

Presentation and Poster Abstracts

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

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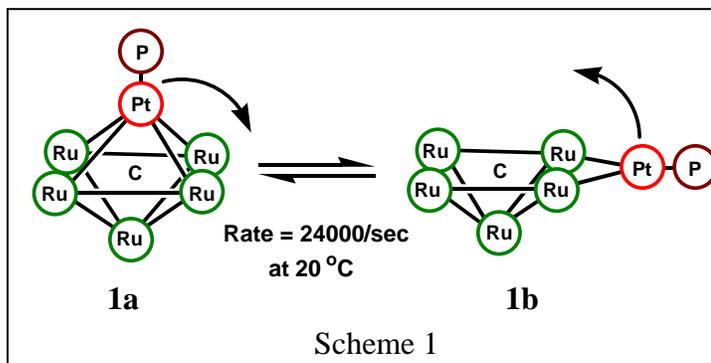
Goals

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

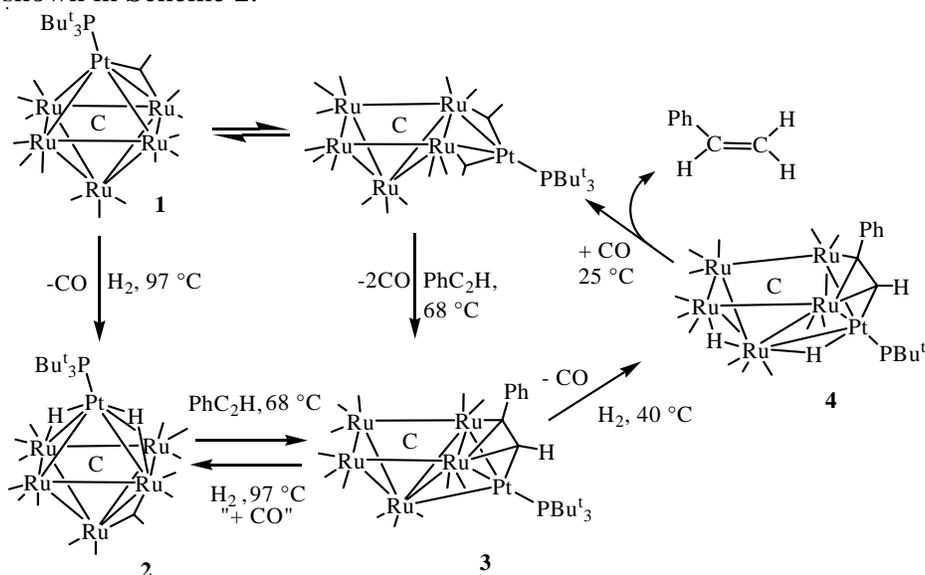
The new hexanuclear cluster compound $\text{PtRu}_5(\text{CO})_{15}(\text{PtBu}_3)(\text{C})$, **1** was obtained from the reaction of $\text{Pt}(\text{P}^t\text{Bu}_3)_2$ with $\text{Ru}_5(\text{CO})_{15}$. Compound **1** crystallizes in two isomeric forms. In one form the cluster consists of a square 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.

Publications for the Years 2002 - 2003.

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- 5) R. D. Adams, B. Captain, W. Fu and M. D. Smith, High Nuclearity Ruthenium-Tin Clusters from the Reactions of Triphenylstannane with Pentaruthenium Carbonyl Carbido Cluster Complexes, *Inorg. Chem.*, **41**, 5593 (2002).
- 6) R. D. Adams, B. Captain, and W. Fu, Germanium-Rich Pentaruthenium Carbonyl Clusters Including $\text{Ru}_5(\text{CO})_{11}(\mu\text{-GePh}_2)_4(\mu_5\text{-C})$ and its Reactions with Hydrogen, *Inorg. Chem.*, **42**, 1328 (2003).
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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.

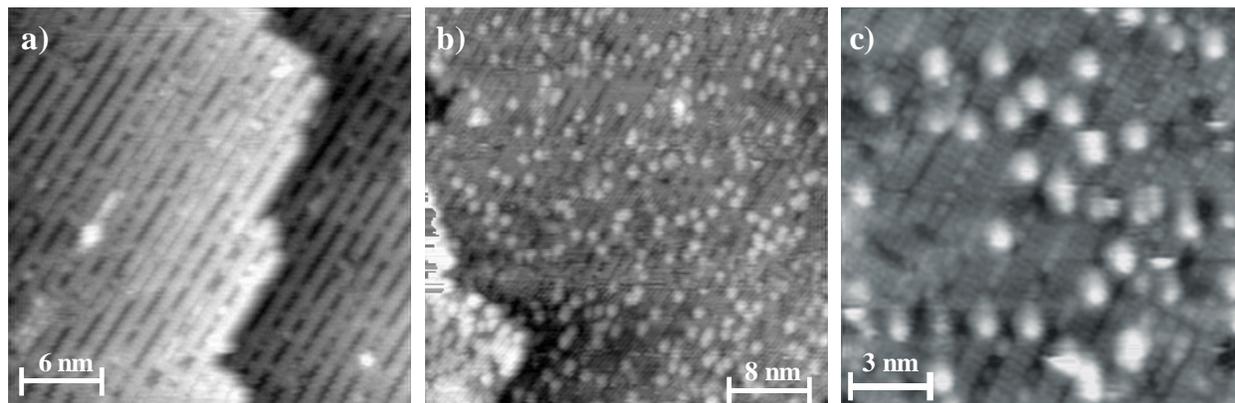


Figure 1. (a) STM image of the $p(n \times 2)$ $\text{WO}_3(100)$ reconstructed surface. In this image, the strand spacing, n , is predominantly 4x though a local 3x spacing can be seen in several places. (b) After exposing this surface to ~ 200 L 1-propanol at 300 K, white dots decorate the tops of 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 (4x1) reconstruction creating (1x1) 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.

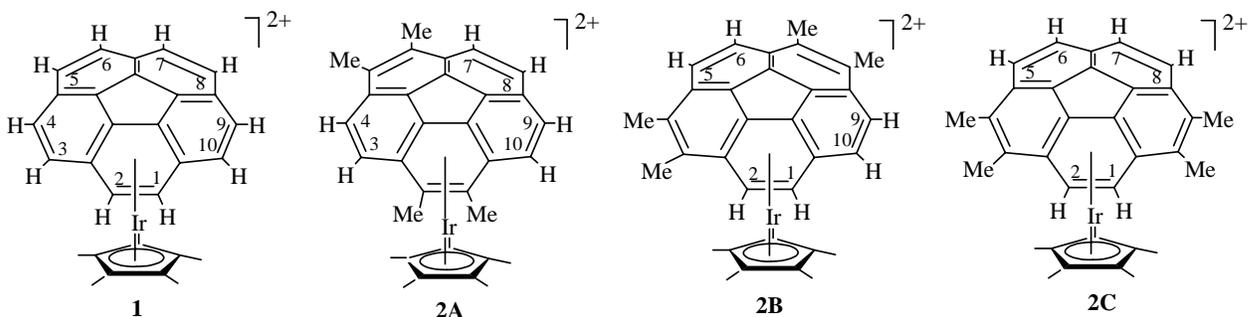
Recent Progress

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

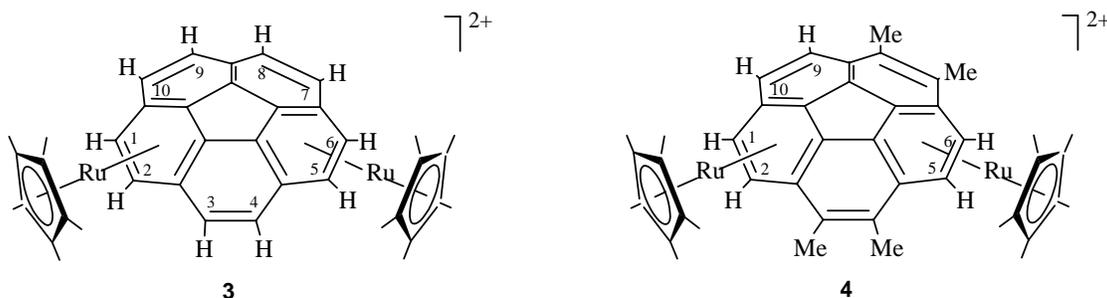
clear whether the migration of the $\text{Cp}^*\text{Ir}^{2+}$ occurs while remaining attached to the surface or by dissociation and re-association.

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.

Publications for 2002-present (supported by BES)

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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).
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6. P. A. Vecchi, A. Ellern and R. J. Angelici, "Synthetic, Structural and Binding Studies of the 4,6-Dimethyldibenzothiophene Complex [(η⁵-C₅Me₅)Ru(CO)₂(η¹(S)-4,6-Me₂DBT)]BF₄: Toward an Understanding of Deep Hydrodesulfurization," *J. Am. Chem. Soc.*, **125**, 2064-2065 (2003).
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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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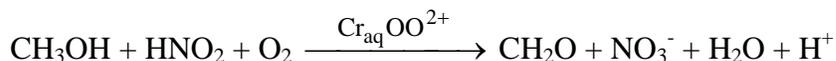
Goal

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

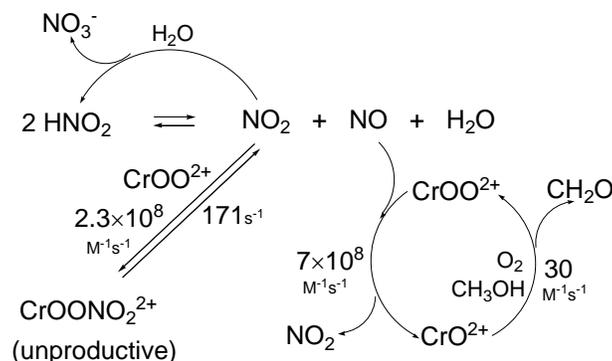
Recent progress:

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 $\text{Cr}_{\text{aq}}^{2+}$.

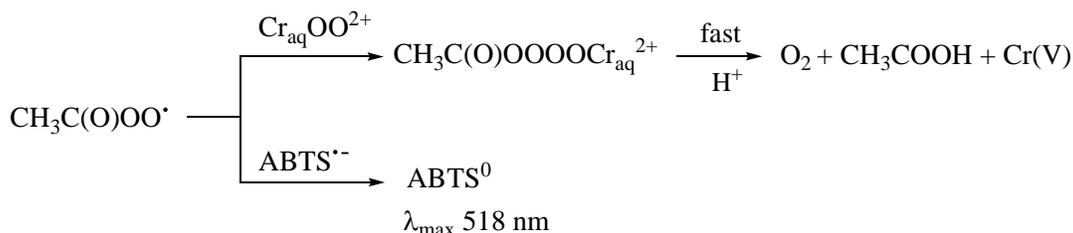


Rapid Cross-Disproportionation of Superoxometal Ions and Acylperoxyl Radicals

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.

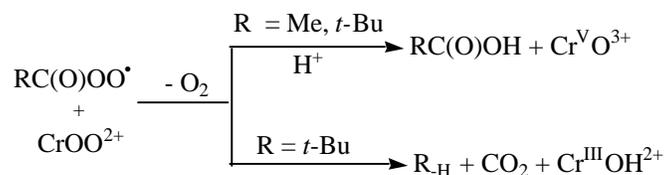
Laser flash photolysis of an organocobalt precursor in the presence of O_2 , $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, and a kinetic probe $\text{ABTS}^{\bullet-}$, yielded the rate constant for cross coupling $k_{\text{cross}} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. After the initial coupling 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.



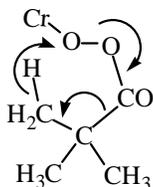
Reactions of Superoxo and Oxo Metal Complexes with Aldehydes

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.



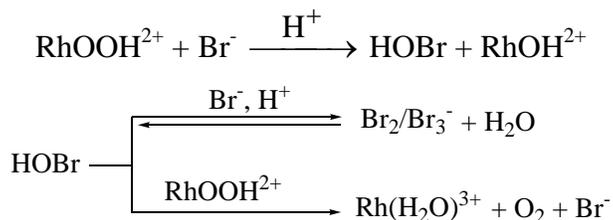
The other products arise from an unprecedented intramolecular hydrogen transfer from *tert*-butyl group to CrO entity, and elimination of CO_2 and O_2 .



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 (NH₃)₄(H₂O)RhOOH²⁺ → 2 (NH₃)₄(H₂O)RhOH²⁺ + O₂, 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)

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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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6. Lemma, K.; Ellern, A.; Bakac, A. "¹H NMR Studies of Ligand and H/D Exchange Reactions of *cis*- and *trans*- ([14]aneN₄)(H₂O)RhH²⁺ in Aqueous Solutions" Inorg. Chem. **2003**, 42, 3662-3669
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Nanostructured Metal Oxide Catalysts via Building Block Syntheses

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

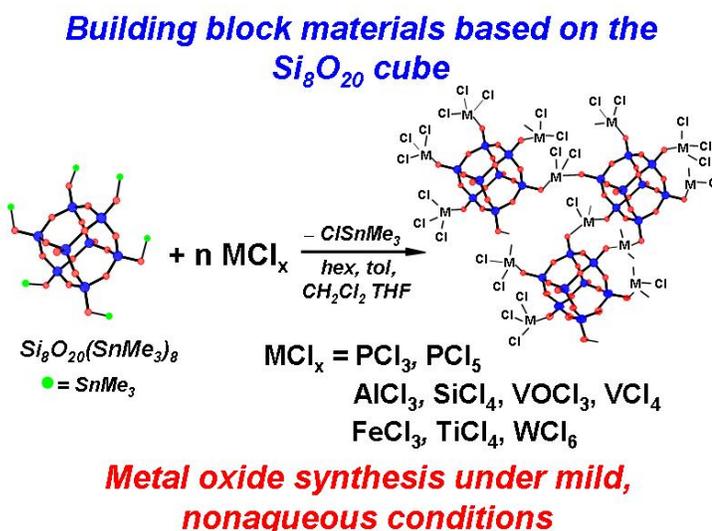
Goal

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-FG02-03ER15468
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

Additional PIs: Douglas J. Buttrey, Jingguang G. Chen, Jochen A. Lauterbach, Raul F. Lobo, Dionisios G. Vlachos (Delaware); James A. Dumesic (Wisconsin)

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 to 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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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.

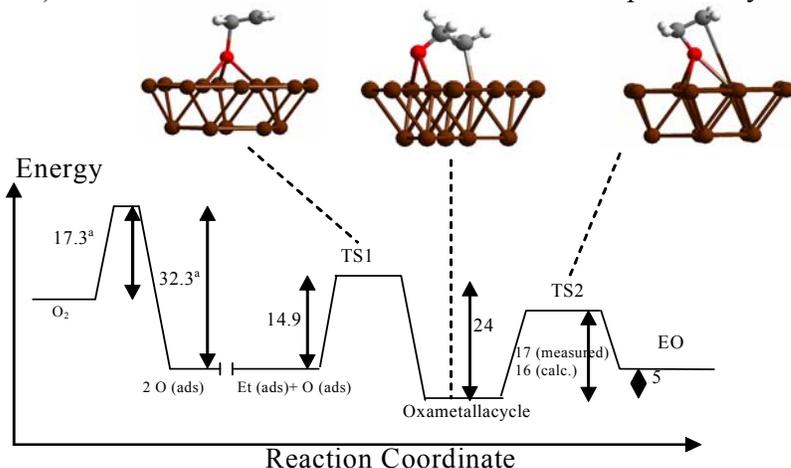


Figure 1. Reaction coordinate for ethylene epoxidation combining results from DFT calculations and surface science experiments.

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.

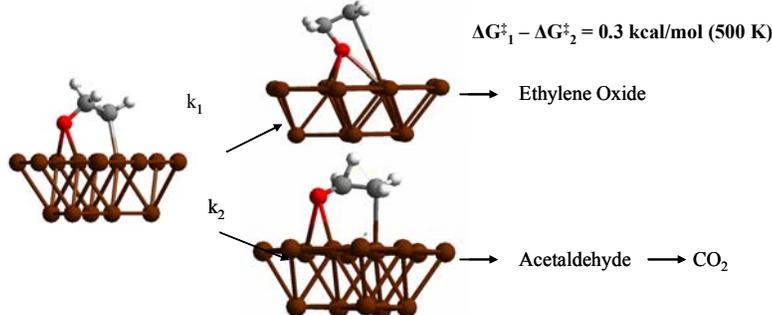


Figure 2. Competing oxametallacycle reaction channels.

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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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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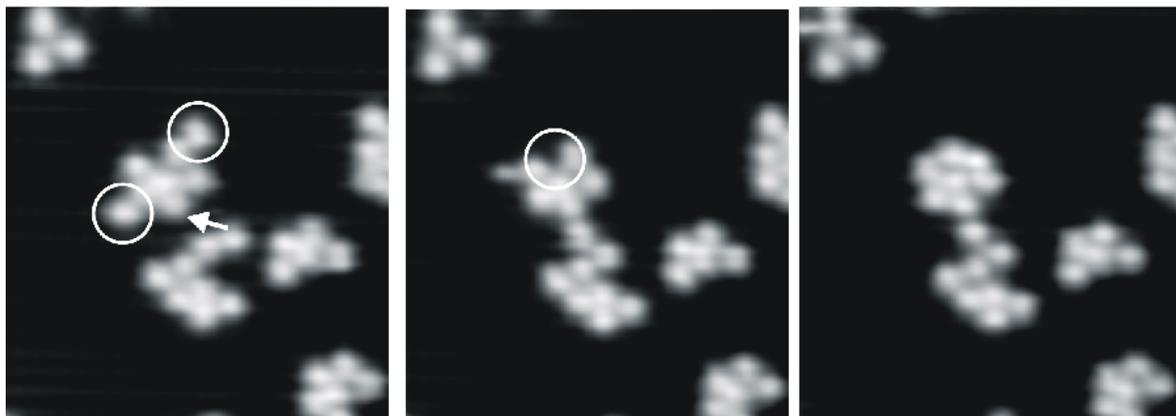
Goal

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:

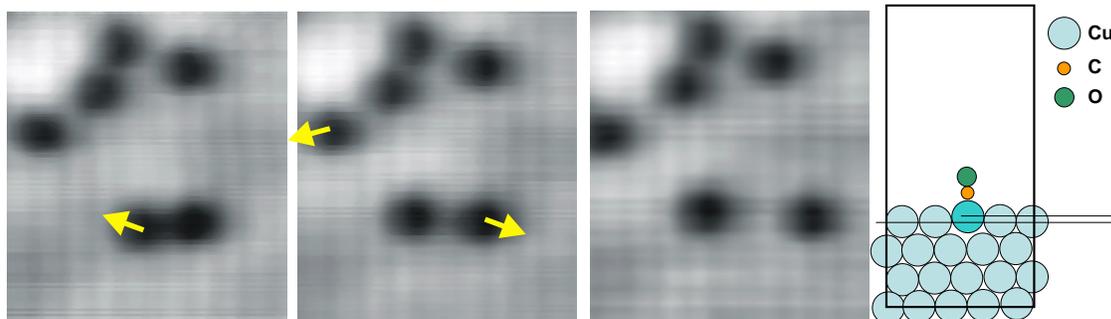
During the first six month of the project, experimental work focused mainly on equipment development and installation, as well as on software development for data analysis as anticipated in the original proposal. In addition, we performed diffusion measurements addressing CO and Thiophenol molecules 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.



