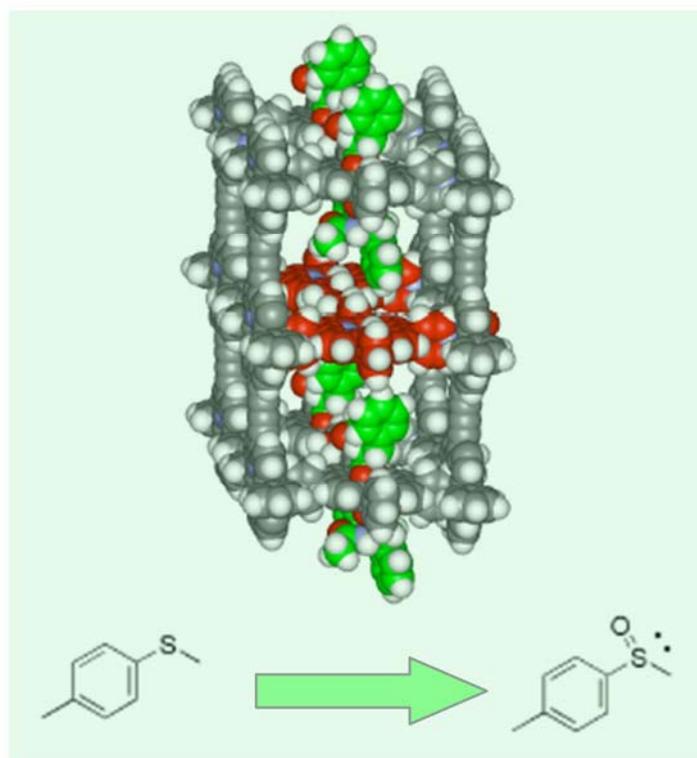
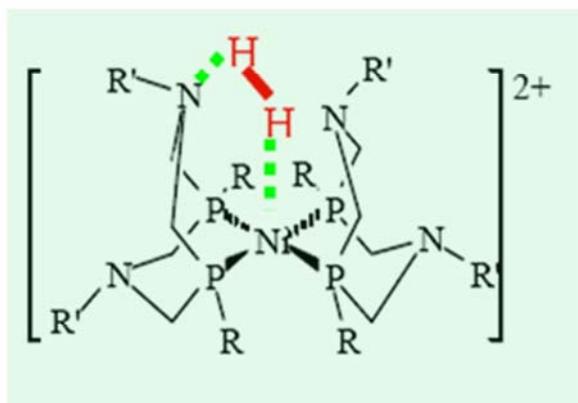
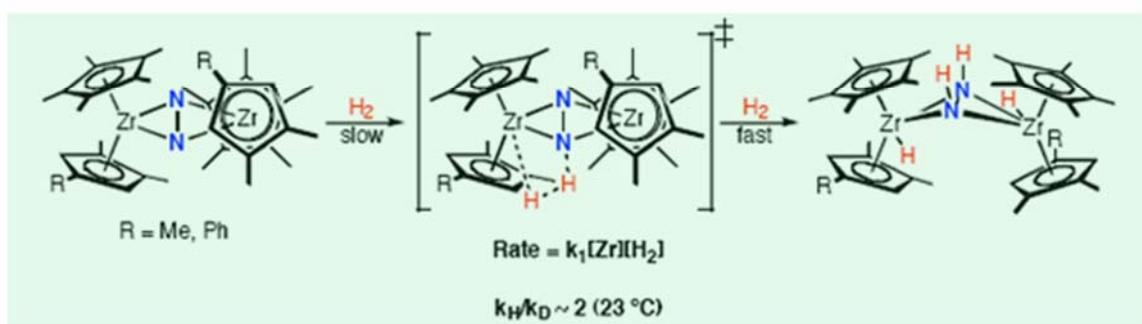


Frontiers in Organometallic, Inorganic, and Bioinspired Chemistry & Catalysis



Meeting of the Catalysis and Chemical Transformations Program
 Chemical Sciences, Geosciences and Biosciences Division
 Office of Basic Energy Sciences
 U.S Department of Energy
 Cambridge, MD
 May 21–24, 2006



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Cover figures (clockwise):

1. P. Chirik: zirconium complexes for nitrogen hydrogenation.
2. J. Hupp, S. Nguyen: metal-porphyrin structure for selective oxidation.
3. J. Franz, D. DuBois, J. Linehan: nickel complex for electrochemical production and oxidation of H₂.

FOREWORD

The 2006 Catalysis and Chemical Transformations Program Meeting is sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (OBES), U.S. Department of Energy. It is being held on May 21-24, 2006, at the Hyatt Regency Chesapeake Bay Hotel, Cambridge, MD. The purposes of this meeting are to discuss the recent advances in organometallic, inorganic and bioinspired chemistry and catalysis, to foster exchange of ideas and cooperation among participants, and to discuss the new opportunities for catalysis and chemical transformations at the interfaces with other disciplines and technologies, including nanoscience, hydrogen fuel generation and storage, solar energy conversion and f-element chemistry.

Catalysis activities within OBES emphasize fundamental research aimed at understanding and controlling the chemical reactivity of fluid and condensed matter. The long-term goal of this research is to discover the fundamental principles and develop the techniques to predict structure-reactivity relations. Such knowledge, integrated with advances in synthesis, instrumentation, characterization, and theory, will help us to control chemical reactions along desired pathways. Ultimately, this new knowledge will result in chemical and materials processes to efficiently convert fossil and renewable resources, or to generate, convert and store energy, with minimum impact to our environment.

Special thanks go to our invited speakers, who will expose us to recent advances in their fields, to the program investigators and their students, postdocs, and collaborators, for their dedication to the continuous success and visibility of the OBES Catalysis and Chemical Transformations Program, and to the session moderators, for their invaluable help. We also thank the Oak Ridge Institute of Science and Education staff, Ms. Sophia Kitts, Ms. Rachel Smith and Ms. Angie Lester, for the logistical and web support and the compilation of this volume.

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²Chemical Sciences, Geosciences and Biosciences Division
Office of Basic Energy Sciences
U.S. Department of Energy

MEETING OVERVIEW				
Catalysis and Chemical Transformations Contractors Meeting				
May 21 – 24, 2006 Cambridge, MD				
Time	Sunday, May 21	Monday, May 22	Tuesday, May 23	Wednesday, May 24
7:00 AM		Continental breakfast * Choptank Side Foyer	Continental breakfast * Choptank Side Foyer	Continental breakfast * Choptank Side Foyer
8:00				
8:30		Monday morning session Choptank Ballroom A/B	Tuesday morning session Choptank Ballroom A/B	Wednesday morning session Choptank Ballroom A/B
9:00				
10:00				
11:00				
11:30				
noon		Lunch buffet * Choptank Side Foyer	Lunch buffet * Choptank Side Foyer	Lunch buffet * Choptank Side Foyer
12:30 PM				
1:00				
2:00				
3:00	Poster set-up begins Chesapeake Ballroom E/F/G			
4:00	Registration Choptank Side Foyer (by the window wall)			
5:00		Posters Chesapeake Ballroom A/B	Posters Chesapeake Ballroom E/F/G	
5:30		Dinner buffet * Choptank Side Foyer	Dinner buffet * Choptank Side Foyer	
6:00	Registration concludes for the day Dinner buffet * Choptank Side Foyer			
7:15	Sunday evening session Choptank Ballroom A/B	Monday evening session Choptank Ballroom A/B	Tuesday evening session Choptank Ballroom A/B	
9:00	Posters Chesapeake Ballroom E/F/G			
9:30		Posters Chesapeake Ballroom E/F/G	Posters Chesapeake Ballroom E/F/G	
				Meeting adjourns

* All meals will be served buffet-style at the Choptank Side Foyer. Seating will be available in the Choptank Ballroom C.

**Frontiers in Organometallic, Inorganic, and Bioinspired Chemistry & Catalysis
Catalysis and Chemical Transformations Program Meeting
May 21-24, 2006 — Hyatt Chesapeake Bay, Cambridge, MD**

Poster presentations – Chesapeake E/F/G
Oral presentations – Choptank A/B

Sunday, May 21, 2006

-- Check-in at Hotel
3:00 p.m. Poster Room available for poster set-up
4:00 – 6:00 Registration in foyer
6:00 Dinner

Sunday Evening Sessions

Session Chair: Jim Franz (Pacific Northwest National Lab)

7:30 – 7:45 Welcoming Remarks
7:45 – 8:25 Bob Crabtree (Yale)
"Normal and Abnormal NHCs as Spectator Ligands in Catalysis"
8:25 – 9:05 Alan Goldman (Rutgers)
"Alkane Dehydrogenation and Tandem Dehydrogenation Systems Using Pincer-Ligated Iridium Complexes"
9:05 Social Hour / Posters

Monday, May 22, 2006

Monday Morning Sessions

7:00 – 8:00 a.m. Continental Breakfast
Session Chair: Guillermo Bazan (UC-Santa Barbara)
8:30 – 9:30 *Keynote Speaker: Richard R. Schrock (MIT)*
"The Controlled Synthesis of Polyenes from 1,6-Heptadiynes"
9:30 – 10:10 Don Tilley (UC-Berkeley)
"Catalysis on the Surface of an Oxide: Well-Defined Catalytic Centers and Oxide Surfaces as Ligands"
10:10 – 10:35 Break
10:35 – 11:15 Tom Autrey (Pacific Northwest National Lab)
"Control of Hydrogen Release and Uptake in Condensed Phases"
11:15 – 11:55 Al Sattelberger (Argonne National Lab)
"Chemistry and Catalysis with the 5f-Elements"
12 Noon Lunch

5:00 – 6:00 p.m. Posters
6:00 Dinner

Monday Evening Sessions

Session Chair:	Karen Goldberg (U. Washington - Seattle)
7:15 – 7:55 p.m.	Paul Chirik (Cornell) <i>"Understanding Nitrogen Fixation"</i>
7:55 – 8:35	Dorothee Kern (Brandeis) <i>"Catalysis, Dynamics and Stability of Enzymes Under Extreme Conditions"</i>
8:35 – 8:50	Break
8:50 – 9:30	Dan Nocera (MIT) <i>"Powering the Planet: The Challenge for Science in the 21st Century"</i>
9:30	Social Hour / Posters

Tuesday, May 23, 2006

Tuesday Morning Sessions

7:00 – 8:00 a.m.	Continental Breakfast
Session Chair:	Rick Kemp (U. New Mexico / Sandia National Lab)
8:30 – 9:10	Rinaldo Poli (Laboratoire de Chimie de Coordination, Toulouse, France) <i>"Controlled Radical Polymerization Mediated by Transition Metal Complexes: New Mechanistic Twists and Perspectives"</i>
9:10 – 9:50	Alexander Katz (UC-Berkeley) <i>"Controlling Inner-sphere Ligation of Oxygen to Ti Using a Surface Organometallic Catalysis Approach"</i>
9:50 – 10:15	Break
10:15 – 10:55	Elena Rybak-Akimova (Tufts) <i>"Toward Mechanism-Based Design of Biomimetic Green Oxidation Catalysts: Identifying Active Species in Oxygen and Peroxide Activation at Non-Heme Iron Centers"</i>
10:55 – 11:35	Oleg Ozerov (Brandeis) <i>"Bond-Breaking and Bond-Making Processes at PNP-Ligated Metal Centers"</i>
12 Noon	Lunch
5:00 – 6:00 p.m.	Posters
6:00 p.m.	Dinner

Tuesday Evening Sessions

Session Chair:	Peter Ford (UC - Santa Barbara)
7:15 – 7:55 p.m.	Jim Mayer (Univ. of Washington - Seattle) <i>"Oxidations of C–H and O–H Bonds by Metal Complexes via Hydrogen Atom Transfer and Possibly Concerted Pathways"</i>
7:55 – 8:35	Ludwig Bartels (UC-Riverside) <i>"Dynamics of Aromatic Species on Copper"</i>
8:35 – 8:50	Break

8:50 – 9:30 Clark Landis (Univ. of Wisconsin)
"Catalytic Alkene Polymerization and Information-Rich Fast Kinetics Methods"

9:30 Social Hour / Posters

Wednesday, May 24, 2006

Wednesday Morning Sessions

7:00 – 8:00 a.m. Continental Breakfast

Session Chair: Tom Rauchfuss (U. Illinois)

8:30 – 9:10 a.m. Brent Gunnoe (North Carolina State Univ.)
"Ruthenium-Mediated C-H Activation and C-C Bond Forming Reactions"

9:10 – 9:50 Morris Bullock (Brookhaven National Lab)
"Carbon-to-Metal Hydrogen Atom Transfer Reactions"

9:50 – 10:15 Break

10:15 – 10:45 Charles Casey (Univ. of Wisconsin)
"Challenges in Homogeneous Catalysis and Organometallic Chemistry in the 21st Century"

10:45 – 11:30 Discussion

11:30 – 11:45 Concluding Remarks

11:45 Lunch

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Sunday Evening Sessions

Normal and Abnormal NHCs as Spectator Ligands in Catalysis

Students: Chianese AR (GS); Li XW (GS); Chianese A (GS); Appelhans LN (GS); Voutchkova A (GS).

Collaborators: O. Eisenstein (France); Alceo Macchioni (Italy); E Peris (Spain)

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phone: (203) 432-3925; Email: robert.crabtree@yale.edu

web page: <http://www.chem.yale.edu/faculty/crabtree.html>

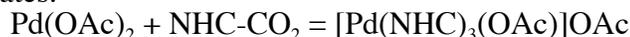
Goal

development of new synthetic routes to NHC complexes, particularly ones having novel structures, for application to catalytic reactions of current interest, such as transfer hydrogenation, hydrosilation, alkyne rearrangement and CH activation.

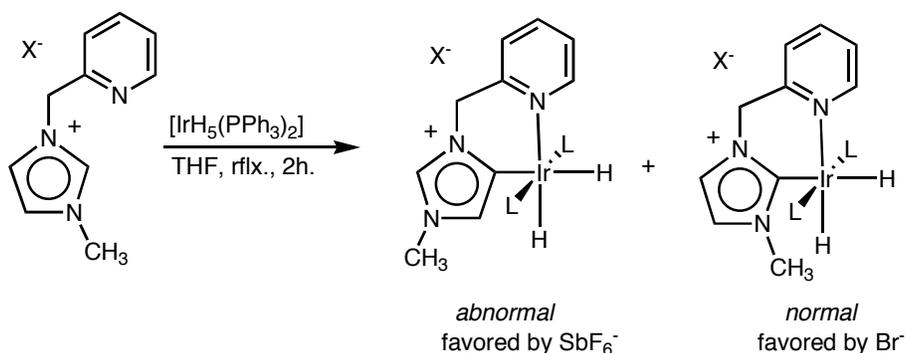
Recent Progress

Synthesis of NHC complexes

NHC-Carboxylate Reagent: In the most recent work, imidazole-2-carboxylates have been shown to be efficient NHC transfer agents to a variety of metal-containing precursors under mild conditions, via beta-elimination of CO₂. Apart from the data published in the JACS communication,¹ where mono- bis- and tris-NHC complexes were found, we now have seen as many as four NHCs being transferred to one metal center, as in the case of IrH₅(PPh₃)₂ which gives HIr(NHC)₄. The tris-NHC complexes of Pt, Pd and Ir that we have synthesized are yet to be tested for catalysis but they seem promising candidates.

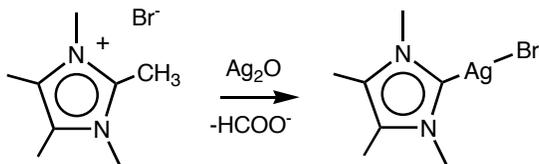


Anion-dependent Switching of NHC Binding Site: Changing the anion in a series of imidazolium salt precursors, entirely switches the outcome of the metallation reaction from normal (C-2) to abnormal (C-4) NHC binding.² Computational work shows that C-4 metallation goes by oxidative addition and shows little anion dependence. C-2 metallation goes via proton transfer from an agostic CH bond of the NHC ring to an adjacent hydride mediated by an ion-paired anion. The energy of this transition state is highly dependent on the anion, leading to the switch noted above.



Unexpected C-C Bond Cleavage: Lin's Ag₂O procedure has proved invaluable for facile metalation of an NHC followed by transmetalation to a transition metal. In order to make an abnormal NHC in this way, we looked at the case of an imidazolium salt blocked at C-2 with a methyl group. Surprisingly, the normal NHC was formed as exclusive product, along with 4 equivs of Ag(0) and formate ion, indicating that the Ag(I)

oxidizes the methyl group to formate.³ Likewise, benzyl was oxidized to benzoate. Transfer to Rh or Ir gives the normal NHC.



Oxidative Addition Route to NHCs: With Peris,⁴ we have shown that metallation of Ir(I) complexes with imidazolium salts and mild base goes via oxidative addition to give an Ir(III) hydride, followed by deprotonation of the metal.

Catalytic Applications

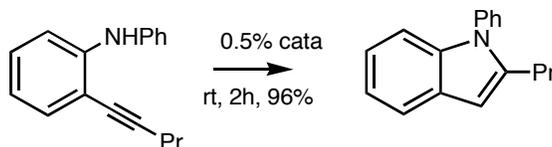
Hydrogen transfer. Hydrogen transfer reduction of ketones is well known but aldehydes and imines are much harder. Some of the complexes formed in our synthetic work prove active for these harder cases, as long as a mild base, K_2CO_3 , is substituted for the usual KOH promoter.⁵

In an extension of this work, we have been able to alkylate amines using the 'green' alkylating agent, $PhCH_2OH$, rather than a tosylate or a halide. This is a problem relevant to commercial drug synthesis where the FDA requires a company to demonstrate that any halide or tosylate alkylating agent is absent from the final product to very strict tolerance limits. The reaction goes via dehydrogenation, transfer of the hydrogen to added acetone, imine formation, then H-transfer reduction from the isopropanol formed in the first step.



Isotope labeling. Our iridium catalysts, discovered in an earlier grant period, have been shown by pharmaceutical chemists to be extremely useful for directed tritium labeling of drugs under chelation control. We have now elucidated the mechanism in a 'rogue' case, in collaboration with the Eisenstein group.⁶

Iridium Catalyzed Alkyne Rearrangements: In a series of related studies relying on catalysts discovered in a previous grant period, we looked at a number of alkyne rearrangements. First we defined the electronic and steric effects in the insertion of alkynes into our iridium(III) hydride.⁷ We next identified an intramolecular oxygen transfer from nitro groups to $C\equiv C$ bonds.⁸ Cycloiridation of alpha,beta-unsaturated ketones and esters was then documented.⁹ By combining the whole set of findings, we have developed a catalyst for intramolecular alkyne hydroalkoxylation and hydroamination.¹⁰



A new axially chiral NHC ligand derived from BINAM has been synthesized and evaluated in asymmetric ketone hydrosilylation.¹¹

Other related papers have also been published, but the work was previously discussed in a DOE report.¹²⁻¹⁵

Recent DOE work continues to be highly cited.¹²

Publications

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2. Appelhans LN, Zuccaccia D, Kovacevic A, Chianese AR, Miecznikowski JR, Macchioni A, Clot E, Eisenstein O, Crabtree RH, An anion-dependent switch in selectivity results from a change of C-H activation mechanism in the reaction of an imidazolium salt with IrH₅(PPh₃)₂. *J. Am. Chem. Soc.*, 2005, 127, 16299-16311.
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6. Clot E, Chen J, Lee D-H, Sung SY, Appelhans LN, Faller JW, Crabtree RH, Eisenstein O, Double Geminal C-H Activation and Reversible α -Elimination in 2-Aminopyridine Iridium(III) Complexes: the Role of Hydrides and Solvent in Flattening the Free Energy Surface. *J. Am. Chem. Soc.*, 2004, 126, 8795-8804.
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9. Li X, Crabtree RH, Cycloiridation of α,β -Unsaturated Ketones, Esters, and Acetophenone, *Organometallics*, 2005, 24, 4810-4815.
10. Li XW, Chianese AR, Vogel T, Crabtree RH, Intramolecular Alkyne Hydroalkoxylation and Hydroamination Catalyzed by Iridium Hydrides. *Org. Lett.*, 2005, 7, 5437-5440.
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Alkane Dehydrogenation and Tandem Dehydrogenation Systems Using Pincer-Ligated Iridium Complexes

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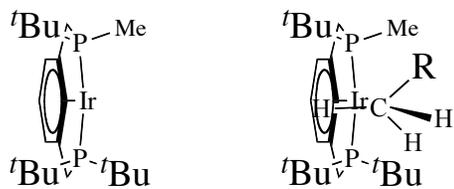
Goal

To develop catalysts for alkane dehydrogenation to give alkenes, particularly with regioselectivity for the terminal position (1° C-H bonds). Other substrates suitable for dehydrogenation include heteroatom-containing species (e.g. amines to give enamines), polymers, and hydrogen-storage materials. Experimental results are used to test computational (DFT) models which are then used iteratively to more fully understand experimental results and to design new catalysts. Steric effects have been found to play a critical role, but only recently has it been possible to meaningfully and accurately model such effects. Accordingly, we plan to develop an understanding of steric effects at a level deeper than is typically considered; i.e. we will explore variations of molecular architecture, rather than the frequently cited one dimensional parameters such as cone angle (or just “increased/decreased bulk”). Tandem systems, in which dehydrogenation is coupled with a useful secondary reaction, are being actively explored.

Recent Progress

Pincer-ligated iridium complexes have shown great promise as catalysts for the dehydrogenation of alkanes. The complex $(^t\text{Bu}_3\text{PCP})\text{IrH}_n$ was first reported by Kaska and Jensen to catalyze the transfer-dehydrogenation of alkanes. Subsequent work in our lab in collaboration with the Kaska and Jensen groups led to the discovery that the kinetic product of dehydrogenation of n -alkanes is the α -olefin, and to the development of systems for “acceptorless” dehydrogenation (in which hydrogen is evolved as H_2 , rather than transferred to a sacrificial acceptor). Other substrates that we have shown can be efficiently and usefully dehydrogenated include poly- α -olefins and tertiary amines. In most cases, the sterically less-hindered complex $(^i\text{Pr}_3\text{PCP})\text{IrH}_n$ was found to give much greater rates; however, the isopropyl groups are found to be susceptible to dehydrogenation-induced decomposition.

In an attempt to reduce steric crowding while maintaining the thermal robustness of t -butyl groups, we considered the use of methyl groups on the ligating phosphorus atoms. Preliminary experiments indicated that the all-methylated analog was too unencumbered and would undergo dimerization or cluster formation. Further consideration led to the



$(\text{Me}/^t\text{Bu}_3\text{PCP})\text{Ir}$ (a) alone, and (b) illustrating the potentially large effect of a single methyl-for- t -butyl substitution on a P atom on the steric congestion in an alkane C-H addition reaction.

hypothesis that steric bulk would be best distributed in an unsymmetrical fashion so as to offer minimal resistance to C-H addition or β -H-elimination, while still preventing cluster dimerization.

Toward this end we have synthesized the new ligands indicated below and the corresponding iridium fragments.

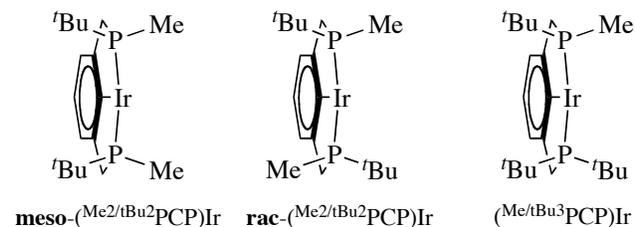


Fig. 1. New pincer-ligated iridium dehydrogenation catalysts.

$(\text{Me}/\text{tBu}_3\text{PCP})\text{IrH}_4$ has been synthesized, isolated and characterized spectroscopically and analytically; reaction with CO gives $(\text{Me}/\text{tBu}_3\text{PCP})\text{Ir}(\text{CO})$ which has been characterized crystallographically. In accord with our hypothesis that an alkane-matched steric environment would yield more favorable catalytic rates, $(\text{Me}/\text{tBu}_3\text{PCP})\text{IrH}_4$ has been found to catalyze dehydrogenation significantly faster than $(\text{iPrPCP})\text{IrH}_n$. Even more importantly, it is found to yield higher turnover numbers, and appears to remarkably stable for such an active catalyst.

Like the “mono-methylated” catalyst, $(\text{Me}_2/\text{tBu}_2\text{PCP})\text{IrH}_n$ shows catalytic activity greater than either that of $(\text{iPrPCP})\text{IrH}_n$ or $(\text{tBuPCP})\text{IrH}_n$, again in accord with the hypothesis of an “alkane-matched” steric environment. The $\text{Me}_2/\text{tBu}_2\text{PCP}$ ligand is a somewhat more complex case than the mono-methylated species, since either meso or rac forms are possible (and were present in the preliminary experiments). The differences between these two forms, which have the identical “total” electronic and steric contributions from the ligands, will be of significant interest in a thorough understanding of ligand architecture, and testing of computational methods, necessary for real-world catalyst design.

We have begun to synthesize one of these enantiomers of $\text{rac-}(\text{Me}_2/\text{tBu}_2\text{PCP})\text{IrH}_n$. Proceeding through the chiral deprotonation of $(\text{tBu})\text{PMe}_2$, we have thus far successfully obtained the R,R enantiomer of the PCP-H ligand. Synthesis of the single enantiomer not only will allow us to distinguish rac from meso activity, we believe that it also affords the possibility of a highly effective and chiral catalyst. Whereas innumerable chiral catalyst fragments have cis-coordinated bidentate groups, $(\text{Me}_2/\text{tBu}_2\text{PCP})\text{Ir}$ offers C_{2v} symmetry but with trans groups. We believe this will result in a more strongly interactive chiral environment than in the case of cis-coordinating bidentate ligands. Other chiral pincers have been developed (with moderate success) but this will be the first example in which the P atoms present two groups as sterically different as t-butyl and methyl. Among the possible reactions, we hope that this will be a rare example of a chiral catalyst for olefin additions (including hydrogenation) that does not require a chelating group on the olefin to achieve enantioselectivity.

The geometry of $\text{rac-}(\text{Me}_2\text{tBu}_2\text{PCP})\text{IrH}_n$ suggests that it would preferentially coordinate trans vs. cis olefins; this preference could easily translate into preferential hydrogenation of trans-olefins, including trans-fatty acids which are believed responsible for 30,000 to 100,000 premature coronary deaths annually (<http://www.hsph.harvard.edu/reviews/transfats.html>).

We also have reason to believe that the methyl-substituted catalysts, and especially $\text{meso-}(\text{Me}_2\text{tBu}_2\text{PCP})\text{Ir}$, will effectively promote C-C coupling reaction with sp^2 -carbons. In other work, we have found that sp^2 -C-C coupling is strongly dependent on the ability of the vinyl or aryl group to rotate so as to "face" an attacking group. Thus, this system offers not only the potential for new C-C coupling catalysts, but also an extraordinary proof of concept and lesson in ligand design.

Tandem catalysis.

During the course of the dehydrogenation reactions the pincer-iridium catalysts initially show excellent rates, which fall off steeply as olefin is produced. We have shown this to be largely due to inhibition by product. An intriguing approach to this problem is to couple dehydrogenation with a secondary reaction that prevents the build-up of olefin; of course the secondary reaction would ideally be useful in its own right.

Successful examples of the tandem principle, including alkane metathesis, will be discussed. Importantly, the new catalysts, $(\text{Me/tBu}_3\text{PCP})\text{IrH}_4$ and $(\text{Me}_2\text{tBu}_2\text{PCP})\text{IrH}_4$, afford significantly better rates for the tandem systems than the parent catalysts.

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Monday Morning Sessions

The Controlled Synthesis of Polyenes from 1,6-Heptadiynes

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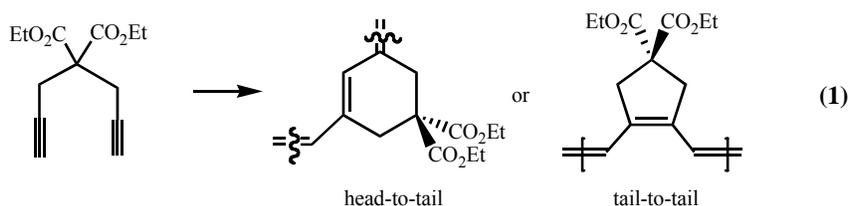
Goal

The goals are to control polymer micro- and macromolecular structures of a variety of poly[1,6-heptadiynes] through living polymerizations that employ well-defined catalysts of the type $M(NR)(CHR')(OR'')_2$ ($M = Mo$ or W) and related species. A second goal is to synthesize long oligomers in a *stoichiometric* fashion and correlate properties with chain length and structure.

Recent Progress

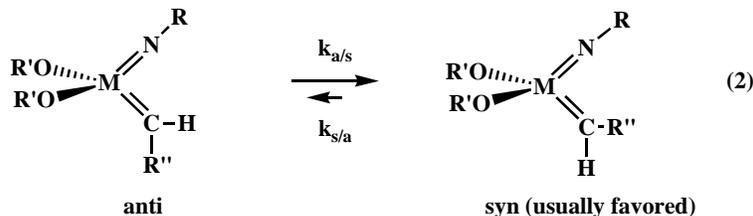
During this past two year grant period we have wound up our investigations concerning the design of catalysts for the living polymerization of olefins and renewed our investigations in the synthesis of soluble polyenes from 1,6-heptadiynes such as diethyldipropargylmalonate (DEDPM), an area that was supported previously by the DOE before we switched to the (then) new living catalysts for olefin polymerizations. The six papers that have appeared (see list at the end) reflect that change in direction.

Controlling polymer microstructure: We have shown that DEDPM, the prototypical 1,6-heptadiyne, can be polymerized in a living fashion to give polyenes that contain a mixture of five- or six-membered rings (equation 1). Five- or six-membered rings are formed as a consequence of initial addition of the first triple bond to a *syn* or *anti*

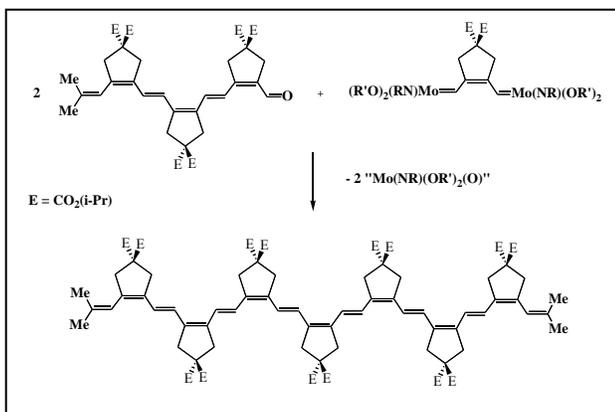


alkylidene to give an α - or a β -substituted molybdacyclobutene intermediate, respectively. The proposal that a greater degree of steric hindrance around the metal will force β -addition led to the design of catalysts that contain carboxylates, in particular $Mo(NAd)(CHCMe_2Ph)(O_2CCPh_3)_2$ ($Ad = 1$ -adamantyl). These catalysts will polymerize DEDPM to yield polyenes that contain all six-membered rings. Conversely polyenes that contain largely (~95%) five-membered rings can be prepared using $Mo(NAr)(CHCMe_2Ph)(O-t-Bu)_2$ catalysts. Since the much higher rate of propagation versus initiation has limited maximum control over the chain length of such polymers, we have now prepared catalysts that are rapid initiators ($k_p/k_i < 1$) and that produce a chain

length that therefore corresponds to the number of monomers added. The structure of a resulting polymer is a sensitive function of the nature of the imido (NR), alkoxide (OR'), and alkylidene (*syn* or *anti*; see equation 2). A large variety of these and related catalysts are being screened in order to determine how polymers can be prepared that contain 100% five-membered rings.



Synthesis of long oligomers with a fixed length: The desire to correlate polymer properties with chain length has led us to develop stoichiometric methods for preparing oligomers with a *single* chain length. For example, we have been able to prepare oligomers that contain all five-membered rings up to and including the red 15 ene shown in the box to the right (where E = isopropyl ester). These oligomers are somewhat air sensitive, but relatively soluble and highly crystalline. We are in the process of preparing the series of both even- and odd-membered polyenes of this type with up to 20-25 double bonds.



