **7/ZRS**, with $N_t = 970 \text{ h}^{-1}$ for **4/ZRS** making this the *most active benzene hydrogenation catalyst yet discovered*. As a function of arene substituent(s), **4/ZRS** exhibits high chemoselectivity, with hydrogenation rates following the order: benzene \gg toluene \gg *p*-xylene ~ 0 . For benzene hydrogenation by **6/ZRS**, kinetic data obey the rate law, $N_t = k_{\text{obs}}[\text{arene}]^0[\text{PH}_2]^1$ with $E_a = 10.3(8) \text{ kcalmol}^{-1}$. Partially hydrogenated products are not detected at partial conversions, with H_2 delivered pairwise to both faces of C_6D_6 , forming all-*cis* and *cis, cis, trans, cis, trans* isotopomers (1:3.1). Protonolytic poisoning experiments reveal that a maximum of $\sim 68\%$ of Zr sites in **4/ZRS400** are catalytically significant for benzene hydrogenation. Relative ethylene homopolymerization rates are: **7/ZRS** $>$ **5/ZRS** $>$ **6/ZRS** $>$ **4/ZRS** for both ethylene (150 psi C_2H_4 , 60 $^\circ\text{C}$), and liquid propylene (20 $^\circ\text{C}$). Studies of similar complexes supported on highly Brønsted acidic sulfated alumina (AIS) reveal analogous chemisorption and catalytic mechanistic pathways. However, we find here that 98% of the **3/AIS** are catalytically significant for benzene hydrogenation and 88% of the sites for ethylene polymerization. To our knowledge, such high percentages of active sites are unprecedented for such catalysts (or any heterogeneous catalyst). Preliminary studies with other classes of sulfated oxides reveals rather different behavior, depending on the innate surface chemical properties of the support.

In related work, ^{13}C CPMAS NMR was employed to investigate the chemisorption of the group 5 hydrocarbyl/alkylidene complexes, $\text{Cp}'\text{Ta}(\text{}^{13}\text{CH}_3)_4$ (**1***), $\text{Cp}_2\text{Ta}(\text{}^{13}\text{CH}_3)_3$ (**2***), $\text{Cp}_2\text{Ta}(\text{}^{13}\text{CH}_2)(\text{}^{13}\text{CH}_3)$ (**3***), and $\text{Ta}(\text{}^{13}\text{CH}^t\text{Bu})(\text{}^{13}\text{CH}_2^t\text{Bu})_3$ (**4***) [$\text{Cp}' = \eta^5\text{-(CH}_3)_5\text{C}_5$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$] supported on partially dehydroxylated silica (PDS), dehydroxylated silica (DS), or dehydroxylated γ -alumina (DA). Mono-Cp Ta hydrocarbyl **1*** undergoes chemisorption to form $\text{Cp}'\text{Ta}(\text{}^{13}\text{CH}_3)_3\text{O-Si}$ μ -oxo species on silica, and 'cation-like' $\text{Cp}'\text{Ta}(\text{}^{13}\text{CH}_3)_3^+$ and $\text{Cp}'\text{Ta}(\text{}^{13}\text{CH}_3)_3\text{O-Al}$ μ -oxo species on DA, via pathways analogous to those established for group 4 and -actinide complexes. When supported on DA, bis-Cp Ta hydrocarbyl **2*** follows the same chemisorption mode as **1***. However, when **2*** is chemisorbed on PDS and DS, a "cation-like" $\text{Cp}_2\text{Ta}(\text{}^{13}\text{CH}_3)_2^+$ species is the major adsorbate product. On PDS, bis-Cp tantalum alkylidene complex **3*** is converted predominantly to a stable $\text{Cp}_2\text{Ta}(\text{}^{13}\text{CH}_3)_2^+$ species, presumably via electrophilic addition of a surface proton from the surface as shown below. In contrast to **3***, Ta alkylidene complex **4*** forms predominantly a $\text{Ta}(\text{}^{13}\text{CH}^t\text{Bu})(\text{}^{13}\text{CH}_2^t\text{Bu})_3\text{O-Si}$ μ -oxo-alkylidene species on PDS.



2. The Significance of Ion-Pairing in on Structure, Activity, and Selectivity of Single-Site Polymerization Catalysts

The solution structures of the zirconocenium homogeneous polymerization catalyst ion-pairs $[\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**1**), $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**2**), $[(\text{Me}_2\text{SiCp}_2)\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$

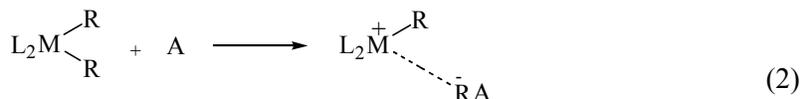
(**3**), $[\text{Me}_2\text{C}(\text{Fluorenyl})(\text{Cp})\text{ZrMe}]^+[\text{FPBA}]^-$ (FPBA = tris(2,2',2''-nonafluorobiphenyl)fluoroaluminate) (**4**), $[\text{rac-Et}(\text{Indenyl})_2\text{ZrMe}]^+[\text{FPBA}]^-$ (**5**), $[(\text{Me}_5\text{Cp})_2\text{ThMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**6**), $[(\text{Me}_2\text{SiCp}_2)\text{Zr}(\text{Me})(\text{THF})]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**7**), $[(\text{Me}_2\text{SiCp}_2)\text{Zr}(\text{Me})(\text{PPh}_3)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**8**), $[(\text{Me}_2\text{SiCp}_2)\text{Zr}(\text{Me})(\text{THF})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**9**), $[(\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{Zr}(\text{Me})(\text{solvent}))]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (solvent = benzene, toluene) (**10**), $[(\text{Cp}_2\text{ZrMe})_2(\mu\text{-Me})]^+[\text{MePBB}]^-$ (PBB = tris(2,2',2''-nonafluorobiphenyl)borane) (**11**), and $[(\text{Cp}_2\text{Zr})_2(\mu\text{-CH}_2)(\mu\text{-Me})]^+[\text{MePBB}]^-$ (**12**), having the counteranion in the inner (**1**, **3**, **4**, **5**, and **6**) or outer (**7**, **8**, **9**, **10**, **11**, and **12**) coordination sphere, have been investigated for the first time in solvents with low relative permittivity such as benzene or toluene by ^1H -NOESY and ^1H , ^{19}F -HOESY NMR spectroscopy. It is found that the average interionic solution structures of the inner sphere contact ion-pairs are similar to those in the solid state with the anion B-Me (**1**, **3**) or Al-F (**5**) vectors oriented toward the free zirconium coordination site. The HOESY spectrum of complex **6** is in agreement with the reported solid-state structure. In contrast, in outer sphere contact ion-pairs **7**, **8**, **9**, and **10**, the anion is located far from the Zr-Me^+ center and much nearer to the Me_2Si bridge than in **3**. The interionic structure of **8** is concentration-dependent, and for concentrations greater than 2 mM, a loss of structural localization is observed. PGSE NMR measurements as a function of concentration (0.1-5.0 mM) indicate that the tendency to form aggregates of nuclearity higher than simple ion-pairs is dependent on whether the anion is in the inner or outer coordination sphere of the metallocenium cation. Complexes **2**, **3**, **4**, **5**, and **6** show no evidence of aggregation up to 5 mM (well above concentrations typically used in catalysis) or at the limit of saturated solutions (complexes **3** and **6**), while concentration-dependent behavior is observed for complexes **7**, **8**, **10**, and **11**. These outer sphere ion-pairs begin to exhibit significant evidence for ion-quadruples in solutions having concentrations greater than 0.5 mM with the tendency to aggregate being a function of metal ligation and anion structure. Above 2 mM, compound **8** exists as higher aggregates that are probably responsible for the loss of interionic structural specificity.

Counteranion effects on the rate and stereochemistry of syndiotactic propylene enchainment by the archetypal C_s -symmetric precatalyst $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrMe}_2$ (**1**; Cp = C_5H_4 ; Flu = C_{13}H_8 , fluorenyl) are probed using the cocatalysts MAO (**2**), $\text{B}(\text{C}_6\text{F}_5)_3$ (**3**), $\text{B}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3$ (**4**), $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**5**), and $\text{Ph}_3\text{C}^+\text{FAl}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$ (**6**), offering greatly different structural and ion pairing characteristics. Reaction of **1** with **3** affords $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrMe}^+ \text{MeB}(\text{C}_6\text{F}_5)_3^-$ (**7**). In the case of **4**, this reaction leads to formation the μ -methyl dinuclear diastereomers $\{([\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrMe})_2(\mu\text{-Me})\}^+ \text{MeB}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$ (**8**). A similar reaction with **6** results in diastereomeric $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrMe}^+ \text{FAl}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$ (**10**) ion pairs. The molecular structures of **7** and **10** have been determined by single-crystal X-ray diffraction. Reorganization pathways available to these species have been examined using EXSY and dynamic NMR, revealing that the cation- $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ interaction is considerably weaker/more mobile than in the $\text{FAl}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$ -derived analogue. Polymerizations mediated by **1** in toluene over the temperature range -10° to $+60^\circ\text{C}$ and at 1.0-5.0 atm propylene pressure (at 60°C) reveal that activity, product syndiotacticity, m and mm stereodeflect generation, and chain transfer processes are highly sensitive to the nature of the ion pairing. Thus, the complexes activated with **4** and **5**, having the weakest ion pairing, yield the highest estimated propagation rates, while with **6**, having the strongest pairing, yields the lowest. The strongly coordinating, immobile $\text{FAl}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$ anion produces the highest/least temperature-dependent product syndiotacticity, lowest/least temperature-dependent m stereodeflect abundance, and highest product molecular weight. These polypropylene microstructural parameters, and also M_w , are least sensitive to increased propylene pressure for $\text{FAl}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$, but highest with $\text{MeB}(\text{C}_6\text{F}_5)_3^-$. In general, mm stereodeflect production is only modestly anion-sensitive; [propylene] dependence studies reveal enantiofacial propylene misinsertion to be the prevailing mm -generating process in all systems at 60°C , being most dominant with **6**, where mm stereodeflect abundance is lowest. For 1,3-dichlorobenzene as the polymerization solvent, product syndiotacticity, as well as m and mm stereodeflects, become indistinguishable for all cocatalysts. These observations are consistent with a scenario in which ion pairing modulates the rates of stereodeflect generating processes relative to monomer enchainment, hence net enchainment syndioselectivity, and also dictates the rate of termination relative to propagation and the preferred termination pathway. In comparison to **3-6**, propylene polymerization mediated by MAO (**2**) +

1 in toluene reveals an estimated ordering in site epimerization rates as **5** > **4** > **2** > **3** > **6**, while product syndiotacticities rank as **6** > **2** > **5** ~ **4** > **3**.

3. Theoretical Studies

Computational efforts centered on understanding catalyst-cocatalyst/cation-counteranion activation processes and subsequent interactions in typical group 4 single-site catalysts, of great technological importance (eq 2).



Mechanistic aspects of ethylene insertion into the Ti-CH₃ bond of the [H₂Si(C₅H₄)(^tBuN)]TiCH₃⁺H₃CB(C₆F₅)₃⁻ ion pair have been analyzed at the ab initio level, employing a double-zeta quality basis set, second-order perturbative Møller-Plesset methods (MP2), and including solvation effects and thermal and pressure corrections to 298 K and 1.0 atm. Three reaction pathways are identified as viable. Ethylene approach from the side opposite the H₃CB(C₆F₅)₃⁻ counteranion is energetically most favored and occurs in a concerted (intermediateless) fashion. The other two pathways involving olefin approach on the same side as the H₃CB(C₆F₅)₃⁻ counteranion are energetically similar, and each occurs via two discrete steps: i) anion displacement with formation of an intermediate π-ethylene complex, ii) ethylene insertion into the Ti-C bond (the slow step). These latter pathways are more strongly solvent-assisted because of the larger attendant ion pair separation. Structural and energetic analysis of the [H₂Si(C₅H₄)(^tBuN)]Ti(*n*-C₃H₇)⁺H₃CB(C₆F₅)₃⁻ insertion product shows the existence of several stable conformations. All such structures can be divided into two different types depending on the [H₂Si(C₅H₄)(^tBuN)]Ti(*n*-C₃H₇)⁺⋯H₃CB(C₆F₅)₃⁻ distance. Structures with short Ti⁺⋯[H₃CB(C₆F₅)₃]⁻ contacts involve metal coordinative saturation by the CH₃ group or an aryl F atom of the counteranion. For structures with longer Ti⁺⋯[H₃CB(C₆F₅)₃]⁻ contacts, the counteranion remains out of the Ti coordination sphere, and these structures exhibit agostic interactions between the *n*-propyl chain and Ti. The relative stabilities of these structures is an index of the preferred olefin enchainment mechanism: chain migratory insertion (dissociated ion pair) versus nonmigratory insertion (associated ion pair). These results are in generally good agreement with the large breath of experimental data now available.

DOE Interest

The catalyst syntheses, mechanistic studies, and product characterization activities that are the central part of this project relate directly to the efficiency, selectivity, and “greenness” of real-world industrial catalytic processes that are practiced on a huge scale and to the ability of these processes to produce cleaner, more environmentally acceptable products. These multifaceted, highly interdisciplinary projects provide ideal training for young scientists needed as part of a highly skilled U.S. technical workforce.

Future Plans

We plan to continue our efforts in all three of the above areas. In the area of novel supports for molecule-based catalysts, we plan EXAFS studies on adsorbate structure in collaboration with Jeremy Kropf of ANL. Systems with virtually 100% active sites present a unique opportunity. We also plan to expand our studies to other types of highly Brønsted acidic supports, to use polymerization reactivity probes of the ion-pairing “tightness,” and to explore tandem supported catalytic processes in which cascade processes are turned on by virtue of the close proximity of the catalytic sites on the surface. In the area of ion-pairing studies, we plan to investigate cocatalyst-selectivity effects in other systems where ion-pairing might be intimately connected with enchainment selectivity. In the theoretical arena, we will explore whether double-layer effects at oxide surfaces may loosen ion-pairing,

hence produce the enhanced reactivities observed. We will also investigate the effects of ion-pairing on enchainment stereochemistry.

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Inorganic-Organic Molecules and Solids with Nanometer-Sized Pores

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Goal

We are constructing porous inorganic-organic hybrid molecules and solids that contain coordinatively unsaturated metal centers.

Recent Progress

We have prepared extended-solid and molecular porous materials based on multifunctional β -diketone ligands.

(a) Extended solids

These materials are constructed by using $M(\text{Pyac})_2$ (see Figure 1) as a "rod"-shaped building block. We completed a study of the coordination of the building block $\text{Cu}(\text{Pyac})_2$ with itself. Meanwhile, we explored the reactions of $\text{Cu}(\text{Pyac})_2$ with other metal ions M' . If M' is capable of binding four pyridine ligands, then a layer with "square-grid" topology results (Figure 2).

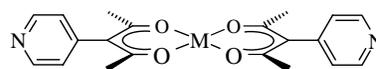


Figure 1. The "rod"-shaped molecule $M(\text{Pyac})_2$.

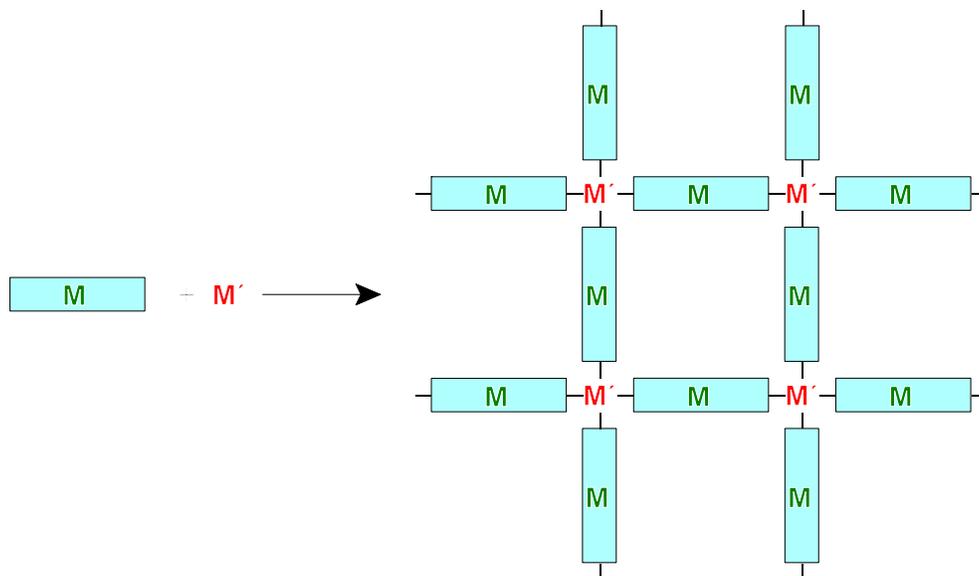


Figure 2. Formation of "square-grid" layer from "rod"-shaped molecules such as $\text{Cu}(\text{Pyac})_2$ (M) and metal "nodes" M' .

We have shown that reaction of $\text{Cu}(\text{Pyac})_2$ with CdCl_2 and $\text{Cd}(\text{NO}_3)_2$ produces 1D and 2D structures based on this square-grid arrangement. In these structures, the pores are ca. 19.7 Å in diameter, with the Cu atoms exposed to the pores.

As an alternative "building block" we have used the iron(III) complex $\text{Fe}(\text{Pyac})_3$. Its three pyridine N atoms are in an approximately trigonal arrangement around the Fe atom. Although this species is coordinatively saturated, it can still be used to construct porous materials. Reaction with AgNO_3 produces a nanoporous bimetallic crystalline solid with a 1-D "ladder" structure, $[\text{Fe}(\text{Pyac})_3]_2[\text{AgNO}_3]_3(\text{solvent})_x$ (abbreviated $\text{Fe}_2\text{Ag}_3(\text{solvent})_x$). Two examples are shown in Figure 3 below, with the solvents of crystallization in their pores (ca. 18 x 21 Å). Not only can the same type of structure be prepared with different solvents/guests, they can be interconverted: $\text{Fe}_2\text{Ag}_3(\text{bromobenzene})_5$ changes to $\text{Fe}_2\text{Ag}_3(1,2\text{-dichlorobenzene})_x$ in a *single-crystal-to-single-crystal transformation*.

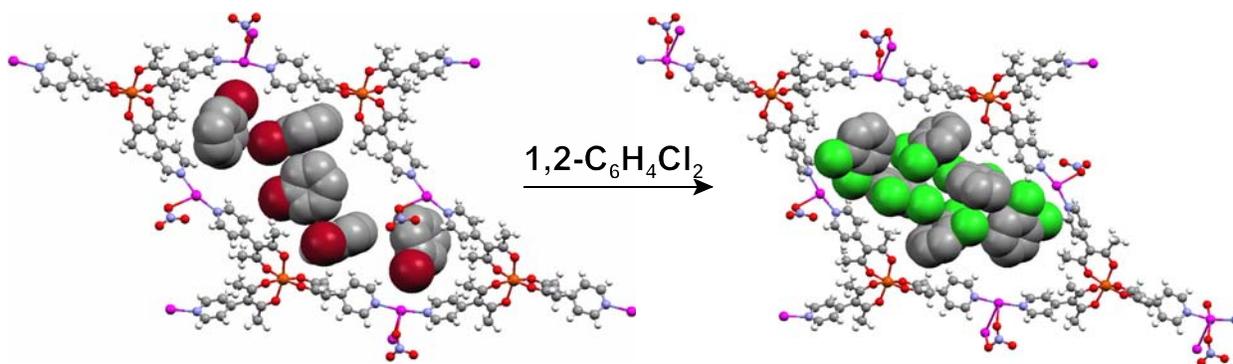


Figure 3. Crystal structures of nanoporous 1-D ladder-structure Ag-Fe compounds. Solvent/guest molecules shown as spacefilling. Crystalline $\text{Fe}_2\text{Ag}_3(\text{bromobenzene})_5$ (*left*) is transformed into crystalline $\text{Fe}_2\text{Ag}_3(1,2\text{-dichlorobenzene})_x$ (*right*) on standing in liquid 1,2-dichlorobenzene.

(b) Molecular materials

We have also studied the reaction of "rods" such as $\text{Cu}(\text{Pyac})_2$ with other metal-containing nodes, including $\text{Re}(\text{CO})_5\text{Cl}$. This reaction is expected to produce "molecular square" species, in analogy with species such as

$[(\text{CO})_3\text{ClRe}(4,4'\text{-bpy})]_4$,

pioneered by Hupp et al.; see

Figure 4. Like Hupp's compounds, our Re-Cu square is expected to be neutral; preliminary results indicate that this compound has UV-vis spectral features approximately as expected for a combination of $\text{Re}(\text{CO})_3\text{Cl}(\text{py})_2$ and $\text{Cu}(\text{Pyac})_2$ moieties.

We are also studying the reaction of $\text{Cu}(\text{Pyac})_2$ (as a "4,4'-bpy equivalent") with other right-angle nodes, such as $\text{Ru}(\text{bpy})_2^{2+}$ and $\text{Pd}(\text{en})^{2+}$. In addition, building on the work of Thomas et al. with "molecular cubes" based on $\text{Ru} + 4,4'\text{-bpy}$, we are carrying out analogous reactions

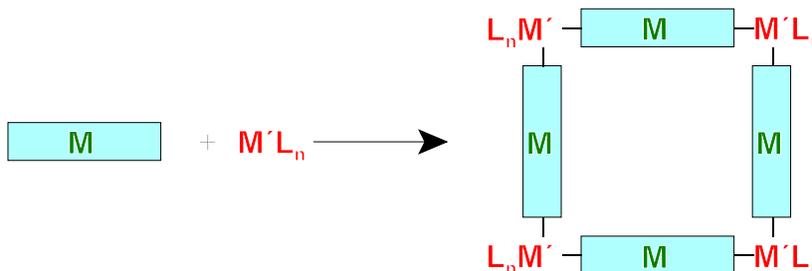


Figure 4. Proposed synthesis of bimetallic molecular squares by reaction of "rods" M with right-angle "nodes" $\text{M}'\text{L}_n$.

with Cu(Pyac)₂. These Re, Pd, and Ru systems are expected to be good molecular analogs of the extended-solid materials mentioned above.

DOE Interest

We expect to use the approaches outlined here to prepare new porous molecules and solids that expose reactive metal sites to the interiors of enclosed cavities and channels. Possible applications of the resulting materials include sensors, thin-film membranes for separations, and catalysts, all of which may derive improved selectivity from the placement of the active metal sites inside the cavities.

Future Plans

For the expended-solid species, we are now working toward porous materials that have both exposed M sites and the ability to exchange guest molecules while maintaining structural integrity. We are also preparing organic "nodes" that are suitable for both molecular and extended-solid products.

Publications

"Solvent-dependent 4⁴ square grid and 6⁴.8² NbO frameworks formed by Cu(Pyac)₂ (bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II))"; Chen, B.; Fronczek, F. R.; Maverick, A. W. *Chem. Commun.* **2003**, 2166-2167.

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(2 others in preparation)

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Reactions of Hydrocarbons on Transition Metal Surfaces

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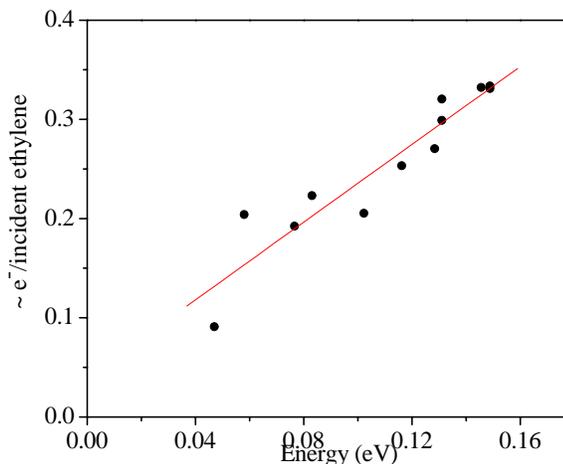
Goal

Improve our understanding of the molecular level processes and the relationships between reactivity, energy transfer, and surface electronic structure associated with hydrocarbon reactivity on transition metal surfaces representative of industrial scale heterogeneous catalysis.

Recent Progress

Reaction induced electronic energy dissipation from olefin adsorption on transition metal surfaces: We have observed reaction induced hot electrons from high energy and low energy chemisorption on several metal surfaces on both M-S Schottky diodes as well as MIS and MOS device structures.¹⁻³ The observation of reaction associated “hot” charge carriers produced by hydrocarbons (low adsorption energy) appears to utilize a different electronic pathway in MOS devices compared to the high energy species (e.g. atomic H, O, NO, etc).^{1,3} With our recently upgraded molecular beam (modified with a redesigned nozzle and skimmer) we have used He seeding to produce a hyperthermal beam to observe the kinetic energy dependence of electronic excitations from ethylene adsorption on Au deposited on a silica capped Si (111) n-type substrate (MIS). The results show a dependence upon the incident molecular kinetic energy and the number of electrons observed associated with the reaction.

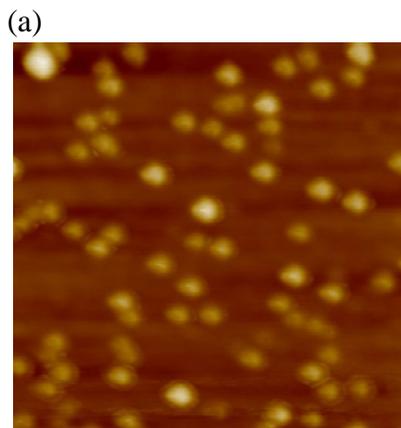
Number of observed electrons per incident ethylene molecule as a function of the ethylene kinetic energy incident upon Au. Ethylene is in a seeded molecular beam incident upon Au on a silica capped Si (111) n-type diode.



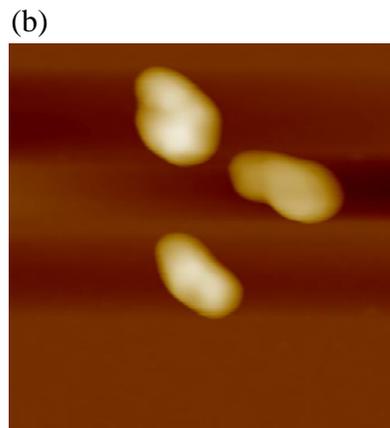
Support and Size Dependent Reactivity of Transition Metal Clusters: The low temperature reactivity of gold clusters (8-22 nm diameter) supported on different metal oxides (titanium dioxide (TiO₂), zinc oxide (ZnO), zirconium oxide (ZrO₂), and silicon dioxide (SiO₂)) was investigated in a high pressure continuous flow reactor. Clusters were encapsulated within polymer in toluene solution, impregnated onto the bulk supports, and reduced by calcination at 300 °C. Support dependent sintering (TiO₂ > ZrO₂ > ZnO) was observed following heating in air at 300 °C. For both propylene hydrogenation and CO oxidation, Au clusters on TiO₂ exhibit the highest activity compared to other supports with activity observed down to room temperature.⁸

There are clearly size dependent changes in the electronic properties of supported metal clusters that alter their catalytic performance. In the case of gold, size selected clusters prepared from micelles as particles with diameters between approximately 1 and 6 nm showed a strong dependence on both the particle size and the support for oxygen reactivity. We observed differences in the formation and stabilization of a metal-oxide, and in the activity for electro-oxidation of carbon monoxide.^{4,5} The smallest particles studied (1.5 nm) were the most active for electro-oxidation of CO and had the largest fraction of oxygen associated with gold at the surface as measured by the Au³⁺/Au⁰ X-ray photoemission intensities. Conducting and semiconducting substrates, ITO-coated glass and TiO₂, respectively, were associated with greater stabilization of Au³⁺ oxide compared to insulating, SiO₂, substrates.

Sintering is the most important limitation to practical utilization of metal cluster catalysts and we have investigated the stability of both supported Ir and Au clusters (1-4 nm diameter) prepared from micelles on several substrates (titania, silica, silicon, alumina). An unexpected, and dramatic increase in the rate of sintering, has been observed on silica and titania substrates under relatively short UV irradiation at room temperature in the presence of oxygen. In contrast, prolonged thermal oxidation in air or oxygen plasmas produced stable non-sintered clusters in all cases in the absence of UV. We have no clear idea, as yet, what is going on.



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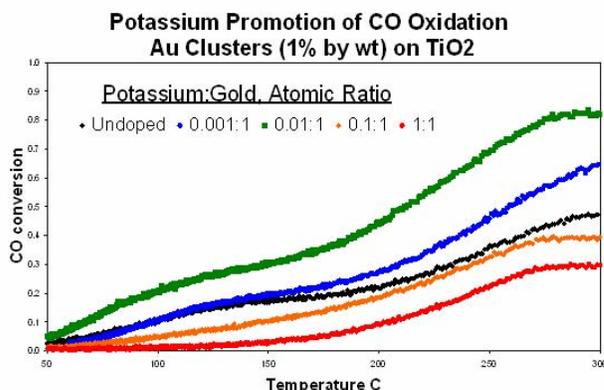


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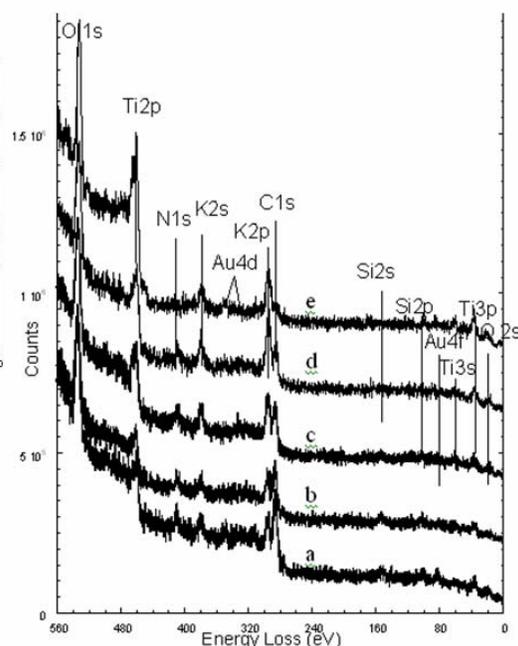
Fig. 2: AFM images of Au nanoclusters deposited from micelles on silica substrates after (a) calcination at 300° C in air, and (b) room temperature UV irradiation in the presence of oxygen.

Activity of Metal Alloy Clusters and Promoted Au Clusters: We are exploring the use of co-metal alloys and promoters to control the electronic structure of metals. Using a micelle deposition method Ag-Au, Pd-Au, Pt-Au and Rh-Au nanoclusters have been deposited on a titania support. Their activity for propylene epoxidation has been screened in a packed bed reactor. The Pd-Au alloy catalyst was found to have unusually high activity for both epoxidation and hydrogenation. The activity of Pt-Au alloys was significantly less and other alloys many of which exhibited no activity.

Initial studies with K promoted Au clusters supported on titania show that there is a significant increase in the activity for high pressure CO activity yet little change in the activation energy in otherwise identical samples (below). A model is under development to explain the kinetics as well as the similar increase in hydrocarbon partial oxidation activity. UHV studies of these potassium-promoted Au-titania catalysts show that in the presence of high pressure oxygen the K appears to “stabilize” Au availability at the surface (a). In the absence of oxygen, K will entirely cover the Au surface (b-d, explaining the observed loss of activity) up to nearly 800 K.



Above: Packed bed reactor (1 atm) activity of K promoted Au. Right: XPS of K/Au/TiO₂ surface taken after a) insert UHV from air, heating to b) 500K, c) 600 K, d) 700 K and e) 800 K. Sample is cooled back to room temperature after each heating cycle.



Investigations of hydrocarbons on transition metals supported on titania and alumina : As a first step in these investigations of partial oxidation and epoxidation in the presence of O₂ and H₂ we investigated the reactivity of TiO₂ (110) and polycrystalline anatase surfaces with molecular and ionized D and H. Thermal Desorption Spectroscopy (TDS), following exposure to more than 100 kL of molecular deuterium, showed a D₂ desorption peak at ~440 K on both single crystal rutile and polycrystalline anatase surfaces. The desorption peak was observed following exposure only at surface temperatures between 140-270 K. Ionized D₂ is significantly more reactive with the titania surface and two desorption peaks at 380 K and ~550 K were observed together with a small D₂O peak observed at ~440 K. Dosing the surfaces with hydrogen and deuterium either in succession or as a mixture showed HD

desorption with no change in the desorption peaks, consistent with dissociative adsorption of both ionized and molecular species. The experimental data was compared to DFT calculations and modeled as a two-step process of hydrogen dissociation at oxygen vacancy sites on TiO₂.⁷

DOE Interests

Understanding and predicting hydrocarbon reactivity on metal surfaces is essential to developing technical strategies to improve and optimize utilization of our fossil hydrocarbon feedstocks (oil, coal, and natural gas) for fuels and chemicals. Investigations connecting fundamental surface science on idealized surfaces to the active surfaces present in industrial scale heterogeneous catalysis are an essential link between the decades of surface chemistry performed in the 20th century and the predictive models to be developed in the 21st century.

Future Plans

In addition to completing the work in progress described above, we intend to pursue the following extensions.

Reaction induced electronic energy dissipation on transition metal surfaces: As proposed, we are now initiating parallel investigations of the incident kinetic energy of several alkanes and olefins on the continuous films and clusters of transition metals on MS and MIS devices.

Support and Size Dependent Reactivity of Transition Metal Nanoclusters: We are now ready to connect the reaction produced hot electrons to catalytic effects on the metal surface in clusters small compared to the mean free path of the electrons. In bulk material and two dimensional films the majority of the electronic energy is driven from the surface ballistically and “cools” by phonon production in the bulk. When mean free path of a hot carrier is on the order of the cluster size (~10-100 nm), multiple interactions of the hot carrier and any adsorbed species are possible. Surface reaction may not be independent of hot carrier production. Using FTIR as *in situ* monitoring tool, we will study the desorption rates of carbon monoxide in presence of inert helium and in presence of strongly physisorbed xenon at adsorption-desorption equilibrium conditions as functions of cluster size and support. We have shown that Xe produces large numbers of carriers compared to He upon collision with the surface. We have completed the installation of a Diffuse-Reflectance Infra-Red accessory (Harrick Scientific) into the external beam path of our FTIR spectrometer and are prepared to make these measurements.

Investigations of hydrocarbons on transition metals supported on titania and alumina : We have developed a complimentary means for depositing size-controlled metal nanoclusters for UHV studies by direct evaporative deposition in vacuum on to surfaces with large concentrations of defects created by sputtering. We will first investigate the size dependent absorption/desorption characteristics of propylene, ethylene, hydrogen, oxygen, and methyl-Br on Au clusters supported on rutile and anatase. Cobalt clusters will be subsequently studied.

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Catalysis on the Nanoscale: Theoretical Studies of the Stability and Reactivity of Metcar Mo_8C_{12} Nanoparticles

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Goal

To explore, as a representative example of early transition metal carbide species, the stability and reactivity of Mo_8C_{12} metcar nanoparticles compared to the extended surfaces $\text{Mo}(001)$, $\text{Mo}_2\text{C}(001)$ and $\text{MoC}(001)$ using density functional theory.

This work was carried out as part of the FWP Catalysis on the Nanoscale: Preparation, Characterization and Reactivity of Metal-Based Nanostructures.

Recent Progress

Considering the utility of metal carbides in catalysis, we are particularly interested in the stability and reactivity of metcar nanoparticles. We have employed density functional theory (DFT) using the DMol³ code in all-electron calculations on the Mo_8C_{12} metcar, and extended surfaces of $\text{Mo}(001)$, $\text{Mo}_2\text{C}(001)$ and $\text{MoC}(001)$ as well as their interaction with several small molecules (CO, SO_2 and thiophene) and S atoms. These calculations were carried out using a double numerical plus d-function basis (comparable in accuracy to a Gaussian 6-31G(d) basis) and the generalized gradient approximation (GGA) with the revised version of the Perdew-Burke-Ernzerhof functional (RPBE).

Our DFT calculations show that: (1) In general, the reactivity of molybdenum carbides decreases in the sequence $\text{Mo} > \text{Mo}_2\text{C} > \text{MoC}$ because of the increasing C/Mo ratio; (2) Owing to their unique geometry, Mo_8C_{12} nanoparticle behave quite differently from the bulk materials; (3) The special geometry of M_8C_{12} attenuates the ligand effect of C atoms on metal atoms, and the nanoparticles interact with CO, S and SO_2 as well as Mo_2C does; and (4) When dealing with thiophene, the steric repulsion of the C_2 groups can overcome the intrinsic reactivity of metal atoms in corner or edge sites, and M_8C_{12} becomes as inert as MoC.

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Surface Chemistry Related to Heterogeneous Catalysis

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Goal

Expand the fundamental understanding of how chemisorption and reaction occur on well-characterized surfaces, composed of metals deposited on oxide films. Of particular interest are oxidation and reduction type reactions on surfaces composed of reducible oxides, and how interactions between the adsorbates, metal and support are manifested in the reaction pathways.

Recent Progress

Our work has focused on how the mechanisms of reactions occurring at model catalyst surfaces depend upon the oxidation state of the support. The principal systems of interest are reducible mixed oxides of cerium and other rare earth elements as supports for Rh, Pt, and Au. Controlled doping of ceria with other rare earth elements or surface modifiers such as K, is used to determine the effect of oxygen vacancies, ionic conductivity, lattice strain and promoters upon support reducibility. We have also been investigating how molecules with more active functionalities, such as –OH or –SH, interact with the reducible oxide surfaces.

Oxygen Mediated Reduction of Ceria by H₂: All previous work on highly crystalline cerium oxide films grown in UHV have shown that these films are very stable to reduction in hydrogen. Addition of Rh to the surface does not enhance reduction, indicating that the mechanism is not limited solely by hydrogen activation. We have found that pre-adsorption of oxygen on Rh leads to facile reduction of cerium oxide films during a subsequent exposure to H₂. The results suggest that a hydroxyl disproportionation at the Rh-ceria interface is a key step in the reduction.

Reactions on Rh Supported on Dysprosium Oxide: Dysprosium oxide films have been prepared in UHV and used as a support to study Rh catalyzed redox chemistry. Unlike Ce, Dy does not have multiple oxidation states and therefore Dy₂O₃ should not readily undergo oxidation and reduction. The surface structure of Dy₂O₃ is believed to be similar to partially reduced ceria and therefore presents a surface containing O vacancies but no reducible cations. When Rh is deposited on the Dy₂O₃ surface, it is not active for the decomposition of CO. This suggests that the presence of O vacancy nucleation sites is not sufficient for activating supported Rh. Surprisingly, CO is produced when C₂H₄ is adsorbed and heated on Rh / Dy₂O₃. There is apparently an excess of O contained in the DyO_x film. Further, following C₂H₄ treatment, the Rh becomes partially active for CO decomposition. This activity can be eliminated following re-oxidation.

Reactions on Rh Supported on Praseodymium Oxide: Both Pr and Ce are divalent (+3 and +4) and form similar oxide structures in the fully oxidized form. Pr is harder to fully oxidize, however, and the sub-oxides have a more complex structure. CO desorption from Rh is similar on oxidized PrO_x and ceria. C_2H_4 adsorption / desorption produces CO indicative of reduction of the oxide, but there initially appears to be little effect on subsequent CO desorption. After extensive reduction by C_2H_4 the Rh does become active for CO decomposition. This behavior occurs over a fairly narrow range of C_2H_4 treatment, however, and excess ethylene exposure poisons CO uptake.

Reducibility of Mixed Oxides: The reducibility of a series of mixed oxides (Ce-X O_2 where $\text{X}=\text{Dy, Gd, Pr}$) both with and without Rh impregnation, have been studied by x-ray absorption near edge spectroscopy (XANES) and temperature programmed reduction. The goal is to understand what factors determine the oxygen storage capability in mixed oxide supports for oxidation catalysts. XANES quantitatively differentiates between Ce^{3+} and Ce^{4+} in high surface area powders. The mixed oxides were synthesized using both a polymer complexation method and a surfactant mediated method that successfully led to single phase mixed oxides. Contrary to expectations, introduction of oxide vacancies by substituting the +3 cations into the fluorite matrix did not strongly affect the reducibility of these oxides. In all cases however the Rh impregnation greatly enhanced reducibility at low temperatures.

Reduction of CeO_2 films studied by positron annihilation spectroscopy: A 100-nm thick CeO_2 film grown on a Si(111) surface was measured with beam positron lifetime spectroscopy and Doppler broadening of annihilation radiation. The positron lifetime spectra were measured before and after the sample was exposed to H_2 at $\sim 10^{-5}$ torr for about three hours at 614°C . The lifetime spectra do not show a clear difference before and after H_2 exposure, indicating that there are no oxygen vacancies generated in the sub layers of the CeO_2 film by exposing H_2 . This is consistent with our XPS experiments, which also shows no reduction of the CeO_2 surface by H_2 exposure alone.

K Co-adsorption with Rh Supported on CeO_2 : The effect of potassium on the adsorption and reaction of CO on Rh supported on CeO_2 was studied by TPD and SXPS. The key findings were that the K did not reduce the Ce^{+4} to Ce^{+3} and did not promote the dissociation of CO on the Rh. The K did promote the formation of carbonate species on the CeO_2 .

Interactions of $-\text{OH}$ and $-\text{SH}$ Groups with Cerium Oxide: The adsorption and reaction of CH_3OH , CH_3SH and H_2S on oxidized and reduced cerium oxide films was studied by TPD and SXPS. CH_3OH was a very effective reductant producing H_2O and CH_2O . H_2S also removed lattice O by producing H_2O but it left the S behind. CH_3SH did not interact strongly with the oxidized film. All of the molecules reacted with a reduced surface by breaking an OH or SH bond and forming a stable species on the surface. CH_3O decomposed to form CO and H_2 at elevated temperatures while CH_3S reacted with surface hydroxyls to form CH_4 . The decomposition of CH_3SH on reduced CeO_x is much more selective than the decomposition on metal surfaces.

DOE Interest

A detailed understanding of the interactions between adsorbates, supported metals and oxide supports is related to many catalytic processes relevant to energy utilization including emission control, lean burn catalysis, and catalysts for fuel cells and hydrogen utilization.

Future Plans

Comparison of Au with Pt and Rh on CeO_x: The work of Haruta and Goodman have established that the reactivity of Au particles on TiO₂ is dependent on the Au particle size. Recent work by Norskov and Besenbacher has shown that the particle size is influenced by the O vacancy concentration on the TiO_x surface. It is likely that O vacancies will serve as Au nucleation sites on CeO_x as they do on TiO_x. We will test the theory proposed by Norskov to generate Au particles of different sizes and to further test the reactivity of these Au particles.

Electronic Structure of Supported Catalytic Particles: The valence band spectra of Pt supported on oxidized and reduced ceria have been recorded. The goal is to understand how the electronic structure of the metal particle is affected by changes in the oxidation state of the support. In collaboration with a computational scientist at ORNL we will seek a correlation between the activity of CO and changes in the electronic structure as exhibited in the VB spectra both with and without adsorbed CO.

Speciation of Adsorbed Molecular Species by FTIR: Previous studies have revealed a rich chemistry that occurs when molecules such as NO or CH₃OH are adsorbed on ceria films or adsorbed on Rh supported by ceria films. SXPS has been useful for identifying the species that occur on the surfaces during the reactions, however in some cases the results are inconclusive. The nature of these species will be further probed by reflection absorption infra-red spectroscopy (RAIRS) in an apparatus which is capable of measuring both the RAIRS and the XPS.

Adsorption of Heteronuclear Aromatics on CeO_x: Our results have shown that hydrocarbons do not interact strongly with oxidized or reduced CeO_x. The presence of a heteroatom such as S or O allows thiols and alcohols to bind to the surface and follow a more selective decomposition pathway than adsorption on metals. A logical extension of this study is to examine heteronuclear aromatics to see if the heteroatom is able to interact with the oxide and whether this leads to selective reaction chemistry. This work will also be extended to N containing molecules since they have been proposed as potential additives for selective catalytic reduction and their interaction with CeO_x needs to be determined.

Adsorption of Alcohol on Rh/ CeO_x: Our recent study of CH₃OH on CeO₂ has shown how the interaction between the alcohol and the oxide is significantly different from the interaction of the alcohol with a metal. When the two materials are combined by supporting the metal on the oxide, new reaction pathways may open up. A desirable result for fuel cell applications may be the production of H₂ and CO₂ from CH₃OH.

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Principles of Selective O₂-Based Oxidation by Optimal (Binuclear) Catalytic Sites

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Goal: To develop combined experimental and theoretical approach to enable molecular-level understanding of the mechanisms of selective (non-radical), reductant-free, O₂-based oxidation of organic substrates catalyzed by polyoxometalates (POMs) with di-metal active sites, virtually the only compounds capable of this chemistry

Progress Report: Experimental work has focused on probing the physical and electronic structures and solution chemistry of one of the 4 known catalysts capable of the low-temperature activation of O₂ for selective (non-radical-chain) oxidations. Three of the four catalysts capable of these practically and environmentally noteworthy processes are transition-metal-oxygen anion cluster compounds (polyoxometalates or “POMs”). These 3 POMs are the gamma-(FeOH₂)₂SiW₁₀O₃₈⁶⁻ complex of Mizuno and co-workers (Fe₂**1**), the (RuOH₂)₂ZnW(ZnW₉O₃₄)₂¹²⁻ sandwich-type complex of Neumann-Dahan (Ru₂**2**) and the recoverable heterogeneous catalyst ((Fe(OH₂)₂)₂(A-α-PW₉O₃₄)₂⁹⁻ supported on cationic silica nanoparticles (Fe₃**3**/CNP) of our group. Initial work has addressed the Fe₂**1** for three reasons: (1) this complex is the simplest of these 3 very complex structures; (2) it shares the Fe₂O₂ active site structural motif with methane monooxygenase (MMO) and other di-iron enzymes under continuing intense investigation; and (3) it is, in some ways the most experimentally tractable.

At the outset, we sought to elucidate whether Fe₂**1** exists in H₂O, and if so, what are its aqueous solution chemistry and catalytic activity in this economically and environmentally optimal medium. The literature studies reported the extremely attractive epoxidation catalyzed by Fe₂**1** via a dioxygenase stoichiometry (alkene + 1/2 O₂ → epoxide). However, prohibitively undesirable chlorocarbon solvents were used.

We have determined that when Fe₂**1** is placed in H₂O at natural pH, an unprecedented trimer, [(gamma-SiW₁₀O₃₆)₃Fe₆(OH)₉(H₂O)₉]¹⁵⁻, forms. The gamma-Keggin units remain largely intact in the trimer, but the Fe atoms move

out of their “pockets” defined by 5 bridging oxygen ligands and now coordinate to hydroxo ligands on the Fe atoms in two adjacent $\text{Fe}_2\text{SiW}_{10}\text{O}_{38}^{6-}$ units. If acetate (a buffer molecule but exemplary of many possible bridging ligands that could be present in such systems either naturally or by design) is present, a structurally related acetate-bridged dimer, $[(\gamma\text{-SiW}_{10}\text{O}_{36})_3\text{Fe}_4(\text{OH})_4(\text{OAc})_4]^{12-}$, forms. Both structures have been solved by X-ray crystallography. Based on many control reactions, the trimer (and not dissociated daughter species) appears to catalyze the selective O_2 -based oxidation of 2-mercaptoethanol in H_2O .

Three different theoretical approaches (models) to study several γ -Keggin POMs, with a general formula of $(\text{MOH}_2)_2\text{SiW}_{10}\text{O}_{36}^{4-}$ ($\text{M}_2\mathbf{1}$) and the lacunary POM $\gamma\text{-}[(\text{SiO})_4\text{W}_{10}\text{O}_{30}(\text{H}_2\text{O})_2]^{4-}$ have been validated. Our computational values of the physical and chemical properties of the low-lying electronic states of $\text{Mn}_2\mathbf{1}$, are in excellent agreement with the available experimental values {*M. Pope and co-workers, Inorg. Chem. 1996, 35, 30*} which substantiates the applicability of the chosen theoretical and geometrical models. These models were then used to elucidate the geometries and energetics of the low-lying electronic states of $\text{M}_2\mathbf{1}$ structures with $\text{M} = \text{Fe}, \text{Mo}, \text{Tc}, \text{Ru}$ and Rh in context with endeavoring to predict the catalytically most active γ -Keggin structures.

Our studies of the lacunary POM indicate that the reported structure (based on X-ray data) $\gamma\text{-}[(\text{SiO})_4\text{W}_{10}\text{O}_{30}(\text{H}_2\text{O})_2]^{4-}$, {*Kamata K. and co-workers, Science, 2003, 300, 964*} should be modified and described as $\gamma\text{-}[(\text{SiO})_4\text{W}_{10}\text{O}_{28}(\text{OH})_4]^{4-}$ with four terminal hydroxy groups.

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Catalytic Applications of H• Transfer from Transition–Metal Hydride Complexes

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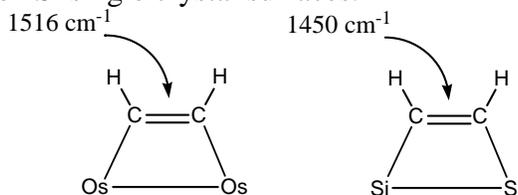
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Goal

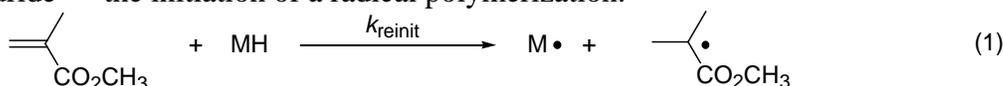
Develop better catalysts for chain transfer during free radical polymerization

Recent Progress

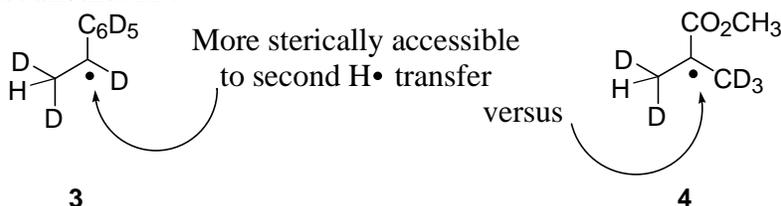
A. A Vibrational Model for Surface Acetylene.³ The vibrational frequencies of the diosmacyclobutene ring in $\text{Os}_2(\text{CO})_8(\mu_2\text{-}\eta^1, \eta^1\text{-C}_2\text{H}_2)$ and its dideuterated isotopologue $\text{Os}_2(\text{CO})_8(\mu_2\text{-}\eta^1, \eta^1\text{-C}_2\text{D}_2)$ have been measured and assigned. The results are an excellent vibrational model for C_2H_2 on Si single crystal surfaces.



B. Transfer of H• from Chromium Hydride Complexes to Methyl Methacrylate and Styrene. Strengths of Cr–H and C–H Bonds¹ The rates of H/D exchange have been measured between (a) the activated olefins methyl methacrylate-*d*₅ and styrene-*d*₈, and (b) the Cr hydrides ($\eta^5\text{-C}_5\text{Ph}_5$)Cr(CO)₃H (**1a**), ($\eta^5\text{-C}_5\text{Me}_5$)Cr(CO)₃H (**1b**), and ($\eta^5\text{-C}_5\text{H}_5$)Cr(CO)₃H (**1c**). Statistical corrections give the rate constants k_{reinit} for H• transfer to the olefin from the hydride — the initiation of a radical polymerization.

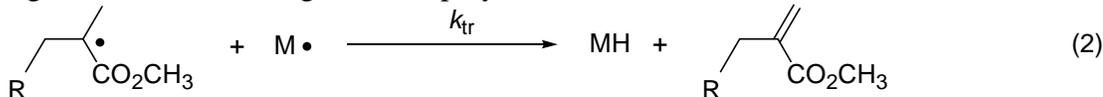


Hydrogenation is insignificant except with styrene and $\text{CpCr}(\text{CO})_3\text{H}$ (which form the intermediate radical **3**); the radical **4** arising from H• transfer to methyl methacrylate is too hindered to abstract another H•.



With MMA, k_{reinit} decreases substantially as the steric bulk of the hydride increases; with styrene, the steric bulk of the hydride has little effect. At longer times, the reaction of MMA or styrene with **1a** gives the corresponding metalloradical **2a** as termination depletes the concentration of the methyl isobutyryl radical **4** or the α -methylbenzyl radical **3**; computer simulation of [**2a**] as a function of time gives an estimate of k_{tr} , the rate constant for H• transfer

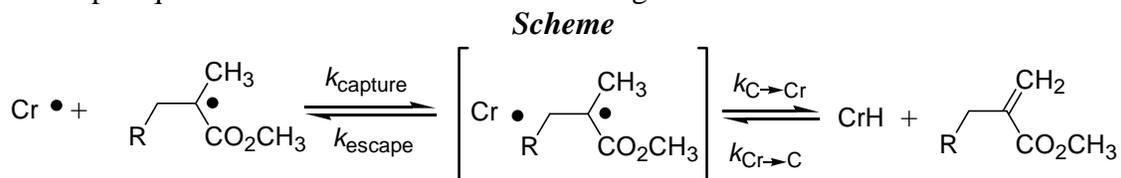
from **3** or **4** back to Cr. The value of k_{tr} measures the effectiveness of a metalloradical in catalyzing chain transfer during a radical polymerization.



The CH_3CN pK_a of **1a**, 11.7, implies a BDE for its Cr–H bond of 59.6 kcal/mol. In combination the rate constants (which give kinetic ΔG values), the experimental BDE for **2a**, and the ΔS values calculated for $\text{H} \cdot$ transfer imply a C–H BDE of 46 kcal/mol for the methyl isobutyryl radical **4**, and a C–H BDE of 48 kcal/mol for the α -methylbenzyl radical **3**.

C. Inverse Temperature Dependence of a Chain Transfer Rate Constant.

Formation of a Solvent Cage. Absence of CIDNP.² There are many reasons to assume that $\text{H} \cdot$ transfers such as k_{reinit} and k_{tr} occur within a solvent cage. (CIDNP has been observed in related reactions.) Such cage effects may explain the difference between the k_{tr} value we obtain by kinetic modeling for methyl isobutyryl radical **4** and the one we obtain from Mayo plots ($1/\text{DP}_n$ as a function of [**2a**]) for the polymer-containing radical **4-P**. We have determined the temperature dependence of k_{tr} by constructing a Mayo plot every 5 degrees between 60 and 80 °C, and have found that k_{tr} *decreases* with increasing temperature. This decrease presumably reflects the preequilibrium formation of the solvent cage in the Scheme.



With the Scheme the observed k_{tr} will be that in eq 3. The cage-forming equilibrium $k_{\text{capture}}/k_{\text{escape}}$ will lie further to the left with increasing temperature, and k_{tr} will decrease.

$$k_{tr} = \frac{k_{\text{capture}} k_{\text{C} \rightarrow \text{Cr}}}{k_{\text{escape}} + k_{\text{C} \rightarrow \text{Cr}}} \approx \frac{k_{\text{capture}} k_{\text{C} \rightarrow \text{Cr}}}{k_{\text{escape}}} \quad (3)$$

We observe no CIDNP even at 58 MHz during the reaction of the chromium hydride **1a** with MMA, presumably because the persistence of the paramagnetic chromium metalloradical **2a** causes loss of spin memory and nuclear polarization.

D. Steric Effect on the Ability of Metalloradicals to Serve as Chain Transfer Catalysts in the Polymerization of MMA.⁴ We have tried the largely monomeric $(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3 \cdot$ (**2b**) as a chain transfer catalyst. A Mayo plot at 70 °C shows activity six times greater than the activity of **2a**. In view of these results we have also measured the activity of $(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3 \cdot$ (**2c**), which dissociates significantly at 70 °C. We have found **2c** to be almost as effective as the best catalyst previously reported.

After testing several other metalloradicals we believe we understand the requirements for effective catalysis of chain transfer during free radical polymerizations. The metalloradical must:

- (a) be stable at the temperature of the polymerization.
- (b) be *just crowded enough to discourage* (i) its own dimerization, (ii) the formation of an M–C bond with the chain-carrying radical, or (iii) the transfer of a second $\text{H} \cdot$ to the chain-carrying radical from its hydride M–H (resulting in hydrogenation). Additional steric hindrance will slow its abstraction of $\text{H} \cdot$ from the chain-carrying radical.

(c) form an M–H bond weak enough to permit the facile transfer of H• to monomer (suggesting that first-row metals may be preferable).

DOE Interest

This project will develop effective metalloradical catalysts for chain transfer during radical polymerizations, thus controlling molecular weight and permitting the efficient synthesis of low-molecular-weight vinyl-terminated oligomers.

Future Plans

Other Metalloradicals We will determine the M–H bond strengths of several other hydride complexes of first-row transition metals, including some water-soluble anions. With that information we will examine the reaction of these complexes with deuterated methyl methacrylate and styrene, and determine the rate of H• transfer. We should be able to predict which hydride complexes will be effective as chain transfer catalysts.

Incorporation of Macromonomers We will label the dimer of methyl methacrylate with deuterium — and see whether are incorporated when a catalyst begins a new chain. We will thus determine whether reinitiation after chain transfer catalysis can occur with oligomers.

Regulation of Molecular Weight with H₂ As some metalloradicals can be converted to the corresponding hydrides with H₂ gas, it should be possible to control the rate and molecular weight distribution of radical polymerizations by varying the H₂ pressure.

Publications (2003-2004)

1. L. -H. Tang, E. T. Papish, G. P. Abramo, J. R. Norton,* M. -H. Baik, R. A. Friesner, and A. Rappé, "Kinetics and Thermodynamics of H• Transfer From (η^5 -C₅R₅)Cr(CO)₃H (R = Ph, Me, H) to Methyl Methacrylate and Styrene," J. Am. Chem. Soc. 2003, 10093-10102.
2. L. -H. Tang, J. R. Norton*, and J. C. Edwards, "Inverse Temperature Dependence of Chain Transfer Rate Constant for a Chromium Metalloradical in Polymerization of MMA." Macromolecules, 2003, 9716-9720.
3. C. E. Anson, N. Sheppard, R. Pearman, J. Moss, P. Stöbel, S. Koch, and J.R. Norton*, "A Vibrational Study of the Dismacrocyclobutene Complex Os₂(CO)₈(μ_2 - η^1 , η^1 -C₂H₂): The Use of Organometallic Complexes as Vibrational Models for Chemisorbed Ethyne." Physical Chemistry Chemical Physics 2004, 1070-1076.
4. L. -H. Tang and J.R. Norton*, "The Effect of Steric Congestion on the Activity of Chromium and Molybdenum Metalloradicals as Chain Transfer Catalysts during MMA Polymerization." Macromolecules, 2004, 241-243.

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Colin Nuckolls, Assistant Professor of Chemistry

Synthesis, Directed Assembly, and Local Probe Measurements of Dipolar, Organic Nanostructures

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The research program outlined below applies organic synthesis and self-assembly to create nanoscale materials. It focuses on self-assembly of complex aromatic molecules at interfaces because this allows electronic and polar properties to be investigated on molecular length-scales.

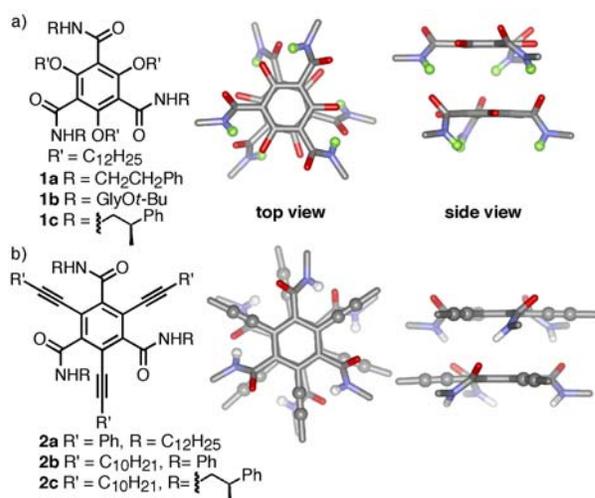


Figure 1. Crowded aromatics that utilize synergistic π -stacking and hydrogen bonding.