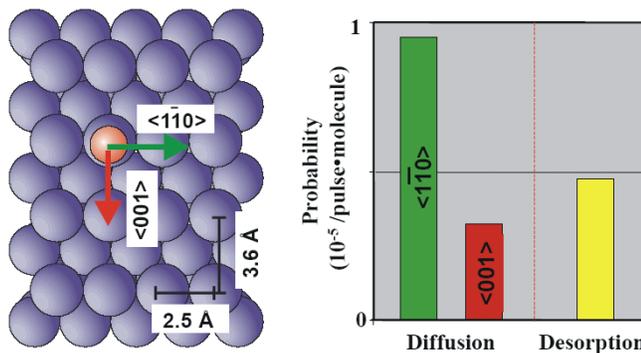
Diffusion and Cluster Formation of Thiophenol on Cu(111) at 90 K (-2V, 0.2 nA, 75x75Å)

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

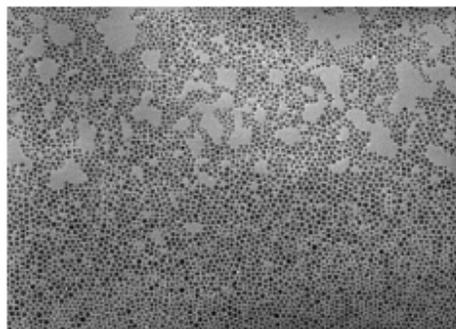
Catalytic reactions have great importance for a broad range of industrial and environmental processes ranging from catalytic CO oxidation in exhaust systems to catalytic hydro-desulfurization of gasoline. This project aims at understanding catalytic processes on the atomic scale by development and applications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

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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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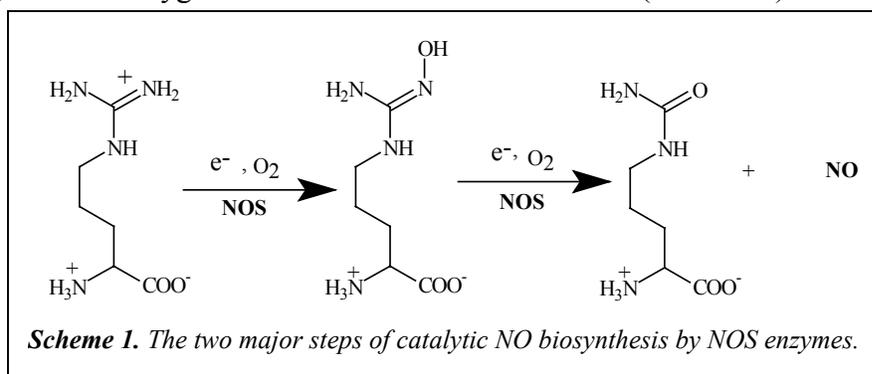
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Goal

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.

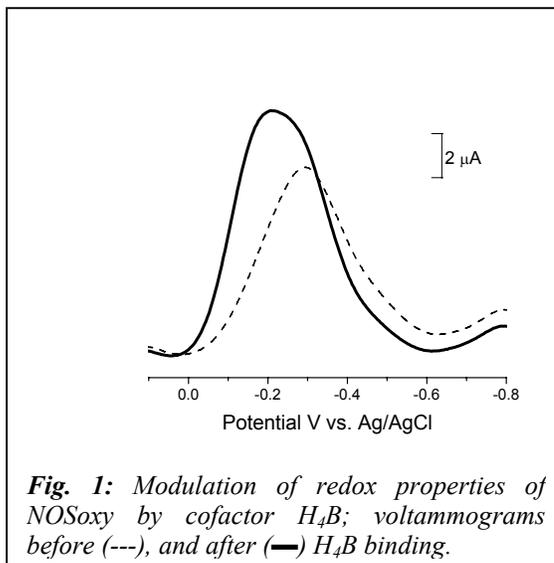
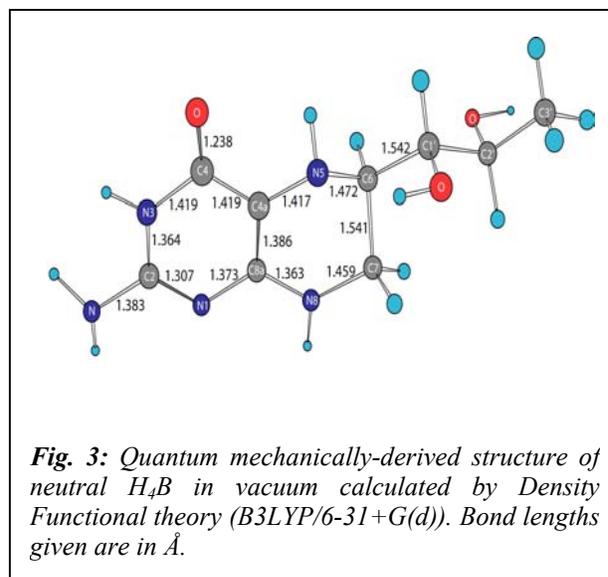
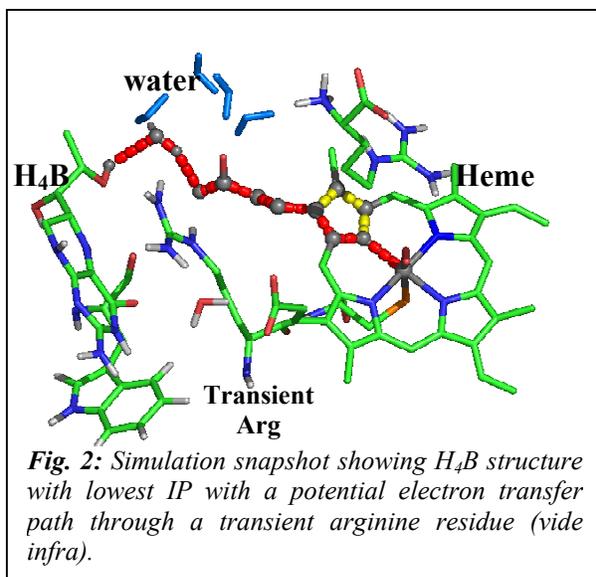


Fig. 1: Modulation of redox properties of NOSoxy by cofactor H₄B; voltammograms before (---), and after (—) H₄B binding.

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.

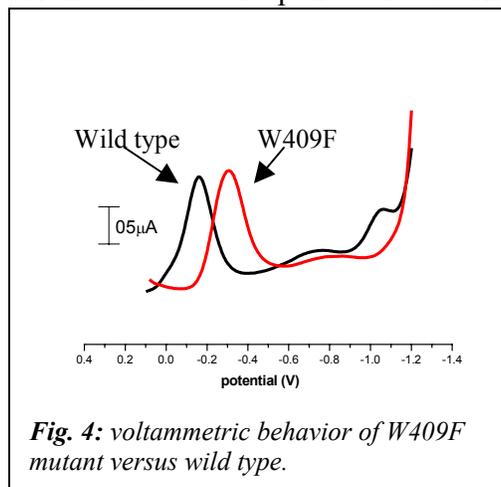


Fig. 4: voltammetric behavior of W409F mutant versus wild type.

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-)

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Catalysts for Selective Olefin Oligomerization and Polymerization

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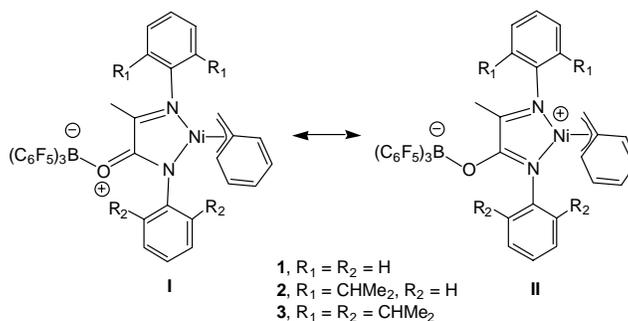
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Goals

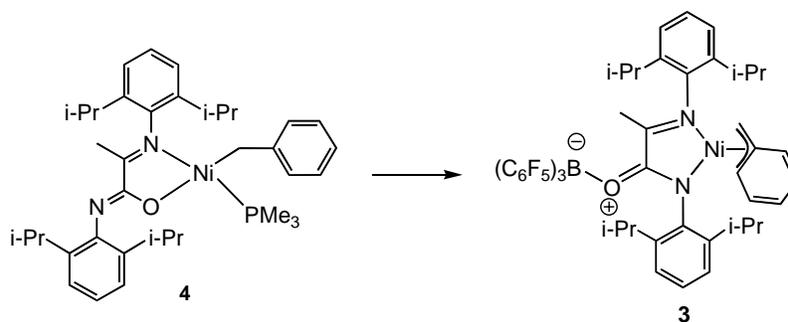
Provide homogeneous organometallic complexes that enable novel olefin polymerization reactions including concurrent tandem catalysis and living polymerization of ethylene with functionalized co-monomers.

Recent Progress

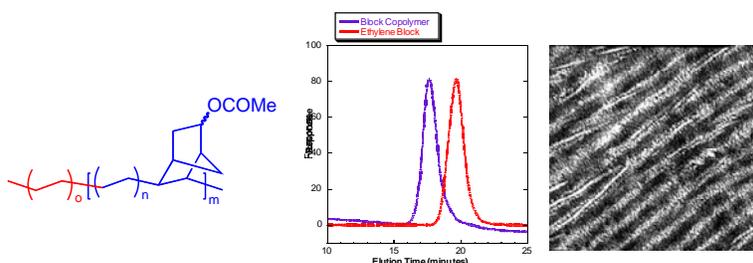
We recently reported the activation of nickel olefin polymerization initiators by attachment of a Lewis acid on the carbonyl functionality at a site removed from the monomer trajectory. Compounds **1-3** were recently prepared in our labs and exemplify our strategy. Resonance structures **I** and **II** 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:

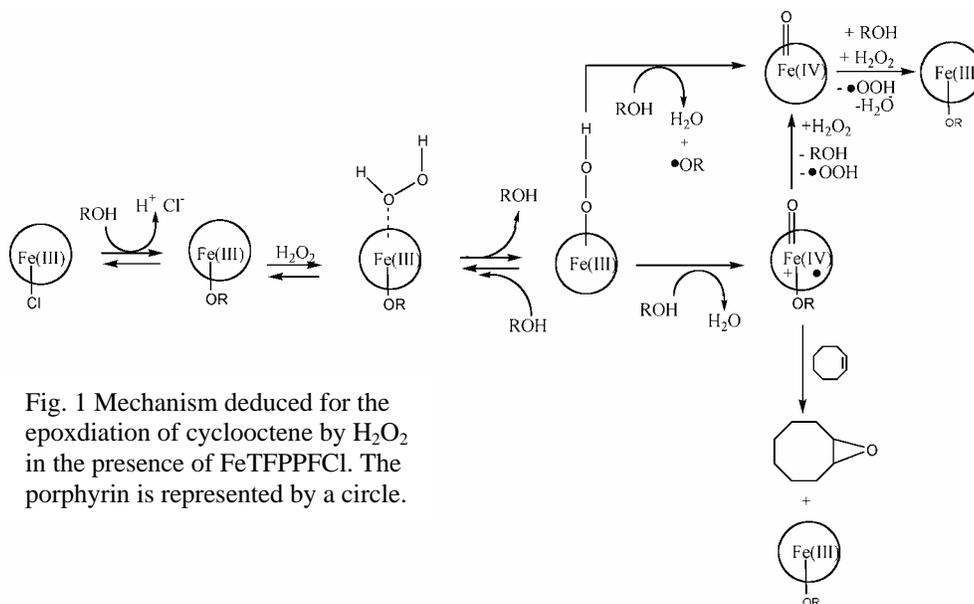


Fig. 1 Mechanism deduced for the epoxidation of cyclooctene by H_2O_2 in the presence of FeTPFPFCl . The porphyrin is represented by a circle.

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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Collaborators: Miller, S. M. (Texas A&M), Green, M. L. H. (Oxford), Green, J. C. (Oxford)

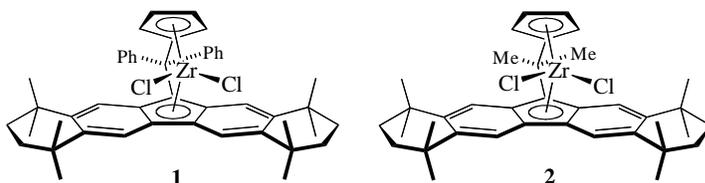
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Goal

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

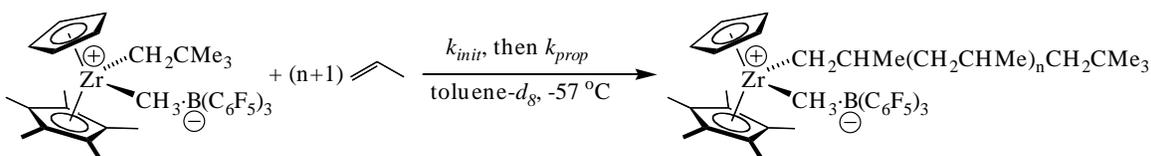
Recent Progress

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)

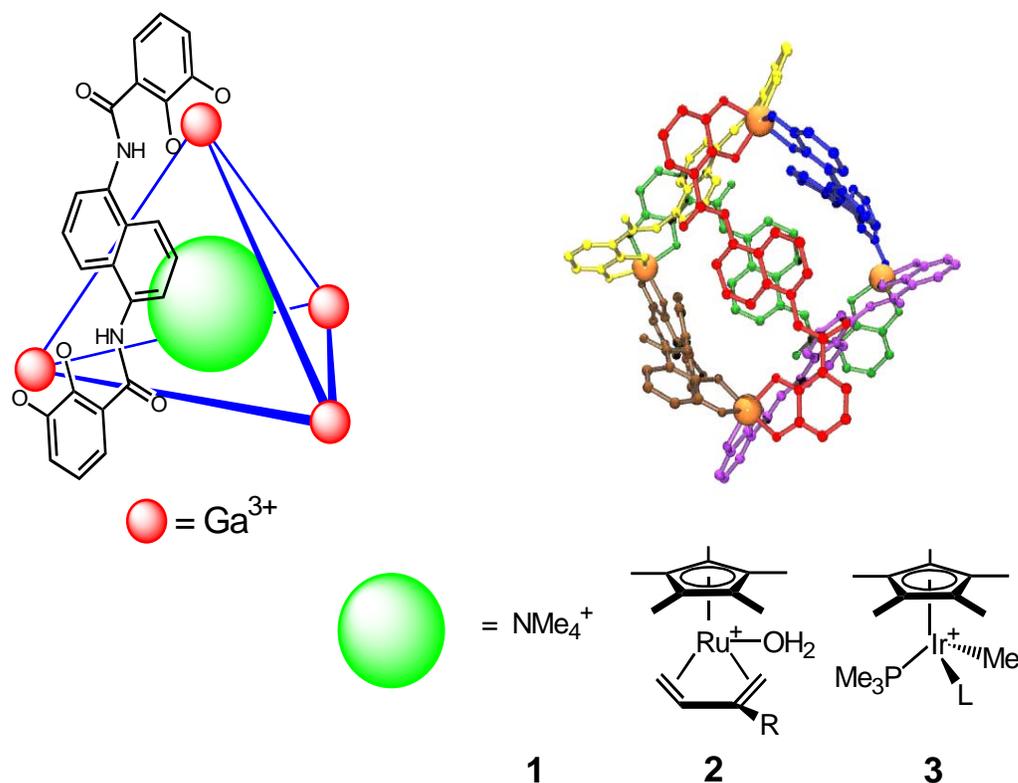


Figure 1. The M_4L_6 assembly illustrated (left) with structure of L and included guest G , and (right) as a molecular model of the full cluster without the encapsulated transition metal guest.

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.

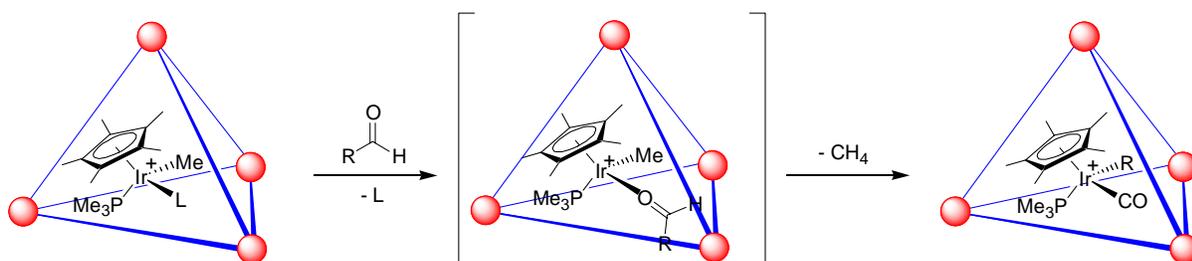
Use of chiral nanovessels in kinetic resolution of planar chiral ruthenium complexes.

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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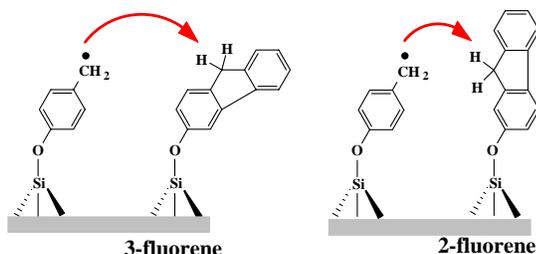
Goal

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

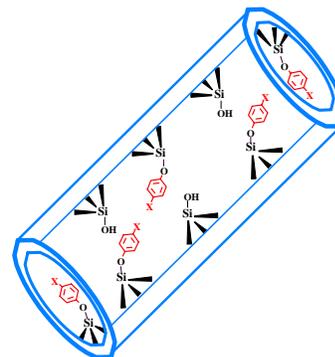
Research focused primarily on two theme areas. First, chemical transformations on surfaces were examined to investigate the impact of restricted mass transport on reaction rates and product selectivities, which can be important in the thermal and catalytic conversion of macromolecular energy resources. 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.



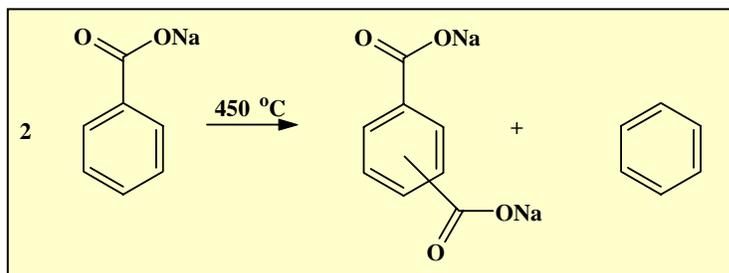
Spectroscopic Studies of Surface-Confined Aromatics. Surprisingly large (megahertz) rotational diffusion rates have been measured for silica-attached 1-pyrene and silica-attached benzene by time dependent fluorescence anisotropy and ¹³C NMR spectroscopy, respectively.³ A remarkable outcome of these findings 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.

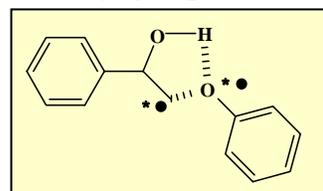
Pyrolysis Studies of Aromatic Carboxylic Acid Esters and Salts. In our efforts to understand cross-linking reactions in low-rank coal, the fundamental reaction pathways for the formation and decomposition of aryl esters were resolved by the study of the pyrolysis of phenyl benzoate.⁹ Aryl esters readily 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 $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_2\text{-OC}_6\text{H}_5$ 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 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{-OC}_6\text{H}_5$, 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

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

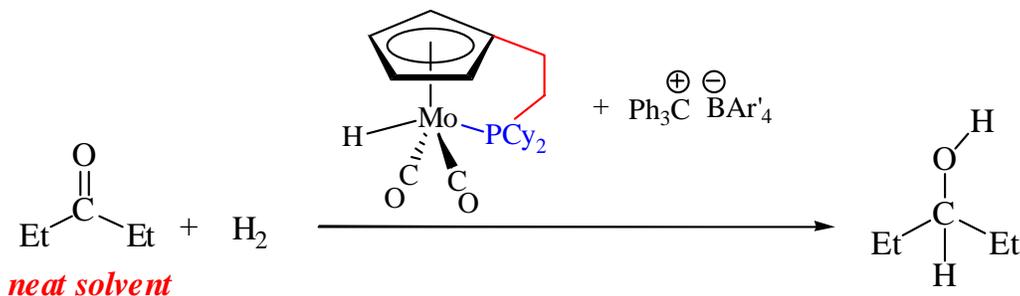
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Goal

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.