DOE Interest

π -Conjugated organic polymers have desirable electronic, linear or non-linear optical and electrochemical (photoconductive or photorefractive) properties. The most efficient method of preparing such species is via polymerization reactions with well-defined alkylidene catalysts. In this manner structures can be controlled and manipulated and the desirable properties maximized. Virtually nothing is known about polyenes with a fixed chain length and a known structure beyond ~12 double bonds.

Future Plans

We want to discover what catalysts will allow us to prepare poly[1,6-heptadiynes] whose structures consist solely of five-membered rings, the most highly conjugated, regular, and rigid structure. Moreover, we want to prepare a series of long oligomers from many other types of 1,6-heptadiynes in order to correlate properties with structure and chain length. We also hope to structurally characterize poly[1,6-heptadiynes] that have a significant chain length in order to further understand the relationship between polymer structure and effective conjugation length and properties.

DOE supported publications that have appeared since 2004.

"Synthesis, Characterization, and Polymerization Behavior of Zirconium and Hafnium Complexes that Contain Unsymmetric Diamido-N-Donor Ligands"

Tonzetich, Z. J.; Lu, C. C.; Schrock, R. R.; Hock, A. S.; Bonitatebus, P. J., Jr.
Organometallics **2004**, *23*, 4362-4372.

"The Optical Spectroscopy of Long Polyenes" Christensen, R. L.; Faksh, A.; Meyers, J. A.; Samuel, I. D. W.; Wood, P.; Schrock, R. R.; Hultsch, K. C. *J. Phys. Chem. A* **2004**, *108*, 8229-8236.

"An Evaluation of Zirconium and Hafnium Complexes that Contain the Electron-Withdrawing Diamido/Donor Ligand, $[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NCH}_3]^{2-}$, for the Polymerization of 1-Hexene" Schrock, R. R.; Adamchuk, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2005**, *24*, 857-866.

"Synthesis, Characterization, and Activation of Zirconium and Hafnium Dialkyl Complexes that Contain a C_2 -Symmetric Diaminobinaphthyl Dipyridine Ligand" Tonzetich, Z. J.; Schrock, R. R.; Hock, A. S.; Müller, P. *Organometallics* **2005**, *24*, 3335-3342.

"Potential Group IV Olefin Polymerization Catalysts that Contain a Diamido Ligand Substituted with Hexaisopropylterphenyl Groups" Tonzetich, Z. J.; Schrock, R. R. *Polyhedron* **2006**, *25*, 469-476.

"Initiators of the type $\text{Mo}(\text{NAr})(\text{CHR}')(\text{OR})_2$ for the Controlled Polymerization of Diethyldipropargylmalonate" Adamchuk, J.; Schrock, R. R.; Tonzetich, Z. J.; Müller, P. *Organometallics* **2006**, *asap* 3/25.

Molecular Precursor Methods for the Controlled Generation of Active and Selective Catalytic Sites on an Oxide Surface

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Goal

The primary goal of this project is to develop molecular chemistry that allows atomic-level and nanoscopic control over the structures of heterogeneous catalysts. Much of this work has targeted the production of multi-component oxides for which high dispersions are expected to give desirable catalytic properties. More recently, extensive efforts have been devoted to use of this chemistry for producing well-defined, single-site catalysts via chemical reactions on an oxide surface.

Recent Progress

Supported titanium and tantalum catalysts for epoxidation: Recent reports have described the surface-modification of epoxidation catalysts with alkylsilane coupling agents to yield hydrophobic materials that exhibit enhanced catalytic activity and selectivity. To investigate such efforts for the epoxidation of olefins with TMP-derived Ti/SiO₂ and Ta/SiO₂ catalysts, we have modified the surface of these catalysts with Me₂N-SiMe₂R (R = Me, ⁿBu, or ⁿOc). These aminosilanes were chosen because (a) they are stronger silylating agents than analogous silyl chlorides and alkoxides, (b) they are monofunctional bonding reagents that will produce a well-defined structure, and (c) the elimination product (Me₂NH) is easily removed. Treatment of the parent M/SiO₂ materials with a solution of the silylating agent at room temperature results in the capping of surface Si-OH and M-OH moieties with coverages ranging from 0.8 to 1.4 silyl groups nm⁻². The parent M/SiO₂ material adsorbs approximately 31 wt% H₂O, while the R_{cap} materials adsorb just 2.4-3.3 wt%. The catalytic performance of the R_{cap} materials was tested in the epoxidation of cyclohexene with aqueous H₂O₂. A significant increase in the selectivity for epoxide was observed for both the Ti and Ta materials. The parent Ta/SiO₂ catalyst was 36 % selective for epoxide after 2 h, and the R_{cap}Ta/ SiO₂ catalysts demonstrated selectivities > 98 % after 2 h with comparable total yield. All of these catalysts retain their high selectivity for epoxide formation (> 95 %) for 6 h of reaction. Spectroscopic and mechanistic studies of these catalysts suggest an important role for M-OSiMe₂R groups.

Catalytic oxidations with supported manganese clusters: Manganese-based materials catalyze a number of useful oxidations. One of the more interesting transformations is accomplished by the polynuclear Mn based oxygen evolving complex (OEC) in photosystem II (PSII), and the development of similar surface-bound species as functional water oxidation catalysts could make a significant contribution to strategies for hydrogen-production systems based on the photochemical splitting of water. Clean

grafting of a dinuclear μ -oxo bridged Mn complex onto mesoporous silica is observed when SBA-15 is treated with an acetonitrile solution of $[\text{Mn}_2\text{O}_2\text{Cl}(\text{O}_2\text{CCH}_3)(\text{H}_2\text{O})(\text{bpy})_2](\text{NO}_3)_2$. Cationic $[\text{Mn}_2\text{O}_2\text{Cl}(\text{O}_2\text{CCH}_3)(\text{H}_2\text{O})(\text{bpy})_2]^+$ is surface bound by a siloxide anion with elimination of HNO_3 . Diffuse reflectance UV-vis, FT-IR, and magnetism measurements confirm that the dinuclear oxo bridged unit remains *intact* after grafting.

DOE Interest

This program is focused on the strategic design of novel catalysts of potential interest for the production of fuels and chemicals in an energy-efficient and environmentally acceptable fashion. Of particular interest is the development of structure-reactivity relationships via the controlled synthesis of catalytic centers, extensive characterization of catalyst structure, and evaluation of catalytic properties. Catalytic centers for water oxidation may be coupled with proton-reduction schemes too provide an efficient process for the production of hydrogen, a renewable and environmentally friendly energy source.

Future Plans

Further mechanistic work is required to provide a complete understanding of the reaction steps involved in selective epoxidation reactions. This will be combined with variations of the support structure, and further structural characterizations of the most selective catalysts, to develop new generations of supported oxidation catalysts. Particular emphasis will be placed on the synthesis and characterization of supported water oxidation catalysts.

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- "Stoichiometric and Catalytic Arene Activations by Pt Complexes Containing a Bidentate Monoanionic Nitrogen-Based Ligand." D. Karshtedt, J. L. McBee, A. T. Bell and T. D. Tilley. *Organometallics*, in press.
- "Single Source Molecular Precursors to Niobia-Silica and Niobium Phosphate Materials." C. G. Lugmair and T. D. Tilley. *Monatshefte für Chemie*, in press.

Basic Research for the Hydrogen Fuel Initiative: Control of Hydrogen Release and Uptake in Condensed Phases

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Goal

The long-term objective of the proposed research is to develop knowledge about hydrogen-rich materials that will provide the basis for developing new hydrogen storage systems. We propose that: (i) hydrogen can be stored reversibly in materials with alternating electron-rich and electron-poor sites, (ii) thermally reversible hydrogen storage can be accomplished with chemical hydrides based on the B,N,C elements, and (iii) nanoscale effects and interfacial interactions can enhance kinetics and modify thermodynamics of hydrogen release and uptake.

Recent Progress

Neutron vibrational studies of di-hydrogen bonding: The low frequency region of the inelastic neutron scattering (INS) spectrum collected at 15 K is shown in Figure 1 for $\text{H}_3\text{N}^{11}\text{BH}_3$, $\text{D}_3\text{N}^{11}\text{BH}_3$, and $\text{H}_3\text{N}^{11}\text{BD}_3$. Specific isotopic labeling of the hydridic and protic positions has allowed for study of the soft dihydrogen vibrational modes.

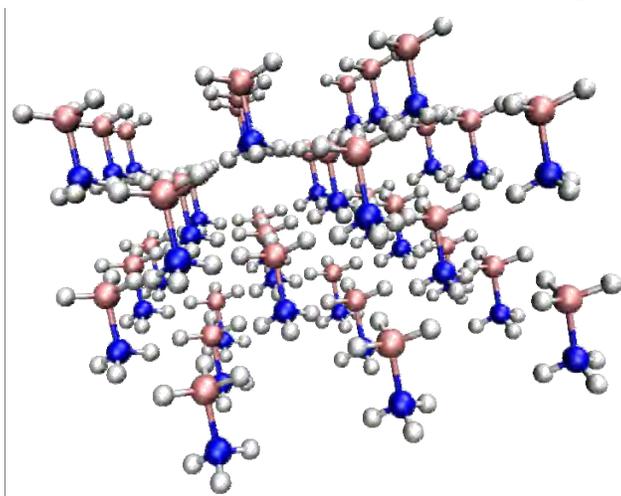


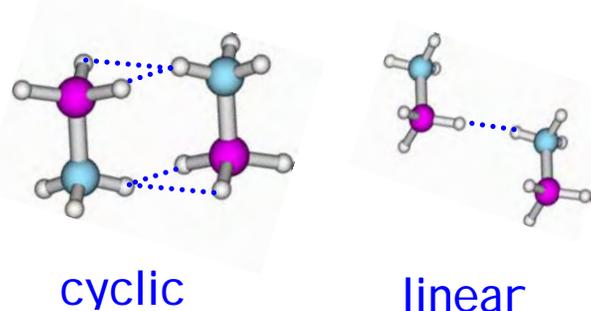
Figure 1. Orthorhombic phase of ammonia borane illustrating extended network of intermolecular dihydrogen bonding between adjacent BH—HN.

Specific isotopic labeling of the hydridic and protic positions has allowed for study of the soft dihydrogen vibrational modes.

In an attempt to predict the change to these vibrational modes with deuteration, we have mapped the N-H...B-H unit involved in dihydrogen bonding to a traditional model of hydrogen bonding. A proton acceptor, proton donor and proton are required for conventional hydrogen bonding. In the case of ammonia borane which has both protic and hydridic hydrogens, we have made the assumption that the proton acceptor includes the

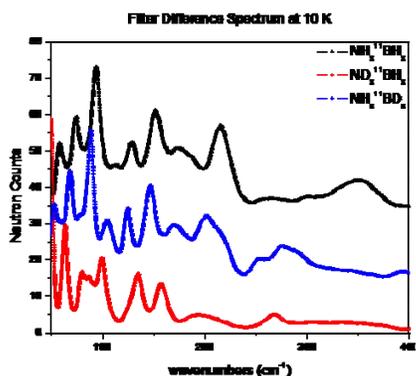
entire (B-H) unit. The nitrogen atom is then the traditional proton donor. Under these constraints, deuteration of the hydridic hydrogen has a weaker effect on the vibrational frequency based solely on the reduced mass change (see Table 1). This model underestimates the softening which results from deuteration of the (B-H) unit, but does predict observed weaker vibrations. Deuteration of the protic positions again results in less energetic vibrations; however, the observed change is far less dramatic than predicted by this model. One explanation may be due to the molecular arrangement in the solid state. The protons are oriented between two hydridic positions of an adjacent molecule. Hydrogen bonding is therefore a cooperative process which involves more than one proton, proton donor, and proton acceptor. This model does predict a weakening on the dihydrogen vibrational energy upon deuteration as observed in the INS spectra.

Our experimental results are compared with various levels of theory for the perprotonated ammonia borane as well as with expected shifts in the vibrational frequency due to isotopic labeling. Experimental and calculated vibrational positions



are tabulated in Table 1. Semi-empirical MP2/aug-cc-VDZ results of the ammonia borane dimer are for each isotopomer reveals the relative changes in the soft modes. Clearly the vibrational frequencies for the dimer are not equivalent to those in the bulk; however, trends in the soft mode frequency changes due to isotopic substitution are

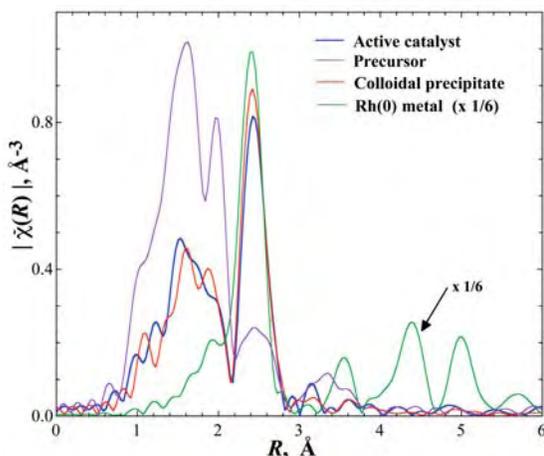
consistent with observed INS results. The dihydrogen symmetric stretching mode (A_g) at 204 cm^{-1} for $\text{H}_3\text{N}^{11}\text{BH}_3$ is relatively stable upon H/D substitution. Further, the bend (A_u) at 93 cm^{-1} and the rocking modes at 150 cm^{-1} (A_g) and 242 cm^{-1} (B_u) for $\text{H}_3\text{N}^{11}\text{BH}_3$ are relatively stable. The other low energy vibrations are assigned to rotational and lattice modes.



		Calculations on AB dimer (MP2)				FDS spectra at 10K (tentative assignments)		
		linear		cyclic				
		NH3BH3	NH3BH3	ND3BH3	NH3BD3	NH3BH3	ND3BH3	NH3BD3
molecular	rock	52				59	64	53
	rock	74				75	81	69
	bend		93	86 [-7]*	84 [-9.5]	94 (+1)	87 [-8]	89 [-5]
						110		105
	torsion		132	101 [-23]	117 [-11]	129 (-3)	99 [-23]	125 [-3]
	rock		150	139 [8]	141 [-7]	152 (+2)	135 [-11]	147 [-3]
	torsion		193	142 [-26]	168 [-13]	180 (-13)	158 [-13]	170 [-6]
	stretch		204	201 [-2]	191 [-6]	211 (+7)	198 [-6]	202 [-4]
	rock		242	224 [-7]	218 [-10]	261 (+19)	-----	218 [-17]
	torsion		256	295	283 [-4]	298 (+3)	269 [-10]	253 [-15]
	torsion		284	327	304 [-7]	327 350 (+23)	317 [-10]	275 [-22]
	v(B-N)					764 (782)	725 (737)	756 (747)

Figure 2. Neutron vibrational spectrum was obtained for there isotopomers of ammonia borane at 15 K to gain insight into the nature of dihydrogen bonding in the solid state. Linear dimer is solid state structure, cyclic dimer is gas phase structure.

Operando Spectroscopy in Catalysis: A combination of operando XAFS and NMR methods were used to elucidate the mechanism of hydrogen release from amine boranes.



XAFS spectroscopy shows that the predominate rhodium species formed under the catalysis conditions is a Rh₄ cluster (diameter of approximately 0.3 nm) rather than a 2 nm-diameter Rh nanoparticle. Knowledge of the Rh structures provides key insights into the catalysis species and the mechanism of the formation of hydrogen from amine borane compounds. We anticipate this class of Rh₄ clusters may play an important role in both dehydrocoupling and hydrogenation reactions.

Figure 2. Comparison of k^2 -weighted $|\tilde{\chi}(R)|$ plots of precursor, di- μ -chloro-bis[(cis,cis- η^4 -1,5-cyclo-octadiene)rhodium(I)]; active catalysis species, Rh₄ cluster; colloidal precipitate; and metallic rhodium standard.

DOE Interest The proposed research will result in knowledge that will provide the basis for development of new materials that release and absorb hydrogen at moderate temperatures and pressures. New theoretical and experimental tools to investigate hydrogen-rich materials will be developed. The proposed work specifically addresses the focus area “Novel Materials for Hydrogen Storage” and peripherally “Design of Catalysts at the Nanoscale” of the Hydrogen Fuel Initiative. These fundamental studies will provide a strong basis for support of DOE’s EERE Centers of Excellence in hydrogen storage.

Future Plans. The long-term objective of the proposed research is to develop knowledge about hydrogen-rich materials (HRM) that will provide the basis for development of new hydrogen storage systems. We propose that 1) hydrogen can be stored reversibly in materials with alternating electron-rich and electron-poor sites, 2) thermally reversible hydrogen storage can be accomplished with chemical hydrides based on the B, N, and C elements, and 3) nanoscale effects and interfacial interactions can enhance kinetics and modify thermodynamics of hydrogen release and uptake. Our research will focus on developing a fundamental understanding of novel hydride systems and providing the foundation for the discovery of new HRM.

Publications.

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Chemistry and Catalysis with the 5f-Elements

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The large size of actinide ions permits coordination numbers and attendant polyhedra that are uncommon amongst the transition elements. For the same set of ligands, a 5f-element ion will be more coordinatively unsaturated than a d-element ion. The availability of 5f valence orbitals also suggests a greater degree of metal-ligand binding possibilities, smaller ligand field stabilization energies, smaller energy barriers to intra- and intermolecular ligand exchange, and a greater degree of ionic character in metal-ligand bonding that leads to more electrophilic metal centers and correspondingly more nucleophilic ligand centers. Modern actinide chemistry is characterized by the existence not only of actinide analogues to many classes of d-transition metal complexes, but increasingly common reports of compounds and types of reactions unique to the actinide series. In this lecture, I will provide an historical perspective on catalysis and chemical transformations involving the 5f-elements and highlight some recent developments in the field that indicate that there is still much to be learned about the chemistry of the heaviest elements.

Monday Evening Sessions

Understanding Nitrogen Fixation

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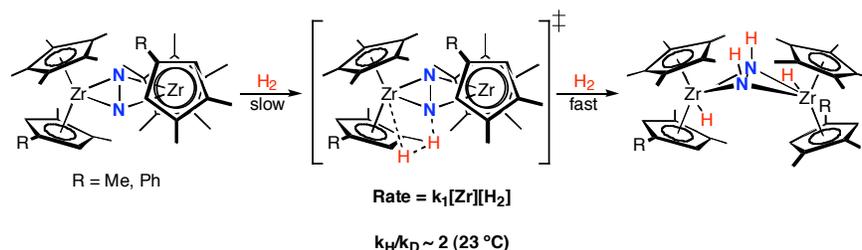
webpage: www.chem.cornell.edu/pc92

Goal

Develop soluble transition metal reagents for the transformation of atmospheric nitrogen into ammonia and other value-added nitrogen-containing molecules. Design and synthesis of these compounds is based on concurrent mechanistic studies aimed at elucidating the factors that govern the reactivity of coordinated dinitrogen.

Recent Progress

Our laboratory has recently discovered a family of bis(cyclopentadienyl)zirconium complexes that activate atmospheric nitrogen for hydrogenation ultimately generating small quantities of ammonia. Computational and mechanistic studies have demonstrated that side-on coordination coupled with a twisted dimeric structure of the metallocene results in significant zirconium-N₂ backbonding facilitating 1,2-addition of non-polar molecules such as dihydrogen and terminal alkynes. Kinetic studies in combination with isotopic labeling studies have established the first H₂ addition as rate determining and established an ordered, four-centered transition structure with concerted H-H bond scission and Zr-H and N-H bond formation.



DOE Interest

The synthesis of ammonia from its elements, N₂ and H₂, is one of the most energy-intensive processes practiced in the chemical industry. The impacts of this energy requirement are profound, rendering crop fermentation products such as ethanol too energetically expensive to replace fossil fuels. A cornerstone to developing new energy efficient stoichiometric and catalytic transformations using atmospheric dinitrogen as a feedstock is understanding how to activate N₂ toward a range of chemical transformations. Our work has focused on early transition metal complexes that promote N-H bond formation.

Future Plans

Our laboratory is currently focused on understanding the mechanisms of N-element bond-forming reactions and expanding the scope of reagents that functionalize coordinated dinitrogen. We have recently discovered reactions that couple the activation of carbon-hydrogen bonds to N₂ fixation. More long term efforts are aimed at developing reagents for the formation of nitrogen-carbon and nitrogen-silicon bonds and elucidating the mechanisms that underpin this reactivity.

Publications 2004-2006

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Catalysis, Dynamics and Stability of Enzymes under Extreme Conditions

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 Collaborators: Joshua Wand (Univ. of Pennsylvania), Martin Karplus (Harvard Univ.)
 Contact: Dorothee Kern, Dept. of Biochemistry, MS 009, Brandeis University, Waltham, MA 02454, E-mail: dkern@brandeis.edu, Phone: (781) 736-2354, Fax: (781)736-2316, <http://www.bio.brandeis.edu/faculty01/kern.html>

Goal

Conformational transitions in proteins are key to function. The long-term goal is to achieve a more general understanding of the physical basis underlying the energy landscape of proteins. We will characterize the influence of external physical parameters such as temperature, pressure and solvent on protein dynamics, stability and the linkage to catalysis on one hand and learn lessons from nature on how proteins have adapted to extreme conditions on the other hand.

Recent progress

Catalytic activities of extremophiles

We chose the enzyme adenylate kinase (adk) as our specific model system. We have cloned, expressed and purified a psychrophilic (Cadk), mesophilic (Eadk), hyperthermophilic (Aadk), halophilic (Hadk) and piezophilic (Padk) adenylate kinase. First we performed activity assays on the psychrophilic enzyme and found that this enzyme has its maximum activity at 25C and unfolds above 25C (Fig. 1). We are in the process of characterizing catalytic activities of all these enzymes under ambient conditions and its extreme conditions (high salt, high pressure).

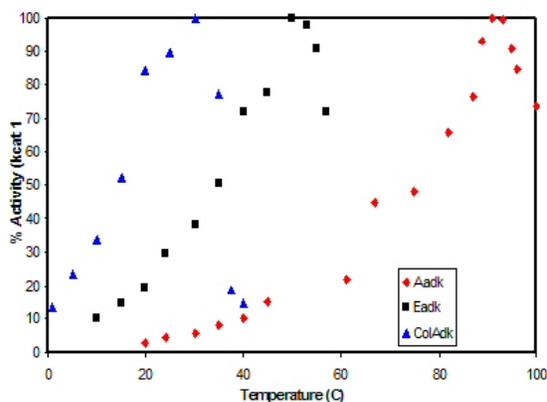


Fig.1 Relative catalytic activities of psychrophilic (blue), mesophilic (black) and thermophilic (red) adk measured with a coupled enzymatic assay).

High-resolution structures of extremophiles

We were able to solve the crystal structure of Hadk bound to the substrate analogue Ap5A (Fig. 2). We are in the process of comparing this structure to the mesophilic analogue (Badk) to rationalize how this enzyme adapts to high salt. This week we obtained small crystals of Padk.

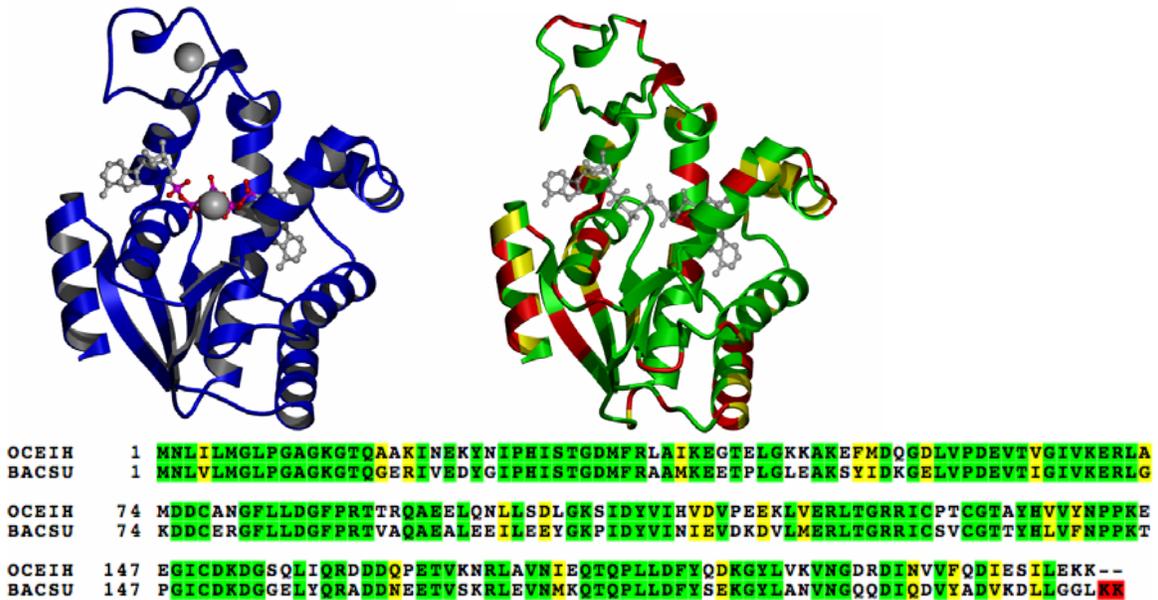


Fig.2: X-ray structure of Padk bound to Ap5A (left) and sequence homology to the Bacillus adk are shown in one letter code (bottom) and color coded onto the structure: identical residues (green), conserved (yellow), different (red).

Dynamics of the extremophiles measured by NMR relaxation

NMR relaxation experiments provide quantitative information about the relative populations of the conformational substates (thermodynamics), the rates of interconversion between them (kinetics) and the chemical shifts of the states (structural information). We performed NMR relaxation dispersion experiments for Eadk and Padk first under ambient pressure and second under 1000 atm pressure using NMR cells that can be pressurized (Fig. 3). Interestingly, the preliminary results indicate a strong influence of the conformational transitions for Eadk but a very small influence on Padk, the piezophilic enzyme.

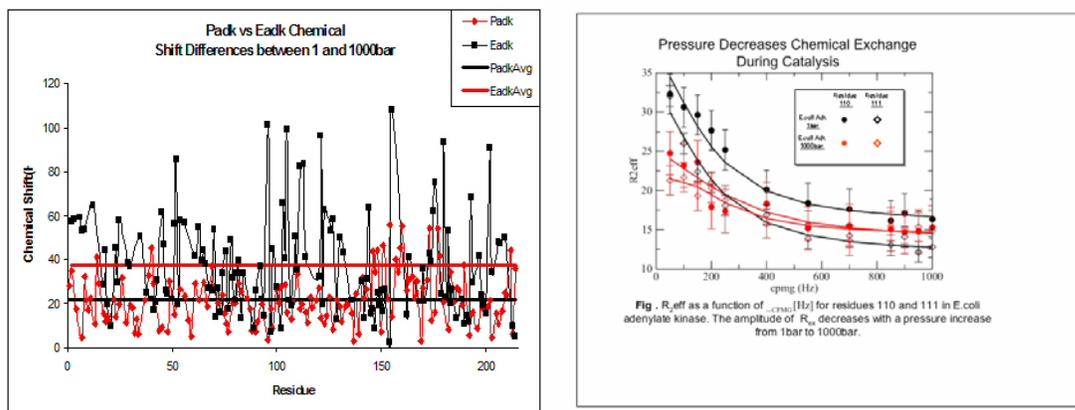


Fig. 3: Left: Changes in chemical shift upon pressure (1000 atm) for Eadk (black) and Padk (red) indicates a much smaller effect on Padk. Right: Comparison of dynamics at 1 atm (black) and 1000 atm (red) for Eadk measured by NMR relaxation experiments. Note that the amplitudes for the dispersion curves have decreased under high pressure indicative of a shift in equilibrium between the interconverting conformations.

Molecular dynamics simulations on extremophiles

To rationalize differences in dynamics and thermal stability of Eadk and Aadk, we performed molecular dynamics (MD) simulations on Eadk and Aadk in explicit solvent for 5ns at both 300K and 350K. The simulations show that the average fluctuation amplitudes of residues in Eadk are more sensitive to temperature than the corresponding residues in Aadk (Fig. 4). Specifically, the residues most sensitive to temperature in Eadk, but not in Aadk, are located 1) at the interface between the AMP and the core domains; 2) the N-terminal of $\alpha 1$ and $\alpha 8$, and 3) the C-terminus of b4 and b5 (Fig. 4).

We selected seven single point residual differences between Eadk and Aadk in these regions to first virtually mutate for MD simulations and second to experimentally test whether these residues indeed are responsible for the thermostability of Aadk. Simulations of the 7-fold mutant of Aadk show that this mutant form is almost as sensitive to temperature as wild type Eadk now (black line in Fig. 4).

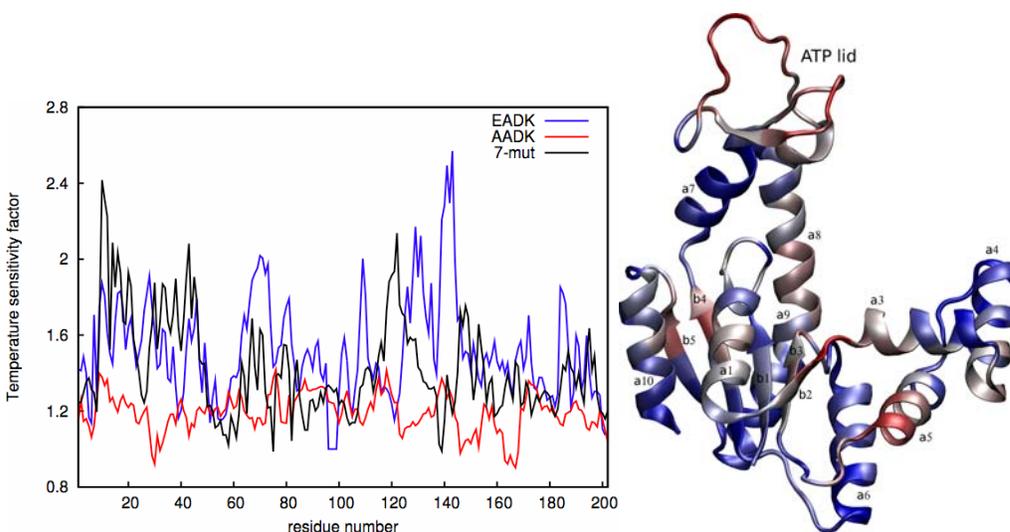


Fig. 4 left: The temperature sensitivity factor (TS) defined as the ratio of the root mean square fluctuation (RMSF) value of a C α atom at 350K and 300K. The blue, red and black lines are for the TS factors of wild type Eadk, wild type Aadk and the 7-fold mutant of Aadk respectively. Right: The ratio of the TS factor of residues in Eadk versus Aadk colored onto the structure of Aadk. Residues are colored continuously from blue to white to red, indicating small to medium to large ratios of TS factors of Eadk over those of Aadk.

We are currently performing explicit solvent simulations on the wild type Eadk at 1atm, 700atm and 1400atm. We do not have the crystal structure of the Padk yet, however since Padk has 76% sequence identity as Eadk, we have built a structure of Padk by homology modeling. We are currently simulating this protein at 1atm, 700atm and 1400atm. The comparison of the simulations of the two proteins at different pressures may reveal the mechanism by which Padk is adapted to high pressure. These simulations will be directly compared to the pressure experiments.

Powering the Planet: The Challenge for Chemistry in the 21st Century

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The greatest challenge facing our global future is energy. Rising living standards of a growing world population will cause global energy consumption to increase dramatically over the next half century. Within our lifetimes, energy consumption will increase at least two-fold, from our current burn rate of 13.5 TW to 28 – 35 TW by 2050 (TW = 10^{12} watts). The challenge for science is to meet this energy need in a secure, sustainable and environmentally responsible way. This additional energy needed for 2050, over the current 13.5 TW energy base, is simply not attainable from long discussed sources – these include nuclear, biomass, wind, geothermal and hydroelectric. The global appetite for energy is simply too much. Petroleum-based fuel sources (i.e., coal, oil and gas) could be increased. However, deleterious consequences resulting from external drivers of economy, the environment, and global security dictate that this energy need be met by renewable and sustainable sources.