It focuses on molecules like **1** and **2** that in their self-assembly allow a synergy between hydrogen bonds and π -to- π interactions (shown in Figure 1). The design principle uses steric crowding to force the recognition groups—amides—out of the aromatic ring-plane and into a conformation that would allow intermolecular hydrogen bonds to form. There are three significant findings. First, the dipole moments of the disks endow the columnar stacks with a macroscopic dipole moment. Polar properties of monolayer films could be measured by means of electrostatic force microscopy. Second, because the association in the stacking direction is stronger than in typical π -stacks, it is possible to create isolated strands of molecules that can be visualized with scanning probe microscopy. Third, it is possible to create the shortest of π -stacks, dimers, on metallic surfaces through noncovalent forces.

Future work will expand the scope of the project to synthesize never versions of these molecules that have larger π -systems that can delocalize charge. In addition the polar and electrical properties will be measured as a function of film thickness from monolayer to multilayers and as the domain size is decreased to near single molecules.

Publications Recognizing Support from DE-FG02-01ER15264

(1) “STM Imaging of Self-Assembled Helical Nanostructures”, T.-Q. Nguyen, R. Martel,

- A. Carlsen, P. Avouris, M. L. Bushey, L. E. Brus, and C. Nuckolls, *in preparation*.
- (2) “Electrostatic Self-assembly of Crowded Aromatics”, T.-Q. Nguyen, J. Dickerson, M. L. Bushey, I. Herman, and C. Nuckolls, *in preparation*.
- (3) “Electric Fields on Oxidized Silicon Surfaces: Static Polarization of PbSe Nanocrystals”, C. Ben-Porat, O. Cherniavskaya, L. Brus and K.-S. Cho and C. B. Murray, *J. Phys. Chem. B.*, *accepted for publication*.
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Nanoscale Materials for Catalysis

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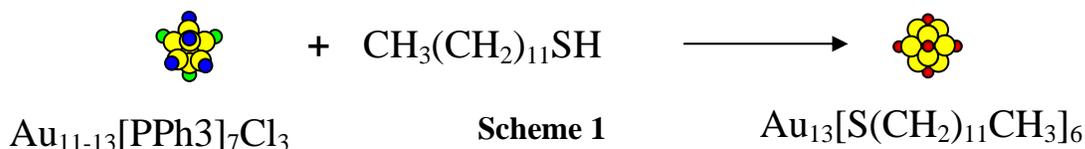
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Abstract

This project involves the characterization of metal nanoparticles with the goal of achieving a fundamental understanding of their dynamical and structural properties and the correlations these have with behavior seen in catalytic chemistry. In addition, the experimental studies are supported with theory and modeling. These studies employ a variety of analytical techniques, highlighted by the complementary use of electron microscopy techniques that probe nanoscale materials properties at the single particle level and x-ray absorption spectroscopy experiments that measure an ensemble of particles. As we will show, this approach has proven especially powerful in identifying metastable geometries and phases not observed in bulk systems. *In situ* studies have identified such metastable structures in several model systems and further elucidated information relevant to the dynamics of their evolution. Efforts to demonstrate the applicability and utility of these techniques to a variety of systems of fundamental and technological interest have led us to focus initially on two classes of model materials. The systems studied include ligand-protected metal nanoparticles as well as catalytically

relevant metal nanoparticles grown on high-surface-area support materials (mostly carbon). The former offers a model system providing experimental control of nanoparticle size and local environment defined by the choice of ligand. The latter is a system of obvious technological interest and also offers greater access to dynamical studies of cluster growth and structural evolution.



Small, monodisperse Au_{13} clusters have been prepared via a ligand exchange reaction of alkanethiols onto phosphine-halide gold clusters (Scheme 1). In one synthetic protocol, two fractions separated with column chromatography exhibit very different UV-visible spectroscopy (Figure 1). The majority fraction of these exchange products showed narrow bands in the UV-visible spectroscopy – a characteristic of a so-called “molecule-like” electronic structure. The minority

fraction showed no bands in the UV-visible spectroscopy but instead exhibited an absorbance profile that increases smoothly into the UV region of the

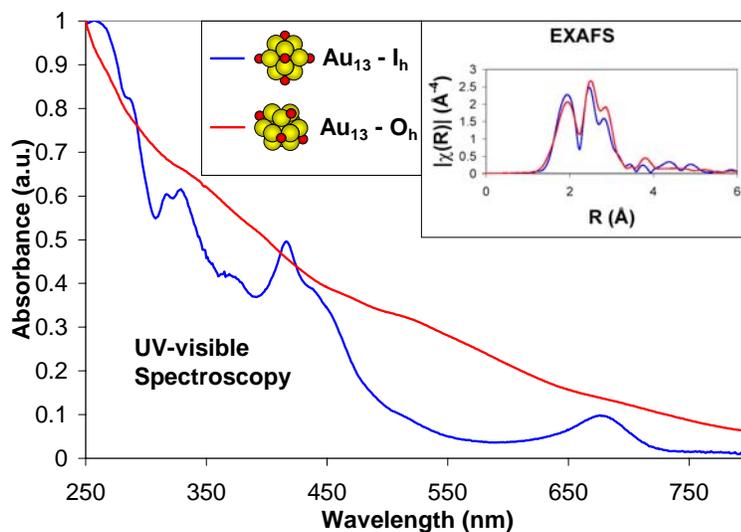


Figure 1

spectrum.

Extended x-ray absorption fine structure (EXAFS) measurements of these two materials (Figure 1, inset) were fit using Au-S and the first nearest neighbor Au-Au scattering paths and found to exhibit two different structures of a Au₁₃ cluster core with a ligand shell of six alkanethiols. The cluster exhibiting a molecule-like UV-visible spectrum (blue curves, Fig.1) was found to have a local structure consistent with an icosahedral core while the cluster with a smoothly varying UV-visible absorption spectrum (red curves, Fig. 1) was determined to be a cuboctahedral Au₁₃ core. This system embeds considerable structural fluxionality as shown by the data given in Figure 2. The EXAFS analysis reveals

that all three samples are icosahedral Au₁₃ clusters, albeit ones exhibiting differences in the average gold-gold bond lengths that

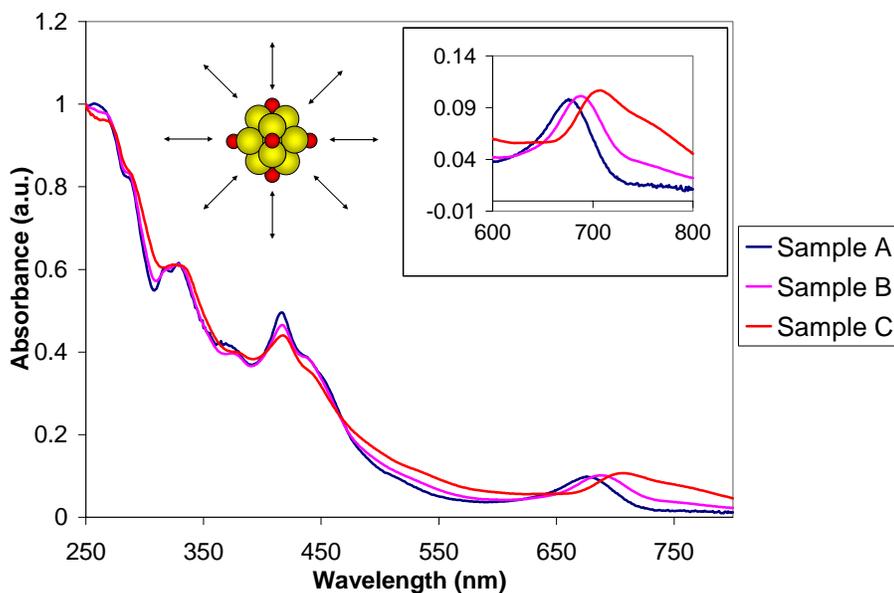


Figure 2

decrease from Sample A to Sample C. The noted differences in the UV-visible spectroscopy are correlated with a progression of structural relaxations of the gold core bonding driven by ligand exchange. The replacement of a thiol ligand with a phosphine (or vice-versa) drives these effects. For example, by replacing a thiol with a phosphine

on the cluster, additional electron density is made available for Au core bonding and a decrease in Au-Au bond lengths is the expected and observed result. Current efforts are focused on using high-resolution electron microscopy techniques to study nanoparticle structures of this sort and compare these data to that obtained at the level of the ensemble using x-ray spectroscopies.

Initial studies by transmission electron microscopy identified both fractions as sub-nanometer, highly monodisperse nanoparticles. Figure 3 is a representative Scanning transmission electron microscopy (STEM) high-angle annular dark-field (HAADF) image of Au clusters. The inset right below is a histogram of the particle size distribution of Au nanoparticles measured from HAADF images taken in different sample regions, where 1025 Au nanoparticles were counted.

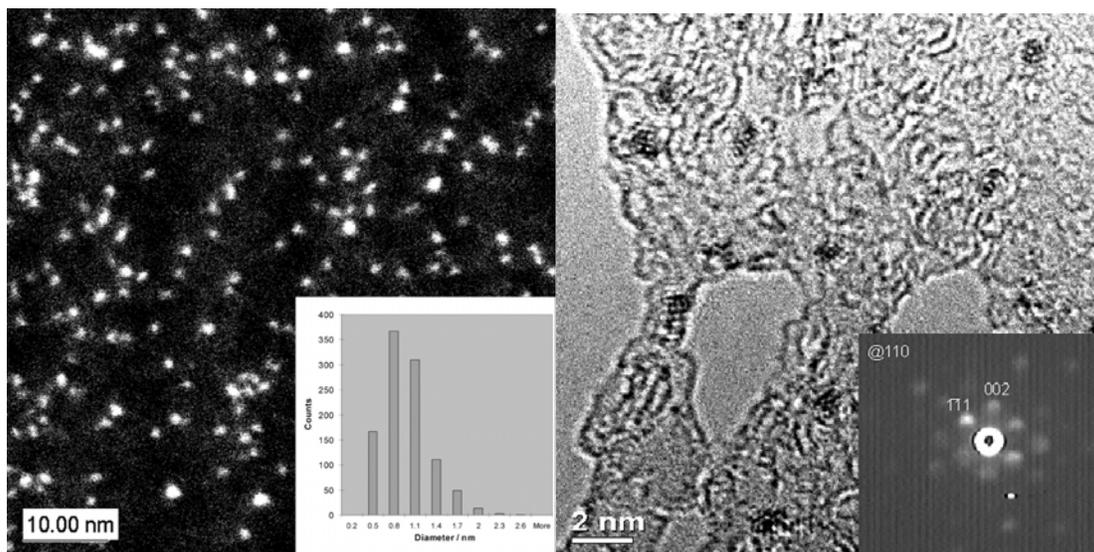


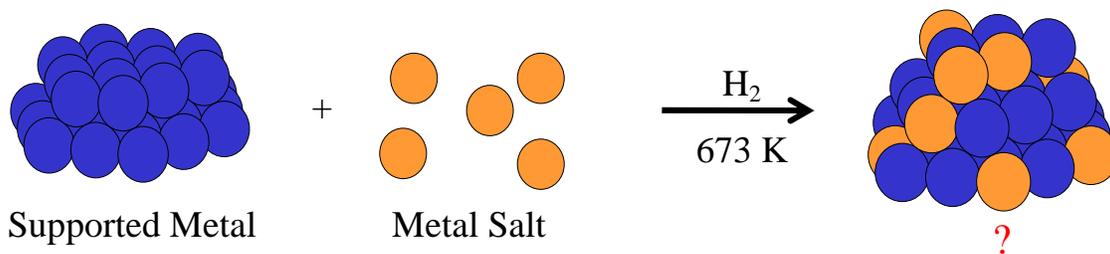
Figure 3

Figure 4

As indicated in the particle size histogram (Figure 3, inset), Au clusters have an average diameter of 0.82 ± 0.34 nm, with a very narrow size distribution, i.e., from 0.5 to 2.0 nm.. The size of the particles seen in this image suggests that the typical particle of gold

contains 13-55 atoms. Quantitative mass spectroscopic analysis is being developed. to provide more details about atoms per cluster.

The nanoparticles microstructure was further studied by electron microdiffraction and high resolution electron microscopy (HREM). Figure 4 is a HREM image of Au clusters in the same sample as scanned by STEM and strong diffraction pattern is seen for these particles with the size larger than 1nm (figure 4, inset). The pattern shown in the figure 4 (and others recorded at the several locations of the sample) is best indexed to an FCC structure with zone axis of 110. The values from the ratios of distances calculated for the FCC Au alloy (where $a=0.407\text{nm}$, $c/a=1.155$, $\theta= 54.74^\circ$) agree closely with those measured from the microdiffractions of a variety of nanoparticles residing in different regions of the samples ($c/a=1.1\pm 0.1$, $\theta = 56\pm 1^\circ$). For smaller particles with the size less than 1nm, the crystal structure can be deduced from HREM images. Figure 4 displays lattice fringes of those ultra small gold clusters with size less than 1nm; the average lattice parameter can be measured as 0.40 ± 0.02 nm, which is in good agreement with the Au-Au bond distance determined by EXAFS techniques. In addition to this, icosahedra Au_{13} clusters can be identified through the analysis of the structure of icosahedrons projected in the zone axis direction as well as HREM image simulation.



Scheme 2

The model system described above has the advantages of being both well-defined and easily characterizable by a variety of physical and spectroscopic techniques, while embedding many of the structural and electronic properties relevant to catalytic systems. Nanoscale catalysts, though, are generally used in complex supported forms and are, as a result, harder to characterize at the same level of detail. To address this deficiency we have begun to explore systems of supported nanoparticles of direct interest to energy technologies. Carbon supported bimetallic nanoparticles (Pt/Ru) are prepared via the high temperature reductive condensation of various metal salt precursors ((CH₃)₂Pt(COD), H₂PtCl₆, and RuCl₃) onto carbon black substrates. The initial goals of the project involve the use of presupported monometallic nanoparticles to template the reduction of the counter metal according to Scheme 2. Using a battery of analytical surface techniques, the composition, atomic structure, and size of these particles were mapped to give a size-correlated binary phase diagram. These nanoscale (2-3 nm) bimetallic alloys show atomic structures not ordinarily seen in the bulk binary phase diagram. Particles with high Ru compositions were seen with FCC structures and particles with high Pt compositions were seen with HCP structures, a phenomenon impacted by the nature of the nascent cluster used. When Pt particles were used as seeds for Ru deposition, the resulting particles tended towards FCC structures at all compositions. The use of Ru seed particles provided some examples of metastable HCP

structures although, as before, the FCC habits were a predominate structural form. The existence of metastable phases in the nanoparticles is suggestive of a complicated energy landscape that contains a number of different atomic environments and correlated chemical natures.

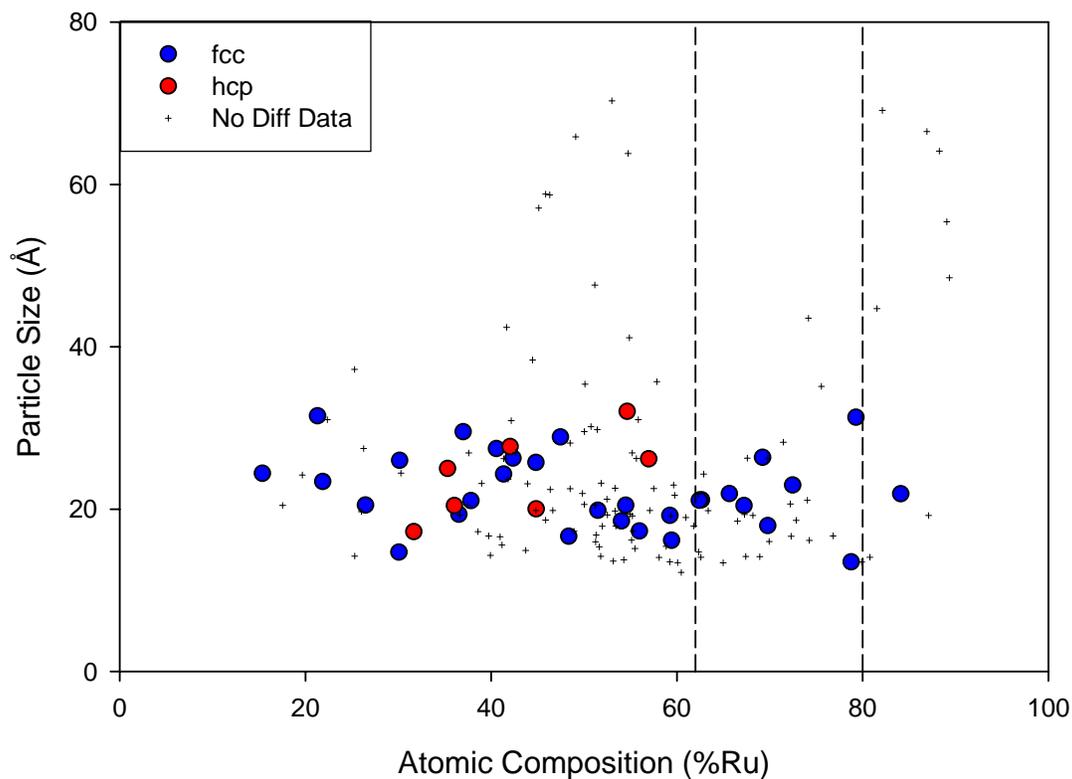


Figure 5. Phase diagram of bimetallic particles formed from the co-reduction of Carbon black + RuCl_3 + H_2PtCl_6 at 673K.

We have carried out direct density-functional-based simulations of Ru-Pt clusters on carbon-based supports. We have identified [3] that the structural properties, including bond lengths and distributions, are dictated by the cluster-substrate interface interactions, even starting with the dimers. In fact, the dimers experience ~25% increase in bond length when in equilibrium on support at zero Kelvin. Figure 4 shows the first-principles calculated bond-lengths relative to bulk Ru-Ru and Pt-Pt bonds for various sized clusters. Note that with and without substrate the dimer bond-length is dramatically affected. Furthermore, magnetism is eliminated as a possible effect that ameliorates the impact on structure.

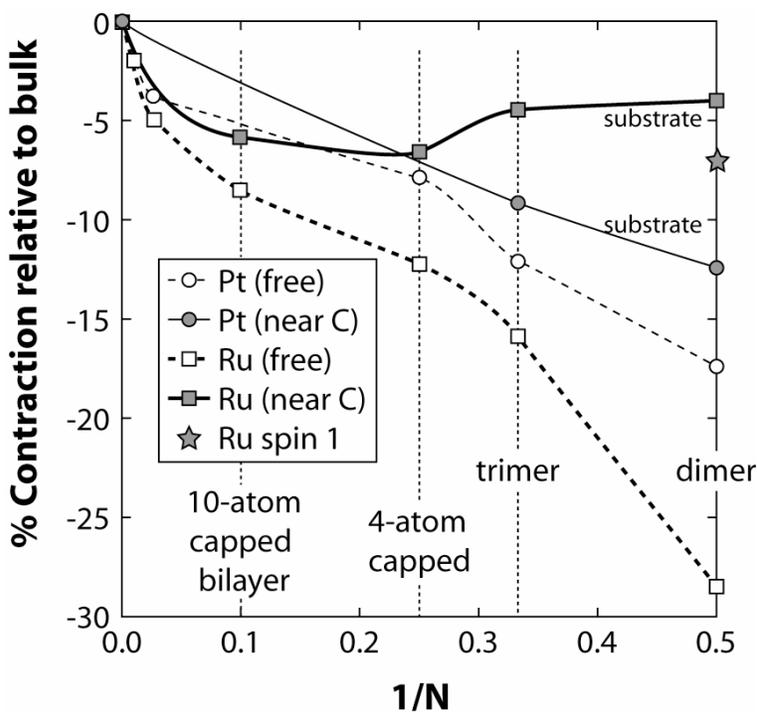


Figure 6. Calculated bond-lengths relative to bulk Ru-Ru and Pt-Pt bonds for various sized clusters with N atoms. The lower-energy spin-polarized Ru-dimer (star) has similar bond-length to non-spin-polarized dimer. Magnetism is not relevant for Ru clusters of ~27 atoms, but does have electronic effects for smaller clusters.

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Columbia University: Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes Through Tailored Nanostructures.

Collaborators: Adzic, Bartels, Feibelman, Heinz, Murray, O'Brien, Rahman

Applied Physics and Applied Mathematics, 200 SW Mudd, 500 West 120th St., New York.

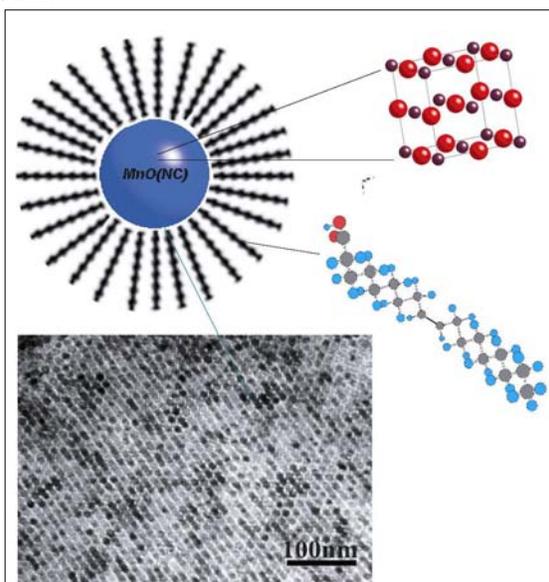
Synthetic Methodologies for Preparing Nanocrystal and Nanocrystal Assemblies with Applications in Catalyzed Oxidation Reactions

1. Transition metal oxide (TMO) nanocrystals

Transition Metal Oxide (TMO) Nanocrystals are nanometer dimension crystals composed of one or more metals from the *d* block of the periodic table and oxygen. The nanocrystals have capping groups which render them discrete, stable, and enable them to be manipulated in a variety of media such as solvents or polymers. The nanocrystals are ideally monodisperse, uniform in composition, crystalline, and can be prepared over a range of sizes from 1-100 nm. The selection of composition for the transition metal oxide (TMO) nanocrystals is based on materials with known catalytic properties in the bulk.

Metal and metal oxide nanocrystals have been prepared by new methods invented in the O'Brien group. Careful attention to purity, the concentrations of the reagents, the rate and order of their addition, and temperature is the minimum requirement for the reproducible formation of nanoparticles in desired composition and size distribution.

We have developed new procedures for the synthesis of new TMO nanocrystals grounded in the use of these techniques. The methods are distinct from sol-gel chemistry and other more traditional methods of producing colloids as discerned by the nature of the product. The capping groups (also called ligands because they bind to the surface of the nanocrystal) are typically long chain alkyl surfactants with heteroatom or polar head groups that react with and bind to the nanocrystal surface via covalent, electrostatic or coordination bonds (or some combination of all three), generally to the metal atoms. The lability of the surface ligand (ease with which it can be exchanged) depends upon the strength of the binding interaction. An extremely important part of the procedure is the ability to control initial conditions of nucleation, with separation from growth. The nanocrystals that result from a successful procedure of this kind can be highly uniform, phase pure, come in high yields with no tendency toward aggregation, and be relatively monodisperse. The absence of water and oxygen



is necessary at the start, and the solvents and ligands have to be dry and pure. In the development of experiments for a particular transition metal oxide, each system will have its own unique set of parameters in need of optimization, and then through a careful survey of several syntheses, we can develop a procedure for obtaining highly uniform particles over a range of sizes.

2. Results

In accordance with our original proposal we are working towards the “ultimate scenario,” in which one can envisage controlling many features through tailoring the nanostructure: control of photophysical properties of the semiconductor by tunability of the band gap by the size of the nanocrystal, control of the nanocrystal architecture by deposition of the materials on substrates.

2.1 Wide band gap semiconductor nanostructures: semiconductor tunability

We report a new synthesis of ZnO nanorods (submitted to J. Am. Chem. Soc.) by thermal decomposition of zinc acetate in organic solvents in the presence of oleic acid, which produces relatively monodisperse ZnO nanorods (ZnO quantum rods) with diameters of 2 nm and lengths in the range 40-50 nm (Figure 1). The diameter is an order of magnitude smaller than previously reported ZnO nanorods prepared by a variety of other methods and near UV absorption and PL measurements were able to determine that quantum confinement effects are present in these rods, with an excitonic ground state of 3.55 eV. We have also prepared nanocrystals of BaTiO₃ and TiO₂. The nanocrystals are prepared via a two step method involving the preparation of a precursor that yield monodisperse 10 nm nanoparticles that can be annealed to make highly crystalline samples on substrates.

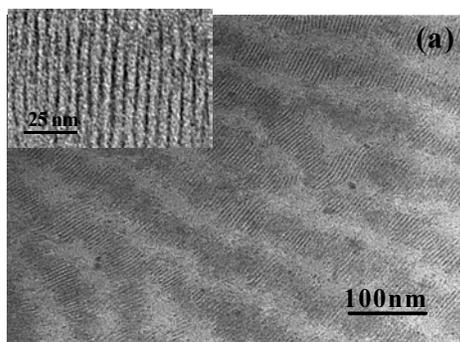


Figure 1. Transmission Electron Microscope Images of Zinc Oxide Nanorods.

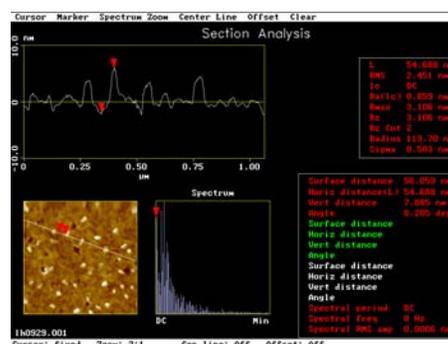


Figure 2. AFM Characterization Nanocrystals of the titanates on n-type silicon.

2.2. Copper oxide nanocrystals in CO oxidation: influence of size dependence at the nanoscale

Carbon monoxide oxidation activities over the Cu-Cu₂O-CuO system have revealed that copper may be a useful potential substitute metal in CO oxidation reactions (includes among others the work of G. A. Somorjai) And there is some discussion in the literature as to the role of the surface lattice oxygen of species non-stoichiometric copper oxides during the course of the reaction. Preparation of nanocrystals using our methods, has demonstrated the ability to control the oxidation state of the metal oxide and/or we have observed the stabilization at the nanoscale of non-stoichiometric oxides which are not normally stable under ambient conditions. We have recently prepared highly uniform nanocrystals of Cu₂O. We believe (although this is to be confirmed) the mechanism for the reaction proceeds via Cu nanocrystals which are subsequently oxidized and therefore we are presented with the opportunity of obtaining copper and copper oxide nanocrystals in different oxidation states. In collaboration with the Heinz and Bartels groups, we plan to try to observe the movement of CO molecules on these nanocrystal surfaces.

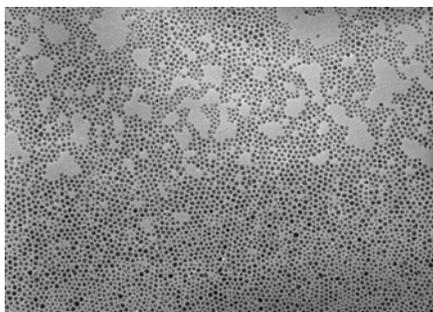


Figure 3. TEM of Cu₂O 5 nm nanocrystals

2.3. Nanocrystal Assemblies of CoPt₃-Iron oxides: Control of the nanocrystal architecture (Collaboration with Murray at IBM Watson)

We have been working to prepare multicomponent binary superlattices of nanocrystals, one of which would be small nanocrystals of metals. We have observed the affinity of small articles to attach themselves to larger ones (Figure 4), thus providing a possible route for making isolated units of catalyst cluster-on-semiconductor-nanocrystal.

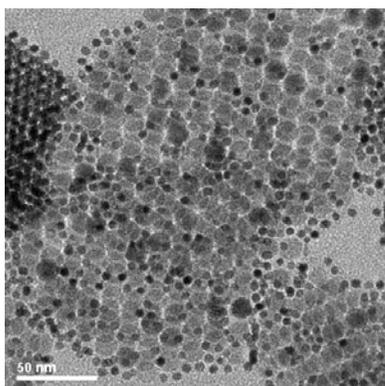


Figure 4. Fe₂O₃-CoPt₃ nanocrystal assemblies. The CoPt₃ are the small darker particles.

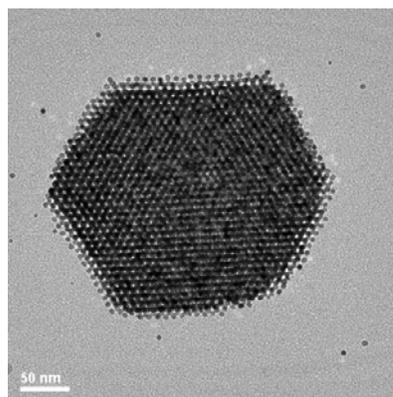


Figure 5. A self-assembled superlattice of CoPt₃ Nanocrystals

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2. "Zinc Oxide Quantum rods" *submitted to JACS*, Ming Yin, Yi Gu, Igor L. Kuskovsky, Tamar Andelman, Yimei Zhu,† G. F. Neumark, and Stephen O'Brien.*
3. "Structural and Magnetic Characterization of Non-stoichiometric Iron Oxides", Redl, F. X., Yin, M., Black, C.T., Murray, C.B.M., O'Brien, S.*, 2004, In preparation.
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Studies of Active Oxygen Species for Hydrocarbon Conversion

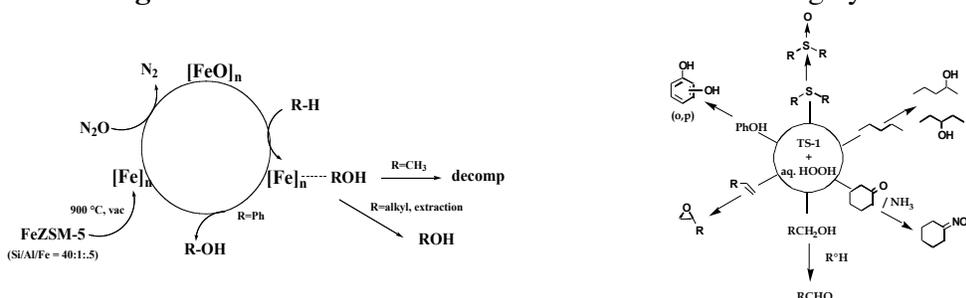
Current postdoctoral researcher: Monika Hartl

Collaborators: Michael Janicke, Juergen Eckert, Thomas Proffen, Neil Henson (all LANL); Prof. Alex Bell, Ben Wood (UC Berkeley); Prof. Tanja Pietrass and Mirka Mecerova (New Mexico Tech).

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Research Goal: Develop an understanding of the local structure at the Fe and Ti sites of the zeolite-based selective oxidation catalysts TS-1 and Panov's catalyst derived from FeS-1, and the closely related, if not identical Fe zeolite catalyst responsible for highly efficient reduction of nitrogen oxides.

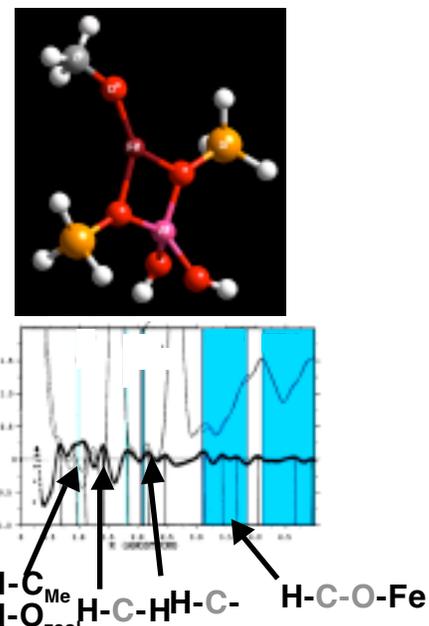
Recent Progress: Ti or Fe sites in or on zeolite frameworks are highly active and selective catalysts



for selective oxidation of hydrocarbon substrates. In both catalysts, the concentration of metal cation is very low, and has made direct spectroscopic and structural studies to report on the local structure of the metal cation sites difficult.

Our previously published work was the first direct determination that Ti and Fe substitute into specific sites within the zeolite framework. Our recent work has been focused on 1). Defining the nuclearity at the iron site (monomer vs. dimer), 2). Determine the interactions of bound intermediates with the iron site (e.g. MeO-Fe), and 3). Correlate this structural information with other catalytic and spectroscopic information to report on details of the highly reactive iron oxo responsible for the insertion into C-H bonds. We have used isotope difference pair distribution function analysis of neutron scattering data to obtain a preliminary description of the putative iron oxo site that has undergone insertion into a C-H bond of methane.

We have prepared several sets of the iron catalyst in which the putative iron oxo has been reacted with either CD₄ or CD₃H at low temperatures to form the zeolite-bound methoxy intermediates. Using total neutron scattering techniques coupled with isotope differences, we have extracted the hydrogen pair distribution function that indicates distances that may be assigned to the C-H, H-C-H, and H-C-O (and possibly H-O-zeol) distances in the bound methoxy intermediate. There are also peaks in the PDF in the region where the H-C-O-Fe distances are expected. Analysis of EXAFS data at the iron edge obtained on these same samples indicates it is unlikely that there is a Fe-O-Fe linkage. We have recently obtained total neutron scattering data on an analogous set of ⁵⁷Fe labeled samples for



comparison with natural abundance Fe samples in an attempt to obtain more specific information in the vicinity of the iron site. This data is currently being analyzed.

DOE Interest: Selective oxidation catalysts are crucial to the production and utilization of fuels. Our study of the local structure of model oxidation catalysts will lead to a better understanding of the electronic and structural requirements to generate high activity catalysts.

Future Plans: Our research will continue to focus on developing the best representation possible of the active site structure of Panov's catalyst and the Ti sites in TS-1.

In the near term, we have a substantial amount of neutron and EXAFS data to interpret from recent neutron scattering and synchrotron X-ray experiments on additional samples of Panov's catalyst, and its precursors. From the ^{57}Fe data sets, we hope to obtain more definitive information regarding the near-neighborhood of the Fe site. We have also just collected EXAFS data on a set of iron zeolite samples where a higher concentration of iron is introduced by sublimation of FeCl_3 . These samples will provide calibration data sets with which to compare our results against published reports that report the iron site is dimeric. Prof. Bell's group has also studied some of our samples that contain Al in the framework, and correlating FT-IR data with different Fe/Al concentrations, they suggest that iron interacts with anionic framework aluminum sites. This would be consistent with the absence of dimeric iron sites in these catalysts that are very dilute in iron.

Electronic structure calculations using small cluster models of the iron site will be performed to guide the interpretation of the PDF data, with the goal of providing a self-consistent model of the reactive iron-oxo site that leads to C-H insertion to form the bound iron methoxy.

In the process of obtaining this data, we will also determine the iron siting that results from different synthetic pathways. We have data which suggests that the iron siting varies with synthetic conditions (high pH, OH^- - vs. near-neutral, F^- - mediated syntheses); this may point to differences in ion pairing arrangements in the zeolite gel state between anionic metasilicate precursors and the cationic structure directing agent. Analogously, with our previous results that describe the Ti siting in TS-1, we will re-examine the siting of Ti as a function of synthetic route. The results of these studies, depending on the outcome, may have implications on the siting of Al and other cations in zeolite frameworks that form the basis of important catalytic processes.

Publications (2002-3):

"Nitrous Oxide Decomposition and Surface Oxygen Formation on Fe-ZSM-5", B. R. Wood, J. A. Reimer, A. T. Bell, M. Janicke, and K. C. Ott, *J. Catalysis* (submitted 9/2003).

"Studies of Methoxy Species Formed on Fe/Al MFI by Direct Oxidation of Methane by Nitrous Oxide", B. R. Wood, J. A. Reimer, M. T. Janicke, and K. C. Ott, *J. Catalysis* (submitted 11/2003).

"NMR Investigations of ^{15}NO and $^{15}\text{NH}_3$ of Gallium-Substituted Zeolites", M. Mearova, N. A. Miller, N. C. Clark, T. Pietrass, and K. C. Ott, *Appl. Cat. B*, (submitted 3/2004).

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"Osmium Carbonyls in Zeolite NaX: Size Differentiation by 129 Xe NMR Spectroscopy" B. Enderle, A. Labouriau, K. C. Ott, B. C. Gates, *J. Phys. Chem. B* **106**, 2109 (2002).

Nanocatalysts: Synthesis, Properties, and Mechanisms

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Collaborators: D. R. Mullins, V. Schwartz, E.W. Hagaman, Jun Xu, S. J. Pennycook, S. Spooner, M. A. Amiridis, Sokrates Pantelides, Craig Barnes

Postdocs: Bei Chen, Wenfu Yan, Haoguo Zhu, Shannon Mahurin, Michelle Kidder, Andrew Lupini, Alberto Franceschetti.

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Goal

Explore and exploit novel synthetic techniques to prepare nanostructured catalysts with high selectivity and activity.

Recent Progress

Synthesis of nanostructured supports and catalysts: We have explored several methodologies to synthesize Au, Pt, and Pd nanoparticles and oxide nanoparticles inside oxide hosts. Stabilization of Au particles in silica supports has been a key challenge. A method was used in which Au precursor is co-assembled along with a template-surfactant and a functional ligand introduced on a siloxy precursor. By this co-assembly method, mesoporous silica networks similar to MCM-41, HMS, and MSU have been prepared with ethylenediamine or diethylenetriamine ligands attached to the pore walls of the mesoporous silica which in turn stabilize highly dispersed Au precursor. Carefully chosen methods of post-treatment to remove the surfactant and reduce the Au are critical to prevent loss of Au or excessive growth of Au particles. In addition to silica supports, a combination of hydrothermal and ultrasonic techniques have been used to prepare titania supports in five different forms (mesoporous, anatase, brookite, rutile) for preparation of Au catalysts by deposition-precipitation (D-P). Mixed mesoporous titania-silica supports with variable ratios of TiO_2 - SiO_2 have been prepared using a templated co-synthesis technique which inhibits rapid selective hydrolysis and precipitation of TiO_2 . These supports contain highly dispersed titanium cations some in tetrahedral sites, which are resistant to crystallization and provide a novel support for Au. A particularly interesting methodology permits layer-by-layer growth of an oxide onto silica supports using two-step non-aqueous chemisorption followed by hydrolysis. This method has been used to prepare single layers of titania, alumina or germania on silica supports, which couple with D-P of Au leads in some cases to extremely active Au catalysts. Co-synthesis techniques have been used to prepare mixed urania-titania and urania-silica nanoparticles inside mesoporous SiO_2 which even without Au or other precious metal are active for oxidation reactions. In addition to oxide supports, Au catalysts have also been prepared in microporous Al phosphate zeolite.

Support and particles size effects in Au catalysts: Five different forms of titania (mesoporous titania and nanocrystalline anatase, brookite, rutile forms and commercial P-25) were used as supports for identically prepared Au catalysts (by deposition-precipitation) to study the effect of crystallite atomic structure upon catalytic activity for CO oxidation. It is found that activities of the as-prepared catalysts are comparable, but brookite exhibits a greater stability towards sintering effects. Using the co-assembly with functional ligand methodology, silica supported Au catalysts were prepared with very small mean size Au particles. Comparison of these catalysts with titania supported catalyst demonstrated much higher activity for the titania supported catalysts indicating that optimal Au particle size is not the only important factor leading to high activity. Au catalysts supported in a microporous aluminum phosphate was found also to be

active for CO oxidation in spite of the fact that no reducible oxide is available for oxygen transfer to Au surfaces. On this catalyst CO oxidation in air deactivates rapidly, but high CO conversion is stabilized if hydrogen is added to the reactant mixture. By this addition, stable and essentially complete conversion of CO is achieved at 298 K while hydrogen conversion is very small.

Characterization of Au catalysts: Au catalysts prepared by the methods described above were characterized by a variety of means. A major emphasis was placed on the determination of particles size and so a XANES/EXAFS was used as well as small angle scattering of both x-rays (SAXS) and neutrons (SANS). XANES proved to be useful for its ability to distinguish the oxidation state of Au and studies of the reduction of the as-synthesized Au precursor catalysts were carried out on a variety of supports. In the active state, the Au on titania support is fully reduced to Au⁰. The activity in this state is comparable to that of the most active titania supported Au catalysts reported in the literature. EXAFS was used to obtain mean coordination numbers, and therefore mean particle size. Comparison with activity data indicates that activity is not clearly linked to particle size, at least over the 0.5 to 5 nm particle range accessible by EXAFS. SANS was also explored as a means of extracting particle size for a Au catalyst supported in mesoporous silica. Using contrast matching, it was possible to remove scattering from silica mesopores thereby permitting analysis of Au particles sizes. Contrast matching in mesoporous titania was less successful. The ORNL aberration corrected microscope has been used to examine several catalysts of interest. For the first time, images with atomically resolved Au atoms have been obtained. The most active state of Au / anatase titania catalysts is associated with thin Au rafts while aggregation of Au rafts into 3-d nanocrystals generally results in a decrease in activity. ¹³C NMR characterization of functionalized MCM-41s at various stages of their synthesis and surfactant removal has illuminated specific reaction paths that occur in the pores of these silicas in the course of forming gold nanoparticles. Polydentate amine functionality tethered in the MCM-41 pores is effective at retaining gold nanoparticles in the silica mesopores. Extensive Hoffmann elimination of retained surfactant is observed during the elevated temperature reduction of chloroauric acid to gold.

Theoretical studies of Au catalysts: Computational studies using density functional techniques have been carried out on free Au clusters and on Au cluster supported on anatase TiO₂. It is found that an oxygen vacancy on the titania stabilizes the adsorption of a Au atom, anchoring small Au rafts. Oxygen adsorption does not occur on single, stable Au adsorbate atoms, but anchored clusters of Au atoms (Au₇ or Au₁₀) do stabilize adsorption of both CO and O₂. Computed adsorption energetics now explain why activity is possible on small clusters but not on large bulk-like crystallites.

DOE interest

New catalysts are needed to achieve incremental or revolutionary improvements in technologies related to emission control, fuel cells and hydrogen utilization. This work provides a research basis for preparing, testing and understanding catalysts with potential application in these technologies.

Future Plans

Layer-by-layer growth of catalysts for control of activity: This synthesis methodology will be investigated extensively and will constitute a major portion of our effort. Layer-by-layer deposition onto nanostructured silica will be applied and the effect of several design factors will be exploited to prepare new Au catalysts. By this methodology and systematic variation, it should be possible to learn how to 1) control morphology using available silica support morphologies, 2) control support chemical activity by depositing different active overlayers such as TiO_x, AlO_x, ZrO_x, VO_x and GeO_x, 3) control placement of metal particles by exploiting capping and functionalization of external vs pore wall surfaces, 4) control pore sizes by sequential layer deposition onto pore walls and 5) control metal particle sizes by confined growth into pores of variable sizes. Layered structures of this type may be expected to exhibit variations in electronic properties (e.g. bandgap, localized electrons, valency) which could modulate catalytic or

photocatalytic behavior. Besides use as a support for Au catalysts, work will shift to include these oxides which themselves may be active catalysts.

Mechanistic studies and characterization of surface chemistry and catalytic performance:

A pulsed reactor with in situ FTIR will be completed and used to study mechanistic aspects of the CO oxidation reaction. It should be possible to simultaneously monitor the chemical nature of surface adsorbates and their time response to changes in the reactant concentration. Work will expand beyond CO oxidation to incorporate extensive studies of selective CO oxidation in the presence of H₂. This process is of high technological importance for fuel cells and the hydrogen economy. This selectivity will be examined on Au catalysts prepared by deposition on a wide variety of supports. Activity and mechanisms for water gas shift and propylene epoxidation reactions will also be examined. In addition to traditional techniques and those mentioned above, positron porosimetry will be developed and applied to the porous catalysts. High resolution Z-STEM will continue to be an important method to provide direct atomic detail of the structure of features on supported catalysts. Emphasis will be placed on using *in situ* and *operando* conditions.

Publications

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Overbury, S. H., L. Ortiz-Soto, H. Zhu, B. Lee, M. D. Amiridis and S. Dai, *Comparison of Au catalysts supported on mesoporous titania and silica: Investigation of Au particle size effects and metal-support interactions*, Catalysis Letters, in press (2004),

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Franceschetti, A., S. J. Pennycook and S. T. Pantelides, *Oxygen chemisorption on Au nanoparticles*, Chemical Physics Letters, 374 (5-6), (2003), 471-475.

Zhu, H. G., B. Lee, S. Dai and S. H. Overbury, *Coassembly synthesis of ordered mesoporous silica materials containing Au nanoparticles*, Langmuir, 19 (9), (2003), 3974-3980.

Zhang, Z. T., M. Konduru, S. Dai and S. H. Overbury, *Uniform formation of uranium oxide nanocrystals inside ordered mesoporous hosts and their potential applications as oxidative catalysts*, Chemical Communications, (20), (2002), 2406-2407.

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Surface Processes in Metal Phosphide Hydrotreating Catalysts

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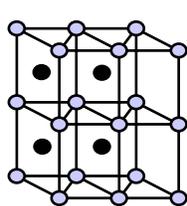
Goal

Study the reactivity of new phosphide catalysts for hydrotreating, and examine the mechanism of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN).

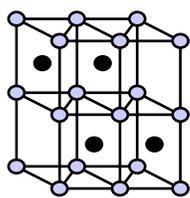
Recent Progress

The high activity of phosphide catalysts continues to attract attention throughout the world, with many groups starting to investigate the activity of this interesting class of new materials. We have identified Ni₂P as the most active of the phosphides and are carrying out extensive studies of its properties.

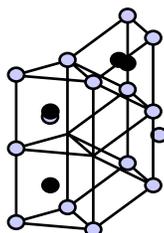
Preparation of Metal Phosphides: The metal-rich transition metal phosphides are a broad class of compounds which combine metallic properties such as conductivity with refractory properties such as hardness. They adopt many types of structure, but in general are not layered so are completely different from standard sulfide catalysts. They offer the possibility of more accessible sites than sulfides, where the basal planes are largely inactive. The phosphides can be prepared readily by the temperature-programmed reduction in H₂ of phosphate precursors



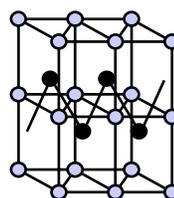
WC
hexagonal
MoP



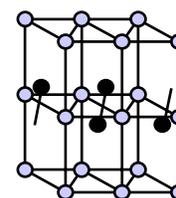
NiAs type
hexagonal
VP



NbAs type
cubic
TaP, NbP



MnP type
orthorhombic
WP, CrP, FeP



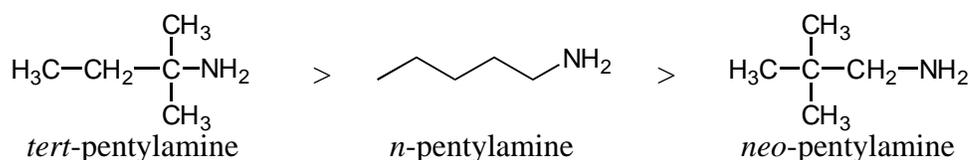
NiP type
orthorhombic
NiP

Ni₂P Supported on K-USY: Ultra stable Y-zeolites have a dual pore structure consisting of standard faujasite cages and a mesoporous system created by the steaming process in the synthesis of the materials. We have found that the USY zeolites with their acidity neutralized by K are effective supports for Ni₂P, giving highly active catalysts. At 30 atm and 613 K the conversion of 4,6-dimethyldibenzothiophene (DMDBT) was 98% compared with 85% for a conventional Ni-Mo-

S/Al₂O₃. The comparison was on the basis of equal number of sites as measured by CO uptake at room temperature for the phosphide and O₂ uptake at dry-ice/acetone temperature for the sulfide.

Studies with Real Feeds: Results with model compounds often do not correlate with those obtained with real feeds because the interactions between the components are complex, so most catalyst development is carried out with actual feeds. In order to evaluate the potential of the new catalyst it was subjected to a test with a hydrotreated gas oil of low sulfur (440 ppm) and nitrogen (8 ppm) contents and moderate aromatics content (27 wt%), which mimics that which would be used in a second-stage hydrotreating process. The measurements were made at realistic conditions (593 K and 3.9 MPa) using a stainless steel reactor of 9.5 mm O.D. (3/8 inch). Comparison was made with a current commercial Co-Mo-S/Al₂O₃ catalyst (Ketjenfine 756) of surface area 218 m²g⁻¹ and containing 11.2 wt.% Mo and 3.1 wt.% Co. For the Ni₂P/SiO₂ the HDS conversion was 85 % (± 2 %) with sulfur content reduced from 440 to 66 ppm. This compares favorably with the results obtained with the commercial Co-Mo-S/Al₂O₃ catalyst, which gives a conversion of 80 % and sulfur content of 86 ppm.

Mechanism of HDN of Pentylamines: The operative mechanism of N-elimination on the phosphide catalysts was investigated on a series of pentylamines of different structure. The following order of reactivity was found



There was no correlation of this order of reactivity with steric hindrance, suggesting that an S_N2 pathway was not involved. Similarly, there was no correlation with the stability of carbocation or carbanion species, suggesting that prior scission of the amine group as in an S_N1 or E1 mechanism was not occurring. However, there was a direct relationship between the order of reactivity and the number of β-hydrogens, and this suggested C-N bond scission by an E2 mechanism on the catalysts.

Calculated adsorbate structure: The mode of binding of alkylamines on Ni₂P surfaces was studied using ethylamine as a probe molecule. Ethylamine is the simplest alkylamine capable of undergoing a β-elimination. Its mode of adsorption was studied by Fourier transform infrared (FTIR) spectroscopy and theoretical molecular orbital calculations. Calculation of the structure of adsorbed ethylamine was performed using the Gaussian 98 program using the HF / 6-31g* basis set. The calculated vibrational frequencies were in excellent agreement with the experimental values.

In Situ EXAFS Studies: We have carried out measurements of the structure of the catalyst in its working state. Our work is unique in that the studies are carried out at high pressure and temperature in the liquid phase. We have verified that the Ni₂P catalyst is stable at reaction conditions.

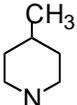
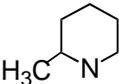
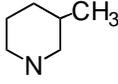
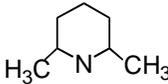
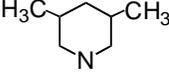
DOE Interest

Commercial hydrotreating catalysts are molybdenum or tungsten sulfides promoted by cobalt or nickel, and supported on alumina. The phosphide catalysts are a completely different class of material and represent a novel direction in hydroprocessing catalysis research.

Future Plans

Mechanism of HDS: A fundamental question in the deep HDS of substituted dibenzothiophenes is the manner in which the reaction proceeds. Two main pathways dominate: a) a direct desulfurization route (DDS) and b) a hydrogenation route (HYD). The mechanism operating on the phosphides will be probed using initial selectivity measurements in a batch reactor.

Mechanism of HDN of Piperidines: The NH_3 elimination step is usually the last step in a sequence of denitrogenation and is relatively facile. A more difficult step is the internal C-N bond hydrogenolysis (CNH) that occurs in heterocycles. A good probe of this reaction is piperidine ($\text{C}_5\text{H}_{11}\text{N}$) and its derivatives

Molecule						
Number of α -H's	4	4	3	4	2	4
Number of β -H's	4	4	7	3	10	2

The various compounds contain different numbers of α and β hydrogens, so are good substrates for identifying the reaction pathways.

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2. J. H. Kim, X. Ma, C. Song, S. T. Oyama, Y.-K. Lee, Kinetic Study of 4,6-Dimethyldibenzothiophene Hydrodesulfurization over Ni Phosphide, NiMo and CoMo Sulfide Catalysts, *ACS Fuel Chem. Div. Prep.* **2003**, 48, 40-41.
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Hydrogen Containing Functional Groups and the Structure of Coal

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Goal

Obtain a fundamental understanding of the structure of coal.

Recent Progress

Recent work has focused on the nature of secondary interactions (e.g., hydrogen bonding, ionic interactions) in coal and the detection of thermal transitions. It has been shown that the amount of pyridine soluble material obtained from many coals is significantly enhanced by washing with weak acids (papers 2 and 3, listed below). This has important implications for the nature of interactions and the structure of these materials. For low rank coals, we have proposed that carboxylate ions and their metallic counter-ions phase separate from the organic component of coal to form micro-domains or clusters, in a similar fashion to synthetic ionomers such as Surlyn. This is important, because randomly dispersed $-\text{COO}^- \text{M}^+$ groups would not affect the swelling and solubility characteristics of a coal, as they do not provide the connectivity necessary to act as some sort of cross-link. In higher rank coals, our results indicated that π -cation interactions are important. These types of interactions have not previously been considered as a significant component of coal structure. As a result of this work, we have proposed that cross-linking in coal should be thought of in a different way and classified into two types; first, "permanent" covalent linkages that cleave only at elevated temperatures or through chemical reaction; second, "reversible" cross-links, largely associated with ionic structures such as carboxylate salts and π -cation complexes.

There is an important school of thought that regards coal as largely an associated structure, rather than a covalent network. However, most of the research supporting this view is based on results obtained from just one or two coals, whose behavior may be anomalous. The most widely studied of these is the APCS Upper Freeport coal, which has a significantly enhanced solubility in the mixed solvent system *N*-methyl-2-pyrrolidinone/carbon disulfide (NMP/CS₂), relative to the individual solvents and "good" solvents like pyridine. The solutions and solvent swollen residues obtained from this coal also display a rich range of complex behavior, forming gels and exhibiting viscoelasticity. The nature of the interactions in this mixed solvent system and the mechanism by which small amounts of certain additional additives further enhance coal solubility remains largely unknown. We recently examined interactions in the NMP/CS₂

mixed solvent system (paper 9, listed below). We demonstrated that this solvent system is capable of forming specific complexes with alkaline earth cations and this leads to color changes and absorptions in the UV/visible spectrum as a result of perturbations to the π -bonds of these molecules. Furthermore, solid complexes that precipitate out of solution are formed at certain solvent/cation molar ratios. We also demonstrated in a separate study that the (1:1) NMP/CS₂ mixed solvent system extracts cations from clays, again forming complexes that turn the supernatant solvent in contact with the clays black (paper 10, listed below). The individual solvents show no color change. It seems likely that the ability of this mixed solvent system to mobilize and complex with cations plays a crucial role in its ability to solubilize certain coals to a greater extent than other solvents.

Finally, it has been claimed that a transition observed near 110°C in Differential Scanning Calorimetric studies of certain coals is a glass transition temperature. This is significant, because many properties and processes (e.g., diffusion) change dramatically if a material is in the rubbery as opposed to the glassy state. However, we are suspicious of any thermal event observed near this temperature in materials that have adsorbed water and therefore decided to use a different technique to study this reported transition. Thermo-mechanical measurements are particularly sensitive to the T_g, as the modulus of a material will change by several orders of magnitude as a material is heated through this transition. The results we obtained by applying this technique demonstrated that there is no T_g near 110°C, but there is a presently undefined small structural rearrangement at 180°C (paper 4, listed below). Coal extraction yields in solvents at temperatures near 200°C (or more) are often enhanced and this transition may be important in these processes.

DOE Interest

A fundamental knowledge of the nature of the interactions in coal and coal/solvent systems is central to an understanding of physical structure, properties and the extent to which soluble material can be obtained from coal by the action of simple solvents.

Future Plans

We believe that our experiments demonstrating that the 1:1 NMP/CS₂ mixed solvent system is capable of forming complexes with certain cations is important and holds the key to not only understanding how the solubility of certain coals is enhanced in this mixture relative to other solvents, but also the nature of strong interactions in coal itself. The nature of the cations present in Upper Freeport (and presumably other coals), which could be organic, inorganic, or perhaps both, remains unknown and needs further investigation.

The nature of certain thermal transitions in coal will also be studied. In recent work a presently undefined transition or structural rearrangement near 180°C has been observed. Solvent extraction yields are considerably enhanced if performed just above this temperature and establishing the nature and significance of this transition is important.

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2. *Ionomer-like Structures and their role in the pyridine-extractability of Argonne Premium Coals*. Opaprakasit, P.; Painter, P. C.; Coleman, M. M.; Scaroni, A.; Div. Of Fuel Chem. Preprints, American Chemical Society, 46(1), 331 – 333 (2001).
3. *Ionomer-Like Structures and π -Cation Interactions in Argonne Premium Coals*. Opaprakasit, P., Painter, P.C. and Scaroni, A. *Energy and Fuels*, 16, 543 – 551 (2002).
4. *Concerning the Glass Transition Temperature of Coal*. P. Opaprakasit, P. C. Painter, *Energy and Fuels*, 17, 354 – 358, (2003).
5. *Intramolecular Screening Effects in Non-dilute Polymer Solutions – an Equation of State Approach*. Berg, L.; Painter, P. C. *J. Polymer Science, Polymer Phys Ed.*, 41, 2911-2922 (2003)
6. *Concerning the Composition Dependence of the SANS χ Parameter in Isotope Blends*. Berg, L.; Painter, P. C. *J. Polymer Science, Polymer Phys.*, 41, 2923-2927 (2003).
7. *The Application of Generalized Two-Dimensional Infrared Correlation Spectroscopy to the Study of Hydrogen Bonded PVPh/PMMA Blends*. Huang, H.; Malkov, H.; Coleman, M. M.; Painter, P. C.; *Applied Spectroscopy* (submitted for publication).
8. *Concerning the Nature of Coal Solutions and Suspensions*. Painter, P.C.; Sobkowiak, M; Mathews, J.; Scaroni, M. *Energy and Fuels* (submitted for publication).
9. *Complex Formation in NMP/CS₂ Mixed Solvents*. Opaprakasit, P.; Painter, P.C. *Energy and Fuels* (submitted for publication).
10. *The Swelling of Clays in NMP/CS₂ Mixed Solvents*. Opaprakasit, P.; Painter, P.C. *Energy and Fuels* (submitted for publication).

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Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

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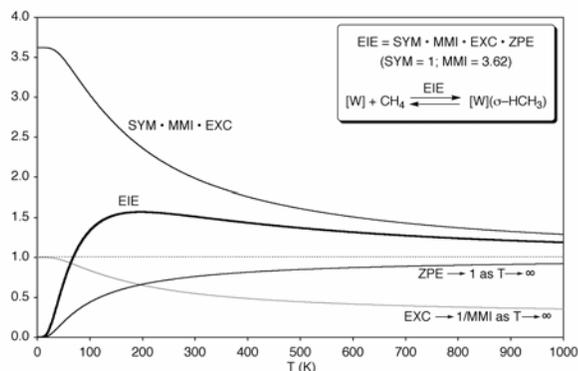
Goals

The specific objectives and research goals of the research performed during the previous grant period have been to obtain information that is relevant to transition metal mediated transformations of organic substrates. Such studies are of importance due to the fact that vast quantities of organic materials are available from natural resources but their full potential is yet to be realized because of synthetic difficulties. Specific issues that were addressed during the course of this research included studies designed to understand (i) the role of molybdenum in hydrodesulfurization and hydrodenitrogenation chemistry, (ii) the factors that influence the kinetics and thermodynamics of the diastereoselective oxidative addition of H₂ to a metal center, (iii) the details of the mechanism of C–H bond activation by molybdenocene and tungstenocene complexes, and (iv) equilibrium isotope effects pertaining to the interaction of H–H and C–H bonds with transition metal centers.

Recent Progress

(1) Transformations of Molybdenum Compounds Relevant to Hydrodesulfurization and Hydrodenitrogenation. With the advent of increasingly stringent regulations pertaining to acceptable levels for the sulfur-containing impurities in gasoline, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) continue to be the largest volume and most important industrial catalytic application of transition metals. Molybdenum is the most essential transition metal component of a typical HDS/HDN catalyst and for this reason we have started to investigate the reactivity of various molybdenum complexes towards heterocyclic sulfur and nitrogen compounds. Hydrodenitrogenation of polycyclic organonitrogen compounds, such as quinoline, may involve hydrogenation of both the heterocyclic and carbocyclic rings. It has, however, been noted that a considerable saving of hydrogen and a more useful ultimate product (namely propylbenzene) would be obtained if the heterocyclic ring of quinoline were to be selectively hydrogenated. Therefore, it is of relevance that $[\eta^6-(C_5N)\text{-quinoline}]\text{Mo}(\text{PMe}_3)_3$ reacts with H₂ to give Mo(PMe₃)₄H₄ and release 1,2,3,4-tetrahydroquinoline, the product of selectively hydrogenating the heterocyclic ring. In contrast, the isomer with quinoline coordinated by the carbocyclic ring, *i.e.* $[\eta^6-(C_6)\text{-quinoline}]\text{Mo}(\text{PMe}_3)_3$, is stable to H₂ under comparable conditions, thereby demonstrating that coordination by the heterocyclic ring facilitates reduction of quinoline.