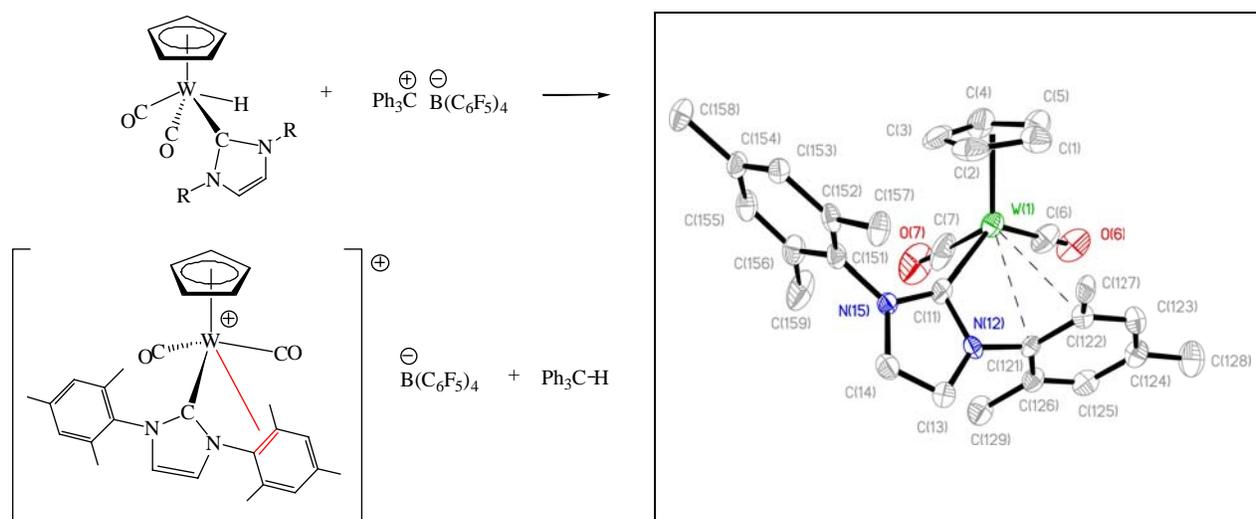
Recent Progress

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

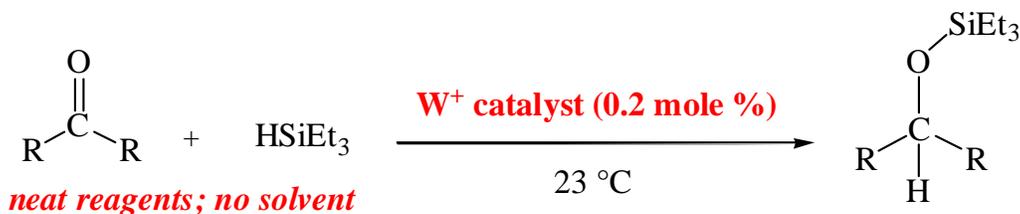


loadings (< 0.4 mole %), higher thermal stability, substantially longer lifetimes (hundreds of turnovers), and hydrogenation of liquid ketones under solvent-free conditions.

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.

Graduate students: Steven Diaz, Steven L. Tait, Lien Ngo, Lijun Xu, Mark Huberty.

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.

Publications (2002-4)

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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-dimethyl-dibenzothiophene (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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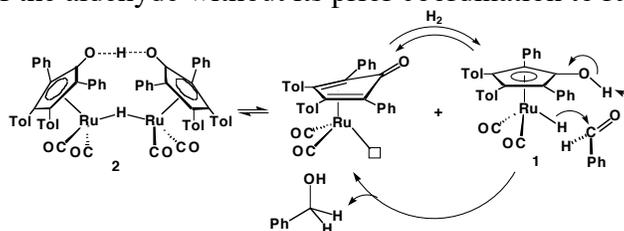
Mechanistic Studies at the Interface Between Organometallic Chemistry and Homogeneous Catalysis

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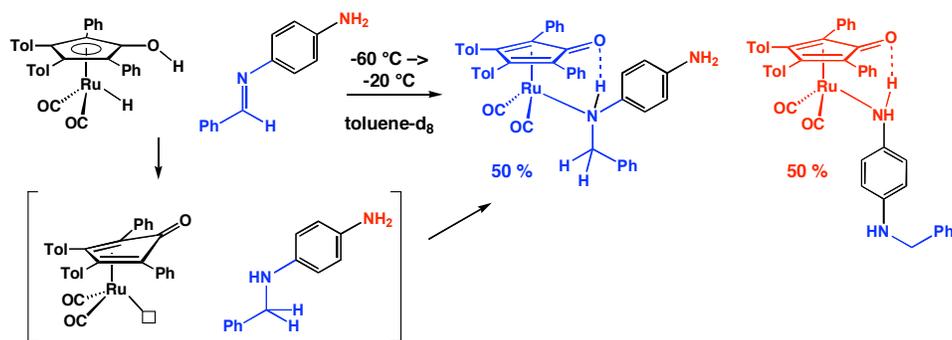
Graduate Students: Susie C. Martins, Jeffrey B. Johnson, Galina Bikzhanova, Sharon Beetner,
 Undergraduate Student: David Priebe

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.

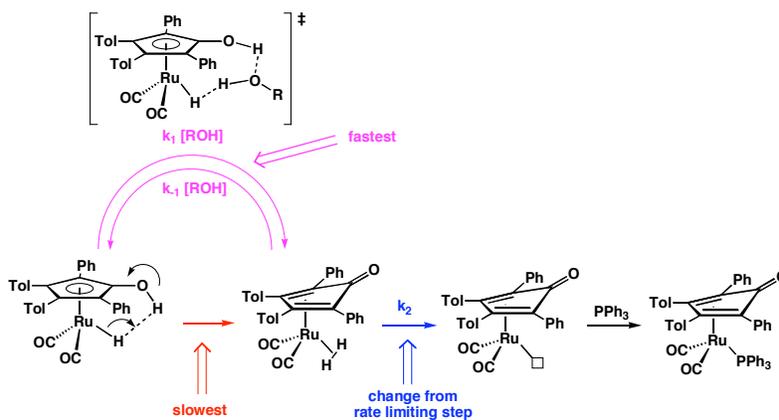
Recent Progress with $(\text{C}_5\text{R}_4\text{OH})\text{Ru}(\text{CO})_2\text{H}$ Hydrogenation Catalysts. Youval Shvo described a remarkable catalytic system in which the key intermediate $(\text{C}_5\text{R}_4\text{OH})\text{Ru}(\text{CO})_2\text{H}$ has an electronically coupled acidic OH unit 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.

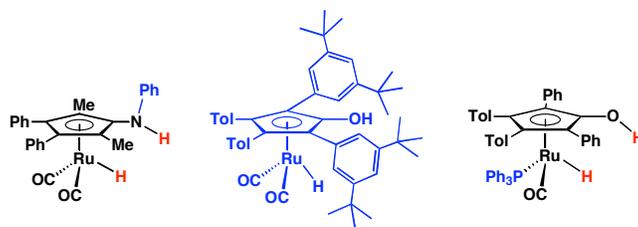


Another important step in the catalysis is the regeneration of **1** from reaction of H_2 with the diruthenium complex **2**. Preliminary studies of the microscopic reverse of this process (hydrogen evolution from **1** which occurs at 80 °C) in the presence of alcohol (the product of aldehyde hydrogenation) 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.



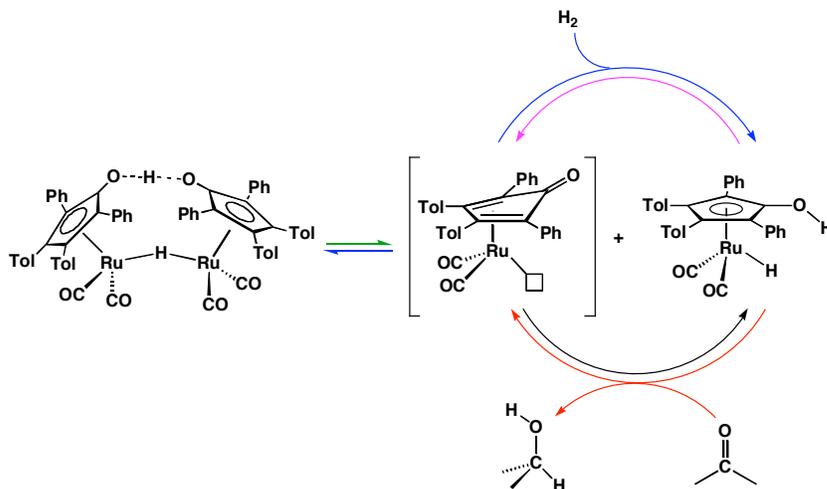
One key to developing more active catalysts is to destabilize the bridging hydride intermediate to prevent its formation or to speed its conversion to a reactive monohydride by reaction with H_2 . We have found three successful ways to sterically destabilize the bridging

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.



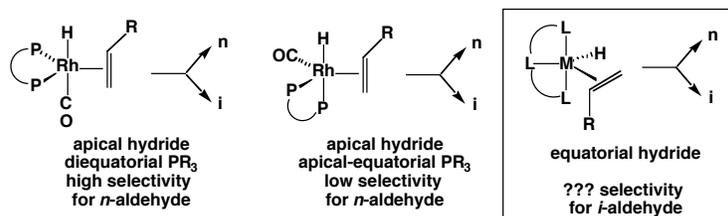
Future Plans

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 LiAlH_4 and NaBH_4 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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John R. Kitchin
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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.

Publications Sponsored by the DOE Grant (2003-2004):

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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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7. J.R. Kitchin, J.K. Norskov, M.A. Barteau and J.G. Chen, "Modification of the Surface Electronic and Chemical Properties of Pt(111) by Subsurface 3d Transition Metals", *Journal of Chemical Physics*, accepted.
8. N.A. Khan, M.B. Zellner and J.G. Chen, "Cyclohexene as a Probe for the Low-Temperature Hydrogenation Activity of Pt/Ni(111) Bimetallic Surfaces", *Surface Science*, accepted.
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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

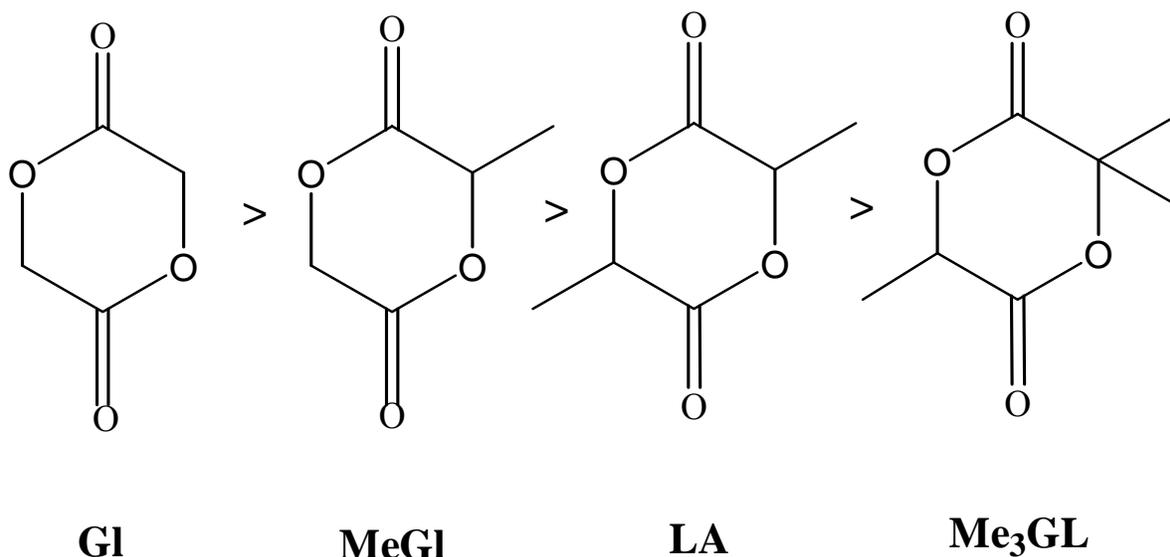
To develop environmentally benign routes to polyoxygenates such as polyesters and polycarbonates by the ring-opening polymerization of cyclic esters derived from renewable resources and the copolymerization of epoxides/oxiranes and carbon dioxide to replace condensation polymerizations involving phosgene.

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.

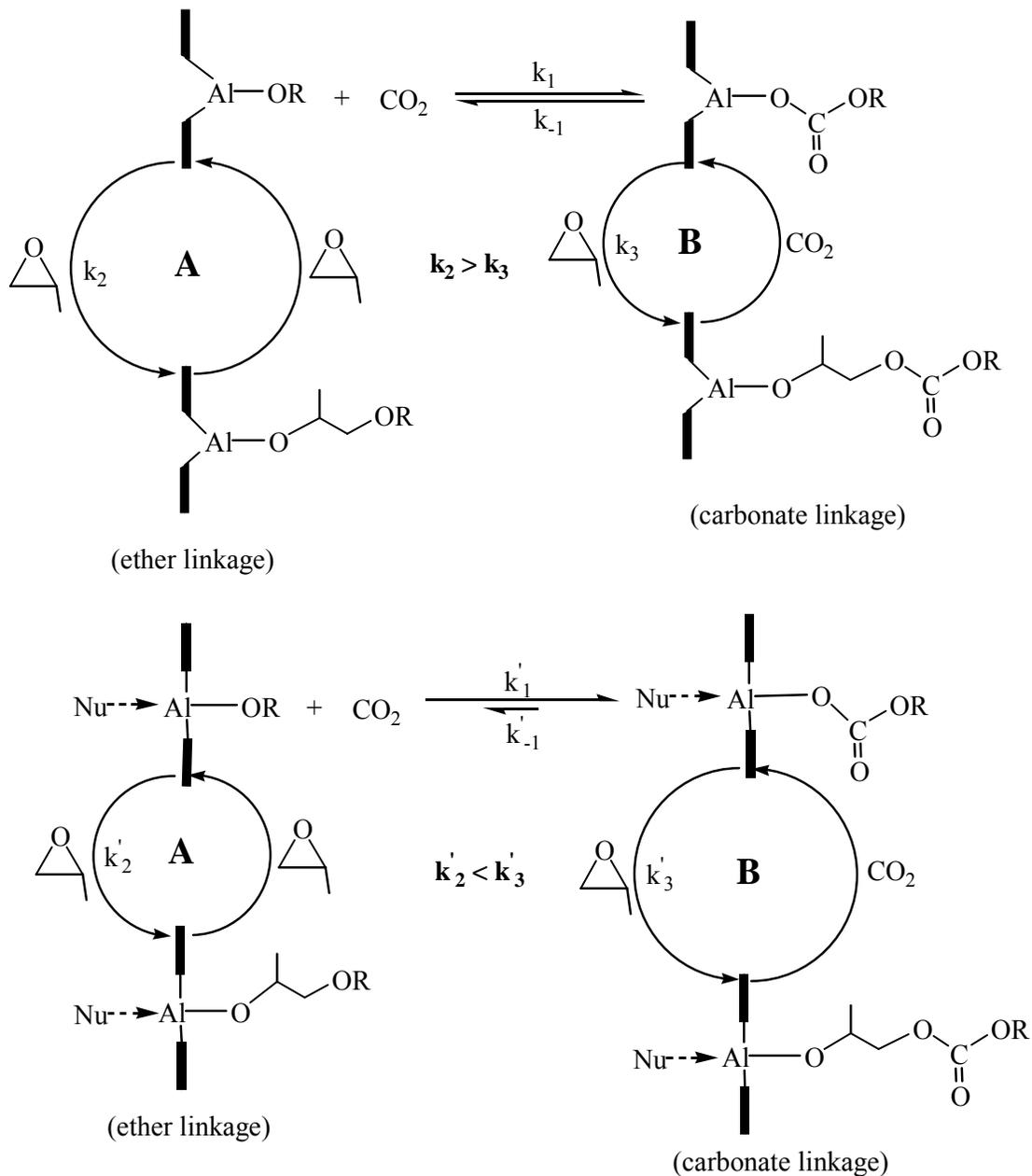
A new series of calcium initiators has been prepared.⁵ The use of the β -diiminate ligand is inappropriate as ligand scrambling can occur to give CaL_2 complexes and loss of single-site control. The use of the bulky *tris*-pyrazolyl borate with ^tBu substituents, $HB(pz^{Bu^t})_3$ prevents this and in 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.

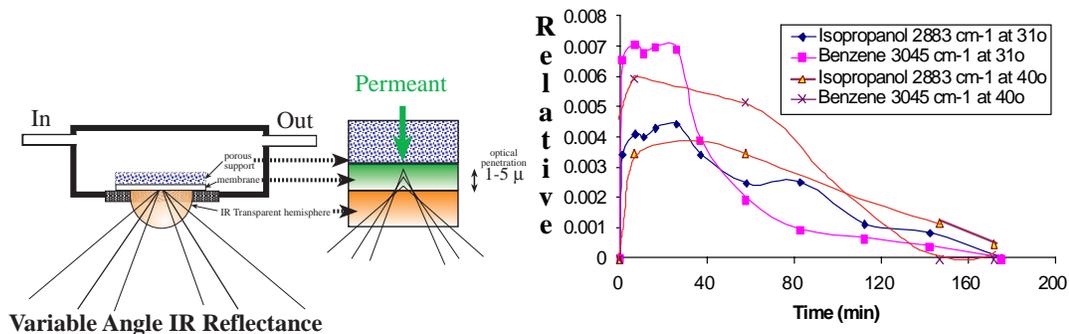


Figure 1 (left): Schematic of variable angle ATR optical path (left) wherein a zeolite membrane is pressed against a ZnSe hemispherical crystal. A pulse of sorbing gas mixture is introduced into the He stream and the composition within the membrane is monitored at different depths by varying the angle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

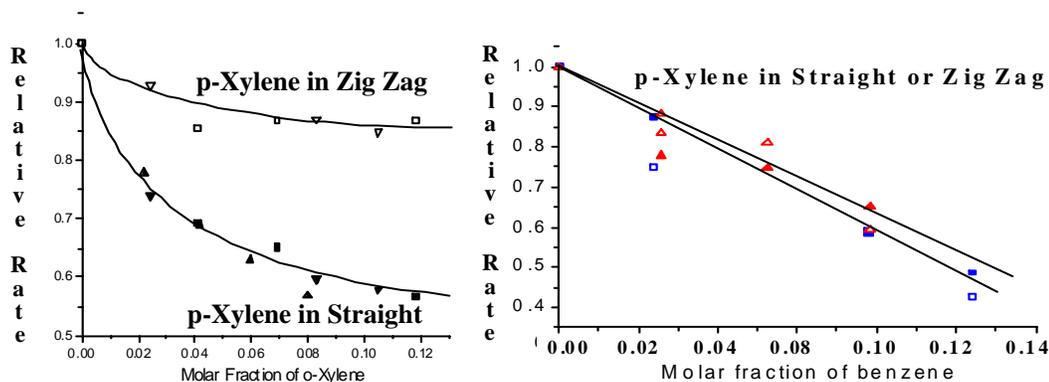


Figure 3 shows that *o*-Xylene has a different effect than Benzene on the two *p*-Xylene diffusion processes, shown on the left. *o*-Xylene impedes the diffusion of *p*-Xylene in the straight channels much more than the diffusion of *p*-Xylene in sinusoidal channels. On the other hand Benzene impedes 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

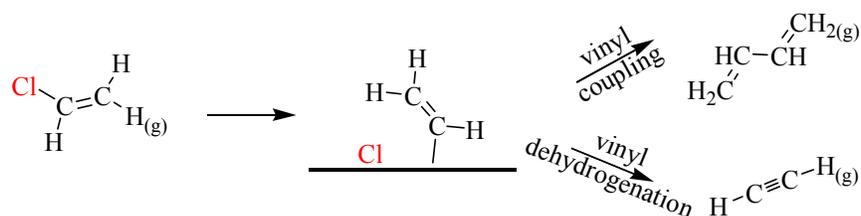
Develop a fundamental understanding of the factors controlling the selectivity of alkane dehydrogenation reactions over metal oxides surfaces.