Of the possible sustainable and renewable carbon-neutral energy sources, sunlight is preminent. If photosynthesis can be duplicated outside of the leaf – an artificial photosynthesis if you will – then the sun's energy can be harnessed as a fuel. The combination of water and light from the sun can be used to produce hydrogen and oxygen. The hydrogen can then be combined with the oxygen in a fuel cell to give back water and energy. In the overall cycle, sunlight is converted to useful energy. But here is the catch. A response to this “grand challenge” of using water and sunlight to make a clean and sustainable fuel to power the planet faces a daunting endeavor - large expanses of *fundamental molecular science* await discovery for light-based energy conversion schemes to be enabled.

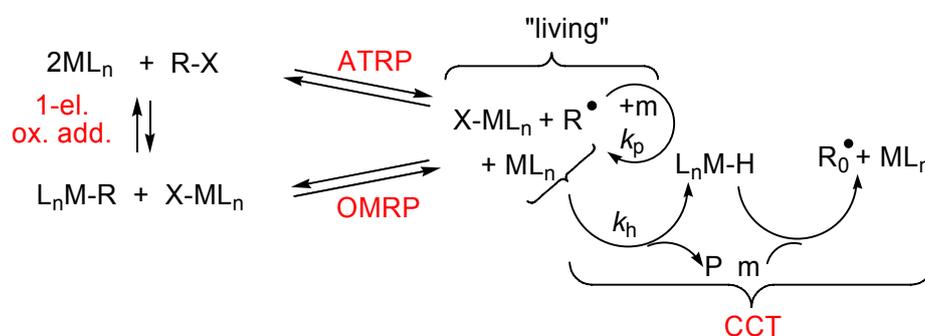
This talk will place the scale of the global energy issue in perspective and then discuss some of the basic science that is needed to emulate photosynthesis. With this basic science in place, the design of catalysts that produce hydrogen and oxygen from water will be presented.

Tuesday Morning Sessions

Controlled radical polymerization mediated by transition metal complexes: new mechanistic twists and perspectives

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The use of metals to achieve a controlled radical polymerization, namely a pseudo-living chain growth process, has been pioneered by Wayland¹ using the reversible formation of metal-carbon bonds (what we call OrganoMetallic Radical Polymerization, OMRP) and by Matyjaszewski² and Sawamoto³ using halogen atom transfer from the chain-end of the polymer dormant species to a metal complex catalyst (Atom Transfer Radical Polymerization, ATRP). Transition metal complexes have also been used to carry out efficient catalytic chain transfer (CCT) in radical polymerization.⁴ We have demonstrated the possible interplay of the three mechanisms and described their relationship with the one-electron oxidative addition process.^{5,6}



Further knowledge in this area has been obtained from electrochemistry, from the synthesis and characterization of oxidized transition metal complex (ATRP spin trap and/or OMRP dormant species), from DFT calculations, and from polymerization studies. Recent developments in this area will be presented.

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Catalysis at the Interface Between Grafted Molecules and Heterogeneous Surfaces

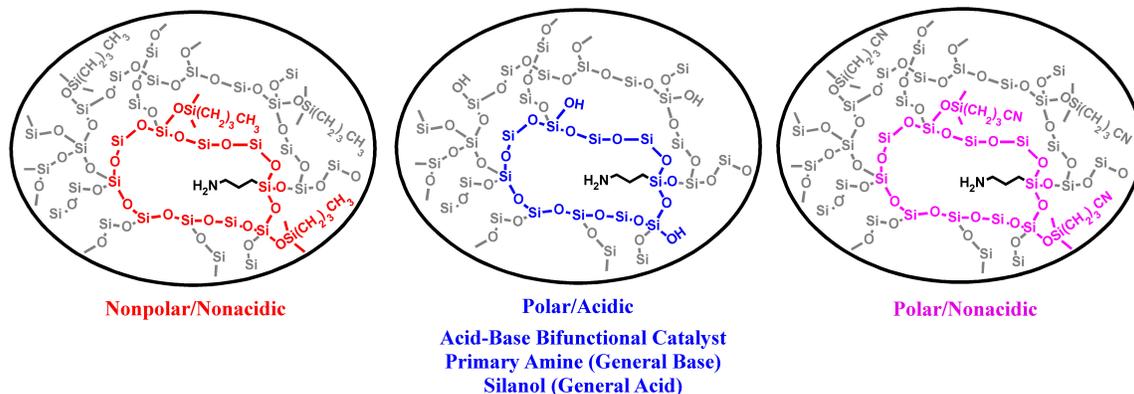
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Goal

Goal is to understand the role of inorganic surfaces in controlling organic and organometallic catalysis, by intentionally exploiting the surface as an active participant within the catalysis mechanism. The subtle interplay between the heterogeneous surface and active site facilitates the synthesis of highly active structures, some of which can be difficult to attain under homogeneous conditions. The knowledge gained in turn enables the synthesis of more globally optimized heterogeneous catalysts – in which the role of the surface as an inner- and outer-sphere ligand is incorporated within the catalyst design.

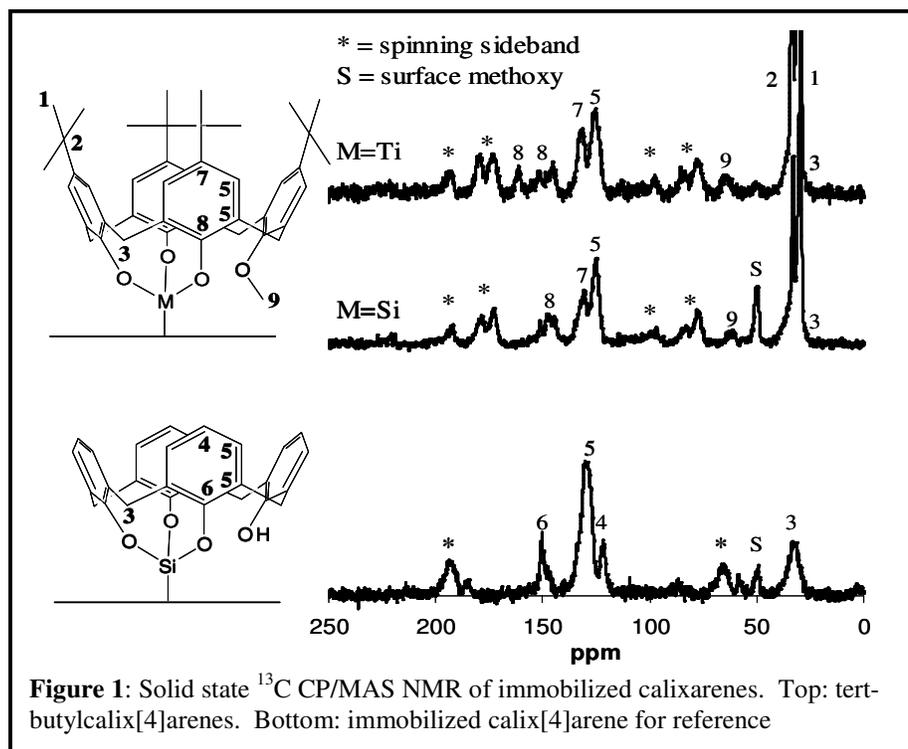
Recent Progress

Surface as Outer-Sphere Ligand: We have elucidated how silanols can cooperate with grafted primary amine base catalyst sites on silica, within the context of promoting versatile acid-base bifunctional heterogeneous catalysis. By capping silanols with cyano (polar/nonacidic) and methyl-terminated (nonpolar/nonacidic) functional groups as shown below, it was possible to separate outer-sphere dielectric effects from acid-base cooperativity for aldol-related catalysis rate and reaction mechanism. Silanol acidity shuttled heterogeneous aminocatalysis via a covalent iminium ion intermediate, which could be observed upon binding salicylaldehyde as a probe molecule. Primary amines located within an aprotic but polar cyano environment had comparable catalytic activity, but instead bound salicylaldehyde as a neutral imine tautomer and followed a previously postulated but experimentally unverified ion-pair catalysis mechanism.



Surface as Inner-Sphere Ligand:

Calixarene macrocycles have been used as robust multidentate ligands for the synthesis of surface organometallic complexes containing Ti on silica. These complexes (shown below) are highly active catalysts for the epoxidation of olefins using organic peroxides. The catalyst was shown to have the same activity, on a per Ti basis, regardless of the synthesized surface density of Ti, justifying the claim of a single-site material. Importantly, the calixarene as ligand remains coordinated to the metal center, even under ligand exchanges processes. This in principle enables steric and electronic control of the heterogeneous catalytic cycle via choice of calixarene ligand.



Future Plans

A direction that is currently being pursued is the synthesis of electron-withdrawing and donating substituents on the calixarene, with subsequent investigation on effect on epoxidation catalysis in the resulting surface organometallic complex with Ti. We have also extended our synthesis method to include the class of hexahomooxacalix[3]arenes. Characterization studies have involved using XANES for characterizing the local environment around the Ti center. Another direction is the role of the support as an inner-sphere ligand. Recent success in extending the synthesis concept to other inorganic-oxide surfaces opens a potentially new method for functionalizing surfaces with calixarene ligands. These new classes of hybrid organic-inorganic materials have tailorable spectroscopic properties and catalytic activities.

Publications 2004-2006

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“Grafted Metallocalixarenes as Single-Site Surface Organometallic Catalysts” by J. M. Notestein, E. Iglesia, and A. Katz*, *J. Am. Chem. Soc.* 2004, 126, 16478-16486. Publication 9 has been highlighted in *C&E News* on September 27, 2004 (volume 82, number 39, p. 24) and as a Science Concentrate in *C&E News* on December 6, 2004 (volume 82, number 9, p. 33).

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“Acid-Base Bifunctional and Dielectric Outer-Sphere Effects in Heterogeneous Catalysis: A Comparative Investigation of Model Primary Amine Catalysts” by J. D. Bass, A. Solovyov, A. J. Pascall, and A. Katz*, *J. Am. Chem. Soc.* 2006, 128, 3737-3747. Publication 16 has been highlighted as a Science Concentrate in *C&E News* on March 6, 2006 (volume 84, number 10, p. 62).

“Bifunctional Thermolytic Imprinting of Silica: Synthesis and Characterization of Discrete Thiol-Amine Functional Group Pairs” by J. D. Bass and A. Katz*, *Chem. Mater.* 2006, 18, 1611-1620.

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Elena V. Rybak-Akimova

Toward Mechanism-Based Design of Biomimetic Green Oxidation Catalysts: Identifying Active Species in Oxygen and Peroxide Activation at Non-Heme Iron Centers

Students: Sonia Taktak, Ivan V. Korendovych, Sergei V. Kryatov, Wanhua Ye, Margaret M. Flook.

Collaborators: Lawrence Que, Jr. (University of Minnesota); William M. Reiff (Northeastern U.); Richard S. Staples (Harvard); Bruce M. Foxman (Brandeis).

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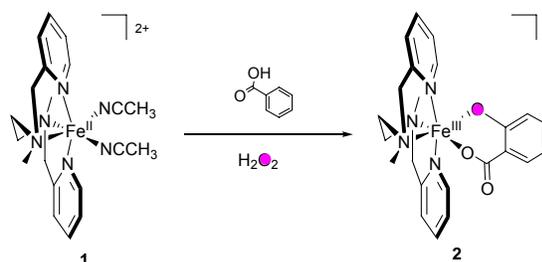
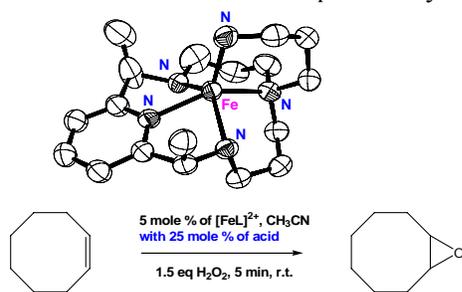
Goal.

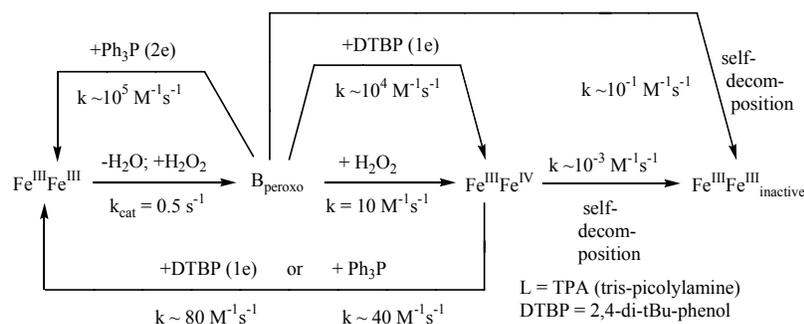
The long-term goal of the project is to develop efficient and selective catalytic systems for green oxidations using hydrogen peroxide or dioxygen as oxidants that do not generate environmentally harmful wastes. Dioxygen and hydrogen peroxide are ideal oxidants because they are readily available and environmentally clean, producing water as the only byproduct. These reagents allow for the most efficient, atom-economy approach to oxidative functionalization of organic molecules, thus saving energy in chemical synthesis. Non-toxic, biocompatible iron complexes will be used as catalysts acting similarly to natural iron-containing oxidative enzymes. Identification of kinetically competent intermediates (transient, very reactive species) is critical for the synthesis of useful, selective and efficient oxidation catalysts utilizing dioxygen and hydrogen peroxide as terminal oxidants.

Recent Progress.

Mononuclear iron(II) complexes with pyridine-containing macrocycles, which were designed as structural models of the active site in iron bleomycin, model oxygen transfer reactions of activated bleomycin. Efficient epoxidation of cyclic and terminal olefins with hydrogen peroxide occurs under mild conditions (Reaction 1). Reactivity is controlled by the concentration of protons, suggesting iron(III)-hydroperoxo species as possible intermediates in oxygen transfer.

Another mononuclear iron(II) complex, Fe(BPMEN)²⁺, promotes highly selective and efficient aromatic hydroxylation with hydrogen peroxide (Reaction 2). Even though both the starting material (1) and the reaction product (crystallographically characterized salicylate 2) contain only one iron center, preliminary kinetic studies indicate that aromatic hydroxylation is second order in iron complex. It is therefore likely that Reaction 2 requires bimetallic activation of hydrogen peroxide. Synthetically useful reaction (2) also provides a unique mechanistic handle, both the hydroperoxo intermediate and the salicylate product have distinct spectroscopic signatures. Scope and mechanism of this reaction will be discussed and related to previously reported catalytic olefin epoxidation and alkane hydroxylation.





Finally, the results of cryogenic stopped-flow studies of oxidation reactions with dinuclear Fe(III)-TPA complexes will be discussed. The diiron hydroperoxo species B(peroxo) is significantly more reactive with phosphines and phenols than the high-valent Fe(III)Fe(IV) intermediate. In diiron systems, coordination of -OOH to one iron(III) center with concomitant substrate binding at the second iron(III)

center appears to yield the most efficient oxidants for various reactions, including aromatic hydroxylation. High selectivity of reactions suggests that metal-based oxidants rather than hydroxyl radicals are involved.

Selected Recent Publications.

S.V. Kryatov, E.V. Rybak-Akimova, S.Schindler. Kinetics and mechanisms of formation and reactivity of non-heme iron oxygen intermediates. *Chem Rev.* **2005**, *105*, 2175-2226 (Invited review for a special issue on inorganic and bioinorganic reaction mechanisms).

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S. Taktak; M. Flook; B. M. Foxman; L. Que, Jr.; E.V. Rybak-Akimova ortho-Hydroxylation of benzoic acids with hydrogen peroxide at a non-heme iron center. *Chem. Commun.* **2005**, *42*, 5301-5303.

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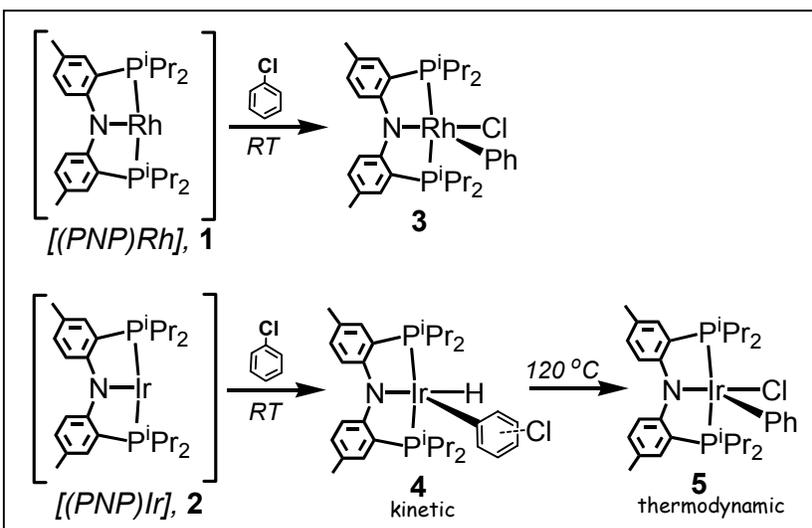
Bond-breaking and bond-making processes at PNP-ligated metal centers

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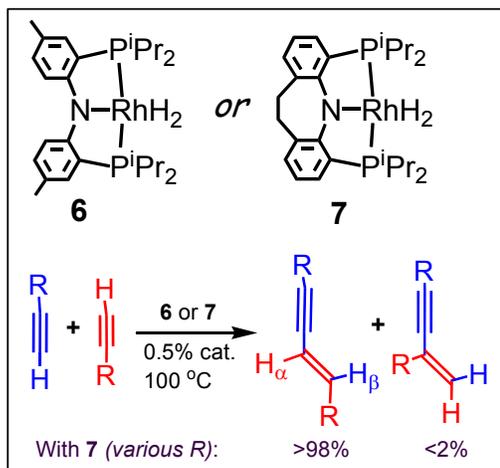
We have recently pioneered several directions in the use of the diarylamido-based PNP ligand class (such as that in **1**). The PNP system is robust and rigid, and binds very strongly (and essentially irreversibly) to late transition metals. Our broad objective is to take advantage of the predictability of the unremitting PNP binding in catalysis.

C-H vs C-X oxidative addition. A great variety of catalytic cycles incorporate oxidative addition (OA) of either C-H or C-X (carbon-heteroatom) bonds to transition metal centers. In some sense, the balance between these two processes is underexplored. We have recently discovered that the unsaturated [(PNP)Rh] (**1**) and [(PNP)Ir] (**2**) fragments (generated in situ) react differently with PhCl and other haloarenes. At room temperature, **1** undergoes exclusively C-Cl OA, while **2** – almost exclusively C-H OA.



Although this difference was rather puzzling at first, we were able to demonstrate that both cases the C-Cl OA is thermodynamically preferred and the observation of C-H OA for Ir is a matter of higher longevity of the kinetic C-H OA products for Ir vs Rh. We have since observed similar reactivity towards C-H vs other C-X bonds (C-O, C-N, C-S, etc.). It is intriguing whether this relationship between kinetic preference for C-H OA and thermodynamic preference for C-X OA is general for Rh/Ir or possibly even for other transition metals.

Alkyne dimerization. We discovered that **6** is an active alkyne dimerization catalyst. A small variation in the ligand (“tied-back” pincer in **7**) led to a substantial improvement of both the reactivity and activity. The influence of this ligand change is of steric, not electronic nature and demonstrates the versatility of the PNP ligand framework.



Tuesday Evening Sessions

Oxidations of C–H and O–H bonds by metal complexes via hydrogen atom transfer and possibly concerted pathways

James M. Mayer, Justine P. Roth, Elizabeth A. Mader, Adam Wu, Karine Valliant-Saunders, Takao Osako, Eric J. Watson S.J., Ahmad Dehestani, Brian C. Bales

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Metal-mediated catalytic oxidation reactions are challenging to develop and study, in part because the nature of the active oxidant is usually not known. Mechanistic understanding will be key to optimizing such reactions. This presentation will describe reactions of a number of stable, isolated oxidants whose properties are well understood, from metal oxides to coordination compounds. These and other studies indicate that the most common mechanism for the oxidation of C–H and O–H bonds is hydrogen atom abstraction. Examples include oxidations of alkylaromatic compounds by a ruthenium oxo complex and oxidations of weak O–H bonds by iron(III) complexes. These reactions involve proton transfer to a ligand concerted with electron transfer to the metal, and their rate constants can often be predicted by Marcus Theory. In the second half of the talk, OsO₄ oxidations of σ bonds (H–H, C–H, Si–H, and O–H) will be described, with the suggestion that at least some of these occur by a concerted [3+2] mechanism. The surprising observation that methane inhibits an aqueous methanol oxidation will also be presented.

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DE-FG02-03ER15464
DE-FG02-03ER15465

Tony F. Heinz, Stephen O'Brien
Ludwig Bartels
Talat S. Rahman

**Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes
Through Tailored Nanostructures.**

Collaborators: R. Adzic (Brookhaven National Lab), P. Feibelman (Sandia), T.F. Heinz (Columbia University), J. Murray (IBM Watson Research Center), S. O'Brien (Columbia University), T.S. Rahman (Kansas State University)

Postdoc: A. Liu, B. V. Rao, A. Thoss, K. L. Wong*, D. Vempaire, R. Fawcett*, K.-Y. Kwon*

Students: R. Frisbee*, T. Jiao*, K.Y. Kwon, X. Lin*, G. Pawin*, R. Perry (together with T.S. Rahman), E. Ulin-Avila, J. Zhang

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Project Start Date: 9/15/03 (* = current)

Project Goal

The overarching goal of this program is to lay the scientific foundations for a new class of heterogeneous catalysts in which materials with nanoscale structuring are utilized to control the flow of reactants to and products from optimized reaction sites and, to the extent possible, to control the flow of energy released in the surface reactions.

Bartels focus in this project is on the investigation and characterization of (a) the dynamic behavior of adsorbates on metal surfaces as a foundation for the development of methods that enhance catalytic activity of supported nanoparticles by steering the diffusion of reactants towards active centers; (b) Substrate-mediated adsorbate excitation and adsorbate-adsorbate excitation transfer that induce/influence relevant surfaces reactions.

DOE Interest

Catalytic reactions have great importance for a broad range of industrial and environmental processes including e.g. catalytic CO oxidation in exhaust systems, 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.

Research Plan and Results

Our vision of a new class of catalysts calls for substrate structures that guide the motion of adsorbates towards catalytically active sites. Realistic catalysts generally consist only to a small fraction of the material to which the catalytic activity is attributed, the remainder being support

and a matrix/binder. This renders efficient transport of the reactants to the active sites an issue with great potential impact.

Guiding Surface Diffusion by Adsorbate-Substrate and Adsorbate-Adsorbate Interactions

In this context, we performed fundamental investigations on a) how the interactions between adsorbate and substrate can guide surface diffusion and b) how interactions with neighboring adsorbates modify surface mobility. Both of these research efforts were conducted on a Cu(111) surface, which offers a top layer of sixfold symmetry (threefold symmetry, if the second layer is included). fcc(111) surfaces are the equilibrium surfaces of many metals (Ag, Au, Cu, Pd, etc.), which renders the hexagonal (111) motif the one most commonly expressed in metallic micro- and nanoparticles. Generally, hexagonal surfaces are regarded as exhibiting the highest symmetry for crystalline media. They are also among the least reactive, which renders transport across them towards sites of greater activity (e.g., step-edges, other surface irregularities, and regions of different composition) even more important.

Surfaces of lower symmetry are known to guide the diffusion of adsorbates along their structural features (e.g., atomic rows on (110) surfaces, step-edges on regularly stepped surfaces, etc.). STM investigations have been tremendously useful in both elucidating and quantifying the details of such processes. Our investigations have shown that similar 1-dimensional guidance can be achieved on the hexagonal fcc(111) surface despite the *absence of structural differences along the three equivalent in-plane directions*. The origin of this guidance effect is completely different from the familiar influence of the inherent surface anisotropy. It arises from the detailed molecule/surface interaction. We demonstrated this effect using a molecule, 9,10-diacetylthioanthracene (DTA), that we designed for this purpose. We found that when deposited on a Cu(111) substrate a DTA molecule diffuses exclusively along the direction in which it is initially aligned. This behavior amounts to a breaking the substrate symmetry. It converts a 2D random walk into a 1D phenomenon. The guiding principle in the design of the DTA molecule was the transfer of the concept of bipedal locomotion (i.e., walking) to the scale of individual molecules. In particular, we could show that if adsorbate-substrate interactions require at least one of a molecule's substrate linkers be attached to the surface at all times, guiding of the molecule's diffusive motion can be achieved (Fig. 1). The novelty of this guided diffusion process earned the findings widespread attention in the scientific community, including mentioning in C&EN news and as one of the 25 'Physics Top Stories for 2005'.

We also addressed the diffusion and reaction of smaller molecules. In this case our interest was to understand distinctive changes in the rates induced by *local changes in the chemical or structural environment of a molecule*. These investigations also included both theoretical and experimental components. The theoretical component was based on the use of Density Functional Theory calculations for a wide range of surface configurations. For example, PI Rahman calculated the barriers for successive abstraction of all hydrogen atoms from ammonia adsorbed at a variety of sites on nickel and palladium surfaces.

On the experimental side, we explored the impact of intermolecular interactions on the surface dynamics in the model system CO/Cu(111). It is generally understood that higher adsorbate coverages lead to

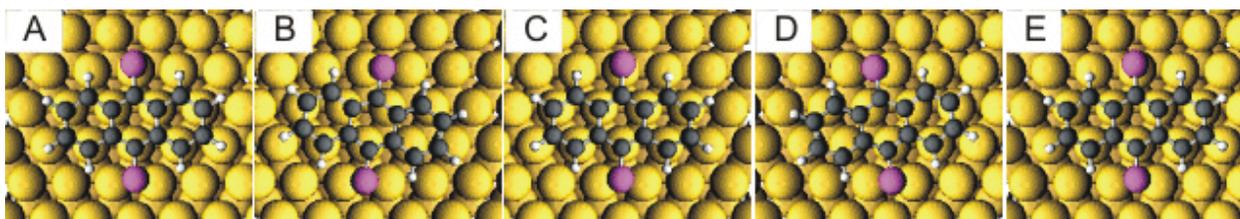


Fig. 1 Molecular configurations during the linear diffusion of DTA on a Cu(111) surface. At any instant either one of the sulfur (purple) substrate linkers is outside a favorable hollow site or the ring system as a whole is misaligned with the substrate.

higher diffusion rates because the diffusion barrier is related to the adsorption energy, which typically decreases with increasing adsorbate coverage. In the literature there is, however, very little direct quantitative evidence to support this view point. The exception are experiments of repeated local

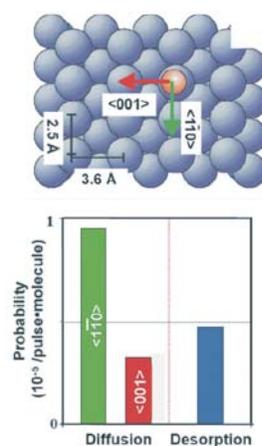


Fig. 3 Distribution of CO reactions following femtosecond substrate heating for the CO/Cu(110) system. The different reactions observed are associated with a wide range of activation barriers.

photodesorption of surfaces and LEEM/PEEM measurements of reaction fronts, which have somewhat limited spatial resolution. We performed STM measurements in which we created local coverage gradients by means of tip-based desorption of CO molecules from a completely covered substrate. By following the diffusion of molecules back into the depleted region, we could measure the surface diffusivity as a function of local coverage. We found that the diffusivity increases by more than a factor of 3 as the coverage increases from the low-coverage limit of isolated molecules (Fig. 2). This finding underscores the impact of the local environment on surface dynamic processes. To probe the intermolecular interactions at the core of this phenomenon, we investigated how the diffusive motion of pairs of CO molecules differs from that of the isolated species. As in literature investigations of Cu/Cu(111) and CO/Pd(111), we found that certain separations for the two partners are preferred. Unlike the earlier studies, we examined diffusive motion as a function of the intermolecular separation. From such data, variations of the adsorption potential and of the diffusion barriers between different adsites can be obtained (Fig. 2) that have a statistical error of $\leq 1\%$ of the total diffusion barrier (i.e., in the sub-meV range for the case of CO/Cu(111)). Data from this investigation can be used to model the acceleration of surface diffusion with increasing coverage up to the point at which collective adsorbate interactions are not well reproduced by a linear combination of pair interactions.

Adsorbate and Energy-Flow Dynamics following Ultrafast Substrate Excitation

The experimental work described above proceeded at cryogenic temperatures in order to limit the diffusion rate of the reactants to a regime compatible with the seconds scanning rate of our STM. Under realistic catalytic conditions, in which the reactant thermal energy is sufficient to induce the chemical transformation of reactants to products, diffusion (with its very low barrier) is expected to be an extremely rapid phenomenon – so rapid that adsorbates cannot be traced by STM. At cryogenic temperatures the branching ratio between diffusion and high-energy processes is very much to the disfavor of the latter and even extensive STM investigations are generally not able to observe chemical transformation of reactants unless other sources of excitation (e.g. the tunneling current) are used. To circumvent this problem, we developed a technique based on alternated imaging of a surface area by STM and femtosecond optical excitation. Although the experiments are conceptually straightforward, success would not have been possible without a combination of the STM-expertise of PI Bartels (e.g. development of dedicated control circuitry to interface the laser and to prevent adverse effects of tip illumination) and the expertise of PI Heinz in optically driven surface processes.

Application of ultra-short high-energy laser pulses at photon energies that are non-resonant to adsorbate transitions does generally not cause adsorbate reactions directly. The photons are rather absorbed by the electrons of the substrate surface, which causes their effective temperature to rise dramatically during a

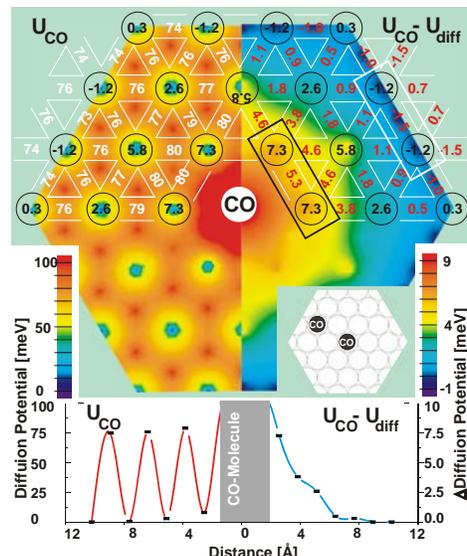
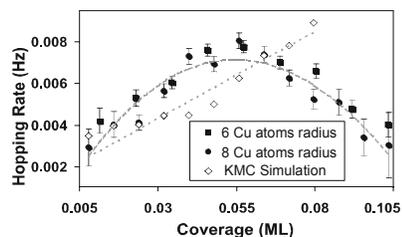


Fig. 2 (top) Variations of CO/Cu(111) diffusivity in dependence on the local coverage; (bottom) The diffusion potential of a CO molecule in the vicinity of another one located at the center of the plot (right) and its variation from the unperturbed potential (left). All values in meV.

short transient until they are able to dissipate the deposited energy via diffusion into the bulk and via coupling to the phononic/vibrational degrees of freedom of the substrate and of adsorbed atoms/molecules. Our measurements for the CO/Cu(110) system showed that under such conditions the rates of desorption and of diffusion along and across the substrate atomic rows are similar (Fig. 3). This is in marked contrast to STM experiments in thermal equilibrium, where only diffusion along the row is observed. Observation of a ratio of the rates for desorption and diffusion of ≈ 10 despite the fact that the barrier for CO-desorption is ≈ 5 times higher than that for diffusion, indicates that (a) a very high excitation level of the adsorbates is reached and (b) that these experiments can provide data on the effectiveness of the energy flow dynamics between different adsorbate modes, the substrate electronic bath and its phononic bath. We wish to explore these phenomena further, experimentally and theoretically. It is also noteworthy that the thermal transient of the substrate electrons is at the same time so brief and so intensive, that energetic surface reactions can occur without being obscured by a massive number of diffusion events.