(2) Equilibrium Isotope Effects (EIEs) Pertaining to the Coordination and Oxidative Addition of C–H and H–H Bonds. We have used a combination of experimental and computational methods to evaluate the isotope effects pertaining to the coordination and oxidative addition of C–H and H–H



bonds. An interesting aspect of these studies is the demonstration that the EIEs do not necessarily exhibit simple van't Hoff behavior by varying in a simple monotonic manner. Rather, the temperature dependence of the EIE may exhibit a maximum as illustrated for coordination of methane. Thus, depending upon the temperature, both normal and inverse EIEs may be obtained for coordination of a C–H bond in the same system.

Potential Impact of Research in Science and Technologies of Relevance to DOE

Our research focuses on several issues pertaining to catalysis that belong to the mission of the DOE. For example, fundamental studies on the reactions of sulfur and nitrogen heterocyclic with molybdenum complexes are directly relevant to HDS and HDN, the catalytic processes that are indispensable for processing and manufacturing fuels.

Future Plans

Future research will be concerned with: (i) The synthesis and structural characterization of well-defined mononuclear molybdenum and polynuclear molybdenum/cobalt compounds which feature the metals in sulfur-rich coordination environments that emulate the catalytic sites of HDS and HDN catalysts, and an investigation of their reactivity towards aromatic heterocyclic sulfur and nitrogen compounds such as thiophene, pyrrole, and pyridine derivatives, and (ii) the application of metallation-resistant *ansa* ligands to an investigation of investigation of intermolecular C–H bond activation reactions.

Publications Citing DOE Support

1. “Carbonyl Abstraction Reactions of Cp*Mo(PMe₃)₃H with CO₂, (CH₂O)_n, HCO₂H, and MeOH: The Synthesis of Cp*Mo(PMe₃)₂(CO)H and the Catalytic Decarboxylation of Formic Acid” by Jun Ho Shin and Gerard Parkin, *J. Organomet. Chem.* **2002**, 642, 9-15.
2. “Synthesis and Structures of Zirconium–Pyrrolyl Complexes: A Computational Analysis of the Factors that Influence the Coordination Modes of Pyrrolyl Ligands” by Joseph M. Tanski and Gerard Parkin, *Organometallics* **2002**, 21, 587-589.
3. “Thiophene and Butadiene-Thiolate Complexes of Molybdenum: Observations Relevant to the Mechanism of Hydrodesulfurization” by Kevin E. Janak, Joseph M. Tanski, David G. Churchill, and Gerard Parkin, *J. Am. Chem. Soc.* **2002**, 124, 4182-4183.
4. “Kinetic and Thermodynamic Preferences For the Diastereoselective Oxidative Addition of H₂ to *trans*-Ir(P*R₃)₂(CO)Cl: Monodentate Chiral Phosphines may Impart Exceptional Degrees of Diastereoselectivity” by Jun Ho Shin and Gerard Parkin, *J. Am. Chem. Soc.* **2002**, 124, 7652-7653.
5. “The Electronic Influence of Ring Substituents and *Ansa* Bridges in Zirconocene Complexes as Probed by Infrared Spectroscopic, Electrochemical, and Computational Studies” by Cary E. Zachmanoglou, Arefa Docrat, Brian M. Bridgewater, Gerard Parkin, Christopher G. Brandow,

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 8. “A Non–Classical Hydrogen Bond in the Molybdenum Arene Complex [η⁶-C₆H₅C₆H₃(Ph)OH]Mo(PMe₃)₃: Evidence that Hydrogen Bonding Facilitates Oxidative Addition of the O–H Bond by Tony Hascall, Mu-Hyun Baik, Brian M. Bridgewater, Jun Ho Shin, David G. Churchill, Richard A. Friesner and Gerard Parkin, *J. Chem. Soc., Chem. Commun.* **2002**, 2644-2645.
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Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials

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Goal

We are employing an integrated experimental/theoretical approach to advance our current ability to understand, design, and control the catalytic and surface chemistry of transition metal oxides, specifically for redox and acid-base chemistries. The approach combines novel solid-state inorganic synthesis, surface science, experimental and theoretical/computational chemical physics, and mechanistic organic chemistry to address this complex and important challenge.

Recent Progress

Materials synthesis and characterization

Ordered mesoporous silica, initially developed in 1992,ⁱ can be synthesized by using a self-assembly approach: surfactant molecules co-assemble with the inorganic materials into sophisticated nanoscale structures through favorable molecular interactions. The resultant nanoscale materials have extremely high surface area (>1000 m²/g), and highly uniform ordered nanoporosity with tightly controlled pore size and shape. These unique characteristics make the self-assembled nanoporous material an attractive candidate for catalytic applications. Previous work at UC-Berkeley (Iglesia and coworkers) and elsewhere demonstrated that WO_x exhibits unique chemical properties for acid-catalyzed reactions. Such catalytic properties are strongly affected by domain size, reducibility, and accessibility of the WO_x clusters when supported on conventional refractory metal oxide supports. However, a systematic investigation between the structural and functional relationship in this catalytic system has not been conducted, primarily due to the difficulties in material synthesis with atomic level control, advanced characterization to understand detailed physical and chemical properties, and interpretation and suggestion of mechanisms guided by advanced theory. Mesoporous silica, particularly SBA-15 type silica, provides a chemically inert and thermally stable scaffold for designing WO_x type model catalysts with controlled cluster size and spatial dispersion.

Our initial work in FY2004 has successfully demonstrated a solution based synthesis approach to highly disperse WO_x on SBA-15 mesoporous silica with excellent thermal stability (Figure 1a). High resolution magic angle spinning ¹H NMR methods are being developed to probe the surface structure and domain size of WO_x clusters supported on SBA-15. With ¹H NMR we have identified the chemical shift which is likely related to the hydroxyl groups associated with the WO_x clusters (Figure 1b), and have also initiated experiments that will potentially provide insight on proton mobility and Brønsted acid strength of WO_x.

We have also been preparing non-silica based mesoporous materials as catalyst supports for WO_x and other acid catalysts, in particular ZrO₂ based mesoporous materials. We are employing two approaches to synthesize ZrO₂-based mesoporous materials. The first approach involves direct synthesis of mesoporous ZrO₂. We are using high molecular weight block copolymer surfactants as the templates following the procedures initially developed by Stucky and coworkers.ⁱⁱ The high molecular weight of block copolymers makes their liquid crystalline structures more stable in the presence of ceramic precursors, so structural control is easier for complex compositions. The large molecules also expand the pore dimensions beyond 10 nanometers. The second approach involves coating mesoporous silica with ZrO₂. This approach may be more flexible because mesoporous silica is easy to make, and the coating can be tightly controlled. Thus, we are developing inorganically functionalized mesoporous structures using both solution based and gas phase based reactions. Once developed, this method can be used to deposit complex active catalytic groups on the pore surfaces as well.

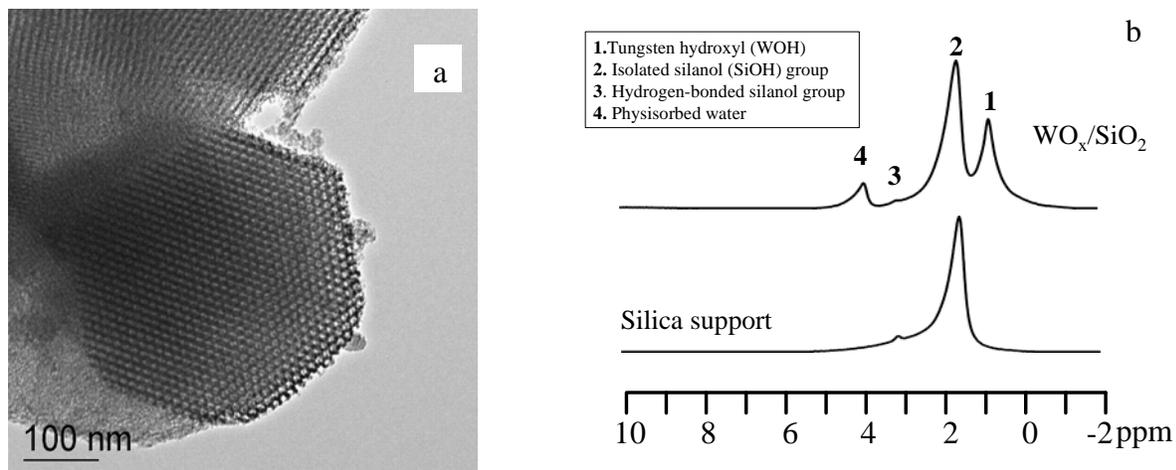


Figure 1: a) High resolution TEM image of 30wt% WO_x/SBA-15 SiO₂ after calcination at 500°C. b) High resolution ¹H MAS spectra obtained at a sample spinning rate of 5kHz.

UHV studies of model TMO catalysts

The initial focus of our UHV studies of model TMO catalysts is aimed at determining the optimum source for the deposition of tungsten oxides films and clusters. Direct evaporation of WO₃ in a molecular beam was found to provide a reliable, carbon-free source, of oxidized tungsten. To test the efficacy of this deposition method, a number of tungsten oxide films (thickness ~1μm) were deposited at various substrate temperatures and deposition angles on optically polished polycrystalline Ta substrates. The oxidation state of tungsten in the films was determined using XPS and was shown to be predominantly the (6+) oxidation state. At high substrate temperatures (> 600K), the films are crystalline and exhibit a cubic crystallographic structure as show by X-Ray Diffraction (XRD). At low substrate temperatures (< 300K) the WO₃ films are amorphous. Films deposited at low temperatures (20 – 300 K) and high deposition angles (> 70°) grow via diffusion limited ballistic deposition and exhibit a filamentous-like structure as shown in Figure 2. The surface area of such films is extremely high, approaching 1000m²/g. Current studies focus on detailed surface area, and binding site distribution measurements of the nanoporous WO₃ films as a function of synthesis and post-growth processing conditions. Parallel studies of WO₃ cluster formation on a TiO₂(110) substrate have just been initiated. These substrates will be used in the molecular beam scattering studies of the proposed research.

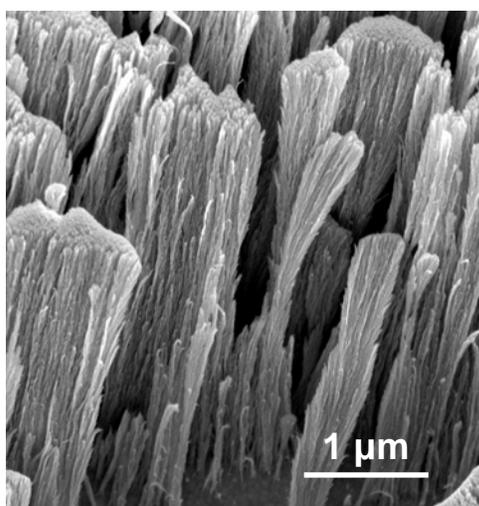


Figure 2: SEM micrograph of amorphous nanoporous WO₃ film deposited at glancing deposition angle of 85° on a Ta substrate at 20K.

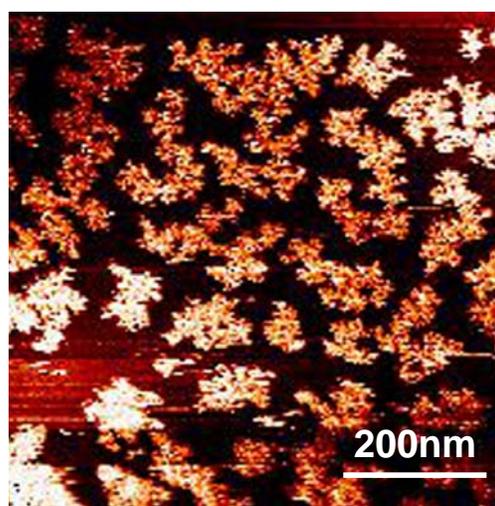


Figure 3: STM image of WO₃ clusters deposited on HOPG at room temperature.

Our initial scanning tunneling microscopy (STM) studies examined the deposition of sub-monolayer quantities of WO_3 on highly-oriented pyrolytic graphite (HOPG). The HOPG substrate provides large terraces with low defect densities and can be imaged relatively easily with atomic resolution. A STM image of WO_3 clusters formed from submonolayer WO_3 deposition at room temperature is shown in Figure 3. The fractal like shape of the clusters suggests that a diffusion-limited aggregation mechanism governs cluster growth. Scanning tunneling spectroscopy indicates that the WO_3 clusters are semiconducting in nature. Current efforts are aimed at understanding how the WO_3 cluster size and morphology depend on initial coverage and substrate temperature. STM studies of WO_3 cluster formation on $\text{TiO}_2(110)$ will begin in May 2004.

Photoelectron spectroscopy of W_xO_y^- clusters

We have been using photoelectron spectroscopy to study small tungsten oxide clusters of the form W_xO_y^- , with $x = 1-4$ and $y = 1-12$. Data have been obtained for WO_y^- ($y = 1-5$) and W_2O_y^- ($y = 1-6$). Theoretical calculations at the density functional theory (B3LYP) and molecular orbital theory (CCSD(T) with large basis sets of aug-cc-pVTZ quality have also been initiated for the WO_y^- series of clusters. Experimental data for the WO_y^- series of clusters showed that the electron binding energies increase with the oxygen content up to WO_4^- and level off beyond that, suggesting a behavior of sequential oxidation, i.e. electron transfer from W to O upon sequential addition of oxygen (see Figure 4: $d - \text{W } 5d$ features; $p - \text{O } 2p$ features). This observation is consistent with the theoretical calculations, which also revealed that WO_4 has a triplet ground state, i.e., a di-radical structure, whereas WO_5 contains a superoxide unit. These results are being prepared for publication.

Computational studies of catalyst systems

We have been using density functional theory to calculate the Brønsted basicities and acidities and Lewis acidities of model V_xO_y , Cr_xO_y , Mo_xO_y , and W_xO_y clusters and bonded to each other and to Si_xO_y or Zr_xO_y clusters. The oxygens are terminated with hydrogen atoms as appropriate to complete the valency. For the Group VIB oxides, we have studied the “+6” state of the metal atom with tetra-coordination (e.g., $(-\text{O})_2\text{W}(=\text{O})_2$), penta-coordination, (e.g., $(-\text{O})_4\text{W}(=\text{O})$), and hexa-coordination (e.g., $(-\text{O})_6\text{W}$). This allows us to explore the role of various surface defect sites. The addition of CH_3OH to the clusters leading to the formation of $\text{CH}_3\text{O}-$ and $\text{H}-$ and then to $\text{CH}_2\text{O}-$ and additional $\text{H}-$ has been studied to determine potential intermediates. In some cases, we find that transfer of the various groups can lead to cleavage of a metal-oxygen bridge bond. Calculations of nmr chemical shifts and of uv-vis absorption spectra at the DFT level for direct comparison to experiment have been initiated. The overall DOE effort in computational catalyst has received a large allocation (1 million node hours) on the new HP Linux cluster with 1980 nodes and 11.7+ peak Tflops in the MSCF in the EMSL at PNNL with M. Gutowski as PI.

DFT calculations with ultrasoft and projector augmented-wave pseudopotentials and gradient-corrected exchange-correlation functionals were done for various oxides, including the catalytic systems WO_3 , MoO_3 , and V_2O_5 , and the supports, TiO_2 , SiO_2 , Al_2O_3 , and MgO . The lattice constants, bulk modulus, and structure of the valence band and semi-core levels for these oxides were calculated in good agreement with experiment but the band gaps are systematically underestimated. The relaxation and corrugation of the (100) surface of WO_3 has been characterized.

NMR

We have measured the solid state ^{183}W magic angle spinning (MAS) NMR Spectra of phosphotungstic acid hydrate $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$. Although this technique is a sensitive probe of structure, it has two shortcomings: (1) Inherent low NMR sensitivity (S/N) combined with long relaxation time \Rightarrow long measuring time and (2) Low $\gamma \Rightarrow$ meaning low resonant frequency. The dead time associated with probe ring down is a big problem. We are developing techniques to improve the signal to noise and to reduce the probe ring down by separating the chip capacitors from the receiver coil.

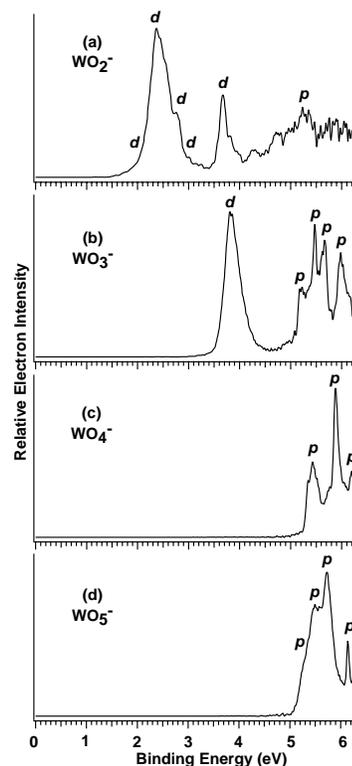


Figure 4:

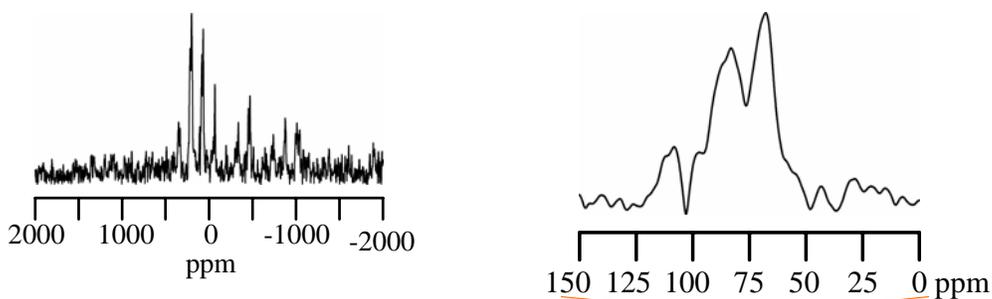


Figure 5: Preliminary Solid State ^{183}W (MAS) NMR Spectra of $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$.

We have demonstrated that we can measure ^{51}V and ^{95}Mo solid state NMR at an 11.7T field strength to probe mixed vanadyl/molybdenyl catalysts. We are in the process of setting-up the ^{51}V - ^{95}Mo MAS distance measurement experiment after demonstrating that we can make good solid state measurements without spinning in the solid state.

DOE Interest

The proportion of chemical industry processes using catalysts exceeds 80%. Current commercial heterogeneous catalysts are structurally and chemically complex and data gathered from them can seldom be interpreted with atomic-level precision. We seek to reduce the complexity of TMO catalysts to levels addressable and controllable at the atomic level, while maintaining intimate linkages with practical catalysis and catalytic materials. The focus of the proposed work is to gain a fundamental understanding of chemical transformations in order to design and construct new catalysts with more precise control of specific chemical reactions. This will enable us to help DOE reach its goals of doing fundamental science to address the energy needs of the country by (1) improving energy conservation by new means of energy conversion and storage; (2) enable direct chemical conversions previously economically unfeasible and produce new routes to novel materials while at the same time minimizing by-products and environmental impact; and (3) protecting the environment

Future Plans

A number of tasks are being planned for the next year. 1) We will continue the PES studies of metal oxide clusters, extending to W_2O_y^- and W_3O_y^- series and substituting Mo and Cr for W and working on the $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{PMo}_{12}\text{O}_{40}^{3-}$, and $\text{SMo}_{12}\text{O}_{40}^{2-}$ Keggin anions. We will perform high level calculations on these ions and neutrals for method benchmark purposes. We will continue to study larger clusters of the metal oxides interacting with CH_3OH and the oxidative dehydrogenation reaction as well as the reductive dehydrogenation of 2-butanol to form butanes and H_2O . We will identify the thermodynamics of the pathways and find transition states to correlate with experimental measurements.

We will link theory, spectroscopic characterizations, and activity studies to calibrate the acid/base chemistry on WO_x catalysts. The methodology established on WO_x will be extended to VO_x and MoO_x catalytic systems for redox induced chemistries. We will also develop synthesis protocols to disperse metal oxides with controlled atomic connectivity and spatial dispersions such as Keggin structured anions on mesoporous silica, and to elucidate their structural and functional relationships for acid/base and redox chemistries. We will use solid state ^{51}V and ^{95}Mo NMR to investigate VO_x and MoO_x catalytic systems. We will continue the development of in-situ NMR capabilities and evaluate the feasibilities of solid state ^{183}W NMR at high and ultra-high magnetic fields available at PNNL.

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Fundamental Studies of Selectivity and Mechanisms of Oxide-Catalyzed Nitrogen Oxide Chemistry

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Goal

Develop a fundamental understanding of catalytic nitrogen oxide (NO_x) reactions on oxide surfaces, with special emphasis on identifying new and unique chemistry associated with molecules containing unpaired electrons in their ground state.

Recent Progress

We completed studies aimed at the identification of optimum parameters for the epitaxial growth of the mixed-oxides films, Ce_{1-x}Zr_xO₂ with x = 0.1, 0.2 and 0.3, by oxygen-plasma-assisted MBE on single crystal Y-stabilized ZrO₂ (YSZ) substrates. The resulting films were characterized by RHEED, LEED, XPS/XPD, XRD, and RBS/C in order to determine their bulk and surface structures and compositions. Pure-phase, epitaxial Ce_{1-x}Zr_xO₂ films readily grew on YSZ(111) without showing any contamination of yttria from the substrate. The resulting epitaxial film surfaces are unreconstructed and exhibit the structure of bulk CeO₂(111). XPS data indicate that both Ce and Zr cations are formally in the +4 oxidation state for all films prepared here. Small differences in the photoemission results for Zr-doped ceria films as compared to those obtained for pure ZrO₂ may be explained by changes in electronic structure when Zr is added to ceria that, in turn, results from longer Zr-O bond distances in the mixed oxides. The minimum yields obtained from the random and channeling spectra of these films also provide evidence that high quality single crystal CeO₂ and Ce_{0.7}Zr_{0.3}O₂ materials were grown. For the Zr-doped films, Zr atoms are shown to occupy the lattice sites of Ce in the bulk structure of CeO₂(111). Indeed, based on minimum yield values, the fraction of Zr substitution for Ce cations in the film was estimated to be 88%.

The interaction of N₂O with TiO₂(110) was studied in an effort to better understand the conversion of NO_x species to N₂ over TiO₂-based catalysts. The TiO₂(110) surface was used as a model system because this material is commonly used as a support and because oxygen vacancies on this surface are perhaps the best available models for the role of electronic defects in catalysis. Annealing TiO₂(110) in vacuum at high temperature (above about 800 K) generates oxygen vacancy sites that are associated with reduced surface cations (Ti³⁺ sites) and that are easily quantified using temperature programmed desorption (TPD) of water. Using TPD, x-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS), we found that the majority of N₂O molecules adsorbed at 90 K on TiO₂(110) are weakly held, and desorb from the surface at 130 K. However, a small fraction of the N₂O molecules exposed to TiO₂(110) at 90 K decompose to N₂ via one of two channels, both of which are vacancy-mediated. One channel occurs at 90 K, and results in N₂ ejection from the surface and vacancy oxidation. We propose that this channel involves N₂O molecules bound at vacancies with the O-end of the molecule. The second channel results from an adsorbed state of N₂O that decomposes at 170 K to liberate N₂ in the gas phase and deposit oxygen adatoms at non-defect Ti⁴⁺ sites. The presence of these O adatoms is clearly evident in subsequent water TPD measurements. We propose that this channel involves N₂O molecules that are bound at vacancies with the N-end of the molecule, which permits the O-end of the molecule to interact with an adjacent Ti⁴⁺ site. The partitioning between these two channels is roughly 1:1 for adsorption at 90 K, but neither is observed to occur for moderate N₂O exposures at temperatures above 200 K. EELS data indicate that vacancies readily transfer charge to N₂O at 90 K, and this charge transfer facilitates N₂O decomposition. Based on this result, it appears that the decomposition of N₂O to N₂ requires trapping of the molecule at vacancies and that the lifetime of the N₂O-vacancy interaction may be key to the conversion of N₂O to N₂.

We performed x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) studies probing the surface chemistry of water on the oxidized and reduced surfaces of a 500 Å epitaxial CeO₂(111) film grown on yttria-stabilized ZrO₂(111). Oxidation with O₂ at 773 K under UHV conditions was sufficient to generate XPS spectra reflective of fully oxidized CeO₂(111). Surface reduction was carried out by annealing in UHV between 773 and 973 K, and the level of reduction was quantified using changes in the Ce3d_{3/2} 4f⁰ photoemission peak at 917 eV. As expected, the level of surface reduction increased with increasing temperature. Annealing at 773 K led to a surface with approximately 1/3rd of its surface Ce⁴⁺ sites reduced to Ce³⁺. The resulting Ce³⁺ sites were primarily in the first layer based on the fact that RT exposure of the film to O₂ resulted in nearly complete conversion of Ce³⁺ to Ce⁴⁺. Annealing at higher temperatures led to complete or nearly complete reduction of the first layer along with substantial levels of subsurface reduction that was not reoxidized by RT exposure to O₂. Comparisons with results in the literature for surface reduction of single crystal CeO₂(111) suggest that the volume of thick (~ mm) ceria crystals, which acts as a reservoir for oxygen vacancies, dictates the severity of reductive conditions required in order to observe significant levels of surface Ce³⁺ sites. In other words, the particular annealing temperatures and times required for a specific extent of surface reduction scales with the thickness of the crystal. Water TPD results indicate strong coverage dependence on the oxidized CeO₂(111) that destabilizes high coverages of water relative to low coverages. The presence of surface reduction (near a full ML of Ce³⁺ based on XPS data) removes much of the coverage dependent behavior. TPD uptake measurements, H₂ TPD spectra and XPS spectra in the Ce3d core level and Ce4f valence band (VB) regions all indicate that little or no irreversible water adsorption or Ce³⁺ oxidation was observed for this reduced surface. In contrast, exposure of water at 650 K promoted reduction of the surface above the level observed from annealing at 650 K in the absence of water, suggesting that water/OH groups may promote removal of lattice oxygen under certain conditions. Because water oxidation of Ce³⁺ surface sites has been observed for reduced ceria powders, but was not observed on the reduced CeO₂(111) surfaces studied here, we propose that the reduced (111) surface is more resistant than non-(111) terminations to being oxidized by water. An explanation based on theoretical arguments in the literature is offered for the resistance of Ce³⁺ sites to being oxidized by water.

We prepared a cubic CeO₂(001) film of thickness equal to ~58 nm was epitaxially grown on Y₂O₃-stabilized cubic ZrO₂ by oxygen plasma assisted molecular beam epitaxy (OPA-MBE). The interface was characterized using high resolution transmission electron microscopy (HRTEM). The interface exhibited coherent regions separated by equally-spaced misfit dislocations. When imaged from the [100] direction, the dislocation spacing is 3.3 ± 0.5 nm, which is slightly shorter than the expected value of 4.9 nm calculated from the differences in lattice constants given in the literature, but is fairly consistent with the 3.9 nm lattice mismatch measured by electron diffraction. Thus, the results indicated that the lattice mismatch between the film and the substrate is accommodated mainly by interface misfit dislocations above some critical thickness.

We have used x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) to probe the surface chemistry of water on the oxidized and reduced surfaces of a 500 Å epitaxial CeO₂(111) film grown on yttria-stabilized ZrO₂(111). Oxidation with O₂ at 773 K under UHV conditions was sufficient to generate XPS spectra reflective of fully oxidized CeO₂(111). Surface reduction was carried out by annealing in UHV between 773 and 973 K, and the level of reduction was quantified using changes in the Ce3d_{3/2} 4f⁰ photoemission peak at 917 eV. As expected, the level of surface reduction increased with increasing temperature. Annealing at 773 K led to a surface with approximately 1/3rd of its surface Ce⁴⁺ sites reduced to Ce³⁺. The resulting Ce³⁺ sites were primarily in the first layer based on the fact that RT exposure of the film to O₂ resulted in nearly complete conversion of Ce³⁺ to Ce⁴⁺. after. Annealing at higher temperatures led to complete or nearly complete reduction of the first layer along with substantial levels of subsurface reduction that was not reoxidized by RT exposure to O₂. Comparisons with results in the literature for surface reduction of single crystal CeO₂(111) suggest that the volume of thick (~ mm) ceria crystals, which acts as a reservoir for oxygen vacancies, dictates the severity of reductive conditions required in order to observe significant levels of surface Ce³⁺ sites. In other words, the particular annealing temperatures and times required for a specific extent of surface reduction scales with the thickness of the crystal. Water TPD results indicate strong coverage dependence on the oxidized CeO₂(111) that destabilizes high coverages of water relative to low coverages. The presence of surface reduction (near a full ML of Ce³⁺ based on XPS data) removes much of the coverage dependent behavior. TPD uptake measurements, H₂ TPD spectra and XPS spectra in the Ce3d core level and Ce4f valence band (VB) regions all indicate that little or no irreversible water adsorption or Ce³⁺ oxidation was observed for this reduced surface. In contrast, exposure of water at 650 K promoted reduction of the surface above the level observed from annealing at 650 K in the absence of water, suggesting that water/OH groups may promote removal of lattice oxygen under certain conditions. Because water oxidation of Ce³⁺ surface sites has been observed for reduced ceria powders, but was not observed on the reduced CeO₂(111) surfaces studied here, we propose that the reduced (111) surface is more resistant than non-(111)

terminations to being oxidized by water. An explanation based on theoretical arguments in the literature is offered for the resistance of Ce^{3+} sites to being oxidized by water.

Multi-layer hetero-structured thin films have been found to possess superior structural and functional properties, especially with respect to ion conductivities. One of the best examples is the dramatically enhanced ionic conductivity in the system of CaF_2 and BaF_2 when they are deposited alternating in thin layers. It is believed that the enhanced ionic conductivity in this type of structure is attributed to the interface defect structures. More recently, researchers have also observed that the ionic conductivity of yttria stabilized zirconia (YSZ) can be enhanced by increased dislocation density. This prompted us to develop pure and doped ZrO_2 and CeO_2 hetero-junction multi-layer thin films for enhanced ionic conductivity. Microstructural features of hetero-multi-layer $\text{ZrO}_2/\text{CeO}_2$ films, with thicknesses of several nanometer for each layer and grown on YSZ substrates, have been studied using TEM, HRTEM, EELS, EDX, and XRD in order to characterize phase, Ce valence state, interface structure, and the nature and number of internal defects. Our results demonstrate that the pure ZrO_2 layers are stabilized as a cubic phase when they are deposited alternating with thin layers of CeO_2 . Electron diffraction combined with dynamical electron diffraction calculations indicates that the oxygens in the pure cubic- ZrO_2 layer of several nanometers in thickness are displaced along the $\langle 111 \rangle$ directions.

Adsorption and reaction of NO on oxidized and reduced $\text{SrTiO}_3(100)$ surfaces have been studied using temperature programmed desorption (TPD). Major desorption peaks for NO from the fully oxidized surface are found at 140 and 260 K, along with a long tail that continues up to 500 K. The desorption features at 140 and 260 K correspond to activation energies of 36 and 66 kJ/mol, respectively, using a simple Redhead analysis. NO reacts non-dissociatively on the fully oxidized surface. Reactivity of reduced $\text{SrTiO}_3(100)$ is relatively higher than that of the fully oxidized surface and is influenced by the adsorption temperature of the NO molecules on the surface. NO and N_2O are the major desorption products following adsorption of NO on the reduced surface at 110 K. Desorption of N_2O from significantly reduced $\text{SrTiO}_3(100)$ indicates that the oxygen atoms of the adsorbed NO molecules are preferentially extracted by the surface oxygen vacancy sites whereas the surface gets oxidized as a result of the de-oxygenation of the adsorbates. Adsorption of NO on the reduced surface at 297 K is followed by breakage of the N-O bond producing adsorbed N and O atoms and recombination of these ad-species results in desorption of NO and N_2 from this surface. Adsorption of NO on the significantly reduced surface at 200 K is followed by desorption of NO, N_2 and N_2O as TPD products and the reactivity of this surface at 200 K presumably is a composite of the behavior observed for NO adsorption at 110 and 297 K.

DOE Interest

Catalysis continues to be vital to the chemical and petroleum industries, and to the development of pollution abatement technologies. The economic impact of catalysis has been estimated to be over 10 trillion dollars per year worldwide. Besides these practical reasons, the U.S. Department of Energy (DOE) has had a longstanding interest in catalysis also for advancing the fundamental understanding for the control of chemical transformations. In all catalyst research, a fundamental understanding of the chemical reaction mechanism(s) that occur on the catalyst surface, including an identification of the catalytic site(s) directly involved in the rate-limiting elementary process(es), is critically important to an effort to rationally develop improved catalysts and catalytic processes.

Future Plans

We will be completing studies of NOx adsorption and reaction on well-characterized $\text{TiO}_2(110)$ and $\text{CeO}_2(111)$ surfaces. These studies will include low-temperature STM measurements that provide a real space view of this chemistry as it occurs. The STM and surface reaction studies on TiO_2 will also focus on the effects of specific oxygen vacancy defects as well as the modification of this chemistry by co-adsorbed atomic and molecular oxygen, water, and hydroxyl groups. We will be initiating experiments that probe the adsorption and reaction of NOx on other important oxide surfaces and will begin to address the effects of support oxides on the observed chemistry of a catalytically active oxide material.

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Microscopy with Single Atom Sensitivity for Solving Catalysis Problems

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Goal

Address fundamental problems in catalytic systems using a combination of Z-contrast STEM with single-atom sensitivity and density functional theory calculations.

Recent Progress

High Catalytic Activity from 1 nm Au clusters on TiO₂: The 0.7 Å diameter beam of the aberration-corrected, 300 kV scanning transmission electron microscope (STEM) at ORNL provides the highest sensitivity for imaging individual atoms. Nanometer-sized gold particles were deposited on a variety of supports (mesoporous titania, anatase, brookite, rutile) in order to investigate the activity for the oxidation of CO. Previous work had associated the activity with ~3 nm sized Au particles and the presence of oxidized Au. However, we found that high activity at low temperatures corresponds to the presence of smaller, ~1 nm, Au particles that are only one or two monolayers thick and fully reduced. Larger (>5 nm) gold particles were far less active. Also, mono-dispersed, single Au atoms were not associated with high activity. First-principles density-functional calculations showed that Au nanoparticles bond only weakly to the stoichiometric anatase (001) surface. Oxygen vacancies in the substrate act as anchors to bond the nanoparticles in place, although at sufficiently high temperatures, the particles can diffuse and coalesce. Using the Au nanoparticle structures seen in the Z-contrast STEM as a starting point, we were able to investigate the catalytic properties. Unlike bulk gold, these nanometer-sized particles are able to adsorb both CO and O₂ molecules. The CO

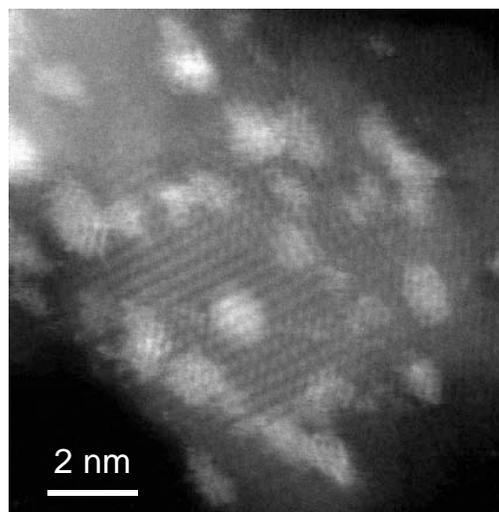


Fig. 3 STEM micrographs of highly active Au / TiO₂ (anatase). Bright patches are Au particles ~ 1nm diameter and mostly one monolayer thick.

adsorbs in an end-on configuration, while the O_2 adsorbs preferentially at the perimeters of the nanoparticles, bonding to both the nanoparticle and the substrate. This suggests that the active sites for O_2 absorption may be at the perimeter of the nanoparticles, explaining the decrease in activity with increasing particle size. In agreement with experiment, single Au atoms adsorbed at vacancies do not bond CO or O_2 . (Submitted to Science)

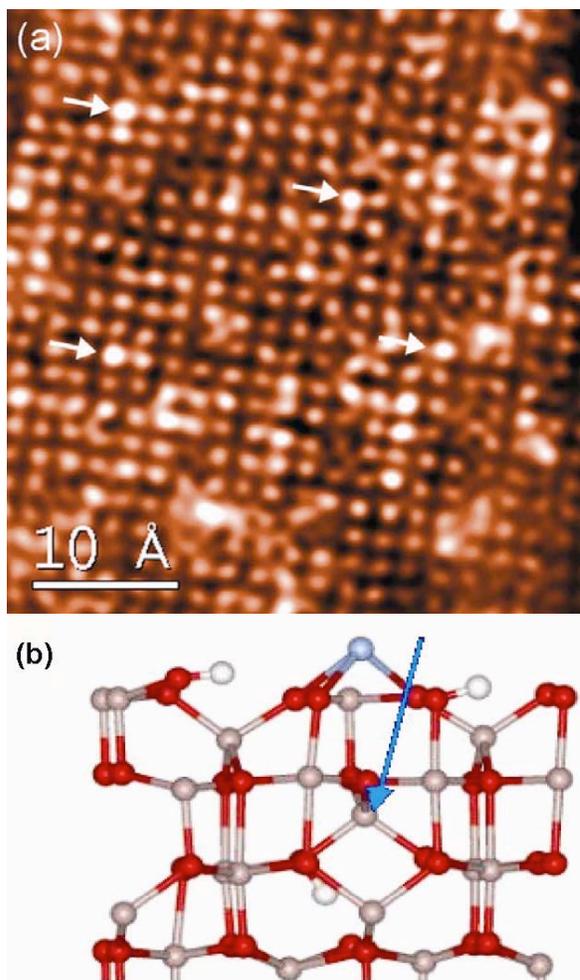


Fig. 2. (a) Z-contrast STEM image of the $\langle 100 \rangle$ surface of $g\text{-Al}_2\text{O}_3$; bright spots correspond to La atoms on the surface; several examples of preferred sites are arrowed. (b) calculated lowest-energy configuration of La atom (blue) on the $\langle 100 \rangle$ surface of $g\text{-Al}_2\text{O}_3$ above an Al-O column; the Al atom displaced by La is arrowed.

Al_2O_3 observed by STEM was shown to correspond to the lowest energy configuration (Fig. 2(b)).

The combination of sub-Ångstrom resolution imaging and theory clearly demonstrates that the stabilization is caused by isolated La atoms that bind strongly to

Mechanism of thermal stabilization of $g\text{-Al}_2\text{O}_3$ catalyst supports by La addition: $g\text{-Al}_2\text{O}_3$, a widely used catalytic support material, undergoes an undesirable phase transition to $\alpha\text{-Al}_2\text{O}_3$ at 1000°C with loss of surface area. Addition of La dopants was previously shown to extend the stability range to 1250°C , but the mechanism of the stabilization was never determined and was speculated to result from the formation of La_2O_3 or LaAlO_3 monolayers on the surface or substitution of Al by La in the bulk. To examine La distribution, samples of La-doped $g\text{-Al}_2\text{O}_3$ were investigated by Z-contrast STEM. It was found that La atoms are distributed on the surface of $g\text{-Al}_2\text{O}_3$ in an uncorrelated fashion; no clusters or ordered monolayers were observed (Fig. 2(a)). On the $\langle 100 \rangle$ surface of $g\text{-Al}_2\text{O}_3$ La atoms were found to occupy predominantly the positions directly above Al-O columns (examples arrowed).

Density functional theory calculations, conducted in parallel, have demonstrated that La atoms have overwhelming preference for the surface positions and are very strongly bound to the surface. In full agreement with the microscopic observations, no tendency towards cluster formation was found. The La site on the $\langle 100 \rangle$ surface of $g\text{-Al}_2\text{O}_3$

the surface of $g\text{-Al}_2\text{O}_3$, thus pinning it and preventing sintering and phase transformation. (Nature Materials, **3**, 143 (2004)).

DOE Interest

Catalysts are now used at some point in a vast number of modern manufacturing processes, from drug or fuel production to catalytic converters in cars, and will be of increasing importance to the worldwide economy. Understanding how and why they act is greatly assisted by the ability to determine individual cluster configurations.

Future Plans

The newly aberration-corrected STEM provides unique sensitivity for imaging the atomic configurations of supported cluster catalysts, and when combined with reaction rate measurements and density-functional calculations promises significant new insight into many previously unresolved issues, including:

The origin of the synergistic effect of bimetallic catalysts: We presently have the ability to distinguish individual second row transition metals from third row metals, eg. Pt/Ru and Au/Pd. We will investigate the preferred configurations of bimetallic clusters with measured reactivities in collaboration with Profs. M. Amiridis and R. Adams, University of S. Carolina.

Examination of different support materials: In collaboration with other groups we will investigate the role of different support materials, both experimentally, where the single atom-resolved Z-contrast microscopy provides unique insight, and theoretically using DFT calculations.

Three-dimensional imaging: We presently have about a 1 nm depth of view which allows us to image individual atoms with sub-Ångstrom lateral resolution and sub-nm depth resolution. We will investigate techniques for 3D visualization of supported catalyst clusters.

In-situ imaging with 3D atomic resolution: A next generation, aberration-corrected STEM with expected 0.4 Ångstrom lateral and 4 Ångstrom depth resolution has been approved by BES Division of Materials Sciences. This microscope will incorporate an in-situ capability for temperatures up to $\sim 800^\circ\text{C}$ under reaction conditions.

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High-resolution homo- and heteronuclear correlation NMR spectroscopy in solid state; applications to heterogeneous catalysis

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Goal

Solid state NMR is used to investigate the materials and chemical reactions involved in heterogeneous catalysis and materials science.^{1-3,9-16,18-20} Development of new NMR techniques is the second major research area.^{4-8,17,21,22} An overview of selected results involving internuclear correlation methods is given below.

Recent Progress

MQMAS-J-HETCOR NMR. We have recently demonstrated a new solid state NMR method that provides high-resolution two-dimensional (2D) heteronuclear correlation (HETCOR) spectra between quadrupolar and spins-1/2 nuclei.²¹ The technique uses multiple-quantum magic angle spinning (MQMAS) NMR to achieve high resolution and *through-bond* (*J*) coupling for polarization transfer. As shown in Figure 1, this method affords a dramatically improved resolution when compared with the standard MAS-based approach. High selectivity, lack of orientational dependence and insensitivity to molecular motion proved useful in exploiting of this method for studying the bond topology and local order in catalysts.

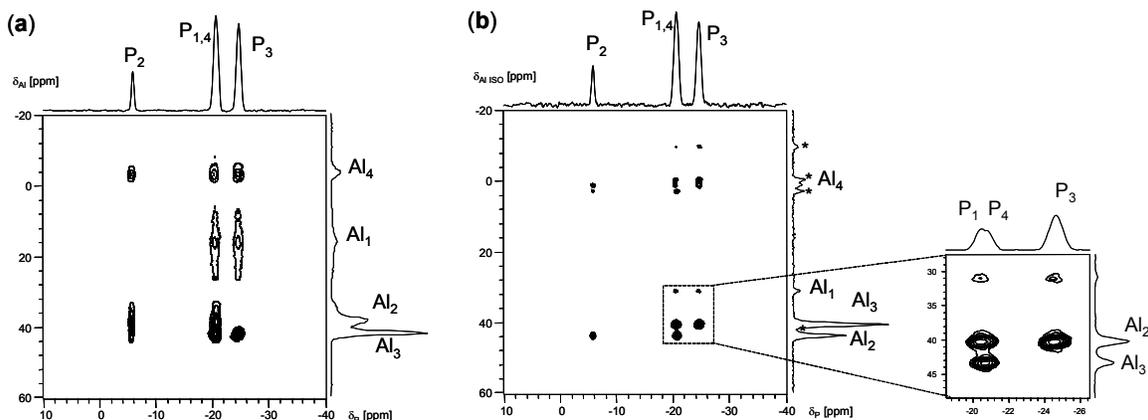


Figure 1. $^{27}\text{Al} \rightarrow ^{31}\text{P}$ spectrum of $\text{AlPO}_4\text{-14}$ catalyst obtained with MAS- (a) and MQMAS-J-HETCOR (b) methods at 14.1 T. All Al and P sites are resolved in spectrum (b), which provides isotropic resolution in both dimensions.

FS-J-RES NMR. We demonstrated the frequency-selective measurements of internuclear *distances* and *J coupling constants* in a multispin system SI_n , where S spin is a quadrupolar (observed) nucleus and I 's represent spin-1/2 nuclei.^{17,22} This method can also be used under high-resolution provided by MQMAS, which offers the possibility of measuring a *complete set of internuclear distances and J couplings in complex systems.*

Heterogeneous catalysts supported on silica materials. We demonstrated the applicability of several hetero- and homonuclear NMR methods to characterize the silica supports before and after tethering with various metal complexes and other functional groups (i.e. ‘gatekeepers’). An example of ^1H - ^{13}C HETCOR spectrum of an MCM-41 silica functionalized with allyltrimethoxysilane (ALTMS) is shown in Figure 2a. A double-quantum ^1H - ^1H correlation spectrum, which emphasizes two-spin correlations in this sample, is shown in Figure 2b.

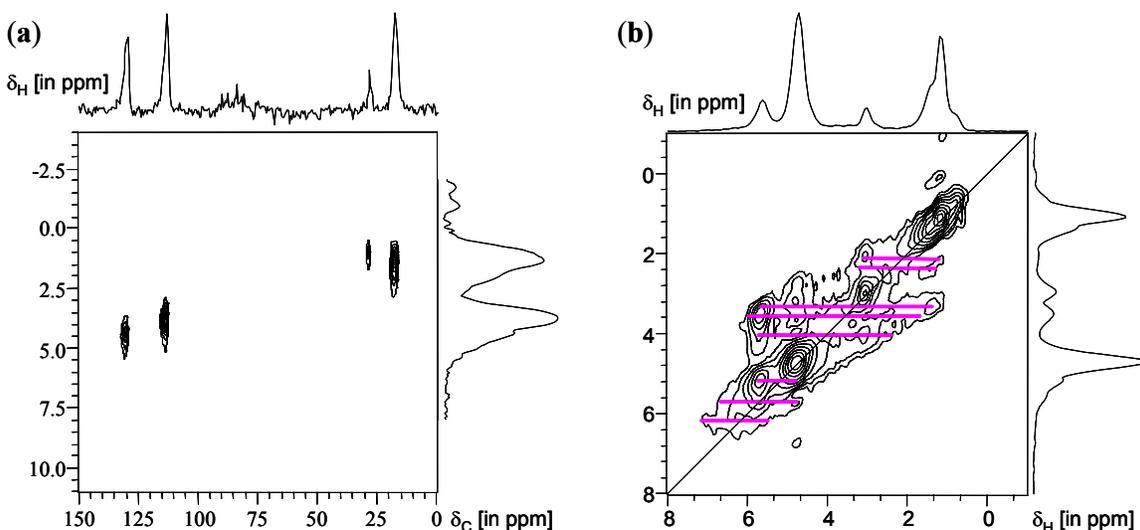


Figure 2. (a) ^1H - ^{13}C CP HETCOR spectrum of MCM-41 functionalized with ALTMS recorded at 9.4 T under 10 kHz MAS, using frequency switched Lee-Goldburg irradiation during ^1H evolution. (b) ^1H DQ MAS NMR spectrum of this sample recorded under 40 kHz MAS at 9.4 T.

DOE Interest

These fundamental studies will result in better understanding of the mechanisms of homogeneous and heterogeneous catalytic reactions, which include the removal or addition of heteroatoms (S, N, O, and Cl) by oxidation or hydrogenation, using primarily transition metal complexes and oxides as catalysts.

Of particular importance to the catalysis program will be the application of multidimensional NMR techniques to determine the structure, concentration, spatial distribution and mobility of various functional groups and reactants on the catalyst surface in 2-D and 3-D controlled environments, e.g., in multifunctional mesoporous materials. Development of state-of-the-art techniques in solid state NMR spectroscopy will provide new tools for these investigations.

Future Plans

Characterization of functionalized silica materials by solid state NMR spectroscopy. Our studies demonstrated that solid state NMR spectroscopy of mesoporous materials yields precise information about the nature of unfunctionalized silica surfaces as well as the structure and distribution of various groups that are anchored on the walls. We will use a suite of 1D and 2D NMR methods, mostly in the solid state, to (a) characterize the silica supports before and after tethering with metal complexes, (b) study the concentration, the conformational details and the mobility of adsorbed (tethered) and reacting species, and (c) monitor the catalytic reactions and the catalysts' stability under various reaction conditions. Some of the studies performed on the solid-liquid interfaces may involve liquid state NMR methodology.

Development of improved NMR methods. We plan to continue the development of improved NMR methods for studying the spin-1/2 and half-integer quadrupolar nuclei. We will explore the experimental strategies for enhancing the efficiency of homo- and heteronuclear correlation NMR spectroscopy in solids via improved methods of polarization transfer and high resolution techniques. Further increase in sensitivity will be achieved by using a higher magnetic field.

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Carbon-13 NMR of Solid State Hydrocarbons and Related Substances

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Goal

Development and exploitation of new solid state carbon-13 experimental techniques to obtain the chemical shift tensors in hydrocarbons and related substances including correlation of these data with advance theoretical constructs. These data are then employed to characterize complex structures and systems that evolve from simple hydrocarbons.

Recent Progress

Spectroscopic developments in our laboratory include a new solid-state **INADEQUATE** method and a new **FIREMAT** variant of a single crystal experiment that has high promise for smaller single crystals. We have also been pleased to note very promising synergism of x-ray powder experiments which, with **REITVELD** analysis, complements our NMR efforts. The extension of our ^{13}C NMR efforts into the ^{15}N NMR field is evolutionary in character and fits nicely into our overall strategy of characterizing molecular structures.

The importance of the chemical shift tensor in modeling molecular structure continues to enjoy success. This is made possible in part by improved theoretical methods for intermolecular lattice effects that become significant whenever the molecule exhibits high charge polarization effects. We therefore are focusing on new experimental methods that provide this information with better reliability and convenience.

Collaborations with personnel at both ANL and LANL on **REITVELD** analysis of powder x-ray data, has demonstrated the power of our **FIREMAT** experiment for estimating the initial structural features of polymorphs of solid organic materials which significantly improves the convergence of the **REITVELD** software. This approach is especially fruitful in powder samples when complete crystallographic data are not presently available from single crystals. The appearance of impurities, mixed crystals, polymorphs, and multiple

molecules per asymmetric unit are readily characterized by solid-state NMR, whereas it is difficult to determine this information directly from micro-crystalline powder diffraction data, especially on materials of unknown structure. Furthermore, chemical shift tensors provide reasonably good estimates of an initial set of vicinal angles that speeds up the data reduction of powder diffraction histograms from several months to merely hours in relatively large molecules that presently are too large to do the analysis without good initial estimates of the conformational angles. There is also some evidence that the chemical shift tensors give a more sensitive estimate of bond distances between directly bonded atoms. The mutual verification of the solid state NMR and diffraction data from the Sector 1 beam line at the Advanced Photon Source (APS) at Argonne exhibits the synergism between the two techniques, and exhibits the success one can have on molecules in the 500 to 2000 Dalton range.

The **INADEQUATE** experiment alluded to above is very useful when more than one molecular isomer is obtained due to mixed crystals and/or multiple molecules per asymmetric unit. The different isomeric molecular structures exhibit closely paired lines at corresponding atomic positions and their assignment into molecular sets is greatly enhanced by the **INADEQUATE** connectivities that link directly bonded atoms. These data are valuable in assigning sets of lines when two or more unique molecular structures are present in the sample.

DOE Interest

Some of our most recent results, not yet in published form, are still exploratory and are woven into our future work. These results document, in large measure, the continuation of present efforts with major emphasis placed on recently developed theoretical and experimental techniques. Synergism with applied efforts is established by our participation in the DOE/ASCI alliance program that continues to employ theory and experimental methods developed largely with DOE/BES support. We will continue to collaborate with staff at: (a) the ANL/APS sector 1 beam line who assist in acquiring powder diffraction data on structures containing more than one molecule per asymmetric unit; (b) we plan to acquire low angle neutron scattering data on the GLAD facility on the ANL reactor to study the structure of amorphous PAH materials and correlate these data with NMR data on the same samples; (c) continue our collaboration with Dr. Randy Winans (Chemistry Division, ANL) on soot samples collected from various pyrolysis/combustion sources in order to maximize the structural information provided by combining NMR and mass spectroscopy data.

Future Plans

Our future plans are focused in three areas. (1) Refinement of the work on single crystal FIREMAT experiments (taken at the icosohedral angle) on small crystals that provide the data needed to determine full chemical shift tensors. (2) Continue to explore the synergism between solid state NMR and X-ray powder diffraction data with special emphasis on molecules which crystallize with more than one molecule per asymmetric unit. (3) Expand the data base on chemical shift tensors to include the effects of ring strain and curvature with an emphasis of cyclopentafused polycyclic aromatic hydrocarbons. Such structures are usually highly toxic and are always found in pyrolysis/combustion environments.

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Bio-inspired Iron Catalysts for Hydrocarbon Oxidations

Project initiated September 1, 2003; 2003-04 budget: \$143,000 total costs

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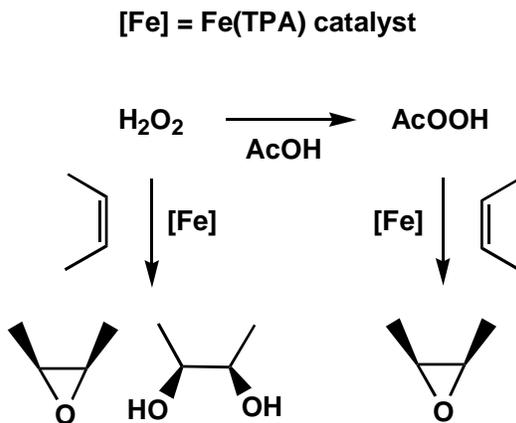
Goal

Develop iron catalysts for hydrocarbon oxidations inspired by nonheme iron oxygenases and to understand their mechanism of action

Recent progress

In situ formation of peracetic acid from H_2O_2 and acetic acid catalyzed by $Fe(TPA)$:

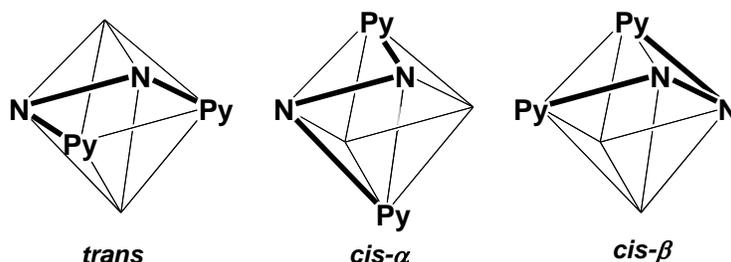
We have previously demonstrated that $Fe^{II}(TPA)$, the iron(II) complex with tris(2-pyridylmethyl)amine, serves as an efficient catalyst for the H_2O_2 -mediated oxidation of olefins to epoxides and cis-diols. In the case of cyclooctene, the oxidations in CH_3CN are stereospecific and an epoxide-to-diol ratio of 1:1.2 is observed. Interestingly, we have found that the addition of increasing amounts of acetic acid results in a shift of the ratio to 16:1 in favor of epoxide with a 7-fold excess of acetic acid over H_2O_2 . The same results are obtained with the use of peracetic acid. We thus conclude that $Fe(TPA)$ catalyzes *in situ* formation of peracetic acid. This method may provide a new route to this important oxidant from its readily available and cheap precursors.



Topological control of the epoxide-to-diol ratio in iron-catalyzed olefin oxidation:

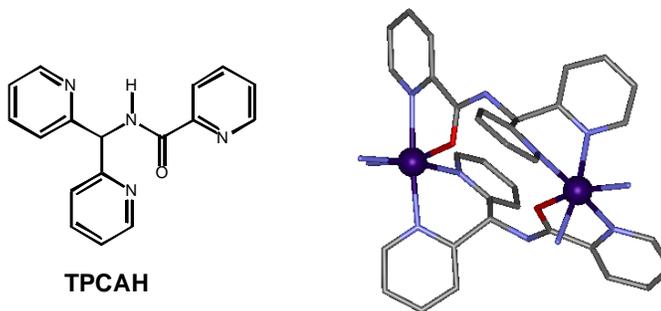
In exploring ligands related to TPA for the catalysis of olefin oxidation, we previously found that the tetradentate BPMCN ligand (BPMCN = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane) forms iron(II) complexes in both the *cis*- α and the *cis*- β topology. Both isomers catalyzed olefin oxidation efficiently but with significantly different epoxide-to-diol ratios. The *cis*- α isomer afforded almost all

epoxide (8:1), while the *cis*- β isomer afforded predominantly diol (1:4). Although both isomers were characterized by X-ray crystallography, the possible participation of a third ligand topology related to the *cis*- α isomer, the so-called *trans* isomer with all four ligating nitrogen atoms occupying the equatorial plane, could not be excluded from consideration. A ligand enforcing such a planar geometry, *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,5-diazacyclooctane, was thus synthesized, and its iron complex made and characterized. As hoped for, this complex catalyzed olefin oxidation and afforded an epoxide-to-diol ratio of 10. This result confirms the importance of ligand topology in determining the course of olefin oxidation by this family of iron catalysts.



New ligand frameworks:

We have initiated a study on the iron complex of TPCAH, a ligand related to TPA in which a benzylic methylene group is converted to a carbonyl moiety. This ligand would be expected to have a weaker ligand field than TPA and may thus favor a high-spin state without the introduction of sterically hindering 6-methyl substituents as in the case of 6-Me₃-TPA. The X-ray crystal structure of the iron(II) perchlorate complex [Fe(TPCAH)N(NCCN₃)₂]₂(ClO₄)₄ reveals that TPCAH acts as a tetradentate ligand but to two metal centers and the complex has a dimeric structure in the solid state. Perhaps surprisingly, the complex nevertheless catalyzes olefin oxidation with H₂O₂ as oxidant with an epoxide-to-diol ratio of 36:1. Isotope labeling studies using H₂¹⁸O₂ and H₂¹⁸O (cyclooctene as a substrate)



displayed a labeling pattern that indicates an epoxidation mechanism resembling that of TPA (Class A low-spin catalyst). Furthermore the use of *cis*- and *trans*-2-heptenes reveals significant retention of configuration in the epoxide, also consistent with Fe(TPA) behavior. However a high-spin iron(III)-alkylperoxo intermediate can be observed upon addition of tert-butyl hydroperoxide at -40°C in acetonitrile, which is typical of a Class B high-spin catalyst. When the minority diol product was examined in isotope labeling experiments, both oxygen atoms derive from H₂O₂, a pattern typical of Class B catalysts. This case thus raises questions with respect to the correlation between the spin-state and

the type of reaction that we have elaborated upon earlier and emphasizes the point that much remains to be learned about the role the iron center plays in these reactions.

Synthesis of chiral ligands:

Efforts to synthesize polydentate ligands containing optically active centers have been initiated but it is premature to report results from these rather recent efforts.

Interest to DOE

Learning to control the activation of dioxygen and its derivatives by biomimetic iron centers to afford oxidants capable of stereospecific hydrocarbon oxidation is an area of potentially enormous environmental and energy-saving impact. Our initial results suggest that this is an avenue worth further exploration.

Future plans

Continued detailed mechanistic studies of the reactions of peroxides with nonheme iron(II) complexes to understand the molecular basis for the observed branching between olefin epoxidation and cis-dihydroxylation.