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

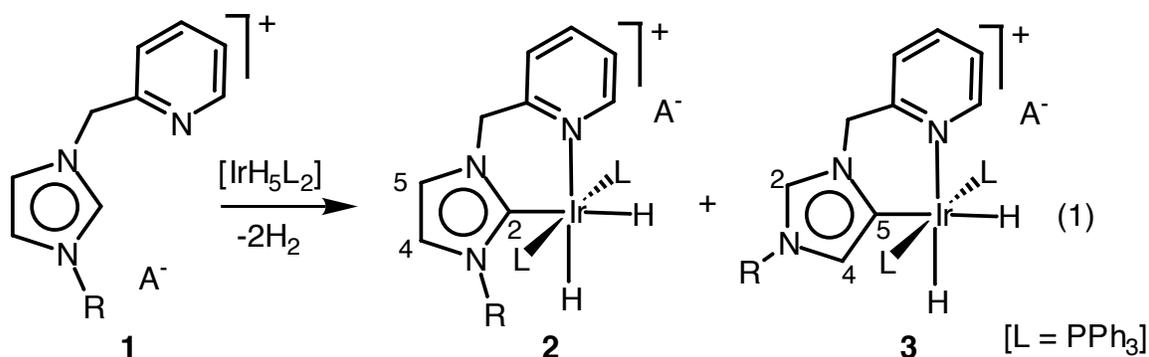
Rising interest in NHCs is suggested by the sharply increasing number of documents found by *Web of Science* under 'NHC or imidazol-2-ylidene': 1998, 17; 1999, 38; 2000, 42; 2001, 55; 2002, 61; 2003, 92. This may be associated with the useful properties often found for such catalysts: air stability, 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

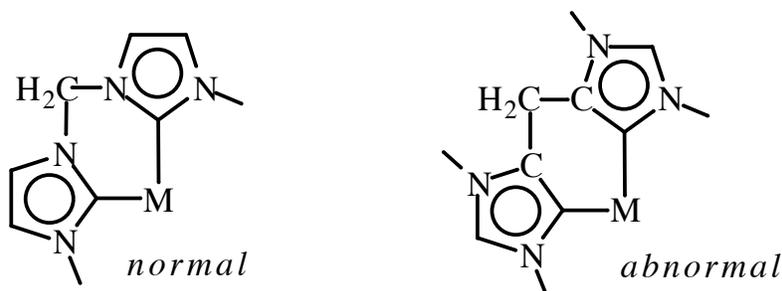
These new catalysts appear to be much more stable to air and thermally than traditional phosphine-stabilized ones and are not easily poisoned by substrate impurities. This could make homogeneous catalysis easier to apply and hence more accessible to a wider user group. NHCs, specially abnormal NHCs have 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.

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

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- Graduate Research Assistants: Tom Klinckman; Yong Zhao; K. A. Pittard
- Undergraduate Research Assistants: M. Danielle Temple; Tom Grimes; Alondra A. Flores

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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

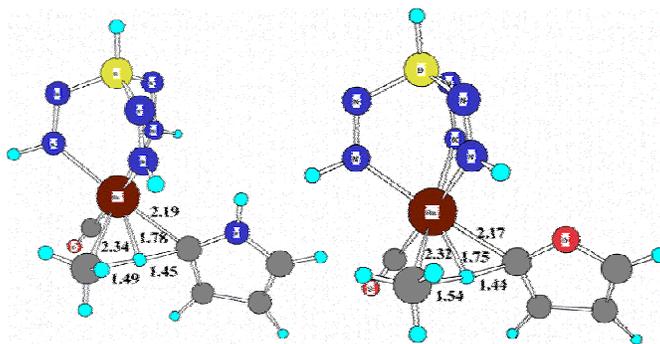


Figure 1. Calculated geometries for C-H activation of furan and pyrrole indicate σ -metathesis transition states.

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.

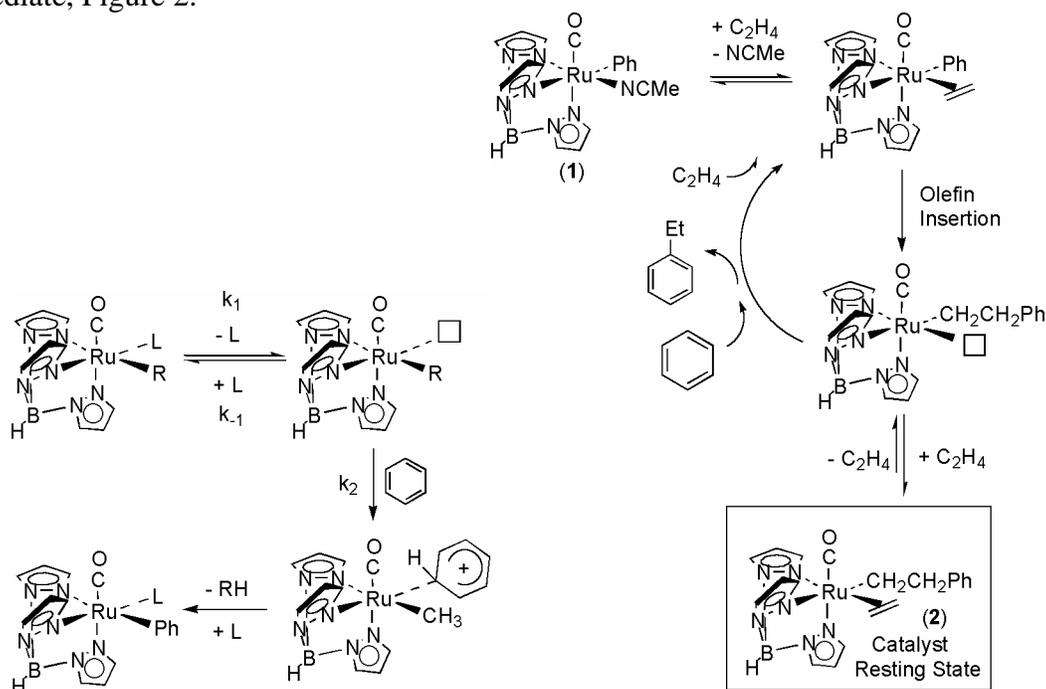


Figure 2. Catalytic cycle for Addition of Arene C-H Bonds to Olefins.

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,

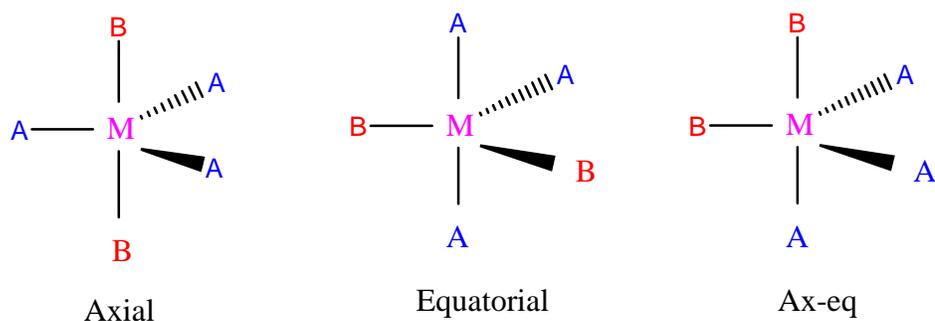


Figure 3. Possible coordination isomers for a trigonal bipyramidal MA_3B_2 complex.

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 $Pd(\text{bulky aryl})_2(\text{biaryl})$ 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 Pd^0 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

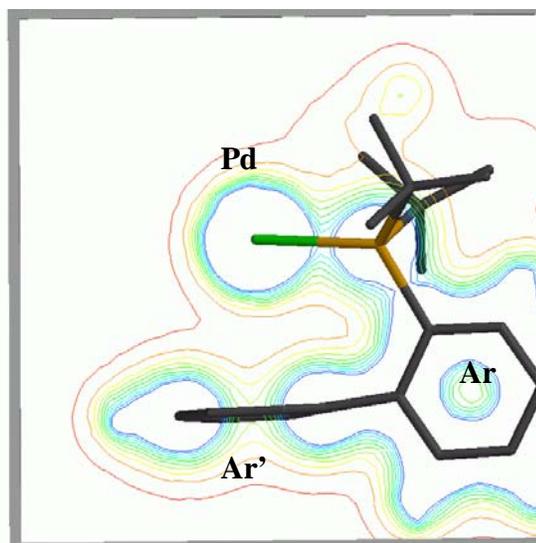


Figure 5. Pd- π -arene interactions in palladium-catalyzed C-C bond coupling.

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.
- R.J. Davis, "Basic Nanostructured Catalysts" in *Encyclopedia of Nanoscience and Nanotechnology*, Marcel Dekker, New York, in press.
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- J. Li and R.J. Davis, "On the Use of 1-Butene Double Bond Isomerization as a Probe Reaction for Cesium-loaded Zeolite X," *Appl. Catal. A.* **239** (2003) 59-70.

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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.
- 5) L. Chen and M. W. Deem, "Strategies for High-Throughput, Templated Zeolite Synthesis," *Mol. Phys.* **100** (2002) 2175-2181.
- 6) M. G. Wu and M. W. Deem, "Monte Carlo Study of the Nucleation Process during Zeolite Synthesis," *J. Chem. Phys.* **116** (2002) 2125-2137.
- 7) M. G. Wu, M. W. Deem, S. A. Elomari, R. C. Medrud, S. I. Zones, T. Maesen, C. Kibby, C.-Y. Chen, and I. Y. Chan, "Synthesis and Structure Determination by ZEFSAII of SSZ-55: A New High-Silica, Large-Pore Zeolite," *J. Phys. Chem. B* **106** (2002) 264-270.

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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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- Titanium Containing Cyclopentadienyl and Aryloxy Ancillary Ligation, *Organometallics*, 2004, 23, xxxx-xxxx.
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 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 siled TS-1 using a solution of tetraethyl orthosilicate in toluene under refluxing conditions. Since the silation coating is thin, we were not able to measure the surface Ti content, but the siled 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, unsilated 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

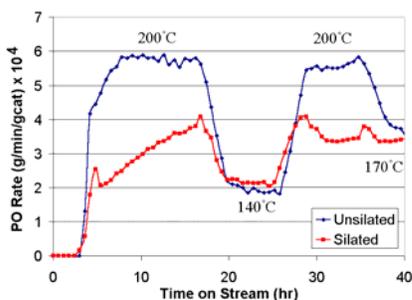


Figure 1: Steady state kinetics for a siled and unsilated catalyst showing the difference in activation behavior.

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.

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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

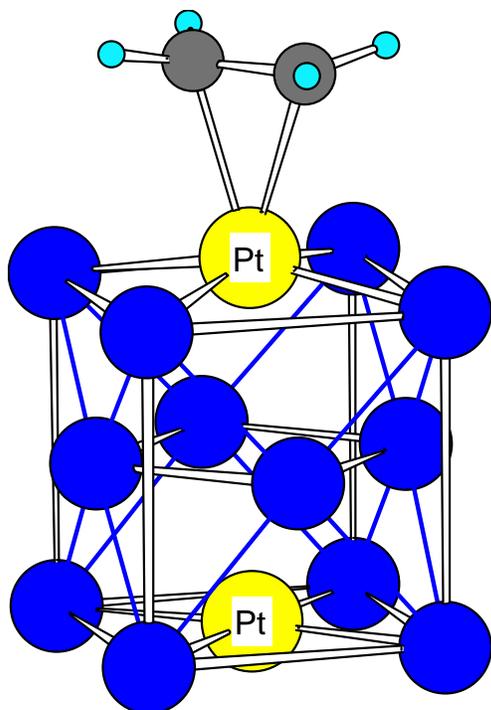


Figure 1. Optimized structure of ethylene adsorbed on a Cu₁₂Pt₂(100) cluster of D_{4h} symmetry.

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. $[\text{Ni}(\text{Et}_2\text{PCH}_2\text{NMeCH}_2\text{PEt}_2)_2]^{2+}$: **A Functional Model for Hydrogenases.** The complex $[\text{Ni}(\text{PNP})_2](\text{BF}_4)_2$ (where $\text{Et}_2\text{PCH}_2\text{N}(\text{Me})\text{CH}_2\text{PEt}_2$ is PNP) is a catalyst for hydrogen oxidation that incorporates both hydride and proton acceptor sites in a single metal complex. Comparison of $[\text{Ni}(\text{PNP})_2](\text{BF}_4)_2$, $\text{Ni}(\text{PNP})_2$, and $[\text{HNi}(\text{PNP})_2](\text{PF}_6)$ 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 $[\text{Ni}(\text{PNP})_2](\text{BF}_4)_2$ 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 ($\text{p}K_a = 10.6$). The NH and NiH protons of this product, $[\text{HNi}(\text{PNP})(\text{PNHP})]^{2+}$, 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 $[\text{HNi}(\text{PNP})_2]^+$ compared to $[\text{HNi}(\text{depp})_2]^+$ 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 $[\text{HW}(\text{CO})_4\text{L}]^-$ Complexes (where $\text{L} = \text{CO}$, PR_3 or $\text{P}(\text{OR})_3$) and Their Reactions with $[\text{C}_5\text{Me}_5\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]^+$.

The hydride-donor abilities of $[\text{HW}(\text{CO})_5]^-$, *cis*- $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$, and *cis*- $[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ (36-40 kcal/mol) were measured in acetonitrile, and the reactions of these complexes with $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]^+$ were studied. The *cis*- $[\text{HW}(\text{CO})_4(\text{L})]^-$ are some of the most powerful hydride donors reported to date for transition-metal hydrides, but it is interesting to note that the neutral $\text{HRh}(\text{dppb})_2$ 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 $[\text{HM}(\text{PNP})_2]^+$ ($\text{M} = \text{Ni}$, Pd , Pt ; $\text{PNP} = \text{Et}_2\text{PCH}_2\text{N}(\text{Me})\text{CH}_2\text{PEt}_2$). The complexes $\text{M}(\text{PNP})_2^{2+}$ ($\text{M} = \text{Pd}$, Pt , Ni and $\text{PNP} = \text{Et}_2\text{PCH}_2\text{N}(\text{Me})\text{CH}_2\text{PEt}_2$) were synthesized, and their thermodynamic properties were determined in acetonitrile. The ΔG_{H^-} values for $[\text{HPt}(\text{PNP})_2]^+$, $[\text{HPd}(\text{PNP})_2]^+$, and $[\text{HNi}(\text{PNP})_2]^+$ are 54.7, 53.8, and 66.7 kcal/mol, respectively. The $\text{p}K_{\text{a}}$ values of $[\text{HPt}(\text{PNP})_2]^+$, $[\text{HPd}(\text{PNP})_2]^+$, and $[\text{HNi}(\text{PNP})_2]^+$ 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 , $\text{C}_5\text{H}_5\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$, and $\text{C}_5\text{Me}_5\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ 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^+ , $\text{NADPH}/\text{NADP}^+$, and FADH/FAD^+ are involved. Similarly, the kinetic hydricities of a series of $\text{CpM}(\text{CO})_2(\text{L})\text{H}$ and $\text{Cp}^*\text{M}(\text{CO})_2(\text{L})\text{H}$ complexes (where $\text{M} = \text{Mo}$ 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 $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ 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 $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$ 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 $[\text{HM}(\text{diphosphine})_2]^+$ complexes ($\text{M} = \text{Ni}$, Pd , Pt), $[\text{HW}(\text{L})(\text{CO})_4]^-$ complexes, transition-metal formyl complexes, NADH derivatives, $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$, and $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{H}$ 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 $[\text{Pd}(\text{diphosphine})_2](\text{BF}_4)_2$ and $\text{Pd}(\text{diphosphine})_2$ 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 $[\text{Pd}(\text{diphosphine})_2](\text{BF}_4)_2$

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:



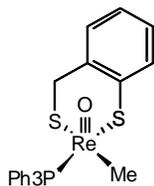
The rate equations for catalysts **1** and **2** are:

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

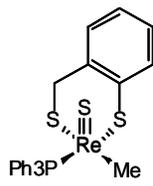
$$-\frac{d[\text{PyO}]}{dt} = k_{2a} \times [\mathbf{2}] \cdot [\text{PyO}]^{1/2} \quad (\Rightarrow \text{a chain mechanism})$$

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

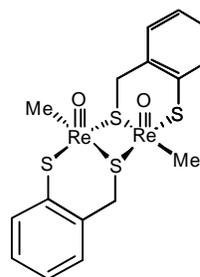
$$\frac{d[\text{RSR}']}{dt} = \left\{ \frac{k_0 + k_1 \cdot K \cdot [\text{PAR}_3]}{1 + K \cdot [\text{PAR}_3]} \right\} \times K_{3P} \cdot [\text{MeS(O)Ph}] \cdot [\mathbf{3}]_{T,t} \quad (\Rightarrow \text{parallel nucleophilic pathways})$$



MeReO(mtp)(PPh₃) **1**



MeReS(mtp)(PPh₃) **2**

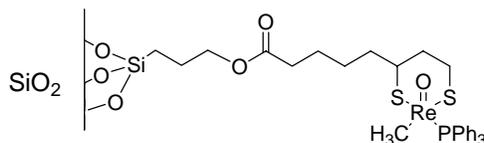


{MeReO(mtp)}₂ **3**

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

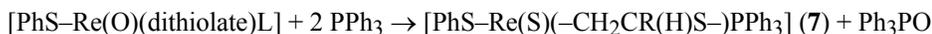
Dirhenium heptoxide, Re_2O_7 , can be used to prepare compounds that are similar to **1** and **3**, above, save that PhS-Re replaces Me-Re . Compounds already characterized crystallographically include the following:



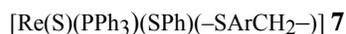
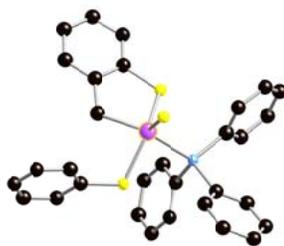
Others, including $[\text{PhS-Re(O)(mtp)(PPh}_3)]$, have been detected by NMR and electronic spectroscopy, and are still being characterized. This transformation will be studied, and compared with the Me-Re case.



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



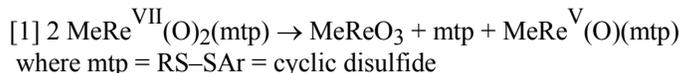
It is the first rhenium(V) compound of this series with a C–Re bond not arising from a methyl group coordinated to rhenium. Moreover, the chemistry by which it was realized will be investigated.



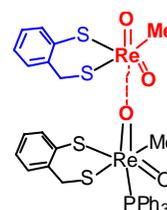
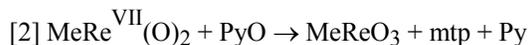
This is a remarkable transformation: a new Re–C bond has been created; a six-membered ring has been converted to a five-membered ring, a thiolate sulfur is now a thio-rhenium group, and the oxo group is now a phosphine oxide. Its mechanism will be studied by kinetics and other methods. The product has 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

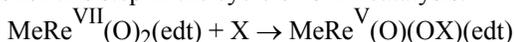
The dimer {MeRe(O)(mtp)}₂, **3**, is 150-fold more reactive as an OAT catalyst than the phosphine monomer **1**. We attribute the enhanced reactivity to the need for **1** to cycle repeatedly though a step entailing loss of the strongly coordinated PPh₃ ligand. Thus we reasoned that MeReO(mtp)Py, with 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.



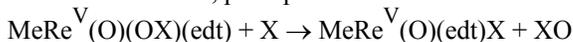
with this net result:



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.

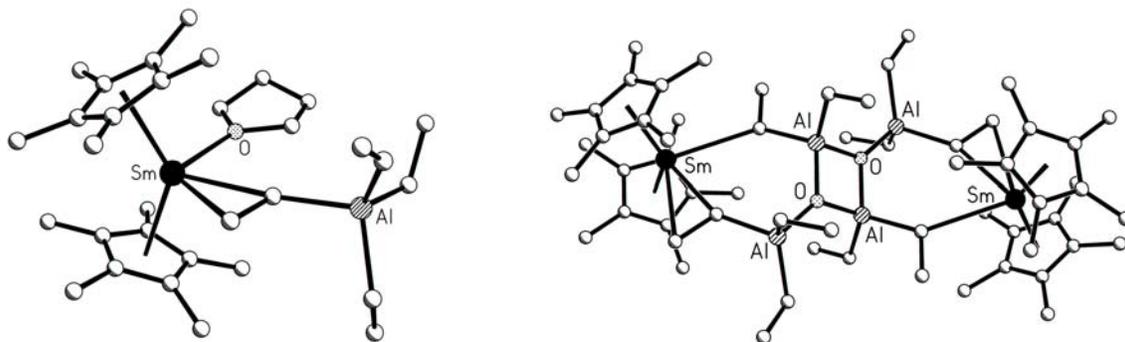
We have synthesized fully characterized lanthanide carboxylates and examined their sequential reaction chemistry with Et_2AlCl and Al^iBu_3 . These well-defined precursors generate catalytically active species that polymerize isoprene to high cis-1,4-polymer. The lanthanide carboxylate/ Et_2AlCl reaction 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 $[(C_5Me_5)_2Sm(O_2CPh)]_2$.