Results with Minor or No Direct Involvement of Bartels

Binary Nanoparticle Superlattices: So far, we focused on combining two *different* types of nanoparticles with the goal of obtaining potentially valuable neighbor-neighbor interactions on the nanoscale. Very little is known about the collective properties of any multicomponent superlattice and there are literally only a few reports in the literature so far. Collaborators O'Brien and Murray are leaders in the materials discovery process and believe that this new class of materials presents opportunities in the rational design of new catalysts.

Catalytic Growth of Carbon Nanotubes: During the current grant period, PI O'Brien has developed advanced CVD growth capabilities. The method can produce single-walled nanotubes with lengths up to the centimeter scale. These nanotubes are highly oriented spatially and their origin is defined by the placement of the catalyst. This allowed high-precision optical investigation of their properties by PI Heinz.

Theoretical Investigation of Nanoparticle Surfaces: Traditional first principles calculations are based on “zero-temperature” and “zero-pressure” techniques, while real catalysts work at finite temperature and in contact with a gas-phase environment at ambient pressure. As shown recently for of RuO₂, exchange of chemical species with the environment causes dramatic modifications of the surface structure, composition and geometry, that in turn change the mechanism of the catalytic reaction fundamentally. We develop *ab initio* thermodynamics approaches capable of treating nanoparticle surface in equilibrium with a gas phase environment.

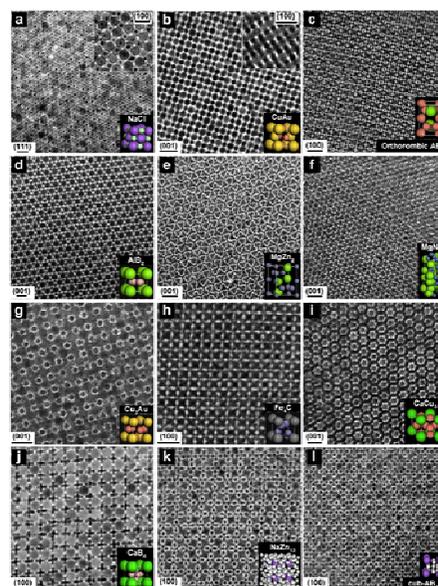


Fig. 4 TEM images of the characteristic projections of the binary superlattices, self-assembled from different nanoparticles, and modeled unit cells of the corresponding three-dimensional structures.

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Mechanism and Design in Homogeneous Catalysis

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Goal

Our primary goal is to understand the fundamental metal-alkyl reactivity patterns that govern activity, selectivity, and catalyst deactivation in catalytic alkene polymerization. Development of new techniques for studying catalysts under realistic conditions play a prominent role in this work. We are developing new NMR and mass spectrometric methods for studying catalytic reactions, with an emphasis on catalytic alkene polymerization. Features of these methods include access to very fast rates (>100 turnovers/s), the ability to determine multiple kinetic parameters and active site counts in a few experiments, and amenability to automated, high-throughput data collection.

Recent Progress

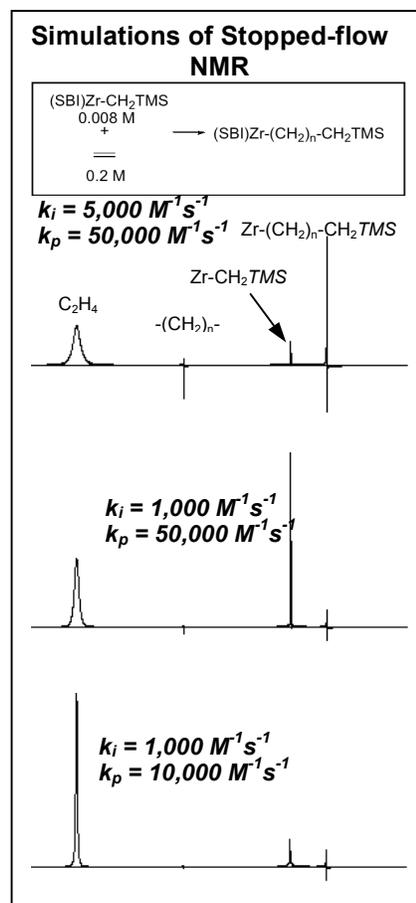
For both metallocene and non-metallocene polymerization catalysts, the ultimate goal is to understand the influence of ligand and counterion structure on the reactivity patterns of metal alkyls with respect to insertion, chain transfer, and catalyst deactivation processes. We recently have completed a thorough examination of the fundamental reactivity of the propagating species in authentic alkene polymerization processes toward different alkenes and dihydrogen. These studies reveal that molecular hydrogen reacts at very different rates with primary and secondary alkyls. Although secondary alkyls, which are formed by relatively rare 2,1-insertion of the alkene into to the metal-polymer bond, have a low steady-state concentration their high reactivity towards dihydrogen means that much of the flux of chain transfer to H₂ may take place through hydrogenolysis of the secondary alkyl. This observation suggests that control of regioselectivity is critical to tuning a catalyst's response to chain transfer to H₂.

Another focus of our work concerns the formation of metallocene-allyls under catalytic polymerization conditions, a pathway that has been purported to remove much of the catalyst from active participation in catalysis. We recently have observed rapid allyl formation under catalytic polymerization conditions. Current data unambiguously demonstrate rapid formation of two diastereomeric Zr-allyls when 1-hexene is polymerized with the catalyst precursor [(*rac*-SBI)ZrCH₂SiMe₃][B(C₆F₅)₄]. Preliminary data are consistent with allyl formation via β -H transfer to metal (to yield a hydrido metal alkene complex) followed by σ -bond metathesis of the allylic C-H bond with the Zr-H bond to yield Zr-allyls and H₂. It appears that the coordinated alkene does not dissociate from the metal during this process.

Catalysis of alkene polymerization, especially under industrial conditions (non-coordinating ions, high alkene concentration, rapid catalysis), illustrate the limitations of current NMR and quenched-flow methods: the time scales are too slow, too little specific information is obtained, and resolution of fundamental questions is too time-consuming. For these reasons we have turned our attention to the development of new methods.

Advances in Rapid Kinetics Methods

Two general problems in catalysis that are particularly relevant to alkene polymerization catalysts are (1) how much of the catalyst is active and (2) what are the rate laws for very fast processes? We have undertaken the development of two methods, stopped-flow NMR and quenched-flow mass spectrometry, to address these issues. Critical attributes of these methods include the ability to resolve active vs. inactive catalysts, data collection at millisecond time scales, and the potential for automated, high-throughput operation. In principle, each method is capable of determining complete kinetic profiles very efficiently: in principle it may be feasible to collect all data needed to determine the rate laws of initiation, propagation, and termination for an industrially relevant catalyst in fifteen minutes.



Although it has not been generally recognized, stopped-flow NMR has the capability of obtaining very fast kinetic data with the resolution and density of information unique to NMR spectroscopy. We have developed the theory for modeling rapid NMR kinetics and probe assembly for collecting data. Data collection and calibration have begun.

Mass spectrometric analysis of polyolefin polymerization kinetics relies on simultaneously quenching polymerization and attaching an ionizable group on the hydrocarbon polymer chain end. We have established that metallocene-polymeryl species react rapidly and quantitatively with aryl isocyanates and various carbodiimides to accomplish both quenching and attachment of an ionizable group. Preliminary data suggest that mass spectral analysis by ESI-MS is feasible, but more work is needed to establish whether the method is quantitative.

DOE Interest

Effective catalysis must be a centerpoint in developing and efficiently utilizing energy sources. We are developing powerful tools for examining catalyst speciation and kinetics and applying them to catalytic alkene polymerization, the largest non-combustive use of hydrocarbon resources that is experiencing rapid growth due to developments in homogeneous catalysis.

Future Plans

Our plans are to continue to push forward the understanding of rapid, catalytic processes through rapid NMR and mass spectrometric methods.

Publications Resulting from DOE Support for This Grant Period

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5. 'Direct Observation of Insertion Events at (EBI)Zr(MeB(C₆F₅)₃)-Polymeryl Intermediates: Distinction Between Continuous and Intermittent Propagation Modes' Clark R. Landis, Kimberly A. Rosaaen, Douglass R. Sillars *J. Am. Chem. Soc.* **2003**, 125, 1710-1711.
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Wednesday Morning Sessions

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

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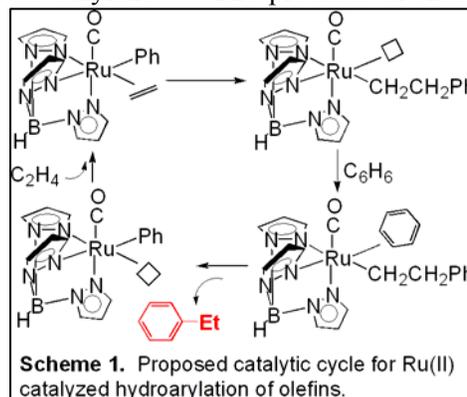
Collaborators: Thomas R. Cundari (University of North Texas)

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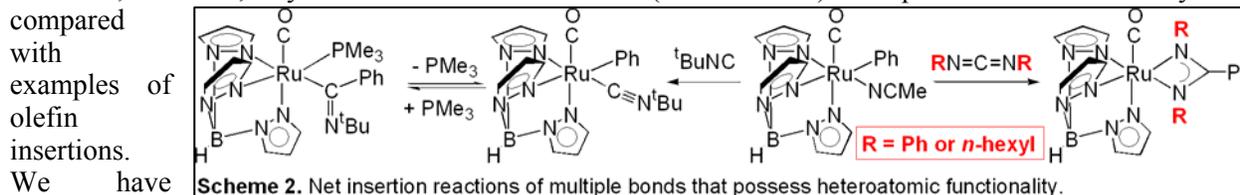
Goals: The overall goal is to increase understanding of fundamental aspects surrounding homogeneous catalysts for the addition of aromatic carbon-hydrogen bonds across multiple bonds (especially olefins). These details will facilitate the rational design of future catalysts for hydroarylation of carbon-carbon multiple bonds and other unsaturated organic substrates. Development of new catalyst systems will increase the scope of available synthetic methodologies for the conversion of C-H bonds into useful materials.

Recent Progress

Catalytic Hydrophenylation: Our initial studies revealed that $\text{TpRu}(\text{CO})(\text{NCMe})\text{R}$ ($\text{R} = \text{CH}_3$, $\text{CH}_2\text{CH}_2\text{Ph}$, Ph , 2-thienyl or 2-furyl; $\text{Tp} = \text{hydridotris}(\text{pyrazolyl})\text{borate}$) complexes serve as catalyst precursors for the addition of aromatic C-H bonds across C=C bonds. For example, $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$ catalyzes the addition of benzene C-H bonds across the double bonds of ethylene and α -olefins, and $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ar}$ ($\text{Ar} = 2\text{-furyl}$ or 2-thienyl) systems catalyze the regioselective addition of the 2-position C-H bond of furan or thiophene across ethylene.¹⁻³ The products of these reactions are alkylaromatic compounds, and the reactions that incorporate α -olefins are moderately selective for linear over branched products. Detailed mechanistic studies reveal that the transformations do not proceed via traditional Friedel-Crafts mechanisms. Rather, the Ru(II) metal center serves to directly mediate both C-H activation and C-C coupling steps (Scheme 1).^{2,3} Since our efforts toward mechanistic elucidation, we have been working to: 1) develop the scope of reactivity accessible with $\text{TpRu}(\text{CO})(\text{NCMe})\text{R}$, 2) study insertion reactions of unsaturated substrates that possess heteroatomic functionality with $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$, 3) prepare systems of the type $\text{TpRu}(\text{L})(\text{NCMe})\text{R}$ ($\text{L} = \text{PMe}_3$, $\text{P}(\text{N-pyrrolyl})_3$ and $\text{P}(\text{OMe})_3$) and $\text{MpRu}(\text{L})(\text{Cl})\text{R}$ ($\text{Mp} = \text{tris}(\text{pyrazolyl})\text{methane}$; $\text{L} = \text{PMe}_3$, $\text{P}(\text{OMe})_3$ or pyridine) and study their ability to initiate stoichiometric and catalytic C-H activation.



Insertion Reactions: Extension of catalytic hydroarylation of olefins to multiple bonds that possess heteroatomic functionality would provide potentially convenient routes to functionalized materials; however, key insertion reactions of C-X ($\text{X} = \text{O}$ or N) multiple bonds are relatively rare compared



with examples of olefin insertions. We have reacted $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$ with imines, isocyanides, aldehydes, ketones, carbodiimides, isocyanates and carboxamides with some results shown in Scheme 2. Combined experimental and computational studies (in collaboration with Prof. Cundari, U. of North Texas) allowed the following conclusions: 1) the scarcity of direct observation of insertion of C-N or C-O multiple bonds into M-H, M-R or M-Ar bonds is not likely attributable *in general* to an inherently substantial activation barriers due to the large BDEs of C-N/C-O multiple bonds; 2) for $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$, the failure to observe imine insertions is proposed

to arise from a substantial activation barrier in combination with an unfavorable change in free energy for formation of the insertion product; 3) the failure to observe insertion of aldehyde C=O bonds is likely due to the highly favorable and kinetically accessible aldehyde C-H activation and subsequent decarbonylation; 4) insertion of isonitrile into the Ru-Ph bond of $\text{TpRu}(\text{CO})(\text{CN}^t\text{Bu})\text{Ph}$ is kinetically accessible yet thermally disfavored (in the absence of Lewis bases to trap the insertion product); 5) similar to imines, the insertion of carbodiimides is likely to proceed with a relatively high activation barrier; however, the insertion is overall thermodynamically favorable and directly observed since formation of the κ^2 -amidinate ligand provides a large enthalpic gain and driving force; and 6) computational studies suggest that the failure to observe insertion of ketones is potentially attributed to weak binding of the ketone and competition with acetonitrile for coordination to Ru. Thus, for systems of the type $\{\text{TpRu}(\text{L})(\text{R})\}$ that have been demonstrated to activate C-H bonds, catalytic reactions that involve the hydroarylation of C-X multiple bonds are potentially viable for some systems (e.g., carbodiimides and isonitriles) if conditions can be found for release of the products of insertion.

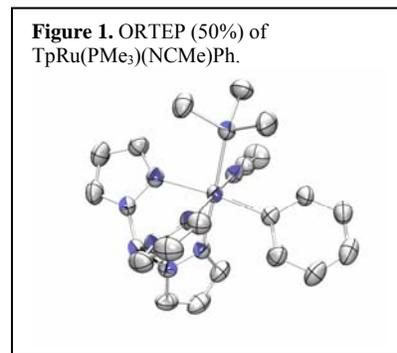
Reactions with Functionalized Olefins: Heating benzene solutions of $\text{TpRu}(\text{CO})(\text{NCMe})\text{R}$ (R = Me or Ph) with electron-deficient olefins (e.g., acrylonitrile, styrene or methylmethacrylate) results in the formation of polyolefins, and we have elucidated that the polymerization reactions likely involve a radical pathway.⁴ Follow-up studies on the stability of Ru(III) systems of the type $[\text{TpRu}(\text{L})(\text{L}')\text{R}]^+$ (L = L' = PMe_3 or L = NCMe and L' = CO ; R = alkyl or aryl) reveal that rapid Ru-R bond homolysis occurs.⁵ Combined with computational studies, we demonstrated that single-electron oxidation of Ru(II) $\text{TpRu}(\text{L})(\text{L}')\text{R}$ complexes to the Ru(III) cations likely decreases the Ru-R bond dissociation energy from ~ 50 kcal/mol to ~ 25 kcal/mol. Thus, at the Ru(III) oxidation state homolysis of Ru-R bonds is rapid, and polymerization of electron-deficient olefins by $\text{TpRu}(\text{CO})(\text{NCMe})\text{R}$ likely involves an initial oxidation to a transient Ru(III) complex followed by facile Ru-R bond homolysis to initiate the radical polymerization.

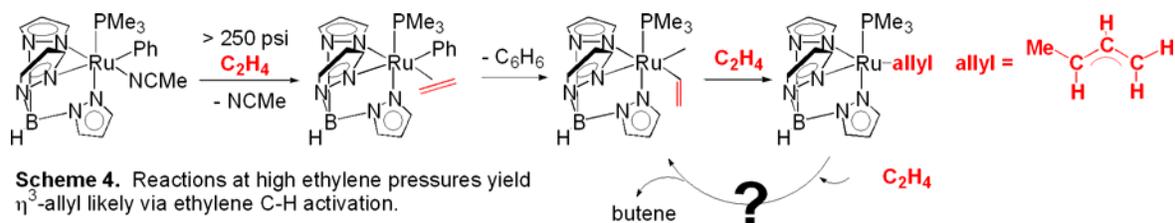
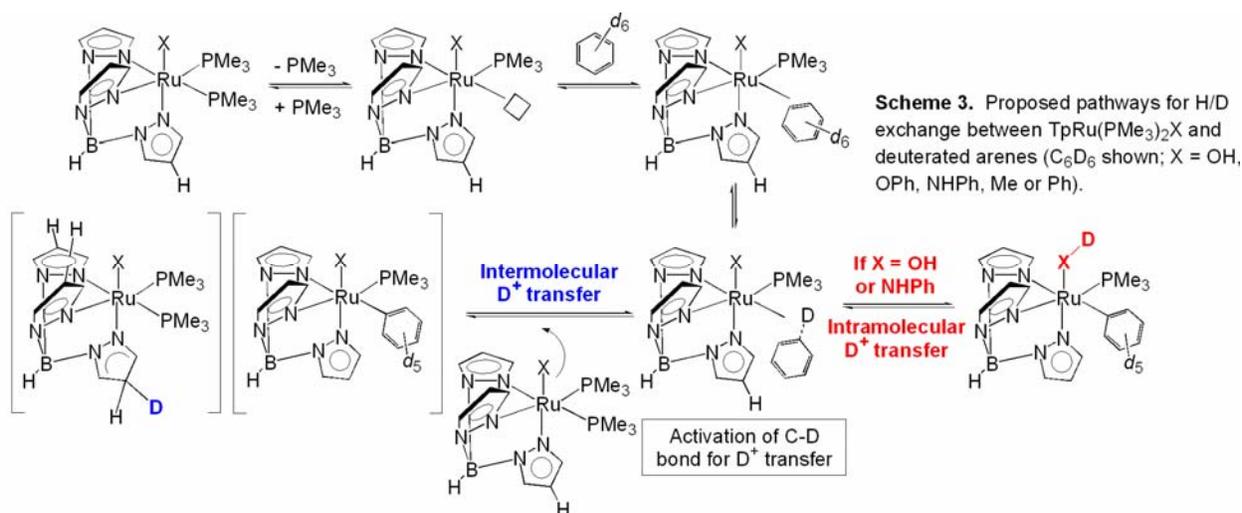
$\text{TpRu}(\text{L})(\text{NCMe})\text{R}$: In an effort to explore the impact of steric and electron properties of the catalyst system on various steps in the catalytic olefin hydroarylation, we have extended our studies to $\text{TpRu}(\text{L})(\text{NCMe})\text{R}$ {L = P(*N*-pyrrolyl), PMe_3 , P(OMe)₃} systems (Figure 1). In particular, we are interested in the impact of the electron donating ability of L on the activation barrier to metal-mediated C-H bond cleavage, the ability of L to control the regioselectivity of olefin insertion based on steric profile (and, hence, control of linear to branched ratios of organic products), and the influence of the identity of R on the activation barrier to C-H activation.

Through a series of mechanistic studies, we have elucidated that systems of the type $\text{TpRu}(\text{PMe}_3)_2\text{X}$ (X = OH, NHPH, OPh, Me or Ph) initiate aromatic C-H(D) activation as depicted in Scheme 3. The thermodynamics dictate that only starting materials are observed; however, isotopic labeling of the aromatic systems allows observation of deuterium scrambling consistent with the pathways shown in Scheme 3. Although the mechanism of the C-H activation step has not been determined in detail, experiments suggest that the metal-mediated C-H activation imparts acidic character to the C-H(D) bond, and the activated H(D) is transferred to a basic site (ligand X, 4-position of pyrrolyl or external substrate) with relative rates likely dependent upon, *inter alia*, the basicity of X or the external substrate.

$\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ has been prepared and provides relatively facile access to the coordinatively unsaturated system $\{\text{TpRu}(\text{PMe}_3)\text{Ph}\}$, which is isoelectronic to our previously studied olefin hydroarylation catalyst $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$. Net substitution of PMe_3 for CO allows us to study the impact of increased steric profile and electron-donor ability on catalysis. $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ activates benzene C-H(D) bonds more rapidly than $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$, and this system has been used to produce ethylbenzene from benzene and ethylene; however, the catalysis is slow and a side reaction with ethylene competes with the ethylene hydrophenylation. For example, reaction of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ with 50 psi of ethylene at 70 °C produces an allyl complex in a reaction that likely proceeds as depicted in Scheme 4.

Figure 1. ORTEP (50%) of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$.





MpRu(L)(Cl)R: For systems of the type $\text{TpRu}(\text{L})(\text{NCMe})\text{R}$, rapid activation of aromatic C-H bonds is limited by competition for coordination to Ru between NCMe and the aromatic substrate. Access to $\text{MpRu}(\text{L})(\text{Cl})\text{R}$ systems {Mp = tris(pyrazolyl)methane; L = PPh_3 , PMe_3 , $\text{P}(\text{OMe})_3$, pyridine or $\text{P}(\text{N-pyrrolyl})_3$ }, and replacement of chloride with a non-coordinating anion will afford access to coordinatively unsaturated systems $[\text{MpRu}(\text{L})\text{R}]^+$. We have prepared several precursors to these systems and will pursue studies of their ability to initiate stoichiometric and catalytic aromatic C-H activation.

DOE Interest: Development of more efficient routes for the conversion of hydrocarbons and other feedstocks derived from petroleum can result in cleaner chemical processes, reduced energy consumption as well as conservation of valuable chemical resources. Access to catalyst technologies for selective conversion of aromatic C-H bonds into functionalized materials is of potential value to both commodity and fine chemical markets. Increased understanding of fundamental aspects surrounding catalytic hydroarylation processes will facilitate the development of new catalysts for aromatic C-H functionalization sequences.

Future Plans: The following studies will be pursued in the near future: 1) Comparison of $\text{TpRu}(\text{L})(\text{NCMe})\text{R}$ systems in stoichiometric and catalytic C-H activation sequences with a focus on impact of electronics on the activation barrier to aromatic and olefinic C-H activation and the influence of steric profile on the regioselectivity of olefin insertion. On the latter topic, Figure 2 shows a space-filling model (from solid-state structure using X-ray diffraction) of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ generated by removing the NCMe ligand (the site where an olefin would bind). Inspection of this model suggests that coordination of an α -olefin with the "R" group oriented in the region between two pyrazolyl rings anti to the phenyl ligand is likely to be favored over either isomer

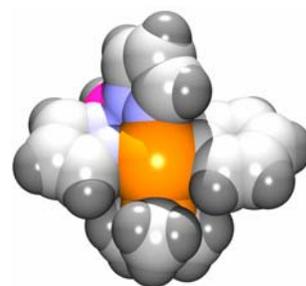


Figure 2. Space filling model of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ with NCMe removed.

with the "R" group syn to the phenyl ligand; 2) ability of [MpRu(L)R]⁺ systems to initiate stoichiometric and catalytic aromatic C-H activation; 3) ability of TpRu(PMe₃)(NCMe)Ph to catalyze intramolecular hydroarylation of multiple bonds that possess heteroatomic functionality (e.g., tethered isonitriles or carbodiimides). Such reactions would provide facile routes to nitrogen or oxygen containing heterocycles.

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Reactivity of Metal Hydrides in Atom Transfer Reactions and Homogeneous Catalysis

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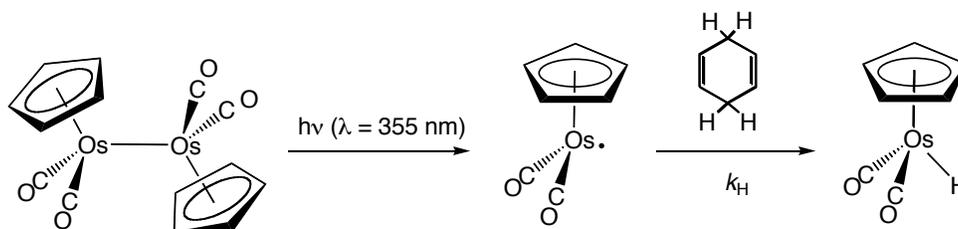
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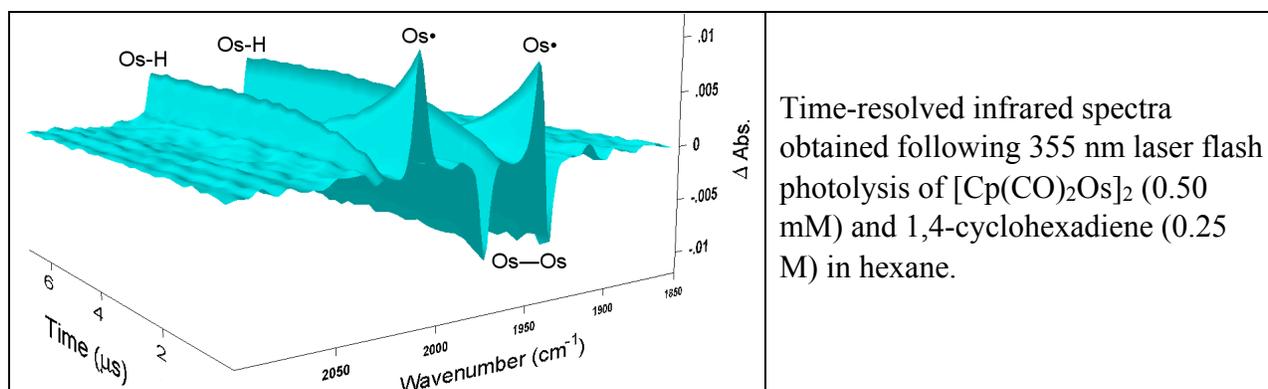
Goal

Improve our understanding of the reactivity of transition metal hydrides and related organometallic complexes. We focus on reactions where M-H bonds are ruptured or formed through transfer of a proton (H^+), a hydrogen atom (H^\bullet) or a hydride (H^-). Systematic studies, including kinetic and thermodynamic data, help to identify trends in reactivity that may be pertinent to a range of homogeneous processes. We seek to use the information gained from kinetic and mechanistic studies to help develop new homogeneous hydrogenation and hydrosilylation 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 or solvent-free processes.

Recent Progress

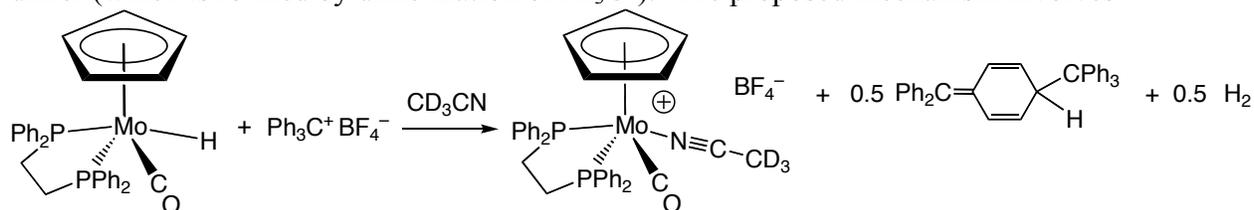
Carbon-to-Metal Hydrogen Atom Transfer Reactions. Hydrogen atom transfer reactions are fundamentally important in a variety of catalytic reactions. Hydrogen atom transfers *from* metal hydrides *to* carbon are known to be involved in certain types of hydrogenation processes, for example. We have begun to investigate the *opposite* process — H atom transfer *from* a C-H bond *to* a metal-centered radical, a reaction that could be pertinent in new schemes to activate C-H bonds. Photochemical homolysis of the metal-metal bond in the dimer $[Cp(CO)_2Os]_2$ produces the osmium-centered radical $Cp(CO)_2Os^\bullet$. In the presence 1,4-cyclohexadiene, carbon-to-metal hydrogen atom transfer occurs, leading to the formation of $Cp(CO)_2OsH$. Using flash photolysis and transient IR detection, the osmium-centered radical $Cp(CO)_2Os^\bullet$ was directly observed. We have determined the second-order rate constant, $k_H = (2.1 \pm 0.2) \times 10^6 M^{-1} s^{-1}$ at 23 °C, for the carbon-to-metal hydrogen atom transfer shown below.





The pK_a of $\text{Cp}(\text{CO})_2\text{OsH}$ in CD_3CN was experimentally determined to be 32.7. This Os hydride is more than 12 pK_a units less acidic than its first and second row congeners $\text{Cp}(\text{CO})_2\text{FeH}$ ($\text{pK}_a = 19.4$ in CH_3CN) or $\text{Cp}(\text{CO})_2\text{RuH}$ ($\text{pK}_a = 20.2$ in CH_3CN). An experimental lower limit of the Os-H BDE as 82 kcal/mol was obtained from a thermochemical cycle. The Os-H bond appears to be the strongest M-H yet determined for a metal carbonyl complex, and is among the strongest for *any* transition metal hydride bond.

Reactions of Metal Hydrides with Ph_3C^+ ; Hydride Transfer vs. One-Electron Oxidation. The kinetics of hydride transfer from a series of metal hydrides to $\text{Ph}_3\text{C}^+\text{BF}_4^-$ were studied previously. Second-order rate constants for hydride transfer span a range of about 10^6 , and mechanistic experiments showed that these were single-step hydride transfers. In contrast, we have found evidence for a different mechanism with a more electron-rich metal hydride. The reaction of $\text{CpMo}(\text{CO})(\text{dppe})\text{H}$ with one equivalent of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ in CD_3CN gives $[\text{CpMo}(\text{CO})(\text{dppe})(\text{NCCD}_3)]^+$ as the organometallic product, along with H_2 and Gomberg's dimer (which is formed by dimerization of $\text{Ph}_3\text{C}\cdot$). The proposed mechanism involves



one-electron oxidation of $\text{CpMo}(\text{CO})(\text{dppe})\text{H}$ by Ph_3C^+ , giving the radical cation complex $[\text{CpMo}(\text{CO})(\text{dppe})\text{H}]^{+\bullet}$. Proton transfer from $[\text{CpMo}(\text{CO})(\text{dppe})\text{H}]^{+\bullet}$ to $\text{CpMo}(\text{CO})(\text{dppe})\text{H}$, loss of H_2 from $[\text{CpMo}(\text{CO})(\text{dppe})(\text{H})_2]^+$, and oxidation of $\text{Cp}(\text{CO})(\text{dppe})\text{Mo}\cdot$ by Ph_3C^+ lead to the observed products. In the presence of an amine base, the stoichiometry changes, with two equivalents of Ph_3C^+ being required for each equivalent of $\text{CpMo}(\text{CO})(\text{dppe})\text{H}$ due to deprotonation of $[\text{CpMo}(\text{CO})(\text{dppe})\text{H}]^{+\bullet}$ by the amine.

DOE Interest

This research is aligned with the DOE goals of obtaining a more comprehensive understanding of the molecular details of homogeneous catalysts. By examining fundamental aspects of atom transfer reactions, we seek an understanding of the factors that influence the rates and mechanisms of atom transfer reactions, particularly those in which C-H or M-H bonds are made or broken. Such mechanistic information that may ultimately help guide the design of improved catalysts.