Investigation of both structural and electronic factors to affect this branching ratio.

Synthesis of chiral ligands for asymmetric olefin oxidation

Publications (2004)

Fujita, M.; Que, L., Jr. "In situ Formation of Peracetic Acid in Iron-Catalyzed Epoxidations by Hydrogen Peroxide in the Presence of Acetic Acid" *Adv. Synth. Catal.* **2004**, *346*, 190-194.

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Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Buckybowls

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Goal

The gram-scale synthesis of polynuclear aromatic hydrocarbons (PAHs) with carbon frameworks that can be identified on the buckminsterfullerene C₆₀ surface (buckybowls), and the use of these bowl-shaped structures as precursors for larger and more complex curved-surface systems.

Recent Progress

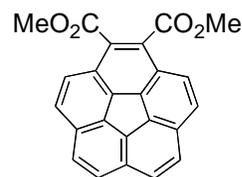
Early work under the DOE sponsored program produced the first “locked” buckybowl by incorporation of an additional five-membered ring onto corannulene, and the first two semibuckminsterfullerenes (C₃₀H₁₂'s) representing half of the C₆₀ surface. While these and other buckybowls were made by our program and others on mg levels, we have more recently developed new methods for the gram-scale synthesis of tetrabromocorannulene (**1**), corannulene (**2**), and corannulene-dicarboxylate (**3**).



1



2



3

DOE Interest

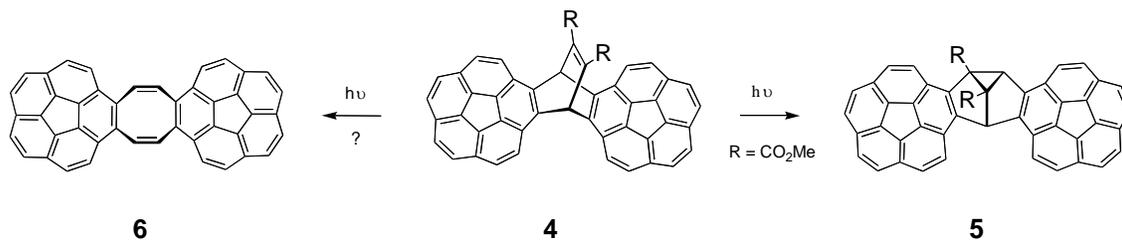
These novel, bowl-shaped structures may be involved in host-guest relationships that have potential in the area of catalysis; they represent the end-caps of closed nanotubes and, as such, could serve as precursors for controlled nanotube synthesis; and they could become an environmental concern if the wide-scale use of fullerenes is ever realized due to potential fragmentation processes of the latter.

Future Plans

Future plans for the program will involve the production of novel, curved PAH systems by (a) applications of the newly developed synthetic methodology, and (b) exploitation of the availability of **1-3** as synthons for further elaboration. Due to space limitations, only a few examples are shown below. However, the availability of new synthetic methodology to produce curved-surface PAHs on gram-scale levels will afford a wide variety of opportunities for the generation of unusual systems. And, while the structural features of these systems are quite interesting, there has been little done to date with the exploration of their chemistry.

Twin Corannulenes

A recent example of the new methodology is the synthesis of twin corannulene **4**. This system is of interest for potential host-guest chemistry (see model below for possible interaction with C₆₀); it also undergoes an extraordinarily facile di- π methane

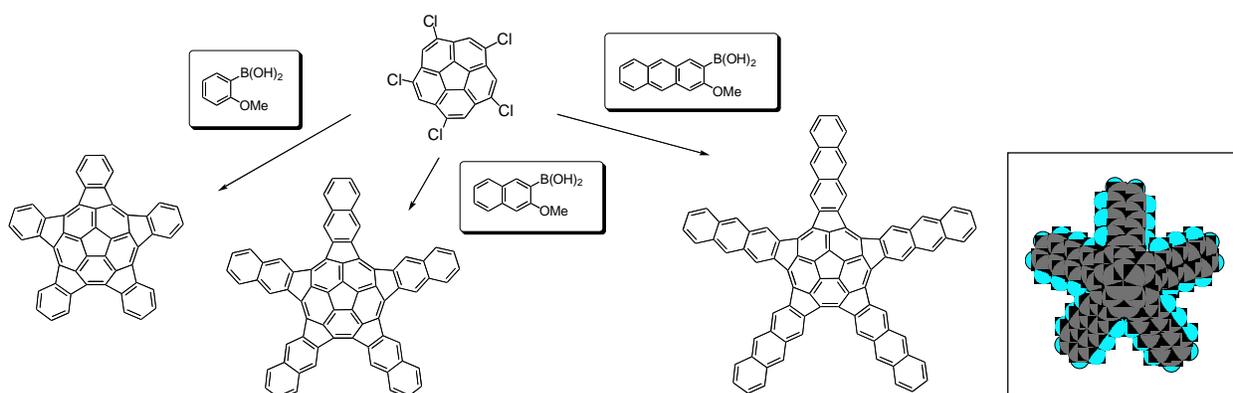


rearrangement to semibullvalene **5**. We plan to convert the R groups to hydrogen or methyl to explore the non-sensitized photochemical conversion, presumably to **6** which has added host-guest possibilities due to the tub-shaped COT ring. It also should have tremendous potential for acceptance of lithium since corannulene readily accepts four electrons and COT forms an aromatic dianion.

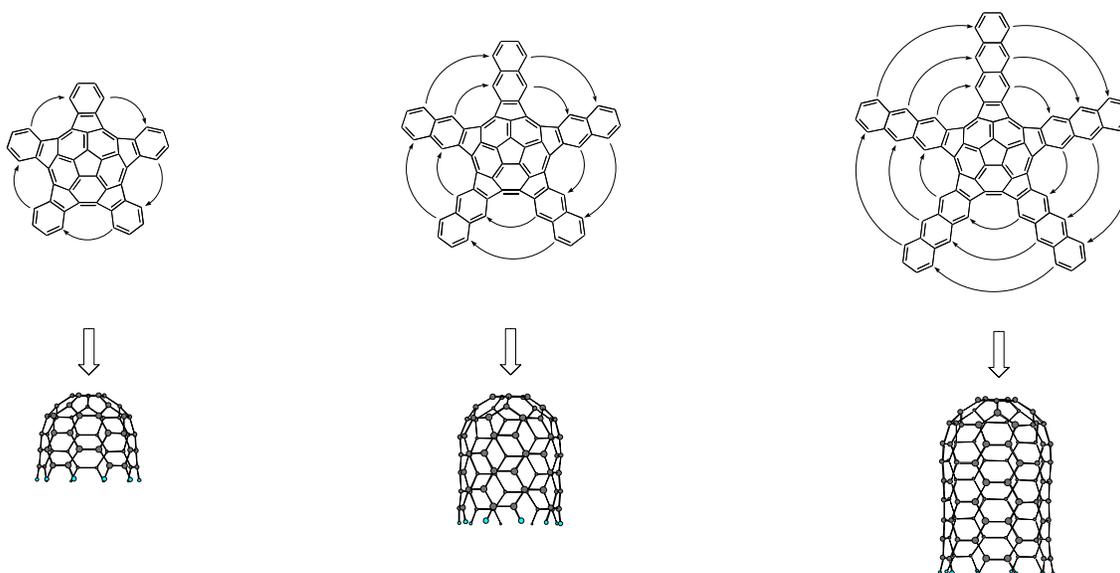


Pentasubstituted Corannulenes as Synthons

The availability of gram quantities of corannulene provides an opportunity to use the easily produced pentachlorocorannulene as a synthon. We have successfully used Suzuki coupling routes with monobromocorannulene to incorporate a single fluoranthene unit. If this can be done at all five sites from a pentasubstituted corannulene, it will produce some remarkable structures as illustrated below for one, two, and three PAH additions. Of course these structures are not planar due to the bowl-shaped inner corannulene core. Moreover, the addition of five-membered rings around the periphery of corannulene will have the effect of “tightening” the core ring system providing an even greater level of curvature (at least to the point where “peri” type interactions may become possible).



Perhaps the most exciting aspect of this project is the possibility that if these “starburst” type PAHs can be formed, they might be induced to “zip up” to form closed-end nanotubes. Of course an organic synthesis of model nanotubes would open the door for a number of studies relating to their properties and behavior.



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2. Z. Marcinow, A. Sygula, P. W. Rabideau, “Improved Synthesis of Benz[a]acephenanthrene,” *Synlett*, 1839 (2002).

3. A. Sygula, R. Sygula, F. R. Fronczek and P. W. Rabideau, "The Addition of Organolithium Reagents to Corannulene and Conformational Preferences in 1-Alkyl-1,2-Dihydro-corannulenes," *The Journal of Organic Chemistry*, 67, 6487 (2002).
4. A. Sygula, S. Karlen, R. Sygula, and P. W. Rabideau, "Formation of the Corannulene Core by Nickel-Mediated Intramolecular Coupling of Benzyl and Benzylidene Bromides: A Versatile Synthesis of Dimethyl 1,2-Corannulene Dicarboxylate," *Organic Letters*, 4, 3135 (2002).
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6. A. Sygula, R. Sygula, A. Ellern and P. W. Rabideau, "A Novel Twin Corannulene: Synthesis and Crystal Structure Determination of a Dicolorannulenobarrelene dicarboxylate," *Organic Letters*, 2003, 5, 2595.

Kansas State University Contribution: Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes Through Tailored Nanostructures.

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Collaborators: Heinz, O'Brien, Bartels

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email: rahman@phys.ksu.edu**Goal**

The overall goal of the project is to pursue the development of new catalysts which may exploit the selective support of specific surface reactions by applying steric and entropic control over the diffusion motion and reaction energy, respectively. Towards this end, Rahman's group has the preliminary goal of understanding the binding, activation energies and diffusion pathways of atoms, molecules and clusters on inhomogeneous (stepped, kinked, with co-adsorbates, etc.) surfaces through theoretical calculations and computer simulations.

Progress during the first 6 Month of the Funding Period:

During the first six month of the project, theoretical work has progressed on several fronts. The first of these is the implementation of a powerful code for the calculation of the electronic structure of adsorbates on surfaces and on nanostructures from first principles using the full potential LAPW (linear augmented plane wave) method. This code, together with the one based on pseudopotentials in the plane wave representation, is now being used in Rahman's group to examine the energetics, changes in electronic structure, diffusion, and reactivity of several systems in conjunction with the work of experimental collaborators on this grant.

Diffusion of CO molecules on Cu(111): Heinz and Bartels groups find interesting changes in the diffusion of CO molecules on Cu(111) as a function of adsorbate coverage. It is conceivable that both activation energy barriers and prefactors are affected. We have obtained preliminary results for the adsorption of CO on Cu(111) which show that for low coverage the strong bond between the CO molecule and Cu atom impacts the local surface structure, as indicated in Fig.1. Our calculational super cell is large enough to allow the examination of changes in the diffusion characteristics as CO coverage is increased.

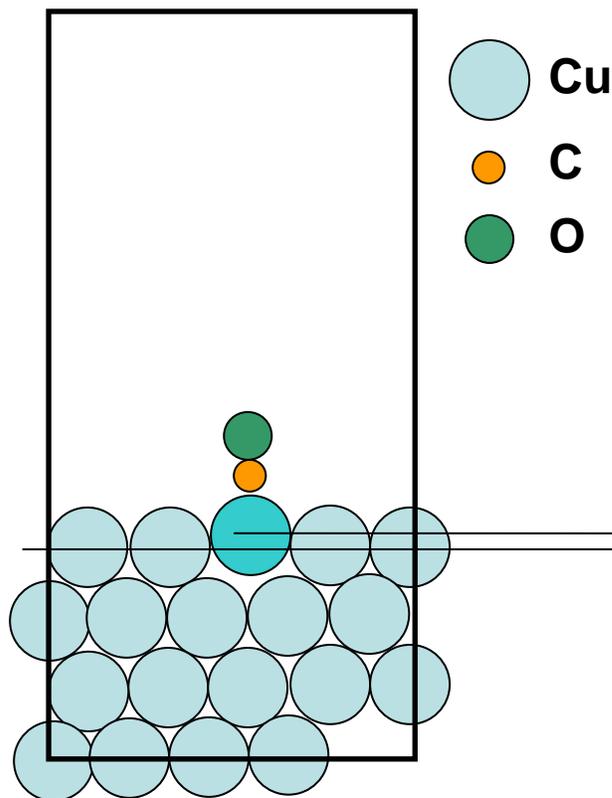


Fig. 1. Side view of the supercell containing 3x5 Cu atoms per layer and a CO molecule (CO coverage of 1/15). We find that the minimum of the total energy corresponds to the adsorption of CO molecule on the top of Cu atom. The adsorption causes a strong atom relaxation, namely the Cu atom located below the molecule undergoes upward shift of about 0.28 Å with respect to the other topmost Cu atoms. The equilibrium C-O bond length is found to be equal to 1.16Å, whereas the C-Cu bond is equal to 1.86Å

Adsorption of ThioPhenol on Cu(111): Motivated by the beautiful experimental observations from Bartels' laboratory, we are carrying out calculations of the nature of the binding of thiophenol molecules on Cu(111). Preliminary results indicate that the adsorption geometry is non-trivial. We are in the process of carrying out similar calculations of thiophenols on Au(111) to understand the rationale for the complex behavior on Cu(111).

Alkali Adsorption on Cu(111) and Pd(111): Complementary work in Rahman's group on S and C adsorption on several types of stepped Pd surfaces have led us to examine the effect of alkali metal adsorption on transition metal surface. Alkali metals are well-known as promoters in heterogeneous catalysis. On adsorption at prototype catalyst surfaces, like that of a transition or noble metal, they substantially increase the rates of various chemical reactions. It is also reported that when alkali adsorb on Cu surfaces they form so-called quantum wells with quasi-two-dimensional electronic states localized along the surface. The ensuing novel properties of the system find many applications, including those in photochemistry and nanotechnology, however, the mechanism responsible for the enhanced reactivity is as yet not understood. We have carried out extensive comparative studies of the adsorption of Na and K on Cu and Pd surfaces. We find that of the several theoretical measures of catalytic activity that have been proposed, the isoelectronic reactivity index $w^N(r)$ is the most reflective of dramatic changes in behavior. For both Cu and Pd surfaces, which are by themselves of varied electronic structure, we find a huge increase and delocalization of $w^N(r)$ on alkali metal adsorption (see Fig. 2). We trace this phenomenon to an unusual feature in the surface potential formed by the adsorbate (see Fig. 3) which may ultimately be the driving force for the "promotion effect" of alkalis. We also find a relationship between the characteristics of the surface potential and the observed unusual optical properties of the quantum wells on these systems. We hope our experimental colleagues can substantiate our predictions through related measurements on these interesting systems.

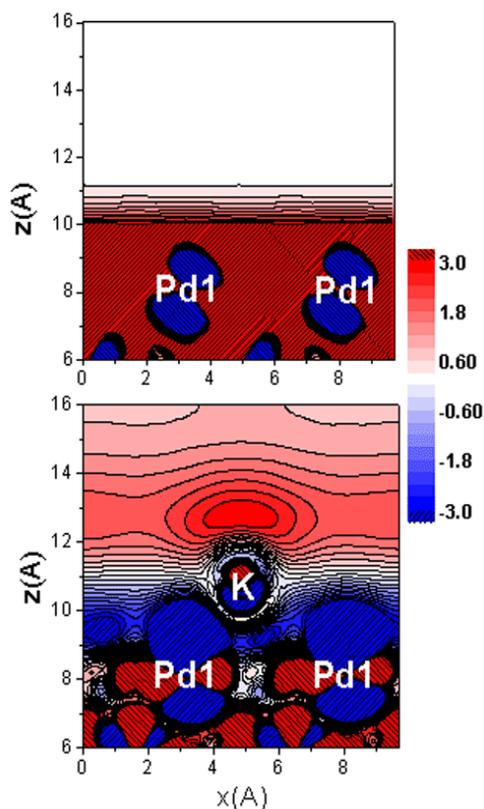


Fig. 2. Plot of $w^N(r)$ for clean Pd(111) (upper panel) and for a 0.25 coverage of K on it ($K_{0.25}/Pd(111)$) (lower panel) along the plane perpendicular to the surface. Pd1 mark the positions of the topmost Pd atoms and K that of potassium atoms. A drastic decrease in $w^N(r)$ is seen for the clean surface (the white area corresponds to $w^N(r) = 0$), while adsorption of K induces a huge increase and delocalization of $w^N(r)$ even at points far from the adsorbate.

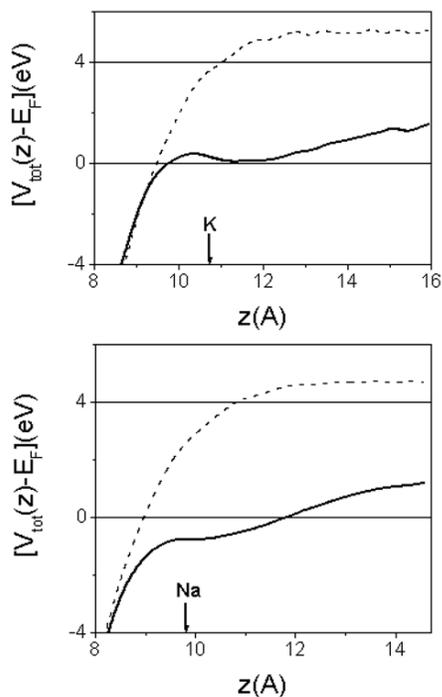


Fig. 3. Self consistent total potential plotted along the surface normal. The upper panel displays the potential for Pd(111) (dashed line) and for a 0.25 K overlayer on Pd(111) (solid line). The lower panel provides the same for Cu(111) (dashed line) and $Na_{0.25}/Cu(111)$ (solid line). Arrows indicate the positions of the alkali atoms. Instead of an expected simple reduction of the surface barrier, the alkali adsorbates form a **groove-like or plateau-like** region of further reduced potential in the vicinity of the surfaces.

DOE Interest

Catalytic reactions have great importance for a broad range of industrial and environmental processes ranging from catalytic CO oxidation in exhaust systems to catalytic hydro-desulfurization of gasoline. This project aims at understanding catalytic processes on the

atomic scale by development and applications of methods that can follow molecular dynamics at high excitation level.

Future Plans

Continuation of the above projects: The two collaborative projects described above require extensive systematic studies in close collaboration with experimentalists. We intend to pursue them. In the case of CO diffusion on Cu(111), we will be examining the influence of increasing CO coverage on the activation energy barriers and diffusion paths. More importantly, we will pay attention to calculations of the diffusion prefactors which are expected to play an important role and cannot be taken to have the same value for all intervening diffusion events. By understanding the most optimal diffusion paths we will be in a position to predict energy-saving reaction pathways. In the case of the structure, adsorption and dynamics of thiophenol molecules on Cu(111), we need to get better insights from adsorption on a substrate like Au(111) on which the energetics is already known from experiments. Such calculations need to be carried out for the Au(111) to gain insights on the nature of the anchoring of the S molecule on the surface.

Transition Metal Oxide Nanocrystals: We are very encouraged by the recent developments in O'Brien's group on the synthesis and characterization of transition metal oxide nanocrystals. We find ourselves well equipped with the tools to carry out theoretical calculations and computer modeling of these useful materials. We will begin by examination of the geometric and electronic structure of small Cu₂O nanocrystals. Some work in this direction has already begun. We will be most interested in investigating the reactivity of these nanoparticles along the lines discussed above for transition metal surfaces.

Kinetic Monte Carlo Simulations: Some members of Rahman's group are engaged in developing a methodology for kinetic Monte Carlo simulations which does not suffer from a priori biasing of the system's temporal and spatial evolution through a set of input energetics. Instead, a data base of the energetics of relevant events and diffusion processes is developed by the system as it evolves. Efforts are underway to generate mapping functions capable of generating the energetics through "self teaching". We plan to implement this novel approach in calculations of the diffusion of CO molecules on Cu surfaces, in collaboration with the experimental work of Heinz and Bartel groups..

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5. S. Durukanoglu, A. Kara, and T.S. Rahman, "Excess and Local Thermodynamic Properties of Stepped Metal Surfaces," *Phys. Rev. B* **67**, 235405 (2003).
6. I. Makkonen, P. Salo, M. Alatalo, and T. S. Rahman, "Characteristics of adsorption of S on Pd vicinal surfaces," *Surf. Sci.* **532-535**, 154 (2003).
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8. T. S. Rahman, A. Kara, and S. Durukanoglu, "Structural relaxations, vibrational dynamics and thermodynamics of vicinal surfaces," *J. Phys. Condensed Matter*, **15**, S3197 (2003).
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10. O. Trushin, A. Kara, T. S. Rahman, "Self-teaching kinetic Monte Carlo technique for simulation of surface phenomena," *Phys. Rev. B*, to be published
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Homogeneous CO Hydrogenation Revisited

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Research Goals and Objectives

The Fluid Catalysis Program explores catalysis mechanisms, new catalytic species, and new catalytic reaction chemistry using an array of in situ spectroscopic and kinetic techniques at the high pressures and temperatures that are frequently used in industrial chemical processes. The Fluid Catalysis Program's research in the area of catalytic chemistry in supercritical media stems from the interesting and favorable physical properties of these media that allow increased scrutiny of catalytic mechanisms by powerful NMR techniques that operate most effectively in low viscosity gas or supercritical-fluid phases. Also, because bond energies are defined in terms of gas-phase chemistry, thermochemical measurements in the gas-like supercritical media are more easily interpretable in terms of the bond dissociation energies of the various bonds in organometallic catalysts. Experimental thermochemical and kinetic data from supercritical fluids is highly amenable to theoretical calculation. We have recently conducted supercritical homogenous CO hydrogenation for the first time and, in related research, uncovered the first cobalt catalyst for the supercritical phosphine-modified hydroformylation of olefins and measured the thermodynamics of the key hydrogen addition step for these catalysts. In research on high-pressure in situ spectroscopic devices, we have developed the toroid-pressure probe, the R&D 100 Award winning toroid-cavity imager, and most recently, a magic-angle-spinning toroid-cavity probe that imparts the high sensitivity and imaging capability of toroids to high-resolution solid-state NMR spectroscopy. In other research, reverse micelles are utilized as nano-sized minireactors to allow catalytic reactions that normally require highly polar solvents to be conducted in the supercritical phase. In this endeavor, the first high-pressure NMR characterization of reverse micelles in supercritical carbon dioxide has recently been achieved.

This abstract describes the Fluid Catalysis Program's recent in situ spectroscopic and kinetic investigations of homogeneous catalytic carbon monoxide hydrogenation in supercritical media.

Recent Progress

Considerable research on homogeneous catalysts for the hydrogenation of CO was undertaken in several laboratories in the late 1970's and early 1980's. The most studied of homogeneous CO hydrogenation catalysis systems is the cobalt carbonyl catalyzed reaction which has been shown to follow a rate law that is first order in both $\text{HCo}(\text{CO})_4$ and H_2 pressure. The reaction is believed to proceed through an early coordinated

formaldehyde intermediate that produces, dependent upon the reaction conditions and solvent, variable amounts of methanol, methyl formate, and ethylene glycol as initial reaction products. In the proposed mechanism, higher alcohols and higher formate esters are produced by secondary homologation and transesterification reactions associated mainly with the initially produced methanol and methyl formate.

Since most of the early kinetic studies on these systems were accomplished using high-pressure autoclaves, it seems possible that recent advances in high-pressure spectroscopic techniques that would allow in situ scrutiny of these systems might provide more information on them, today. We recently tested the use of a high-pressure toroid NMR probe on the cobalt carbonyl catalyzed CO hydrogenation in supercritical carbon monoxide medium for the first time. Use of a single-phase homogeneous supercritical system containing catalyst and reactant gases was utilized to avoid gas-liquid mixing problems that might otherwise interfere with kinetic studies in an unstirred NMR pressure vessel using conventional liquid media.

The reaction rate and products and the cobalt containing species associated with the catalytic reaction were measured in situ at 180 and 200 °C and at total pressures of hydrogen and carbon monoxide near 260 atm. The second order rate constant at 200 °C, $12 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$, measured in supercritical carbon monoxide is close to the reported value for the nonpolar solvent, benzene ($15 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$) and considerably smaller than that reported in the more polar solvent, 2,2,2-trifluoroethanol ($84 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$). The products of the reaction including methanol and methyl formate were quantified by in situ ^1H NMR, while in situ ^{59}Co NMR revealed cobalt carbonyl hydride and dicobalt octacarbonyl as the only detectable cobalt species. Preliminary measurements yielded an approximate activation barrier of 34 kcal/mole. Separate experiments established that the homologation of methanol, the pathway for production of higher alcohols under CO hydrogenation conditions in polar solvents, did not occur to a measurable extent in the nonpolar supercritical CO medium used here.

DOE Interest

In earlier high-pressure kinetic studies, the Fluid Catalysis Program demonstrated the first mononuclear catalyst for homogeneous carbon monoxide hydrogenation and determined the rate law and the currently accepted mechanism for the $\text{HCo}(\text{CO})_4$ catalyzed reaction (see F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Sixth Edition, 1999, p. 1253). In the past year, in research aimed at experimental and theoretical parameterization of the reaction coordinates of this mechanistically important reaction, it conducted kinetic measurements on homogeneous catalytic carbon monoxide hydrogenation, in situ, in an NMR probe for the first time. Also, supercritical carbon monoxide was used as a gas-like reaction medium (to aid in the theoretical calculations) for the first time in homogeneous CO hydrogenation.

This program pioneered the use of homogeneous catalysts in supercritical fluids and invented supercritical hydroformylation catalysis. To conduct in situ spectroscopic studies of supercritical and other high-pressure industrial process chemistry, it developed the toroid-pressure probe, the R&D 100 Award winning toroid-cavity imager, and most recently, a magic-angle-spinning toroid-cavity probe that imparts the high sensitivity and

imaging capability of toroids to high-resolution solid-state NMR spectroscopy. This program recently reported the first high-pressure NMR characterization of reverse micelles in supercritical carbon dioxide.

Future Research

In future work on homogeneous CO hydrogenation, accurate determinations of such parameters as activation barriers and kinetic isotope effects, afforded by high-pressure NMR in a gas-like medium that is highly amenable to theoretical (density functional) calculations will allow scrutiny of the early steps in this important reaction. The earlier work with autoclaves had established a strong temperature coefficient and a significant isotope effect on this system, but the uncertainties and complexities associated with sampling from autoclaves discouraged attempts to accurately determine these parameters with the high-pressure techniques available at that time. Evaporation of the volatile $\text{HCo}(\text{CO})_4$ into the autoclave headspace increased by removal of liquid samples, and uncertain quenching of samples containing this unstable species are problems associated with autoclave sampling methods that are alleviated by the high-pressure NMR technique used here.

Publications 2003-2004

Cobalt(I) Salt Formation in Hydroformylation Catalysis

J. W. Rathke, R. J. Klingler, M. J. Chen, R. E. Gerald II, and K. W. Kramarz
The Chemist **80(1)**, 9-12, 2003

Ionic Species in Cobalt-Catalyzed Hydroformylation

J. W. Rathke, R. J. Klingler, M. J. Chen, and R. E. Gerald II
In *Chemical Engineering Division Annual Technical Report 2002*, ANL-03/13,
pp. 77-78, 2003

Two Dimensional B1-Gradient NMR Imager

Rex E. Gerald II, Rafael L. Greenblatt, and Jerome W. Rathke
U. S. Patent 6,538,444 Issued March 25, 2003

Nuclear Magnetic Resonance Imaging Apparatus

Rex E. Gerald II, Robert J. Klingler, and Jerome W. Rathke
U. S. Patent 6,674,283 Issued January 6, 2004

In Situ High Pressure NMR Studies of $\text{Co}_2(\text{CO})_6[\text{P}(\text{p-CF}_3\text{C}_6\text{H}_4)_3]_2$ in Supercritical Carbon Dioxide: Ligand Substitution, Hydrogenation, and Hydroformylation Reactions, M. J. Chen, R. J. Klingler, J. W. Rathke, and K. W. Kramarz, *Organometallics*, accepted for publication.

Supercritical Catalytic CO Hydrogenation

J. W. Rathke, R. J. Klingler, and M. J. Chen, *The Chemist*, accepted for publication.

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Organometallic Cyano-Cages as Scaffolds, Ligands, and Sequestrants

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Ph.D. students: Kuhlman, M. L.; Boyer, J.; Contakes, S. M.

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Goal:

Develop new metal-rich ensembles for applications in catalysis and in separations.

Background:

In 1998 we discovered an efficient route to organometallic cages with box-like structures. Specifically tricyanides $fac\text{-}L_nM(\text{CN})_3$ were found to condense with facial tritopic Lewis acids to give $M_8(\text{CN})_{12}$ species, e.g. $\{[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Rh}]_4\}^{4+}$. Such species were the first cyanometallate cages ever described after literally hundreds years of research on cyanide coordination chemistry. Related reactions afforded “incomplete” or “defect” boxes consisting of $M_7(\text{CN})_9$ frameworks such as $\{[\text{Cp}^*\text{Rh}(\text{CN})_3]_4[\text{Cp}^*\text{Rh}]_3\}^{2+}$. $[\text{Cp}^*\text{Rh}(\text{CN})_3]$ was subsequently found to condense with $\text{Mo}(\text{CO})_3$ sources to give inclusion complexes $\{M\text{-}[\text{Cp}^*\text{Rh}(\text{CN})_3]_4[(\text{CO})_3\text{Mo}]_4\}^{3-}$ ($M = \text{Cs}^+, \text{K}^+$). The presence of alkali metal cations M^+ is required for cage stability. Competition studies showed that Cs^+ binds more tightly than K^+ by $>10^4$. The incorporation of alkali metal centers into organometallic frameworks is an unusual supramolecular motif. This research also demonstrated the versatility of the cage-building process, i.e. vertices can range from $M(\text{CO})_3$ to $(\text{C}_5\text{R}_5)\text{M}^{2+}$. The specific finding that Cs^+ binds more tightly than K^+ points to fundamental concepts related to Cs^+/K^+ separations. The work also highlights the considerable advantage to the organometallic approach to cage-forming processes, because the versatility of organometallic reagents allows greater control over the charge on the cage.

These architecturally novel species represent the starting point for development of fundamental but still application-oriented studies described in a stepwise manner below.

Recent Developments

Non-labile M-CN linkages are critical to cage formation

Findings: We examined condensations where the M-CN bonds are labile: box-like structures do *not* form, rather one obtains smaller trigonal bipyramidal or tetrahedral cages. These condensations formally involve $[\text{Mo}(\text{CN})_3(\text{CO})_3]^{3-}$, but in this species the Mo-CN bonds are labile. With K^+ and Cs^+ one obtains trigonal prismatic $\{\text{Cs}\text{-}[(\text{CO})_3\text{Mo}]_6(\text{CN})_9\}^{8-}$ whereas with smaller alkali metal cations one obtains smaller tetrahedranes such as $\{\text{Na}\text{-}[(\text{CO})_3\text{Mo}]_4(\text{CN})_6\}^{5-}$.

Implications: It was unknown if the box and defect box motifs would spontaneously form when metal electrophiles were presented with 1.5 equiv of cyanides. Clearly the use of preformed $[L_nM(CN)_3]^{n-}$ building blocks is critical. This study also demonstrated that the size of the alkali metal cation strongly influences the cage architecture - small ions give smaller cages. This work strongly suggests that the ability of the boxes to discriminate between Cs^+ vs. K^+ is due to the poor fit of the latter in the cage. The overarching implication is that rigid, 3-dimensional architectures display higher selectivity for ion complexation than do flexible ligands. Most ligands in use are flexible, hydrocarbon-based species, thus a considerable opportunity exists for the design of rigid inorganic frameworks.

Charge-neutral organometallic boxes display high affinities for alkali metal cations

Finding: Charge-neutral cages bind cations very well. This result came from our discovery of a templated synthesis of $[CpCo(CN)_3]_4[Cp^*Ru]_4$, which binds Cs^+ , Rb^+ , NH_4^+ , K^+ , Tl^+ , $N_2H_5^+$, and $MeNH_3^+$. The affinity for Cs^+ vs. K^+ remains high, and K_{Cs} is estimated $>10^{10}$. Neither Na^+ nor any dication binds to these cages. Ion exchange kinetics are first order in the filled box, i.e. rate-determining loss of the cation followed by rapid uptake of the new cation. Ion-binding to empty cages follow first order kinetics in terms of the concentrations of both box and the alkali metal cation. K^+ inserts into the box more quickly than does Cs^+ .

Implications: The fact that anionic cages bind alkali metal cations at their interiors is unsurprising given the electrostatic forces involved and the 3-dimensional enclosure provided. Particularly encouraging and somewhat unexpected is the fact that *charge-neutral* cages display high affinities for cations. In fact, it is increasingly clear that *cationic* cages also bind cations, which is unprecedented.

Encapsulated guests display modified reactivity

Finding: The 1H NMR spectrum of $\{MeNH_3[CpCo(CN)_3]_4[Cp^*Ru]_4\}^+$ displays the full complement of 1H - ^{13}C , ^{13}C - ^{14}N , and 1H - ^{14}N couplings, which indicates that the cation is shielded from solution, thereby suppressing intermolecular exchange processes. Further evidence of the ability of the box to protect guests is the absence of H-D exchange of the encapsulated NH_4^+ with D_2O . Finally, the ammonium ions are immune to attack by strong base.

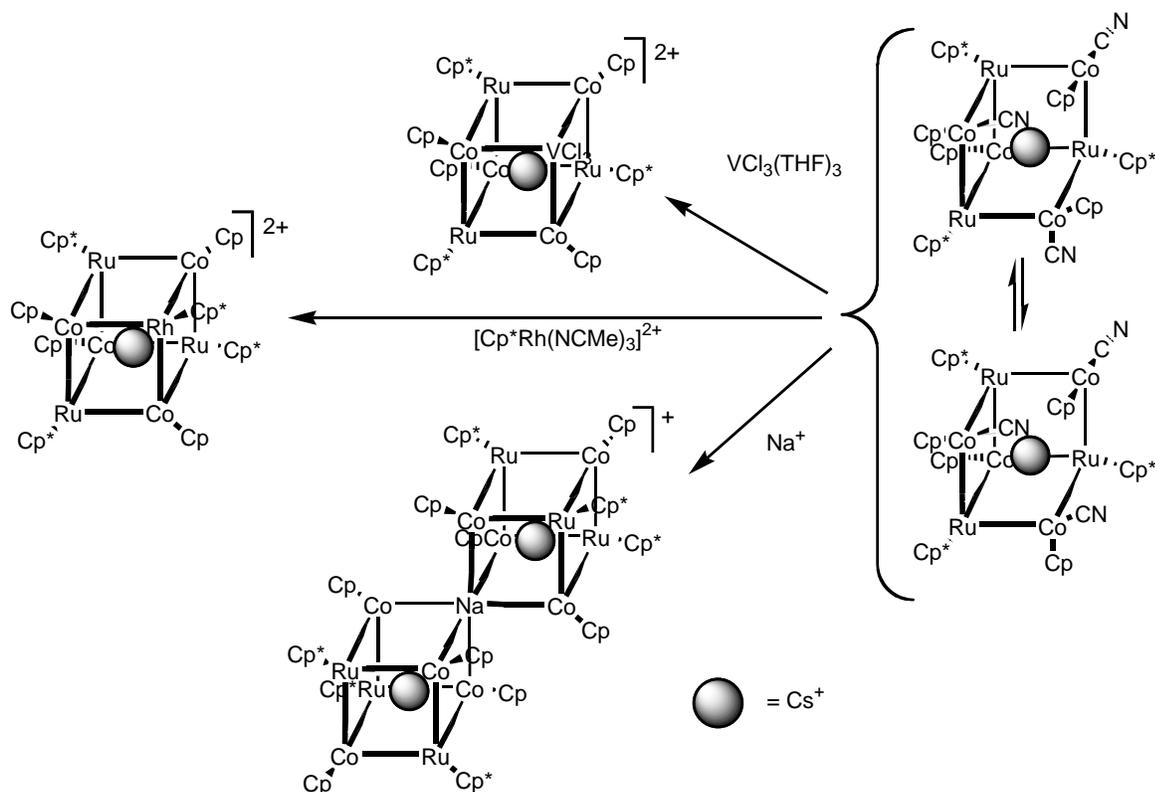
Implications: The unusual environment provided by the box suggests that unusual chemistry could be performed inside such containers. Many host-guest species are known, but it is rare to see slow in-out exchange of the guest molecules in solution.

Incomplete boxes are excellent ligands

Finding: Parallel with the preparation of $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_4\}^+$, routes were developed to the defect box $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3\}$, which is missing one metal vertex (Ru_3 vs. Ru_4). This species possesses three terminal cyanides suitable for further complexation. Indeed the defect box binds a range of metal electrophiles to give boxes. Using this "box-completion" reaction, one can generate boxes containing terminally bound reactive ligands, e.g. $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3VCl_3\}$. One can also construct nano-scale cages such as the double boxes, e.g., $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3\}_2Fe^{2+}$, and the cluster-fused boxes, e.g., $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Ru_3S_2(arene)_2\}^{2+}$.

Implications: The box completion process (see Scheme) establishes that the defect boxes perform like Tp^- , Cp^- , and other tridentate ligands. Insofar as facially binding tridentate

ligands are central to many catalytic reactions, this new family of multimetallic ligands is a promising source of novel ligands for catalytic applications.



Scheme: Box-completion reactions demonstrating the tridentate character of the “defect” boxes.

Tetrahedral $L_nM(CN)_3$ vertices give larger cages

Finding: This subproject began with the synthesis of the new ligands $[RB(CN)_3]^-$, where R = alkyl, aryl. Condensation of these anions with Cp^*Rh^{++} sources affords the hexagonal prismatic cage $\{[PhB(CN)_3]_6[Cp^*Rh]_6\}^{6+}$.

Implications: At issue in any synthetic advance, i.e. the development of cyanometallate boxes, is the scope for expanding the concept to broader range of products. The $B_6Rh_6(CN)_{12}$ cage has greater internal volume vs. the aforementioned boxes, as demonstrated by the inclusion of THF at the cage interior. Furthermore the solubility of these species allows thorough characterization.

DOE Interest

The new cages demonstrate unparalleled selectivity for Cs^+ vs. K^+ , relevant to DOE-specific separations issues. The boxes and incomplete boxes present revolutionary or at least very novel designs. The work demonstrates new classes of ligands that incorporate supramolecular interactions. These efforts are relevant to the development of new supports, ligands, and scaffolds for catalysis.

Future Plans

- 1) Electro-active boxes, i.e. cages that undergo redox changes at mild potentials, allowing electrochemically switchable behavior. By changing the charge on the cluster, one could switch an ion-binding cage to a container that is no-longer ion binding. This approach could underpin ion-specific sensors as well as recyclable sequestrants for guest ions of interest to DOE nuclear research, e.g. $^{137}\text{Cs}^+$. Key to progress in this area are redox-active vertices, and promising advances are being made.
- 2) New, inexpensive vertices. To enable broader applications of the cage chemistry, we are interested in new kinds of vertices that might be more readily (easily, cheaply) prepared than say $[\text{CpM}(\text{CN})_3]^-$. The species $[\text{PhB}(\text{CN})_3]^-$ and analogues are being examined to this end.
- 3) Proton-box interactions. Organometallic cages, such as $\{[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_4\}$ can apparently undergo reversible tetraprotonation. Furthermore the boxes interact in an outer-sphere manner with alkyl ammonium ions ($R > \text{Me}$), without incorporation. Such interactions may open the way for the binding of boxes to ammonium-rich environments. The outer-sphere interaction of organic substrates and organometallics is an area of both fundamental and topical interest.
- 4) Catalytically active boxes. Species of the type $\{\text{Cs}_c[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\text{ML}_n\text{Cl}/\text{H}/\text{R}\}$ ($M = \text{Ti}, \text{V}, \text{Ru}, \text{etc.}$), derived from box-completion reactions, are potential catalysts.

Selected publications

1. "Structural and Mechanistic Studies on Ion Insertion into the Molecular Box $[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_4$ " Ramesh, M.; Rauchfuss, T. B. *J. Organometal. Chem.* **2004**, in press.
2. "Synthesis and Characterization of the Hexagonal Prismatic Cage $\{\text{THF}_c[\text{PhB}(\text{CN})_3]_6[\text{Cp}^*\text{Rh}]_6\}^{6+}$ " Kuhlman, M. L.; Yao, H.; Rauchfuss, T. B. submitted 2004.
3. "Hybrid Cluster-Cages Formed via Cyanometallate Condensation: $\text{CsCo}_4\text{Ru}_6\text{S}_2(\text{CN})_{12}$, $\text{Co}_4\text{Ru}_9\text{S}_6(\text{CN})_9$, and $\text{Rh}_4\text{Ru}_9\text{S}_6(\text{CN})_9$ Frameworks" Kuhlman, M. L.; Rauchfuss, T. B. *Inorg. Chem.* **2004**, *43*, 430-435.
4. "Tricyanometallate Building Blocks and Organometallic Cyanide Cages" Contakes, S. M.; Klausmeyer, K. K.; Rauchfuss, T. B. *Inorg. Synth.* **2004**, *34*, 00.
5. "Structural Chemistry of "Defect" Cyanometallate Boxes $\{\text{Cs}_c[(\text{C}_5\text{R}_5)\text{M}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}$ ($M = \text{Co}, \text{R} = \text{H}; M = \text{Rh}, \text{R} = \text{Me}$)" Kuhlman, M. L.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **2003**, *124*, 10084-92.
6. "Membership Rules for a Molecular Box: the Admission Process and Protection Provided to Guest Molecules", Hsu, S. C. N.; Ramesh, M.; Espenson, J. H.; Rauchfuss, T. B., *Angew. Chem. Int. Ed.* **2003**, *42*, 2663-6.
7. Systematic Assembly of the Double Molecular Boxes: $\{\text{Cs}_c[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}$ as a Tridentate Ligand", Contakes, S. M.; Kuhlman, M. L.; Ramesh, M.; Wilson, S. R.; Rauchfuss, T. B., *Proc. Nat. Acad. Sci.* **2002**, 4889-4893.

Controlling Structural Characteristics of Single-Walled Carbon Nanotubes (SWNT) by Tailoring Catalyst Composition and Synthesis Conditions

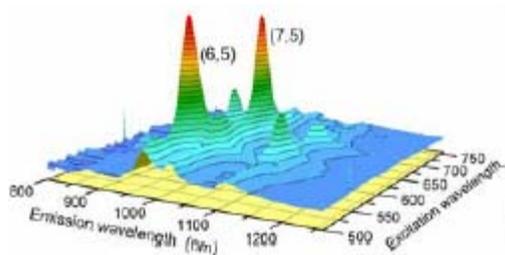
Students: Olga Rueda, Jose E. Herrera, Liang Zhang
 Collaborators: R. B. Weisman (Rice), L. Balzano (SWeNT), O. Matarredona (SWeNT), C. Lieber (Harvard), M. Strano (Illinois), P. Balbuena (South Carolina), Ming Zheng (Dupont)
 Contact: D. Resasco, 100 E. Boyd St, Norman OK 73019;
 phone: (405) 325-4370; Email: resasco@ou.edu
 web page: www.ou.edu/engineering/nanotube

Goal

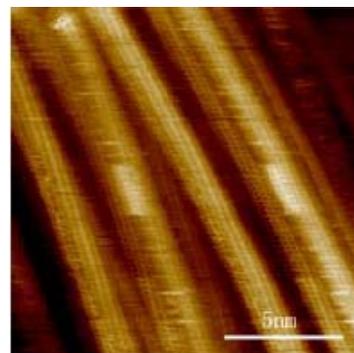
Advance the knowledge of the mechanisms responsible for the formation of single-walled carbon nanotubes to get control over their structural parameters (diameter and chirality). Through a detailed knowledge of the growth mechanism it will be possible to produce SWNT with tailored properties that are directly related to the structural parameters.

Recent Progress

Controlled Synthesis of SWNT: We have produced single-walled carbon nanotube samples with very narrow distribution of diameters and chiralities (n,m). By controlling the rate of metal agglomeration, it was possible to keep the nanotube diameter at $0.8 \text{ nm} \pm 0.05 \text{ nm}$. The narrowness of the diameter distribution of our samples was corroborated at Rice University. Spectrofluorimetric measurements that can be used to identify the (n,m) structure of all the semiconducting nanotubes present in the sample revealed that this sample comprised mostly the (6,5) and (7,5) nanotubes. This is the narrowest distribution of nanotube types ever produced. The diameter of these tubes is 0.75 and 0.83 nm, respectively. Noteworthy, not only the diameter distribution but the distribution of chiral angles is remarkably sharp. The angles of these two nanotubes are 27 and 24.5°, respectively; close to the chiral angle of the arm-chair nanotubes (30°). These conclusions were further confirmed by studies at Illinois (Raman) and Harvard (STM). The characteristics of the SWNT are illustrated below.



Spectrofluorimetric analysis of SWeNT (Left) and competing (Right) SWNT samples. Courtesy of Dr. Bruce Weisman at Rice



STM Image of SWNT produced by SWeNT™'s low temperature method. Courtesy of Dr. Charles Lieber at Harvard University

Incorporation of SWNT in matrices and study of their properties: With these high-quality, well-characterized SWNT materials we have expanded our studies to explore the interactions of nanotubes of narrow-diameter-distribution with surfactants, polymers, DNA and other organic molecules. We have investigated the electrical, mechanical, and thermal properties, as well as their field emission characteristics to determine relationships between the diameter and chirality of the nanotubes and their physical properties. In addition, we are investigating the use of these tailored SWNT as unique catalyst supports with high thermal and electrical conductivities for applications as fuel-cell electrodes.

(n,m) Speciation of SWNT: One of the most sought after capabilities that will open many opportunities for SWNT in nanoelectronics is to separate monodispersed samples of specific (n,m) characteristics. Only those SWNT for which n-m is a multiple of 3 are metallic and within the semiconducting, each (n,m) pair has a characteristic band gap and electronic response. To produce nanodevices it is important to be able to use specific (n,m) nanotubes. We have recently collaborated with researchers at Dupont who have been able to obtain from our SWNT monodispersed (6,5) nanotubes by selective interaction with DNA molecules of specific sequence (i.e. d(C,G)_q with q=16-40).

DOE Interest

Single-wall carbon nanotubes (SWNT) can be considered as one of the building blocks for nanoscale science and nanotechnology. They exhibit exceptional chemical and physical properties. Among the various synthesis methods investigated, the catalytic decomposition of carbon-containing molecules over solid catalysts appears as a promising technique since it has the potential to be scaled-up at a relatively low cost. A number of researchers have investigated different catalyst formulations and operating conditions. Yet, obtaining high quality SWNT has not been possible with this method. By focusing on tailoring the catalyst formulation and operating conditions, we have obtained high yields and selectivities to SWNT, and what is most remarkable, a high degree of control on nanotube diameter and chirality. Such control may open a vast number of opportunities for research on specific nanotubes structures. It may also generate technological applications in diverse fields such as nanoelectronics, nanosensors, field emission, fuel cell electrodes, tailored catalyst supports, etc.

Future Plans

We plan to continue improving our ability to control of producing nanotubes with specific (and varying) (n,m) structure by manipulating catalyst composition and reaction conditions. At the same time, we will continue investigating the reaction mechanisms responsible for the SWNT growth. To help us in this task, we are collaborating with a theorist who is conducting molecular dynamics and Monte Carlo simulations of the growth process. Our plan is provide her with detailed experimental kinetic parameters to compare with the theoretical calculations. At the same time, we plan to continue working on the dispersion, functionalization, and separation of SWNT with the ultimate goal of separating metallic from semiconducting nanotubes, and even further produce different monodispersed samples of individual (n,m) characteristics.

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Fundamental Studies on the High Temperature Kinetics for the Catalytic Combustion of Methane

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Goal

Understand the catalytic chemistry for the reaction of combustion of methane on palladium catalysts.

Recent Progress

We have completed most of the work using foils and single crystals of Pd. We have established the kinetics of methane combustion on the metal and oxide phases of Pd. The next step is to study the effect of the support. We have studied water-gas shift reactions also.

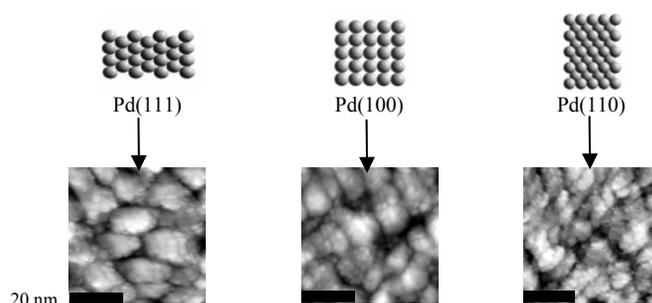
*Studies of water gas shift reactions*¹ The kinetic parameters for water-gas shift reaction on Cu based catalysts were measured under fuel reformer conditions for fuel cell applications (7% CO, 8.5% CO₂, 22 % H₂O, 37 % H₂, and 25% Ar) at 1 atm total pressure and temperature in the range of 200 °C. The rate per unit of Cu surface area at the stated concentrations was $0.8 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ at 200 °C. The overall reaction rate as a function of the forward rate (r_f) is $r = r_f(1-\beta)$, where $r_f = k_f[\text{CO}]^{0.8} \cdot [\text{H}_2\text{O}]^{0.8} \cdot [\text{CO}_2]^{-0.7} \cdot [\text{H}_2]^{-0.8}$, k_f is the forward rate constant, $\beta = ([\text{CO}_2] \cdot [\text{H}_2]) / (K \cdot [\text{CO}] \cdot [\text{H}_2\text{O}])$ is the approach to equilibrium, and K is the equilibrium constant for the water-gas shift reaction. This expression indicates a strong inhibition on the forward rate by H₂ and CO₂. When ceria was added to the catalyst, it decreased the Cu surface area and did not increase the rate per unit of Cu surface area, suggesting that ceria is not a promoter. The addition of ZnO did not increase the rate per unit of Cu surface area either. Thus, Cu is the active site for catalysis. It was proposed that the kinetics can be explained based on the “Redox” mechanism with $\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2^* + *$ as the rate-determining step.

*Increase of Pd surface area by O₂ oxidation*² By a combination of supported and model catalyst studies, surface science and TEM (in collaboration with Professor A.K. Datye) measurements we observed an increase in the Pd surface area by oxidation of Pd. This result is important in rationalizing the data in supported catalysts for the combustion of methane.

*Coverage of Palladium by Silicon Oxide during Reduction in H₂ and Complete Oxidation of Methane*³ The interaction between silica and palladium following complete

oxidation of methane or following reduction in H_2 was investigated on a polycrystalline palladium foil and on supported Pd/SiO₂ catalysts. During methane oxidation, oxidized silicon covered the palladium oxide surface as observed by TEM on Pd/SiO₂ catalysts and by XPS on palladium foil. On the Pd foil, the source of silica was a silicon impurity, common on bulk metal samples. The migration of oxidized silicon onto PdO deactivated the catalysts by blocking the active sites for methane oxidation. Silicon oxide overlayers were also observed covering the Pd surface after reduction of Pd/SiO₂ by H_2 at 923 K.

*The rate of methane combustion is not sensitive to the structure of the catalyst*⁴ We have measured the rates and kinetics on Pd(111), Pd(100), Pd(110), and Pd foil. Based on the constancy of rates and the similar structure of the catalysts after reaction, we concluded that the kinetics is not sensitive to the structure of the catalyst.



STM pictures of single crystals after combustion reaction

*Rates of reaction at high temperatures*⁵ We measured the kinetics at high temperatures using non-porous model catalysts. These data will be benchmark values for catalytic combustion at high temperature. Under the reaction conditions used, supported porous catalysts would have been limited by heat and mass transport limitations. The high temperature conditions are important in practical applications. We have found that the turnover rate for oxidation on PdO is 10 times higher than on Pd at 907 K. Water inhibition is not present at the higher temperatures.

DOE Interest

Catalytic combustion can generate energy with minimum production of NO_x. Palladium is the most active metal for the catalytic combustion of methane. The understanding of the catalytic chemistry for this process will help in the design of commercial systems.

Future Plans

Preparation of flat oxide supports For the preparation of model catalyst we will need flat alumina and zirconia supports. We are constructing an atomic layer epitaxy device to prepare thin (50 layers) of alumina and zirconia over Si(100). It is imperative that the oxide be atomically flat so we can distinguish the metal clusters by AFM.

Preparation of metal clusters We will prepare metal clusters by spin coating and by evaporation. The aim is to prepare clusters in the range 1-10 nm with a size distribution of 1 nm.

Specific studies of metal clusters on oxides:

- Does the PdO interact strongly with the support (alumina or zirconia) causing it to lose activity?
- What is the cause for deactivation of catalysts?
- How does the support (ZrO_2 and Al_2O_3) affect the shape and morphology of metal particles? How do structural defects on the support affect particle uniformity, dispersion?
- How does the support (ZrO_2 and Al_2O_3) affect the thermal stability of Pd particles? How does the rate of sintering change depending on environment: vacuum, O_2 , steam, CO_2 , and reaction conditions?
- How do the shape and morphology of metal particles change under reaction conditions depending on the nature of the support? How do these changes correlate with catalytic activity?

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DeNOx and DeSOx Reactions on Oxide and Carbide Surfaces: Experimental and Theoretical Studies

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Abstract

In this talk examples will be presented that illustrate the use of synchrotron-based photoemission, x-ray absorption spectroscopy, and time-resolved x-ray diffraction in the characterization of catalytic systems that involve metal oxides and metal carbides [1-5]. Density-functional calculations were used to help in the interpretation of experimental results and the prediction of chemical behavior [6]. Nowadays a major effort in environmental catalysis is focused on reducing the content of sulfur and nitrogen oxides in the atmosphere. NOx and SOx species are common air pollutants produced during the combustion of fuels in automotive engines, factories and power plants. Sulfur dioxide results from the burning of S-containing impurities present in all oil and coal derived fuels. On the other hand, nitrogen oxides are produced by the thermal fixation and oxidation of nitrogen in combustion operations that use air as an oxidant. In our industrial society, there is a clear need to develop methods with a high efficiency for the removal or destruction of SOx (DeSOx processes) and NOx (DeNOx processes) compounds. Studies have been carried out to investigate the fundamental chemistry of sulfur and nitrogen dioxides on single-crystal surfaces and bulk powders of several oxides and carbides. We have found that metal-doped MgO and carbides of titanium and molybdenum are very useful for the control of environmental pollution. These studies reveal several aspects that can be useful for facilitating the breaking of S-O and N-O bonds and enhancing the efficiency of DeSOx and DeNOx catalysts [1-6].

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Project : Chemical Interactions in Multimetal/Zeolite Catalysts

Project Code: DE FG02-87ERA 13654

Principal Investigators: Wolfgang M.H. Sachtler,

Abstract

This two-year project has led to a significant improvement in the fundamental understanding of the catalytic action of zeolite-supported redox catalysts. Fe/MFI catalysts have been studied for two prototype reactions:

- (1) One step oxidation of benzene to phenol with N_2O as the oxidant
- (2) Reduction of nitrogen oxides to N_2 with hydrocarbons.

The mechanism has been studied for both prototypes and the crucial active sites have been identified by EXAFS, TPR, FTIR and isotopic labeling.

Chemical vapor deposition has been used to obtain catalysts with high Fe content

Hydrothermal synthesis followed by dealumination was used to obtain catalysts with very low Fe content in accessible positions.. To discern the catalytic action of Fe sites from those of acid sites, selective poisoning of Fe by H_2S was used

The most important conclusion of this research is that Fe-oxo ions are the active sites in both prototype reactions.

For benzene oxidation to phenol highest activity is achieved with **mono-nuclear** Fe-oxo-ions ;

For NO_x reduction to N_2 , **dinuclear ions**, such as $[HO-Fe-OH]^{2+}$ are active sites.

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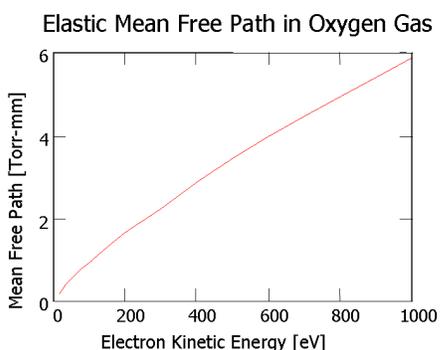
**New instrumentation bridges the “pressure gap” in catalysis studies:
Fundamental studies of catalyst surfaces under relevant pressure conditions**

Miquel Salmeron, D. F. Ogletree, Hendrick Bluhm, Eleonora Hebenstreit, Felix Requejo,
Hongjian Wang and Guido Ketteler
Lawrence Berkeley National Laboratory. Berkeley, CA. USA

Catalytic phenomena require the investigation of surfaces in contact with gases under pressures ranging from millibars to several atmospheres. This applies also to fields such as environmental chemistry, electrochemistry, and biology. The investigation of those phenomena calls for experimental techniques that are not only surface sensitive, but also can operate under elevated pressures.

Several surface science methods fulfill these requirements and can provide information of the structure under equilibrium conditions with the gas phase. Chief among them are:

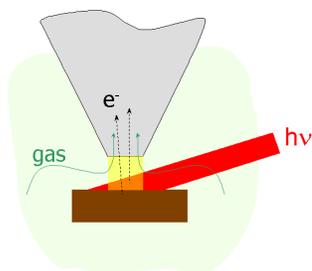
- 1) Scanning probe methods, which can reveal atomic scale topographic and spectroscopic details of a surface and can operate at gas-liquid and liquid-solid interfaces [1].
- 2) Optical methods like sum-frequency generation (SFG), which owe their surface sensitive to selection rules that requires the absence of inversion symmetry. For centro-symmetric media this happens precisely at interfaces. In this manner the gas phase does not contribute directly to the signal. [2,3].
- 3) Photoelectron spectroscopies (PES), including XPS (or ESCA), X-ray absorption and emission (XAS, XES), etc. are widely used for studies of the electronic structure of surfaces. They provide information about surface elemental composition and chemical bonding. Although traditionally PES has been used under high vacuum conditions, today, thanks to developments initiated at the Lawrence Berkeley Laboratory, it is



possible today to perform studies under high pressure⁴. Because of its novelty, high-pressure PES (HPPES) is the subject of the current presentation.

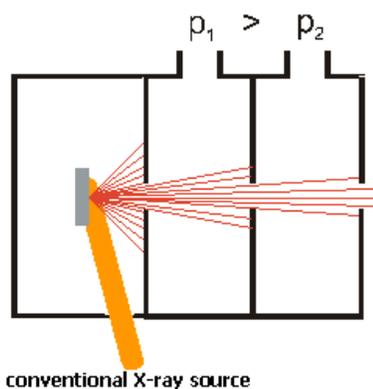
The main problem with PES is that electrons are strongly attenuated by collisions with the gas phase, to such an extent that the mean free path of 500 eV

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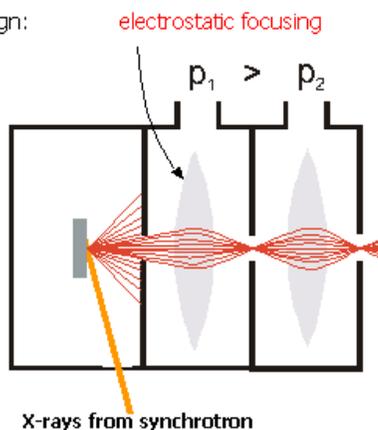


electrons in 4 torr of gas is about 1 mm. In our instrument the sample, in the reaction chamber, is located at a distance of the about 1 mm from an aperture (see diagram on the left) that communicates with another chamber pumped to a vacuum that is 2 to 3 orders of magnitude lower. For example if the pressure in the reaction chamber is 1 Torr, the pressure in the second chamber is about 10^{-2} torr. Traditional differential pumping schemes collect only electrons in a very small solid angle (line-of-site). In our method we used electrostatic focusing, such that the orifices separating the differentially pumped chambers are part of a lens system and are located at the focal points of several electrostatic lenses. Using this method we increased the

Previous designs:



New design:



collection efficiency by 3 orders of magnitude.