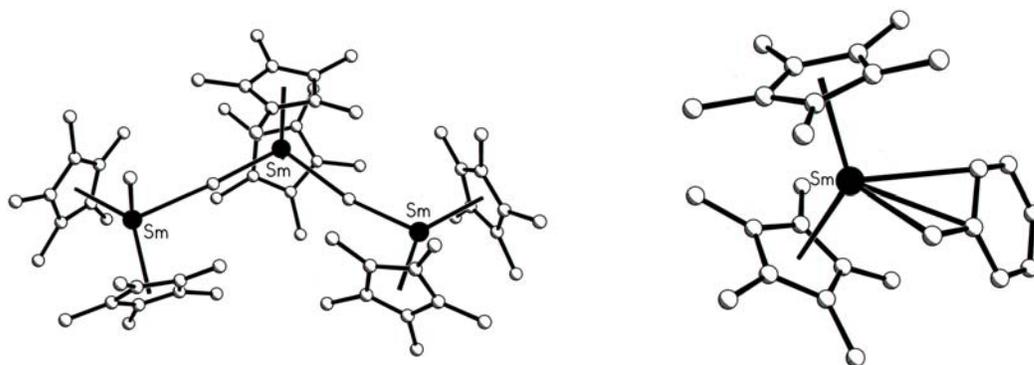
In each of these complexes, the ethylaluminum variation is providing extra coordination via side-on bonding in a coordination mode not identically available with Me and iBu analogs. Such a weak interaction could explain how the bimetallic ethyl-containing Al/Nd complexes isolated in the metal carboxylate/ 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.

DOE Funded Research Published Under This Grant

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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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Studies Relevant to Catalytic Activation of Small Molecules

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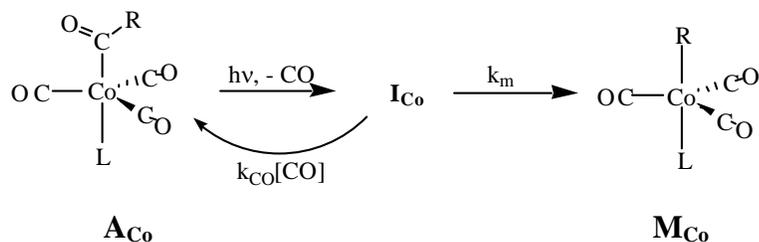
Goal

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

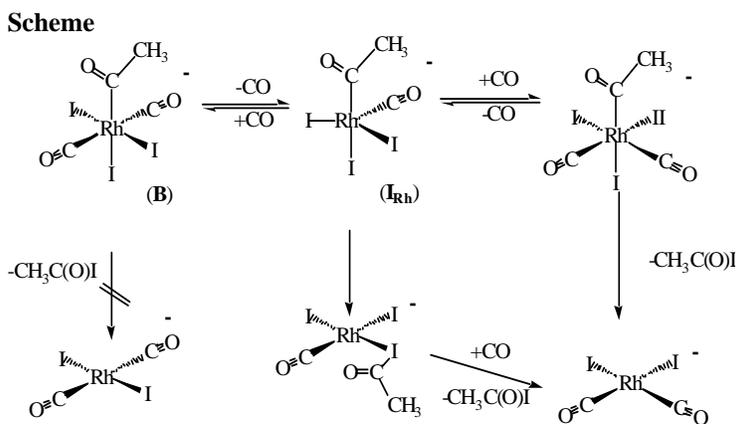
of reactive intermediates generated by flash photolysis of $\text{RC(O)Co(CO)}_3\text{L}$ ($\text{R} = \text{CH}_3, \text{CD}_3, \text{ or Et}$; $\text{L} = \text{PPh}_3 \text{ or P}^n\text{Bu}_3$) in several solvents.

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.

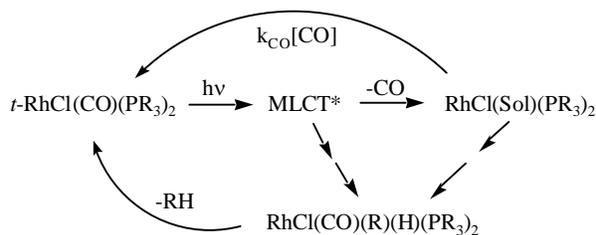
Visiting researcher Verena Mertens (U. Münster) carried out a similar investigation for the analogous reactions of $\text{Mn(CO)}_4(\text{C(O)R})$ intermediates (**I_{Mn}**) generated from flash photolysis of the manganese pentacarbonyl models $\text{Mn(CO)}_5(\text{C(O)R})$ ($\text{R} = \text{CH}_3 \text{ or CD}_3$) (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

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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.

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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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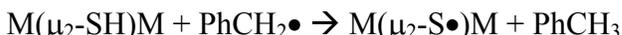
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Goal

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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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.

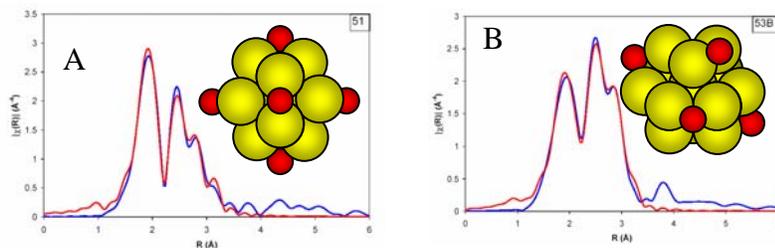


Figure 1. Icosahedral (top) and cuboctahedral (bottom) models of atomic packing in $\text{Au}_{13}[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_6$. Shown also are EXAFS data and FEFF fits for the sample A (with band gap) and B (without the band gap) that were best fit by using the 13-atom icosahedral and cuboctahedral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

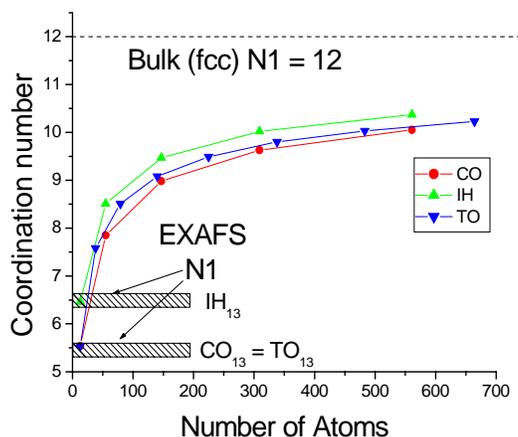


Figure 2. Simulated sequences of the first nearest neighbor Au-Au coordination numbers as functions of “magic numbers” corresponding to the cuboctahedral (CO), icosahedral (IH) and truncated octahedral (TO) models. Small particles show dramatic difference in

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.

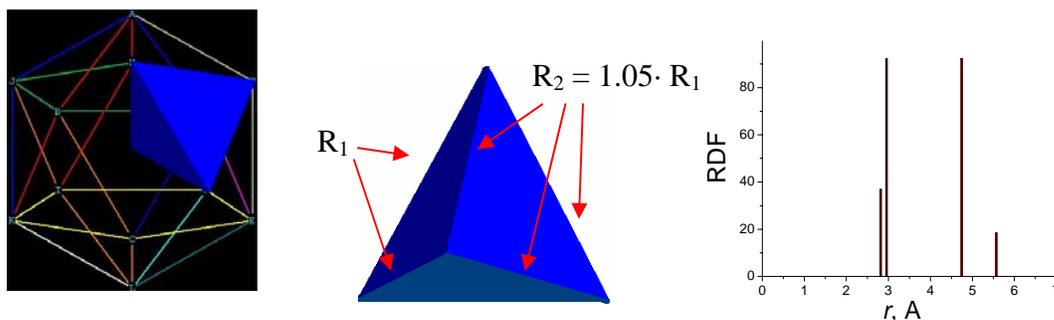


Figure 3. Schematic of the icosahedron that is made of 20 face sharing pyramids. Each pyramid is symmetrically distorted so that the distances R_2 are ca. 5% longer than R_1 . The plot in the right is the calculated radial distribution function for the icosahedral structure that demonstrates two subshells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

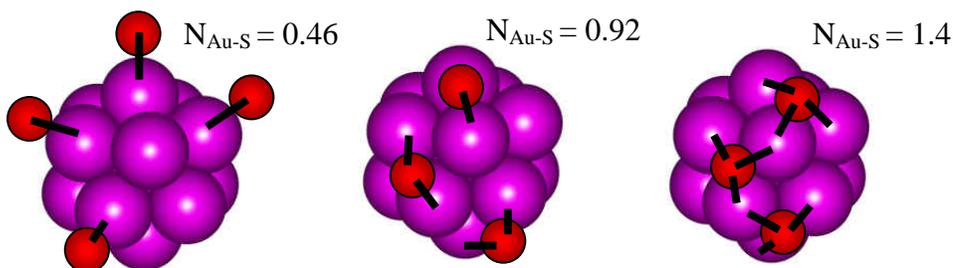


Figure 4. Different models for Au-S bonding geometry.

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

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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 MoO₃ and TiO₂ nanostructures; and, (2) reactive studies of NO_x and possible intermediates in hydrocarbon-assisted NO_x reduction on oxide thin-films grown on 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 MoO₃ and TiO₂ using the Au(111)-“herringbone” surface as a template (Figures 1). We have completed detailed studies of the MoO₃ nanostructures, thus far. Detailed investigations of the TiO₂ are currently underway.

The MoO₃ nanostructures are crystalline and one layer high as determined using both scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Furthermore, the MoO₃ forms a c(4x2) superlattice on the Au and lifts the herringbone reconstruction of the Au under the oxide nanocrystals. The Mo is ~94% Mo⁶⁺, 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 MoO₃ to a 1:1 mixture of Mo⁶⁺: Mo⁵⁺ with no other oxidation states detected in XPS. Shear planes develop in order to accommodate the Mo⁵⁺. We are currently in the process of studying the chemical behavior of these materials.



Figure 1: STM image of MoO₃ nanostructures grown on 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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‡Supported by DOE

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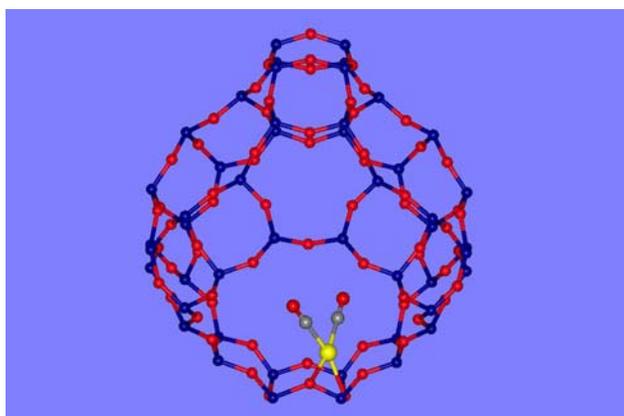
SPECTROSCOPY, THEORY, AND IMAGING OF NANOCATALYSTS ON CRYSTALLINE SUPPORTS: REPRESENTATION OF METAL-SUPPORT-ADSORBATE COMBINATIONS AS MOLECULAR ANALOGUES

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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:

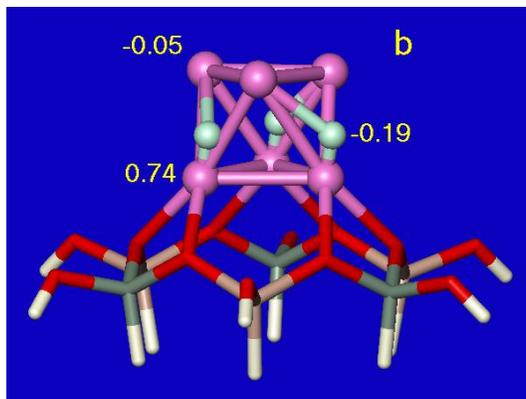


We characterized the complex by IR and EXAFS spectroscopies and density functional theory, with the results being in good agreement with each other and demonstrating the strong chemical bonding between the Rh atom and oxygen atoms of the support surface. The data identify crystallographically specific 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,



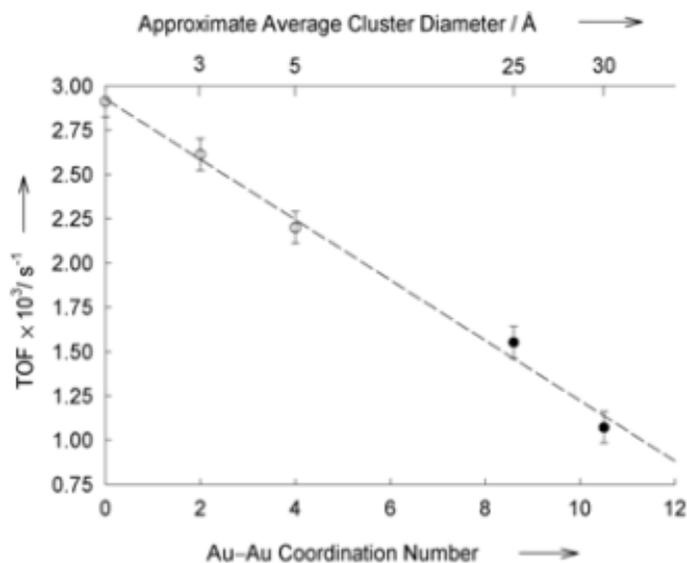
shows that the Rh atoms at the interface with the support are positively charged (with about +0.74 electronic charge per atom, although the Rh atoms farther removed from the support bear hardly any charge), which explains the metal–oxygen distance (the theoretical and experimental values agree, being 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.

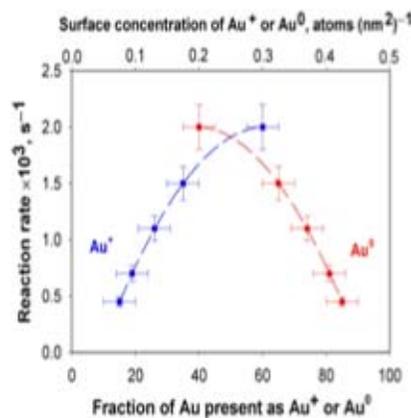
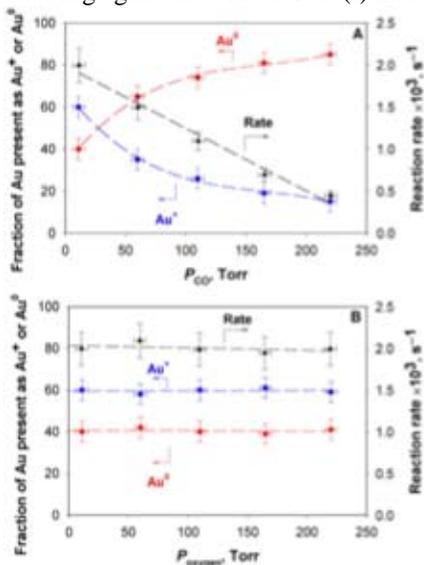
There has been a high level of excitement generated by recent discoveries of high activities of highly dispersed supported gold catalysts for reactions such as CO oxidation. We have emphasized work on these catalysts in our DOE project and plan more gold work in the proposed continuation. Most interpretations 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.



PUBLICATIONS (2002-PRESENT) FROM DOE PROJECT:

1. "Synthesis and Structure of Tetrairidium Clusters on TiO₂ Powder: Characterization by Infrared and Extended X-ray Absorption Fine Structure Spectroscopies," J. F. Goellner, J. Guzman, B. C. Gates, *J. Phys. Chem. B*, **106**, 1229 (2002).
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3. "Imaging of Nearly Uniform Os₅C Clusters Dispersed on MgO Powder," L. F. Allard, G. A. Panjabi, S. N. Salvi, B. C. Gates, *Nano Lett.*, **2**, 381 (2002).
4. "Simultaneous Presence of Cationic and Reduced Gold in Functioning MgO-Supported CO Oxidation Catalysts: Evidence from X-Ray Absorption Spectroscopy," J. Guzman and B. C. Gates, *J. Phys. Chem. B*, **106**, 7659 (2002).
5. "Nanoclusters in Nanocages: Platinum Clusters and Platinum Complexes in Zeolite LTL Probed by ¹²⁹Xe NMR Spectroscopy," B. A. Enderle, A. Labouriau, K. C. Ott, B. C. Gates, *Nano Lett.*, **2**, 1269 (2002).
6. "Structure and Reactivity of a Mononuclear Gold Complex Catalyst Supported on Magnesium Oxide," J. Guzman and B. C. Gates, *Angew. Chem. Int. Ed.*, **42**, 690 (2003).
7. "Oxidation States of Gold in MgO-Supported Complexes and Clusters: Characterization by X-ray Absorption Spectroscopy and Temperature Programmed Oxidation and Reduction," J. L. Guzman and B. C. Gates, *J. Phys. Chem. B*, **107**, 2242 (2003).
8. "Oxidation of Supported Rhodium Clusters by Support Hydroxyl Groups," G. N. Vayssilov, B. C. Gates, N. Rösch, *Angew. Chem. Int. Ed.*, **42**, 1391 (2003).
9. "Reaction of Au(CH₃)₂(acac) on γ -Al₂O₃: Characterization of the Surface Organic, Organometallic, Metal Oxide, and Metallic Species," J. Guzman and B. C. Gates, *Langmuir*, **19**, 3897 (2003).
10. "Alkene Hydrogenation Catalyzed by Rhenium Carbonyls Bonded to Highly Dealuminated Y Zeolite: Spectroscopic Characterization of the Working Catalyst," B. Enderle and B. C. Gates, *J. Mol. Catal. A Chem.*, **204**, 473 (2003).
11. "Supported Molecular Catalysts: Metal Complexes and Clusters on Oxides and Zeolites," J. L. Guzman and B. C. Gates, *J. Chem. Soc. Dalton Trans.*, **2003**, 3303. [Dalton Perspective]
12. "Synthesis and Structural Characterization of Iridium Clusters formed Inside and Outside the Pores of Zeolite NaY," F. Li and B. C. Gates, *J. Phys. Chem. B*, **107**, 11589 (2003).
13. "A rhenium carbonyl bonded to highly dealuminated zeolite Y: structure determination by infrared and X-ray absorption spectroscopies," B. Enderle and B. C. Gates, *Phys. Chem. Chem. Phys.*, in press (on web) 2004.
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Carbon-Hydrogen Bond Functionalization Catalyzed by Transition Metal Systems

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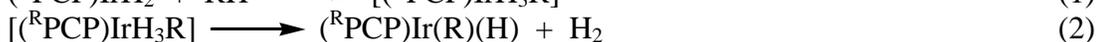
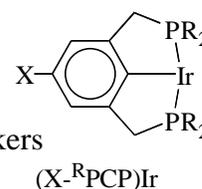
Goal

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

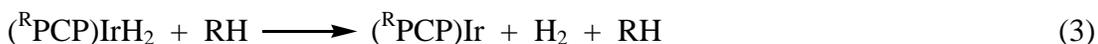
Recent work has focused on two major areas: (i) the dehydrogenation of alkanes and alkyl groups, including an elucidation of mechanism, the development of improved catalysts, and efforts to expand applications beyond alkanes; (ii) development of a fundamental understanding of the factors that govern 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)

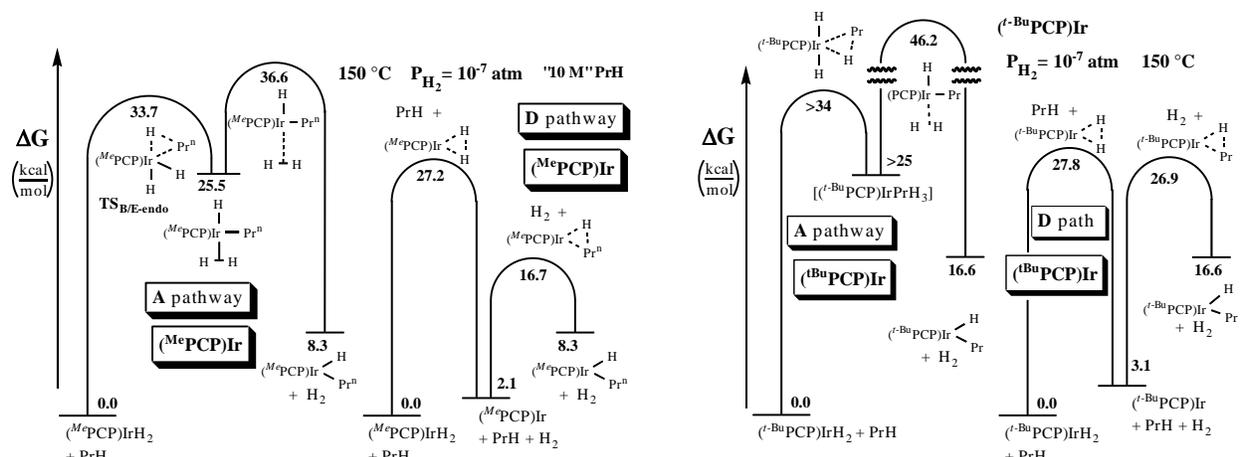
An alternative pathway (eqs 3-4), an Ir(I) mechanism, involves H₂ loss prior to C-H addition. Clearly these pathways are different at the most fundamental level; therefore distinguishing which one (or ones) is operative is critical to catalyst design.