Future Plans

Carbon-to-Metal Hydrogen Atom Transfer. Laser flash photolysis and time-resolved infrared spectral measurements will be used to determine rate constants for a series of carbon-to-metal hydrogen atom transfers from hydrocarbons to photochemically generated metal-centered radicals. We seek to understand how the rate constant changes as the thermodynamics (bond dissociation energy of the C-H bond being cleaved) change, as well as to assess steric effects that may influence these hydrogen atom transfers. Rate constants will be measured for chlorine atom transfer from CCl_4 to metal-centered radicals, for comparison to the H atom transfers. Quantum yield measurements may help us to understand the details of the photochemical processes. Further studies are planned on $[\text{Tp}(\text{CO})_2\text{Os}]_2$, since initial experiments show that this complex, with a tris(pyrazolyl)borate ligand, reacts with hydrocarbons photochemically to cleave C-H bonds stronger than those found to work thus far with related dimers, e.g., $[\text{Cp}(\text{CO})_2\text{Os}]_2$. Determining how strong of a C-H bond can be cleaved in this type of reaction is a long-term goal.

Ionic Hydrogenations; Proton Transfer and Hydride Transfer Reactions of Metal Hydrides.

We previously found that hydride abstraction from $\text{CpW}(\text{CO})_2(\text{IMes})\text{H}$ (IMes = the N-heterocyclic carbene ligand 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) gives $\text{CpW}(\text{CO})_2(\text{IMes})^+$, a catalyst precursor for hydrogenation and hydrosilylation of ketones. In the solvent-free hydrosilylation of aliphatic ketones by HSiEt_3 , the catalyst precipitates at the end of the reaction, facilitating recycling and reuse of the catalyst. Ongoing and future experiments will vary the counterion and other changes in the metal complex, as we seek to understand the factors that influence catalyst self-precipitation and recycling.

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Poster Presentations

Silane Activation on a Single-Site Oxorhenium(V) Oxazoline Catalyst: A New Mechanistic Paradigm for Hydrogen Production and Hydrosilation

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Goal

Establish reaction dynamics, mechanisms, and the utility of oxorhenium coordination catalysts in reduction reactions and hydrogen production from organic liquids and water. Advance the synthetic methodologies available for preparing these single-site catalysts.

Recent Progress

Synthesis of cationic oxorhenium(V) complexes containing oxazoline and salen-type ancillary ligands: We have developed efficient, readily accessible, and high yielding (70-90% overall) pathways for preparing cationic oxorhenium(V) complexes with oxazoline and salen ancillary ligands. The oxazoline active catalyst, $[\text{Re}(\text{O})(\text{hoz})_2(\text{Solv})][\text{B}(\text{C}_6\text{F}_5)_4]$, is prepared from the chloride precursor via halide abstraction with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. In the case of rhenium salen complexes the most readily accessible compounds are dinuclear m-oxo bridged rhenium(V). Even though these dinuclear rhenium compounds have been known in the literature for two decades, they have not been employed in catalytic reactions because of their lack of activity. We have been able to synthesize mononuclear cationic complexes from these dinuclear rhenium compounds via oxo abstraction (Figure 1). The mononuclear cationic oxorhenium complexes are highly active catalysts for reduction of organic carbonyl compounds and for kinetically controlled hydrogen evolution from organosilanes and water. All of the rhenium catalysts investigated in have been fully characterized by spectroscopic methods (NMR, IR, MS), elemental analysis, and X-ray diffraction.

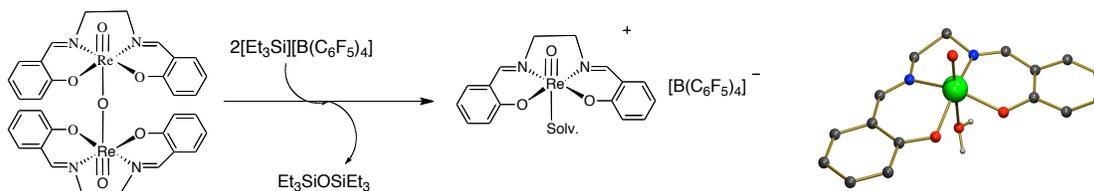
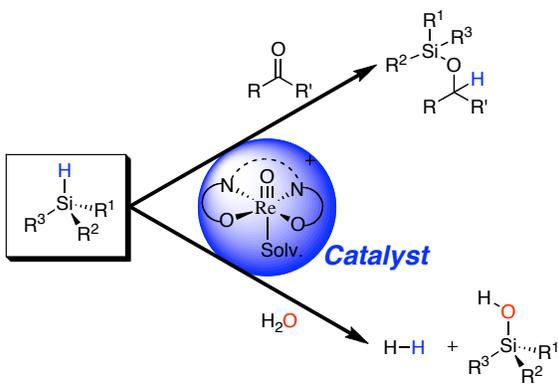


Figure 1. Preparation of mononuclear oxorhenium(V) salen and its structure with a water ligand.

Catalytic reduction of organic carbonyl compounds and hydrogen evolution: Metal oxo complexes are ubiquitous in catalytic oxidations. However, their use in catalytic reduction

has only been realized very recently. We discovered that cationic oxorhenium(V) complexes with an open coordination site (which is occupied by a solvent molecule) are high active catalysts for the reduction of organic carbonyl compounds and for the production of



hydrogen from dehydrogenative oxidation of organosilanes (Figure 2). The highlights of these catalytic reaction are low catalyst loading, ambient conditions, and no solvent is required. The versatility of substrates is quite high. Tertiary, secondary, primary, polymeric, etc. organosilanes are effective for both reactions. In reduction reactions aliphatic as well as aromatic aldehydes and ketones are reactive. The catalysts tolerate many functional groups including alkenes, alkynes, and ethers, to name a few. Product yields are quantitative.

Figure 2. Oxorhenium catalyzed reactions.

Mechanism: We have characterized the kinetics in detail for the oxorhenium(V) oxazoline catalyst, $[\text{Re}(\text{O})(\text{hoz})_2(\text{Solv})][\text{B}(\text{C}_6\text{F}_5)_4]$. In the hydrolysis of organosilanes, the experimental rate law is first-order in catalyst and organosilane but zero-order in water. Isotope-labeling experiments showed that molecular hydrogen in the product is made of one hydrogen atom from organosilane and the other from water. The silanol contains exclusively oxygen from water even under stoichiometric conditions. A primary kinetic isotope effect of 1.35 is observed for Si-H versus Si-D, and no kinetic isotope effect is observed for D_2O . These results are in agreement with a mechanism in which the oxo ligand on rhenium is a spectator.

As for the hydrosilation reaction, the experimental rate law is first-order in catalyst and organosilane and zero-order in aldehyde or ketone. Furthermore, the primary kinetic isotope effect for Si-H versus Si-D is 1.30. These findings are consistent with the hypothesis that both catalytic reactions (reduction and hydrogen evolution) occur via a common mechanism in which the rate-determining step is Si-H bond activation.

Real time evolution of hydrogen: Reaction rates of gas evolution are often measured by volume displacement or by employing pressure transducers, which have several limitations. Neither method provides identification of products. Measuring pressure change can be done properly only over a narrow dynamic range as maintaining a constant temperature becomes more difficult per $PV = nRT$. The price of a minimal commercial MS system (~\$50K) is somewhat prohibitive for a single laboratory. We have found that using commercially available components, a mass spectrometer can be implemented for approximately \$20K. An RGA was installed in a small vacuum system with a differentially pumped inlet, allowing real-time monitoring of reactants and/or products from reaction systems near atmospheric pressure. An added benefit is that we are able to perform isotope analyses in real time. The MS is a universal detector, and analysis is rapid and very sensitive.

DOE interest

Research in the chemical sciences can contribute to energy solutions in three ways, new sources of energy, preferably renewable; methods of energy storage and production via making and breaking of chemical bonds; and increased efficiency of chemical reactions (atom economy, mild conditions, 'green' chemistry, etc.). It is evident that chemical catalysis would play a central role in the latter two areas. Besides the immediate benefit of advancing a new mechanistic knowledge for the reactivity of organosilanes with transition metal oxo complexes, our research has broader impact in the areas of hydrogen storage and production on-demand, and "green" and facile catalysis.

Future plans

We will continue our investigation of the reaction mechanism and discern whether the terminal oxo ligand plays a role in activating organosilane. Analogous rhenium imido and alkylidene complexes will be prepared and their catalytic chemistry explored. We will be probing the rate insensitive step that involves the organic carbonyl substrates by determining electronic effects (Hammett correlation) using competition kinetics. Various organosilane substrates that contain multiple Si-H bonds will be investigated in the context of hydrogen evolution. With the mononuclear rhenium salen complexes in hand, we plan to prepare chiral catalysts and investigate their utility in asymmetric hydrosilation reactions. We also plan to expand the scope of using oxorhenium catalysts in reductions to include hydrogenations with molecular hydrogen.

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Synthesis and Studies of Bimetallic Catalysts in Solution and on Supports

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Goal

The principal objectives of this project are: 1) to design, prepare and characterize new stoichiometrically precise heterometallic cluster complexes for use as precursors for nanoscale supported heterogeneous catalysts; 2) to prepare and test heterometallic nanoscale catalysts derived from the cluster complexes on supports for oxidation and reduction reactions of economically important organic compounds of interest to the energy mission; 3) investigate the structures and bonding of nanocatalysts derived by activation of these cluster complexes on selected supports including the new families of mesoporous silicas.

Recent Progress

A new family of highly electron deficient platinum-rhenium complexes containing sterically encumbered phosphine ligands have been prepared and shown to exhibit facile activation of hydrogen that is reversible under certain conditions. A number of high nuclearity platinum-iridium carbonyl cluster complexes have been obtained from the reaction of $\text{Ir}_4(\text{CO})_{12}$ with $\text{Pt}(\text{PBU}^t_3)_2$. Also, the compound $\text{PtRu}_5(\text{CO})_{15}(\mu\text{-SnPh}_2)(\mu_6\text{-C})$ has been prepared and shown to be a precursor to highly dispersed nanoparticles with the same metal composition PtRu_5Sn . These supported nanoparticles exhibit the highest activity and selectivity observed to date for the hydrogenation of dimethylterephthalate to cyclohexanedimethanol under mild conditions. The catalytic performance of cluster-derived PtFe/SiO_2 bimetallic catalysts for the oxidation of CO has been also examined in the absence and presence of H_2 (PROX) and compared to that of Pt/SiO_2 . $\text{PtFe}_2/\text{SiO}_2$ and $\text{Pt}_5\text{Fe}_2/\text{SiO}_2$ samples were prepared from $\text{PtFe}_2(\text{COD})(\text{CO})_8$ and $\text{Pt}_5\text{Fe}_2(\text{COD})_2(\text{CO})_{12}$ organometallic cluster precursors, respectively. Heating in H_2 led to complete decarbonylation of the supported clusters at approximately 350°C and the formation of Pt-Fe nanoparticles with sizes in the 1-2 nm range. A higher degree of metal dispersion and more homogeneous mixing of the two metals were observed with the cluster-derived samples, when compared to a PtFe/SiO_2 catalyst prepared through a conventional impregnation route. The cluster-derived $\text{PtFe}_2/\text{SiO}_2$ and $\text{Pt}_5\text{Fe}_2/\text{SiO}_2$ samples were more active than Pt/SiO_2 and the conventionally-prepared PtFe/SiO_2 sample for the oxidation of CO in air.

DOE Interest

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 expand these studies of the synthesis of bimetallic clusters by combining new platinum and palladium complexes, such as Pt(COD)₂, Pd(PBu^t)₂ and Pt(PBu^t)₂, with other noble metals from the transition series. Incorporation of tin into the bimetallics seems to be important anchoring the clusters on to supports, and efforts will be expanded to introduce tin ligands into the bimetallic cluster complexes. The catalytic activity of these nanoparticles for reactions such as alkane hydrogenolyses, selective hydrogenations, selective oxidation of CO, and oxidation of alcohols will be investigated and as well as the relationships between the structure and composition of the nanoparticles and their catalytic activity.

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Gold Metal-Catalyzed Reactions of Isocyanides with Primary Amines and Oxygen

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Abstract

Despite its generally-poor catalytic properties, bulk gold metal is observed to catalyze reactions of isocyanides ($C\equiv N-R$) with primary amines (H_2N-R') and O_2 to give carbodiimides ($R-N=C=N-R'$) at room temperature and above. Detailed infrared reflection absorption



spectroscopic (IRRAS) and kinetic studies show that the reaction occurs by initial η^1 -adsorption of the isocyanide on the Au surface, which activates the isocyanide to attack by the amine. This attack is the rate-determining step in the catalytic cycle and has characteristics very similar to those of amine reactions with coordinated isocyanides in transition metal complexes. However, the metallic Au surface provides a pathway involving O_2 to give the carbodiimide product, whereas homogeneous metal ion catalysts give formamidines [$HC(=NR)(NHR')$].

Selective and Efficient Catalysis in 3-D Controlled Environments and New Developments in Homogeneous Catalysis

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Goal

Develop and characterize multifunctionalized mesoporous silica materials with well-defined pore/particle morphology and surface properties for heterogenization of single-site catalysts, and study the selectivity, reactivity and kinetics of these catalytic systems. Develop an understanding of homogeneous oxygen activation by transition metal complexes, explore kinetics and mechanisms of such reactions, and detect and characterize intermediates involved.

Recent Progress

(1) We have developed synthetic methods¹⁻⁶ for multifunctionalization of mesoporous silica supports to test the feasibility of the major research goals of this project.

(a) We have examined the surface of *non-functionalized* MCM-41-type mesoporous silica nanoparticles (MSNs) prepared under low surfactant concentration by solid-state NMR spectroscopy.⁷ The surface species, which included weakly adsorbed water, silanol groups and the residual surfactant (CTAB) molecules, were precisely quantified and characterized using ultrafast ¹H MAS, ¹H-¹H homonuclear correlation (double quantum, exchange and RFDR) and ¹H-²⁹Si heteronuclear correlation (HETCOR) NMR. Water was hydrogen bonded to the silanol groups, all of which were involved in such bonds under ambient humidity. Specific structures involving these SiOH-(H₂O)_n species were proposed for various stages of thermal treatment, which included dehydration, dehydroxylation and subsequent rehydration. The study also showed that the CTAB molecules, which remained in the pores after acid extraction, assumed prone positions along the pores, with the tailgroup being most mobile.

(b) We have developed synthetic approaches¹⁻⁶ that allow efficient *multi-functionalization* with precise control of the relative concentrations of functional moieties, and provide means to modify the particle and pore morphology. As depicted in Figure 1, our method involves the utilization of organotrialkoxysilanes with various anionic, hydrophobic, or hydrophilic functional groups that can provide different non-covalent interactions, e.g., electrostatic attractions, hydrophobic interactions, with the cationic CTAB surfactant micelles in a NaOH-catalyzed

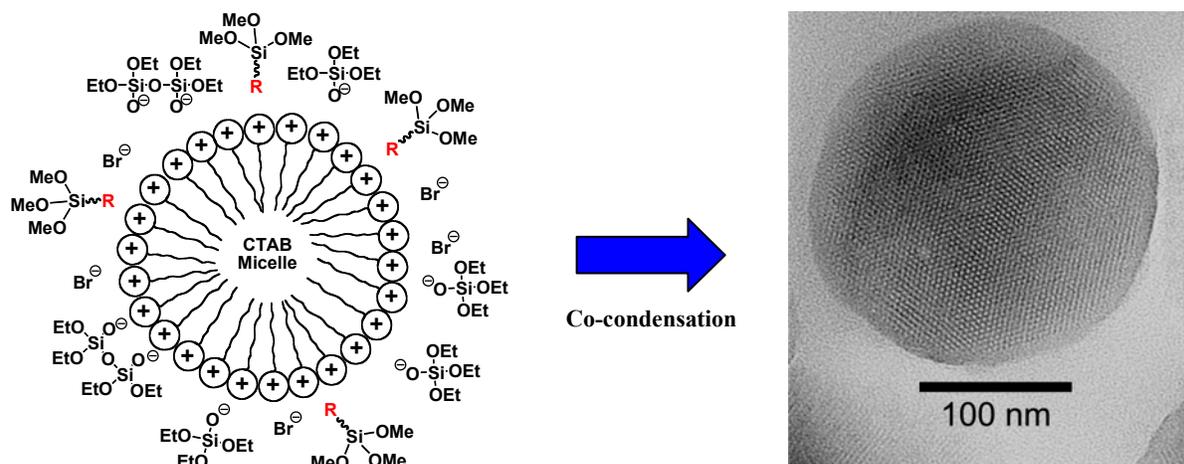


Figure 1. Schematic representation of the utilization of various organoalkoxysilanes ($R\text{-Si}(\text{OMe})_3$, R = anionic, hydrophobic, and hydrophilic organic groups) for controlling the functionalization of the MSN materials. The MCM-41 type mesoporous structure is illustrated by the hexagonally packed light-colored dots shown in the TEM micrograph of an organically functionalized MSN material.

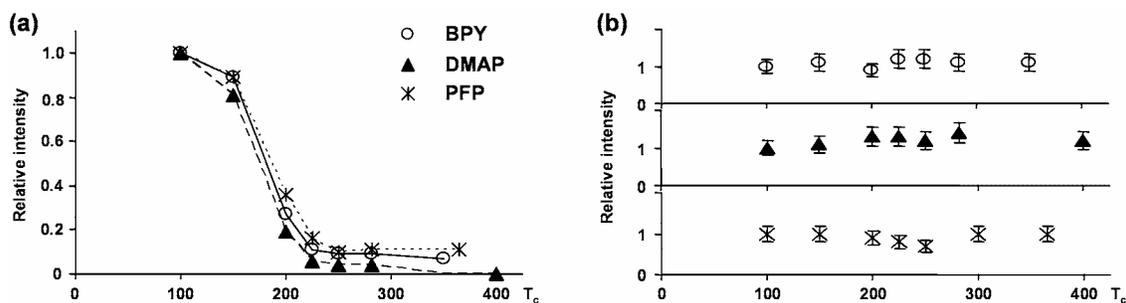


Figure 2. Concentration of CTAB (a) and the organic functional groups (b) versus the temperature of thermal treatment in samples functionalized with BPY, DMAP and PFP. The experimental points represent integrated intensities of all ^{13}C resonances for each species.

condensation reaction of tetraethoxysilane (TEOS).¹⁻⁶ By carefully designing the interfacial interaction between the surfactant head groups and the desired organic functional group precursors, we have reported that the extent of organic functionalization as well as the particle shape and size of MSNs can be controlled and fine-tuned. A series of organically functionalized MSN materials with spherical, tubular, and rod-like particle morphologies and narrow particle size distributions could be easily synthesized via our method.^{1,2,6}

(c) We have systematically investigated the *template removal* and *thermal stability* of organically functionalized MCM-41-type mesoporous silica nanoparticles. The samples, functionalized with 2,2'-bipyridine (BPY), 4-dimethylaminopyridine (DMAP) and pentafluorobenzene (PFP) by a co-condensation method, were studied by solid-state NMR following a series of heat treatments between 100 and 400 °C.⁸ The ^{13}C and ^{29}Si NMR spectra of these materials showed that the structures and concentrations of these functional groups remained unaffected by the heat treatment (Figure 2b). Furthermore, it has been demonstrated that the surfactant template, cetyltrimethylammonium bromide (CTAB), could be effectively removed from these materials at ~ 250 °C (Figure 2a), without disrupting the covalent bonds between the functional groups and the silica surface. The chemical accessibility and reactivity of the organic functionalities were also preserved after heating. We envision that this temperature-controlled heating process could be further developed into an economical and environmentally friendly method for surfactant-removal from other organically functionalized materials.

(d) We have tested the feasibility of the major research goal of this project, i.e., controlling the reaction selectivity of mesoporous catalysts by using the novel concept of *gatekeepers*.^{3,4} Specifically, by introducing two organoalkoxysilanes as precursors in our co-condensation reaction, we utilized one precursor with *stronger structure-directing ability* to create the desired pore and particle morphology and employed the *other* for selective immobilization of catalysts.³ This strategy allowed us to generate a series of multi-functionalized mesoporous silicas with *control of both morphology and degree of functionalization*. As a proof of principle, we have synthesized and reported a series of bifunctionalized MSN-based heterogeneous catalysts for nitroaldol (Henry) reaction.³ As shown in Figure 3, a common 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) primary group and three different secondary groups, ureidopropyl (UDP), mercaptopropyl (MP), and allyl (AL) functionalities, were incorporated into these mesoporous silica materials by introducing equal amounts of AEP-trimethoxysilane with UDP-, MP- or AL-trialkoxysilane precursors to the aforementioned co-condensation reaction. The AEP group served as a catalyst and the other secondary groups provided different non-covalent interactions to reactants and thereby controlled the reaction selectivity. We discovered that the selectivity of a nitroaldol reaction of two competing benzaldehydes reacting with nitromethane could be simply tuned in these bifunctionalized MSN catalysts by varying the physicochemical properties of the pore surface-bound secondary groups, i.e., polarity and hydrophobicity.³

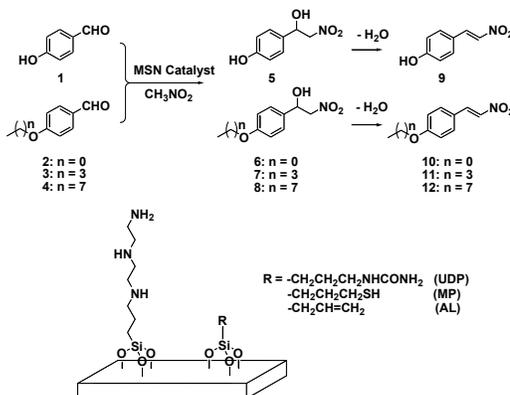


Figure 3. Bifunctionalized MSN catalysts for competitive nitroaldol reaction. The reaction selectivity is dictated by the chemical nature of the secondary functional groups (R).

(e) We have developed a new *cooperative catalytic system* comprised of a series of bifunctionalized mesoporous silica nanosphere (MSN) materials with various relative concentrations of a general acid, UDP group, and a base, AEP group,³ as depicted in Figure 4. Three bifunctional AEP/UDP-MSN catalysts with the initial molar ratio of the organoalkoxysilane precursors, AEP/UDP = 2/8, 5/5, and 8/2, were synthesized via the co-condensation method and

thoroughly characterized by solid-state NMR.⁵ The syntheses and characterizations of the mono-functionalized MSNs with either AEP or UDP functionality were also reported.⁵ We have demonstrated that these AEP/UDP-MSN bifunctional materials could cooperatively activate substrates in catalyzing the aldol, Henry and cyanosilylation reactions. By fine-tuning the relative concentrations and proper spatial arrangements of different cooperative functional groups, we were able to regulate the turnover numbers of these important carbonyl activation reactions.⁵

(f) We have successfully synthesized and characterized a new nucleophilic catalytic system comprised of dialkylaminopyridine-functionalized mesoporous silica nanosphere (DMAP-MSN).⁹ Successful functionalization of DMAP on mesoporous silica surfaces has never been reported prior to our study. This could be attributed to the undesired protonation of the pyridyl group of various trialkoxysilyl-derivatized dialkylamino pyridines by the surface silanol groups during the conventional post-synthesis grafting reaction. We have demonstrated that the DMAP-MSN material is an efficient, selective and recyclable heterogeneous catalyst for Baylis-Hillman, acylation, and silylation reactions.⁹ We envision that this material can also serve as an effective heterogeneous catalyst for many other catalytic nucleophilic reactions.

(2) We used a variety of *solid-state NMR methods* to characterize the MCM supports before and after functionalization, to study the structure and absolute/relative concentration of various moieties in the mesopores, and to determine their spatial distribution and orientation with respect to the surface.^{1-5,8,9} In addition, two extensive investigations of MSN silicas were carried out in order to develop and/or adapt the solid state NMR methods that are specifically dedicated to the studies of functionalized surfaces.^{7,10}

(a) The fast MAS (40-50 kHz) approach proved very profitable in the studies of *functionalized* silica surfaces, especially in HETCOR NMR spectroscopy involving protons and low-gamma nuclei.¹⁰ In the case of ¹H-¹³C and HETCOR NMR, the spectra of surface functional groups on silica could be obtained without the isotopic enrichment using small (less than 10 μL) sample volumes. In ¹H-²⁹Si HETCOR NMR spectroscopy, a sensitivity gain of more than *one order of magnitude* has been achieved by incorporating the CPMG train of π pulses into the standard HETCOR pulse sequence. The ¹H-¹³C and ¹H-²⁹Si HETCOR methods provided detailed characterization of the surface of MSN silicas functionalized with allyltrimethoxysilane (≡SiCH₂CH=CH₂) in the absence of templating molecules (Figure 5). Similar methods are being currently applied in the studies of surfaces functionalized with more complex molecules. Access to smaller surfaces and/or lower molecular concentrations can be gained by using isotopically enriched samples. Further advances were also made in *J* spectroscopy of solids.¹⁰⁻¹⁴ For example, we have developed new methods for measuring high-resolution HETCOR spectra between spin-1/2 and quadrupolar nuclei.^{11,12} One of these methods allows for probing ²⁹Si-²⁷Al correlations in aluminosilicate materials.¹²

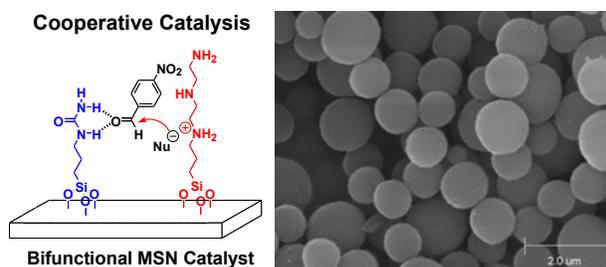


Figure 4. A new cooperative catalytic system which consists of a series of bifunctionalized mesoporous silica nanosphere (MSN) materials with various relative concentrations of a general acid, ureidopyrrolidone (UDP) group, and a base, 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) group.

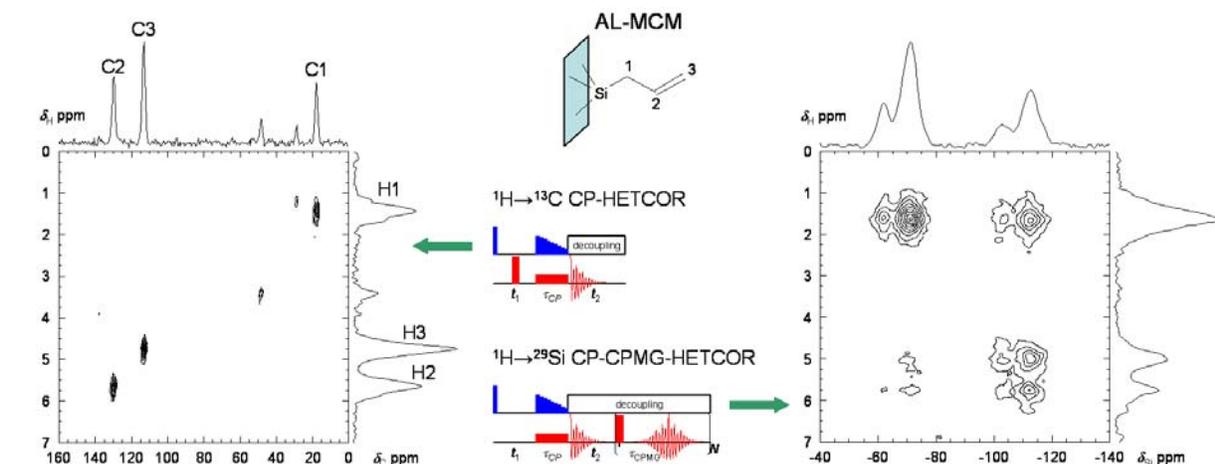
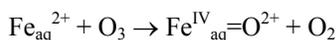
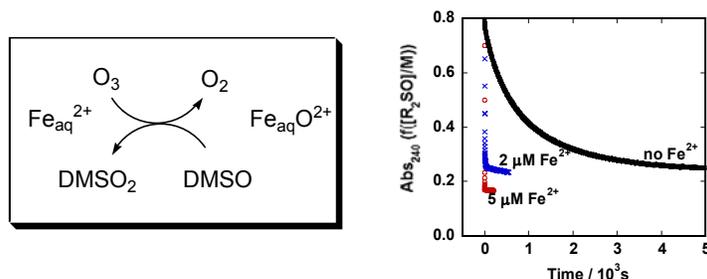


Figure 5. Two-dimensional heteronuclear ¹H→¹³C (left) and ¹H→²⁹Si (right) correlation spectra of an allyl group (-CH₂-CH=CH₂) covalently bound to the pore walls of a MCM-41 type silica material taken using schemes shown in the middle of the figure.

(3) We have generated aqueous Fe(IV) ions from $\text{Fe}_{\text{aq}}^{2+}$ and O_3 in acidic aqueous solutions.¹⁵



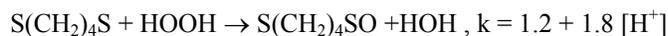
Mössbauer and XAS spectroscopies, conductivity measurements, kinetic studies, and DFT calculations have established the formula $\text{Fe}_{\text{aq}}^{\text{IV}}=\text{O}^{2+}$ for this short-lived (half-life 7 seconds at room temperature) but extremely reactive species.¹⁵⁻¹⁷ The oxidation of alcohols, ethers, and carboxylic acids takes place in parallel hydrogen atom and hydride abstraction reactions, but sulfoxides (R_2SO) are oxidized exclusively by oxygen atom transfer. This reaction is the product-forming step in the oxidation of R_2SO by ozone catalyzed by $\text{Fe}_{\text{aq}}^{2+}$:



The strong catalytic effect of several micromolar $\text{Fe}_{\text{aq}}^{2+}$ on the ozone/dimethyl sulfoxide reaction has enabled us to determine the rate of oxo-oxygen exchange between $\text{Fe}_{\text{aq}}^{\text{IV}}=\text{O}^{2+}$ and ^{18}O -labeled solvent water, $k = 1.5 \times 10^3 \text{ s}^{-1}$ at 25°C .¹⁷

(4) Having a *bona fide* aqueous Fe(IV) species at hand has allowed us to examine its reactivity and compare it to that of hydroxyl radicals. As a result, we have resolved a century-old mystery regarding the nature of the active intermediate in the ubiquitous Fenton reaction, i. e. the reaction between $\text{Fe}_{\text{aq}}^{2+}$ and H_2O_2 in aqueous solution. We have developed criteria that allowed us to rule out $\text{Fe}_{\text{aq}}^{\text{IV}}=\text{O}^{2+}$,¹⁶ leaving HO radicals as the most likely candidate.

(5) Several hydroperoxorhodium(III) complexes were found to be extremely efficient oxygen-atom transfer reagents in aqueous solutions.¹⁸⁻²⁰ Oxygen transfer is exclusively H^+ -catalyzed, in contrast to the reactions of unactivated H_2O_2 which utilizes both H^+ -independent and H^+ -catalyzed pathways.



(6) We have established the nature of various complexes of rhodium and rhenium tethered to silica surfaces to form catalysts for enantioselective hydrogenation and selective oxidation reactions.^{21,22}

(a) Rhodium complexes of the chiral chelating phosphine (2*S*,4*S*)-4-(diphenylphosphino)-2-(diphenylphosphino-methyl)pyrrolidine (X-PPM) tethered on silica (SiO_2), tethered on silica with supported palladium (Pd- SiO_2), and in solution were characterized by ^{31}P NMR and IR spectroscopies.²¹ The (X-PPM)Rh(COD)⁺ complex, which is highly enantioselective for the hydrogenation of the prochiral olefin methyl- α -acetamidocinnamate (MAC), retains its composition in the tethered catalysts regardless of its mode of preparation or the presence of Pd on the silica surface. The chiral diphosphine ligand remains coordinated to the rhodium during the reaction. The catalysts were examined for their arene hydrogenation activity. It was established that Pd in the (X-PPM)Rh(COD)⁺/Pd- SiO_2 catalyst causes the reduction of any uncomplexed Rh to metallic species during the hydrogenation reactions. It was these metallic Rh species that were responsible for the toluene hydrogenation activity of the tethered catalysts.