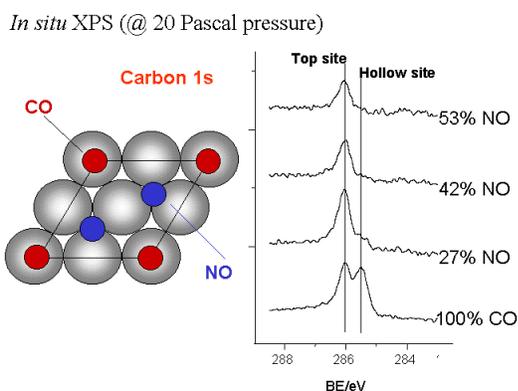
Several benefits derive from this novel instrument, among them:

- Possibility to perform PES studies at high pressures, of up to 10-20 Torr at present.
- Gas flow and variable sample temperature, from -100°C to 600°C (higher and lower values possible).
- Elimination of charging problems in insulators, due to neutralization by ions in the gas phase generated by the incoming X-ray beam.
- Spectra of gas molecules located between sample and aperture excited by the incoming X-ray beam are obtained, in addition to that of the surface species. This makes possible to detect reactant and products a few tenths of mm from the catalyst surface.
- Finally, there is an exciting and still an unexploited feature of this instrument. This is the possibility to detect hot gas species desorbing from the surface before they

collide with other molecules in the gas phase or with the walls. These “hot” molecules carry information of the energetics and dynamics of the reaction. They could be analyzed downstream of the molecular jet escaping through the first aperture by mass spectrometry and time of flight measurements. Crossed with a Laser beam, it should be possible to excite molecules through single or multiple photon absorptions for studies of the internal excited modes.

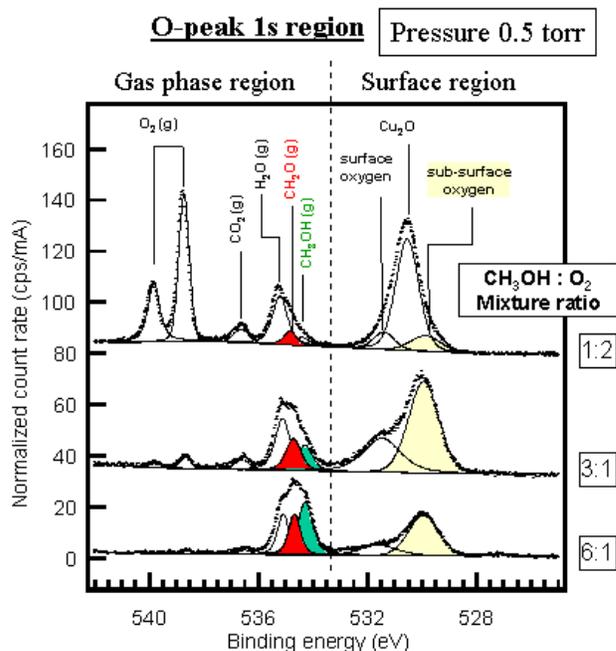
We give here examples of studies we carried out over the last 3 years:

- a) Determination of the structure of the ice surface through its melting transition. XAS was used to determine the amount of water molecules with unsaturated H-bonds. This can be detected by the increased X-ray absorption at energies near the absorption edge of oxygen (from the O1s to the H₂O 4a₁-derived orbitals) [5].
- b) CO+NO equilibrium structures over Rh(111). XPS of C, N and O was used to determine the adsorption site of CO and NO molecules in equilibrium with mixed gases in the torr pressure range. As the NO partial pressure increased it displaced CO from hollow sites first and from top sites at higher pressure [6].



- c) Partial oxidation reaction of methanol to formaldehyde on Cu catalyst. The intensity of the gas phase products (H₂O, CO₂ and CH₂O) was followed as a function of substrate temperature and reactant pressure. It was shown that there is a linear correlation between the catalytic activity of the sample and the presence of a sub-surface oxygen species that can only be observed *in situ* [7].
- d) Structure and equilibrium phase diagram of PdO formed over Pd(111) under high O₂ pressure.

Cu-catalyzed oxidation of methanol



At present there exist three HPPES instruments of this kind in the world, two at the Advanced Light Source in Berkeley, the third one at BESSY, Berlin. The first was built in 1999 in line 9.3.2 of the ALS. This was followed by an improved second generation of instruments built in a joint collaboration between Berkeley and the Fritz-Haber Institut in Berlin, Germany. The second Berkeley instrument is part of the Molecular Environmental Science beam line 11.0.2. At the ALS the HPPES instruments are receiving numerous user applications, both for

catalysis and for environmental studies projects. While at present only the prototype instrument is open to the general public, the new instrument is expected to be available in a few months.

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Homogeneous-Heterogeneous Reactions: Thermal and Chemical Coupling

DE-FG02-88ER13878

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Hydrogen from Ethanol

We show that ethanol can be converted directly into H₂ with >80% selectivity and >95% conversion by catalytic partial oxidation at contact times <5 milliseconds over Rh and Rh-Ce catalysts. This can be made to occur by rapid vaporization and mixing with air using an automotive fuel injector at temperatures sufficiently low and times sufficiently fast that homogeneous reactions producing acetaldehyde, ethylene, and total combustion products can be minimized. The reaction can also be run with or without added water to increase H₂ and optimize operating conditions. This process has great potential for low cost H₂ generation in fuel cells for small portable applications where liquid fuel storage is essential and where systems must be simple, robust, and capable of repeated startup and shutdown. We show that carbohydrates can be converted economically into hydrogen at efficiencies exceeding 80% by the combination of fermentation to produce ethanol and millisecond reactors to produce H₂. This provides a convenient, transportable, liquid fuel for efficient generation of electricity from biomass.

Olefins from Biodiesel

The methyl esters derived from soy oil can be converted into olefins with up to 80% yield at high conversions by partial oxidation with air on a Rh-Ce catalyst in an autothermal reactor at residence times of ~5 milliseconds. These results are compared to the corresponding reactions of *n*-hexadecane which is a related fossil fuel used in steam cracking of naphthas to produce olefins. At lower C/O ratios, biodiesel also produces up to 90% yield of H₂. Yields of both lower olefins and H₂ are nearly identical with both the ester and alkane, even though the former has double bonds that might be expected to lead to carbon formation.

The results suggest that the process is initiated by surface reactions near the front face of the catalyst which consumes all of the O₂. Olefins are formed primarily by homogeneous pyrolysis later in the catalyst, and rapid quenching within 20 milliseconds prevents secondary reactions that make many products. While hexadecane forms up to 80% *n*-olefins at even higher C/O, biodiesel forms comparable amounts of smaller olefinic esters and *n*-olefins containing 8 to 10 carbon atoms. Evidently the attack of the esters occurs preferentially near the double bond location on the long chain fatty acid producing these fragments.

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Catalysts for the Living Polymerization of Olefins

Recent Students: Mehrkhodavandi, P.; Adamchuk, J.; Pryor, L. L.; Gabert, A.; Tonzetich, Z. J.; Schrodi, Y.

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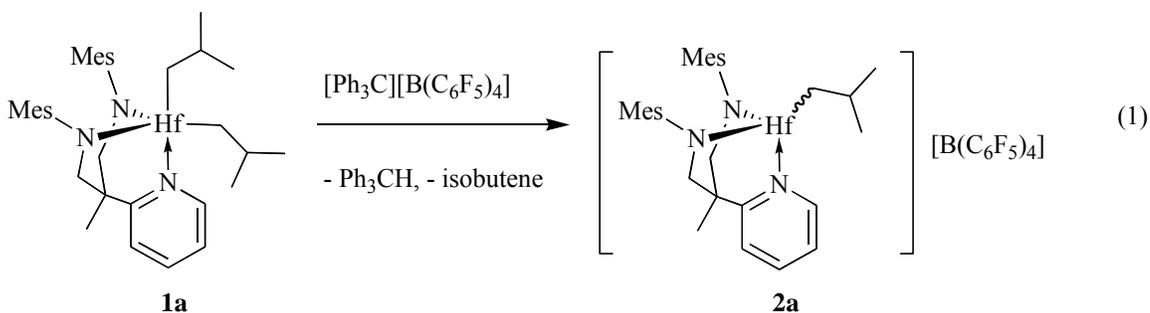
Goals

The overall research goals are to explore the chemistry of zirconium and hafnium complexes that contain diamido/donor ligands in order to develop new olefin polymerization catalysts, and in particular, living polymerization catalysts. Ultimately we also hope to control the structure of the polyolefins prepared by well-defined catalysts through the use of asymmetric ligands that would lead to isotactic structures, and to polymerize olefins that contain a protected functionality.

Recent Progress

Recently we have focussed on (i) kinetic and mechanistic studies of the polymerization of 1-hexene by zirconium and hafnium catalysts that contain a [(MesitylNCH₂)₂C(CH₃)(2-C₅H₄N)]²⁻ ([MesNpy]²⁻) ligand (see **1a** in eq 1); (ii) catalysts that contain related [(2,6-X₂C₆H₃NCH₂)₂C(CH₃)(2-C₅H₄N)]²⁻ (X = Cl or F) ligands; and (iii) zirconium and hafnium catalysts that contain an asymmetric diamido/donor ligand in an attempt to effect stereocontrol of 1-hexene polymerization.

We have found that {[MesNpy]Hf(isobutyl)}⁺ initiators (**2a**, equation 1) are essentially perfectly living catalysts for polymerization of up to 600 equivalents of 1-hexene



at 0 °C in bromobenzene or chlorobenzene, and that certain bulky bases (diisopropylether, tributylamine, and triethylamine) are well-behaved inhibitors of 1-hexene polymerization. Dimethylaniline and diphenylether are not well-behaved inhibitors as a consequence of deactivation of the cationic alkyl by CH activation in the phenyl ring adjacent to the basic functionality.

Related catalysts that contain [Ar_{X2}Npy]²⁻ ligands in which the aryl ring (Ar_{X2}) contains ortho halides (X = Cl or F) are progressively worse catalysts than the mesityl-substituted species; they react more slowly with 1-hexene and they are more prone to β hydride elimination processes. In general, ortho-fluorides were found to interact with the metal, even in five-

coordinate neutral dialkyl precursors (Figure 1). Attempts to prepare some $[\text{Ar}_{\text{F}_2}\text{Npy}]^{2-}$ complexes resulted in exchange of one or two dimethylamino groups with one or two ortho fluorides. Activation of dimethyl species with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in bromobenzene led initially to the formation of dimeric monocations such as $\{[\text{Ar}_{\text{X}_2}\text{Npy}]_2\text{M}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$, which are inactive for polymerization of 1-hexene. The $\{[\text{Ar}_{\text{X}_2}\text{Npy}]_2\text{M}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ compounds react further with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to give $\{[\text{Ar}_{\text{X}_2}\text{Npy}]\text{MMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ species, which are active for polymerization of 1-hexene. The living characteristics of the polymerization therefore are compromised to varying degrees when ortho halides are employed in the aryl ligands ($\text{F} > \text{Cl}$).

Similar studies have been completed with diamido/donor ligands of the type $[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NMe}]^{2-}$. We found that Zr systems of this type were well-behaved, but the Hf systems were plagued by relatively slow rates of initiation relative to propagation.

Most recently we have completed a study of Zr and Hf complexes that contain two new unsymmetric diamido-N-donor ligands, H_2A and H_2B . The Zr and Hf complexes that have

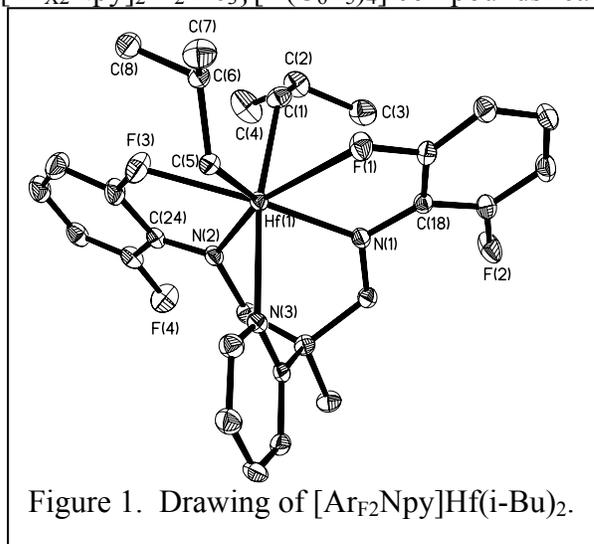
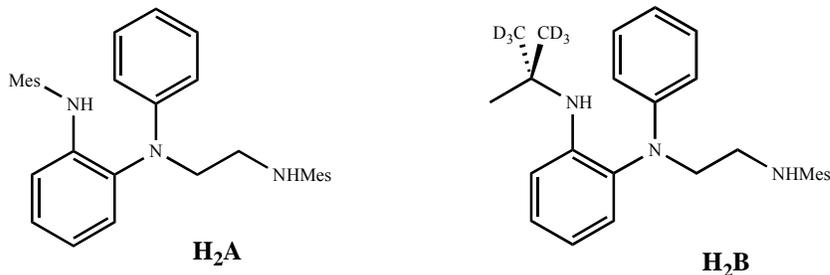


Figure 1. Drawing of $[\text{Ar}_{\text{F}_2}\text{Npy}]\text{Hf}(\text{i-Bu})_2$.



been isolated include $[\text{A}]\text{MX}_2$ ($\text{M} = \text{Zr}$ or Hf , $\text{X} = \text{NMe}_2$, Cl , or Me) and $[\text{B}]\text{MX}_2$ ($\text{M} = \text{Zr}$ or Hf , $\text{X} = \text{NMe}_2$, Cl , Me). Methyl abstraction in $[\text{A}]\text{MMe}_2$ ($\text{M} = \text{Zr}$ or Hf) with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ gives rise to cationic complexes which are active initiators for the polymerization of 1-hexene. Similar activation of $[\text{B}]\text{MMe}_2$ ($\text{M} = \text{Zr}$ or Hf) species gives rise to dimeric monocations that eventually break-up and react further to yield cationic monomethyl species. Unfortunately, in all cases the poly[1-hexene] produced was found to be atactic. It is postulated that the central donor can dissociate from the metal, invert, and reassociate in order to produce the opposite enantiomer at a rate that is competitive with insertion into the metal-alkyl bond.

DOE Interest

The consequences of this work are expected to be the synthesis of sophisticated or "smart" new materials from ordinary and functionalized olefins in high yield in the form of diblock or triblock copolymers.

Future Plans

Future research will focus on C₁ ligands related to those we have investigated to date that contain a racemic chiral auxiliary and on new types of racemic C₂ symmetric diamido ligands.

Publications (2001-present)

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3. "A Kinetic Investigation of the Polymerization of 1-Hexene by the {[t-BuNON]ZrMe}[B(C₆F₅)₄] Initiator" Goodman, J. T.; Schrock, R. R. *Organometallics* **2001**, *20*, 5205.
4. "Synthesis and Structures of Zirconium and Hafnium Alkyl Complexes that Contain [H₃CC(2-C₅H₄N)(CH₂NAr)₂]²⁻ ([ArNpy]²⁻; Ar = Mesityl or Triisopropylphenyl) Ligands" Mehrkhodavandi, P.; Schrock, R. R.; Bonitatebus, P. J. Jr. *Organometallics* **2002**, *21*, 5785.
5. "Living Polymerization of 1-Hexene by Cationic Zirconium and Hafnium Complexes that Contain a Diamido/Donor Ligand of the Type [H₃CC(2-C₅H₄N)(CH₂NMesityl)₂]²⁻. A Comparison of Methyl and iso-Butyl Initiators." Mehrkhodavandi, P.; Schrock, R. R.; Pryor, L. L. *Organometallics* **2003**, *22*, 4569.
6. "Zirconium and Hafnium Complexes that Contain the Electron-Withdrawing Diamido/Donor Ligands, [(2,6-X₂C₆H₃NCH₂)₂C(2-C₅H₄N)(CH₃)]²⁻ (X = Cl or F). An Evaluation of the Role of ortho-Halides in 1-Hexene Polymerization." Schrock, R. R.; Adamchuk, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2003**, *22*, 5079.
7. "Synthesis, Characterization, and Polymerization Behavior of Zirconium and Hafnium Complexes that Contain Unsymmetric Diamido-N-Donor Ligands" Tonzetich, Z. J.; Lu, C. C.; Schrock, R. R.; Hock, A. S.; Bonitatebus, P. J., Jr. *Organometallics*, submitted.

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High Temperature Chemistry of Aromatic Hydrocarbons

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Collaborators: de Meijere, A.; Diederich, F.; Guldi, D.; Hirsch, A.; Jennekens, L. W.; Petrukhina, M. A.; Rabinovitz, M.; Schleyer, P. v. R.; Willner, I.; Wudl, F.

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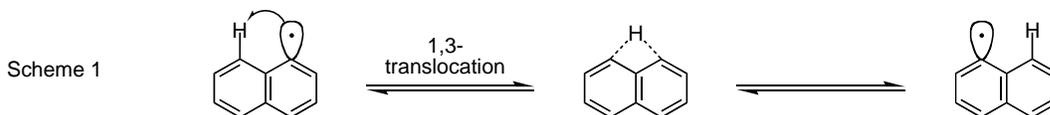
Goal

The primary goal of this research is to uncover all the principal reaction channels available to polycyclic aromatic hydrocarbons (PAHs) at high temperatures in the gas phase and to establish the factors that determine which channels will be followed in varying circumstances. New structure-property relationships for PAHs are also studied.

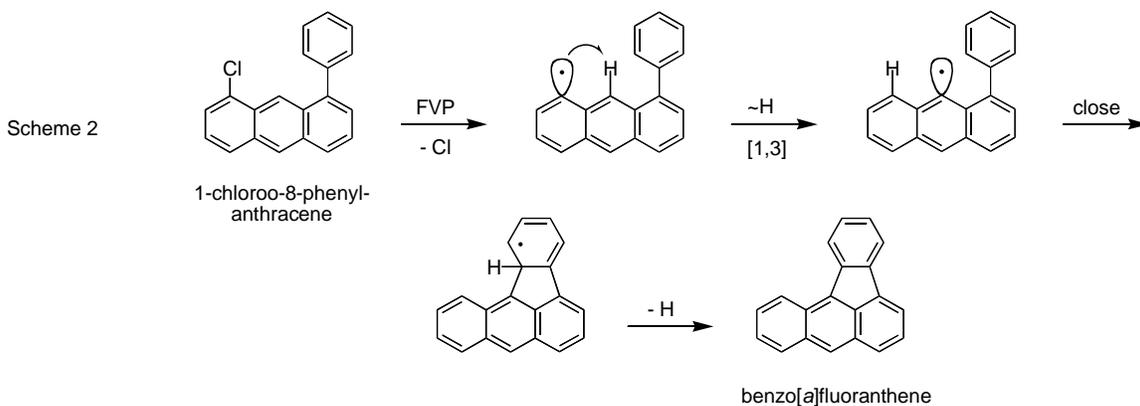
Recent Progress

The latest results from three representative projects are summarized here (all still unpublished).

1,3-Translocation of hydrogen atoms in aryl radicals. Earlier in this project, we predicted, demonstrated, and published the first unambiguous example of a hydrogen atom 1,2-shift in an aryl radical at high temperatures in the gas phase [*JACS* **1999**, *121*, 5444]. Our subsequent calculations have predicted that a hydrogen atom should also be able to “jump,” with comparable facility, from one ring to the next by a 1,3-translocation to a *peri*-radical center (Scheme 1).

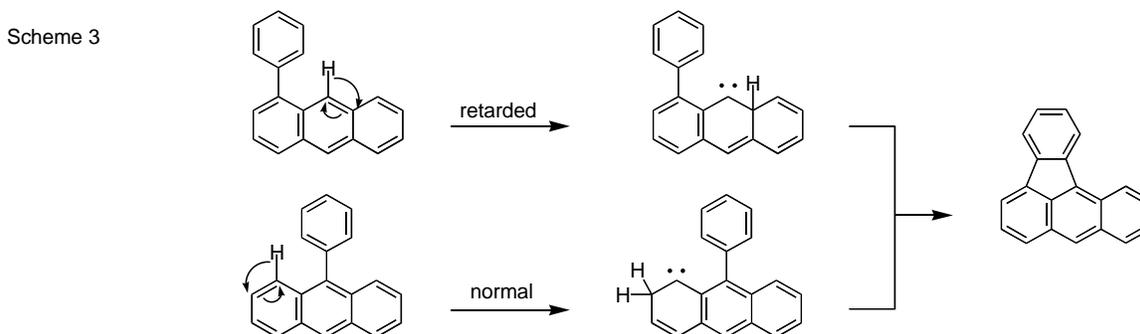


Since this process would be degenerate in the 1-naphthyl radical, we have examined a less symmetrical system. Structural features were incorporated to provide an opportunity for the rearranged radical (but not the starting radical) to close a new ring and aromatize to an easily identifiable product. As shown in Scheme 2, flash vacuum pyrolysis (FVP) of 1-chloro-8-phenylanthracene gives benzo[*a*]fluoranthene, presumably by the predicted 1,3-translocation of a *peri*-hydrogen atom to the radical center created by homolysis of the C–Cl bond.



Control experiments show that very little benzo[*a*]fluoranthene is formed by FVP of the corresponding unchlorinated hydrocarbon, 1-phenylanthracene. Deuterium labeling studies are now underway to prove that the hydrogen atom attached at the position vacated by the chlorine atom is the one that originated at C(9).

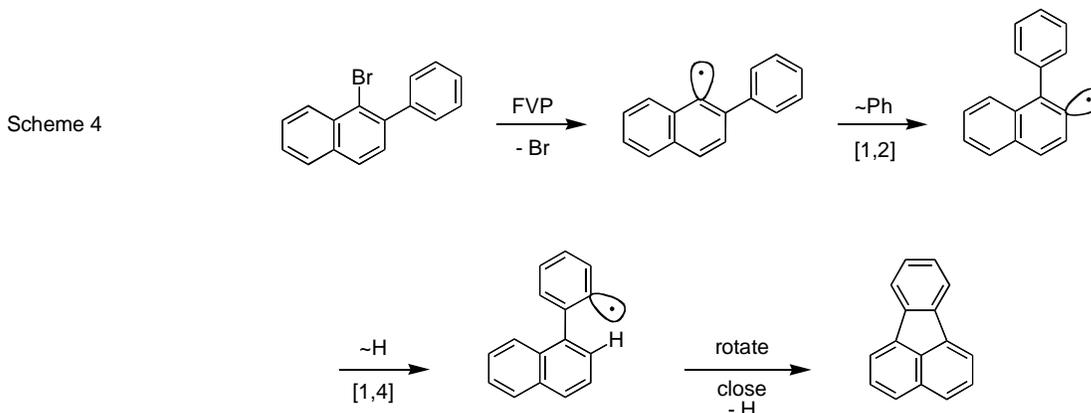
Cyclodehydrogenations to form 5-membered rings. At high temperatures in the gas phase, PAHs bearing peripheral phenyl groups commonly suffer cyclodehydrogenations to produce more highly condensed PAHs. The mechanism(s) by which these cyclizations occur and the hydrogens are lost, however, are not well established. We have previously shown that hydrogen atoms on the rims of intact PAHs can shift reversibly to *ortho*-positions, thereby generating transient carbenes [*JACS* **1991**, *113*, 9692], and it seems reasonable that such hydrogen shifts could trigger many cyclodehydrogenations. In agreement with this hypothesis, we have found that the thermal cyclodehydrogenation of 1-phenylanthracene to benzo[*a*]fluoranthene is significantly slower than formation of the same product by thermal cyclodehydrogenation of 9-phenylanthracene, under the same conditions (Scheme 3).



Generation of the proposed carbene intermediate by a hydrogen shift in the former case would simultaneously disrupt the aromaticity of two rings, whereas the same reaction in the latter case would disrupt the aromaticity of only one ring, which should be energetically less costly. The observed rate difference is difficult to explain by other mechanisms, *e.g.*, cyclization of an aryl radical that results from loss of a hydrogen atom.

Phenyl group 1,2-shifts in aryl radicals. To determine whether or not a phenyl group can migrate along the rim of a PAH radical, we have generated the 2-phenyl-1-naphthyl radical in the gas phase by FVP of 2-phenyl-1-bromonaphthalene (Scheme 4).

As predicted, a 1,2-shift moves the phenyl group over next to the ring junction where, following 1,4-translocation of a hydrogen atom, the radical cyclizes to form fluoranthene. The isolation of fluoranthene in this experiment constitutes the first good evidence that 1,2-shifts of phenyl groups are feasible in aryl radicals at high temperatures (Scheme 4).



DOE Interest

An understanding of the fundamental molecular transformations, rearrangements, and interconversions of PAHs at high temperatures in the gas phase, as revealed by careful studies on small, well-designed, molecular systems, provides insights into the underlying chemistry of many processes that are more complex and critically important to life in the twenty-first century, such as the generation of energy by the combustion of fossil fuels, the uncatalyzed gasification and liquefaction of coal, the production of fullerenes in fuel-rich flames, and the formation of soot and carcinogenic pollutants in smoke. The rational control of any of these processes, whether it be the optimization of a desirable process or the minimization of an undesirable one, requires a clear knowledge of the basic chemistry that governs the fate of the species involved.

Future Plans

We plan to repeat our experiments on the 1,3-translocation of hydrogen atoms in aryl radicals (Scheme 2) using a deuterated starting material, to demonstrate that the hydrogen originating on the central ring ends up at the site vacated by the chlorine atom. Further studies on thermal cyclodehydrogenations to form 5-membered rings are planned, and we also plan to test the generality of phenyl group 1,2-shifts in aryl radicals. New studies will be initiated on thermal cyclodehydrogenations to form 6-membered rings and on the mechanism by which phenyl groups are lost at high temperatures.

Publications (last 2 years)

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- 2) "Stability and Aromaticity of the Cyclopenta-Fused Pyrene Congeners," Havenith, R. W. A.; Jiao, H.; Jenneskens, L. W.; van Lenthe, J. H.; Sarobe, M.; Schleyer, P. v. R.; Kataoka, M.; Nacula, A.; Scott, L. T. *J. Am. Chem. Soc.* **2002**, 124, 2363-2370.
- 3) "From Bifluorenylidine Dianion to Dibenzo[*g,p*]chrysene Dianion: Sensitivity of Anisotropy Changes to Bonding Structure," Shenhar, R.; Beust, R.; Hagen, S.; Bronstein, H. E.; Willner, I.; Scott, L. T.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **2002**, 449-454.
- 4) "An Insight into the Aromaticity of Fullerene Anions: Experimental Evidence for Diamagnetic Ring Currents in the Five-Membered Rings of C₆₀⁶⁻ and C₇₀⁶⁻." Sternfeld, T.; Thilgen, C.; Hoffman, R. E.; Heras, M. d. R. C.; Diederich, F.; Wudl, F.; Scott, L. T.; Mack, J.; Rabinovitz, M. *J. Am. Chem. Soc.* **2002**, 124, 5734-5738.
- 5) "A Four-Step, Alternating Reductive Dimerization/Bond-Cleavage of Indenocorannulene," Aprahamian, I.; Hoffman, R. E.; Sheradsky, T.; Preda, D. V.; Bancu, M.; Scott, L. T.; Rabinovitz, M. *Angew. Chem. Int. Ed. Engl.* **2002**, 41, 1712-1715.
- 6) "Transition Metal Complexes of an Open Geodesic Polyarene," Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. *Angew. Chem. Int. Ed. Engl.* **2003**, 42, 3375-3379 (highlighted on the cover).
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- 9) "Methods for the Chemical Synthesis of Fullerenes," Scott, L. T. *Angew. Chemie*, an extensive review submitted at the request of the editor.

Design of olefin metathesis catalysts for unfunctionalized and functionalized olefins

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Goal

Olefin metathesis is a powerful method for forming new C=C bonds. However, the full potential of heterogeneous metathesis catalysts has yet to be exploited, because supported metal oxides show low rates of activation and rapid deactivation. The goal of our project is to create fundamental knowledge about how carbene active sites are formed and how they are lost in supported metal oxide catalysts, in order to increase metathesis activity and impart functional group tolerance.

Recent Progress

A well-defined organometallic complex, methyltrioxorhenium (CH_3ReO_3 , MTO), generates metathesis activity without high temperature activation (calcination) when supported on certain inorganic oxides, although it is inactive in solution. The mechanisms by which MTO is grafted and activated and the nature of the MTO-support interaction are unknown, but may be directly relevant to the problems of inorganic metathesis catalysts.

Methyltrioxorhenium is unreactive towards the mildly acidic surface hydroxyls of silica. It does chemisorb onto the surfaces of niobia and silica-alumina powders, to give supported catalysts which are different in their electronic structure. Niobic acid, transformed to niobia by calcination at 450°C , turns purple at room temperature in the presence of white MTO. Grafting MTO onto silica-alumina (13 wt.% alumina, $500\text{ m}^2/\text{g}$) leads to a color change of the solid from white to orange when silica-alumina is not subjected to thermal treatment, or dark yellow-brown when the solid is pretreated under vacuum at 450°C . The color change may be associated with oxidation state or coordination sphere changes at Re.

The uptake of Re is self-limiting during gas phase grafting, yet stabilizes at values (ca. 15 wt.%) higher than might be expected for a deposition reaction limited by the availability of surface hydroxyl sites. Indeed, the hydroxyl sites appear not to be the point of attachment for MTO, since methane is not generated and the ^1H MAS NMR spectrum of MTO/silica-alumina shows a strong signal due to unreacted $\equiv\text{SiOH}$ at 1.7 ppm, in addition to signals for the methyl ligand (2.7 ppm) and adsorbed water (5.3 ppm), Figure 1a. The high loading of MTO suggests oxide-induced polymerization, similar to the formation of poly-MTO observed by Herrmann in acidic aqueous solution.

^{13}C CP/MAS NMR with natural abundance ^{13}C indicates the presence of multiple carbon sites for MTO grafted onto silica-alumina, Figure 2b. Our computational studies are aimed at understanding this complexity by developing models for the binding of MTO to oxide supports. We are simultaneously investigating the energy of the

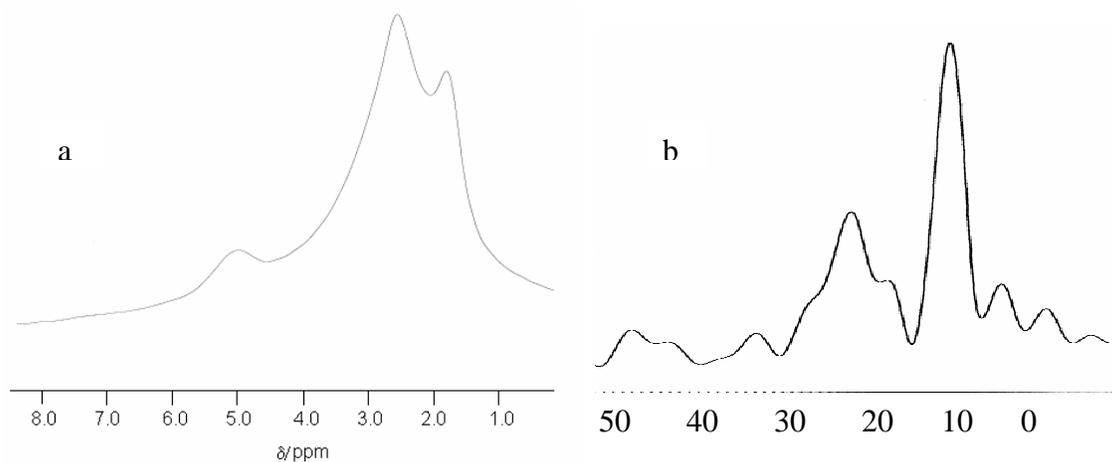


FIGURE 1. NMR of MTO on silica-alumina: (a) ^1H MAS NMR (hydroxyls partially D-exchanged); (b) ^{13}C CP/MAS NMR; 24 hour data acquisition with spinning at 10 kHz.

methylidene tautomer, a potential initiating site. Using clusters to represent silica, silica-alumina and niobia surfaces, energy minimizations have been carried out (Gaussian98) using DFT methods and various basis sets to investigate MTO and its tautomer interacting with the oxide surface via two O atoms, Figure 2. In our preliminary studies, we consistently find a significant lowering of the energy of the supported tautomer relative to adsorbed MTO, by comparison to the unsupported molecules. More sophisticated models for the silica-alumina and niobia surfaces are currently being developed.

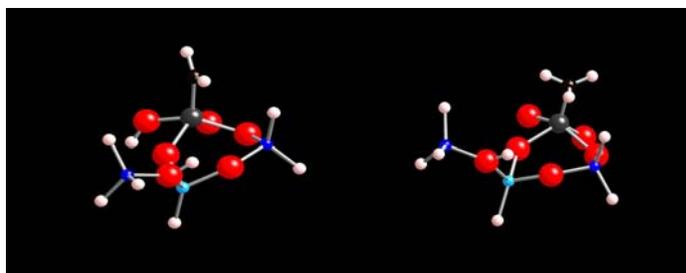


FIGURE 2. Cluster models of MTO (right) and the methylidene tautomer (left) on silica-alumina. The difference in energy between the two structures is 46 kJ/mol, compared with 108 kJ/mol for the isolated molecules.

Frequency calculations for MTO on all-silica and silica-alumina clusters show a dramatic decrease (by as much as 100 cm^{-1}) of the methyl torsional frequencies relative to the bulk solid. This result has been confirmed qualitatively by vibrational spectroscopy using Inelastic Neutron Scattering (INS), Figure 3. Note the large number of bands in the region below 250 cm^{-1} for surface-grafted MTO, which not only confirm the lowering of the methyl torsional frequency, but also suggest the existence of multiple MTO species on the surface. INS is particularly sensitive to low-frequency motions involving H atoms of adsorbed or bound species. Furthermore, such spectra can readily be calculated (Figure 3b) from the frequencies and amplitudes obtained for our models. We expect to be able to derive information on the binding of MTO by an iterative comparison of observed INS spectra and those calculated from different structural models.

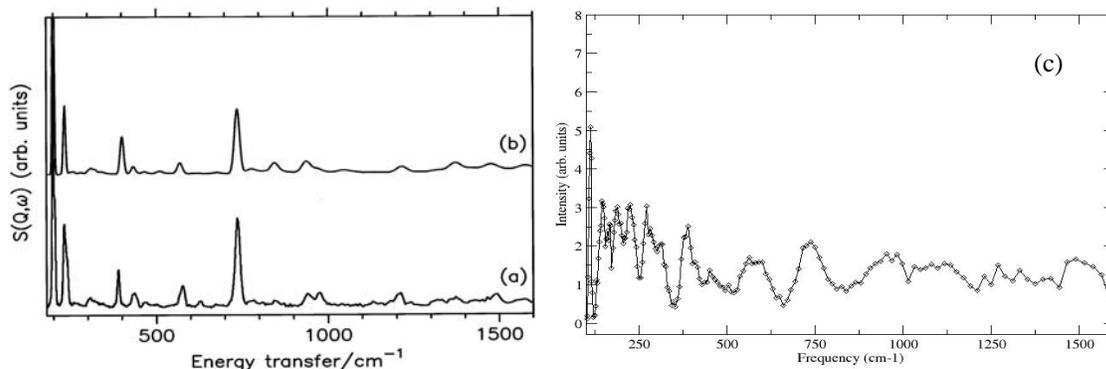


FIGURE 3. INS spectra of MTO (observed (a) and calculated (b)) and MTO grafted on silica-alumina. Spectrum (c) recorded at 20 K. (Left: S.F. Parker and H. Herman, *Spec Acta* A56 (2000) 1123)

We are also investigating the structure of grafted MTO using X-ray absorption spectroscopy, Figure 4. Analysis of the EXAFS is underway to provide information about the coordination environment of Re and bond distances, which will allow us to perform more definitive calculations.

DOE Interest

Supported perrhenate catalysts are of particular interest for olefin metathesis, because they are active at much lower temperatures and are more functional group-tolerant than either Mo- or W-based catalysts. These properties make them potentially useful in liquid phase reactions involving biorenewable feedstocks, such as seed oils.

Future Plans

We plan to mitigate deactivation by attaching rhenium to silica or silica/alumina via protolytically stable Re-C-Si linkages. This objective is being pursued via a co-condensation synthesis to produce vinyl-functionalized SBA-15, on which the surface organic groups will be used to anchor rhenium oxide. Characterization of grafted complexes will be undertaken using multidimensional solid-state NMR.

Inhibiting the adsorption of polar impurities or reaction by-products will be achieved with surface silylation. Sn incorporation into the oxide support is being pursued in order to promote functional group tolerance without enhancing deactivation or precluding reactivation of the active sites. This goal is particularly important as we work towards the design of metathesis catalysts for biorenewables.

Publications (2003 -). This project began 9/15/2003. No publications have appeared at this time (3/15/2004).

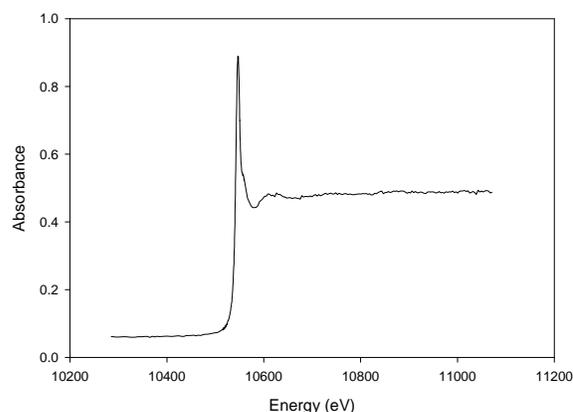


FIGURE 4. X-ray absorption at the Re L_{III} edge (10,535 keV) for MTO supported on silica-alumina pretreated at 450°C. This spectrum was acquired at CAMD (Baton Rouge, LA).

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Title: Transition Metal Mediated Transformations of Small Molecules

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Goals and Objectives

Catalytic polymer synthesis by metal compounds is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The theme of the proposed research is the design of new metal-based systems for the synthesis of novel classes of polymers. In the process, we hope to address key questions concerning the steps involved in such polymerization reactions.

Significant Recent Achievements and Results

Below we briefly summarize some of our recent research achievements. Further details regarding our work can be found in the publications and patents listed at the end of this section.

A significant fraction of the work during the current grant period has been devoted to catalytic systems for the homo and copolymerizations of norbornene derivatives and acrylates. A new palladium-based catalyst was found for the vinyl addition polymerization of norbornene derivatives, including those with pendant oxygen functionalities. For norbornene, a polymerization rate of 1000 tons norbornene/mol Pd•hour was observed at 25°C. However, the polymerization rate was found to decrease for norbornene derivatives with pendant functionalities. *Endo*-substituted norbornenes are polymerized more slowly than their corresponding *exo* isomers. The size of the substituent plays a role. However, the coordinating ability of the functionality plays an even bigger role in attenuating polymerization than its size. The formation of chelates upon the coordination of the *endo*-functionalized norbornene is responsible, in part, for the observed decrease in polymerization rate. A further and, even greater, reason for the diminution of activity of *both* the *endo* and the *exo*-functionalized isomers is simply the coordination of the functionality to the metal center.

We have also investigated a novel acrylate copolymerization system. A neutral palladium complex was found to effect the polymerization of acrylates. Over 10 mol% incorporation of 1-hexene in the polymer was achieved when the latter was added together with methyl acrylate. The polymerization occurs by a free radical mechanism that is tied to a β -H elimination chain termination/transfer step.

Finally, a copper-mediated procedure for the synthesis of random copolymers of methyl acrylate with 1-alkenes, ranging from ethene to 1-decene, as well as norbornene derivatives, has been discovered. Copolymers with greater than 20 mol% incorporation of the 1-alkene are formed. The system is *living*, thereby allowing the synthesis of novel block terpolymers of methyl acrylate with 1-alkenes and/or norbornenes by the sequential addition of the latter monomers.

Future Plans

During the upcoming year we intend to follow, for the most part, the lines of research outlined in the most recent proposal. This will involve investigations of homogeneous metal-catalyzed processes for the synthesis of polymers and copolymers. The principal goal of the proposed research will be the design of new metal-catalyzed systems for the formation of polymers with interesting architectures. The research will focus on two specific areas: (A) metal-mediated homo and copolymerization of functionalized vinyl monomers and (B) metal-catalyzed polypeptide synthesis through alternating copolymerization of imines with carbon monoxide.

Impact on Science and Technologies of Relevance to DOE

Catalytic polymer synthesis by metal compounds is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. Indeed, several high-volume commercial polymers are only accessible through metal-mediated routes. Hence, the achievement of a fundamental understanding of all aspects of such catalysis is an important goal. The Technology Vision 2020 report also cites the importance of developing new catalysts for customizing polymer properties. The theme of our research is the design of new metal-based catalytic systems for the synthesis of novel classes of polymers. For example, the copolymerization of functionalized vinyl monomers with non-polar alkenes remains an area of great interest in synthetic polymer chemistry, because the addition of functionalities to a polymer which is otherwise non-polar can greatly enhance the range of attainable properties. One particular area of interest is the homopolymerization of norbornene derivatives and their copolymerization with acrylates to form materials suitable for deep UV photolithography. Polyacrylates show good adhesion and have been used extensively as photoresist materials, but suffer from poor dry etch resistance. On the other hand, polynorbornenes exhibit superior etch resistance and thermal stability. Thus, norbornene homo and copolymers may provide the optimum properties.

Refereed Publications and Patents Based on DOE Grant (2001-present)

1. "Grafting of Syndiotactic Polystyrene by Branched Oligoethene Using $[\text{Ni}(\pi\text{-methylallyl})(\text{Br})]_2/\text{AlCl}_3$ Catalyst," Shengsheng Liu and Ayusman Sen, *J. Polym. Sci., A: Polym. Chem.*, **2001**, 39, 446.

2. "Synthesis of Novel Linear Polyethene-Based Graft Copolymers by Atom Transfer Radical Polymerization," Shengsheng Liu and Ayusman Sen, *Macromolecules*, **2001**, *34*, 1529.
3. "New Olefin Polymerization and Copolymerization Catalysts. Effect of Coordinating Functionalities," Ayusman Sen, *Pure Appl. Chem.*, **2001**, *73*, 251.
4. "Transition Metal Phthalocyanine and Porphyrin Complexes as Catalysts for the Polymerization of Alkenes," Gregory S. Long, Benjamin Snedeker, Kyle Bartosh, Michelle L. Werner, and Ayusman Sen, *Can. J. Chem.*, **2001**, *79*, 1026.
5. "A Novel, Efficient, Palladium-Based System for the Polymerization of Norbornene Derivatives: Scope and Mechanism," April D. Hennis, Jennifer D. Polley, Gregory S. Long, Ayusman Sen, Dmitry Yandulov, John Lipian, George M. Benedikt, Larry F. Rhodes, and John Huffman, *Organometallics*, **2001**, *20*, 2802.
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11. "Diametrically Opposite Trends in Alkene Insertion in Late and Early Transition Metal Compounds: Relevance to Transition Metal-Catalyzed Polymerization of Polar Vinyl Monomers," Myeongsoon Kang, Ayusman Sen, Lev Zakharov and Arnold L. Rheingold *J. Am. Chem. Soc.*, **2002**, *124*, 12080.
12. "Copolymerization of Ethene with Norbornene Derivatives Using Neutral Nickel Catalysts," George M. Benedikt, Ed Elce, Brian L. Goodall, Heather A. Kalamarides, Lester H. McIntosh, Larry F. Rhodes, K. T. Selvy, Robert A. Shick, Cecily Andes, Karl Oyler, and Ayusman Sen, *Macromolecules*, **2002**, *35*, 8978.

13. "Strategies for Catalytic Polymerization of Polar Monomers," Ayusman Sen and Myeongsoon Kang in "Late Transition Metal Polymerization Catalysis," Wiley-VCH, Weinheim, 2003, p. 307.
14. "Trends in Alkene Insertion in Late- and Early-Transition Metal Compounds: Relevance to Transition Metal-Catalyzed Polymerization of Polar Vinyl Monomers," Myeonsoon Kang, Ayusman Sen, Lev Zakharov, Arnold I. Rheingold, In "Beyond Metallocenes: Next-Generation Polymerization Catalysts," *ACS Symp. Ser.*, **2003**, 857, 143.
15. "The Addition Polymerization of Functionalized Norbornenes: The Effect of Size, Stereochemistry and Coordinating Ability of the Substituent," Jeffrey K. Funk, Cecily E. Andes, and Ayusman Sen, *Organometallics*, 2004, *in press*.

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1. "Preparation of Highly Branched, Liquid Polymers of Ethylene and/or α -Olefins in the Presence of Aluminum-Based Catalyst Systems," Ayusman Sen, Louis M. Wojcinski, and Shahid Murtuza, *U. S. Patent*, 6,232,257 (2001).
2. "Transition Metal-Free Olefin Polymerization Catalyst," Ayusman Sen, Louis M. Wojcinski, and Shengsheng Liu, *U. S. Patent*, 6,291,387 (2001).
3. "Palladium(II) Catalyzed Polymerization of Norbornene and Acrylates," Ayusman Sen and April Hennis, *U. S. Patent*, 6,300,440 (2001).
4. "Metal Catalyzed Synthesis of Hyperbranched Ethylene and/or α -Olefin Polymers," Ayusman Sen, Jang Sub Kim, James H. Pawlow, Shahid Murtuza, Smita Kacker, and Louis M. Wojcinski, *U. S. Patent*, 6,303,717 (2001).
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6. "Alkyl Magnesium Catalyzed Synthesis of Ethylene and α -Olefin Polymers," Ayusman Sen and Jang Sub Kim, *U. S. Patent*, 6,407,299 (2002).
7. "Catalyst and Methods for Polymerizing Cycloolefins", John-Henry Lipian, Larry F. Rhodes, Brian L. Goodall, Andrew Bell, Richard A. Mimna, John C. Fondran, Jayaraman Saikumar, April D. Hennis, Christine N. Elia, Jennifer D. Polley, and Ayusman Sen, *U. S. Patent*, 6,455,650 (2002).
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9. "Preparation of Highly Branched, Liquid Polymers of Ethylene and/or α -Olefins in the Presence of Aluminum-Based Catalyst Systems," Ayusman Sen, Louis M. Wojcinski, and Shahid Murtuza, *U. S. Patent*, 6,518,384 (2003).
10. "Palladium(II) Catalyzed Polymerization of Norbornene and Acrylates," Ayusman Sen, Smita Kacker, April Hennis, and Jennifer D. Polley, *U. S. Patent*, 6,593,440 (2003).

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Alkene Oxidation with Platinum Oxo Complexes and Gold Cluster Complexes as Models for Supported Gold Cluster Catalysts

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Students: Endre (Andy) Szuromi

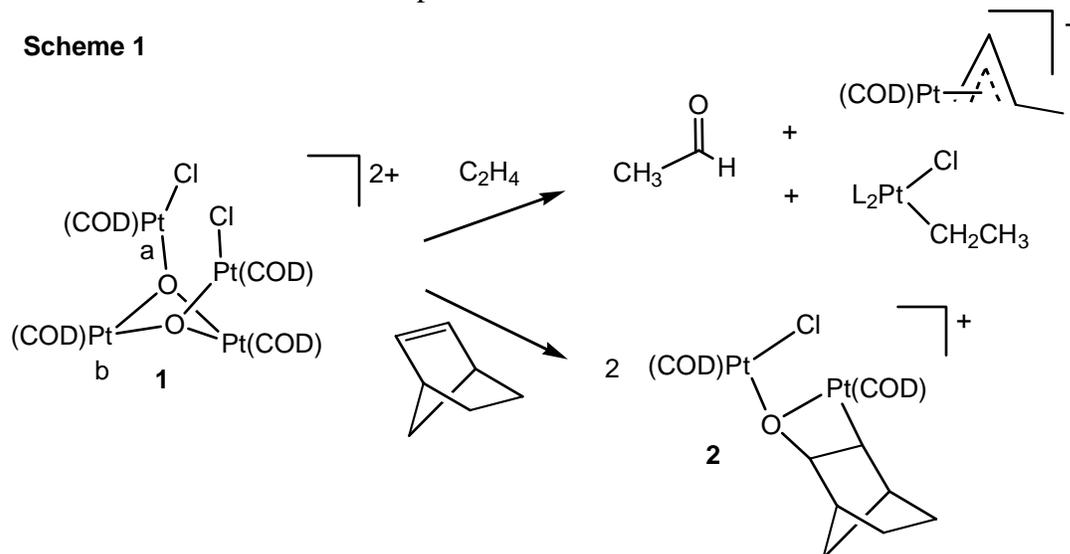
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Goals

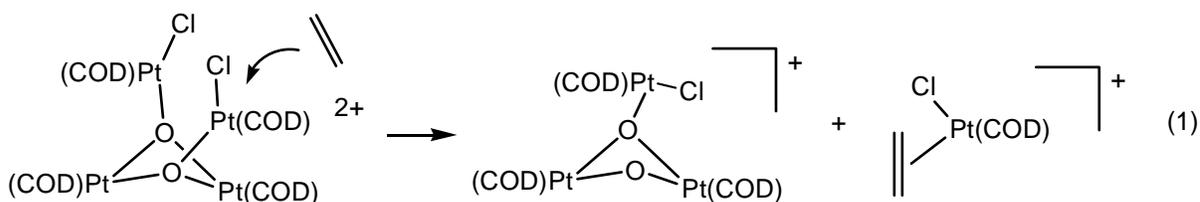
1) Understand the factors in late transition metal oxo complex reactions with alkenes and other unsaturated substrates and 2) improve understanding of supported gold cluster catalysts by the preparation and study of gold complexes and gold cluster complexes containing Au-M (M = Al, Ga, Si, Ge, Ti) and Au-O bonds.

Recent Progress

Alkene oxidation chemistry. Oxo complex $[(1,5\text{-COD})_2\text{Pt}_2(\mu^3\text{-O})_2\{(1,5\text{-COD})\text{PtCl}\}_2]^{2+}$ (**1**) oxidizes ethylene to acetaldehyde (Scheme 1). This is a complex reaction and we sought an alkene that would give a more clearly defined reaction. Norbornylene is such an alkene and gives, in quantitative yield, platinaoxetane **2** (Scheme 1), the first metallaoxetane to be formed from the reaction of an oxo complex with an alkene.

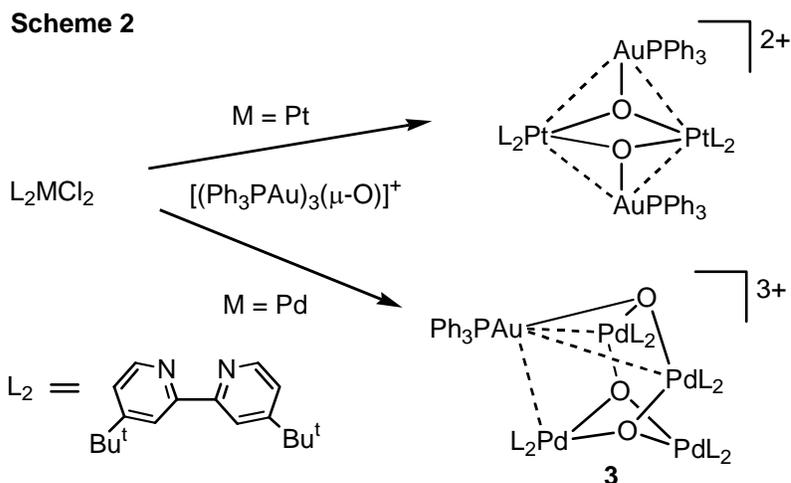


Mechanistic studies of the norbornylene reaction are in progress. Preliminary kinetic studies indicate that the reaction is first order in alkene. DFT calculations to determine the alkene attack site (Pt(a) or Pt(b) in Scheme 1) have begun. Charge distribution favors attack at Pt(b) but product stability strongly favors attack at Pt(a) with formation of $[(\text{COD})\text{PtCl}(\text{C}_2\text{H}_4)]^+$ and $[(1,5\text{-COD})_2\text{Pt}_2(\mu^3\text{-O})_2\{(1,5\text{-COD})\text{PtCl}\}]^+$ (**3**) (eq 1). These highly CPU intensive calculations are continuing and will help us understand the reactions of **1**.



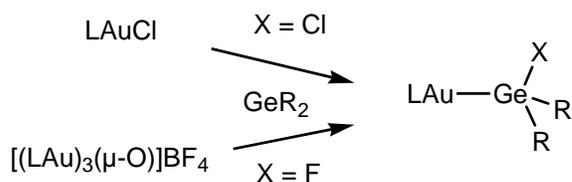
Modifications to **1** and reactions with other substrates have also been undertaken. We have successfully prepared the bromide analog of **1** and find that its reactions parallel those of **1**. Styrene, propene, cyclopentene, and diethylacetylene react readily with **1**. The propene reaction is analogous to the ethylene reaction and gives acetone, though in low yield. The platinum containing products have not yet been identified. The styrene reaction is complex and the major platinum-containing product is CODPtCl₂. The cyclopentene and diethylacetylene look very promising giving CODPtCl₂ and one other platinum-containing complex.

New oxo complexes. Parallel with the above studies on **1** we have been expanding our inventory of similar oxo complexes for possible alkene reactions. New complexes are given in Scheme 2 and include our first example of a Pd oxo complex **3**, which bears considerable resemblance to **1**. Unfortunately, the new complexes appear not to react with alkenes.

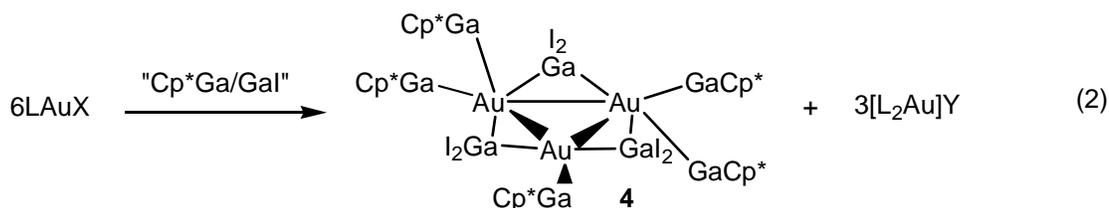


Gold-electropositive metal clusters. Work in this new area began with reactions of LAuCl (L = a phosphine) with GeR₂ (R = N(SiMe₃)₂) (Scheme 3). For all L examined, insertion of GeR₂ into the Au-Cl bond was observed giving the new complexes LAu-Ge(Cl)R₂. To obtain the more desirable chloride free analog ([LAu-GeR₂]⁺), [(LAu)₃(μ-O)]BF₄ was treated with GeR₂. LAu-Ge(F)R₂ was obtained, presumably by fluoride abstraction from BF₄⁻.

Scheme 3



The remarkable cluster **4** with gold bonded solely to Ga was formed in the reaction shown in eq 2. Isolation of this cluster bodes well for the synthesis of a new family of group 13 ligated gold cluster complexes. Preliminary DFT calculations on **4** indicate strong polarization of the Cp*Ga-Au bond and essentially neutral gold atoms.



DOE Interest

The improved understanding of the chemistry of metal oxo complexes and gold cluster complexes that will be gained by studying the reactivity and formation of the above complexes will increase our fundamental understanding of critical interactions in important catalytic processes. The benefits could be many, including increased efficiency, new processes, and less pollution.

Future Plans

We will continue our work on the platinum alkene oxidation chemistry. Our objectives are to complete the kinetic studies of the norbornylene reaction with [(1,5-COD)₂Pt₂(μ³-O)₂{(1,5-COD)PtCl₂}₂]²⁺ (**1**) and derivatives and to prepare new examples of oxo complexes which are capable of alkene oxidation. DFT studies will be continued to assist in our search. Our objectives in the gold cluster area are to prepare the aluminum analog of **4** and to elucidate the reactivity of the cluster complexes. The aluminum analog of **4** is expected to show even greater charge transfer from aluminum to gold giving negatively charged gold centers.

Publications (2002-present)

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“A Gold-Gallium Cluster Complex with Gold Bonded only to Gallium” Anandhi, U.; Sharp, P. R. *Inorg. Chem.* submitted.

Growth of Metal and Semiconductor Nanostructures Using Localized Photocatalysts

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Goal

Develop photocatalytic synthesis methods for producing metallic nanostructures.

Recent Progress

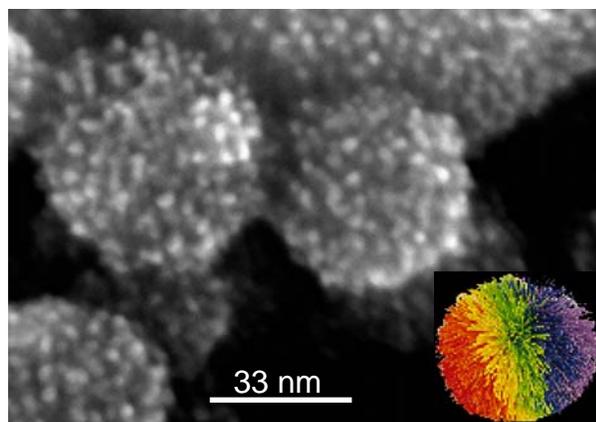
Our main objective is to understand and develop a new and novel light-driven approach to the controlled growth of unique metal and semiconductor nanostructures and nanomaterials. In this bio-inspired photochemical process, porphyrin photocatalysts provide metal nucleation and growth centers at which metal salts are reduced from aqueous solutions at ambient temperatures to produce desired metal nanostructures. Photocatalyst molecules are pre-positioned at the nanoscale to control the location and morphology of the metal nanostructures that are grown. Self-assembly, chemical confinement, and molecular templating are some of the methods used for nanoscale positioning of the photocatalyst molecules. When exposed to light, a photocatalyst molecule repeatedly reduces metal ions from solution, leading to deposition in the vicinity of the photocatalyst molecule and the formation of the nanostructure or nanomaterial.

This new synthetic approach has proven to be very successful for producing metal nanostructures and nanostructured materials, giving a number of amazing new and novel metal nanostructures. Of particular note are the platinum metal Koosh-ball like nanodendrites and the platinum-lace foams and foam balls (which were extensively reported in the scientific media) and, most recently, the gold- and platinum-decorated porphyrin nanotubes. In fact, the discovery of porphyrin nanotubes by our group was also an indirect outcome of the DOE research effort in photocatalytic growth of metal nanostructures. The nanomaterials resulting from these studies will have applications in nanoelectronics, photonics, sensors, catalysis, and microelectromechanical systems.

Another of our goals has been to elucidate the processes involved in the photocatalytic growth of metal nanomaterials and provide the scientific basis for controlled synthesis of a wide variety of nanomaterials, and we have made considerable progress in this effort as well. In this regard, we have fully elucidated the mechanisms associated with the growth of the platinum and palladium nanodendrites.

Surfactant-Templated Platinum and Palladium Nanostructures: We have discovered and extensively studied a porphyrin-based photocatalytic method for controlling the growth of

Figure 1. Globular platinum nanodendrites grown on Brij-35 micelles. The size distribution is very broad when porphyrin photocatalyst is absent. Nanodendrite size and uniformity is easily controlled by using a micelle-bound porphyrin (SnOEP) to photocatalytically grow a large initial population of platinum seed nanoparticles, which then grow autocatalytically by oxidation of ascorbic acid into the nano-Koosh balls.
Inset: A Koosh® ball.



novel platinum metal nanodendrites templated on surfactant assemblies containing the photocatalyst. When the porphyrin photocatalyst is localized in the micelles, three-dimensional globular dendrites of dimensions between 3-100 nm have been produced. A transmission electron microscopy (TEM) image of these platinum nano-Koosh-balls is shown in Figure 1. The size and uniformity of these nanodendrites can be controlled by altering the platinum-to-photocatalyst concentration ratio and/or the light exposure. Control is realized because the micelle-bound porphyrins (SnOEP) photocatalytically grow a large initial population of platinum seed nanoparticles, which then become catalytic at a certain size and grow into the nano-Koosh balls by Pt-catalyzed oxidation of ascorbic acid and reduction of Pt ions. These platinum nanodendrites were shown to be active catalysts for H₂ evolution from water.