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 TΔS 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.

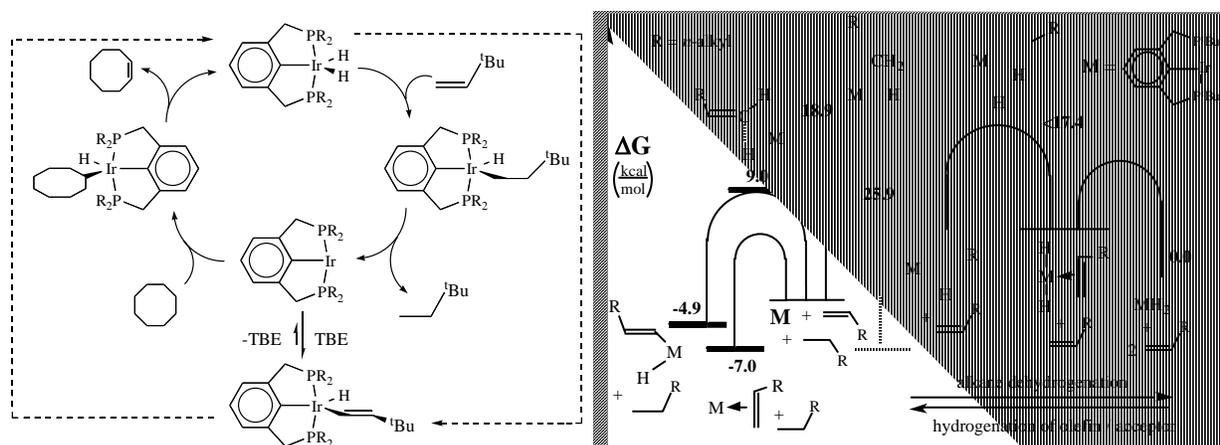
The Ir(V) (**A**) pathway requires a very unfavorable C-H addition (eq 1). This uphill step must be followed by loss of H₂, which is also endothermic. The entropic “payback” is only realized after this full “free-energy-price” is paid in the course of the **A** pathway (Scheme 1). In contrast, the **D** path involves initial loss of H₂, 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 (^RPCP)Ir, occurs with a lower barrier than the back reaction of H₂ under the reaction conditions. Accordingly calculations with the truncated ^{Me}PCP ligand reveal a significantly lower overall barrier for the **D** path (27.2 vs. 36.6 kcal/mol). When the full ^{tBu}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 (^{tBu}PCP)IrH₂ undergoes facile H/D exchange with C₆D₆, and slow exchange with *n*-octane, no H/D exchange is observed with C₆D₁₂ 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 $R-H = \text{propane}$, 150 °C, $P(\text{H}_2) = 10^{-7} \text{ atm}$ and 10 mol/L alkane for the reaction of alkane with (^{Me}PCP)IrH₂ (left) and (^{t-Bu}PCP)IrH₂ (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.

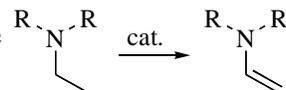


Scheme 2. Mechanism of COA/TBE transfer-dehydrogenation cycle (left); free-energy profile for *n*-alkane/ α -olefin couple (right), experimentally extrapolated from COA/TBE profile.

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).

2-year Publications (June 2002 - present)

1. "On the Mechanism of (PCP)Ir-catalyzed Acceptorless Dehydrogenation of Alkanes: a Combined Computational and Experimental Study " K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. Achord, and A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 11404-11416.
2. "Computational and Experimental Studies of the Mechanism of (PCP)Ir-catalyzed Acceptorless Dehydrogenation of Alkanes" K. Krogh-Jespersen, M. Czerw, and A. S. Goldman, *J. Mol. Cat., A*, **2002**, *189*, 95–110 (Special issue on Selective C-H Bond Functionalization).
3. "DFT Calculations on the Mechanism of (PCP)Ir-catalyzed Acceptorless Dehydrogenation of Alkanes: Realistic Computational Models and Free Energy Considerations" Krogh-Jespersen, K., Czerw, M. and Goldman, A. S in *ACS Symposium Series: Activation and Functionalization of C-H Bonds*; K. I. Goldberg and A. S. Goldman, Eds. 2004; Vol. 885; in press.
4. "The Mechanism of Alkane Transfer-Dehydrogenation Catalyzed by a Pincer-Ligated Iridium Complex" K. B. Renkema, Y. V. Kissin and A. S. Goldman, *J. Am. Chem. Soc.* **2003**, *125*, 7770 -7771.
5. "Alkane Transfer-Dehydrogenation Catalyzed by a Pincer-Ligated Iridium Complex" Goldman, A. S., Renkema, K. B., Czerw, M. and Krogh-Jespersen, K. in *ACS Symposium Series: Activation and Functionalization of C-H Bonds*; K. I. Goldberg and A. S. Goldman, Eds. 2004; Vol. 885; in press.
6. "Novel synthesis of enamines by iridium-catalyzed dehydrogenation of tertiary amines" X. Zhang, A. Fried, S. Knapp, and A. S. Goldman, *Chem. Comm.*, **2003**, (16), 2060-2061.
7. "Introduction of C-C double bonds into aliphatic polymers by Iridium-catalyzed Dehydrogenation" Ray, A.; Renkema, K. B.; Coates, G. W.; Goldman, A. S.; Zhu, K. *Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003* **2003**, INOR-445 and manuscript in preparation.
8. "What factors govern relative metal-carbon bond strengths and the thermodynamics of C-H addition?" Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. 223rd National Meeting of the American Chemical Society, Orlando, FL, 2002; INOR-352 AN 2002:189955; and manuscript in preparation.

9. "C-H Bond Activation by Transition Metals: An Introduction" Goldman, A. S., Goldberg, K. I. and Shilov, A. E. in *ACS Symposium Series: Activation and Functionalization of C-H Bonds*; K. I. Goldberg and A. S. Goldman, Eds. 2004; Vol. 885; in press.
10. "Distinct Thermodynamics for the Formation and Cleavage of N-H Bonds in Aniline and Ammonia. Directly-Observed Reductive Elimination of Ammonia from an Isolated Amido Hydride Complex" M. Kanzelberger, X. Zhang, T. J. Emge, A. S. Goldman, J. Zhao, C. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 13644-13645.
11. "Dehydrogenation - Homogeneous", *Encyclopedia of Catalysis*, John Wiley & Sons, **2002** <http://www.mrw.interscience.wiley.com/enccat/articles/eoc072/frame.html>
12. "Synthesis and Crystal Structure of a Coordinatively Unsaturated Organomercury Iridium Complex (PCP)Ir(HgPh)Cl (PCP = η^3 -2,6-(^tBu₂PCH₂)₂C₆H₃)" X. Zhang, T. J. Emge, A. S. Goldman, *J. Chem. Cryst.* **2003**, *33*, 613-617 (Special issue on Mercury Chemistry).

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Toward an Understanding of Catalysis by Supported Metal Nanoclusters

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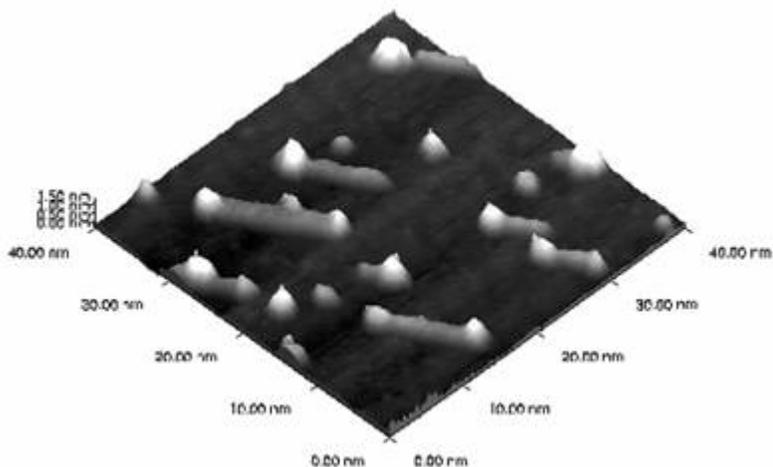
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Goal

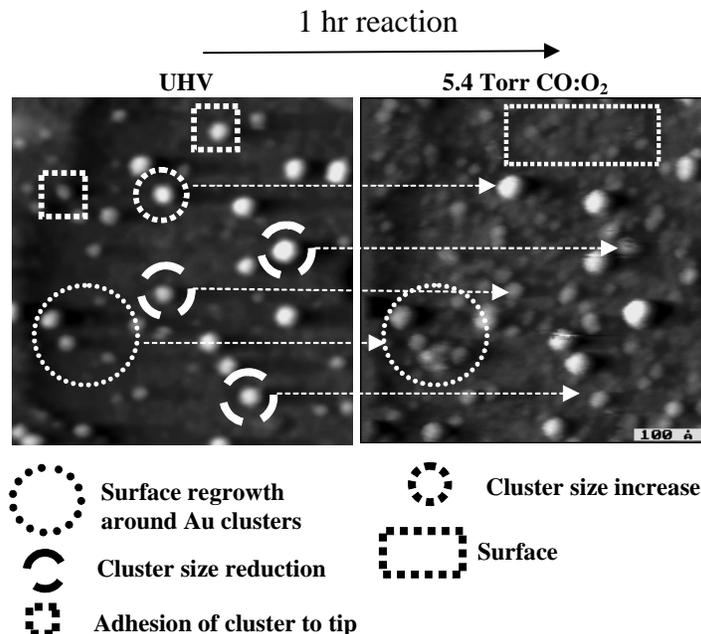
Develop an atomic-level understanding of catalysis by supported metal nanoclusters

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.

Publications Citing DOE/BES (2002-4)

1. "Characterization of C₂(C_x H_y) Intermediates from Adsorption and Decomposition of Methane on Supported Metal Catalysts by In-Situ Inelastic Neutron Scattering Vibrational Spectroscopy", C. Sivadinarayana, T. V. Choudhary, L. L. Daemen, J. Eckert and D. W. Goodman, *Angewandte Chemie*, 41, 144-146 (2002).
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12. "Characterization of MgO(100) Thin Film Growth on Mo(100)", Y. D. Kim, J. Stultz and D. W. Goodman, Surf. Sci., 506, 228-234, (2002).
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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.

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Joint NMR and Diffraction Studies of Catalyst Structure and Binding

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Goals

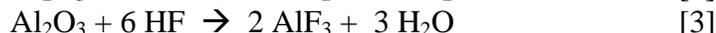
Research carried out under DOE support focuses on two areas. Our first goal is to develop and then use a combination of structural probes to characterize catalytic surfaces and how they change during the catalytic reaction. In the second project, we use novel NMR methods to characterize gas binding,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

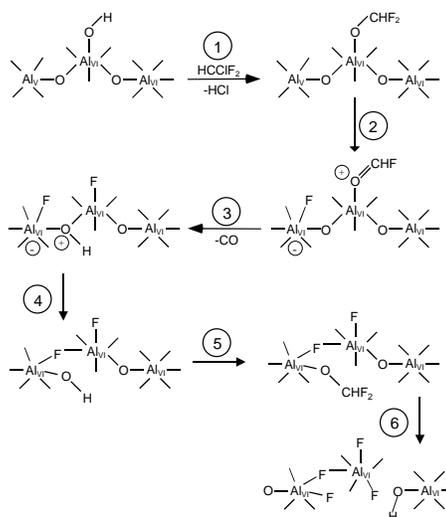
Study of the effect of the fluorinating agent on catalyst structure

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.

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Ruthenium Mediated C-H Activation and C-C Bond Formation Reactions

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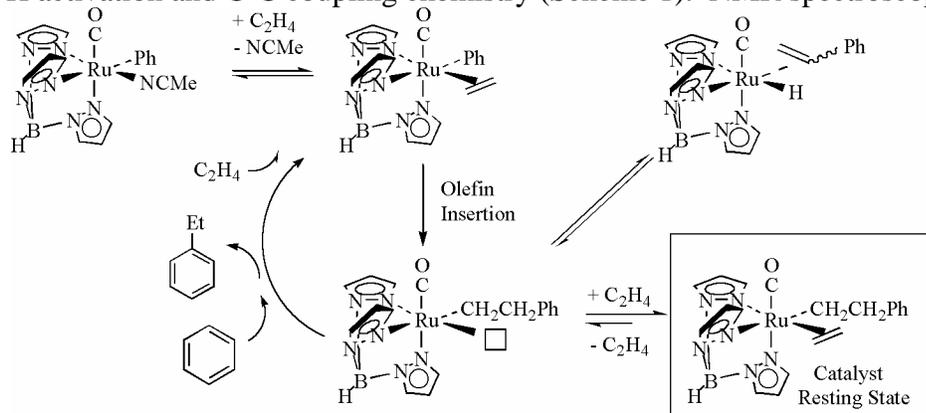
Goals

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.

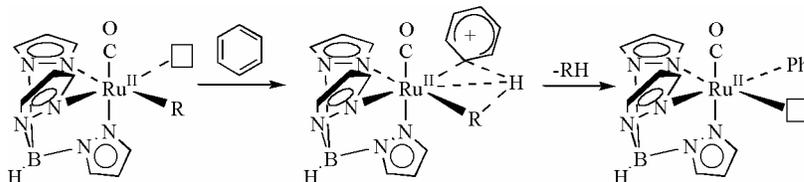
Mechanism of Hydrophenylation: The catalytic hydrophenylation reactions do not proceed via a traditional Friedel-Crafts mechanism. Rather, the Ru(II) metal center serves to mediate C-H activation and C-C coupling chemistry (Scheme 1). NMR spectroscopy indicates



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.

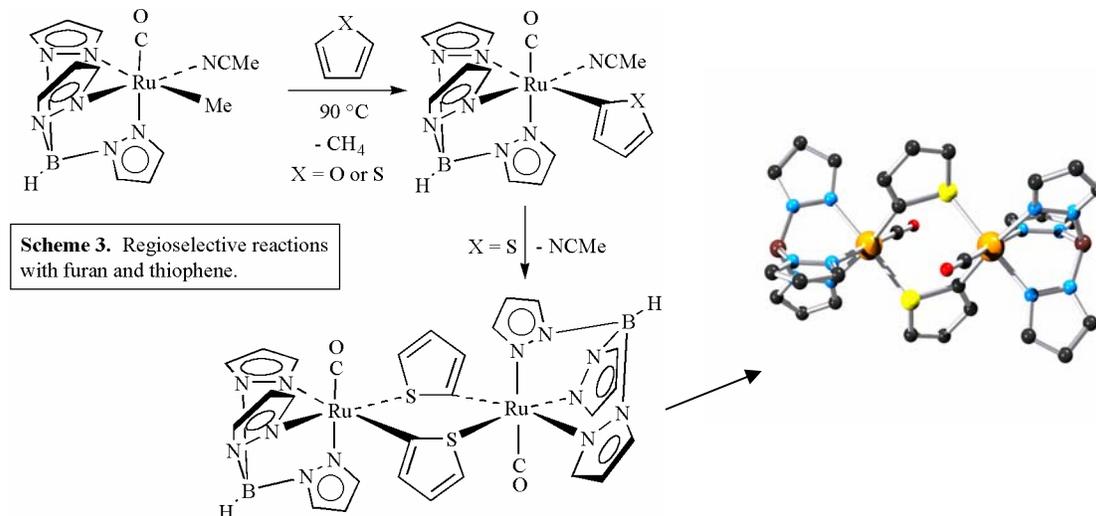
Consistent with the proposed metal-mediated C-H activation, the reaction of $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ with C_6D_6 produces CH_3D . In addition, catalytic reactions of C_2H_4 in C_6D_6 produce $\text{C}_6\text{D}_5\text{CH}_2\text{CH}_2\text{D}$, while catalysis in a 1:1 molar 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.

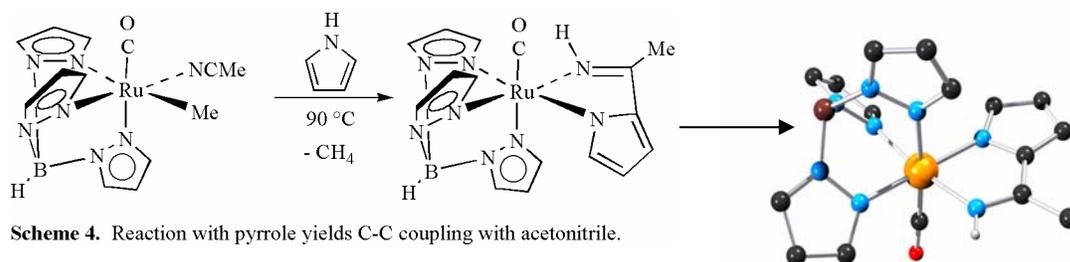
activation step is consistent with the regioselectivity of reactions with five-membered heterocycles (see below). In addition, calculated transition states reveal Ru-H interactions. Thus, the transition states exhibit "oxidative" character.

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

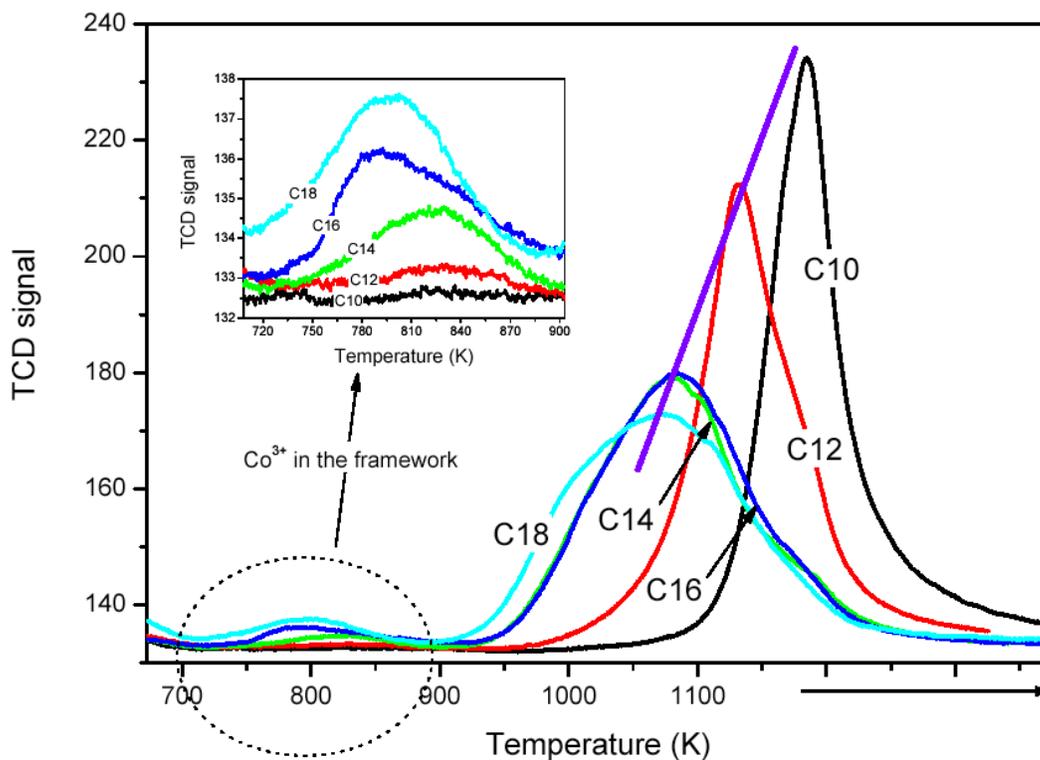


Figure 1

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.