(b) A silica-tethered version of the oxorhenium(V) dithiolate oxidation catalyst [-S(CH₂)₃S-]Re(O)(Me)(PPh₃) was prepared and characterized by solid state ^{13}C and ^{31}P NMR.²² This tethered complex (SiO₂-RTA)Re(O)(Me)(PPh₃) catalyzes the selective oxidation of methyl(*p*-tolyl)sulfide (MTS), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) to sulfoxides and sulfones by *tert*-butylhydroperoxide (TBHP). Although the rate of oxidation catalyzed by the immobilized catalyst is about a factor of three times lower than the homogeneous analog [-S(CH₂)₃S-]Re(O)(Me)(PPh₃), the supported catalyst is much more long-lived achieving approximately 3,000 turnovers in the oxidation of DBT at 100 °C. The immobilized catalyst effectively catalyzes the oxidation of DBT and the hindered 4,6-Me₂DBT to their sulfoxides or sulfones in simulated petroleum feedstocks.

DOE Interest

Developing catalytic systems that can coherently unite the best features of the homogeneous and heterogeneous areas of catalysis has been a key interest of the DOE. By controlling the structure, reactivity and morphology of the mesoporous solid support and its interaction with the active sites, these studies provide truly unique opportunities for the design of a new generation of highly efficient and selective catalysts. The development of novel homogeneous reactions, such as activation of oxygen and its use in catalytic oxidations is also one of the top DOE priorities. Research in both homogeneous and heterogeneous areas provides new fundamental knowledge about catalysis in general by deconvoluting the key factors that affect selectivity, reactivity and kinetics.

Future Plans

- *Influence of the mesopore environment on catalyst selectivity and activity.*²³ Our ability to anchor two types of groups on mesopore walls allows us to tether not only the catalyst but also other functional moieties. The influence of these auxiliary groups will be directed toward achieving various catalyst functions, such as enantioselectivity. These studies will use the concept of gatekeepers, which will be tested in the development of catalysts for the stereochemically controlled polymerization, selective hydrolysis, etc.
- *Cooperative catalysis inside mesopores.* To study how various functional groups could synergistically catalyze a reaction in a 3-D controlled environment, we will functionalize the surface of mesopores with two to three different types of catalytically active moieties and vary the relative ratio and spatial distribution of these functionalities. As a proof of principle, functional groups that can serve as general acid and base will be introduced to study the selective carbon-carbon bond formation in, for example, aldol, Diels-Alder, and hetero-Diels-Alder (HDA) reactions that involve carbonyl activation.
- *Control of the orientation and activity of tethered transition metal complex catalysts.* In order to understand the activity and selectivity of metal complex catalysts tethered on the walls of mesopores, we will characterize and control the location and the exact structure of the tethered catalysts on the surface.
- *Catalyst characterization.* Solid state NMR techniques will be further developed to better characterize the catalytic surfaces, especially to probe the spatial organization of the surface species and to provide key dynamic information about catalysts that will be prepared and tested during the next stages of this research. We will focus on further exploitation of J-spectroscopy, ^1H - ^1H multiple quantum NMR methods and the CPMG-based schemes for enhancing the sensitivity.
- *Theory, modeling and simulation of transport and reaction in mesopores.* Theoretical and computational tools will be developed to allow analysis of electronic structure and dynamics for the complex silica surface + functional group + reactant + solvent systems. Second, statistical mechanical models will be proposed for the relevant many-particle transport and reaction processes in silica nanopore geometries, ideally utilizing energetic and dynamic information from the above electronic structure studies.
- *Catalytic oxidations with molecular oxygen, hydrogen peroxide, and ozone.* Kinetic and mechanistic studies of transition-metal catalyzed oxidation reactions will be carried out, with an emphasis on iron-based systems. We will search for new potential catalysts and oxygen-activating complexes, and focus on detection and characterization of reactive intermediates and reaction pathways. The discovery and understanding of factors that facilitate two-electron transformations involving $\text{Fe}^{\text{II}}\text{-Fe}^{\text{IV}}$ (or $\text{Fe}^{\text{III}}\text{-Fe}^{\text{V}}$) pairs is expected to lead to the development of iron-based catalysts to replace the expensive noble metals (mostly rhodium, palladium and platinum) that are currently in use.

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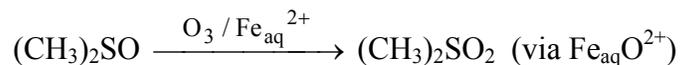
Chemistry of Aqueous Iron(IV) Ions, $\text{Fe}^{\text{IV}}_{\text{aq}}\text{O}^{2+}$

Andreja Bakac and Oleg Pestovsky

Ames Laboratory, Iowa State University

Abstract

Oxidation of $\text{Fe}_{\text{aq}}^{2+}$ with ozone in acidic aqueous solutions generates the strongly oxidizing $\text{Fe}^{\text{IV}}_{\text{aq}}\text{O}^{2+}$ which was characterized chemically and spectroscopically. $\text{Fe}^{\text{IV}}_{\text{aq}}\text{O}^{2+}$ utilizes hydrogen atom and hydride abstraction pathways in reactions with alcohols, ethers, and carboxylic acids, but oxidizes phosphines and sulfoxides exclusively by oxygen atom transfer. The latter is one of the central steps in $\text{Fe}_{\text{aq}}^{2+}$ -catalyzed oxidation of sulfoxides by ozone.



$\text{Fe}^{\text{IV}}_{\text{aq}}\text{O}^{2+}$ rapidly exchanges its oxo-oxygen with solvent water, $k = 1.5 \times 10^3 \text{ s}^{-1}$ at 25^o C. The Fenton reaction, i. e. the oxidation of $\text{Fe}_{\text{aq}}^{2+}$ with hydrogen peroxide in aqueous solution, does not generate $\text{Fe}^{\text{IV}}_{\text{aq}}\text{O}^{2+}$ as an intermediate.

Nanostructured Metal Oxide Catalysts via Building Block Syntheses

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Goals: To develop a general synthetic methodology by which well defined metal oxide catalysts can be incorporated into the surface structures of support materials. These heterogeneous catalysts will be nanostructured in the following ways: All catalyst sites will be identical (“single site axiom”); all will be well separated from one another (“site isolated axiom”); and the support surface will be nanostructured for optimum binding between the catalyst ensemble and the support. Following the development of the synthetic methodology and detailed characterization of supported catalysts, our final goal is to directly connect these single site, nanostructured catalysts to catalytic activities which will address the question: what effect does nanostructuring have on the catalytic activity of a catalyst.

DOE Interest: One of the operational definitions of “next generation catalysts” is that they be “ultra selective” in the products derived from the catalytic transformation. An important area of catalysis that would benefit from such next generation catalysts is the selective oxidation of unactivated hydrocarbon chemicals (e.g. methane) to more useful feedstocks for chemical synthesis (formaldehyde or methanol). Traditional approaches to supported metal catalysts on metal oxide supports usually yield a variety of supported species with different activities, but more importantly with different selectivities with respect to oxidation chemistry. A general synthetic approach to the creation of well defined supported metal catalysts in which all the sites were, by design, the same would represent a significant advance in the science of supported catalysts and would represent an important new approach to the efficient use and management of many valuable natural resources.

Research Plan

The three main phases of this research program are as follows: Phase one involves the elucidation of the synthetic principles by which nanostructured metal oxide matrices may be constructed in which single metal ions or metal clusters play a role in structuring the matrix. Phase two involves detailed characterization of the both the matrix and catalyst sites. Two critical questions must be answered: first, can the catalyst be described as single site in nature and second, what is the nature of the catalyst sites in the building block matrix. Other questions that are

important in this context are whether the building block is intact in the matrix, and the availability of catalyst sites on the inner and outer surfaces of the porous matrix. The final phase of the project involves establishing a connection between a designed, single site catalyst and its properties (activity, selectivity, longevity) as a catalyst. Currently, we have completed phase one of the project for atomically dispersed titanium and vanadium centers in a silica building block matrix and are working on phases two and three for both of these metals. We have also begun to study aluminum and tungsten based catalysts within the context of solid acid and oxidation reactions.

Recent Progress:

1. Optimization of synthetic methodology and characterization of supported metal (Ti, V, W) catalysts on silicate building block supports. We have now optimized the general approach for creating atomically dispersed metal sites within a porous silicate building block matrix. The basic tenets of the synthetic strategy are the following: 1) a suitably functionalized metal oxide building block must be chosen that will be the major structure directing element in the matrix. The use of a nanometer or larger building block also ensures isolation of the catalyst sites in the matrix. 2) Linking chemistry must be developed which involves the reaction of complementary functional groups (e.g. A and B) on the linkers and building blocks, respectively, in which A will react with B but neither A nor B can self react (avoids the problem of self condensation and phase separation that is frequently observed in sol-gel approaches to mixed metal oxide syntheses). 3) The preparation of single site catalysts is effected by control of two further synthetic variables: the stoichiometric ratio of building blocks to linking entities and the addition sequence chosen to insert catalyst centers and cross link the matrix into solid material. An overview of this approach to the synthesis of nanostructured catalysts will be presented in the poster along with supporting characterization data (IR, Raman, SSNMR, EXAFS).
2. A micro catalysis reactor has been constructed consisting of: 1) mass flow controllers to produce flows of carrier or substrate gases (He, O₂, CO, alkanes, alkenes,) into the reactor; 2) a temperature programmable reactor that can ramp smoothly from room temperature to ~1000°C; 3) both gas chromatographic and mass spectrometric analysis instrumentation to separate product mixtures into components and identify each by mass and GC retention time. Construction and testing of this reactor is now completed. Preliminary results from selective oxidation studies will be presented.

Future Plans: We will continue to explore the catalytic oxidation chemistry of atomically dispersed titanium and vanadium in silicate building block matrices. Both V(V) and V(IV) species will be studied. Additionally, we are studying the properties of these high valent centers within the context of solid Lewis acid catalysts. Other solid acid catalysts that we are investigating are atomically dispersed tin(IV), aluminum and phosphorus in silica. Finally we have begun to investigate the insertion of tungsten(VI) and chromium(VI) centers into building block matrices as potential oxidation and polymerization catalysts.

Publications Supported by DOE-BES Funding:

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**, 856-857

Synthesis and Structure of Functional Spherosilicate Building Block Molecules for Materials Synthesis, Jason C. Clark, Suree Saengkerdsub, Geoff T. Eldridge, C. Campana, Craig E. Barnes: *J. Organomet. Chem.*, in press.

A Synthetic Methodology for Preparing Nanostructured Metal Oxide Glasses, Jason Clark and Craig E. Barnes, manuscript in preparation.

CATALYSIS SCIENCE INITIATIVE: Electron transfer, Oxygen Activation, and NO Biosynthesis: An Integrative Electrochemical, Biochemical, and Computational Approach

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Goals:

Biocatalysis embodied by the sophisticated reactivity of enzymes remains a fertile ground for the catalysis community to learn how these molecular machineries perform their function with exquisite control and, by all standards, with the best selectivity and efficiency, defeating all possible reaction side paths. Despite advances made in the understanding of enzymes' functions, the catalytic aspects of this field is yet to be fully exploited by chemists, and particularly by the catalysis community, to unravel the dynamic mechanisms by which these enzymatic entities carry out their function, and to draw new paradigm mechanisms for catalysis. It is in this context that the teams involved in this project investigate the nitric oxide synthase (NOS) catalytic reaction, a complex biocatalytic platform with the potential to reveal kinetic, thermodynamic, and exquisite structural control of reactivity at the atomic level. Understanding the biocatalytic function of complex enzymes has much rewarding outcomes, including discovery of new paradigm mechanisms for catalysis and catalytic transformations, and rational design of catalysts inspired from biological molecules. The same fundamental understanding will also pave the way to systematically address other challenging aspects such as truly integrating biological and chemical catalysis.

Specific goals for the current funding period are as follows: We planned to conduct detailed investigation of the thermodynamic and kinetic modulation of charge transfer to NOS oxygenase in the presence of the pterin cofactor, the arginine substrate, or their surrogates. We were particularly interested in rationales for the modulation of electronic properties at the atomic level. We therefore planned to carry out computational studies in synergy with direct electrochemical measurements to understand how the electronic modulation is executed at the

atomic level and identify residues that play the key role in this process. Specific goals also included the NOS-catalyzed oxygen activation process. We particularly planned to electrochemically identify active oxygen complexes involved in oxygen activation by NOS using environments with very low and controlled water/proton content. On the electrochemically-driven catalysis front, our goal, as originally planned in this period, was to compare and contrast the behavior of nNOSoxy versus iNOSoxy, and address the kinetics of the overall process. Another specific aim included the study of feedback inhibition by self-generated product NO, and particularly comparing two isoforms. In a related goal, we planned to closely study the electrocatalytic reduction activity of the product nitric oxide catalyzed by NOS oxygenase with particular emphasis on the characterization of the NOS nitrosyl/nitroxyl redox couple. Plans also included the expression/purification followed by biochemical and electrochemical investigation of some mutants identified in the previous period; the mutants identified interrogated the role of residues in the petrin cofactor binding pocket. We planned to closely study how kinetic and thermodynamic modulations by cofactor binding are affected in these mutants compared to wild type. We also wanted to understand long range cooperative effects, if any, starting relatively far at the binding pocket of the petrin cofactor and influencing the binding of arginine immediately above the heme.

DOE Interest:

Design of the next generation of catalysts integrating smart molecular features, found for instance in the function of enzymes, remains a challenge, in part because of our limited fundamental understanding of how elemental steps of complex enzymatic reactions are controlled. Therefore, developing a molecular-level understanding of the catalytic function of nature's best catalysts (i.e. enzymes), their dynamic structural flexibility, and long-range ultimate control of reactivity and selectivity, is a pre-requisite to integrate these important concepts in the challenge of molecular design of next generation of catalysts.

Research Plan:

The catalytic molecular machinery that orchestrates the production and delivery of NO is structurally impressive and functionally very complex. The research teams in this project adopt a cross-disciplinary plan that coordinates efforts among core areas to address the complex function of the biocatalytic synthesis of nitric oxide. In this unique setting, and as explained before, hypothesis-driven explorations of one team provide feedback or input information for finer exploration in the other. Our synergistic efforts revolve around experimental measurements of redox properties of various states of the oxygenase domain of NOS as well as critical intermediates in the catalytic cycle. Our direct electrochemical and spectro-electrochemical investigations are carried on both wild-type and mutants prepared by site-directed mutagenesis. The mutants that are successfully expressed/purified and tested experimentally are typically identified based on molecular dynamics and other computational efforts. Likewise, experimental observations and measurements will provide feed-information for more computational MD and QM/MM investigations. This, in turn, yields to insights on structural information vital to NOS catalysis, and that can be tested experimentally.

The Bayachou lab at CSU conducts all direct electrochemical and spectro-electrochemical efforts. This includes enzyme immobilization and development of stable interfaces to study direct electron transfer, interface characterization, *in situ* assays of activity, fast-scan electrochemical investigations, as well as kinetic and thermodynamic measurements using electrochemical methods. The Gogonea lab carries out computational investigations with

close feedback with the Bayachou lab. The Zhou lab conducts all aspects of biochemical and molecular biology efforts, including expression and purification of wild type and mutants of NOS-oxygenase. Molecular biology efforts are mainly guided by findings from direct electrochemical investigations in close interaction with the computational calculations. This system-approach that we adopted is powerful and is suitable with the challenges of the NOS biocatalytic platform that we have chosen in order to develop an understanding of some aspects of molecular controls over catalytic steps such as electron transfer and oxygen activation, as well as kinetic control of key intermediates involved in the NOS catalytic cycle.

Direct electrochemical tools are used to investigate of the thermodynamic and kinetic modulation of charge transfer to NOS oxygenase by the pterin cofactor or arginine substrate. The investigation takes place on purified recombinant NOS oxygenase immobilized in bilayered thin films on pyrolytic graphite electrodes. The structural integrity of NOS oxygenases is addressed by spectroscopic characterization in the film. In fact, the characteristic low-to-high spin shift of the iron-heme known to occur when substrate arginine and/or pterin cofactor bind to NOSs in solution are also typically observed for NOS heme oxygenase in the lipid bilayered thin film as evidenced by difference spectra in the Soret region. Our fast and reversible direct electron transfer between NOS oxygenases and underlying electrodes, allows us to carefully investigate issues such as cofactor- and substrate-assisted modulation of redox activity of NOS oxygenases. Electronic properties of the iron-heme redox-active center in NOS oxygenase are sensitive to the structure and content of the binding pocket. Electrochemical measurements are therefore very powerful in studying substrate binding to enzymes that are also redox active, as is the case of nitric oxide synthases. Not only can these methods reveal differential kinetics of binding of a particular substrate to various NOS isoforms, but they can also accurately measure dynamic affinities of a substrate towards oxidized versus reduced state of the same isoform.

Electron transfer to the resting state of NOS enzymes, i.e. the first electron transfer to the Fe^{III}-heme form, is the actual gate to the whole catalytic cycle; the kinetics of this event and how the rate for electron transfer is modulated by the substrate and/or cofactor binding are of particular importance to the biocatalytic properties of NOS enzymes. In fact, kinetics reflects in a way transient dynamics of the protein and residues around the prosthetic groups of NOS including the heme active site. Therefore, as a part of this specific aim, we have planned to thoroughly characterize the kinetics of electron transfer to the Fe^{III} forms (i.e. resting state) of NOS isoforms. Whether binding of cofactor and substrate affect the kinetics of electron transfer is the main question that we began to address here. To this end, the rate constant k^0 for the heterogeneous electron transfer to the Fe-heme in NOSoxys in bilayered thin films on electrodes can be determined routinely in our labs using cyclic voltammetry methods. Anodic-to-cathodic peak separation, ΔE_p , as a function of scan rate, for the reversible redox couple Fe^{III}/Fe^{II}-heme in NOS oxygenases provides a measure of the rate of the electron transfer. The collective set of ΔE_p measured over an appropriate window of scan rates (dictated by how fast or slow the electron transfer process in question) is then used with digital simulations in our labs, to provide the rate of heterogeneous electron transfer.

Computational insights and particularly quantum mechanical calculations can be used to explore this cofactor-driven modulation as well as the differential affinities for oxidized and reduced iron-heme. In this type of exploration, we typically consider different configurations of charge and spin for the iron (Fe) atom in the heme active site. The heme and the cofactor H₄B are taken in the iNOSoxy environment in this case. In these calculations, we take advantage of our hybrid QM/MM interface that we developed in this project. The interface

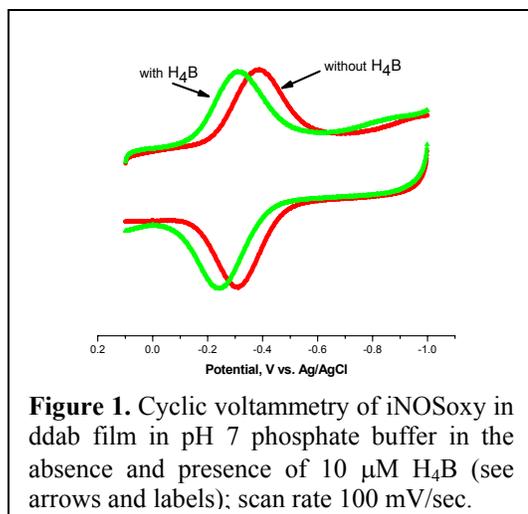
couples Gromacs and Car-Parrinello Molecular Dynamics (CPMD) codes for MM and QM parts respectively. The heme group (Fe-protoporphyrin) and part of the cysteine thiolate group are partitioned in the QM system, while the H₄B, the rest of the protein and the surrounding water are partitioned in the MM system.

The NOS-catalyzed oxygen activation process is key to NOS biocatalysis; identifying active oxygen complexes involved in this process is critical to full understanding of NOS molecular mechanism. In this regard, we developed a system using an ionic liquid as medium with extremely low water content to conduct direct electrochemical reaction in the presence and absence of oxygen. Although this is preliminary, this system allows us to have a better control on proton transfer steps which are critical in the overall oxygen activation process. Electrochemical tools such as cyclic voltammetry and square wave voltammetry are used in the Bayachou group to address electrochemically-driven catalysis and feedback inhibition of various NOS isoforms. Scan rate dependence along with digital simulations provide a direct assessment of the kinetics of the overall process.

Recent Progress

Considerable progress has been made on all fronts mentioned above. We provide below brief description of results in each specific goal.

Kinetic and thermodynamic effects on NOSoxy redox behavior: We have already shown that substrate-arginine and cofactor-H₄B act as modulators of redox properties of the heme-Fe^{III} in NOSoxys. The binding of H₄B shifts the formal potential of the heme in NOSoxy towards more positive potentials, and indicates 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.



Kinetics of electron transfer to Fe^{III}-heme in NOSoxys and effect of binding: The oxidation-reduction peak splitting provides a measure of the rate of the electron transfer. The collective set of ΔE_p measured over an appropriate window of scan rates in conjunction with digital simulations in our labs provide the rate of heterogeneous electron transfer. For our wild type iNOS oxygenase, a rate constant $k^0 = 5.3 \pm 0.1 \times 10^{-3}$ cm/s was determined at room temperature. This rate speaks to a relatively fast electron transfer to iNOS oxygenase in ddab films. We also explored the kinetics of electron transfer to the heme in NOS oxygenases in the presence of the H₄B cofactor. In this regard, Figure 2 shows our preliminary analysis of collective data measured on iNOSoxy in ddab films in the presence and absence of the cofactor H₄B. These results show that

the rate of heterogeneous electron transfer to the heme with bound H₄B is $12.8 \pm 0.1 \times 10^{-3}$ cm/s.

Computational insights on redox modulation and redox-driven affinity: In this exploration, different configurations of charge and spin for the iron atom in the heme active site were considered. With Fe^{II}-heme, after energy minimization, the H₄B cofactor is found to form hydrogen bonding with the propionate group of the heme, Figure 3. Similar calculations are carried with Fe^{III} state. The overall outcome of these results can be summarized as follows: First, our calculated interaction energies indicate that the minimum difference in the interaction energy of H₄B with the heme active site (QM) with Fe^{II}-heme on one hand, and Fe^{III}-heme on the other, is about 5.2507×10^{-3} au or 3.30 kcal/mol. We find that this energy difference is due mainly to the change in charge on the Fe-atom (i.e. oxidation state) and not the spin state. Second, close analysis of QM/MM optimized structure with the Fe^{III}-heme indicates that the hydrogen bond, previously observed for the reduced form Fe^{II}-heme, is weakened for the Fe^{III} oxidation state with an increase in H₄B-heme distance. This is consistent with our experimental observation and measurements.

Oxygen activation, low water environment, and cooperative influence of residues: We have previously shown that NOSoxy-modified electrodes catalytically reduce O₂ when the latter is added to buffer solutions. Irreversible catalytic voltammograms are obtained at moderate scan rates, indicating rapid reaction of O₂ with the reduced form Fe^{II}-heme-NOSoxy. We have previously shown that the ferrous-dioxy active intermediate is difficult to track by transient voltammetry. We have developed a system allowing us to conduct direct electrochemical measurements on protein thin films in low-water ionic liquid environments, which provide better control over proton transfer reactions. Figure 4 shows the typical cyclic voltammogram of iNOSoxy/ddab film immersed in the ionic liquid 1-butyl-3-methyl imidazolium tetrafluoroborate (BMIM BF₄) in the presence and absence of O₂. While there is a slight shift towards positive potentials upon addition of oxygen, there is absolutely no catalytic activation of oxygen as we observe in aqueous solution. The same is true even at scan rate as low as 10mV/sec, where one would expect maximum catalysis. This behavior is very interesting, and does indeed speak to a very ideally dry medium, where the protein keeps its structural integrity as evidenced by spectroscopy, and where one can add the source of protons in a controlled manner and interrogate the kinetics of the proton-limited

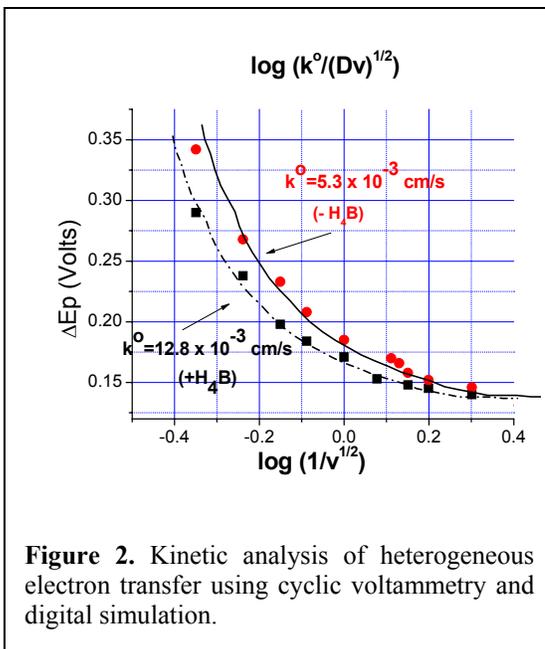


Figure 2. Kinetic analysis of heterogeneous electron transfer using cyclic voltammetry and digital simulation.

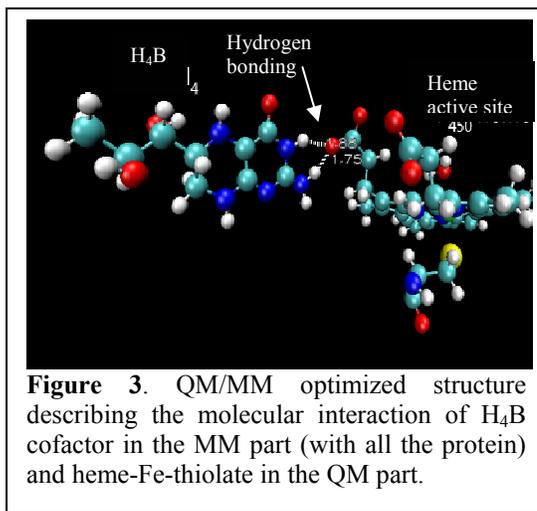


Figure 3. QM/MM optimized structure describing the molecular interaction of H₄B cofactor in the MM part (with all the protein) and heme-Fe-thiolate in the QM part.

oxygen reductive activation. We are now using this system to track the ferrous-dioxy intermediate and to study proton transfer-mediated activation.

We have explored an interesting aspect in regards to the interaction of H₄B with the catalytic oxygen activation by molecular dynamics simulation. The most important of a number of simulations is the fact that the significant change in the ionization potential and electron affinity of H₄B in the protein environment is due to the multipole electric field created by charged residues around H₄B and it is affected by protein dynamics; this is consistent with our previous electrochemical results pointing to a very high oxidation potential of H₄B, leaving transient dynamics a viable driving force, may be the only one, for an electron transfer to occur.

Catalysis, isoform behavior, mutants, and feedback inhibition: In regards to catalysis, we have closely studied the behavior of modified electrodes with iNOSoxy versus nNOSoxy proteins as far as the formation of the ferrous nitrosyl complex and the catalytic reduction of the product NO. Figure 5 shows for instance the catalytic reduction of exogenous nitric oxide, NO, on iNOSoxy-modified electrodes. From voltammetric studies and digital simulations, we noted that the ferrous-nitrosyl complex is significantly unstable in the case of iNOSoxy compared to nNOSoxy. We have now an expanding array of useful mutants identified, expressed and purified over the last two years based on both experimental and computational insights. We already started to thoroughly study their electrochemical behavior, as far as cofactor-induced redox modulation, oxygen activation, and feedback inhibition and nitrosyl complex stability.

Future Plans

Investigate in detail redox properties multiple site mutants: We plan to study double and multiple-site mutants that we have identified to closely study the cooperative effects of some amino acid residues on dynamic substrate and cofactor binding, oxygen activation and reactivity in the two steps of the NOS reaction.

Proton Transfer by both experimental and computational tools: We will closely investigate how proton transport occurs during critical steps of the NOS catalysis and how it is coupled to electron transport. Proton transport is a critical event in oxygen activation and it is by far the least understood.

First versus second step in electrochemically-driven reactivity of wild type and mutants: We will investigate the differences of electrochemically-driven NOS catalytic reactions with N-hydroxy-arginine (i.e. second step) as opposed to the case of substrate L-

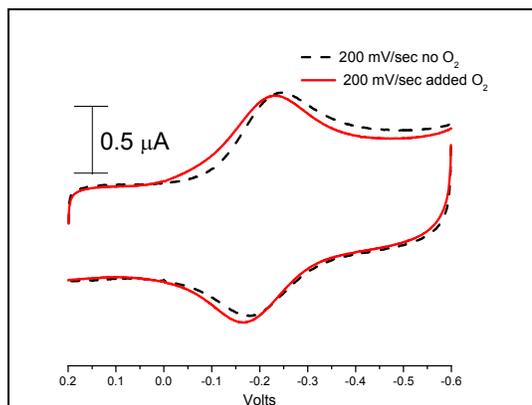


Figure 4. Cyclic voltammetry of iNOSoxy/ddab in very dry ionic liquid with, at 200 mV in the presence (—) and absence (---) of dioxygen.

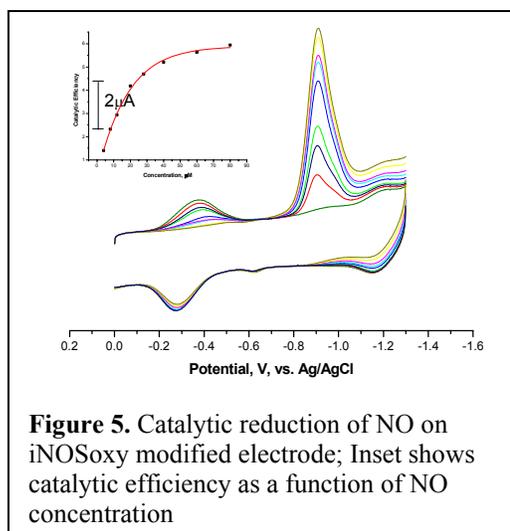


Figure 5. Catalytic reduction of NO on iNOSoxy modified electrode; Inset shows catalytic efficiency as a function of NO concentration

arginine (i.e. the first step), on NOS-modified electrodes that we developed in the first cycle of this project; computational insights and mutagenesis interrogation will continue to guide our efforts in this area. Study NO interaction with NOS oxygenase in the context of NO-feedback inhibition and measure redox properties of NO-heme complexes for various NOS-oxygenase isoforms. These studies aim to better understand the differential behavior of isoforms and correlate structure and function in terms NO-feedback inhibition of NOS oxygenases.

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Catalyst-Modified Carbon Pastes for Real Time Hydrodynamic Quantification of Nitric Oxide Generated Electrochemically on NOS Modified Electrodes.

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The biocatalytic synthesis of nitric oxide (NO) is mediated by enzymatic machineries called Nitric Oxide Synthases (NOS). The NO synthesis pathway is very complex and we use NOS-modified electrodes to gain mechanistic and kinetic insights into this catalytic reaction, which oxidizes in two steps the substrate arginine into nitric oxide and citrulline. Quantifying the end product NO accurately in real time on our NOS-modified electrodes is critical for both kinetic and mechanistic investigations.

Methods currently available to measure these products in real time are relatively complex, and their sensitivity and selectivity is not suitable for our project, which focuses on gaining insight into elemental steps of the NOS reaction on NOS-modified electrodes.

We have previously developed modified carbon microfiber electrodes with for very sensitive NO detection and quantification on our NOS-modified electrodes *in situ*. However, these electrodes provide only a “single-point” collection near the macroscopic NOS modified electrode. For better quantitative measurement of NO generated on our NOS-modified electrodes, we decided to develop carbon pastes modified with colloidal metal catalyst particles as NO sensors with enhanced detection capability. The NO-sensitive carbon paste is to be used as a ring around NOS-modified electrodes for efficient hydrodynamic NO measurement on a rotating ring-disc electrode. The NOS-modified disc is acts as NO generator and is driven electrochemically, while the colloid-modified carbon paste ring acts as the NO collector. The preparation of catalyst-modified carbon pastes have been optimized and characterized. Electrocatalytic oxidation of the NO on the modified versus original pastes was assessed by cyclic voltammetry, amperometry in standing solutions, and in flow injection analysis. The catalyst-modified carbon paste showed superior electrocatalytic behavior compared to regular carbon paste, with a sensitivity of about 13x higher, and a limit of detection in the ~100 pM range. The performance of this catalyst-modified paste on ring-disc rotating electrodes for hydrodynamic NO detection is now exploited to accurately quantify our electrochemically driven NOS catalysis.