In contrast with the micelles, localization of the porphyrin within the bilayers of unilamellar liposomes and exposure to white light initiates the growth of dendritic sheets of platinum. Depending on the illumination conditions and the concentrations of porphyrin and Pt, the growth of these Pt sheets leads to either thin (~2-nm) flat circular dendrites of 50-200-nm diameters or extended Pt foam-like materials. The morphology of the Pt foams is easily photocatalytically controlled to give individual Pt-coated liposomes, Pt foam balls, or monolithic Pt foams. The Pt foam balls and monolithic foams are shown in scanning electron microscopy (SEM) images in Figure 2(a) and (b), respectively.

Porphyrin-Nanotube-Templated Platinum and Gold Nanostructures: One of the most

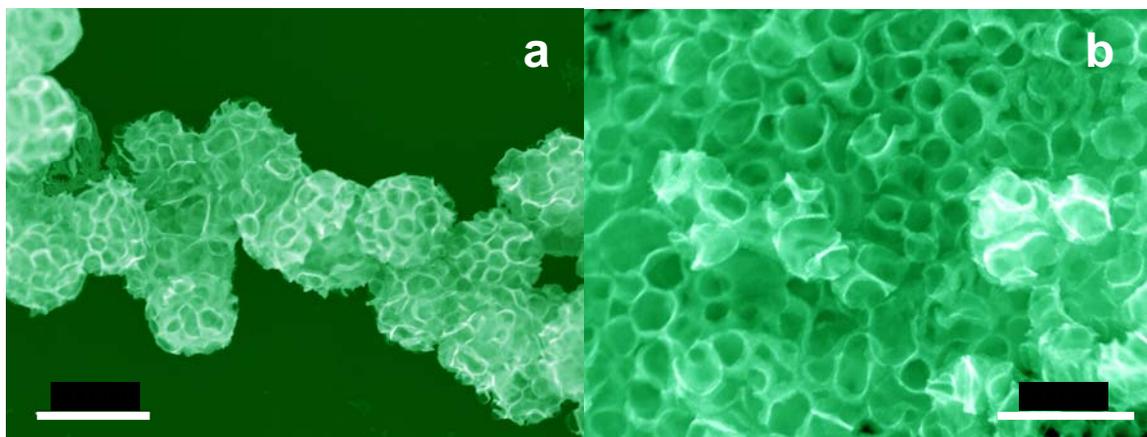


Figure 2. Platinum foam balls (a) and monolithic platinum foams (b) composed of 2-nm thick dendritic platinum sheets coating aggregated liposomes.

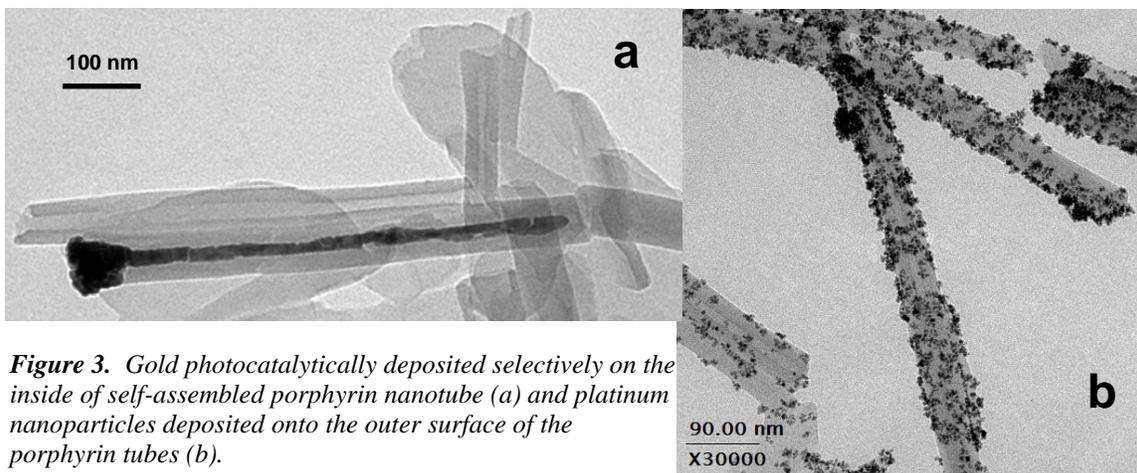


Figure 3. Gold photocatalytically deposited selectively on the inside of self-assembled porphyrin nanotube (a) and platinum nanoparticles deposited onto the outer surface of the porphyrin tubes (b).

exciting discoveries made during the course of the DOE work is that porphyrins can be self-assembled into well formed nanotubes. These nanotubes are composed of mixtures of two porphyrins—one anionic and the other cationic. The diameters of the porphyrin tubes are monodisperse and the tube diameter can be varied by altering the molecular structure of the porphyrins making up the tubes. Furthermore, one of these porphyrins can be made to be a photocatalytic metal derivative, making possible the use of the nanotubes as templates for the photocatalytic growth of metal-nanotube composite structures.

Figure 3 shows typical TEM images of two examples of the photocatalytic deposition of metals onto one type of the porphyrin nanotubes. We suspect the selectivity for gold deposition inside the tubes and platinum on the outside the tubes is based on the opposite charges of the metal ions—the Au(I) complex is positively charged and the Pt(II) complex is negatively charged. The porphyrins making up the tube walls are expected to be active in electron and energy transfer since the porphyrins are self-assembled as *J*-aggregates, which give interesting collective electronic properties such as intense resonance light scattering. The possibility of energy and light conductivity is supported by the lack of gaps in the gold nanowires.

Peptide Nanotube Templates: We have also been investigating the possibility of using peptide nanotubes as templates for photocatalytic metal deposition. Currently, we have synthesized these nanotubes and grown platinum nanoparticle inside the apparently porous walls of the tubes in a dense and homogeneously distributed fashion. Very recently, we have succeeded in making ‘pink’ tubes, which incorporate a photocatalytic porphyrin. We now plan to use the porphyrin-impregnated peptide nanotubes to grow various metal nanostructures.

DOE Interest

The research has led to highly nanoengineered materials for applications in catalysis, nanoelectronics, photonics, MEMS, and nanomagnetic systems. These nanomaterials are composed of platinum, palladium, and gold, and they may potentially be made from other useful metals and semiconductors. The development of a fundamental understanding of the uses and limitations of biomimetic photocatalysis as a means of producing metal and semiconductor nanostructures and nanomaterials is progressing and is expected to lead to further new applications of this new nanotechnology. The work has led to a relationship with InfraSUR LLC, a small business that is developing our photocatalytic metal reduction processes for

environmental remediation. We are also in discussions with a major automotive manufacturer concerning the potential use of the platinum nanodendrites in fuel cells.

Future Plans

Platinum Nanostructures and Nanostructured Materials: We need to further explore the synthetic possibilities of these types of materials and improve our understanding of the factors that control their morphology. Our main objectives will be to produce new nanomaterials for specific applications and gain additional expertise in controlling their nanostructure. Specifically, we will investigate additional templating materials (e.g., porphyrin nanotubes and fibers, polymers, and silicates), develop new alloyed metal nanostructures (Pt,Pd,Ni,Fe,Rh), formulate new composite nanostructures by sequential addition of different metals, determine the minimum size of nanoparticles that can be made, incorporate metal nanoparticles and nanosheets at specific locations in polymer electrolytes and other materials (for fuel cells), and determine the thermal and mechanical stability, porosity, and other materials properties relevant to these specific applications. Experimental techniques to be used include high-resolution electron microscopy (TEM,SEM), XRD, UV-visible, fluorescence and Raman spectroscopy.

Porphyrin-Nanotube Templated Nanostructures We will focus a large part of our work on making new metal-nanotube composite structures and investigating their catalytic, optical, and electronic properties. For example, we expect the platinized porphyrin nanotubes to be excellent nanostructures for evolving hydrogen, given that they may already incorporate light-harvesting and electron-transport functionality coupled with photosynthetic reaction centers and hydrogenase catalytic function (Pt nanoparticles) in optimal proportions. The plasmonic properties of metal nanostructure grown inside and/or outside of the tubes will be investigated.

Other Methods of Localizing Photocatalyst Molecules We will use the peptide nanotubes with incorporated photocatalytic porphyrins to grow metal nanostructures and investigate their structure and properties. We will investigate other ways of positioning porphyrins at the nanoscale for fabrication of metal and semiconductor nanostructures.

Other Metals and Semiconductors We will investigate the photocatalytic reduction of other metals and semiconductors for applications in waste treatment, nanoelectronics, nanotagging, nanophotonics, and nanomagnetism.

Publications (2003-4)

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3. Song Y, Singh A K, Qiu Y, Shelnutt J A, Photocatalytically Nanoengineered Foam-Like Platinum Materials Templated on Liposomes *Angew. Chem., Int. Ed.* In preparation.
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Self-Assembly of Polyelectrolyte Structures in Solution:
From Atomic Interactions to Nanoscale Assemblies

Co-Investigators: P. F. Britt, A. Habenschuss, B. K. Annis, A. A. Chialvo, G. D. Wignall, Y. B. Melnichenko (ORNL); J. W. Mays (UT/ORNL); M. Muthukumar (U. Mass., Amherst), P. T. Cummings (Vanderbilt)

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Goal

Predict and control the nanoscale structures formed by polyelectrolytes in solution based on a fundamental understanding of extent and importance of the full range of interactions from atomic to nanoscale dimensions.

Recent Progress

Research is aligned along parallel, complementary efforts in synthesis of model polyelectrolytes, detailed characterization at the atomic and macromolecular length scales, and fundamental theoretical and computational models of structure and interactions in solution.

Polyelectrolyte synthesis. The goal of this task is to synthesize novel polyelectrolytes designed to highlight specific interactions in solution that lead to significant differences in the observed conformation, interactions with counterions, and self-assembly of nanoscale structures. Building on an extensive base of literature studies of polystyrene sulfonate (PSS), we have focused on the synthesis of poly(cyclohexadiene) sulfonate (PCHDS). For this material the stiffer chain will permit determination of the effect of this important variable on structure and interactions in solution.

Sulfonation of well-defined (molecular weight: ~8,000g/mol, PDI: ~1.06) poly(1,3-cyclohexadiene) polymers (PCHDS) was accomplished by using SO₃/dioxane, SO₃/triethyl phosphate complexes or acetyl sulfate (acetic anhydride in sulfuric acid) in various solvents. The degree of sulfonation can be controlled by varying the ratio of sulfonation agent to monomer units. Synthesis of deuterated PCHD, needed for small-angle neutron scattering studies of polymer conformation in solution, was found to depend strongly on the synthesis of the deuterated 1,3-CHD monomer. While proton exchange of 1,4- or 1,3-cyclohexadiene with DMSO-d₆ gave impure product material that could not be purified, an alternate synthetic approach starting from cyclohexanol was successful for the production of undeuterated 1,3-CHD in 60% yield (~99.8% purity). Using this approach, we have synthesized perdeuterated PCHDS of varying molecular weight for investigations of the effect of chain length on polyelectrolyte conformation and self-assembly. We have also synthesized short-chain (~2000 molecular weight before sulfonation) PSS samples for studies of local order of counterions near charged sites on the polyelectrolyte chain.

Structural studies in solution. Both short-range (atomic dimensions) and longer scale (macromolecular) interactions contribute to polyelectrolyte self-assembly. We are investigating the

interaction of polyelectrolytes with counterions and solvent molecules (water) through wide-angle neutron diffraction with isotopic substitution (NDIS) and laboratory-based X-ray scattering. Initial NDIS experiments on a ternary model system including polyethylene oxide (PEO), water (D₂O) and lithium iodide indicate that the ether oxygens of PEO do not compete effectively for solvation sites near the lithium ion in solution.¹ Total structure factors $G(r)$ were obtained using laboratory X-ray scattering techniques for ternary LiI-D₂O-PEO mixtures at the same concentrations as the wide-angle neutron studies. Preliminary assignments of the observed structural features from these experiments are consistent with the neutron scattering results, and include additional information on pair correlation distances (i.e., those not involving Li). Future studies will add to our understanding of this competitive solvation effect through investigation of water-poor ternary mixtures, where insufficient water is available to form complete solvation shells.

Small-angle neutron scattering (SANS) is being used to probe details of macromolecular conformation and the formation of self-assembled structures. Initial studies with PCHDS indicated only a poorly defined “polyelectrolyte peak” with a surprisingly weak dependence on ionic strength in solution. Parallel light-scattering studies of PCHDS indicated significantly stronger aggregation of PCHDS in solution as compared with PSS. This aggregation, extensive even at very low polyelectrolyte concentration, leads to the poor resolution of the polyelectrolyte peak in the SANS experiments. The newly synthesized perdeuterated PCHDS enables additional definitive SANS studies of this system through contrast matching.

In collaboration with Professor E. R. Zubarev, Iowa State University, SANS studies were carried out at Forschungszentrum Jülich (Germany) on amphiphilic heteroarm star polyelectrolytes. These polyelectrolytes included 12 arms (6 uncharged polystyrene, 6 polyacrylic acid), each incorporating an average of 25 monomer units. In a “nonselective” solvent (70% chloroform, 30% methanol) the observed dimensions ($R_g \sim 26\text{Å}$) reflect the size of the unimer, while in D₂O/dimethyl formamide, self-assembled core-shell micelles form at the lowest concentrations. In chloroform the radii of gyration indicate aggregation of about 3 unimers at infinite dilution, and larger self-assembled micelles at higher concentrations.

Theory, Modeling and Simulations. Both coarse-grained approaches and atomistically-detailed simulations are being applied to understand short-range interactions and their contributions to nanoscale conformation and assembly. Detailed molecular dynamics (MD) simulations are currently in progress on interactions of PSS and PEO with ions and solvent molecules. Detailed Brownian dynamics simulations showed that the counterions condense on the polymer backbone by an adsorption mechanism, yielding a degree of ionization of about 0.3 for a flexible polyelectrolyte. The simulations predict that the degree of ionization increases with increasing chain stiffness. Studies of stiff-chain polyelectrolytes show that either, or both, hydrophobic interactions between incompletely-sulfonated chain segments and hydrophilic (e.g., counterion sharing) interactions can contribute to self assembly in solution, and that the extent of aggregation is sensitive to chain stiffness.

DOE Interest

The fundamental knowledge gained from this research contributes to the scientific foundation required for tailoring the macromolecular structure and self-assembly of complex nanoscale polyelectrolyte structures. This ability to predict and control structure will enable a clearer understanding between the relationships between structure and function in ionic polymer systems.

Future Plans

Our capabilities for investigation of chain conformation and self-assembly will be significantly enhanced through the availability of the deuterated polyelectrolytes. In addition to synthetic progress within this program, we will collaborate with staff and users of the Center for Nanophase Materials Science through a recently-approved Partner User proposal, making available additional facilities and expertise for synthesis of deuterium-labeled and perdeuterated polyelectrolyte samples. We will focus near-term studies of macromolecular conformation and self-assembly on deuterated PCHDS with varying degrees of sulfonation, and with changing ionic strength and counterions. Understanding the structural results from these studies will depend on understanding and controlling the extent of aggregation as a function of polymer and salt concentrations. Theoretical and Brownian-dynamics simulation studies will focus on representing and predicting effects of changing backbone stiffness, degree of functionalization (e.g., sulfonation) and solution ionic strength on macromolecular conformation and the extent of self-assembly.

We will take advantage of the high solubility of LiCl to extend studies of competitive solvation in PEO-D₂O-LiCl ternary mixtures to systems with insufficient water (Li:D₂O ratio greater than 1:4) in order to gain further insight into the competitive solvation of counterions in solution. Our studies of short-range interactions in short-chain polysulfonate oligomers will focus on lithium salts, with further studies highlighting the effect of changing charge density (valency) of the counterion. Simulation studies of the binary and ternary mixtures will give insight into details of local structure, as well as indications of the nature (e.g., hydrated ion layers) of possible electrostatic bridges in self-assembled structures. The combination of the wide-angle neutron scattering with X-ray measurements will give insight into both the local environment around the counterion in solution and the effects of these counterions on local structural features of other interactions, such as chain charge-site solvation.

Publications for 2002-2004 (This program began at the end of FY 2002.)

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Ferrocene-Based Nanoelectronics

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Goal

Synthesize and investigate the conduction physics of a variety of proposed ferrocene diode / transistor designs in order to address the fundamental question; can electron transport within nm-length scale molecular structures be modulated in a controlled and reversible fashion?

Recent Progress

Ferrocene-based molecular components for nanoelectronics offer a number of distinct advantages relative to all carbon frameworks, including lower and tunable redox properties. During the past year, substantial progress towards achieving the stated goal has been made by surmounting a number of scientific and technical obstacles. More specifically, a concise and general synthetic route to the requisite 2,5-diethynylpyridyl-linked diferrocene dithiols and monothiols has been achieved that now allows for the directed and controlled assembly of metal/organometallic/metal test structures and the fabrication of self-assembled monolayers (SAMs) on Au(111) that are amenable to quantitative electrochemical characterization of electron-transfer rates. Methods have also been developed for the construction of the key Au nanoparticle (Au NP)/ferrocene dithiol/Au(111) test structures shown in Figure 1 that will be used to acquire current / voltage (I/V) characteristics for the ferrocene molecular components. Complementing this approach, an alternative test structure based on the fabrication of a molecularly-bridged nanogap between two gold electrodes has also now been successfully fabricated. This test structure schematically shown in Figure 2 has the additional feature of possessing a novel aluminum oxide gate electrode, and in preliminary studies,

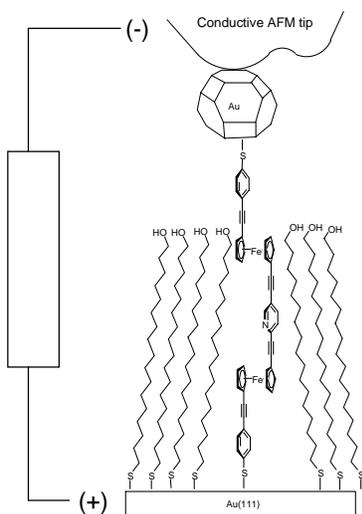


Figure 1. Schematic of experimental design for measuring I/V characteristics of ferrocene-based single molecules.

reproducible I/V data for one of the ferrocene dithiol molecules have been collected which exhibit surprisingly high conduction for a molecular species at a remarkably low bias of only 50 mV. Importantly, this conductance responds to application of a gate voltage in a predictable manner.

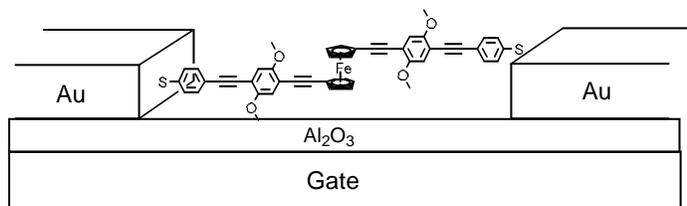


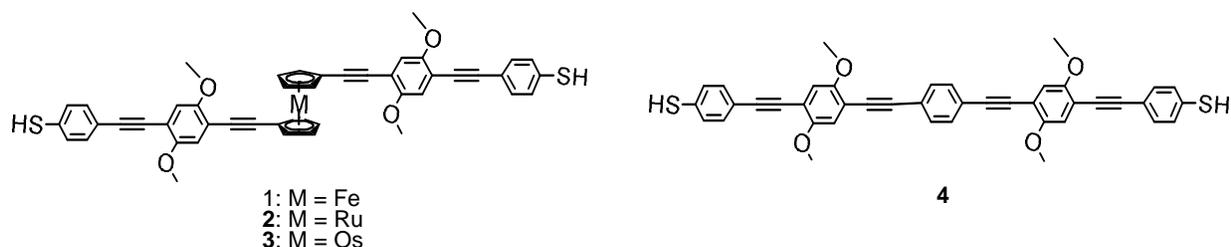
Figure 2. Schematic of a nanogap test structure to measure the I/V characteristics of ferrocene-based single molecules

DOE Interest

The successful realization of the goals of this project should play an important role in the continued evolution in design of molecular components for nanoelectronic devices, which in turn, will have a positive impact on the science and potential technologies associated with these systems.

Future Plans

The first credible, reproducible I/V data for one of the ferrocene molecules using a nanogap test structure, namely compound **1**, has been acquired, and these data have already provided exciting preliminary results in the form of remarkably high observed conductance. In the next year, one of the primary objectives will be to better understand the data that have obtained for **1** by placing it on a firm theoretical foundation. More specifically, it was originally thought that the ferrocene unit in the molecular construct would be electronically localized, i.e., conduction would occur through electron-hopping rather than via through-bond tunneling. The electrochemical studies that have been carried out now point to the opposite conclusion that the ferrocene unit in **1** is, in fact, well coupled electronically to the conjugated organic fragments, and overall, the organometallic framework provides a very low barrier to electron tunneling. The high observed conduction for **1** is further attributed to being due to the Fe center's d orbitals being in close proximity to the Fermi levels of the Au electrodes. To provide additional experimental and theoretical support for this hypothesis, two avenues of research will be pursued during the next year. First, compound **4** will be synthesized and its I/V characteristics compared with that of **1**. Second, Carlos Gonzalez, a theoretical chemist at NIST and Harold Baranger, a physicist at Duke, who both specialize on the theory of conduction through molecules, have been enlisted to computationally investigate the predicted properties of **1** and **4** at the theoretical level. By replacing the first row Fe center in **1** by the analogous second and third row group 8 metals, Ru and Os, i.e., compounds **2** and **3**, respectively, the relationship of the metal's d orbital energy levels on transmission efficiency will be investigated.



New Chemical Routes to Advanced Ceramic Materials: Metal Catalyzed Syntheses and Polymerization Reactions of Alkenylpolyborane Single Source Precursors

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Goal

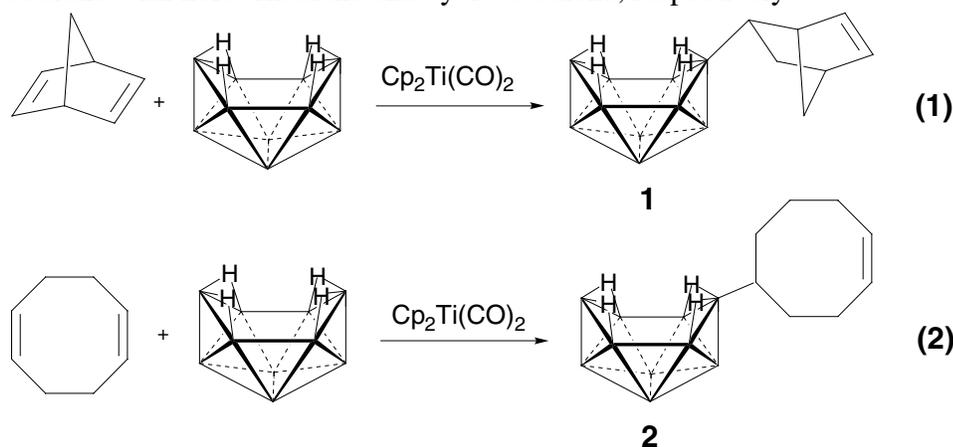
Develop new metal-catalyzed routes to single-source precursors to technologically important solid-state materials.

Recent Progress

New Routes to Organodecaborane Polymers via Ruthenium-Catalyzed Ring Opening Metathesis Polymerization

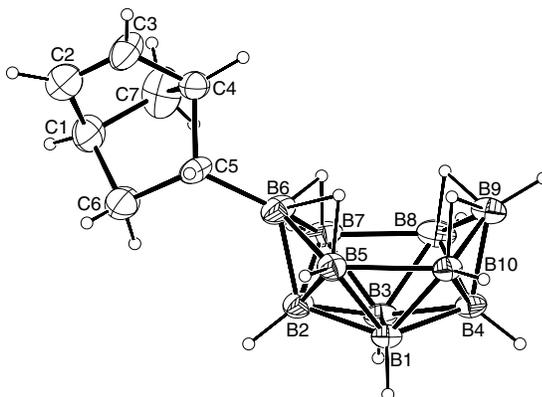
As a part of our interest in the design of new polymeric precursors to non-oxide ceramics, we have been investigating the development of new general metal-catalyzed methods for the synthesis of polyborane polymers. We have found during the last year that ruthenium-catalyzed ring opening metathesis polymerization (ROMP) of organodecaboranes containing cyclic-olefin substituents provides a new efficient route to poly(organodecaborane) polymers.

As shown in **Eqs. 1** and **2**, the high yield syntheses of the key decaboranyl-substituted norbornene and cyclooctene monomers were achieved by employing the titanium-catalyzed reaction of decaborane with norbornadiene and cyclooctadiene, respectively.

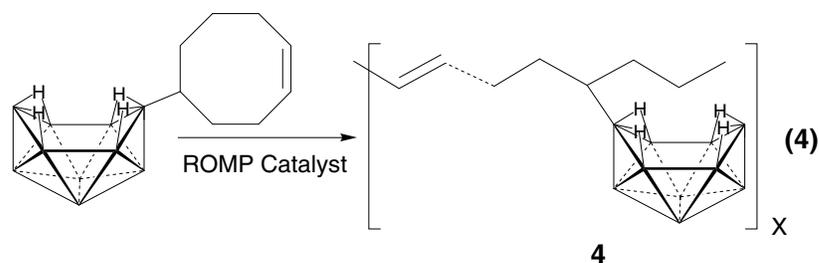
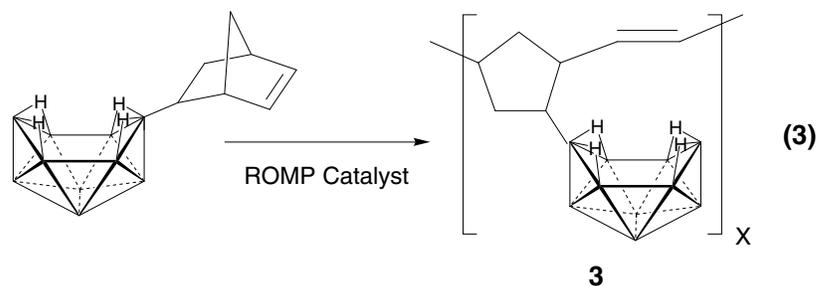


Typical conditions involved the reaction of a large excess of the olefin with decaborane in the presence of ~3 mol% catalyst at 90°C for 72 h. The products were easily isolated in pure form and excellent yields (**1**, 98% and **2**, 96%) from the metal catalyst by filtration through silica gel. As shown in the figure below, a single crystal X-ray determination of **1** confirmed a 6-

substituted norbornenyl-decaborane structure resulting from the titanium-catalyzed hydroboration of the norbornadiene C5-C6 double bond.



Because of their air stability and tolerance to various functional groups, “Grubbs-type” ROMP catalysts appeared to be ideal candidates for the syntheses of polyborane polymers. Indeed, ROMP of monomers **1** and **2** with either the first-generation (**I**) or second-generation (**II**) catalysts readily yielded the poly(organodecaborane) polymers shown in **Eqs. 3** and **4**.



Both the **I** and **II** catalysts polymerized **1** efficiently, giving ~90% conversions in the 1 h reaction time. Molecular weight studies by size exclusion chromatography employing both multi-angle light scattering and DRI detectors showed that molecular weights with M_n in excess of 30 KDa can be readily obtained with polydispersities (PDI's) between 1.1 and 1.8.

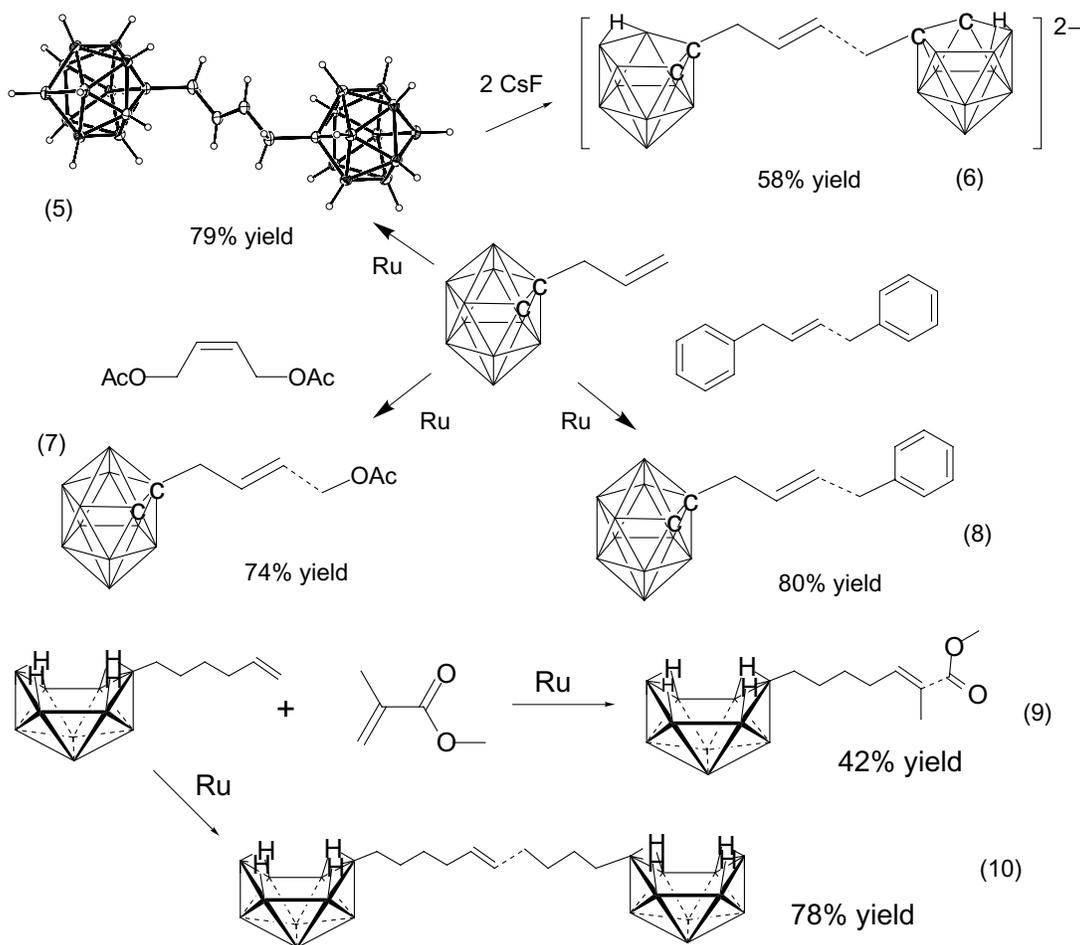
TGA studies of samples of **3** and **4** (each having M_n of ~32 KDa) indicated that for both polymers weight loss begins near 100°C and is essentially complete for **3** by 500°C and for **4** by 700°C to give final char yields of 72% and 70%, respectively. Given that DSC studies show that the T_g 's of both polymers are in the 65-70°C range, these polymers have excellent potential for applications requiring molten processing. We are currently studying the ceramic conversions and the properties of the derived ceramics.

Future Studies

The results presented above clearly demonstrate that ruthenium-catalyzed ROMP reactions are important new methods for the systematic formation of polyborane polymers. Since ruthenium-based ROMP catalysts work with a wide variety of functionalized olefins, we will now explore the use of these reactions to produce more complex poly(organopolyborane) polymers and copolymers than possible with our previously developed methods.

Ruthenium Catalyzed Alkenylpolyborane Metathesis Reactions: New Routes to Functionalized Polyboranes.

Metal-catalyzed olefin metathesis has become a widely used synthetic tool for carbon-carbon bond formation. Recent studies in our laboratory of both the homometathesis and cross-metathesis of alkenylboranes catalyzed by Grubbs-type catalysts have now shown that ruthenium catalyzed metathesis reactions are efficient high yield methods for the synthesis of organopolyboranes. The scheme below presents some results from our initial studies of the reactions of allyl-*o*-carborane and 6-hexenyldecaborane. Both compounds readily undergo homometathesis (Eqs. 5 and 10) to produce olefin-bridged compounds. As shown at the upper left, an X-ray study of the linked carborane confirmed the central double bond (1.35(2)Å).



Our initial studies have also shown efficient cross-metathesis of both compounds with a variety of olefins, including allylbenzene, allylacetate, allyltrimethylsilane, methyl acrylate, styrene and stibene. Thus, the cross-metathesis reactions provide important new routes to functionalized decaborane and *o*-carborane compounds. As also depicted in the scheme, we have now converted the olefin-linked carborane to the bis(dicarbollide) compound by deboronation with fluoride anion.

Future Studies

We plan to explore the deboronation reactions of the cross-methasis products to develop general routes to functionalized dicarbollides and then investigate the coordination chemistry of these new anions. We will likewise explore the use of the functionalized decaboranes as starting materials for the synthesis of boron-substituted derivatives of other important cage systems, including for example, $3\text{-RC}_2\text{B}_{10}\text{H}_{11}$, $\text{RCB}_{11}\text{H}_{11}^-$, $\text{RB}_{10}\text{H}_9^{2-}$ and $\text{RB}_{12}\text{H}_{11}^{2-}$.

Impact on Science and Technologies of Relevance to DOE

The development of efficient methods for the production of complex structural and electronic materials in usable forms with controlled structures, orders and porosities ranging over different length scales is one of the most challenging and important problems of modern solid-state chemistry and materials science. This research program is focused on the design, syntheses and applications of new processible chemical precursors to non-oxide ceramics, including boron carbide, silicon carbide and boron-carbide/silicon-carbide composites, that will allow the formation of these technologically important materials in forms, such as films, fibers and nanostructures, that have been unattainable with conventional methods.

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3. Moraes, K.; Vosburg, J.; Wark, D.; Interrante, L. V.; Puerta, A. R.; Sneddon, L. G.; Narisawa, M. "The Microstructure and Indentation Fracture of SiC-BN Composites Derived from Blended Precursors of AHPCS and Polyborazylene" *Chem. Mater.* **2004**, *16*, 125-132.
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Nanoscience and Nanoparticles for 100% Selective Catalytic Reactions

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Goal

The research conducted in the project is designed to develop new heterogeneous catalysts with 100% selectivity for the development of clean manufacturing processes that do not produce waste byproducts.

Recent Progress

Heterogeneous catalysts are nanoparticles. They are utilized in most industrial chemical processes in the form of metal clusters dispersed on high surface area oxide supports. Recent breakthroughs in nanotechnology have created the ability to control material structures on scales that are relevant for catalyst design (e.g. the diffusion length of molecular intermediates in a bifunctional catalyst, ca. 5 nm). Here we study the structure, composition and dynamic properties of catalysts to achieve 100% selectivity in multipath surface catalyzed reactions.

Synthesis and Characterization of High Surface Area Model Catalysts: Uniform shape and size Pt nanoparticles encapsulated in mesoporous silica (SBA-15) were prepared by a novel two-step method. It consists of the preparation of the metal nanoparticles by H₂ reduction of aqueous K₂PtCl₄, followed by addition of a tri-block copolymer and Si precursor which results in the development of a mesopore-structure of type SBA-15 around the nanoparticles. The studies indicate that the incorporation of small metal particles does not disrupt the hexagonal ordering of the SBA-15 channels. Coupled with TEM measurements, gas adsorption experiments confirm that the Pt nanoparticles are located in the internal structure (i.e. pores and walls) of the mesoporous silica. In parallel, Rh nanoparticles were synthesized using a reverse-micelle method. TEM and HRTEM revealed that the particles are close to monodisperse and highly crystalline. The Rh particles were supported on SBA-15 to form an active high surface catalyst that is currently being studied for catalytic ethylene hydrogenation and ethane hydrogenolysis.

An important aspect of the design of 3-D metal nanoparticle catalysts is variation and control of the chemical nature of the porous oxide support. We have explored modification of the SBA-15 silica pore surface by introducing a vanadium oxide layer. Structural aspects of the overlayer were elucidated by UV-Raman, UV-Vis DRS, XRD, TEM, and physisorption measurements. For these as well as all mesoporous materials with encapsulated metal particles, SAXS measurements at SSRL provide crucial

information on the pore diameter and the structural integrity of the material upon chemical processing.

Rh and Pt nanoparticles encapsulated into SBA-15 were synthesized by sonicating dispersed metal particles with the mesoporous silicate in solution (collaboration with Prof. Peidong Yang, UCB). Weight loadings of over 10% were obtained. The effect of sonication on mesoscale order, pore size distribution, and surface area was evaluated. FT-IR and UV-Raman were used to investigate changes in the silica framework caused by sonication and by sample preparation methods such as pellet pressing.

The study of a new class of metal/metal oxide core-shell structures for heterogeneous catalysis has been initiated (collaboration with Prof. Paul Alivisatos, UCB). Pt nanoparticles are used as the core, and Co_3S_4 or CoO as the shell. HRTEM indicates that the CoO shell is multicrystalline, furnishing access of gas molecules to the core by diffusion along grain boundaries as evidenced by the observation of C_2H_4 hydrogenation at low temperature.

Development of New and Sensitive Probes of Chemical Reactions on Metal and Metal Oxide Nanocluster Assemblies: XPS studies have revealed the first valence band photoemission spectra of Au nanoparticles as a function of size and separation. Quantum size effects are observed by a decrease of the density of states at the Fermi level when the particle size is below 1.7 nm. This reduction can have implications on the chemical activity and selectivity of nanoparticles that we are planning to explore. We also observed a metal-to-insulator transition when the small nanoparticles (< 1.7 nm) are separated by more than 10 Å. For Co nanoparticles, the first X-ray absorption and emission spectra have been obtained *in situ* in liquid suspension as function of particle size (measurements conducted at the ALS). Using resonant inelastic X-ray spectroscopy, the build-up of d-d electron transfer excitation was observed as function of size in the 3 to 9 nm diameter range. The purpose of these experiments is to determine the quantum size effects on electronic structure that may affect the catalytic properties of monodispersed nanoparticles.

In-Situ Reaction Studies of Nanoengineered Catalysts: Ethylene hydrogenation and ethane hydrogenolysis were studied on Pt/SBA-15. Low temperature (190-230 K) ethylene hydrogenation was investigated in a microreactor with plug-flow hydrodynamics. Kinetic measurements on Pt/SBA-15 materials with Pt particle size varying from 1.7–7 nm confirmed the structural insensitivity of this reaction. For ethane hydrogenolysis to proceed, both C-H and C-C bond activation must occur. The structure sensitivity of the reaction has previously been demonstrated on Ni catalysts. Detection of methane did not occur until temperatures > 573 K, indicative of the high activation of bond breaking that must occur. The activity of the Pt/SBA-15 materials was found to be insensitive to Pt particle size. The severe conditions (> 573 K, high pressures of ethane and hydrogen) employed in this study demonstrated that our model catalysts are robust.

Monitoring of heterogeneous catalysis by time-resolved vibrational spectroscopy is essential for the elucidation of the detailed mechanisms under reaction conditions. We have developed a method based on time-resolved FT-IR spectroscopy that affords observation of the lifetime of intermediates of hydrocarbon conversions over supported metal catalysts for the first time. The approach builds on a reactor design in which a

continuous gas flow of one reactant merges with a short (> 300 microsec) pulse of a second reactant, synchronized with the FT-IR spectrometer, in close proximity to the catalyst. Using ethylene hydrogenation over a supported Pt catalyst as a first example, two intermediates were detected: One is the well-established spectator surface ethylidyne ($1339, 2880\text{ cm}^{-1}$) showing a decay time of 300 msec (473 K). A transient absorption at 1200 cm^{-1} revealed the presence of a second surface species with a lifetime shorter than 100 msec. Based on these observations and the detection of accompanying CH stretching absorption at 2875 and 2860 cm^{-1} known from steady-state spectroscopy, we attribute the transient to surface ethyl species. $\text{CH}_3\text{CH}_2\text{Pt}$ has been proposed as the kinetically relevant reaction intermediate of ethylene hydrogenation. This is the first observation of the lifetime of $\text{CH}_3\text{CH}_2\text{Pt}$ under reaction conditions.

DOE Interest

The development of heterogeneous catalysts with 100% selectivity is a high priority goal for energy-efficient and environmentally friendly chemicals manufacturing.

Future Plans

New synthetic methods will be developed with the goal of generating monodisperse Rh and other metal or metal oxide particles with well-defined geometry and surface structure, including routes to 'naked' nanoparticles that obviate the need for stabilizing ligands. Comparison of catalytic activities versus surface structure could lead to the development of highly selective catalysts. We will expand microporous oxide supports for nanoparticles to include titania, alumina and zirconia. Research on our core/shell structures will be extended to different core materials such as Al_2O_3 , SiO_2 , or TiO_2 , with focus on improving the thermal stability.

The development of new and sensitive probes of chemical reactions on nanocluster assemblies will, along one direction, build on X-ray photoelectron spectroscopies at the ALS for measuring the size effects on the electronic structure of nanoclusters. Moreover, a high-pressure reaction cell will be built for the study of gas chemisorption on the nanoclusters. *In-situ* Raman and IR reflectance spectroscopy will be employed for the study of mesoporous silica-supported metal particles in a reactor cell. Time-resolved FT-IR spectroscopy for hydrocarbon conversions under reaction conditions will be expanded to the microsecond and nanosecond time range by employing the step-scan technique. Methods will be developed for the triggering of catalysis with sub-microsecond reactant pulses.

Future *in-situ* studies of nanoengineered catalysts will focus on the effect of particle size on reaction selectivity, in addition to activity. The hydrogenation/dehydrogenation of cyclohexene is a multi-path reaction currently under study. A fully automated reactor system for investigating the particle size effect on n-hexane reforming is in progress. Time-resolved FT-IR experiments on the same systems will be conducted for identifying and determining the lifetime of transient surface intermediates. Sum frequency generation measurement of metal nanoparticle catalysts will be pursued based on a total internal reflection cell.

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In-situ and Time-Resolved Characterization of Working Catalysts by Ultraviolet Resonance Raman Spectroscopy

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Goal

Characterize and understand heterogeneous catalysts and catalytic chemistry using in-situ and time-resolved Raman spectroscopy

Recent Progress

Ultraviolet Raman spectroscopy continues to develop as a powerful tool for the in-situ study of catalysts and catalytic chemistry. Experiments have shed light on the nature and mechanism of coke formation during acid-catalyzed reactions in zeolites. The effects of resonance enhancement have been used to detect and discriminate catalytic sites and subtle changes in molecular structure induced by adsorption in catalyst pores.

Mechanism and Topology of Coke Formation:
UV Raman spectroscopy is useful for monitoring the chemical intermediates in coke formation, and distinguishing polyolefin from polyaromatic coke. Moreover, the observed intensity pattern in the UV Raman spectra of coke is diagnostic for whether aromatic coke has a 1-Dimensional, chain-like or 2-Dimensional sheet-like topology. Coke formed during the methanol-to-hydrocarbons reaction (MTH) catalyzed by zeolite H-MFI has the 1-D topology characteristic of fused aromatic chains; coke formed on alumina-supported chromia has the 2-D topology (Fig. 1).

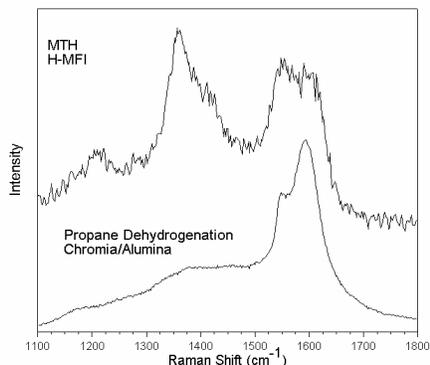


Figure 1 UV Raman spectra of coke.

Chemical Behavior of Catalytic Peroxides and Superoxides: Resonance enhancement makes it possible to detect and study chemically active peroxide and superoxide species adsorbed on iron clusters in zeolite H-MFI using UV Raman spectroscopy. The thermal and chemical stability of these species were found to be strongly dependent on the hydroxyl

content of the iron clusters. In particular, on highly dehydroxylated Fe/MFI samples peroxide and superoxide species are stable to at least 250°C where catalytic reactions occur.

Nature of Adsorbed Benzene from Resonance Raman Spectroscopy: Normal Raman spectroscopy involves transitions that occur on the ground electronic potential energy surface. Resonance Raman spectroscopy involves electronically excited states in the Raman scattering process. Consequently, resonance Raman spectroscopy is a sensitive tool for probing electronic excited states. The UV resonance Raman spectrum of benzene adsorbed in MFI silicalite is dramatically different than the spectrum of the free molecule (Fig. 2).

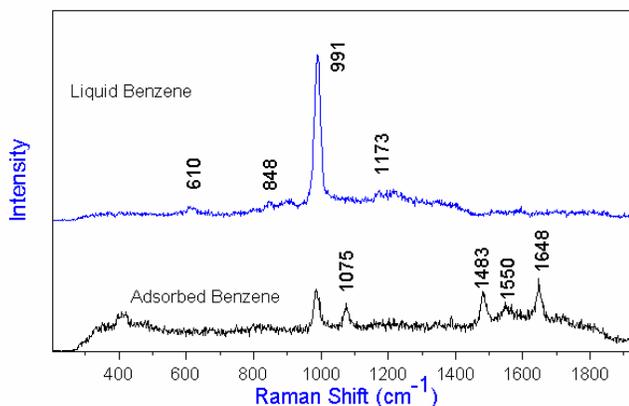


Figure 2 UV Raman spectra of benzene.

2). The spectrum reveals that the point group of benzene changes in the excited electronic state to either D_{2h} (planar elongated) or D_{3d} (chair) due to steric interactions with the channel walls.

DOE Interest

These new UV resonance Raman spectroscopy measurements provide a view of molecular adsorption, active sites, and catalytic chemistry within zeolites, one of the most important catalytic materials for energy production and utilization.

Future Plans

Quantitative Raman Spectroscopy: Due to variations in scattering volume, Raman spectroscopy is not generally a quantitative analysis technique. With zeolites, however, the TOT bending vibration provides an internal standard that can be used to adjust for scattering volume changes. Measurements on a series of adsorbed hydrocarbons will be used to develop a quantitative calibration of Raman intensity vs. adsorbate loading.

Time-Resolved Raman Spectroscopy: Using a pulsed infrared laser, it is possible to rapidly activate and quench catalytic reactions within zeolites. Since diffusion is slow on the timescale of the heating and quenching, the zeolite pores behave like a constant volume reactor during these experiments. We plan to use this method to follow hydrocarbon reaction pathways with unprecedented time resolution.

Simultaneous Spectroscopy/Performance Experiments: By interfacing a gas chromatograph to the fluidized bed reactor used for in-situ Raman spectroscopy

measurements, it will be possible to monitor the performance of a catalyst during reaction while measuring the Raman spectrum at the same time.

Multi-Wavelength Raman Spectroscopy: From a comparison of visible and ultraviolet laser excited Raman spectra it is apparent that resonance enhancement is operative for many molecule and materials systems of interest in catalysis. In a mixture the species that are resonance enhanced are selectively displayed in the measured Raman spectrum. In order to obtain a more comprehensive view of the species present in catalytic mixtures, Raman spectra will be recorded at a series of excitation wavelengths in the visible and ultraviolet wavelength regions.

Recent Publications

1. UV-Raman characterization of Iron peroxo adsorbates on Fe/MFI catalyst with high activity for NO_x reduction, Z. X. Gao, H. S. Kim, Q. Sun, P. C. Stair and W. M. H. Sachtler, *J. Phys. Chem. B.* **105**, 6186-6190 (2001).
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10. Vibrational Spectra of Alumina- and Silica-Supported Vanadia Revisited: An Experimental and Theoretical Model Catalyst Study, N. Magg, B. Immaraporn, J. B. Giorgi, T. Schroeder, M. Bäumer, J. Döbler, Z. Wu, E. Kondratenko, M. Cherian, M. Baerns, P. C. Stair, J. Sauer, H.-J. Freund, *J. Catal.* Submitted.

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Institute for Environmental Catalysis

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Goal

Advance the molecular level understanding of catalytic chemistry designed to reduce human impact on the environment.

Highlights

The Institute for Environmental Catalysis supports six (6) research projects that address, broadly, topics in catalytic oxidation.

The Surface Structure – Chemistry Relationship: This surface science project includes the synthesis of metal oxide and mixed-metal oxide single crystals, surface structure determination of oxide surfaces using diffraction (x-ray & electron) and microscopy techniques, and associated surface chemistry studies. Recent accomplishments include the synthesis of large magnesium orthovanadate and hematite single crystals suitable for surface structure analysis, the structure determination of several SrTiO₃ surfaces, and studies of the structure and composition dependence in methyl group chemistry on hematite surfaces.

Novel Selective Oxidation Catalysis: The selective oxidation of CO by supported gold nanoparticles and the novel synthesis of supported gold catalysts by Jet Enhanced Nanoparticle Deposition (JEND) have been studied. Focusing on gold supported on alumina, a combination of catalytic, in-situ spectroscopic, and electron microscopy results indicate that

surface hydroxyl groups play an important role in the active site for CO oxidation. At the same time XANES measurements show mostly metallic gold. These results can be reconciled by postulating an active site consisting of a hydroxyl group bonded to a gold cation that is embedded in an otherwise metallic gold cluster. The first samples for catalytic studies were synthesized by the JEND method. This method involves a gas phase condensation and reaction between atomic gold, aluminum and oxygen to produce highly uniform, alumina supported gold nanoparticles.

Nano-structured Membrane Oxidation Catalysts: Novel selective oxidation catalysts have been synthesized using nano-structured organic and alumina membranes as the catalyst host. These catalysts have been studied both experimentally and computationally. Manganese-based catalysts, active for the enantioselective epoxidation of olefins, have been shown to be exceptionally robust against deactivation when incorporated into molecular square frameworks. Vanadium oxide supported in alumina membranes made by anodic aluminum oxidation demonstrates remarkable selectivity for the oxidative dehydrogenation of cyclohexane to cyclohexene. On conventional Vanadia/alumina catalysts only small amounts of cyclohexene are produced compared to the deeper oxidation products benzene, CO, and CO₂.

Low Temperature NO_x Reduction for Diesel Engine Exhaust Abatement: The reaction mechanism for NO₂ reduction by acetaldehyde catalyzed BaNa-Y zeolite has been studied by FTIR and isotopic labeling. A key intermediate in this reaction is proposed to be O₂NCH₂NO₂⁻, which is formed by a sequence of reactions starting with the formation of acetate ions and subsequently the aci-anion of nitromethane. Further reaction with NO₂ forms the O₂NCH₂NO₂⁻, which is stabilized by ionic environment in the zeolite. This intermediate leads to ammonia via reaction with water, and N₂ is formed by well-known reactions between ammonia and NO₂.

Gas Phase Photocatalysis: The mechanism of photocatalytic oxidation of volatile organic compounds and chlorinated hydrocarbons by TiO₂ is under investigation. From a combination of spectroscopic evidence localized “hot spots” in the photocatalytic activity have been attributed to the interface region of rutile and anatase crystals of TiO₂.

Metal Oxides in Aquatic Systems: In aquatic systems manganese oxides (MnO_x) are formed primarily by biological processes and have been shown to have unique chemical properties. However, their structures are often difficult to determine owing to intimate association with a complex nucleation medium, small particle size, lack of long-range order, and diversity of structure types. Syntheses of well-characterized MnO_x model compounds are underway in order to provide standards for establishing spectroscopic and x-ray scattering signatures.

DOE Interest

These projects represent a broad attack on the development and fundamental understanding of catalytic systems for selective oxidation. Success in this area is expected to impact energy technology in diverse ways, ranging from the clean-up of hydrogen for fuel cell applications to the more efficient and cleaner use of energy in chemical manufacturing.

2003 Publications

1. Agrios, A. G., Gray, K. A. & Weitz, E. Photocatalytic Transformation of 2,4,5-Trichlorophenol on TiO₂ under Sub-Band-Gap Illumination [Erratum for Langmuir 2003, 19, 1402-1409]. *Langmuir* **19**, 5178 (2003).
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MICROPOROUS AND MESOPOROUS NANO-SIZE TRANSITION METAL OXIDES: PREPARATION, CHARACTERIZATION, AND APPLICATIONS

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Collaborators: Hanson, J.; Iton, L. E.; Navrotsky, A.; Tsapatsis, M.; Howell, A. R.; Aindow, M.; Marquez, M.; Ching, S.; Satyapal, S.; Rusling, J. F.; Malz, R.

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Goal

To synthesize porous nano-wires, helices, lines, patterns, powders, and other morphologies for selective catalytic oxidations.

Recent Progress

Much of our research has concerned the synthesis of porous octahedral molecular sieves (OMS) and octahedral layered (OL) materials that are nano-size. Synthesis and characterization of nano-materials of porous manganese oxides in various surface areas and morphologies has been a major research effort. Applications of such systems in catalysis and as sensors have also been pursued.

A major focus of our research has been to produce nano-size porous manganese oxide materials. Tetraalkylammonium manganese oxide sols have been prepared using phase transfer techniques with mixed aqueous/organic solvents. Such sol-gel syntheses can also involve the sole use of organic solvents. These precursor sols are extremely stable and have been used to prepare a variety of novel materials with interesting morphologies, including helices,²⁻⁴ nano-lines, and nanopatterns.¹ Such colloidal sols can also be used to form thin films that have excellent ion-exchange properties with 100% of cations being exchanged in a 3 sec period.⁴ This fast exchange is likely due to the presence of interconnected micro-, meso-, and macropores. The nano-lines on glass surfaces have been characterized with a variety of methods including atomic force microscopy (AFM) and electron paramagnetic resonance (EPR).²

Novel porous inorganic helices have been synthesized by slow heating of these colloidal (~ 15 Å diameter hexagonal plates as determined by small angle neutron scattering) sols and high resolution transmission electron microscopy of the sol precursors. The helices are excellent semiconductors, and can be ion-exchanged and heated to produce new compositions and structures that retain their helical macrostructure. Mechanistic studies of formation of these helices via magnetic resonance imaging (MRI) methods suggest that buckling of the gel occurs via gravitational forces.¹ A patent has issued on these helical materials.^A

Nano-lines have been prepared by slow evaporation of the colloidal precursor TMAMnO₄ by dip coating procedures. The complicated nature of these lines shows that the lines are actually composed of a series of lines. Cross sections via X-ray fluorescence imaging of manganese concentrations show that the mid sections of the widths of the lines are thicker than the edges of the lines, leading to the formation of columns of semicircles.

Another synthesis effort has focused on the preparation of nano-size manganese oxide octahedral layered (OL) materials of birnessite, OL-1. These materials have been pillared with organic amine species.⁸ Synthesis and X-ray absorption studies of nanosize OL-1 materials having tetramethylammonium cations as templates have been a large focus of our recent efforts. Another thrust has been the incorporation of Fe³⁺ species in the framework of octahedral

molecular sieve (OMS) cryptomelane, known as OMS-2.^{5,22} Many natural manganese oxide nodule materials are composed of iron and manganese, however, it has been difficult to achieve framework substitution of iron due to instability problems until our recent studies.

A novel synthesis of bulk OMS materials with an asymmetric 2x4 tunnel structure having a pore size of dimensions 4.6 Å by 9.2 Å and having a tunnel diagonal as large as 10.3 Å has been prepared.¹⁰

Incorporation of manganese colloids into MCM-41⁸ and into layered double hydroxides (LDH)⁹ materials has also been done in order to produce manganese in specific locations in mesoporous and layered materials, respectively. These materials afford various coordination environments and potential unique physical and chemical properties not available in OMS and OL materials. Nanoparticles of mordenite zeolite materials have been made.¹⁰ All of these systems have an emphasis on preparation of nanomaterials.

Related synthetic efforts include the use of layer by layer films of alternating polymer, myoglobin (heme containing) proteins, and manganese oxides. Such films are prepared by using alternating layers of positively and negatively charged species and monitoring the thickness with an *in situ* quartz crystal microbalance. Multi-layer films made from tetralkylammonium permanganate are also readily exchangeable, show more reversible electrochemistry of intercalated dye molecules than corresponding bulk powders, and are uniform. Colloids, helices, and patterned films have been made as an extension of this work by incorporating myoglobin into manganese oxide precursors since the earlier work suggested an association between these systems.¹² Some recent work in this area of manganese oxide layer by layer films in the absence of myoglobin show excellent activity for the selective oxidation of styrene to styrene oxide.¹³ There is a clear interaction of H₂O₂ with the manganese oxide films, which leads to enhanced oxidation of styrene.

(1) Catalysis and Other Applications.

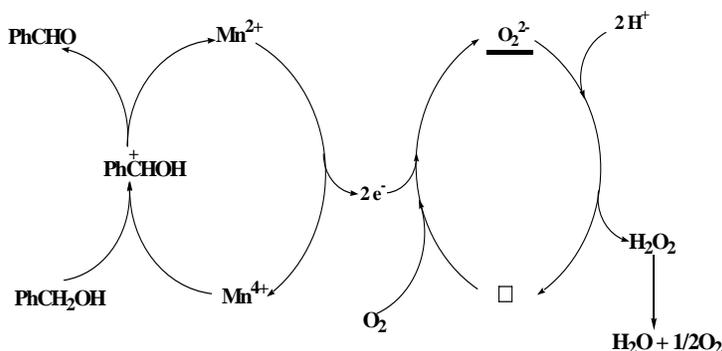
Our major efforts have focused on the use of several OMS and OL materials in the selective oxidation of alcohols.¹⁴ These catalysts are outstanding materials for the selective aerobic catalytic oxidation of alcohols. The selectivity in almost all cases is 100%. We believe that these materials and processes have commercial value and a patent application has been submitted in this area.^B A two-step Mars-van Krevelen model involving an exchange between gas phase oxygen and lattice oxygen of the OMS-2 catalyst was found to give a better fit. This was further corroborated by an oxygen isotope labeling study. The changes in the ¹⁶O and ¹⁸O content of the product water confirm this observation.

Kinetic isotope effects are used to ascertain if the oxidative attack on the alcohol molecule is at the secondary hydrogen atom or at the hydroxyl hydrogen atom. The fact that C-H and C-D bonds differ in their zero-point energies is used to make this distinction. The presence of an isotope effect greater than 1 implies that the benzyl alcohol substrate reacts much faster than its di-deuterated analogue. The presence of a large kinetic isotope effect implies that the removal of a secondary H atom is indeed the rate-controlling step. A mechanism in which the abstraction of the secondary H atom leads to the formation of a free radical is not feasible as shown by experiments using quinone as a radical trap. These results point to an electron-deficient carbon center in the intermediate formed in the rate-determining step.

Not many examples of oxidations are known to occur by the Mars van Krevelen pathway in the liquid phase due to competition from readily generated free radicals. Our proposed mechanism indicates a multi-electron redox event occurring in the liquid phase (See Fig. 1). This result coupled with the potential of shape-selectivity in the regularly ordered tunnels makes these OMS-2 materials an interesting new class of oxidation catalysts. Nano-ribbon porous manganese oxide materials are also useful in these selective oxidation reactions.¹⁵

Two key recent studies regarding selective oxidations have been done. First, hollow spheres of OMS-2 containing H⁺ ions lead to a doubling of the rate for selective oxidation of alcohols.¹⁶ These data clearly show that morphology is important as regards rate and that an interplay of

micro-, meso-, and macropores may be important in improving the rate of transport. The second study is an extension of the ^{18}O labeling experiments that clearly show that the rates of these reactions are related to the surface area of the catalyst, to the incorporation of H^+ via NH_4^+ exchange, and to the lability of surface oxygen in the manganese catalysts.¹⁷ A combination of labeling, mass spectrometry, temperature programmed desorption, and synthetic and microanalytical experiments were done to come to these conclusions. A review of the synthesis and applications of OMS and OL materials with an emphasis on catalysis has been prepared.¹⁸ Fig. 1, Proposed Mechanism for Aerobic Oxidation of Alcohols using OMS-2.



Manganese oxide nanoparticles can also be used for the degradation of nerve gas simulants. The Department of defense is currently exploring use of such systems for real chemical warfare agents. These systems have been patented in collaboration with United Technologies Research Center (UTRC).^D

A process for the synthesis of 2,2,6,6-tetra-methyl-4-oxopiperidine from acetone and ammonia-donor compounds in the presence of CaY zeolite catalysts has also recently been developed.¹⁹ This process is being licensed by Crompton. In related research we have used zeolite type materials for the alkylation of aniline.²⁰ A final application of porous manganese oxide nanomaterials (films) is their use as sensors in detection of halogenated hydrocarbons.²¹ This process is being used by Olin for applications in monitoring chlorinated species in swimming pools.