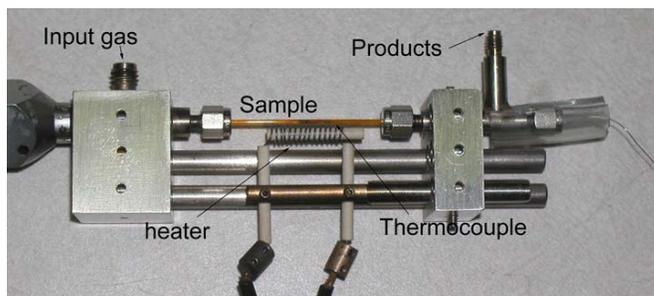


Fig. 1. Flow cell for *in situ* X-ray diffraction and EXAFS measurements.

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 - MnO_2 synthesis, metal carbide formation by methane carburization of metal oxides, nanoparticle cubic ZrO_2 formation from amorphous ZrO_2 , 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 , Cu_2O , MoO_3 , CoMoO_4 , NiMoO_4 , CeO_2) 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 $\text{Cu}^{+1}/\text{Cu}^0$ 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 H_2 or CO usually does not produce significant amounts of Cu_2O (or Cu_4O_3) intermediates before metallic copper forms. However, if one limits the flow of the reductant gas (H_2 or CO), then a Cu_2O intermediate is formed (see Fig. 2). The Cu_2O phase formed under these conditions shows extra oxygen in the cavities of the lattice structure. We have also shown that a Cu_2O phase is required during the water shift reaction.

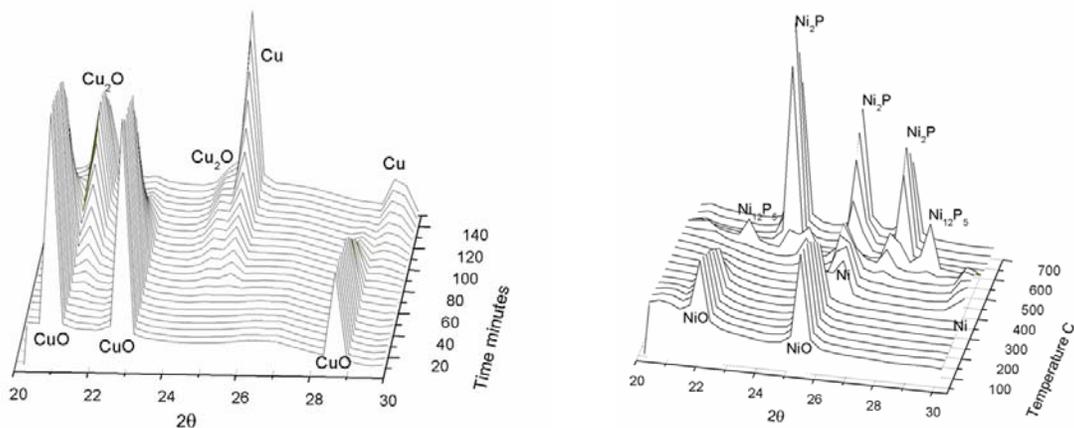


Fig. 2. *In situ* diffraction patterns during the reduction of CuO with limited CO flow (left); *in situ* diffraction patterns during the synthesis of HDS catalysts (right).

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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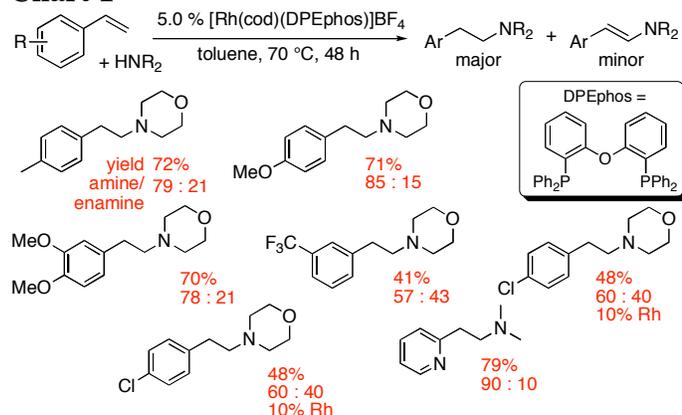
Goals

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.

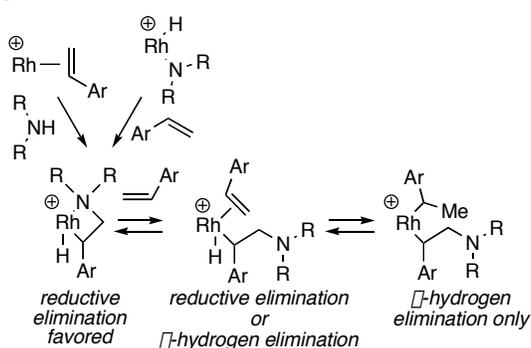
Recent Progress

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.

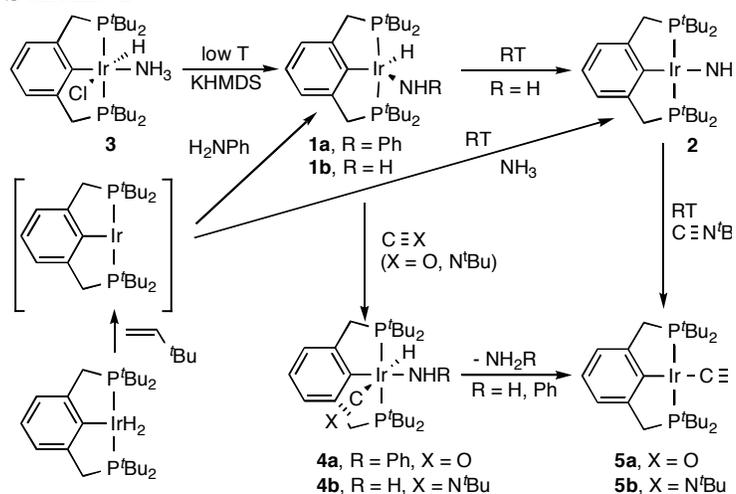


Reactions of morpholine, *N*-phenylpiperazine, *N*-Boc-piperazine, piperidine, 2,5-dimethylmorpholine, and perhydroisoquinoline reacted with styrene to form the amine product in 51-71% yield. Reactions of a variety of vinylarenes with morpholine generated amine as the major product. Reactions of morpholine 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.

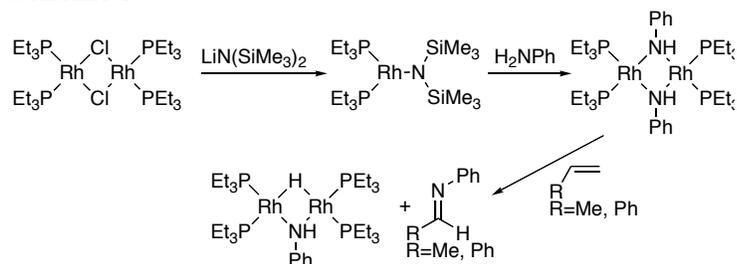
2) *Thermodynamics of Oxidative Addition and Reductive Elimination of Ammonia.* To help identify viable pathways for the hydroamination of olefins catalyzed by complexes of the cobalt triad, we studied oxidative additions and reductive eliminations of ammonia from (PCP)Ir fragment (PCP=1,3-di-*tert*-butylphosphinobenzene) 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

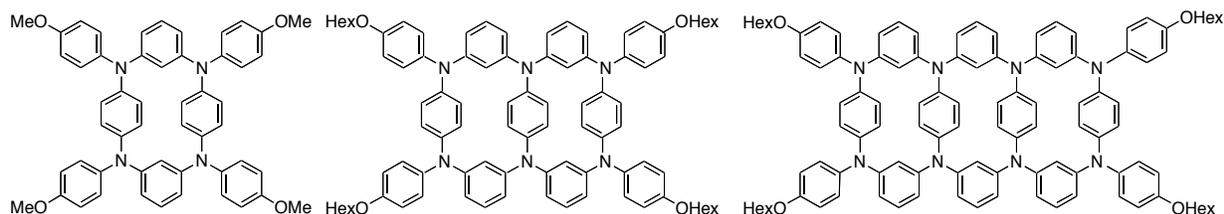


have found in unpublished work the first examples of such a transformation. As shown in Scheme 2, we prepared a dimeric rhodium anilide complex bound by trimethylphosphine. This complex reacted with styrene and alkenes, such as propylene to form the corresponding imine product from Markovnikov addition. 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



Publications

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3. Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. "Distinct Thermodynamics for the Formation and Cleavage of N-H Bonds in Aniline and Ammonia. Directly-Observed Reductive Elimination of Ammonia from an Isolated Amido Hydride Complex" *J. Am. Chem. Soc.* **2003**, *125*, 13644-13645.
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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.

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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

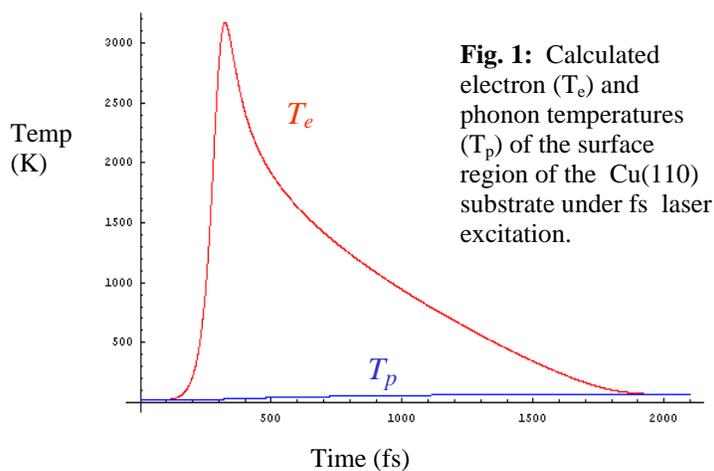
adsorbate/substrate electronic coupling, the isotopic mass of a molecule does determine its dynamics on a given potential energy surface, since its acceleration varies inversely with mass for the prescribed force.

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.

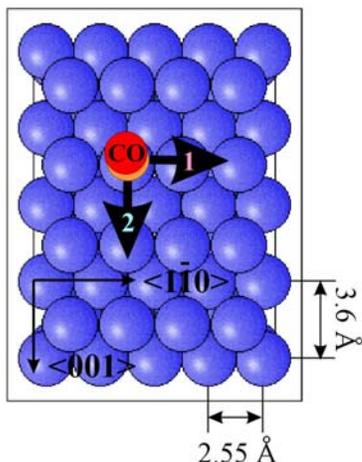


Fig. 2: Migration of CO molecules parallel (1) and perpendicular (2) to the atomic rows of the Cu(110) surface was observed by direct STM measurements.

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

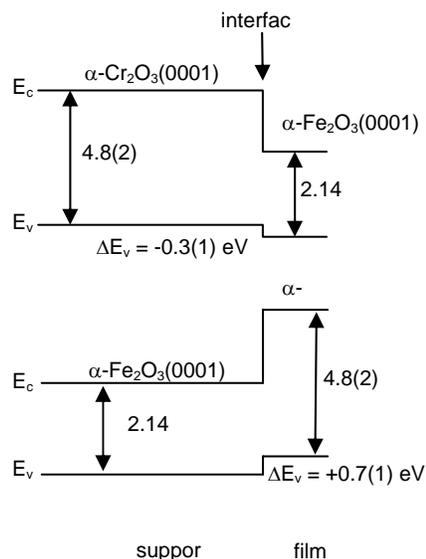
Explore the impact of nanoscaling the dimensions of a supported semiconducting metal oxide on its ability to promote photochemistry. Effective electron-hole pair separation can be achieved between a supported semiconducting metal oxide and its semiconducting host support when a band offset heterojunction 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

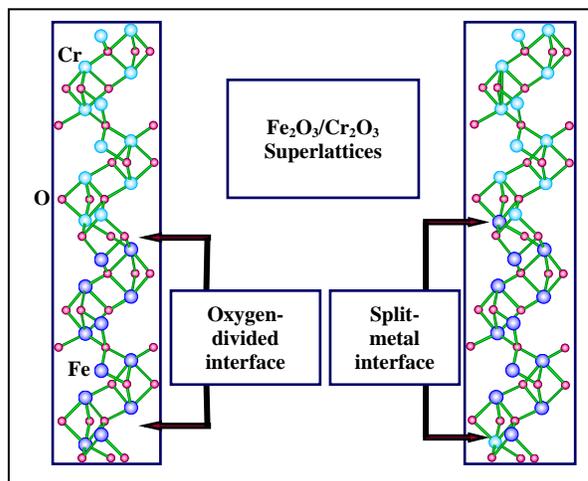
Advance basic understanding of heterogeneous photocatalysis with an emphasis on using nanotechnology to promote reactivity of supported oxide on oxide systems.

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

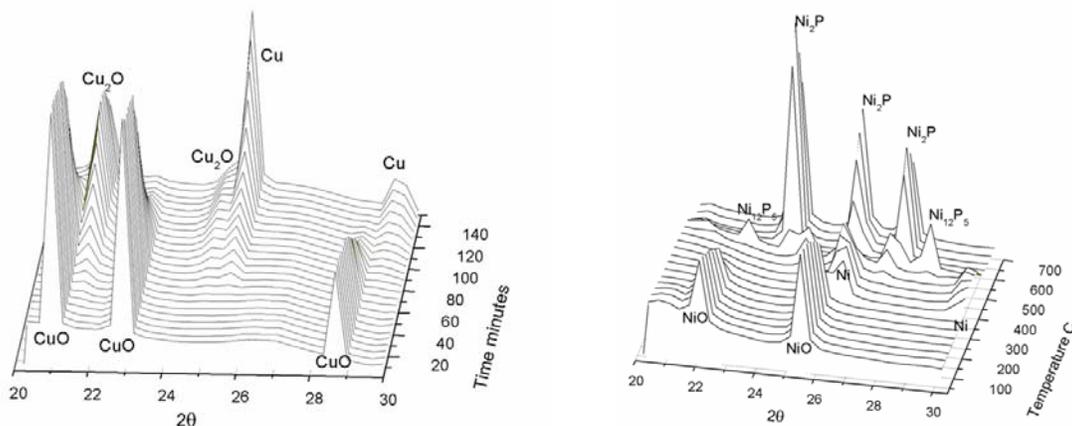
In the last three years our Catalysis group has been very actively investigating the generation of active sites on oxide surfaces through the creation of oxygen vacancies (TiO_2 , NiO , MgO , CeO_2) and metal doping ($\text{Cr}_x\text{Mg}_{1-x}\text{O}$, $\text{Zr}_x\text{Ce}_{1-x}\text{O}_2$). These 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. $\text{C}_2\text{H}_6\text{-C}_2\text{D}_6\text{-O}_2$ 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. $^{16}\text{O}_2\text{-}^{18}\text{O}_2\text{-C}_2\text{H}_6$ 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 $^{16}\text{O}_2\text{-}^{18}\text{O}_2\text{-C}_2\text{H}_6$ 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 Al₂O₃ 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 Al₂O₃, ZrO₂, SiO₂, and SnO₂ 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 O₂ 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

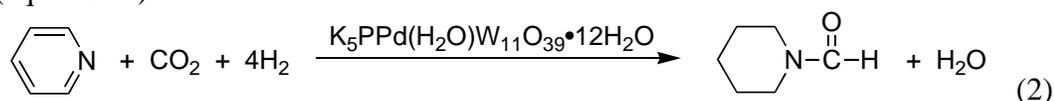
The development of new or more efficient methods for the conversion of CO₂ into useful organic products, via the design or discovery of new catalysts, ligands, solvents, and methods.

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.



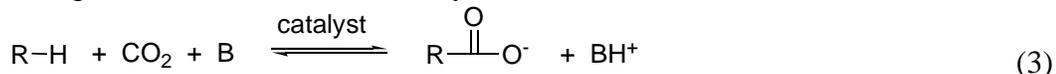
The co-hydrogenation of CO₂ and aromatic amines catalyzed by a Pd/W cluster was found to give alkylformamides via simultaneous hydrogenation of C=C, C=N and C=O double bonds (equation 2).



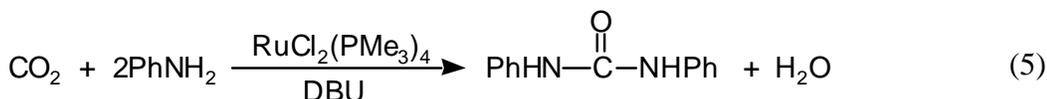
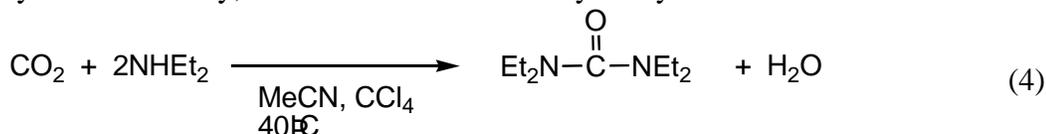
Spectroscopic and crystallographic studies of the catalysts for CO₂ hydrogenation: The group of Dr. John Linehan (PNNL) and the Jessop group together determined the structures of some of the complexes generated from the catalyst precursors RuCl(OAc)(PMe₃)₄ and RuCl₂(PMe₃)₄, identified most of the major 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

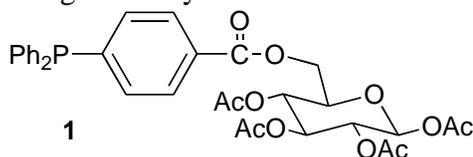
has not been reported for compounds containing significantly less acidic C-H bonds. We have used high-throughput screening methods to identify catalysts capable of promoting this reaction. Early screening has given us several promising hits, which we are now working to confirm using conventional-scale 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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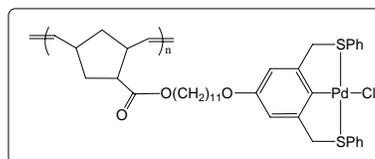
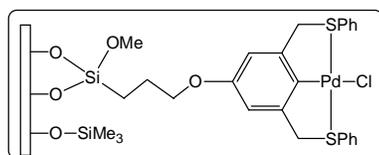
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Goal

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.

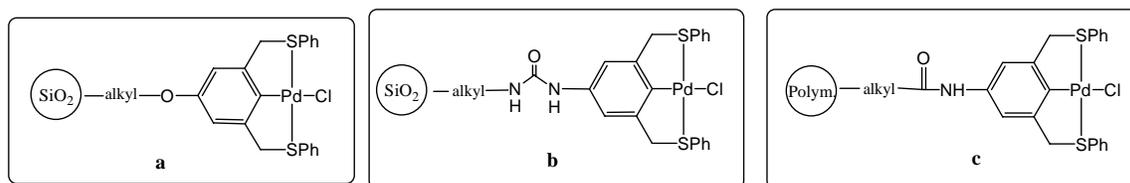


Heck Couplings with Pd-SCS pincer complexes: There are several reports in the literature that have identified Pd(II) pincer complexes as ideal catalysts for immobilization to allow for recoverable and reusable Heck catalysts. This idea stems from the observation that the complexes are stable at high 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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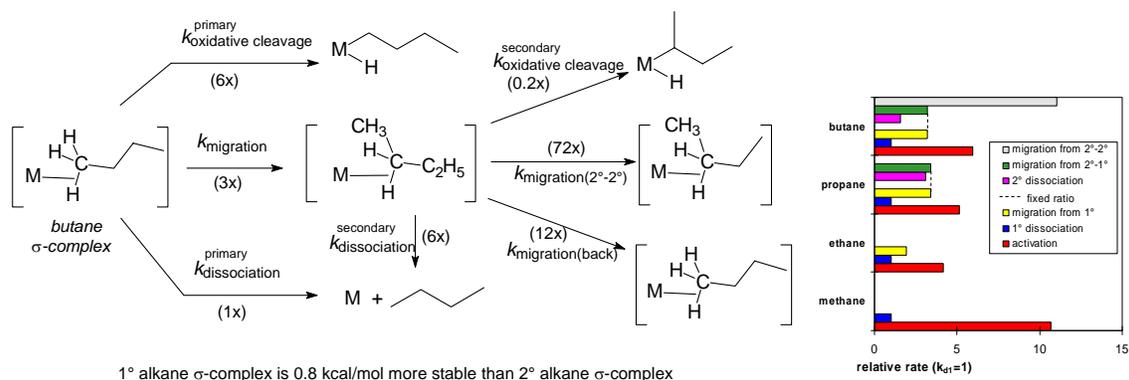
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Goals

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.