Direct detection of Nitric Oxide on Modified Carbon Fiber Electrode: Cooperative effect of Electrochemically conductive Polymer (PDOT) and a Transition Metal Catalyst.

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Nitric oxide (NO) is a free radical with multiple physiological functions; it is synthesized by heme-flavoenzymes called nitric oxide synthases (NOS) in a two-step catalytic process with exquisite structural and kinetic control. The mysterious elemental steps of this catalytic process triggered vigorous research aiming at shedding more light on how the biosynthesis of this reactive molecule is catalyzed by the NOS molecular machineries. Our project uses direct electrochemical methods combined with molecular biology and computational insight to develop an understanding of the NOS catalysis at the atomic level. The detection and quantification of nitric oxide on NOS-modified electrodes is key for our mechanistic and kinetic investigations. Although we have recently developed transition metal-modified carbon fiber electrodes for NO measurement on NOS-modified electrodes, the sensitivity of these fibers was limited. We therefore developed a new generation of modified carbon fibers for NO detection consisting of a hybrid matrix containing consecutive layer-by-layer electropolymerized 3, 4-ethylenedioxythiophene (EDOT) and electrodeposited metal oxide catalyst on 7- and 30- μm carbon fiber electrode (CFE). The layer-by-layer modified fiber is characterized by SEM and elemental analysis. Its electrocatalytic detection of NO was characterized by cyclic voltammetry and amperometry. Our data indicate that the modified microelectrode has rapid and reproducible response to NO at relatively low applied potential (0.5V vs. Ag/AgCl). The metal catalyst-PEDOT (Poly EDOT)-modified carbon fiber exhibits great response for NO, with a sensitivity 130-times higher than the bare fiber. In addition to sensitivity, we show that this "third generation" electrocatalytic NO sensor provides excellent linearity on a wide range, including low concentrations (sub-nanomolar) of NO, which can be used for reliable detection of NO. Preliminary results and application in the context of our larger project will be presented and discussed.

Catalysts for Selective Olefin Oligomerization and Polymerization

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Goal

To develop organometallic polymerization initiators that increase the options available for chemical synthesis and industrial processes and that contribute toward a better management of petrochemical resources.

Recent Progress

i) α -Iminocarboxamide Nickel Complexes: Synthesis and Uses in Ethylene Polymerization. A series of nickel complexes containing α -iminocarboxamide, η^1 -benzyl and PMe_3 ligands were synthesized to identify structural features of neutral Ni complexes that are employed in ethylene polymerization and ethylene/functionalized norbornene copolymerizations. Variations in steric bulk on aryl substituents in the α -iminocarboxamide framework were used to probe N,N - vs. N,O -binding modes. When the steric bulk is sufficiently large, as in $[N-(2,6\text{-diisopropylphenyl})-2-(2,6\text{-diisopropylphenylimino})\text{-propanamidato-}\kappa^2N,O]\text{Ni}(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)$ (**1**), $[N-(2,6\text{-diethylphenyl})-2-(2,6\text{-diethylphenylimino})\text{-propanamidato-}\kappa^2N,O](\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)\text{nickel}$ (**2**), $[N-(2,6\text{-methyl-isopropylphenyl})-2-(2,6\text{-methyl-isopropylphenylimino})\text{-propanamidato-}\kappa^2N,O](\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)\text{nickel}$ (**3**), one observes N,O -binding. In the case of $[N-(2,6\text{-dimethylphenyl})-2-(2,6\text{-dimethylphenylimino})\text{-propanamidato}][(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)\text{nickel}$ (**4**), both N,O - and N,N -bound can be obtained and isolated; the N,N structure is the thermodynamic product. N,N products are observed with smaller ligands, as in $[N\text{-phenyl-}2-(2,6\text{-diisopropylphenylimino})\text{-propanamidato-}\kappa^2N,N](\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)\text{nickel}$ (**5**) and $[N-(2,6\text{-diisopropylphenyl})-2\text{-}(\text{phenylimino})\text{-propanamidato-}\kappa^2N,N](\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)\text{nickel}$ (**6**). Ethylene polymerization, upon activation with $\text{Ni}(\text{COD})_2$, is observed only with the N,O -bound species. NMR spectroscopy shows that addition of $\text{Ni}(\text{COD})_2$ to **5** and **6** results in removal of the phosphine and the formation of an η^3 -benzyl fragment. Furthermore, the phosphine-free complex $[N-(2,6\text{-diisopropylphenyl})-2-(2,6\text{-diisopropylphenylimino})\text{-propanamidato-}\kappa^2N,N](\eta^3\text{-CH}_2\text{Ph})\text{nickel}$ (**7**) is also inactive toward ethylene polymerization. These observations suggest that ethylene polymerization are preferentially initiated by nickel complexes with N,O -bound α -iminocarboxamide ligands.

ii) **Tapered Block Copolymers Containing Ethylene and a Functionalized Comonomer.** Gradient, or tapered, copolymers have a chemical structure with a gradual change of composition along the polymer chain, from one comonomer to the other. If the average chain length is sufficiently long, the degree of incompatibility between the two monomers is high and the gradient profile provides chain ends that contain mainly one type of monomer, then microphase separated structures similar to those observed in traditional block copolymers can be observed. This special class of gradient copolymers, called tapered block copolymers (TBCs), are of importance, in particular they are efficient compatibilizers of polymer blends and may be superior to block copolymers for this application. The phase morphology and interfacial energy in TBCs is modulated by the length and sharpness of the composition gradient.

In view of the motivations given above, we developed and optimized the synthesis of tapered block copolymers of ethylene with 5-norbornen-2-yl acetate (**8**) by the nickel catalyst system $[N-(2,6\text{-diisopropylphenyl})-2\text{-}[(2,6\text{-diisopropylphenylimino})\text{propanamide}]\text{Ni}(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)$ (**1**) and $\text{Ni}(\text{COD})_2$ (bis(1,4-cyclooctadiene)nickel), as shown in Figure X.

Polymerization takes place when ethylene is added and is terminated after a chosen reaction time.

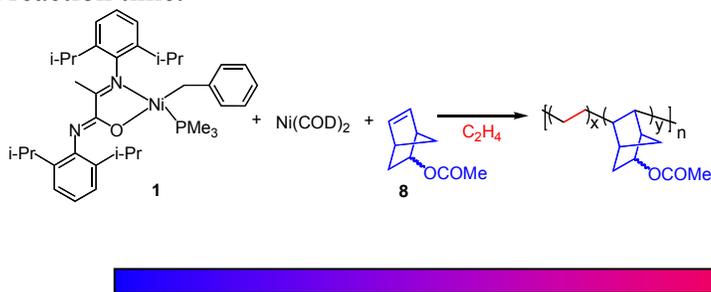


Figure X. Gradient copolymerization method. The ratio (x/y) increases as a function of n . The gradient bar illustrates the compositional variation from segments rich in **1** (blue) to segments rich in C_2H_4 (red).

This technique utilizes a one-pot semi-batch copolymerization in which ethylene is continuously added while **8** is depleted by incorporation into the polymer chain. The simplicity of this technique allows the construction of a polymer library, which enabled us to study the effect of polymer composition and chain length on solid-state morphology and mechanical and thermal properties. From these studies we were able to derive a profile relating the probability of **8** insertion versus degree of polymerization (X_n). Under proper experimental conditions, these tapered polymers form ordered microphase-separated morphologies where the phase morphology is modulated by the polymer chain length. The percent crystallinity and storage modulus of the polymers was found to be chain length dependent.

DOE Interest

Polyolefins constitute a large fraction of materials derived from petrochemical resources. Better methods for their preparation and processing thus improve our management of oil and its derivatives. Additionally, materials that modulate the

interfacial energies of polyolefins and polar commodity plastics should substantially increase the scope of applications for polyolefins by allowing their incorporation into polymer “alloys”.

Future Plans

We plan to continue exploring the development of initiators that incorporate polar monomers into polyolefin chains with a focus on polypropylene. There are a couple of promising leads based on variations of the α -iminocarboxamide ligands, which support the active metal center via a spectator olefin adduct. Additionally, the quasi-living characteristics of the polymerization reactions mediated by activating **1** with Ni(COD)₂ should allow us to create novel polymer architectures, such as tetrablock and tapered tetrablock structures.

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

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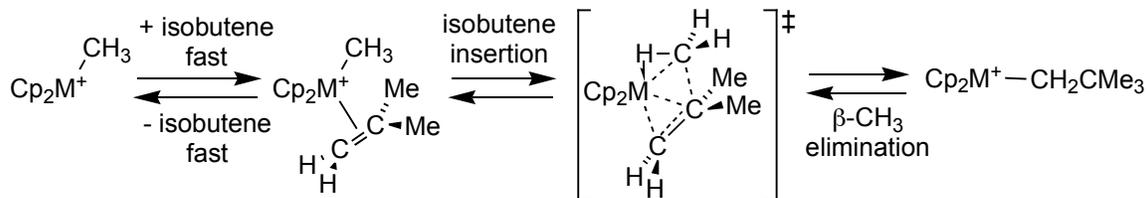
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Goal

Advance (1) understanding of fundamental principles of polymerization catalysis such as ligand effects on stereochemistry, elementary rates, and co-anion effects on stereochemistry for metallocenium cation-catalyzed olefin polymerization in order to guide development of superior catalyst systems, and (2) the development of catalysts capable of kinetic resolution of chiral 1-alkenes.

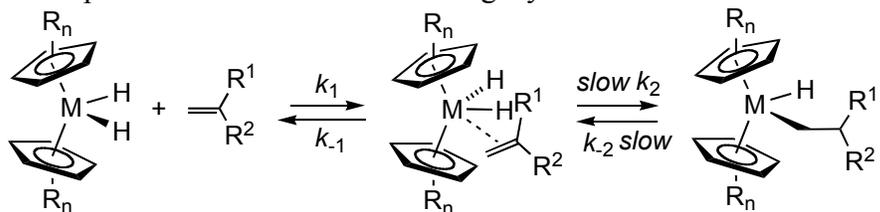
Recent Progress

We have reported some experimental evidence for γ -agostic assistance in β -methyl elimination, providing additional evidence for the microscopic reverse of α -agostic assistance in the chain propagation step of olefin polymerization. Isotopically labeled zirconocene(methyl)(neopentyl) complexes of the formula, $(\text{CpR}_n)_2\text{Zr}(\text{CH}_3)(\text{CH}_2\text{C}(\text{CH}_3)_2\text{CD}_3)$, when treated with $\text{B}(\text{C}_6\text{F}_5)_3$ result in β -methyl elimination forming the ion-paired species $[(\text{CpR}_n)_2\text{Zr}(\text{CH}_3)][\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]$ along with isotopologs of isobutene. The relative amounts of d_3 - and d_0 -isobutene afford the isotope effect (1.40(2) has been measured at 23 °C) for β -methyl elimination.



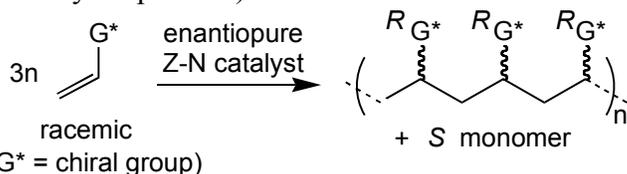
We have also investigated cyclopentadienyl and olefin substituent effects on the rates and thermodynamics of olefin insertion and β -H elimination for group 4 metallocene systems. Whereas the effects of metallocene symmetry on polymer stereochemistry are fairly well-understood, a predictive correlation between cyclopentadienyl substitution pattern and polymer molecular weight has not yet been established. For $\text{Cp}^*_2\text{HfH}_2$, the relative rates of olefin insertion have been found to be 1-pentene > styrene \gg *cis*-2-butene > cyclopentene > *trans*-2-butene > isobutene. The rate of isobutene insertion into $\text{Cp}^*(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{ZrH}_2$ is 3.8×10^3 times greater than that for $\text{Cp}^*_2\text{ZrH}_2$ at 210 K, demonstrating the striking steric effect for isobutene insertion imposed by a tenth methyl substituent on the two cyclopentadienyl ligands. A primary k_H/k_D of 2.4(3) at 23 °C and a linear free energy correlation to σ ($\rho = -0.46(1)$) for

para-substituted styrene insertion indicate that insertion into a Zr-H bond proceeds via rate determining hydride transfer to coordinated olefin, with small positive charge buildup at the β carbon of the inserting styrene.



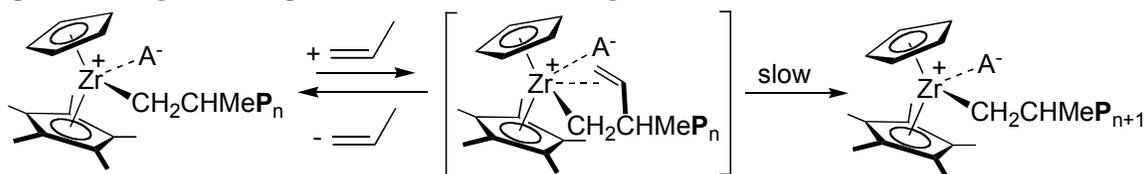
The rates of β -H elimination for the series $(R_n\text{Cp})_2\text{Zr}(\text{CH}_2\text{CHR}')(\text{H})$ have been measured via rapid trapping of the intermediate zirconocene dihydride with 4,4-dimethyl-2-pentyne: (a) $k_H/k_D = 3.9 - 4.5$ and (b) a linear free relationship for the phenethyl hydride series, $\text{Cp}^*(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Zr}(\text{CH}_2\text{CH}_2\text{-}p\text{-C}_6\text{H}_4\text{-X})(\text{H})$ ($X = \text{H}, \text{CH}_3, \text{CF}_3, \text{OCH}_3$), $\rho = -1.80(5)$.

A major project during the last funding period was directed toward the development of a catalyst system that effects the *kinetic resolution* of chiral olefins (e.g. 3-methyl-1-pentene).



Some of metallocenium catalysts that we have developed are extremely active, particularly the doubly $[\text{SiMe}_2]$ -linked zirconocenium systems, producing in many cases $>10^4$ kilograms of polymer/g of metal·hr. Syntheses of the $\{(1,2\text{-SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_2\text{-4-R})(\eta^5\text{-C}_5\text{H-3,5-CHMe}_2)\}$, "R-Thp", ligand using an enantiopure chiral substituent R has been carried out to give the C_1 -symmetric, (*S*)-methylneopentyl-ThpZrCl₂. When activated with methylaluminumoxane, these metallocenes show unprecedented activity for the polymerization of bulky racemic monomers bearing substitution at the 3- and/or 4-positions. These catalyst systems do indeed effect kinetic resolutions: $s = k_{\text{faster}}/k_{\text{slower}} \sim 2$, but in one case, the polymerization of 3,4-dimethyl-1-pentene, high levels of separation were obtained ($s > 15$).

We have completed a first phase of our kinetic investigations of chain propagation and transfer via direct observation of the kinetically relevant metallocene catalytic species using low-temperature NMR monitoring.



$\text{A}^- = [\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$; P_n = polymer chain of n monomers

Second order initiation (k_i) and propagation rate constants (k_p) for the polymerization of propene and a series of 1-alkenes catalyzed were measured by ¹H NMR spectroscopy in toluene-*d*₈ at low temperatures. Comparisons of the measured values of propagation rate constants for propene and other alkenes at -45 °C reveals that k_p decreases with

increasing chain length and steric influence: propene ($105(10) \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$) > 1-butene ($27(5) \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$) > 1-pentene ($18(1) \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$) > 1-hexene ($15(1) \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$) > 1-undecene ($7.8(7) \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$) > 4-methyl-1-pentene ($4.3(5) \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$). The overall activation parameters for propene propagation determined from an Eyring analysis are $\Delta H^\ddagger = 8.5(3) \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -25(2) \text{ eu}$. The propagation rate was found to increase in the presence of $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ counteranion (but not in an integral kinetic order manner) and in a more polar toluene- d_8 /chlorobenzene- d_5 solvent system. The experimental results are most consistent with propagation mechanism that does not involve the formation of outer-sphere ions for alkene polymerization by this catalyst system.

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

With regard to kinetic resolution of chiral olefins, we plan to explore more fully the role of chain end control in stereoselection and to develop new enantiopure, C_2 -symmetric catalysts that will avoid stereo-errors generated with the C_1 -symmetric systems that we have explored earlier. We will examine the effects of the counteranion on stereocontrol and activity in olefin polymerizations with a group 4 metallocenium cation. Our new strategy employs a tethered anion constrained to reside on only one side of the metallocenium wedge. Finally, we will pursue semi-rigid, non-metallocene catalysts based on two highly substituted phenoxide or anilide groups connected at the *ortho* positions via semi-rigid, ring-ring (sp^2 - sp^2) linkages to a flat cyclic linker that presents another donor (either L-type or X-type); these resemble metallocene systems. We will explore their utility as polymerization catalysts, as well as their abilities to control polymer tacticity and conceivably even fluxional enantiomeric site-control.

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2. Kinetic Resolution of Chiral α -Olefins Using Optically Active Ansa-Zirconocene Polymerization Catalysts, C. R. Baar, C. J. Levy, E. Y.-J. Min, M. W. Day, and J. E. Bercaw *J. Am. Chem. Soc.* **2004**, *126*, 8216.
3. Experimental Evidence for γ -Agostic Assistance in β -Methyl Elimination, the Microscopic Reverse of α -Agostic Assistance in the Chain Propagation Step of Olefin Polymerization, P. J. Chirik, N. F. Dalleska, L. M. Henling, and J. E. Bercaw *Organometallics* **2005**, *24*, 2789.
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Highly Selective Organic and Organometallic Reactions in Water-Soluble Host-Guest Media

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Postdoctoral

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Goal

Although a great deal of work has been done on the synthesis of self-assembled molecular systems that encapsulate smaller species, much less is known about how such systems can be developed to function as catalysts. The present project was designed to combine the expertise in supramolecular chemistry in the Raymond group and the knowledge of organometallic catalysis in the Bergman group, to determine whether catalysts can be incorporated in self-assembled systems and used to strongly modify the rates and selectivities of the reactions that take place inside the assembly cavities.

Recent Progress

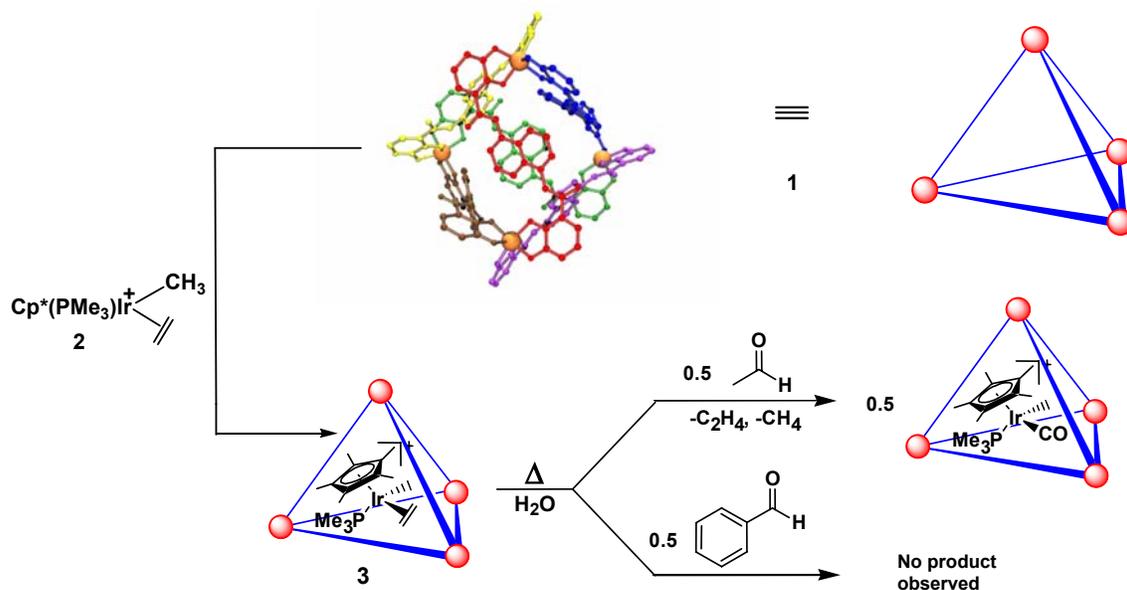
Several years ago, workers in the Bergman group discovered some of the first "C-H activation" reactions that involve reactive Ir(I), Rh(I) and Re(I) complexes in the conversion of alkanes into isolable metal complexes. More recently, the higher-valent methyliridium(III) cation $[(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{IrCH}_3]^+$ has been uncovered that also is capable of hydrocarbon C-H bond activation. These transformations also proceed by initial C-H oxidative addition, in this case to give very high oxidation state iridium(V) intermediates, followed by reductive elimination. Often the initially-formed products undergo rearrangement—aldehydes (RCH=O), for example, give the decarbonylated complexes $[(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Ir}(\text{CO})(\text{R})]^+$ as final products. Concurrently, work in the Kenneth Raymond group has led to the self-assembled synthesis of water-soluble chiral clusters or "nanovessels" constructed from metal salts and dicatecholate bridging ligands. These polyanionic assemblies (**1**) contain cavities that are capable of encapsulating organic and organometallic ions that have appropriate size and shape and carry a single positive charge.

Because both the nanovessel assemblies and C-H activating iridium cations are water soluble, we recently initiated a collaborative project aimed at determining whether the Ir cations described above would bind into the cavities of the nanovessels and carry out selective C-H activation reactions inside the assemblies. This effort has been successful, and we have observed the first "intravessel" C-H activation reactions of several classes of organic compounds, including aldehydes, aromatic compounds, and ethers. Substantial size- and shape selectivities (e.g., with encapsulated assembly **3**, as illustrated in Scheme 1) have been observed in these reactions.

Most recently, we have turned to the determination of whether rearrangement reactions of cationic organic substrates would take place inside nanovessel cavities. We first focused on [3,3]-sigmatropic rearrangements of unsaturated enammonium ions e.g., compound **4** in Scheme

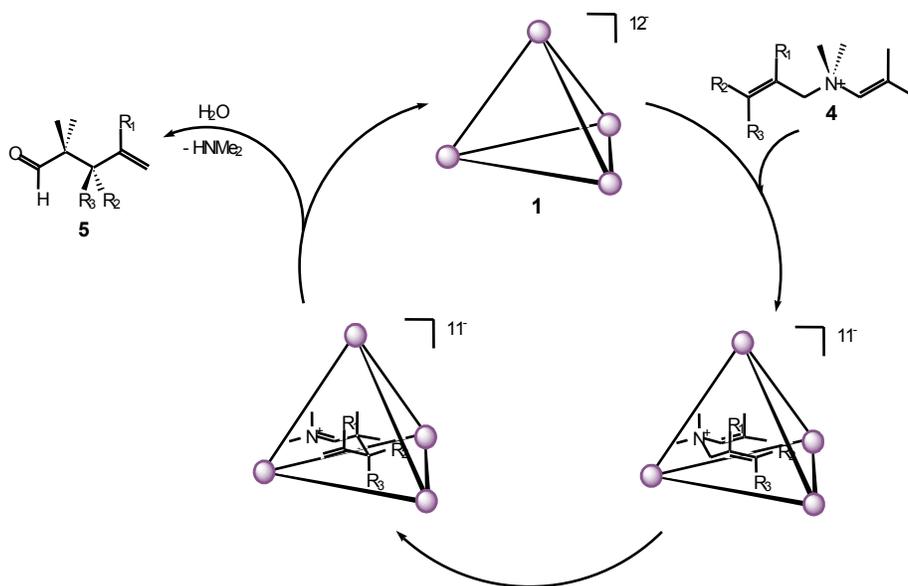
2). These rearrangements have not only been found to proceed in the nanovessels, but the reactions proceed more rapidly than they do under ordinary solution conditions.

Scheme 1



This fact, and the ability of the products of these reactions to undergo rapid hydrolysis to give **5**, results in our ability to carry out the reactions in a catalytic fashion (Scheme 2). The nanovessels catalyze the rearrangement/hydrolysis of the aza-Cope substrates with up to 1000-fold rate acceleration.

Scheme 2



DOE Interest

Work on this project responds to the interest of DOE in (a) development of new carbon-hydrogen bond activation reactions, leading to the more efficient use of organic molecules in fuels and chemical synthesis, (b) understanding how rate acceleration and selectivity are controlled in catalytic active sites of specific size and shape, such as those in heterogeneous systems and enzymes, and (c) development of ways to use this understanding to devise new control methods for catalysis selectivity.

Future Plans

In the part of this work involving encapsulated metal complexes, we plan to move from stoichiometric to catalytic reactions, with plans to bind catalytically active metal complexes into nanovessel cavities and use these sites to control the rates and selectivities of reactions catalyzed by the sequestered complexes. To exploit our finding that the capsules themselves can be catalytically active, we plan to determine the physical basis for this catalysis, use this information to enhance the catalytic rates, and investigate other organic and organometallic reactions that can be catalyzed by nanovessel incorporation. Longer-range plans involve the synthesis and exploration of catalytic properties of larger nanovessels that can encapsulate a wider range of molecules, as well as enantioresolved assemblies that should be capable of carrying out catalytic asymmetric transformations.

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Organic Chemical Transformations at Interfaces

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Goal

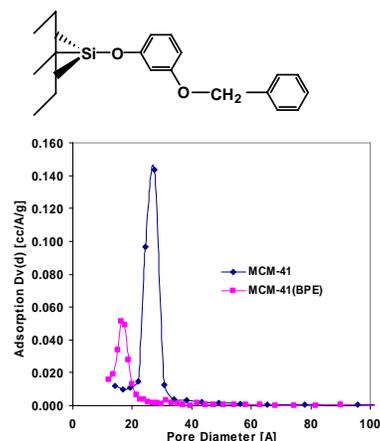
The objective of this program is to develop new fundamental understanding of the key features that govern organic molecular interactions and selective transformations at solid interfaces with an emphasis on mesoporous metal oxides.

Recent Progress

Research in this program focused on three principal themes. First, the impacts of pore confinement, size, and surface properties in mesoporous solids (silica, silica-titania, etc.) on organic free-radical and ionic reactions were explored with an emphasis on covalently assembled hybrid materials. Second, the impact of hydrogen bonding of organic molecules (ethers, alcohols, etc.) in the gas phase and at metal oxide surfaces on their high temperature ($> 250\text{ }^{\circ}\text{C}$) chemical transformations was systematically explored. Computational studies involving electronic structure calculations were employed to help unravel the complex free-radical pathways. Third, the relationships between structure and dynamics of the organic-inorganic interface and resultant chemical reactivity was probed with spectroscopic techniques such as C-13 and O-17 solid-state NMR, as well as steady-state and time-resolved fluorescence techniques employing probe molecules. Quasielastic neutron scattering studies coupled with molecular dynamics simulations was investigated to provide additional insights into molecular motion under pore confinement. A few examples are provided below.

Effects of Pore Confinement on Free-Radical Transformations.

Hexagonal mesoporous silicas are conveniently functionalized with aromatic phenols whose subsequent thermally induced, free-radical chemistry can be explored as a function of pore size and grafting density.^{1,2} Studies of 1,3-diphenylpropane (DPP) at $375\text{ }^{\circ}\text{C}$ revealed that the rates of the free-radical chain reaction were accelerated in the mesoporous solids and increased with decreasing pore size ($5.5 - 1.7\text{ nm}$), suggesting increased rates for key hydrogen transfer steps on the surface.² Pyrolysis of benzyl phenyl ether (BPE), a model for α -aryl ethers in lignin, confined in mesoporous silicas was investigated at $275\text{ }^{\circ}\text{C}$ as a function of pore diameter ($1.7 - 2.7\text{ nm}$).¹ The reaction rate was slightly slower than previously observed on non-porous silica (Cabosil) as a consequence of a reduced rate for initial radical formation (O – C homolysis) in these nanoporous solids. The two



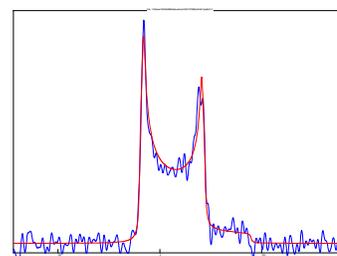
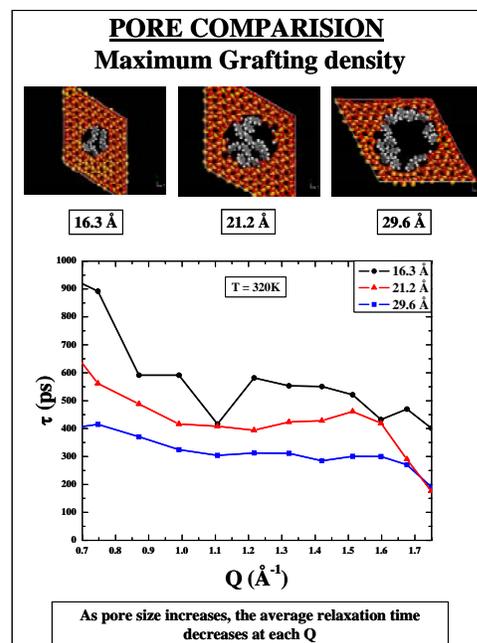
rearrangement pathways previously detected on the Cabosil surface account for an even larger fraction of the products in the MCM-41 silicas, and the selectivity between the two pathways was only slightly affected by the pore confinement. Current studies on the pore-confined lignin model structure, phenethyl phenyl ether, indicate that pore confinement, molecular grafting density, and the presence of co-attached rigid spacer molecules (biphenyl) on the surface can significantly alter product selectivity through steric hindrance of a radical rearrangement pathway. Molecular modeling and dynamics simulations suggest that hydrogen bonding to the surface is also playing a role.

Impact of Pore Confinement on Molecular Motion. The motion of hydroxy-1,3 diphenylpropane affixed to the surface of silicas (mesoporous and non-porous) by covalent attachment via a silyl aryl ether linkage and through hydrogen bonding of the phenol to surface silanol functionality has been characterized by variable temperature ^{13}C NMR spin lattice relaxation and Nuclear Overhauser Enhancement (NOE) measurements. The studies have shown that the organic moiety exhibits rapid average reorientation rates even at high molecular densities. The organic molecules covalently attached to the surface are more restricted than molecules held by hydrogen bonding, reflecting two additional degrees of freedom in the hydrogen-bonded complex.

Neutron scattering experiments investigating the dynamics of 1,3-diphenylpropane (DPP) molecules tethered in mesoporous silicas were initiated in collaboration with Dr. Ken Herwig (ORNL, SNS) on the high flux backscattering spectrometer at NIST. Initial studies examined the effect of both MCM-41 pore size and DPP grafting density on the dynamics over a wide temperature range. Initial results from quasielastic neutron scattering measurements indicate that there is more molecular motion in the larger pores, as perhaps expected, but also at higher grafting densities. The latter observation suggests that DPP molecules are interacting more with the surface at lower grafting densities, and extensive molecular dynamics simulations (Dr. Alan Chaffee, Monash University) are in progress to aid in the interpretation of the neutron scattering data.

Steady state and time-resolved fluorescence and fluorescence anisotropy techniques have been employed to study the effect of pore confinement (using various pore diameter MCM-41 and SBA-15 silicas) on the emission and dynamics of fluorescent probe molecules 1-hydroxypyrene (HPy) and 1-pyrenebutanol (PyBu) chemically attached to these surfaces. Spectroscopic data indicate that excimer (formed from the interaction of a ground-state pyrene with an excited singlet state of pyrene and/or excitation of a ground-state pair) formation and emission is dependent on pore size, probe/molecular spacer (biphenyl) ratio, and probe chain length. The excimer emission increases as these parameters are increased. The observation that PyBu exhibits more excimer emission than HPy for similar probe/spacer ratios in the same pore diameter reflects the additional “reach” provided by the butyl tether present in PyBu.