List of Publications of S. L. Suib, Acknowledging DOE Support

January 1, 2002 – February 5, 2004

1. Giraldo, O.; Durand, J.P.; Ramanan, H.; Laubernds, K.; Suib, S. L.; Tsapatsis, M.; Brock, S. L.; Marquez, M. Dynamic Organization of Inorganic Nanoparticles into Periodic Micrometer-Scale Patterns, *Ang. Chem., Int. Ed.*, 2003, **42**, 2905-2909.
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Small Molecule Activation with Sterically Hindered Tris(pyrazolyl)borate Metal Complexes

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Goal

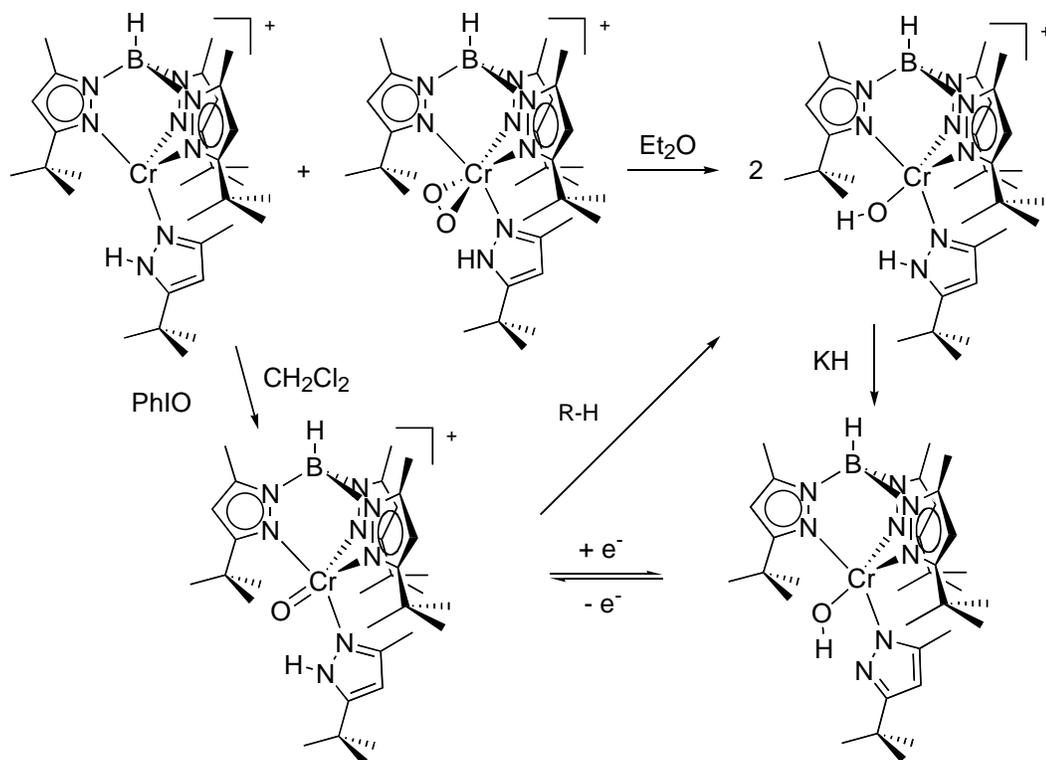
Develop catalysts for the activation of O₂ and its use as terminal oxidant in the functionalization of organic molecules.

Recent Progress

Chromium Dioxygen Complexes: We have prepared a series of chromium(III) superoxide complexes via binding of O₂ to coordinatively unsaturated chromium(II) precursors.¹ These complexes are the first structurally characterized representatives of their kind (i. e. chromium(III) superoxide complexes), and they all adopt the rare ‘side-on’ binding mode of superoxide that we first discovered in Tp^{tBu.Me}Co(O₂).

Dioxygen Activation: Reaction of the dioxygen complexes with their precursors results in splitting of the O-O bond and the formation of reactive chromium(IV) oxo intermediates. Avoiding all hydrogen atom donors in the reaction of [Tp^{tBu.Me}Cr(pz'H)]BARF with PhIO has allowed the isolation and full characterization of [Tp^{tBu.Me}Cr(O)(pz'H)]BARF.² The redox chemistry of the latter was investigated in collaboration with Prof. D. H. Evans, in order to estimate the affinity of the oxo complex for a hydrogen atom.⁶

Hydrocarbon Activation: [Tp^{tBu.Me}Cr(O)(pz'H)]BARF reacts with organic molecules containing weak C-H bonds ($D_{C-H} < 90$ kcal/mol) by hydrogen atom abstraction to yield the chromium(III) hydroxide [Tp^{tBu.Me}Cr(OH)(pz'H)]BARF. Activation parameters and isotope effects for several reactions have been determined. For example, the kinetic isotope effect for the hydrogen atom abstraction from 9,10-dihydroanthracene at 293 K is $k_H/k_D = 25.2$. Determination of the temperature dependencies of the H- and D-abstraction reactions revealed large differences ($\Delta\Delta H^\ddagger = 7.5(5)$ kcal/mol and $A_H/A_D = 10^{-4.3(1.1)}$). These values indicate a significant contribution of quantum mechanical tunneling to the hydrogen atom transfer. H-atom tunneling has been invoked for several oxidation enzymes, and this small molecule reaction provides a valuable model system for the study of H-atom tunneling.



Cobalt Imido Complexes: Our investigation of cobalt dioxygen chemistry has yielded evidence for the intermediacy of the terminal cobalt oxo species $\text{Tp}^{\text{tBu.Me}}\text{Co}=\text{O}$ in several reactions; however, This compound is apparently too reactive for even spectroscopic detection. We have thus pursued the chemistry of isoelectronic imido complexes, $\text{Tp}^{\text{tBu.Me}}\text{Co}=\text{NR}$, as chemical models. For example, reaction of $\text{Tp}^{\text{tBu.Me}}\text{Co}(\text{N}_2)$ with Me_3SiN_3 yielded a cobalt(III) amido species resulting from hydrogen atom abstraction from the ligand by the inferred imido complex $\text{Tp}^{\text{tBu.Me}}\text{Co}=\text{NSiMe}_3$.⁵

Stable Cobalt imido complexes: To our surprise, tertiary alkyl azides (e. g. $\text{R} = \text{}^t\text{Bu, Ad}$) have produced isolable cobalt(III) imido complexes. However, the thermal reactivity of these compounds also includes the functionalization of ligand C-H bonds. The mechanism of this C-H activation and the exact nature of the unusual products are currently under investigation.

Peroxynitrite chemistry: The recent interest in peroxynitrite led us to explore the synthesis of stable peroxynitrite complexes by the reactions of $\text{Tp}^{\text{tBu.Me}}\text{Co}(\text{O}_2)$ with NO and $\text{Tp}^{\text{tBu.Me}}\text{Co}(\text{NO})$ with O_2 . We have gathered spectroscopic evidence for an unstable intermediate, but could only isolate the nitrate isomer $\text{Tp}^{\text{tBu.Me}}\text{Co}(\text{O}_2\text{NO})$.³

Tris(pyrazolyl)borate Iron chemistry: The prevalence of iron in oxidation enzymes and the position of this element between chromium and cobalt has motivated some exploration of $\text{Tp}^{\text{tBu.Me}}\text{Fe}$ chemistry. Thus we have prepared $\text{Tp}^{\text{tBu.Me}}\text{Fe}(\text{CO})$ (from $\text{Tp}^{\text{tBu.Me}}\text{Fe}-\text{R}$) and we have strong evidence for the formation of $\text{Tp}^{\text{tBu.Me}}\text{Fe}(\text{N}_2)$. The latter compound should provide entry into dioxygen chemistry of the $\text{Tp}^{\text{tBu.Me}}\text{Fe}$ fragment.

DOE Interest

O₂ is a readily available and environmentally benign oxidant. Catalytic oxidations using O₂ (including those proceeding in fuel cells) are of critical importance to chemistry and electricity generation.

Future Plans

Generation and reactivity of metal oxo complexes: The coordination and cleavage of O₂ by metal (Cr, Co) complexes yields metal oxo species that can activate and functionalize C-H bonds (as do isoelectronic imido complexes). We plan to measure the hydrogen affinities of relevant compounds (D_{MO-H}), and to study the kinetics and mechanism of the hydrogen atom transfer. We hope to learn more about tunneling contributions to those reactions.

Oxidation resistant ligands: Some of the C-H bond activation we have seen has involved substituents of our ligand system (the tris(pyrazolyl)borates – ‘Tp^R’). We plan to explore the chemistry of Tp-ligands with amide groups in the 3-position, in the hope of preventing ligand destruction.

Iron chemistry: We are just beginning the exploration of iron complexes and hope to find informative parallels and differences to what we have learned with cobalt and chromium.

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Molecular Precursor Methods for the Control of Structure in Heterogeneous Catalysts

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Goals

The primary goal of this project is to develop molecular chemistry that allows atomic-level and nanoscopic control over the structures of heterogeneous catalysts. Much of this work has targeted the production of multi-component oxides for which high dispersions are expected to give desirable catalytic properties.

Recent Progress

Molecular Precursor Routes to Heterogeneous Catalysts. The synthesis of a variety of multi-component oxide materials with tailored properties employed a molecular building-block approach referred to as the *thermolytic molecular precursor* (TMP) method. This molecular precursor approach employs metal complexes containing oxygen-rich ligands, such as those with the general formulas $L_nM[\text{OSi}(\text{O}^i\text{Bu})_3]_m$ and $L_nM[\text{O}_2\text{P}(\text{O}^i\text{Bu})_2]_m$, where L_n = alkoxide, amide, alkyl, etc. Such compounds function as excellent single-source precursors to carbon-free, homogeneous mixed-element oxide materials of the types M/Si/O and M/P/O, respectively. Although the sol-gel process and the TMP method both represent low-temperature routes to metastable materials, the TMP method offers several advantages. Firstly, the use of high purity and well-defined species allows accurate control over the stoichiometry of the final material. Also, the preexistence of M-O-E groups maximizes the homogeneity of the final material and leads to a high concentration of heterolinkages. The TMP method also offers benefits with respect to surface properties, since the use of nonpolar solvents minimizes pore collapse upon drying, thus providing high pore volumes and surface areas. Additionally, the use of nonaqueous media prevents M-O-E cleavage via hydrolytic means, a common occurrence in sol-gel processes that leads to inhomogeneity. Finally, the precursor complexes may serve as soluble molecular models for single-site catalysts involving a metal center on the surface of an oxide support.

Studies on aluminosilicate materials obtained by the TMP route indicate that the molecular precursor method results in a higher dispersion of Al and Si, and therefore a greater surface acidity, than related aluminosilicates obtained by sol-gel methods. Related investigations targeted vanadia-silica materials, and determined that precursors with the lower oxidation state (+4) gave more homogeneous structures. Routes to boron-containing materials were enabled with the synthesis of a rare example of a boronous acid, $\text{HOB}[\text{OSi}(\text{O}^i\text{Bu})_3]_2$. This species was used to obtain various metal-containing precursors. Molybdenum-containing precursors to Mo/P/O, Mo/P/Si/O, Mo/P/B/O and Mo/Bi/Si/O catalysts for oxydehydrogenation were investigated. Along similar lines, the new precursor $(^i\text{BuO})_3\text{CrOSi}(\text{O}^i\text{Bu})_3$ was used to obtain chromium-containing catalysts of the type Cr/Si/Al/O and Cr/Si/Zr/O. Upon calcinations, these materials contain mostly Cr^{6+} centers. These exhibit modest activities for propane ODH, and excellent activities and selectivities for the dehydrogenation of propane.

Production of Well-Defined, Single-Site Catalysts. Attempts to develop general routes to catalysts with tailored and improved properties are based on the application of molecular chemistry in the fine control of structures for the catalyst active site. Single-site titanium catalysts are the most active and selective for various hydrocarbon oxidation reactions. $\text{Ti}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$ serves as an excellent reagent for introduction of isolated, surface-bound titanium sites for epoxidation. Results suggest that the siloxide ligands provide an important and beneficial effect on the structure of the supported catalytic site. Precursors with various Ti:Si ratios, $\text{Ti}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$, $(^i\text{PrO})\text{Ti}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ and $(^t\text{BuO})_3\text{TiOSi}(\text{O}^t\text{Bu})_3$, were supported onto MCM-41 and SBA-15, and the structures of the active sites were probed via spectroscopic methods. These catalysts give the best results reported so far for the epoxidation of cyclohexene with titanium-based catalysts.

Molecular Precursor Route to Hybrid Inorganic/Organic Materials. It was shown that new types of hybrid inorganic-organic materials (which are promising as new catalyst supports) may be obtained by the thermolytic molecular precursor approach. Cothermolyses of $\text{Zr}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$ with various organosilanes (e.g., $(\text{EtO})_3\text{SiC}_6\text{H}_4\text{Si}(\text{OEt})_3$) gave these materials, which were thoroughly characterized.

Homogeneous Catalysis with Methane. A new effort in this program targets the homogeneous, catalytic functionalization of methane. This chemistry takes advantage of the ability of early transition metal, d^0 complexes to mediate σ -bond metathesis chemistry. The scandium neopentyl derivative Cp^*_2ScNp ($\text{Np} = \text{CH}_2\text{CMe}_3$) is highly reactive toward C-H bond activation processes. For example, it reacts with benzene to produce neopentane and the phenyl derivative Cp^*_2ScPh . In addition, it reacts more rapidly with methane than does the methyl derivative Cp^*_2ScMe . The mechanism of this activation has been explored, and the chemistry involving the non-degenerate exchange of alkyl groups at scandium has been extended to the design of catalytic cycles.

DOE Interest

The programs described above provide a useful vehicle for the training of students and postdocs in technologies that impact the fields of catalysis, materials chemistry, and reaction chemistry/dynamics. In particular, it provides a rare opportunity for coworkers to gain experience in application of the diverse fields of inorganic synthesis, materials characterization, and reaction engineering in solving problems in catalysis. Most of this work has targeted the development of new catalysts for the selective conversions of hydrocarbons to more valuable products. Since such processes contribute significantly to the world economy, the potential impact is large. Our studies should lead to superior catalysts for various hydrocarbon transformations, including selective oxidations and carbon-carbon bond formations.

Future Plans

Molecular Precursor Routes to New Catalytic Materials. The use of molecular design concepts will be employed in studies to develop routes to new, catalytically active compositions such as VP_xO_y and VSb_xO_y . In addition, we will continue studies toward the achievement of control over the surface structures of heterogeneous catalysts. In one aspect of this work, molecular precursor species will be used to carry metal-based functional groups onto the surface of a support. This method will be explored in the context of extending the structural control that is currently available, by use of new copolymer templates. There is also a strong need for new synthetic methods for producing catalytic, oxide nanoparticles of controlled size and shape. Initial results indicate that the thermolytic molecular precursor route may be useful in this regard. We will also continue to investigate the use of this method in the preparation of isolated,

single-site catalysts on the surface of an oxide support. Recently prepared precursors, such as $V[\text{OSi}(\text{O}^t\text{Bu})_3]_2(\text{O}^t\text{Bu})_2$ and $\text{O}_2\text{Mo}[\text{OSi}(\text{O}^t\text{Bu})_3]_2$, are being studied in the synthesis of well-defined single sites involving vanadium and molybdenum. Such catalysts may prove to be selective hydrocarbon oxidation catalysts.

Transformations of Hydrocarbons via σ -Bond Metathesis. The homogeneous methane activation chemistry described above will be pursued further with attempts to obtain more active catalysts via manipulation of ligands on Sc and related metals. We will probe the mechanisms of methane activations in related systems, to learn as much as possible about the factors that influence activity and selectivity. Since there are a number of possible competing reactions (e.g., beta-hydrogen elimination and sp^2 C-H activation in the olefin), the influence of catalyst structure, and the electronic properties of ancillary ligands, will be extensively explored with respect to their influence on reactivity. We intend to examine these effects in complexes involving Lu, Y, and Sc, and for cationic complexes of Zr and Hf.

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Well-Defined, Single Site Iron Centers and Heterobimetallic Systems for Catalytic Transformations of Hydrocarbons

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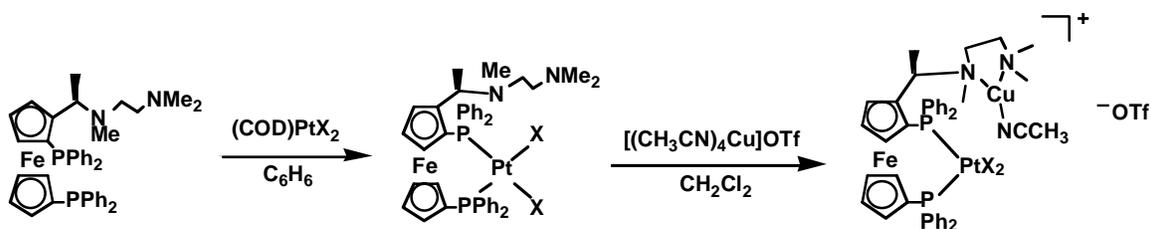
Goals

The iron-containing zeolite FeZSM-5 has attracted considerable attention due to its high activity as a catalyst for the selective oxidation of hydrocarbons with nitrous oxide as the oxidant. Although there is no consensus on the nature of the iron centers in this catalyst, it seems clear that some type of isolated iron site plays an important role in the selective processes catalyzed by FeZSM-5. Given the increasing interest in the structure and catalytic chemistry of supported iron centers, and related chemistry observed for iron-containing enzymes, we are pursuing the development of reliable routes to stable, well-defined inorganic iron species bound to an oxide support. A second aspect of this program involves attempts to develop new homogeneous catalysts based on heterobimetallic systems.

Recent Progress

Routes to Single-Site Iron Catalysts. For the introduction of single-site iron species onto silica, the precursor molecule $\text{Fe}[\text{OSi}(\text{O}^t\text{Bu})_3](\text{THF})$ is bonded to the surface of SBA-15 via protonolysis, which occurs with loss of $\text{HOSi}(\text{O}^t\text{Bu})_3$. Calcination then leads to stable, isolated inorganic Fe sites. The new site may be partially supported by the few equivalents of silica that are introduced by the molecular precursor, and in this way, stabilized. The resulting materials are catalysts for selective oxidations of alkanes, alkenes, and aromatic compounds with hydrogen peroxide as the oxidant.

Bifunctional Ligand for Pd/Cu and Pt/Cu Complexes. In designing the ligand framework for these catalysts, our attention was drawn to Kumada's ferrocene-based ligand (shown below). This ligand had previously been used for monometallic asymmetric catalysis. We reasoned that bimetallic complexes supported by this ligand might be readily synthesized in a stepwise fashion via the initial formation of a bisphosphine-Pd or -Pt complex and subsequent chelation of Cu(I) by the diamine moiety (see below; X = Me, Cl).



We have prepared bimetallic Pt-Cu complexes, and have devised a means for activating the Pt center toward the binding of organic substrates by abstracting the CH₃ groups with [Ph₃C][PF₆]. In attempting to prepare Pd-Cu complexes, we discovered an interesting

isomerization process in which the initially formed (P,P)-Pd complex was converted predominantly to the (P,N)-Pd complex over time. We have further probed the coordination chemistry of this ligand system by preparing a bimetallic Pd-Mg complex, in which Pd is (P,P)-bound and Mg is (N,N)-bound.

Heterobimetallic Pt/Ag System for the Hydroarylation of Alkenes. A new methodology for the hydroarylation of simple olefins (propylene, 2-butene, norbornene) with benzene and other arenes was developed. This process exhibits high yields and mild reaction conditions (80 °C, 2 h). The catalyst systems consist of a Pt(II) complex and a Ag(I) salt, such as AgOTf or AgBF₄. A variety of Pt precursors can participate in this process, including the complexes [2-(2-pyridyl)indolyl]PtCl(C₂H₄), containing a bidentate nitrogen donor ligand, and (1,5-cyclooctadiene)Pt(OTf)₂, containing a diolefin ligand. Control experiments demonstrate that the role of the Ag(I) salt extends beyond halide abstraction, and possibly involves arene activation. Pt complexes, on the other hand, may act as Lewis acids toward olefin substrates, as demonstrated by the exclusive formation of the branched product cumene from benzene and propylene. The potential catalytic role of strong protic acids, which could be formed via hydrolysis of metal triflates by adventitious water, has been ruled out with mechanistic experiments.

DOE Interest

These projects represent challenging research problems that are relevant to issues in biology, and to development of chemical processes that could have a significant impact on the economy. Hydrocarbons are an important source of chemical feedstocks, and their selective reactions with oxygen have the potential to provide valuable chemicals. In addition, an increased understanding of the reactivity of oxygen in catalytic oxidation processes should aid in the elimination of wastes and in maximizing the efficiency of hydrocarbon utilization to provide transportation fuels and chemicals. The training of students and postdocs in this field should add to the technological capability of the nation.

Future Plans

Routes to Single-Site Iron Catalysts. Our initial focus has been on mononuclear single-site catalysts that activate oxygen. We would like to like to expand this effort by looking at support (i.e., "ligand") effects on the reactivity of the isolated iron sites. For example, the FeZSM catalysts of Panov appear to contain iron in an aluminosilicate framework. We would therefore like to generate well-defined, single iron sites on high-surface-area aluminosilicates. It is also of interest to develop routes to diiron sites, since these have been implicated in the Panov chemistry and are clearly important for selective oxidation catalysis in biology. Initial efforts in this direction have produced molecular precursors to diiron species, including [NEt₄]₂{[(^tBuO)₃SiO]₃Fe-O-Fe[OSi(O^tBu)₃]₃}.

Heterobimetallic Catalyst Systems for Transformations of Hydrocarbons. Further investigations with the new homogeneous Pd/Cu and Pt/Cu complexes will focus on the role of these species as olefin oxidation catalysts. Studies will be designed to probe the ability of the copper center to activate oxygen, and the activation of olefins by the other metal center. Later work will also involve redesigns of the ligand platform, as appropriate, and immobilization of the catalytic centers. The new Pt/Ag catalyst system will be studied in detail. Considerable effort will be devoted to establishment of the mechanism of this bimetallic system. In addition, we intend to explore the generality of this transformation, and the use of this catalysis in hydroarylations with functionalized substrates.

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Probing Surface Chemistry under Catalytic Conditions: Hydrogenation and Cyclization

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Goal

To obtain a fundamental understanding of the catalytic reaction pathways for palladium-catalyzed hydrocarbon conversion reactions by relating the chemistry observed in ultrahigh vacuum to processes occurring under catalytic conditions.

Recent Progress

Ethylene and acetylene hydrogenation and acetylene cyclotrimerization provide ideal candidates for fundamental mechanistic studies since these reactions occur both in ultrahigh vacuum, where products are formed in temperature-programmed desorption, and also at high pressures where the catalytic reaction kinetics of the supported systems are mimicked by a model Pd(111) single crystal catalyst. The nature of the surface is monitored under reaction conditions using photoelastic modulation reflection-absorption infrared spectroscopy (PEM-RAIRS) where we have demonstrated that the infrared spectrum of a monolayer of CO can be measured in the presence of over 200 Torr of gas-phase CO. A method has also been developed for measuring the structures of disordered overlayers using low-energy electron diffraction (LEED) by measuring the I/V curves of the substrate (1×1) Bragg spots of disordered overlayer-covered surfaces. It has been shown theoretically that the effect of an adsorbate on the substrate diffraction spots is about two orders of magnitude larger than the diffuse background scattering and is therefore much easier to measure. The resulting I/V data are analyzed using conventional LEED methods and the method has been tested by comparing the structure measured from both disordered and ordered overlayers of acetylene on Pd(111) with identical structures being obtained by both methods

Both LEED and RAIRS measurements show that ethylene adsorbs on clean Pd(111) in a di-**F** configuration in a structure that is in good agreement with DFT results. A significant improvement in Pendry R-factor was found for a surface containing ~15% of a tilted species with a geometry that is in excellent agreement with the calculated structure for vinyl species on Pd(111) suggesting that some dehydrogenation takes place following ethylene adsorption in clean Pd(111). Vinyl species grafted onto Pd(111) using vinyl iodide either hydrogenate to yield ethylene or react to form ethylidyne on Pd(111) suggesting a possible route for ethylidyne formation.

Ethylene adsorption on hydrogen-saturated Pd(111) has also been studied using RAIRS and LEED revealing the formation of a **B**-bonded species, which is oriented with the C=C axis parallel to the surface and adsorbed on an atop site. Again, the measured structure is in excellent agreement with the results of DFT calculations. The proportion of **B**- and di-**F**-bonded ethylene varies with hydrogen coverage such that only di-**F**-bonded ethylene is present on the clean surface, while

ethylene is exclusively **B**-bonded on a hydrogen-saturated surface. Since hydrogen can adsorb both on and below the surface, the question of whether surface or subsurface hydrogen affects the nature of adsorbed ethylene was investigated. The ratio of surface to subsurface hydrogen depends on temperature and it was clearly demonstrated that subsurface hydrogen is exclusively responsible for inducing the formation of **B**-bonded ethylene. TPD experiments revealed that **B**-bonded ethylene desorbs with an activation energy of 50 kJ/mol compared with 79 kJ/mol for di-**F**-bonded ethylene so that the adsorption of ethylene is substantially weakened by the presence of subsurface hydrogen.

The chemistry of the ethyl intermediate to ethylene hydrogenation was also investigated on Pd(111) to identify the rate-limiting step in the sequential addition of hydrogen. In this case, the adsorbed ethyl group, formed by exposing the surface to ethyl iodide, reacted with hydrogen to form ethane in TPD at ~160 K compared to the desorption peak temperature for the hydrogenation of ethylene itself of ~270 K. This indicates that the addition of the first hydrogen to (**B**-bonded) ethylene is the rate-limiting step, and that the resulting ethyl group reacts rapidly once it is formed.

Strongly bound ethylidyne species are present on the surface during ethylene hydrogenation. In spite of the presence of this ethylidyne overlayer it has been shown that ethylene, acetylene and CO all adsorb onto ethylidyne-saturated Pd(111). Ethylene is di-**F**-bonded on ethylidyne-covered Pd(111) and **B**-bonded on ethylidyne-covered Pd(111) pre-dosed with hydrogen indicating that ethylidyne acts as a spectator species.

The kinetics of ethylidyne formation from ethylene have been measured on Pd(111), with an activation energy to ethylidyne formation of 92 ± 4 kJ/mol and a formation rate constant k_1 at 300 K of $\sim 7.1 \times 10^4 \text{ s}^{-1} \text{ Torr}^{-1}$. The ethylidyne removal kinetics by high pressures of hydrogen were measured, both on clean Pd(111) as well as on alumina supported palladium and showed that the initial removal rate is first order in hydrogen pressure for both a Pd(111) single crystal and alumina-supported palladium. Assuming that the initial rate of ethylidyne removal is given by $k_2 \text{P}(\text{H}_2)$ (ethylidyne) yields a value of $k_2 = 3.1 \pm 0.3 \times 10^{-2} \text{ Torr}^{-1} \text{ s}^{-1}$ at 300 K. The activation energy for ethylidyne removal varies between ~150 and 200 kJ/mol, depending on coverage.

The ethylidyne coverage on Pd(111) was measured under reaction conditions, using PEM-RAIRS, as a function of $\text{P}(\text{H}_2)/\text{P}(\text{C}_2\text{H}_4)$, the ratio of the hydrogen to ethylene pressure and showed that the ethylidyne coverage decreases from 0.25 in pure ethylene ($\text{P}(\text{H}_2)/\text{P}(\text{C}_2\text{H}_4) = 0$) to ~0.08 as the ethylene to hydrogen ratio increases to ~2, and remains constant for higher hydrogen to ethylene ratios. Since the rates of ethylidyne removal and formation have been measured independently, assuming that these rates are identical under reaction conditions, and that the system is at steady state yields a relative ethylidyne coverage under reaction conditions given by $\theta(\text{ethylidyne}) = (k/r)/(1+(k/r))$ where r is the ratio $\text{P}(\text{H}_2)/\text{P}(\text{C}_2\text{H}_4)$ and $k = k_1/k_2$. Using the values of k_1 and k_2 measured above suggests that the ethylidyne coverage should be constant over the range of $\text{P}(\text{H}_2)/\text{P}(\text{C}_2\text{H}_4)$ used experimentally, in contrast to what was found experimentally. Possible origins for the apparently lower value of k_1 are first that the presence of subsurface hydrogen results in the formation of **B**- rather than di-**F**-bonded ethylene and second, that saturation of the surface by hydrogen limits the surface sites available to accept hydrogen and lowers the extent of vinyl formation.

DOE Interest

These results provide a deeper understanding of the nature and reactivity of the surface species that participate in palladium-catalyzed hydrogenation and cyclization reactions. A combination of LEED intensity versus energy measurements of disordered overlayers with infrared spectroscopy has allowed us to measure the structures and reactivities of the key intermediates and identify rate-limiting steps in the reaction pathway. In particular, we have identified the complex role of hydrogen in these reactions, which can act to modify the nature of the strongly bound carbonaceous layer (consisting of ethylidyne or vinylidene) or the nature of the reactant by converting di-**F** into **B**-bonded ethylene. Measurements of the nature of the model catalyst surface under reaction conditions will allow a close connection to be made between the surface species and reaction steps identified in ultrahigh vacuum with the catalytic pathway occurring under realistic conditions.

Future Plans

Surface Structure Determination: The structures of surface species, particularly ethylidyne and vinylidene will be measured using LEED methods. We will examine the structure of vinylidene species as a function of surface coverage since the saturation coverage of these species ($\theta_{\text{sat}} = 1$) suggests that their geometry may change as a function of coverage. The method we have developed for examining disordered overlayers is ideally suited for examining such coverage dependent structural changes. We are collaborating with Professor Matthew Neurock who is carrying out DFT calculations for these structures as a function of coverage to compare with these structural measurements.

Analysis of Surfaces Under Reaction Conditions: We will continue to measure the composition of the Pd(111) single crystal under reaction conditions using PEM-RAIRS initially focusing on the behavior of ethylidyne species since the strong infrared absorbance of the methyl bending mode makes this an ideal candidate for such studies, and also on the more crowded surface formed from propylene. The surface structure will be measured as a function of pressure and temperature.

Modeling of Elementary Reaction Steps: The measured ethylidyne coverage under during ethylene hydrogenation cannot be reproduced using the individually measured ethylidyne formation and removal rates indicating that the rate of ethylidyne formation is substantially lowered by the presence of surface hydrogen. This effect will be explored by measuring the rate of ethylidyne formation on hydrogen-covered surfaces. We will collaborate with Professor Neurock, who has already carried out and published the results of DFT and Monte Carlo calculations on Pd(111)-catalyzed hydrogenation reactions, to model the elementary reactions steps to compare with the experimental data. Such a close interplay between experiment and theory will provide a framework for fully understanding catalytic reaction pathways.

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6. Structure and Reactivity of Propylene on Clean and Hydrogen-covered Pd(111), D. Stacchiola, L. Burkholder and W.T. Tysoe, *Surface Science*, **542**, 129 (2003)
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Potentially Catalytic and Conducting Polyorganometallics

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Goal

To design and execute synthetic routes to novel oligometallic arrays held in unprecedented configurations and to explore their physical and chemical, particularly potentially catalytic properties.

Recent Progress

Molecular Synthesis of Carbon Nanotubes from Alkyne–Metal

Complexes

A method for the quantitative solid-state conversion of Co and Ni alkyne and biphenylene complexes at 550-700 °C for 0.5 to 3 hours into freestanding films of multiwalled carbon nanotubes has been developed. The process is unique in its use of defined molecular entities with controlled metal to carbon ratio as starting materials, the avoidance of specialized apparatus, the locospecific coverage of other structures, the emerging control of morphology of the produced ordered carbon, and the relatively mild conditions employed. The assembly of a library of structurally similar (oligo)alkynyl-arene transition metal complexes has been completed, including the metals Fe, Co, Ni, Pd, Pt, and Mo. A novel approach for the synthesis of complex alkyne ligands was developed based on tungsten catalyzed alkyne metathesis. The catalytic activity of the as-produced metal encapsulating carbon nanotubes in the Pauson-Khand reaction, Fischer-Tropsch synthesis, and shape-selective hydrogenation of nitroarenes is notable.

To probe the scope and limitations of the transition metal catalyzed side hydration of alkyne starting materials, when moist, in this synthesis, a study of their controlled reaction with water to give ketones was completed. This transformation depended strongly on the steric and electronic nature of the alkynes and other attached ligands (e.g. phosphines).

To probe the occurrence and fate of potential hydrocarbon intermediates, a FVP investigation of a biphenylene analog was concluded, leading to the isolation of five isomeric PAHs. Their mechanism of formation was probed in detail by extensive ¹³C labeling experiments.

Potentially Catalytic Oligocyclopentadienylmetals

The total synthesis of (pentaferrocenyl)CpMn(CO)₃ and its (C₅H₄Mn/Re)₅CpMn(CO)₃ congeners was accomplished (X ray structures), reaching the long sought goal of making permethylated (pentacyclopentadienyl)cyclopentadienyl complexes. The key was the use of (C₅H₄M)₂Zn reagents that could be induced to undergo fivefold Pd-catalyzed coupling with C₅I₅Mn(CO)₃ in up to 58% yield. Access to these remarkable hexanuclear clusters held in “unnatural” configurations, has opened up their exploration as potential catalysts and other functional materials. The generality of the method was demonstrated in the pericyclopentadienylmetalation of tetraiodocyclobutadieneFe(CO)₃ and hexaiodobenzene. The X-ray structures of the complexes reflect the extremely crowded nature of the persubstituted periphery of the core. Access to these remarkable clusters held in “unnatural” configurations has opened up their exploration as potential catalysts and other functional materials. The investigation of their chemistry has begun and has led to novel chemistry and structural configurations. Thus, [C₅H₄Mn(CO)₃]₅CpMn(CO)₃ undergoes photodecarbonylation to render the first stable and structurally characterized [CpMn(CO)₂]₂(CO) fragment, held together by the rigid ligand frame. In addition, (pentaferrocenyl)CpMn(CO)₃ can be selectively demanganesylated in high yield providing the novel potential ligand (pentaferrocenyl)cyclopentadiene, a highly crowded assembly endowed with five strongly electron donating substituents. Finally, single and double annealing of the Cp-substituents in (pentaferrocenyl)CpMn(CO)₃ can be effected by Lewis acids to generate intermediates on route to metallated semibuckminsterfullerene, C₃₀H₁₀, critical milestones in a projected rational synthesis of endohedral metallafulerenes.

A study of the metallomeric equilibrium between (η⁵:η⁵:η⁵-1,1':3',1''-terCp)[M¹M²(CO)₆][M³(CO)₃]⁻ X⁺ and (η⁵:η⁵:η⁵-1,1':3',1''-terCp)[M³M²(CO)₆][M¹(CO)₃]⁻ X⁺ has yielded a first X-ray structure of a heterotrimetallic (W-W-Mo) anion system and quantitative activation and equilibrium parameters. The data allow an estimation of relative metal–metal bond strengths in cyclopentadienylmetals, leading to a revision of the literature values for the W-W bond. The investigations feature the system as uniquely suitable for the study of such hitherto mechanistically inaccessible manifolds that represent, in essence, molecular wires and models for minisurfaces.

The photochemistry of FvRu₂(CO)₄ with dimethyl *cis*- or *trans*-butene- and butynedioate has been detailed, leading to the isolation of novel complexes FvRu₂(μ-η²:η⁴-CRCRCRCR)₂(L) (R = CO₂CH₃, L = CO, THF, *cis*-CHR=CHR, thiophene, PPh₃, DMSO). Kinetic experiments point to dissociative substitution of L.

Experimental and structural details of a range of fulvalene(Fv)W₂sulfur complexes have been determined, including the bridging disulfide FvW₂(μ-S₂)(CO)₆ and the monosulfide FvW₂(μ-S)(CO)₆.

Finally, the search for a synthetically conveniently accessible fulvalene* analog of Cp* (i.e. Me₅Cp) has led to syntheses of tetrakis(*tert*-butyl)- and tetrakis(trimethylsilyl)fulvalene. These ligands should enable the isolation of and structural characterization of previously observed FvM₂-CH activation products and open up the potential for catalytic transformations.

Future Plans

Metal-Catalyzed Routes to Carbon Nanotubes: A library of organometallic homo- and heterobinuclear complexes of $(C_6H_5C_2C_6H_5)$ will be screened for selectivity in defined wall, especially single wall, nanotube assembly. Efforts will be initiated in the construction of devices using this methodology. Extensions to the synthesis of BN and other heterotubes will be sought.

Potentially Catalytic Oligocyclopentadienylmetals: The electrochemical properties of radial CpM clusters, in particular the series based on cyclopentadienyl as the core, will be subject to continuing investigation. The ability of these potentially multichelating assemblies to provide the first isolable and structurally characterizable C-H σ -complexes of, e.g., methane will be tested. Preliminary observations of multiple C-H activations will be subject to scrutiny. Further effort will be made to effect complete annealing to the semibuckminsterfullerene core. Extensions of the synthetic methodology to decahaloferrocene and ruthenocene should provide access to decametallated metallocenes containing the topology of C_{60} and thus constituting excellent precursors to endohedral metallofullerenes. The novel free ligand pentaferrocenyl(cyclopentadiene), a highly electron rich (by virtue of the five Fc substituents) analog of Cp*, suggests an extensive exploration of its potential in the construction of electronically stabilized cationic and/or electron poor (16 or 14e) metals for catalysis (e.g. titanocenes for olefin polymerization, 16e-Cp*RuL⁺ for a large range of catalytic C-C bond formations).

Future work on the tercyclopentadienyl trimetallic core is directed toward manipulation of the ligand (e.g. a central indenyl fragment, to probe potential ring slippage) and the trimetallic array (e.g. rendition of an M-M'-M sequence for consonance with Marcus theory) for mechanistic purposes, and the juxtaposition of metal pairs judiciously chosen to allow for the determination of their relative intermetallic bond strengths.

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Propane Oxidation/Amoxidation Reactions over Mixed Metal Oxide Catalysts: Nature of Surface Sites and Their Relationships to Reactivity/Selectivity Properties

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Goals: Determination of the (1) nature of surface sites (surface composition, molecular structures, oxidation states and redox/acidic/basic sites) for mixed metal oxide catalysts (bulk mixed metal oxides and model supported metal oxides), (2) influence of the reaction environments on the active surface sites, and (3) molecular structure-reactivity/selectivity relationships for propane reactions oxidation, amoxidation and autothermal reactions.

Recent Progress: There is currently much interest in the activation of propane over mixed metal oxide catalysts to numerous reaction products: propylene, acrolein, acrylic acid, acrylonitrile and generation of H₂. However, there is currently very limited fundamental information about the nature of these active surface sites, especially under reactions conditions, and their relationships to the catalytic activity and selectivity. Two methods have been advanced and developed to obtain information about the surface composition of mixed metal oxides: low energy low energy ion scattering spectroscopy (LEISS) and CH₃OH-temperature programmed reaction (TPSR) spectroscopy. The elemental surface composition of mixed metal oxides was determined with a special LEISS procedure and revealed, *for the first time*, that bulk mixed metal oxides can exhibit surface segregation of certain elements (especially oxides of Mo and V). Additional information about the surface composition and reactivity was provided by CH₃OH-TPSR experiments that revealed the nature of the active surface sites (elemental composition, oxidation states, participation of surface and bulk lattice oxygen, redox/acidic/basic sites and their reactivity/selectivity relationships).

Molecular structural and oxidation state information about the active surface sites and surface reaction intermediates under reaction conditions were determined with *in situ* Raman, IR and UV-Vis spectroscopy for the model supported metal oxide catalyst systems. For propane oxidation reactions to propylene over supported vanadium oxide catalysts, the surface metal oxide species retained their fully oxidized dehydrated molecular structures with only a minor fraction becoming reduced by the reaction conditions. Under these reaction conditions, the surfaces exhibit no detectable surface reaction intermediates. For propane autothermal reforming to H₂ over supported Rh/Al₂O₃ catalysts, the development of UV Raman spectroscopy with a special *in situ* cell was required to be able to monitor the catalysts, *for the first time*, at temperatures of 1000 °C. The active surface species under these severe reaction conditions was rhodium oxide. No surface reaction intermediates were present at 1000 °C, but surface carbonaceous deposits were present on the catalyst at lower reaction temperatures.

Propane oxidative dehydrogenation was found to require one redox surface metal oxide site and was promoted by the specific oxide support (Zr > Ti > Nb > Al > Si) due to the participation of the bridging V-O-Support bond. Propane oxidation to acrolein, via propylene

oxidation, was found to require two surface sites and was also promoted by the specific oxide support (Zr > Ti > Nb > Al > Si) due to the participation of the bridging M-O-support bond. Thus, it appears that the promotion by the specific oxide support is a general phenomenon for oxidation reactions over supported metal oxide catalysts and that the number of required active surface sites is specific to each reactant molecule and product. These conclusions are also expected to play a role during oxidation reactions over bulk mixed metal oxide catalysts.

DOE Interest: The efficient use of natural gas hydrocarbon feedstocks for production of chemicals and energy over mixed metal oxide catalysts is of great interest to many catalytic applications. The more selective the chemical oxidation reactions, the smaller will be the amounts of environmentally undesirable by-products. The more selective the autothermal reactions to produce hydrogen, the more energy efficient will be the technology and by-product formation minimized. The key to achieving these goals is the establishment of molecular structure-reactivity/selectivity relationships for various mixed metal oxide catalysts employed for such oxidation reactions. Such fundamental molecular level information is needed for the development of theoretical models of mixed metal oxide catalysts for numerous alkane hydrocarbon oxidation reactions.

Future Plans:

1. Investigate propane/propylene oxidation to acrylic acid with well-defined bulk and supported mixed metal oxide catalytic materials.
2. Investigate propane/propylene oxidation to acrylonitrile with well-defined bulk and supported mixed metal oxide catalytic materials.
3. Continue to advance spectroscopic techniques that can provide composition and oxidation state information about the outermost surface of bulk mixed metal oxides.
4. Continue to advance molecular spectroscopic techniques that can provide molecular structures and oxidation states under reaction conditions.

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Catalytic Hydrogenation of Carbon Monoxide

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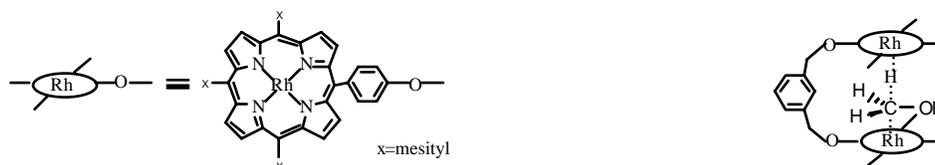
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Abstract

This program encompasses a series energy research issues associated with conversion of carbon monoxide and hydrocarbons to organic oxygenates from reactions of CO, H₂, CH₄, C₂H₄, O₂, and H₂O. Diverse substrate reactions of group nine (Co, Rh, Ir) metalloporphyrins including formation of metallo-formyl complexes, methane and water activation are guiding the design of new catalyst materials with properties modified for improved rates and selectivity for applications in both organic and aqueous media. One of the current focus areas is the design and synthesis of diporphyrin ligands that form dimetal complexes capable of preorganizing transition states for substrate reactions that involve two metal centers. Dimetallo radical diporphyrin complexes are observed to manifest large rate increases over mono-metalloradical reactions of H₂, CH₄, CO and other small molecule substrates. One particularly important result is that bimetallo radical carbon-hydrogen bond activation can be designed to give kinetic preference for methane activation over that of both methanol and ethanol¹. Another current focus of this program is to explore the range of organometallic transformations that can be achieved in aqueous media. Water soluble group nine metalloporphyrins manifest remarkably versatile substrate reactivity in aqueous media which includes producing rhodium formyl (Rh-CHO) and hydroxy methyl (Rh-CH₂OH) species.² One of the most complete descriptions of equilibrium thermodynamics for organometallic reactions in water is emerging from the study of rhodium porphyrin substrate reactions in aqueous media.^{2,3} Current directions for this program include developing new strategies to obtain anti-Markovnikov addition of water, amines and alcohols with olefins, and evaluating catalytic reactions of CO that yield formamides and formic esters.

Overview of recent progress**m-xylyl tethered dirhodium(II) biporphyrins**

Bimetallo-radical complexes of rhodium (II) have been prepared and evaluated with porphyrin units that prohibit intermolecular and intramolecular Rh(II)-Rh(II) bonding and a tether unit that has an appropriate size and flexibility to permit the two metal centers to reach the transition states for intramolecular substrate reactions.

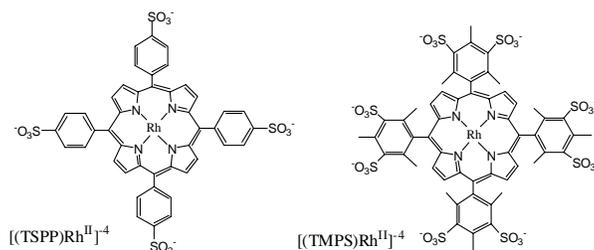


The primary initial objectives for designing bimetallo-radical species were to test the strategy to obtain rate enhancements for metallo-radical substrate reactions by converting termolecular metallo-radical processes to bimolecular reactions with reduced activation entropy while retaining selectivity. These objectives have been realized in the reaction of $\cdot\text{Rh}(\text{m-xylyl})\text{Rh}\cdot$ with methane, which occurs as a bimolecular process with reduced activation entropy compared to the reaction of methane with $(\text{TMP})\text{Rh}\cdot$. Realization of additional rate enhancements and substrate selectivity in this system requires reducing the activation enthalpy through designing bimetallo-radical structures that more closely emulate the transition state structures.

Organometallic Reactions of Group 9 Porphyrins in Water

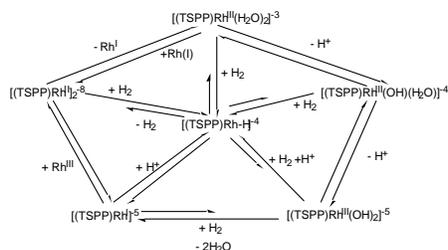
Studies of rhodium porphyrins in aqueous solution

Growing interest in applying organometallic reactions for processes in water and the utilization of water as a substrate are primary motivations for the study of rhodium porphyrin chemistry in aqueous media. Sulfonation of tetraphenyl porphyrin derivatives provides a convenient entry point into water-soluble porphyrin complexes.



Reaction of (TSPP) Rh^{III} species with H₂ in H₂O

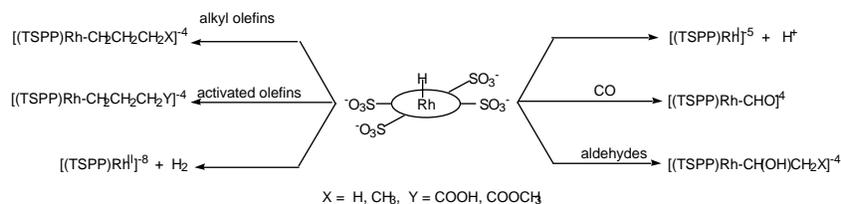
The set of species formed in aqueous solution in the reactions of H₂ with rhodium(III) porphyrins is illustrated in Scheme I.



Scheme I: Interrelationships of reactive Rh(I), Rh(II) and Rh(III) species

Reaction of [(TSPP)Rh-H]⁻⁴ with CO, aldehydes and olefins in H₂O

Reactions of (TSPP)Rh-H with CO, aldehydes and olefins that produce formyl, α-hydroxy alkyl and alkyl derivatives are summarized in Scheme II.



Scheme II: Reactivity patterns of [(TSPP)Rh-H]⁻⁴ species

(TSPP)Rh-H reacts rapidly with a wide range of olefins (CH₂=CHX; X = H, R, C₆H₅, CN, CO₂R) to give anti-Markovnikov addition of the Rh-H unit. This set of olefin reactions establishes the foundation to obtain anti-Markovnikov addition of H₂O to alkenes by addition of (por)Rh-H to the olefin to form (por)Rh-CH₂CH₂R and then nucleophilic displacement of (por)Rh⁻ by OH⁻ to produce the primary alcohol (HO-CH₂CH₂R).

Thermodynamic studies in water

Equilibrium constants have been evaluated for a wide variety of substrate reactions of rhodium porphyrins in water. Most of the reactions in Scheme I and Scheme II have been studied and many additional reactions of (por)Rh-H and (por)Rh-OH are currently being evaluated. This research will provide an unprecedented range of metal-substrate (M-H, M-R, M-OR) thermodynamic measurements. Reactivity and thermodynamic studies are currently being extended to the (TMPS)Rh and electron withdrawing porphyrin systems.

Publications:

- 1) “Bimetallo-Radical Carbon-Hydrogen Bond Activation of Methanol and Methane”, Weihong Cui, X. Peter Zhang, and Bradford B. Wayland, *J. Am. Chem. Soc.* **2003**, *125*, 4994.
- 2) “Aqueous Organometallic Reactions of Rhodium Porphyrins: Equilibrium Thermodynamics”, Xuefeng Fu, Leah Basickes and Bradford B. Wayland, *Chem. Commun.* **2003**, 520.
- 3) “Equilibrium Thermodynamic Studies in Water (1): Reactions of Dihydrogen with Rhodium(III) Porphyrins Relevant to Rh-Rh, Rh-H and Rh-OH Bond Energetics”, Xuefeng Fu and Bradford B. Wayland, *J. Am. Chem. Soc.* **2004**, *126*, 2623-2631.

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Non-Thermal Reactions of Gas-Phase Oxygen Atoms with Atoms Adsorbed on Transition Metal Surfaces

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Goal

The reactions of gas-phase oxygen atoms at transition-metal surfaces are important in catalytic oxidation processes occurring at high temperature and with plasma activation. Due to the strong bonding of oxygen on metals, the collision of an oxygen atom with a metal surface results in significant energy release that can stimulate a variety of non-thermal reactions, including direct atom abstraction and collision-induced reactions. Such processes could play a central role in the surface chemistry occurring in extreme environments and are therefore important to understand. The goal of this project is to elucidate the mechanisms and to quantify the kinetics of non-thermal reactions between gas-phase oxygen atoms and atoms adsorbed on transition-metal surfaces, and to advance the fundamental understanding of the effects of adsorbate and surface properties on the predominant non-thermal processes.

Recent Progress

The initial focus of this project has been to design, assemble and test an apparatus for generating beams of thermal energy oxygen atoms that will be used in reactive scattering experiments in ultrahigh vacuum (UHV). The beam system consists of a plasma source that is mounted in a two-stage differentially-pumped chamber and coupled to an UHV chamber (Figure 1). Gaseous oxygen atoms are produced in this system by dissociating O₂ in a microwave plasma that is confined to a small volume at the end of the plasma source. Species exit the plasma volume through small holes at the end of the source, thus forming a beam that is directed toward the sample surface held in the UHV chamber. In the first pumping stage, the beam passes between charged parallel plates that deflect ions from the beam flux. After flowing through a thin-walled orifice separating the first and second pumping stages, the species travel down a quartz tube before entering the UHV chamber. The purpose of the quartz tube is firstly to collimate the beam so that the atomic oxygen flux can be confined to the sample surface. In addition, collisions at the inner walls of the tube are known to significantly reduce the fraction of atoms and molecules in vibrationally and electronically excited states. Thus, the beam flux reaching the sample should consist almost exclusively of thermal energy (~0.05 eV), ground-state atomic and molecular oxygen, with the fraction of oxygen atoms in the flux expected to lie between 45 and 65%. The quadrupole mass spectrometer (QMS) shown in the figure is available for characterizing the beam flux and

composition. Finally, a shutter is located in the first pumping stage to enable control over beam introduction into the main UHV chamber.

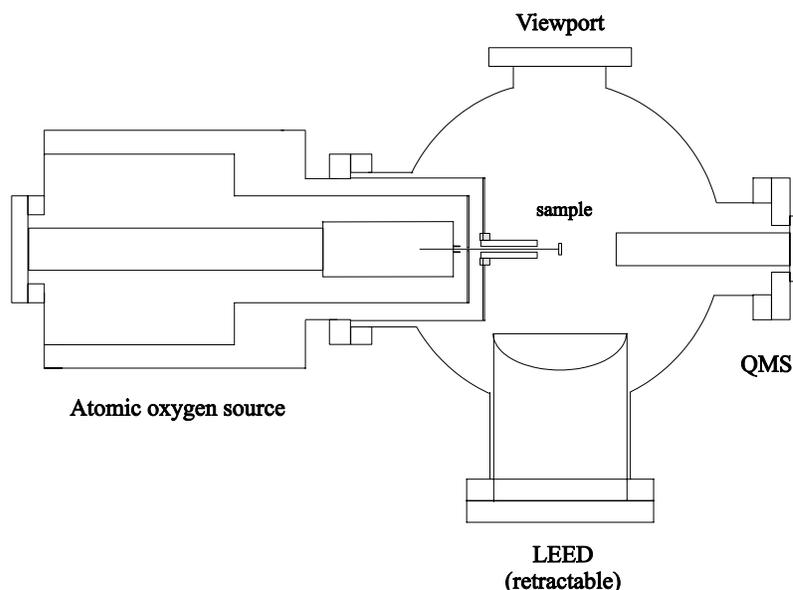


Figure 1. Schematic of atomic oxygen beam source attached to UHV system.

The new beam source was installed at the end of 2003 and its performance has recently been benchmarked by examining the oxidation of Si(100). Using X-ray photoelectron spectroscopy, the uptake of oxygen by Si(100) was measured as a function of exposure to oxygen beams generated with and without plasma activation. As expected, the rate of oxygen uptake was significantly enhanced when the plasma was activated. In addition, the saturation oxygen coverage that could be reached on Si(100) held at room temperature was about twice that achieved by exposing the surface to a pure O₂ beam. Analysis of the uptake results obtained with and without plasma activation indicates that the atomic oxygen flux at the sample location was in the range of 0.4 to 1.2 x 10¹⁴ atoms/cm² sec for the beam conditions employed. This range is ideal for measuring atom abstraction rates using direct mass spectrometric analysis of the desorbing products. Experiments using appearance potential mass spectrometry are currently underway to further characterize the atomic oxygen content of the beam.

DOE Interest

Understanding of the mechanisms that govern the surface reactions of gaseous oxygen atoms, and quantification of the associated reaction cross sections, is important to the design and modeling of catalytic processes that occur under extreme conditions, including processes such as surface combustion and plasma-assisted catalysis.

Future Plans

Atom abstraction from Pt(111). We have recently begun an investigation of the interactions of thermal-energy oxygen atoms with clean and adsorbate-modified Pt(111). The exposure of clean Pt(111) to atomic oxygen is expected to generate high coverage adsorbed phases and possibly oxide structures that will be characterized using several surface analysis techniques. We then plan to investigate the non-thermal reactions that occur between gas-phase oxygen atoms and various atoms (O, C, N, H) adsorbed on the Pt(111) surface. The general aim is to elucidate the mechanisms for these reactions and to investigate how adsorbate-surface bond strengths and interactions between adsorbates affect the kinetics for the non-thermal reactions that occur.

Hyperthermal oxygen atoms. We also plan to investigate the surface reactions induced by oxygen atoms generated with hyperthermal kinetic energies (~ 5 eV). Our approach for producing hyperthermal atomic oxygen involves the continuous permeation of oxygen atoms through a silver membrane followed by electron stimulated desorption of the oxygen atoms as they emerge on the vacuum side of the membrane. By investigating the surface reactions induced by both thermal and hyperthermal oxygen atoms, we seek to determine the main effects that incident energy has on the mechanisms and kinetics of the surface reactions of gas-phase oxygen atoms.

Substrate-mediated effects. The reactions between gas-phase oxygen atoms and atoms adsorbed on different metal surfaces will be investigated to determine how the non-thermal surface reactivity of oxygen atoms is influenced by the metal substrate. The reaction kinetics and branching among reaction channels may vary from metal to metal due to changes in the efficiency of energy exchange between energetic oxygen atoms and the surface.

Publications (2003-4)

No publications have yet resulted from this work.

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Polymer Supported Palladated Pincer Ligands in Catalysis

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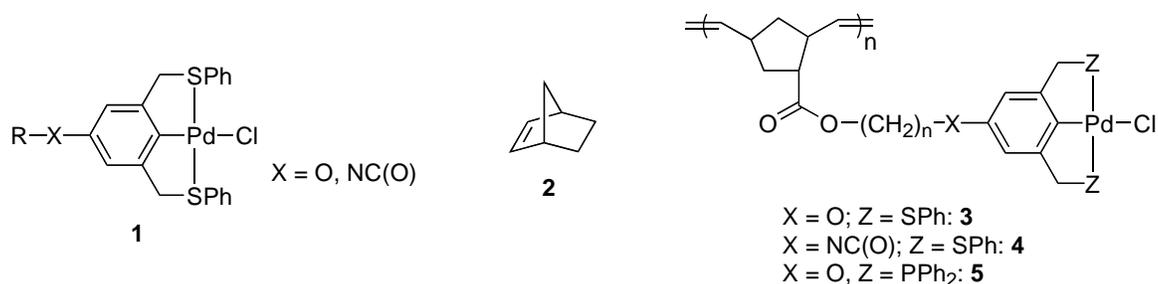
Goal

To develop a fundamental understanding of the interactions between soluble catalyst supports such as polymers and soluble nanoparticles and well-defined transition metal catalysts, in particular catalysts for organic transformations such as carbon-carbon bond formations and epoxidations.

Recent Progress

This project is part of a larger DOE funded initiative to elucidate the basic design principles that govern the interactions between well-defined transition metal catalysts and supports ranging from polymers to porous silica. Initially, we focused our efforts on the synthesis of polymer supported palladium/pincer complexes and studied their catalytic activity as well as their potential catalyst decomposition.

Heck Couplings with Pd-SCS pincer complexes: Supported palladated pincer complexes have been identified in the literature as potential well-defined catalysts for a variety of carbon-carbon bond formations including the Heck reaction. In particular so called Pd(II) SCS pincer complexes (**1**) have been described as outstanding Heck catalysts by a number of groups in the literature. Over the last six months, we have synthesized a variety of novel polymer supported Pd(II) pincer complexes. In contrast to previously published polymers supports that contain only one or two catalytic active moieties per polymer strand, our polymers are based on norbornene as polymerizable unit (**2**) thereby allowing for the controlled polymerization via ring-opening metathesis polymerization. The resulting polymers contain one catalytic site per repeating unit creating the highest supported Pd(II) pincer catalyst loading reported to date. A variety of poly(norbornene)s containing different supported Pd(II) pincer complexes were synthesized (compounds **3** - **5**). These polymer-supported catalysts vary slightly in their attachment of the catalytic moiety to the monomer unit and/or the elements that undertake the dative bonds to the palladium center.



Using a variety of characterization methods including NMR spectroscopy, targeted catalyst poisoning and IR, we have unequivocally determined that the supported polymer/Pd(II) pincer catalyst system **3** decomposes under standard reaction conditions for the Heck catalysis of iodo-arenes with acrylates. Furthermore, we were able to identify that the active catalytic species is a homogeneous molecular Pd(0) source. These findings are in contrast to reports in the literature and clearly demonstrated that these catalysts are not reusable and/or recoverable. Interestingly, preliminary investigations on the use of **4** as Heck catalyst suggest that this polymer Pd(II) system does not decompose or only partially decompose under standard reaction conditions. Investigations into the true nature of the catalytic species of **4** are currently being carried out.

Synthesis of Poly(norbornene)s Containing Terminal N-heterocyclic Carbenes as Ligands in Catalysis. We started on the synthesis of norbornene-based monomers containing terminal N-heterocyclic carbene ligands. These carbenes have been identified as outstanding ligands for a variety of catalysts for organic transformations including carbon-carbon bond formations such as olefin metathesis and the Heck reaction. Initially, we have synthesized a number of novel carbene ligands with a variety of alkyl spacers containing terminal functional groups such as thiols, alcohols, and olefins. Currently, we are actively pursuing the attachment of these carbenes onto norbornenes and soluble gold nanoparticles.