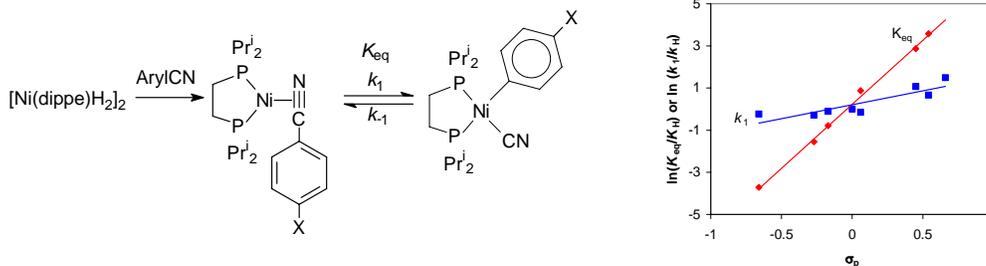
Recent Progress

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.

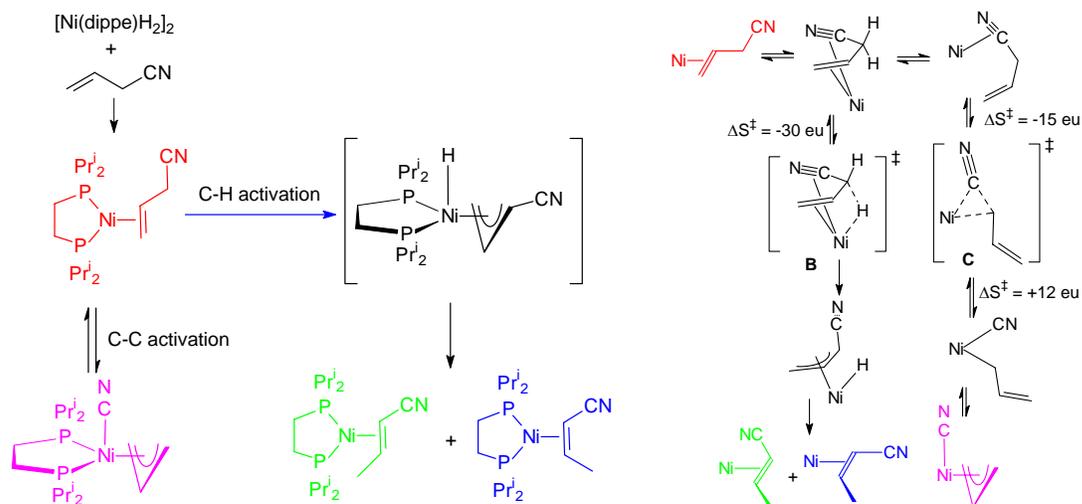


C-C Bond Cleavage Studies-C-CN cleavage in aryl nitriles. We have discovered that aryl nitriles undergo sp^2 - sp C-CN cleavage when reacted with NiL₂ fragments, and η^2 -nitrile adducts can be observed as reaction intermediates. The reaction is quite general, and can be controlled via the electronic demands of the aryl group as shown in

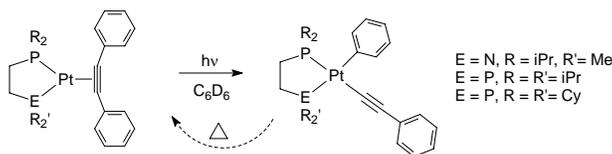
the equation below. K_{eq} was found to be strongly dependant ($\rho = +6.1$) on the electronics, whereas the rate of cleavage k_1 was found to be less dependant ($\rho = +1.3$).



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.

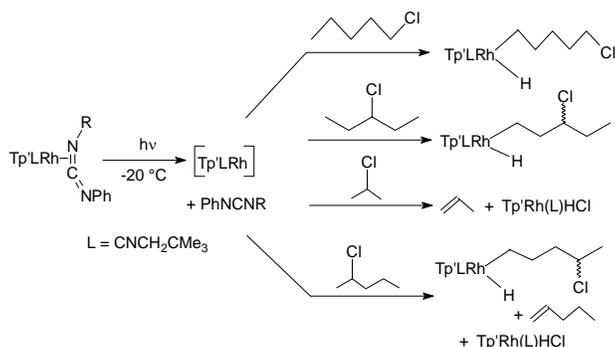


C-C Bond Cleavage Studies-C-CN cleavage in arylacetylenes. We have also discovered an important new type of C-C bond oxidative addition, cleavage of sp - sp^2 C-C bonds in aryl acetylenes. This is a *new class* of C-C bond cleavage, and offers many exciting possibilities. We have found that irradiation of either P-P or P-N chelate complexes of Pt-(diphenylacetylene) leads to the clean and quantitative formation of the oxidative addition product.

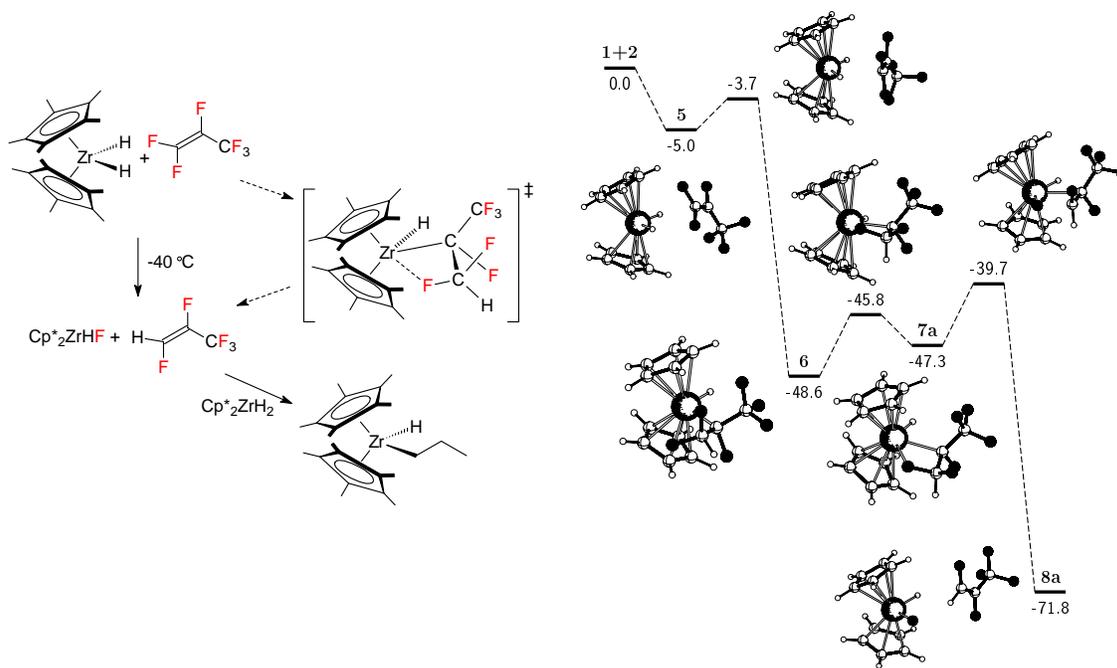


The reaction works for all complexes we have examined to date. Furthermore, the oxidative cleavage reaction is reversible, in that heating the Pt(II) complexes results in their reversion to the Pt(0)-alkyne complexes. Consequently, we now have methodology to break and make C-C≡C bonds, and further development 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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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

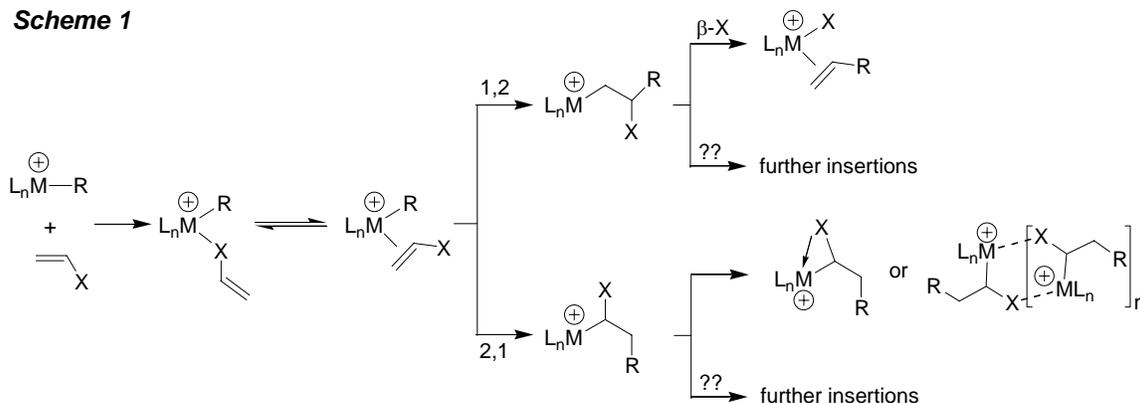
The polymerization of olefins by insertion chemistry using single-site metal catalysts provides a powerful approach to the synthesis of polyolefins with exquisite control of composition and structure. The development of metal catalysts that are capable of polymerizing or copolymerizing *functionalized 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.

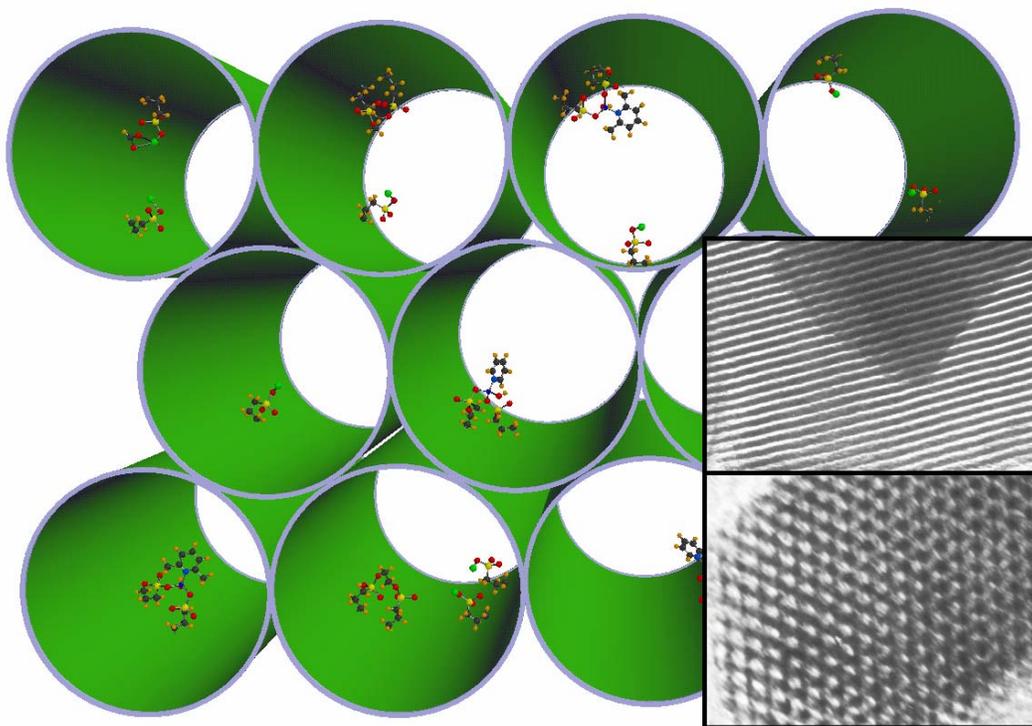


Fig. 1. Schematic of the mesoporous SBA-15 material with intrapore complexes formed at the wall-anchored propylsulfonic acid sites and TEM (inset with mag. = 50,000x) of the improved, highly ordered propylsulfonic acid-derivatized mesoporous SBA-15 catalyst was subsequently synthesized that contained 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 $-\text{H}\dots\text{N}\equiv$ 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.

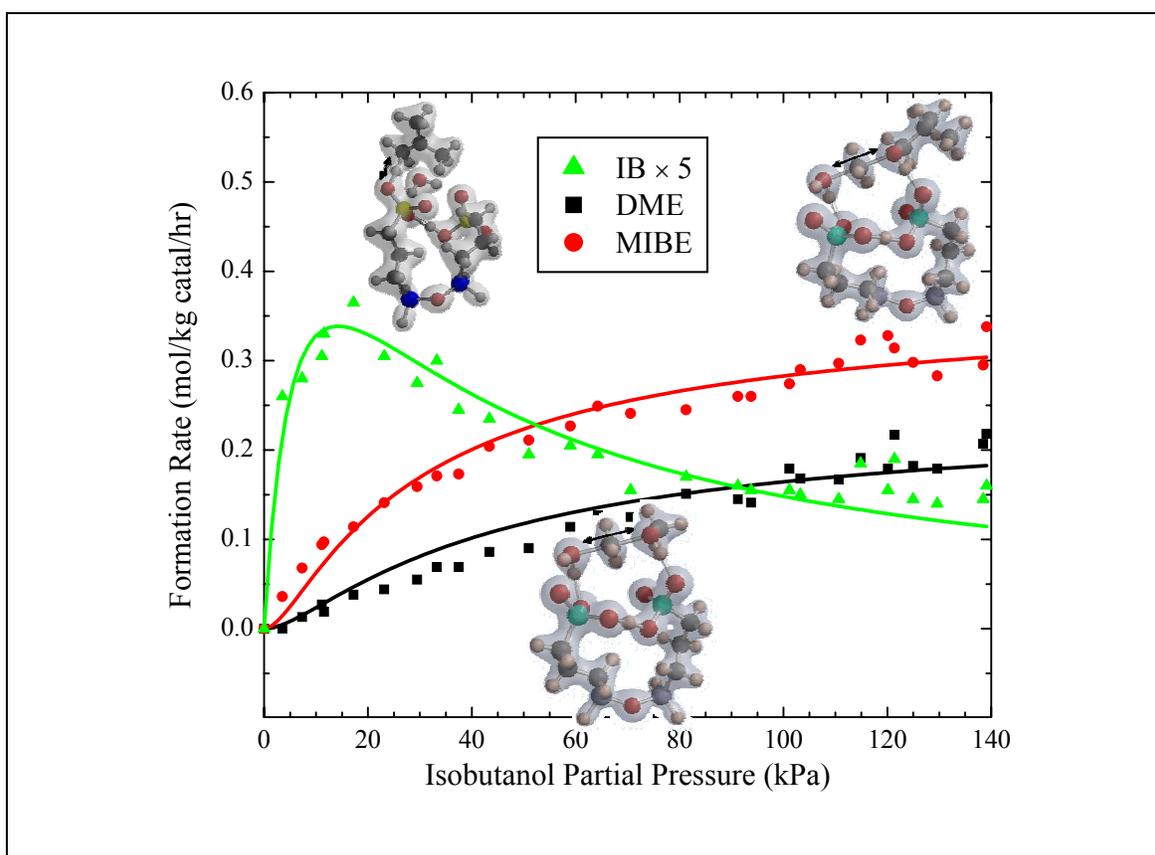


Fig. 2. Rates of MIBE, DME, and isobutene formation from MeOH/i-BuOH = 12.3/6.2 mol/kg catal/h at 404K in N_2 carrier gas as a function of i-BuOH partial pressure. Also shown are the computationally determined TS for the overall reaction pathways yielding MIBE, DME, and isobutene. The TS shows a planar 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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TRANSITION METAL-MEDIATED REACTIONS OF SMALL MOLECULES

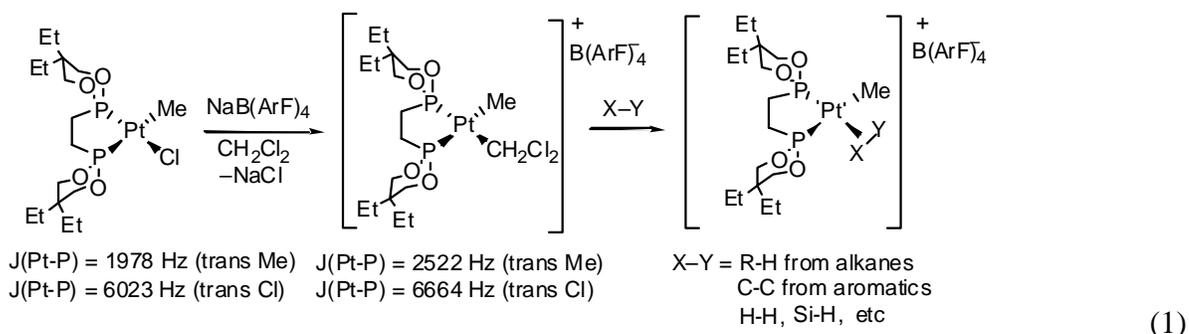
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Research Goals. The main goal is to study the binding and heterolytic cleavage of σ bonds on highly electrophilic cationic complexes to provide groundwork for applications ranging from hydrogen storage to the design of new catalysts to convert methane 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.



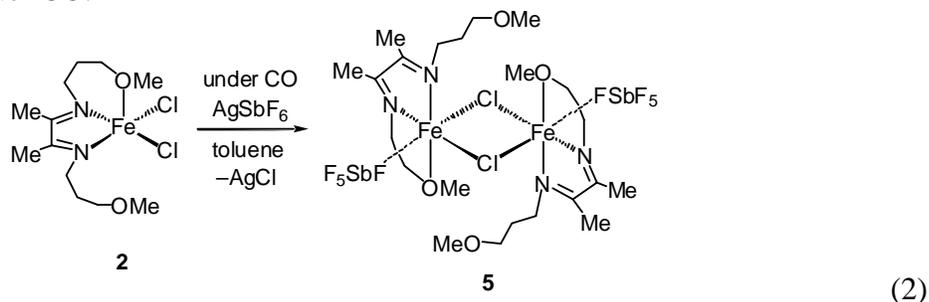
The extremely large NMR $J(\text{Pt-P})$ values for these complexes reveal that the Pt center is very electron poor, especially for the cation with bound dichloromethane. The latter is more electrophilic than $[(\text{depe})\text{PtMe}(\text{OEt}_2)]^+$ that gives C–H activation and C–C coupling of arenes (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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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

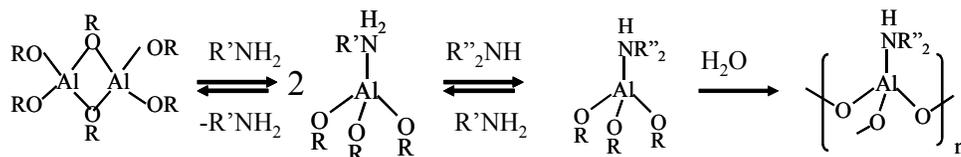
Develop synthetic concepts to control the surface chemical and catalytic properties of oxide by directing the chemistry during their preparation.

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).

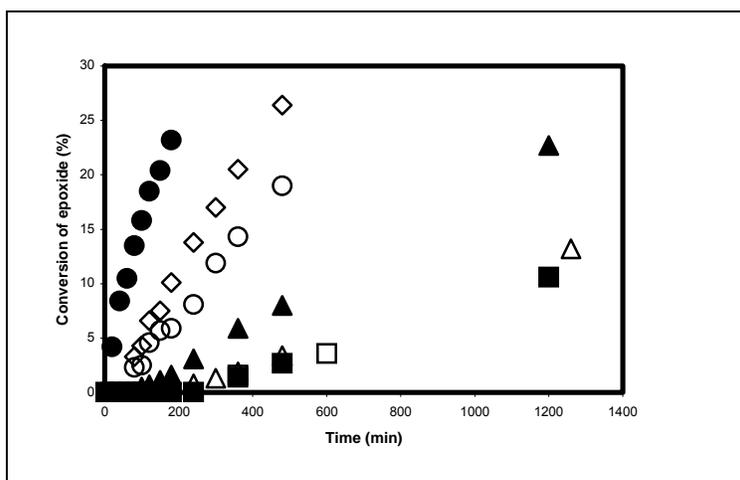


Figure 1: Conversion of cyclopentene oxide in reaction with piperidine catalyzed by various aluminas. ● PPD-Al₂O₃, ◇ SG-Al₂O₃-200, ○ SG-Al₂O₃-500-H₂O-200, ▲ SG-Al₂O₃-500-H₂O, △ PA-Al₂O₃-500-H₂O-200, ■ PA-Al₂O₃-500-H₂O, □ blank.

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.

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