DOE Interest

A detailed understanding of the underlying design principles that dictate the interactions between a supported catalyst and its support are of utmost importance in catalysis. This research will improve the rational design of reusable and recyclable supported catalysts that are able to use the current basic carbon-hydrogen feedstock to create complex molecules and important precursors for drugs and polymers and it is therefore of general interest to the DOE.

Future Plans

Elucidating the Catalytic Species of Different Polymer Supported Pd(II) Pincer Catalysts. Using polymers **3** - **5** and similar polymers, we hope to identify the catalytic species of polymer supported Pd(II) pincer catalysts. Furthermore, we will investigate which factors influence the formation of the catalytic species using a combination of computational methods and experiments.

Influence of Polymer Backbone Structure on Catalyst Accessibility: We are investigating the role of the polymer backbone, its structure in solution (rigid rod versus

random coil) and ultimately the accessibility of the catalyst using poly(norbornene)s and poly(octene)s via a combination of computational methods and experimental characterizations such as two-dimensional NMR spectroscopy.

Investigations into the Use of Soluble Nanoparticles as Catalyst Support. Soluble gold and silver nanoparticles will be functionalized with thiol containing Pd(II) pincer complexes and their catalytic activity will be investigated. In a second step, these activities will be compared to the analogous polymer supported Pd pincer complexes and again, using a combination of computational methods and experiments the underlying design motifs will be elucidated.

Publications (September 2003-present)

- 1) Yu, K.; Sommer, W.; Weck, M.; Jones, C. W.; Silica and Polymer-Tethered Pd-SCS-Pincer Complexes: Evidence for Precatalyst Decomposition to Form Homogeneous Catalytic Species in Mizoroki-Heck Chemistry, manuscript submitted, March 12 2004.

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Morphological and Kinetic Aspects of Surface Processes

Postdocs: Huang, W.X., Ni, J.

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Goals

Using model systems, our goals are to prepare and characterize intermediates postulated to play important roles in heterogeneously catalyzed reactions, to characterize ordered overlayers of organic species chemisorbed on single crystal metals, and to prepare and characterize the structural and chemical properties of metal nanoparticles on planar model oxide substrates.

Recent Progress

Thermodynamics of decanethiol on gold. The coverage-dependent phase behavior of the thiolate formed from decanethiol, $\text{CH}_3(\text{CH}_2)_9\text{SH}$, on Au(111) was studied at 0°C using variable-temperature scanning tunneling microscopy and compared to analogous results for temperatures between 25 and 65 °C.^{1,2} The effects that a reconstructed (herringbone) and stepped Au(111) surface have on the structure of submonolayers of decanethiolate were also studied between 25 and 60 °C.² At 25 °C, formation of lattice gas (α) species at low coverages alters the herringbone structure by shortening the periodicity of the elbows from 25 to 15 nm. In addition, small β phase islands nucleate and grow anisotropically in regions of fcc stacking. These domains grow by incorporating nearby lattice gas species, consuming herringbone ridges and altering the remnant ridges that surround them. For a coverage that saturates the β -phase (~0.25 of the closest packing achievable), raising the temperature to 30 or 40 °C increases the average size of the β -phase islands by condensation of neighboring islands with no evidence, at the selected coverage, for the presence of any other thiolate phase. At 60 °C, well above the thiolate melting point to form the ϵ -phase, small β -phase domains remain.

Electron-induced dissociation of tert-butyl nitrite adsorbed on Ag(111). Non-thermal methods for generating catalytically interesting intermediates is a sug-goal of our project. The electron-induced chemistry of *tert*-butyl nitrite (TBN, $(\text{CH}_3)_3\text{CONO}$), adsorbed on Ag(111), or over a CH_3OH spacer layer, was studied at 90 K using three kinds of measurements—the time dependence of ejected fragments during 70 eV electron irradiation, temperature-programmed desorption (TPD) after irradiation, and X-ray photoelectron spectroscopy before and after irradiation.³ Only NO is detected during 70 eV electron irradiation, and the initial total cross-section for loss of TBN is quite large,

$3.3 \times 10^{-15} \text{ cm}^2$. Post-irradiation TPD, after dissociating ~90% of a saturated TBN monolayer, reveals residual TBN and a number of products, including NO, C₄H₈ (isobutene), CH₃COCH₃ (acetone), (CH₃)₃COH (*t*-butyl alcohol), CO and H₂O. Interestingly, there is no evidence for H₂ in TPD. Illustrating a central role for the Ag(111) substrate, electron-induced dissociation of monolayer TBN adsorbed over 10 ML of methanol was less efficient, by a factor of 4, than 1 ML TBN on clean Ag(1 1 1).

Reactions of hydrocarbon species on silver. Silver is an ideal substrate for modeling many aspects of heterogeneous reactions of hydrocarbons, e.g., partial oxidation of propene. The interactions of propene, itself, with Ag(111) were examined using TPD and RAIRS.⁴ At 100 K, propene reversibly adsorbs, with chemisorbed desorption peaks at 161, (α_1) and 145 K (α_2), and a multilayer peak at 123 K (α_3). Repulsive interactions drive a change from α_1 - to α_2 -propene during adsorption and desorption. The three adsorption states are distinguished by RAIRS on the basis =CH₂ wagging vibration frequencies at 924, 918 and 908 cm⁻¹, respectively. Vibrational spectroscopic and thermal desorption evidence describing the behavior of propene on oxygen-modified Ag(111) at 100 K indicates a gradual transition from π -bonded to *di*- σ -bonded propene as the oxygen adatom coverage increases.⁷

Reactions of propene on oxygen modified Ag(111) surface were also investigated.⁵ In the presence of oxygen adatoms, interactions of propene with the substrate are strengthened. The reaction between propene and oxygen adatoms (0.086 ML) produces not only total oxidation products (CO₂ and H₂O), but also partial oxidation products (CO and acetone). The formation of chemisorbed hydroxyl groups is identified by RAIRS when coadsorbed propene and oxygen adatoms are annealed to 200 K. The formation of hydroxyl is ascribed to the abstraction of methyl hydrogen by oxygen adatoms.

Nitrogen oxides on silver. The interactions of NO₂ with Ag(111) at various temperatures were investigated by means of temperature programmed desorption and reflection-adsorption infrared spectroscopy and found to be sensitively coverage- and temperature-dependent.⁹ During dosing at 508 K, NO₂ decomposes into NO(g) and O(a) whereas at 215 K NO and O remain adsorbed. The NO(a) occupy threefold-bridged sites and atop sites in sequence. Orientations of the NO(a) axes are affected by neighboring O(a).

Cross-coupling of C₁ groups on silver. The cross-coupling reaction between CH₂ and CF₃ on Ag(111) to form adsorbed CF₃CH₂(a) was, for the first time, spectroscopically identified as an intermediate in the reaction to form CF₂CH₂.¹⁰ It is formed by migratory methylene insertion into Ag-CF₃. CF₃CH₂(a) undergoes β -fluoride elimination to form CF₂CH₂. These results provide direct new fundamental insight into Fischer-Tropsch synthesis.

Chemistry of carboxylates on TiO₂. In collaboration with scientists at Pacific Northwest National Laboratory, the thermal and photochemical properties of trimethyl acetate (TMA) on TiO₂(110) have been examined.¹¹⁻¹³ Deprotonation occurs at or below 300 K to form trimethyl acetate, (CH₃)₃CCOO⁻, is bound to exposed Ti⁴⁺ cations, and

OH^- involves a bridging oxygen atom of the substrate. On the basis of temperature-programmed desorption and isothermal reaction mass spectrometry, the desorbing products include $(\text{CH}_3)_3\text{CCOOH}$, isobutene ($i\text{-C}_4\text{H}_8$), carbon monoxide, and water. Much of the $(\text{CH}_3)_3\text{CCOO}^-$ is relatively stable and decomposes to release mainly carbon monoxide and isobutene above 550 K with a maximum rate at 660 K. Thermal desorption to 750 K leaves a carbon-free surface that is indistinguishable from the initially clean surface. During dosing at 550 K, a steady-state reaction condition is realized with about half the adsorption sites being occupied at any instant.

The behavior of H_2O on clean and trimethyl acetate (TMA)-covered $-(1 \times 1)$, prepared with or without oxygen vacancies and associated Ti^{3+} , reveals the hydrophilic nature of clean surfaces and the hydrophobic nature of TMA-covered surfaces. UV irradiation of a hydrophobic surface in the presence of 10^{-6} Torr of O_2 removes TMA and rapidly restores hydrophilicity. The presence of oxygen atom vacancies does not detectably alter the hydrophilicity of either clean or TMA-covered $\text{TiO}_2(110)$.

Metal nanoparticle synthesis. As a strategy for synthesizing metal nanoparticles, thermally evaporated Ag was deposited onto a thin (~ 1.2 nm) crystalline ice layer on an inert oxide substrate--hafnia (HfO_2) at 100 K.⁸ The Ag atoms penetrate into the ice matrix but do not reach the underlying HfO_2 substrate. After controlled thermal desorption of water by heating to 300 K, atomic force microscopy reveals Ag particle formation. Figure 1 illustrates for one set of preparation conditions.

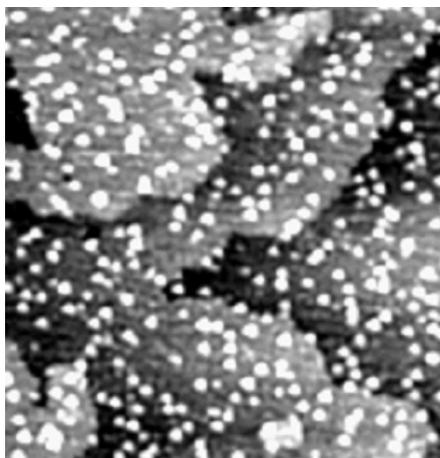


Figure 1. 200 x 200 nm image of Ag nanoclusters on a $\text{TiO}_2(110)$ surface. The sample was prepared by dosing 0.2 ML (effective) on solid water film (~ 10 ML thick). Water and Ag were deposited on 100 K surface. Water was then desorbed by warming to 300 K.

Instrumentation. As an integral part of this project, we have made improvements to standard UHV surface analysis tools that allow *in-situ* elevated temperature real time analysis of insulator substrates. For real-time analysis during thermal annealing, a continuous wave CO_2 infrared laser was coupled to a surface analysis system equipped

for x-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS).⁶ The laser beam was directed into the vacuum chamber through a ZnSe window to the back side of the sample. With 10 W laser output, the sample temperature reached 563 K. The chamber remained below 10^{-8} Torr during annealing and allowed XPS and ISS data to be gathered as a function of time at selected temperatures. As a test example, real time Cu₂O reduction at 563 K was investigated.

Future plans.

Ir nanoclusters. Motivated to develop the basic science of catalytically activating C-H and C-halogen bonds at the surfaces of metal nanoclusters, we plan to prepare surfaces comprising size-selected Ir nanoclusters, some involving other metals, supported on planar oxide supports; to characterize the surfaces structurally using scanning tunneling microscopy; and to study the chemical properties of the supported clusters employing molecular beam reactive scattering techniques, complemented, as needed, by electron microscopy and standard surface science spectroscopies.

DOE Interest

Controlled deposition and characterization of metal nanoclusters are central issues in developing the basic science of highly selective catalytic systems that involve C-H and C-X bond activation.

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1. W.P. Fitts, J.M. White and G. E. Poirier, "Thermodynamics of Decanethiol Adsorption on Au (111): Extension to 0°," *Langmuir*, **18**(6), (2002) 2096-2102.
2. W.P. Fitts, J.M. White and G.E. Poirier, "Low coverage decanethiolate structure on Au(111): Substrate effects," *Langmuir*, **18**(5), (2002) 1561-1566.
3. Ilkeun Lee, S. K. Kim, Wei Zhao, and J. M. White, "Electron-induced dissociation of *tert*-butyl nitrite adsorbed on Ag(111)," *Surface Sci.*, **499** (2002) 53-62.
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6. Q. Wang, Y.-M. Sun, W. Zhao, J. Campagna and J.M. White, "In-situ Laser Annealing System for Real Time Surface Kinetic Analysis," *Rev. Sci. Instr.*, **73** (2002) 3916.
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propene on O-modified Ag(111) *Langmuir*, **18**(25), (2002) 9622-9624.

8. X.-M. Yan, J. Ni, M. Robbins, H. Park, W. Zhao and J.M.White, "Silver nanoparticles synthesized by vapor deposition onto an ice matrix", *Journal of Nanoparticle Research* **4**(6), (2002) 525-533.

9. W.X. Huang, J.M. White, "Revisiting NO₂ on Ag(111): a detailed TPD and RAIRS study", *Surface Science*, **529** (2003) 455-470.

10. W.X. Huang and J. M. White, "Direct Spectroscopic Evidence of the Cross-Coupling Reaction between CH₂(a) and CF₃(a) on Ag(111)", *J. Am. Chem. Soc.*, **125**(36), (2003) 10798-10799.

11. White. J.M., Szanyi, J., and Henderson, M.A., "The Photo-Driven Hydrophilicity of Titania: A Model Study Using TiO₂(110) and Adsorbed Trimethyl Acetate", *J. Phys. Chem. B.*, **107** (2003) 9029-9033.

12. Henderson, M., White, J., Uetsuka, H., Onishi, H., "Photochemical Charge Transfer and Trapping at the Interface Between an Organic Adlayer and an Oxide Semiconductor", *J. Am. Chem. Soc.*, **125** (2003) 14974-14975.

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Catalysis on the Nanoscale: Preparation, Characterization and Reactivity of Metal-Based Nanostructures

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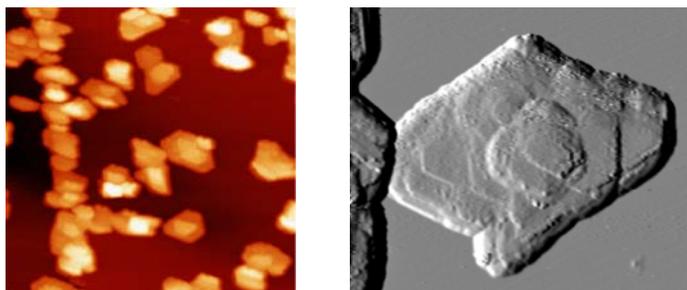
Goal

Explore and manipulate the size, morphology and chemical environment of metal-containing nanoparticles with the goal of modifying their reactivity.

Recent Progress

Model Ru/C catalyst for ammonia synthesis: New-generation ammonia-synthesis Ru catalysts are more active at lower temperatures and pressures than iron-based catalysts used worldwide in this large-scale industrial process. Industrial Ru catalysts are synthesized using a carbonyl precursor and oxide, nitride or graphite substrates. To prepare a model Ru catalyst, we have grown Ru particles using chemical vapor deposition of $\text{Ru}_3(\text{CO})_{12}$ as a precursor on a highly oriented pyrolytic graphite (HOPG) surface. HOPG has been modified with one-atomic-layer-deep holes mimicking an activated carbon support by mild sputtering and oxidation in air. At low Ru surface concentrations, the Ru particles (~2 nm) have a round shape, while at higher Ru surface concentrations, the Ru forms flat layered crystallites (~3 nm high and ~40 nm wide) with the (0001) facet parallel to the graphite surface (see Figure).

A reactivity study of a model Ru/C catalyst was carried out to advance the understanding of this structure sensitive reaction where dinitrogen dissociation is the rate-limiting step. The N_2 desorption maximum occurs at ~650 K for the small particles and 500 K for the larger crystallites. The higher temperature desorption has its origin at opened Ru surfaces which dominate the small round particles; the lower temperature desorption comes from terraces of the Ru(0001) surface, which



Crystalline Ru nanoparticles on HOPG (200 nm x 200 nm) [left]; morphology of a single Ru nanoparticle (73 nm x 50 nm) [right].

are predominant for the large flat crystallites. The initial sticking coefficient for N₂ dissociative adsorption on the Ru/HOPG model catalyst is 1×10^{-7} , ~4-5 orders of magnitude larger than Ru single crystal surfaces.

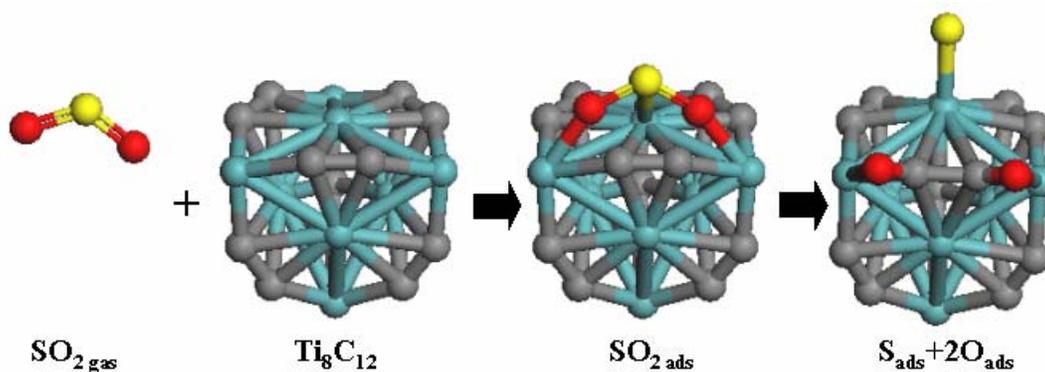
Activation of gold nanoparticles on oxide surfaces: Gold nanoparticles deposited on metal oxides display an unexpected high reactivity. A priori, it is not clear if this phenomenon is a consequence of the size of the nanoparticles or the result of interactions with the oxide support. To address this issue we examined and compared the destruction of SO₂ on Au/Ti(110) and Au/MgO(100) surfaces. Synchrotron-based high-resolution photoemission and first-principles density-functional slab calculations were used in the studies. We found that the dissociation of SO₂ on Au/MgO(100) is very limited due to weak Au↔MgO interactions. On the other hand, the deposition of Au nanoparticles on TiO₂(110) produces a system with an extraordinary ability to adsorb and dissociate SO₂. Neither MgO(100) nor TiO₂(110) are able to dissociate SO₂ on their own. On both oxide supports, the largest activity for the full dissociation of SO₂ is found in systems that contain Au coverages smaller than 1 ML when the size of the Au nanoparticles is below 5 nm. The data clearly show how important can be the effects of the oxide support for the activation of Au nanoparticles.

M_mX_x nanoparticle formation and deposition: Our recent laser ablation studies on the Mo_nX_m (X= C, N, S) clusters suggest that gas-phase cluster methods can generate an extensive array of transition metal compounds with a wide range of particle size, stoichiometry and structure. Our ultimate goal is to use such a source to deposit mass-selected nanoparticles onto a substrate, e.g., graphite or TiO₂, and thereby prepare a model catalyst system whose particle size distribution is precisely known. Much of the effort this year has been spent on constructing a deposition apparatus and characterizing the magnetron sputtering cluster source which will be used in place of laser ablation in the first generation instrument. Using a high-mass quadrupole spectrometer, we have demonstrated the ability to form a wide range of bare metal, metal carbide and metal sulfide cluster ions with resolvable masses up to 10,000 amu, e.g., Mo₁₀₅. Transition metals studied include Ti, V, Zr, Nb and Mo. Of significant interest is the observation of “magic number” Metcar clusters (M₈C₁₂, M≡Ti, Zr) as well the observation of nearly stoichiometric niobium carbide nanocrystallites, e.g., Nb₁₄C₁₃. For molybdenum, a “magic number” sulfide cluster, Mo₃S₉, was also observed. The Mo₃S₉ cluster has been implicated as a structural unit in amorphous phase of molybdenum sulfide which is particularly active for desulfurization. Future work will focus on the deposition of size-selected clusters onto well-defined substrates under UHV conditions for characterization by thermal desorption and photoemission.

Theoretical studies of the structure and properties of M₈C₁₂ metallocarbohedrenes (metcars): We have extensively studied the geometric and electronic structure of the “metallocarbohedrenes” (metcars) Ti₈C₁₂ and Mo₈C₁₂ using fully *ab initio* and density functional methods. We were particularly interested in how these systems might serve as model heterogeneous nanocatalysts with precisely defined size and active sites. We examined these issues through calculations employing a hierarchy of levels of theory and the correlation of the molecular orbitals as the symmetry of the cluster is systematically reduced.

Our most important discovery in these calculations was that it required the highest levels of theory to identify the correct electronic ground state (1A_1), symmetry group in its equilibrium geometry (D_{2d}) and principal orbital configuration of the Ti_8C_{12} metcar. The structure consists of an outer tetrahedron of Ti atoms (formal oxidation state “+1”) connected by C_2 units, and a smaller inverted tetrahedron of Ti atoms (formal oxidation state “+2”) bound directly to each other and with each of them η^2 -bonded to three of the C_2 units comprising the outer tetrahedron.

Density functional theory was also employed to study the interaction of SO_2 with the Ti_8C_{12} and Mo_8C_{12} metcars. The S – O bonds of SO_2 spontaneously break on Ti_8C_{12} ($\Delta E \approx 3.8$ eV) and Mo_8C_{12} ($\Delta E \approx 2.9$ eV). The products of the decomposition reaction (S, O) interact simultaneously with metal and C sites. The C atoms are not simple spectators and they play an important role in the energetics for the dissociation of SO_2 . The theoretical calculations indicate that the metcars are more reactive towards small molecules (CO , NH_3 , H_2O and SO_2) than $TiC(001)$ and $MoC(001)$ surfaces. The particular geometry of the metcar attenuates the ligand effects of C on Ti and Mo.



Dissociation of SO_2 on a Ti_8C_{12} metcar. Ti atoms are shown as blue spheres, while gray spheres represent C atoms.

Future Plans

Future work will focus on nanostructured carbides, nitrides and sulfides of the Group 4-6 transition metals (*e.g.*, Ti, V, Nb, Mo, Zr), which have been observed to exhibit catalytically active bulk surfaces and/or unique gas-phase cluster structures. Such materials may offer advantages over supported noble metal catalysts in terms of selectivity and resistance to poisoning and sintering. A major objective is to understand how nanoparticle size, support and alloy formation effect the electronic environment of the metal active sites and their chemical reactivity.

DOE Interest

Understanding how to modify the metal active site through manipulation of nanostructured materials can provide a basis for development of new catalytic materials.

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Chemical Transformation Mechanisms

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Goal

The three programs described here seek to elucidate mechanisms pertinent to both the synthesis and deactivation of catalysts. The chemistry of synthetic clays is being studied to understand how a particular heterogeneous nanoporous catalyst is formed, and to exploit this knowledge for tailoring the characteristics of the catalytic material. Mechanisms of the formation of aromatic precursors that can lead to carbonaceous deposits on acidic catalysts, on nano-sized metal clusters on surfaces, and on metal nanoparticles within synthetic clays are being explored.

Recent Progress

The first subtask has been an on-going program in DOE for several years, whereas the second and third are new programs this year. As a result, the first subtask has had significant progress whereas the second and third subtasks have only preliminary data at this time.

Fundamental Studies of the Design of Nanoporous Silicate Catalysts. Several new mesostructured synthetic clay (MSC) materials were prepared and evaluated for their potential use as catalysts. Textural porosity was determined as a vital parameter to understand for catalytic, as well as for polyelectrolyte, applications. It was found previously that using a silica sol creates a MSC with high surface area morphological features (textural porosity), whereas use of other silicon sources creates a more traditional layered clay catalyst that is not as active. After extensive characterization, it was determined that the unique features of the MSCs, including especially their thermally stable mesoporosity, would lend themselves to selective catalysis. One area where selectivity could be crucial is the efficient hydrodesulfurization (HDS) of low-quality hydrocarbon feedstocks. In order to make strides towards this goal, we have begun with model compound studies.

New MSCs were prepared as a function of the size, pH, and counterion (and therefore the surface chemistry) of various silica sol precursors. XRD showed slight differences in crystallinity, surface areas ranged from 195-293 m²/g with either H2 or H3 hysteresis loops, pore volumes varied from 0.31-0.49 cc/g, and TEM showed sol particle sizes slightly different in some cases from values provided by the manufacturer. For HDS, the conversion of dibenzothiophene (DBT) to biphenyl was examined using Co/Mo/S-loaded MSC supports. The catalysis was accomplished in collaboration with C. Marshall of the Chemical Engineering Division at ANL. The most active clay was derived from silica sol AS30, with an activity of 65% DBT conversion (vs. 86% for a commercial alumina catalyst). This sol has a nominal particle diameter of 22 nm and it

yields the highest observed synthetic clay pore volume at 0.49 cc/g, which may be related to the high activity.

For deep HDS activity, the conversion of 4,6-dimethyldibenzothiophene (DMDBT) was tested in collaboration with C. Song at Pennsylvania State University. A commercial catalyst displays 11.4% conversion. This value is nearly attained (10.5%) for the Co/Mo/S-loaded mesostructured clay derived from AM30 silica sol. A Co/Mo/S clay catalyst made from laponite, a hectorite clay of typical platelet morphology, has very low activity (3.0%), indicating that the unique morphology of the mesostructured clays is important. Contrary to the HDS data above, the most active deep HDS catalyst is derived from AM30 silica sol, which has a 12 nm size and yields a synthetic clay with the lowest pore volume observed (0.31 cc/g). Deep HDS data nearly as good were obtained with the AS30 sol described above, with DMDBT conversion at 9.5%. The one feature that clays from both AS30 and AM30 sols share is an H3 N₂ isotherm hysteresis loop, whereas the rest have H2 loops. The importance of this textural porosity feature to catalytic activity will be examined in future studies.

The sol of smallest particle size (7 nm, SM30) showed poor results in both HDS tests, although we had expected that the smaller size would allow more dissolution and perhaps more incorporation into the matrix. Upon close examination of the x-ray powder diffraction (XRD) results, it appears that the most crystalline clays are AM30, AS30, and HS30, which are also the most active. The materials were also provided to G. Sandi for testing as polymer-clay nanocomposite membranes for lithium ion transport in secondary batteries.

Aromatic Molecule Formation Mechanisms on Homogeneous and Heterogeneous Acidic Catalysts: New proposal.

Aromatic Formation Mechanisms on Metal Nanoclusters: New proposal.

DOE Interests

The chemistry of synthetic clays is being studied to understand how a particular heterogeneous nanoporous catalyst is formed, and to exploit this knowledge for tailoring the characteristics of the catalytic material. In terms of catalyst deactivation processes, the formation of polycyclic aromatic compounds is a key step. Our studies probe both homogeneous and heterogeneous catalysts, initially polyphosphoric acid and zeolites, which are active for such transformations as methanol to hydrocarbons. This will provide detailed information regarding mechanisms of reaction for a specific substrate initially; however, these methods are applicable to a number of mechanistic problems in catalysis.

Future Plans

Fundamental Studies of the Design of Nanoporous Silicate Catalysts. We have had enormous success in the past exploiting solid-state ²⁹Si and ¹³C NMR to examine formation of the synthetic clay catalysts. We will again make use of these methods to probe the crystallinity of the various silica sol samples made for HDS and compare the results with those from XRD. The issue to determine is why certain silica sols foster greater crystallinity in the clay catalysts. Another important question to address is whether the absence of silica impurity hastens or otherwise affects the clay crystallization mechanism and subsequent porosity and catalytic behavior. A complete understanding of such mechanisms leads to better catalyst design. In situ SAXS experiments using a new flow cell are underway in order to aid in this understanding.

We will exploit our prior knowledge gained from mechanistic determinations to synthetic clays that contain a catalytically active metal component. Bifunctional catalysts contain both an acidic component (typically for hydrocarbon cracking) and a metal

component. We will probe the mechanism of formation of clay catalysts, including metal-lattice substituted materials and nanocomposites created with small metal and metal oxide particles, via NMR, in situ time-resolved small angle X-ray scattering (SAXS), anomalous SAXS, microscopy, and other techniques. A comparison of the clay catalysts after a catalytic reaction will then be made in order to assist in understanding the role of the metal nanoclusters in the particular catalytic reaction.

Organosilanes are of special interest because of their now demonstrated ability to be incorporated into the framework of clay as it is crystallizing. One natural extension of this process for us to study is the simultaneous incorporation of templating molecules such as polymers, and their effect on porosity or network structures. We will also compare and contrast the mechanism of formation of organo-grafted clays with silane-derived hectorite and silica sol-derived hectorite.

Aromatic Molecule Formation Mechanisms on Homogeneous and Heterogeneous Acidic Catalysts. This program has four main objectives: (1) to elucidate the mechanisms of aromatic hydrocarbon formation that are often the first step in catalyst deactivation in important industrial processes (2) to probe the aromatic species formed in both heterogeneous and homogeneous acidic catalysis of methanol to hydrocarbons (3) to develop an approach for studying the mechanisms of catalyst deactivation that will be applicable to other important systems and (4) to advance the use of in situ methods (including UV-Raman, NMR and SAXS) for these pioneering studies. Initially, the methanol to hydrocarbon reaction in polyphosphoric acid solution and on acidic zeolites will be compared and contrasted. The approach will take information defined on the homogeneous system and compare and contrast it with comparable experimental and computational data measured on the heterogeneous systems. Note that this approach does not presume that the two systems have much in common; it simply makes use of the homogeneous system as a definable and logical basis for comparison of results and a reasonable preliminary guide to experimentation on the heterogeneous process. In this approach, how the systems differ from each other is as important as features they might have in common.

Aromatic Formation Mechanisms on Metal Nanoclusters. This program encompasses several primary objectives: (1) to elucidate mechanisms of aromatic formation on metal catalysts in deactivation reactions involving olefins (2) to study nano-sized metal catalytic clusters from micelle directed synthesis in terms of formation and reactivity (3) to elucidate the mechanisms of deactivation of well-defined metal clusters supported on acidic surfaces (4) to study the deactivation of metal nanoparticles on polymer-clay nanocomposite membranes, and (5) to bridge the gap between homogeneous and heterogeneous catalysis in terms of synthesis and functionality. Initially, the metal of choice for all of these studies will be Pt(0) and propene will be the carbon source. Techniques including TEM, NMR, SAXS, and GISAXS will be used to follow the preparation of the clusters and to characterize them prior to the reactivity studies. These methods, plus Raman spectroscopy and *ex situ* MS, will be used to elucidate the mechanism of aromatic formation on the catalyst.

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Surface Bonding of Molecules, Their Reaction and Confinement Effects in the Chemisorbed Layer

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Goal

To understand the role of surface defects on the reactive chemistry of chemisorbed molecules of interest in heterogeneous catalysis.

Recent Progress

A. Adsorption and Dissociation of CO on the Atomic Step Sites on Ru(109).

Metallic Ru surfaces are known to effectively catalyze the production of linear alkanes from CO and H₂ in the Fischer-Tropsch reaction [1,2]. It is very likely that the first step of this process is the dissociation of the CO bond in chemisorbed CO. We have studied the Ru(109) single crystal surface using reflection IR, temperature programmed desorption, isotopic mixing, and low energy electron diffraction methods with a special aim to evaluate the role of the atomic step sites which this crystal presents.

The Ru(109) surface formally possesses single atomic height step edges separating Ru(001) terraces of 5 Ru atom width. Our LEED investigations have shown that step doubling in fact occurs, yielding double atom-height step sites separated by 10 atom-wide terrace sites [3]. Figure 1 shows a portion of the LEED pattern, generated by stacking LEED

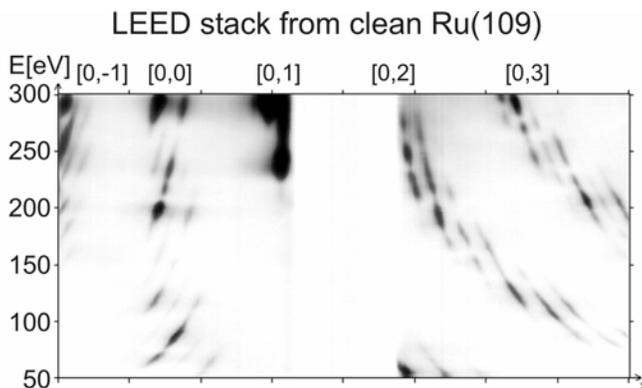


Figure 1. LEED Stack Measurement of the Ru(109) Surface. The [0,0] beams are identified by the lack of horizontal displacement as the electron energy is changed.

measurements at different primary electron beam energies. These measurements are compared with dynamical simulations of the LEED patterns for both single atom-height step sites and for double atom-height step sites, shown in Figures 2 and 3.

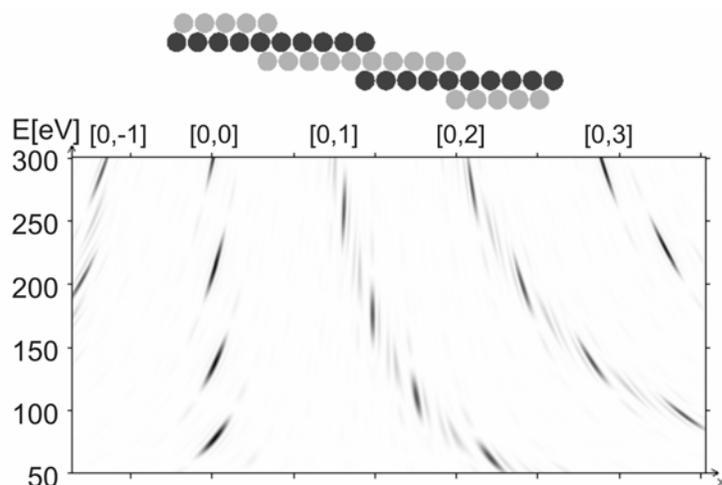
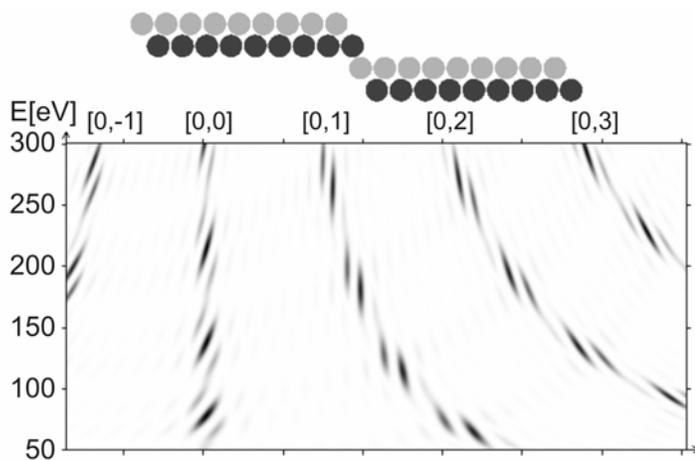


Figure 2. Kinematic LEED Simulations of the Ru(109) Surface with Single-Height Steps as Shown.

Figure 3. Kinematic LEED Simulation for Ru(109) Surface with Double-Height Steps as Shown. Comparison with the experiment in Figure 1 strongly favors the double height step geometry for the Ru(109) surface.



A model of the stepped Ru(109) surface is shown in Figure 4. The orientation of the trigonally-arranged step atoms is $\langle 101 \rangle$.

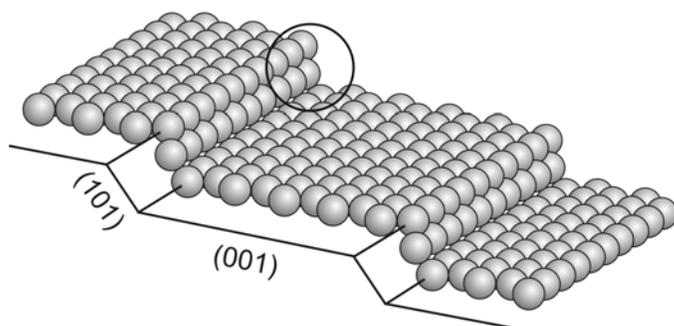


Figure 4. Structure of the Ru(109) Surface

The kinetics of adsorption of CO on the Ru(109) surface has been studied using the collimated and absolutely calibrated capillary array doser, and the results

are shown in Figure 5. At 88 K, an initial sticking coefficient of unity is measured, and most importantly, the sticking coefficient remains above 0.9 for the main range of adsorption. This behavior suggests that adsorption occurs via a mobile precursor mechanism up to near saturation coverage of 0.5 CO/Ru.

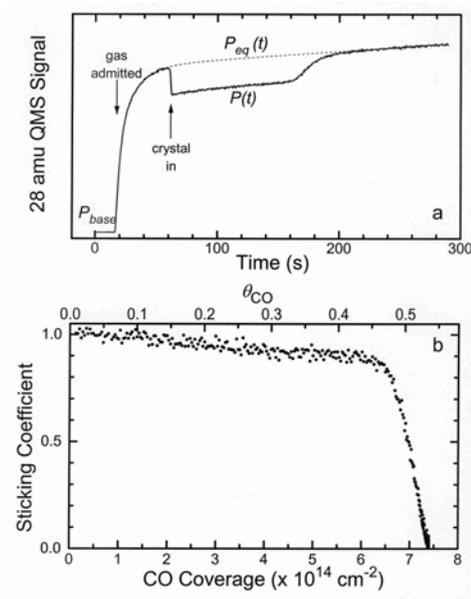


Figure 5. Uptake Curve for CO Adsorption on Ru(109) and Sticking Coefficient Derived from the Uptake Curve.

The reflection IR spectral developments during CO adsorption are shown in Figure 6. A C-O stretching mode, initially observed at 1973 cm^{-1} intensifies and shifts to higher wavenumber. There is an uncanny resemblance between this family of infrared spectra and those obtained on the flat Ru(001) crystal surface by others [4-6], suggesting that the 10 Ru atom wide terraces are similar to the infinitely wide Ru(001) plane in-so-far as the vibrational behavior of chemisorbed CO is concerned. One might ask why specific CO modes associated with the step sites are not seen, and we believe that these modes are invisible because of strong intensity sharing effects with the dominant CO phase on the terraces.

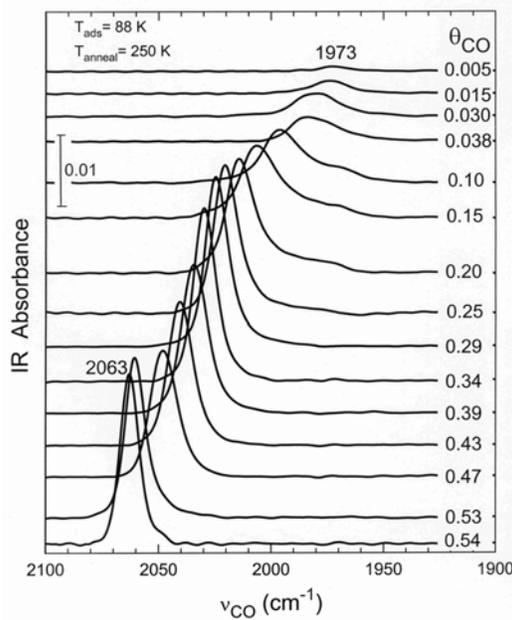


Figure 6. IR Spectral Development for $^{12}\text{C}^{16}\text{O}$ Chemisorption on Ru(109).

In contrast to the similarity between Ru(109) and Ru(001) when viewed from the infrared behavior of chemisorbed CO, the temperature programmed desorption spectra for the two surfaces differ markedly. Figure 7 shows the results for Ru(109).

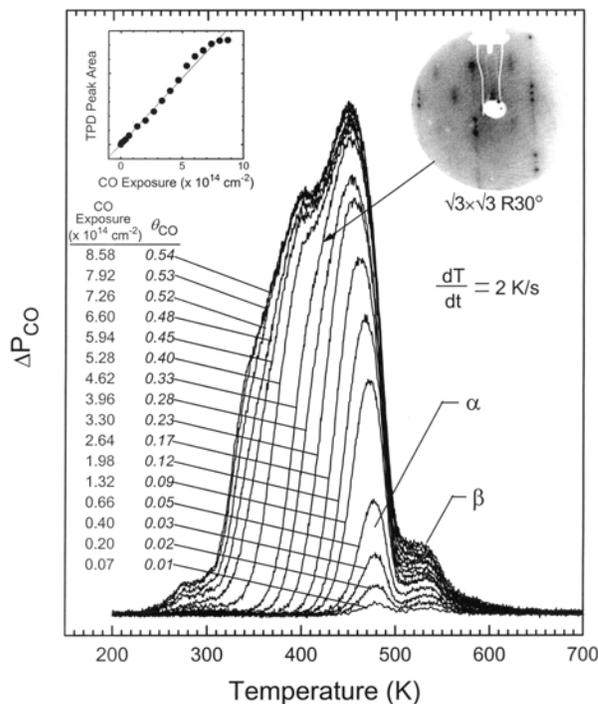


Figure 7. TPD Spectra for CO on Ru(109). The insert shows the LEED pattern obtained for 1/3 monolayer coverage on the Ru(109) terraces.

The TPD spectra reveal that a high temperature CO desorption state (β -CO) is dominant at lower CO coverages, and persists up to saturation coverage. A lower temperature state (α -CO) dominates the desorption process at higher CO coverages, and ultimately is composed of several features. The behavior in the coverage region where α -CO dominates is very different from that observed on Ru(001), where the classic studies of the Menzel group show that a CO-surface phase transition causes dramatic variations in the rate of CO desorption in the temperature range of α -CO desorption.

The unique β -CO desorption process (Figure 7) is of special interest since it is produced as a result of chemical processes at the atomic step sites on the Ru(109) surface. The β -CO state begins to desorb near 480 K; **careful studies by reflection IR indicate that at this temperature, all observable CO has disappeared from the surface, yet CO is observed to desorb in the range 485 K - ~580 K.** The β -CO desorption process is not observed on the smooth Ru(001) surface [4-6]. Thus, we infer that β -CO results from recombination of dissociated fragments of C(a) and O(a) which have been produced on the step sites. This postulate was confirmed by studies of isotopic mixing between doubly-labeled CO isotopomers, and as shown in Figure 8, isotopic mixing is indeed a process which occurs solely in the temperature range of the β -CO desorption process.

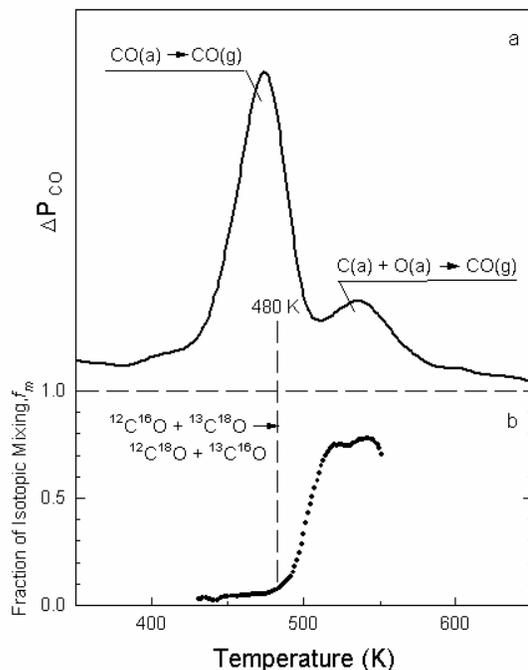


Figure 8. CO Isotopic Mixing During TPD from Ru(109).

These results suggest that the classic Fischer-Tropsch catalytic activity of Ru is a specific property of the defect sites on this element. The "nascent" carbon produced by low temperature CO dissociation on defect sites is likely to participate in reaction with hydrogen to initiate alkane synthesis. The carbon produced on the defect sites

can also recombine with oxygen atoms at very low temperatures on the surface due to the mobility of one or both of these species. These observations suggest that preparative procedures for high area Ru catalysts, which enhance the fraction of low Ru-Ru coordination at defect sites, will probably show enhanced catalytic activity in the Fischer-Tropsch reaction.

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DOE Interest

Because of the widespread use of Ru catalysts in the Fisher Tropsch synthesis we decided to try to learn something about the atomic details of the key reaction necessary for the FT synthesis- the dissociation of CO. We found, interestingly, that atomic step defect sites on Ru are much more active for CO dissociation than smooth surfaces. Thus, for maximum kinetic rate, the practical Ru catalyst should be prepared to expose a maximum fraction of defect sites.

Future Plans

The role of Pt adatoms on the chemisorption behavior of the atomically-stepped Ru(109) surface will be investigated by reflection IR and by thermal desorption kinetics. The goal is to determine whether the Pt atoms (probably located at atomic step sites) behave as isolated atomic sites with their own electronic character, or whether they behave as more delocalized electronic entities. Understanding this will aid in understanding alloy catalysts as often used, for example, in Ru/Pt fuel cell electrodes.

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Molecular Design of Hydrocarbon Oxidation Catalytic Processes

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Goal

To understand the molecular-level mechanistic factors that define selectivity in the catalysis of oxidation of hydrocarbons, of alkanes and alcohols in particular.

Recent Progress

Our past research has relied on a combination of modern surface-characterization techniques with well-defined surfaces under ultrahigh vacuum (UHV) conditions to look into the elementary steps that comprise catalytic oxidations. Our general conclusion based on that work is that the selectivity of those reactions is defined by the regioselectivity of dehydrogenation steps from alkyl and alkoxide surface intermediates. Figure 1 illustrates the reaction diagram underpinning this central hypothesis. Two sets of reactions are presented in this diagram to account for both oxidative coupling and chain growth in alkanes (left) and oxidation and dehydrogenation of alkanes and alcohols (right), and a common alkoxide intermediate, the result of either oxygen insertion into alkyl-surface bonds or α -dehydrogenation from adsorbed alcohols, is also indicated. In terms of dehydrogenation versus dehydration in alcohols, direct β -hydride elimination to aldehydes or ketones (the dehydrogenation product) was determined to be the preferred pathway on late transition metals. On the other hand, promotion of γ -hydride elimination may lead to the production of an oxametallacycle instead. That intermediate can then undergo oxygen extrusion to the olefin (the dehydration product). Some of our recent studies have focused on this idea.

This project was initiated with the use of 2-propyl iodide to prepare 2-propyl surface groups on a Ni(100) single crystal surface. It was found that 2-propyl moieties can easily incorporate oxygen atoms to form 2-propoxide groups, even if only on surfaces with submonolayer oxygen coverages emulating defective oxides. It was also shown that similar 2-propoxide species can be prepared by decomposition of 2-propanol. The resulting 2-propoxide moieties are stable on both clean and oxygen-treated Ni(100) surfaces up to ~ 325 K, but decompose via β -hydride elimination above that temperature to yield acetone. Additional temperature programmed desorption (TPD) experiments indicated that propene does not convert directly to acetone on these O/Ni(100) surfaces, a thought-provoking conclusion given that alkene partial oxidation is in fact performed industrially by using oxide catalysts. Our results suggest that such a process may occur via an initial hydrogenation of the alkene to an alkyl intermediate on a metal center followed by a sequence of oxygen migratory insertion and β -hydride elimination steps.

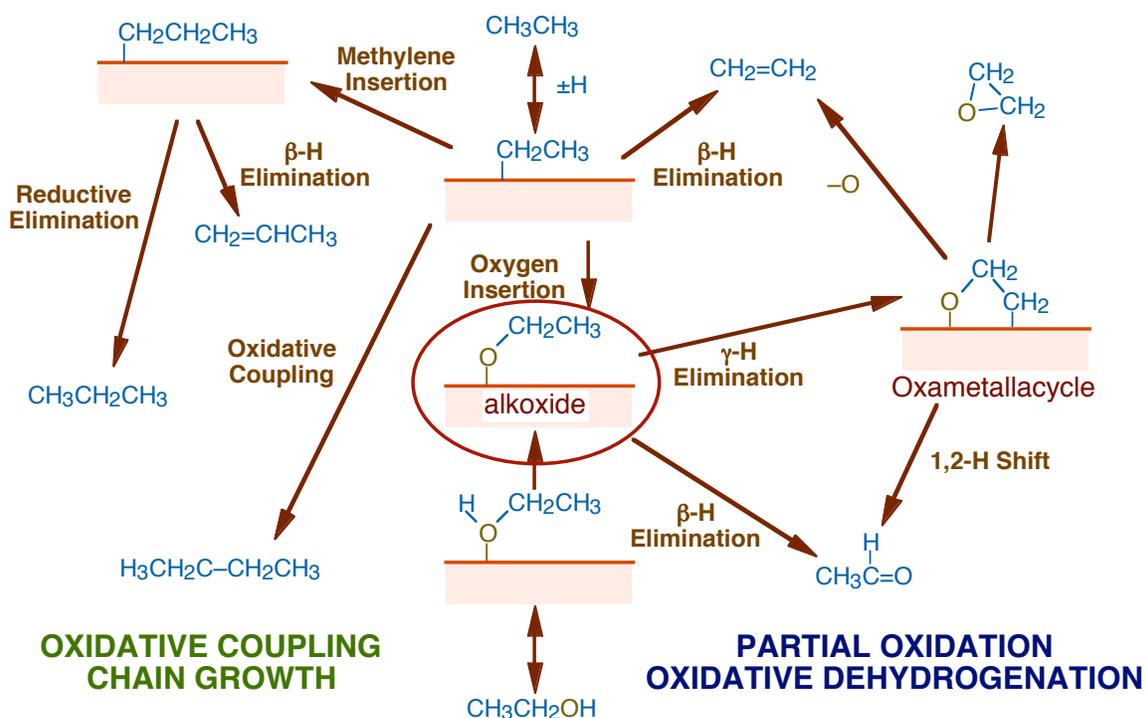


Figure 1

The chemistry of $\text{HOCH}_2\text{CH}_2\text{I}$, a precursor to surface oxametallacyclobutane, was also studied on $\text{Ni}(100)$. It was determined that a low-temperature decomposition channel of the adsorbed $\text{HOCH}_2\text{CH}_2\text{I}$ produces small amounts of ethylene (together with water) around 140 K. The activation of the remaining species occurs around 150 K to yield $-\text{O}(\text{H})\text{CH}_2\text{CH}_2-$ and 2-hydroxyethyl intermediates. The $-\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{I}-$ intermediate dehydrogenates around 160 K to produce the desired $-\text{OCH}_2\text{CH}_2\text{I}-$ surface oxametallacycle, and that later isomerizes via a 1,2 hydrogen shift to yield acetaldehyde. The 2-hydroxyethyl intermediate, on the other hand, reacts around 160 K via two competing steps, a reductive elimination with surface hydrogen to produce ethanol, and a β -hydride elimination to yield surface vinyl alcohol. The vinyl alcohol converts further on the surface either by losing its oxygen atom to produce ethylene or by tautomerizing to acetaldehyde. Overall, these studies have proved that oxametallacycles may be intermediates towards the production of alcohol dehydration products (olefins), but could also lead to dehydrogenation (aldehydes and ketones).

In a separate study, the possibility of activating γ hydrogens in surface alkoxy species was explored. Preliminary work using tert-butyl alcohol on $\text{Ni}(100)$ has suggested that, indeed, γ -H elimination may occur in those systems. Alternatively, the β carbon of the alkoxy species may be deactivated via inductive substitutions. TPD results from studies with 1,1,1-trifluoro-2-propanol have shown an increase in activation energy for β -hydride elimination of approximately 10 kcal/mol, and the opening up of a second dehydration pathway for the adsorbed alcohol, which results in a desorption peak for 3,3,3-trifluoropropene at 437 K in TPD experiments.

DOE Interest

The combination of the results from our reactivity studies with additional work on the nature of the catalytic surface has provided us with a tentative list of characteristics for the active sites involved in hydrocarbon oxidation catalysis: (1) the need for surface metal atoms to induce the initial bond-activation of the reactant; (2) the need of a proximity between the resulting alkyl/alkoxide intermediates and oxygen surface atoms, which may require unique unsaturated coordination to be reactive; (3) the tuning of the electronic properties of the metal site to set the relative rates of β - versus γ -dehydrogenation steps, and with that the selectivity between dehydrogenation and dehydration reactions; and (4) the enhancing ability of surface hydroxides toward oxygen insertion reactions (and possibly dehydrogenation steps) on surface alkoxides. A more detailed list of this sort, which we are in the process of developing, should be helpful for the design of specific and selective hydrocarbon oxidation catalysts.

Future Plans

Regioselectivity of dehydrogenation steps as they relate to hydrocarbon oxidation processes. New experiments will involve tert-butyl species to characterize γ -H eliminations, 2-bromo-1-propanol, 1-bromo-2-propanol, and 1-chloro-2-methyl-2-propanol to test the reactivity of oxametallacycle intermediates as a function of the extent of substitutions at particular locations within the carbon backbone, allyl alcohol to explore changes in selectivity due to the weakening of the C–O bond, and propene and propyl halides to investigate the reactivity of allylic hydrogens.

Chemical reactivity on oxide and oxygen-treated metal surfaces toward chain growth processes. Experiments will be carried out with mixtures of methylene and methyl precursors and with coadsorbed ethylene to explore the potential insertions into metal-carbon bonds in competition with alkyl coupling and oxygen insertion steps. Selective deuterium isotope labeling will be employed to differentiate among the different possible mechanisms. Systematic studies will be carried out as a function of the coverages of each of the surface species involved as well.

Reactivity of different types of oxygen-based surface sites. Different preparations will be tried on several crystallographic orientations and by modifying NiO films via sputtering and/or annealing. The nature of the resulting sites will be characterized by chemical titrations and physical (XPS, PAX) methods. Their reactivity towards hydrocarbon surface species will be probed, and their effect on modifying the surface mobility of the reactants will be tested using selective isotope labeling. Differentiation among the different oxygen species will be attempted by oxygen isotope labeling. The reactivity of surface hydroxide species will be probed.

Contrasting of the chemistry on nickel versus vanadium oxides. Oxygen treatments for the preparation of different oxygen sites on vanadium will be developed, and the resulting surfaces characterized by using methodology similar to that developed for nickel. The reactivity of those surfaces toward different reactions with alkyls, allyls, alkenes and alcohols will be tested. Vanadium oxides are central components in many oxidation catalysts. Nickel and vanadium oxides are expected to represent opposite extremes within the range of oxides available for hydrocarbon oxidation catalytic applications.

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Molecular Level Design of Chiral Heterogeneous Catalysts

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Goal

To prepare surfaces having chiral structures of different origin and optimize their enantioselectivity for adsorption and catalysis.

Recent Progress

Surfaces having chiral structures at the atomic scale can catalyze reactions enantioselectively. Naturally chiral surfaces can be created either by starting with a chiral bulk structure or by taking an achiral bulk structure such as that of a metal and cleaving along a plane that exposes a chiral surface. Chiral surfaces can also be made by templating an otherwise achiral surface with chiral organic molecules. The enantioselectivity of surfaces prepared in these ways is being explored through the use of a number of chiral molecular probes.

Previous work has shown that the adsorption of R- or S-2-butanol on the Pd(111) surface can be used to create an enantioselective, templated chiral surface. The enantioselectivity has been probed by the adsorption of R- or S-propylene oxide where coverages are measured from both its desorption spectrum and its infrared-absorption spectrum. Enantioselective adsorption of the propylene oxides is observed over a narrow range of the 2-butanol coverage near $\Theta_{2\text{-ButO}} \sim 1/2$ monolayer. The enantioselective ratio for adsorption of the propylene oxides on the templated surface is defined as

$$ER_{2\text{-ButO}} = \frac{\Theta_{\text{R-PropyleneOxide}}}{\Theta_{\text{S-PropyleneOxide}}}$$

and can reach a value as high as $ER_{2\text{-Butanol}} = 2$.

Recent work has made use of R- and S-2-methyl butanoic acid as the chiral template on Pd(111) and has shown that for this templating agent there is no enantioselective adsorption of propylene oxides ($ER_{2\text{-Methyl Butanoic Acid}} = 0$). This may arise from the fact that the chiral butyl group is now located further away from the surface than in the case of the 2-butanol templates and can rotate more freely, thus reducing its chirality. Functionalizing the butyl group with an amine (2-amino butanoic acid) anchors the butyl group to the surface and restores enantioselectivity for the adsorption of propylene oxide,

$ER_{2\text{-Amino Butanoic Acid}} = 1.75 \pm 0.15$. Using amino acids of various types it has been possible to observe enantioselectivity ratios as high as $ER_{\text{Amino Acid}} \approx 2$ on Pd and Pt surfaces. Initial work with other amino acids suggests that the ER value decrease as the size of the functional group on the amino acid increases. This may be due to the formation of larger “chiral” pockets.

Initial work using Density Functional Theory (DFT) to explore the structures of adsorbed amino acids has begun with the Cu(110) and Cu(100) surfaces in order to resolve known issues regarding the structures of the ordered overlayers that they form on these surfaces. Earlier experimental studies of glycine and alanine adsorption on these surfaces showed that both molecules form highly structured adlayers, but the determination of the structures of these adlayers from experimental data was controversial. For glycine/Cu(110), the existence of two distinct adlayer domains, one heterochiral and one homochiral, was suspected based on STM images. This conclusion has been called into question by x-ray photoelectron diffraction (XPD) data that did not support the existence of multiple distinct adlayers. DFT calculations show unequivocally that the heterochiral adlayer is the only structure that appears on Cu(110), and that the multiple domains observed with STM can be understood as rotationally equivalent domains of this single adlayer. In contrast, calculations for glycine on Cu(100) show that two structurally distinct adlayers appear with essentially equal energies. Both of these structures are consistent with the extant XPD data from glycine/Cu(100). Similar calculations for alanine adlayers on Cu(110) and Cu(100) have shown that the binding footprint of glycine on Cu surfaces provides an excellent starting point for describing the binding of alanine and other amino acids.

The most widely studied enantioselective heterogeneous catalyst is based on the templating of Pt with cinchonidine. This catalyst is used in solution for the enantioselective hydrogenation of ketoesters. Infrared spectroscopy has been used to study the adsorption of cinchonidine, lepidine and other small models of cinchonidine on Pt surfaces. The properties of the template are influenced by the solvent. For example, the thermal stability of cinchonidine adsorbed from CCl_4 is increased by dissolution of hydrogen into the solution. The solvent also has a strong influence on the enantioselectivity of templated hydrogenation catalysts. The polarity of the solvent has been found to influence the kinetics of cinchonidine desorption into solution in a manner that is correlated to its influence on the enantioselectivity of the templated catalyst.

Adsorption of the cinchonidine template on Pt is very sensitive to the concentration in solution. At low concentrations little cinchonidine is adsorbed. At intermediate concentrations the cinchonidine is adsorbed with the quinoline ring parallel to the surface while at high concentrations the ring is tilted away from the surface. The optimum enantioselectivity occurs under conditions that are consistent with a template adsorption geometry having the quinoline ring parallel to the surface.

Finally, naturally chiral surfaces have been prepared by exposing high Miller index planes of fcc metals such as Cu. Electron diffraction has shown that these are indeed chiral and desorption studies have shown that their enantioselectivity originates with kinks on the surfaces. The most recent work has extended this work to studies of reactivity on these surfaces. Using chiral 2-bromobutane it has been possible to create chiral 2-butyl groups on naturally chiral Cu surfaces. The kinetics of their -hydride elimination has been found to be enantioselective.

DOE Interest

Enantioselectivity is perhaps the most subtle form of chemical selectivity. Understanding enantioselective surface chemistry can have broad impact on our understanding of selectivity in many other heterogeneous catalytic processes. Enantioselectivity is critical to the production of numerous fine chemicals used for bioactive applications such as pharmaceuticals. Heterogeneous catalysis has a number of attractive features that offer opportunities for its use in fine chemical synthesis.

Future Plans

Future work is centered on exploration of the enantioselectivity of surfaces templated with amino acids, related compounds, and naphthylethylamine (a model for cinchonidine). Pt, Pd and Cu surfaces will be templated with these chiral compounds in order to explore the influence of substrate on their enantioselectivity. In addition, efforts will be made to explore the use of new chiral probes such as 3-methylcyclohexanone, 2-chlorobutane, and 2-aminobutane. DFT calculations will be used to model the interaction of these probes with amino acids in the gas phase and with amino acids on Cu surfaces. Amino acids are also known to induce the reconstruction of Cu surfaces to expose high Miller index facets which are naturally chiral. Efforts are being made to develop a process to prepare high surface area Cu powders with surfaces that are homochiral and thus can be used at a macroscopic level for enantioselective separations and catalysis.

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