Solid-State ^{17}O NMR. ^{17}O MAS and MQ/MAS NMR spectroscopy has been used to characterize a series of silica “cubes” based on the Si_8O_{12} framework in collaboration with Dr. Craig Barnes (University of Tennessee). The figure shows the ^{17}O -NMR spectrum of $(\text{Me}_3\text{Si}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$ (Fit: $C_Q = 4.95$ MHz; $\eta = 0.0$; $\delta = 33.5$ ppm). The results allow the interpretation of more complex products of functionalized, condensed polymers built on this framework. The work is also relevant to our understanding of the framework silica contribution to reactions on silica surfaces.



DOE Interest

The organic molecules examined in this research are typically models for important functional groups present in biomass, a renewable organic energy resource of interest as a potential alternative source of fuels and chemicals, and the mesoporous metal oxides studied are often used as catalyst supports. This research provides fundamental knowledge that will contribute to advances in many fields such as heterogeneous catalysis, separations, and the synthesis and properties of nanostructured materials, for which the interface is paramount.

Future Plans

Pyrolysis studies of pore-confined phenethyl phenyl ether (PPE) will be studied in more detail since recent studies have shown the product selectivity to be very sensitive to the structure of the interface. Investigations will include an examination of the impact of rigid molecular extenders that move the PPE molecules away from the surface, and the presence of a second spacer molecule on the surface that is either rigid or flexible. In addition, the potential role of pore curvature on the efficiency of hydrogen transfer to free radicals will be explored through the study of the pyrolysis of 1,3-diphenylpropane (DPP) in the presence of co-tethered hydrogen donor molecules. MCM-41 mesoporous silicas will be employed with initial pore sizes in the 1.7 – 3.0 nm range. Hydrogen donors, 2-fluorene and 3-fluorene, will be employed since recent studies on nonporous Cabosil showed that the rate of hydrogen transfers, and resulting DPP pyrolysis rates, were sensitive to molecular orientation of the hydrogen donor.¹¹

Neutron scattering experiments investigating the dynamics of organic molecules tethered in mesoporous silicas will be expanded. The focus will be on examining phenethyl phenyl ether (PPE) derivatives in mesoporous silicas as a function of grafting density and temperature to explore the potential role of hydrogen bonding to the surface on the PPE molecular motion. This information will be correlated with molecular dynamics simulations and pyrolysis results to gain a more complete understanding of pore confinement effects on molecular motion and chemical transformations.

¹⁷O NMR techniques will continue to be developed as probes of chemical interactions and reactivity at interfaces. This nucleus is ideally suited for interface studies on metal oxide surfaces. Specific isotopic enrichment by chemical means highlights the surface and targets the reactivity zone where interesting chemistry occurs. This work has direct impact on understanding of the structure of solid/liquid and solid/solid interfaces. Hydrogen bonded complexes between phenols and metal oxide/hydroxide surfaces will be investigated. The latter are important in relation to the use of mixed metal oxides as catalytic surfaces and provide a way to explore the metal particle/ surface interaction of real catalysts.

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Nanoporous Silicate Catalyst Design

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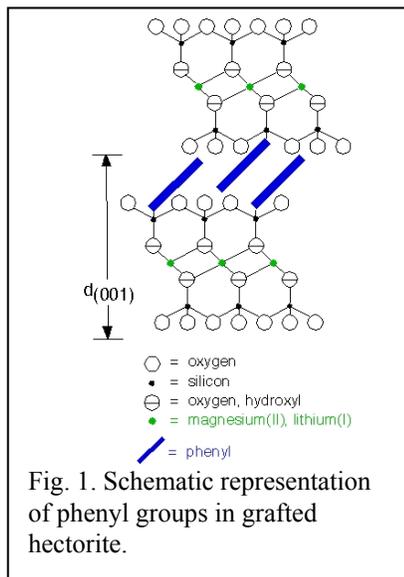
Goal

To develop fundamental, basic understanding of the relationship between the synthesis of a heterogeneous catalyst and the resulting surface structure, reactivity and selectivity of the catalyst. Tailored silicate materials then comprise the central focus of testing hypotheses about the role of metal particle morphology in catalysis. Only after a full understanding of formation processes is achieved can synthetic control be utilized to tune the properties for a particular application.

Recent Progress

Synthetic Catalyst Design.

(1) *Mechanisms of Catalyst Support Formation.* We have successfully completed the first in situ small angle x-ray scattering (SAXS) study of layered silicate crystallization. While some mechanistic information has been obtained from ex situ SAXS in the past, more complete information can be expected from in situ time-resolved SAXS experiments. For this purpose, a variable temperature flow cell was designed and optimized at APS Sector 12-ID. A successful run of silane-hectorite crystallization was completed. Data were collected every 5 min during 20 hr of hydrothermal crystallization over $Q = 0.1 - 0.03 \text{ \AA}^{-1}$. The data, similar to an ex situ silane-hectorite experiment, modeled best with the general unified fit using two structural levels. R_g values are observed to triple over the first 10 hr of reaction, after which they level off. Another synthetic approach pursued during this term involved co-condensation methods to introduce organic functionality grafted to the layered support. Fig. 1 shows a schematic representation of an experiment performed using phenyltriethoxysilane (PTES), which yields surfaces that are derivatized with phenyl groups throughout the gallery space. Variation of the density of organic groups was demonstrated by using mixtures of tetraalkoxysilane (TEOS) and PTES as precursors.



(2) *Tailored Supports for Metals, Metal Sulfides and Metal Oxides.* This portion of the program has begun to examine whether tailored mesostructuring of synthetic layered silicate supports has any effect on metal sulfide or metal nanoparticle size and shape. Small Pt(0) rafts (1.7 x 10 nm) were observed within the interlayer galleries of silica-hectorite via TEM (see Fig. 2). In contrast, Pt(0) spheres of 5 nm are observed on polymer-clay nanocomposite supports. These samples were prepared via a chemical method, wherein a Pt-salt is dispersed and followed by reduction under H₂ at 150°C. Au(0) also has been prepared on synthetic silica-hectorite via the chemical method and is being studied by XRD, UV-vis and TEM. The polydispersity of the spherical nanoparticles is fairly high but 93% Au(0) are < 10 nm and 62% are within 2-6 nm.

Catalytic Activity. The activity of CoMoS-loaded mesostructured silica-clays was greater than on layered silane-clays for both HDS and deep HDS. Furthermore, there is an optimum mesoporosity for the silica-clays. Mesoporosity can be controlled by the size of the precursor silica sol in the clay synthesis. A variety of precursor silica sol sizes (12 to 22 nm) was employed to synthesize the clay supports. Catalytic activity peaked with 15 nm sols. The 15 nm sols also foster the most crystalline materials (from XRD & TEM) and the optimum mesostructure (in terms of textural porosity from porosimetry data) of the clay catalyst support. We speculate that there is an optimum CoMoS-species size and/or shape for HDS catalytic activity, and a 15 nm sol-derived synthetic clay allows CoMoS species to most closely attain that optimum. This speculation can be clarified by more extensive HR-TEM imaging of metal loaded catalysts. Fig. 3 shows that an unusual multilayered CoMoS “banding” structure is evident in the most active HDS catalyst. NiMoS particles are more catalytically active for deep HDS because Ni catalyzes a pre-hydrogenation step. We have begun studies on NiMoS synthetic clays, focusing initially on the optimum 15 nm silica-hectorites for CoMoS particles. As expected, results show that deep HDS conversions increased by 30-50% over CoMoS depending upon reaction temperature.

Polymer-Clay Nanocomposites. Because membranes in general are important to catalysis and because adding polymer can change drastically the characteristics of clays, we began to investigate whether PCN-film morphology leads to unique catalytic sites (metal nanocluster morphology) and activity. Initial studies have been directed at metal nanoparticle PCN films which can be contrasted to the analogous powders. In contrast to intra-gallery Pt(0) raft formation in the pure clays, spherical 5 nm Pt(0) nanoparticles form that are dispersed primarily within the external polymeric matrix. An in situ SAXS study of the reduction process was performed. An R_g component which appears only after 120°C is assumed to arise from the reduced Pt(0) nanoparticles that form in situ during reduction. This experiment demonstrated that SAXS alone (without anomalous methods) can be used to follow the growth of a metal nanoparticle in situ. A similar, preliminary, study was also carried out using the grazing incidence method. This served to show that studies on the surfaces of PCN films are possible. The GISAXS data reveal that, at

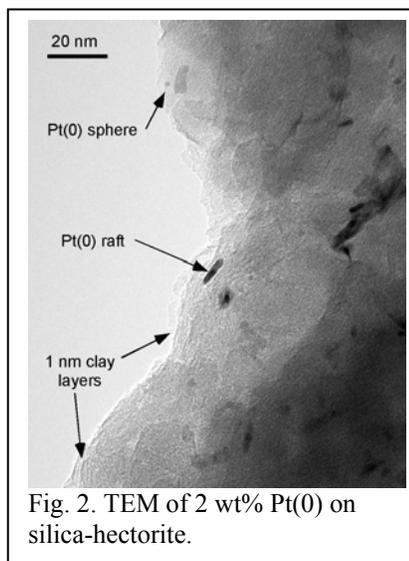


Fig. 2. TEM of 2 wt% Pt(0) on silica-hectorite.

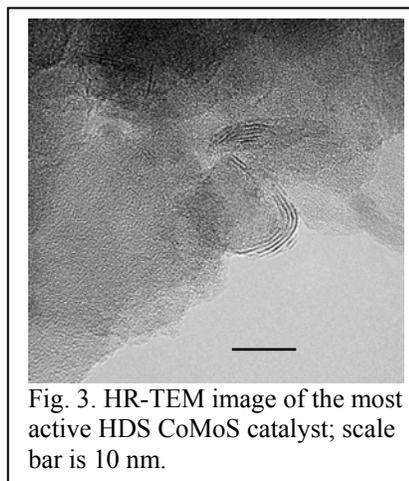


Fig. 3. HR-TEM image of the most active HDS CoMoS catalyst; scale bar is 10 nm.

low wt% Pt, the nanoparticles reach and maintain a maximum size (2.9-3.4 nm). At high loadings, however, the nanoparticles continue to coalesce past 200°C.

DOE Interest

This program seeks to address fundamental questions that arise during the formation of catalytic materials. Synthetic materials offer designed synthesis controls over pore size distribution, volume, surface area, etc., specific compositions devoid of trace impurities, and controlled particle size. For these reasons, synthetic layered silicates, specifically clays, become of interest; they also offer unique surface chemistry and constrained environments, and therefore present a wealth of opportunity in strategic design alternatives. Tailored silicate materials comprise the central focus of testing hypotheses about the role of metal particle morphology in catalysis. Of paramount interest are (1) whether the mechanism of formation and catalytic reactivity of these materials can be monitored in situ, (2) examination of reliably produced metal particle morphologies and their effects in a variety of catalytic reactions and (3) whether differences between powder and film morphologies can offer insight into catalytic reactivity and transport mechanisms.

Future Plans

We plan to follow the intricate chemistry that occurs during the synthesis of layered silicates, and the development of specific metal nanoparticle shapes and sizes upon them, using TEM, solid-state NMR and advanced in situ SAXS techniques. The metals will be added via chemical reduction, sputtering, or deposition, and the clay surfaces will be modified using co-condensation methods with organosilanes to facilitate incorporation as necessary. Catalysis efforts will concentrate on HDS, hydrogenation or oxidation as appropriate, including an exploration into the entirely new direction of *operando* SAXS. Furthermore, polymer-clay nanocomposite films will be examined for potential use as membranes in catalytic applications. Theoretical chemistry will be employed to guide the synthesis and lend insight to operative transport mechanisms.

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Mechanistic Studies at the Interface Between Organometallic Chemistry and Homogeneous Catalysis

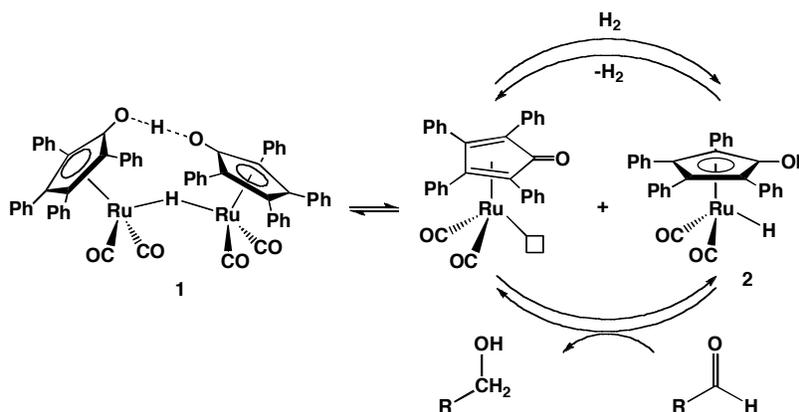
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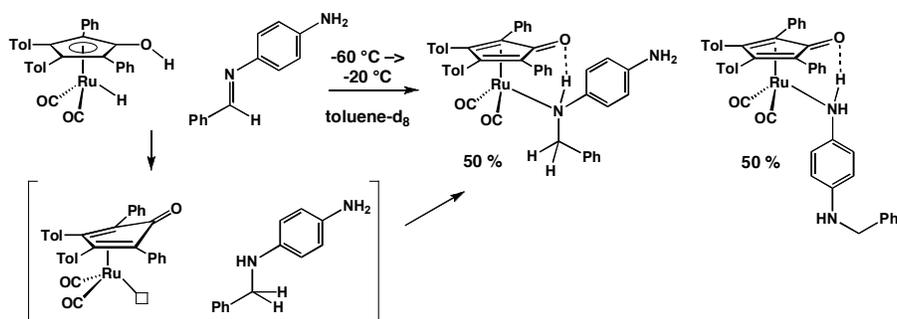
Research Goals and Specific Objectives. Our goal is to learn the intimate mechanistic details of reactions involved in homogeneous catalysis and to use the insight we gain to develop new and improved catalysts. Our work centers on the hydrogenation of polar functional groups. Specifically, we are concentrating 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 hydrogenation of ketones and aldehydes is a modern green alternative to reductions by LiAlH_4 and NaBH_4 which require extensive work-up procedures.

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.

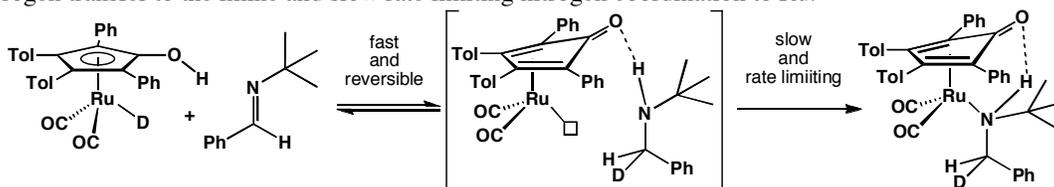
Our work with Shvo's diruthenium bridging hydride catalyst (**1**) has shown that the active reducing agent is a hydroxycyclopentadienyl ruthenium hydride (**2**) which reacts with benzaldehyde at -15°C . The observation of primary deuterium isotope effects for transfer of both OH and RuH to benzaldehyde provided evidence for a concerted mechanism occurring outside the coordination sphere of the metal.



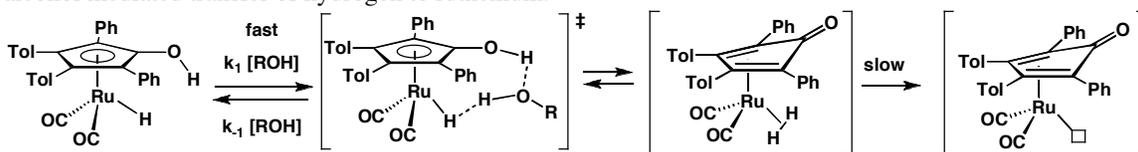
An alternative mechanism for aldehyde and imine reduction involves ring slippage and coordination of the substrate to Ru prior to hydrogen transfer. This ring slip mechanism has alcohol or amine “born in the coordination sphere of the metal” while transfer of hydrogen without prior coordination would give a trappable coordinatively unsaturated intermediate. 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.



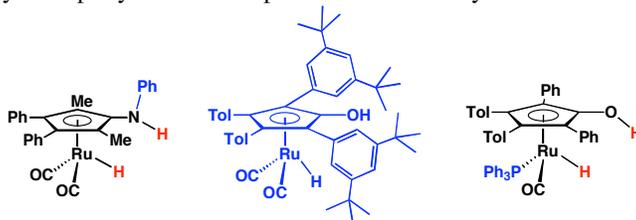
Studies of *N*-alkyl imines establish a different rate limiting step for reduction. Inverse isotope effects, imine isomerization, and deuterium scrambling results are all consistent with rapid and reversible hydrogen transfer to the imine and slow rate limiting nitrogen coordination to Ru.



Another important step in the catalysis is the regeneration of **2** from reaction of H_2 with the diruthenium complex **1**. Studies of the microscopic reverse of this process (hydrogen evolution from **2** which occurs at $80^\circ C$) 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 mediated 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 CpNHP group successfully prevented formation of a bridging hydride. Catalysis of aldehyde reduction at room temperature by these CpNHP catalysts is accomplished in the presence of acid. Second, the large *t*-butyl groups on the aryl rings of the (C_5R_4OH) 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 and are very selective for aldehydes over ketones.

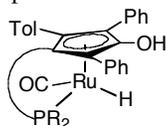


Future Plans

Our mechanistic studies of hydrogenation catalysts related to **1** are now concentrating 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.

We are also in the process of synthesizing chiral analogs of the ruthenium phosphine complex in which a phosphine is linked to the Cp ring as potential enantioselective catalysts.



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Bioinspired Oxidation Catalysis of Energy Consequence

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Goal

The long-term goal of this research program is to develop bioinspired synthetic catalysts for oxygen- and nitrogen-based reactions that rely on cheap and plentiful first-row transition metals. Of particular interest are multielectron, multiproton oxygen and nitrogen activation, functionalization, and evolution pathways that form the basis for natural and synthetic carbon-neutral energy conversion cycles, with water splitting as the holy-grail catalytic reaction. Synthetic designs are biomimetic and guided by principles of natural metalloenzymes, which exert exquisite control over substrate reactivity at first-row transition metal sites by dual management of proton and electron inventories. This program seeks to capture the functional essence of biological energy conversion systems and extend their chemistry beyond the constraints of the protein environment.

Recent Progress

We have developed several new types of nitrogen-based ligand templates for first-row transition metal centers and have elaborated their coordination chemistry. A unifying design feature for all these scaffolds is the use of “soft” amide donors that are electronically compatible with coordination to early, mid, or late metals. Included are pyrrolide, carbazolid, and diphenylamide donors incorporated into chelating frameworks. The synthesis and structural characterization of a variety of unsaturated trigonal bipyramidal and pseudo-tetrahedral complexes has been achieved without resorting to excessive steric bulk. The resulting iron and copper compounds are competent for stoichiometric and catalytic group transfer reactions.

DOE Interest

The proposed research program in bioinspired energy catalysis addresses the overall BES scientific/technical mission of developing predictive catalyst design principles by advancing three frontiers of catalytic research: (i) multielectron chemistry at cheap and abundant first-row transition metal centers, (ii) bond-making and bond-breaking reactions at energy-poor substrates, and (iii) coupling electron and proton transfer for catalytic transformations.

Future Plans

Characterization of intermediates along stoichiometric and catalytic pathways will be pursued. The second-sphere coordination chemistry of available templates will also be

explored. In particular, introduction of second-sphere hydrogen-bond pendants will probe the effects of acid-base functionalities on metal-bond formation and cleavage reactions. Reactions with other small-molecule substrates of energy consequence, including carbon dioxide, hydrogen, water, and protons, will also be evaluated.

Synthesis, Characterization, and Catalytic Properties of Bimetallic Dendrimer-Encapsulated Nanoparticles

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Goals

The overall goal of this project is to synthesize and structurally characterize well-defined, bimetallic catalysts. These materials, which we call dendrimer-encapsulated nanoparticles (DENs), are synthesized within dendrimer templates by coordination of metal ions to the interior tertiary amines of the dendrimer, followed by reduction. This approach yields monometallic and bimetallic nanoparticles that have a high degree of uniformity in size, structure, and composition.

The specific goals of this project are to evaluate the homogeneous and heterogeneous catalytic activity of bimetallic nanoparticles prepared by the dendrimer templating approach. We are particularly interested in the effect of nanoparticle size, composition, and structure on catalytic rates and product distributions.

Recent Progress

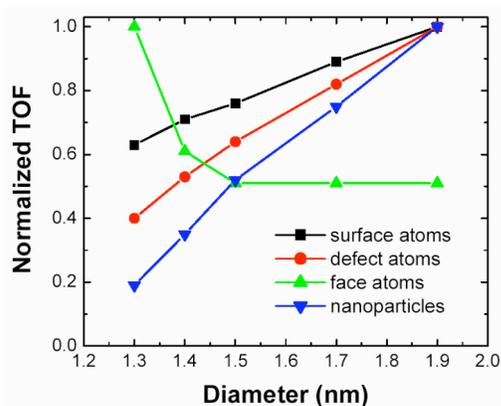
The Effect of Pd Nanoparticle Size on the Catalytic Hydrogenation of Allyl Alcohol

We have found that the rate of hydrogenation of allyl alcohol is a function of the diameter of the Pd nanoparticles (1.3 – 1.9 nm) used to catalyze the reaction. Furthermore, kinetic data indicate that this effect is electronic in nature for particles having diameters <1.5 nm, but for larger particles depends primarily on their geometric properties. This is a significant finding, because it represents a particle-size effect for hydrogenation over unsupported Pd nanoparticle catalysts in a size range that has not been widely studied.

The procedure used to prepare Pd dendrimer-encapsulated nanoparticle (DEN) was developed by our group in the late 1990s. For the experiments reported here, sixth-generation, hydroxyl-terminated PAMAM dendrimers (G6-OH) were used to synthesize Pd DENs containing an average of 55, 100, 147, 200, or 250 Pd atoms (G6-OH(Pd_n), where n is the average number of atoms per particle). These particles have measured (by

TEM and calculated (in parentheses) diameters of 1.3 (1.2), 1.4 (1.4), 1.5 (1.6), 1.7 (1.8), and 1.9 (1.9) nm, respectively.

The TOFs shown in the Figure are given in units of mol H₂ per mol of surface, defect, or face atoms (or number of particles) per hour, and then each data point is



normalized to the highest TOF for each series.

For three of the four plots, there is a monotonic increase in the TOF as the particle size increases. This indicates that there is no correlation between the TOF (calculated based on the total number of surface atoms, the number of defect atoms on the surface, or the number of nanoparticles) and the geometric properties of the DEN catalysts.

However, when only face atoms are considered, the plot attains zero slope for particle diameters ≥ 1.5 nm. Because this TOF is calculated in terms of the number of face atoms (mol H₂/mol face

atoms-h), it means there is a 1:1 correspondence between the rate of hydrogen uptake and the number of face atoms for particles in this size range.

To summarize, we have shown a correlation between catalyst size and TOF for the hydrogenation of allyl alcohol. This structure/function relationship is a direct consequence of the nanoscale size of the catalysts. The hydrogenation reaction is sensitive to both the electronic and geometric properties of the catalytic Pd nanoparticles, both of which change quickly in the 1.3 to 1.9 nm-diameter size range. Our analysis indicates that the hydrogenation kinetics are dominated by electronic effects for the smallest particles (<1.5 nm diameter) and by geometric effects for larger particles (1.5 to 1.9 nm diameter). Results of the type described here are enabled by the high degree of monodispersity resulting from the dendrimer templating approach to nanoparticle synthesis. We are presently obtaining measurements similar to these for bimetallic DEN catalysts.

Electrocatalysts based on dendrimer-encapsulated nanoparticles.

Platinum dendrimer-encapsulated nanoparticles (DENs) were prepared within fourth-generation, hydroxyl-terminated, poly(amidoamine) dendrimers and immobilized on glassy carbon electrodes using an electrochemical immobilization strategy. X-ray photoelectron spectroscopy, electron microscopy, and electrochemical experiments confirm that the Pt DENs are about 1.4 nm in diameter and that they remain within the dendrimer following surface immobilization. The resulting Pt DEN films were electrocatalytically active for the oxygen reduction reaction (ORR). The films are also robust, surviving up to 50 consecutive cyclic voltammograms and sonication. Monometallic Pd DENs were also prepared and found to have little catalytic activity for the ORR. However, PtPd bimetallic DEN alloys had catalytic activity nearly identical to that found for Pt-only DENs. This indicates an overall catalytic enhancement for the bimetallic electrocatalysts.

DOE Interest

The dendrimer templating approach is an effective route to the synthesis of chemically and structurally well-defined bimetallic catalytic nanoparticles. We envision that these materials

will provide excellent experimental models for developing the next generation of catalytic materials. The partnership with the University of Delaware and University of Wisconsin groups allows us to guide future development of highly selective bimetallic catalysts according to theoretical models and study their catalytic properties in depth.

Future Plans

Current investigations are focused on three aspects of this project. First, we are examining the effect of the bimetallic nanoparticle size (in the range of 1 to 3 nm), composition, and structure (alloy vs. core/shell) on homogeneous catalytic reactions. For example, we are determining if there are quantum-size effects on the rates of chemical reactions (hydrogenations and carbon coupling reactions) catalyzed by monometallic and bimetallic nanoparticles. Likewise, we want to know if there are synergistic effects arising from the presence of the two metals and if so why. Second, as mentioned earlier, we have discovered that dendrimer-encapsulated Pt nanoparticles catalyze the reduction of oxygen, and this opens the door to the study of bimetallic DENs for fuel cell applications. In particular, we are interested in finding metal combinations of metals that could substitute for Pt, and we wish to know if there are particle-size effects on the catalytic efficiency of the oxygen reduction reaction.

In collaboration with Dr. Anatoly Frenkel at the NSLS, we have just (April, 2006) finished our first EXAFS experiments on mono- and bimetallic DENs. At the time this abstract was written we had not fully analyzed the data, but the results will be provided at the contractors' meeting. During the coming two years we have been granted additional synchrotron time, and we plan to use it to more fully characterize the bimetallic DENs and also to obtain in-situ catalytic measurements using these materials.

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CATALYSIS SCIENCE INITIATIVE: Catalyst Design by Discovery Informatics

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Goal:

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

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. Though the emphasis here is on catalytic applications, the general approach has broad application to materials design and even process improvement. The informatics and data visualization tools developed in this effort also have broad application to knowledge extraction from virtually any large data set.

Research Plan:

The heart of our *Discovery Informatics* approach is the *forward model*, designed to quantitatively connect chemical, structural and higher level descriptors of a catalytic material to its kinetic performance for a specified reaction [2, 3]. The forward model, comprised of a catalytic chemistry component and a microkinetic model, then enables a guided stochastic *inverse search* of the descriptor space to identify trial catalyst materials predicted by the forward model to best satisfy the catalytic performance goals. Discrepancies between the predictions and high throughput evaluation of the trial catalysts can then be used to improve the model. Iteration of this cycle will continue to improve the model until it converges on a set of catalytic materials that meet the design goal. Our research objectives include building the computational, informatics,

data visualization, and experimental infrastructure to support this design algorithm and to further develop the approach through application to three diverse problems.

Aryloxide catalysts for polyolefin production - This homogeneous catalyst system offers the significant advantage of a well-defined, single catalytic site. We are focusing on cationic alkyls of the group 4 metals with cyclopentadienyl and substituted aryloxide ligands [1, 6, 11]. By varying ring substituents and the associated anion, we alter the rate and stereochemistry of the olefin polymerization catalyzed by these cationic compounds. Careful measurements of rates of monomer loss and molecular weight distribution in batch experiments are analyzed to give propagation rate constants and ratios of k_p to initiation, chain transfer, and catalyst deactivation rate constants to provide a rich data set for linking chemical descriptors to reaction performance [5]. We have focused first on the propagation rate for 1-hexene polymerization. This work is closely supported by DFT calculations and is our primary testbed for development of informatics and visualization tools to aid model building and the discovery of appropriate descriptors and for full closure of the discovery informatics cycle.

Aromatization of paraffins over zeolites - In this study, we have focused on zeolites because their crystallinity qualifies them as “molecular” heterogeneous catalysts, i.e., ones for which we can compute properties because we have a good starting point for assigning atomic positions. The reaction, conversion of propane to aromatics has a high level of complexity and thus is a demanding test of the reaction modeling suite, a set of tools for kinetic model building..

Hydrogen generation via the water-gas shift (WGS) reaction - For fuel cell applications, the stability of the catalyst against upsets is paramount. To gain robustness, the active, but fragile, Cu/ZnO catalyst must be replaced by appropriately promoted supported metal catalysts. This is a case where the reaction is stoichiometrically simple, but the combinatorial complexity of the catalyst is substantial with choices for support, metal, and multiple promoter oxides. We have started with mechanistic studies of the reaction over single supported metals to establish the Kinetic Model and with construction of a four reactor system that will speed the production of high quality data. That data, together with DFT calculations of the properties of proposed catalyst sites will drive the discovery informatics process.

Infrastructure – There are two additional research thrusts that support this effort. The first is *parallel mass spectroscopy* for at least semi-quantitative speciation on the timescale of seconds to minutes rather than hours. A four channel device has been designed and constructed, and will be used first for parallel characterization of catalysts using temperature programmed methods. The second concerns *informatics*, the hardware, software, and middleware involved in data management, data analysis, model building, data visualization and the extraction of knowledge from data.

Recent Progress:

Olefin Polymerization over Single-Site Catalysts – Using a combination of experimental measurements, kinetic modeling and DFT computations, we have developed a model for the relationship between descriptors of the catalyst chemistry and structure and the measured propagation rate constants [13]. 1-Hexene polymerization kinetics were measured by NMR at 20 °C for 18 Ti and 2 Zr based aryloxide-Cp (or Cp*) ligated catalysts with tetra- and tris-perfluorophenyl counterions. For example, polymerization kinetics for 1-hexene catalyzed by [Cp*Zr(OC₆H(Ph)_{4-2,3,5,6}(CH₃))] [H₃C-B(C₆F₅)₃] was followed by ¹H NMR in C₆D₅Br at 20 °C. The zwitter-ionic catalyst was prepared from the zirconium dimethyl precursor and tris-pentafluorophenylborane activator. Bromobenzene was the solvent of choice because the cationic catalyst failed to polymerize 1-hexene in toluene or benzene, presumably due to tight ion pair association in nonpolar solvent. Typical time profiles of [1-hexene] versus time for different catalyst concentrations are given in Figure 1.1. The kinetic data deviate from first-order behavior particularly at lower catalyst concentration. Initiation for this catalyst was not sufficiently slower than propagation to enable its determination by NMR. The deviation from linearity clearly shows

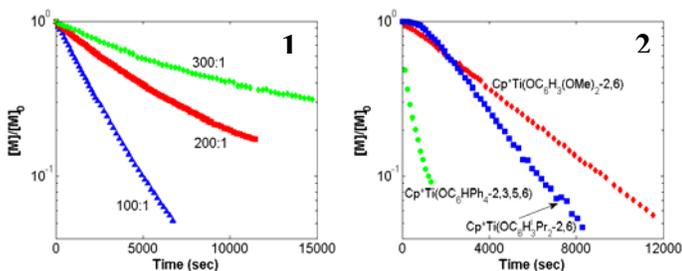


Fig. 1. 1-hexene consumption at 20°C for (1) $\text{Cp}^*\text{Zr}(\text{Ph}_4\text{OAr})\text{Me}_2$ at different monomer-to-catalyst ratios; (2) three catalysts at 200:1 monomer-to-catalyst ratio. Activator: $\text{B}(\text{C}_6\text{F}_5)_3$; monomer: 1M 1-hexene in bromobenzene (1) and toluene (2).

to identify the degradation mechanism and extract k_p from $M(t)$, a set of kinetic models was developed that included initiation, propagation, and catalyst deactivation that was either 0th or 1st order in monomer. For each of the aryloxy catalysts, models have been fit to the data, models that are unable to fit the data were eliminated, new experiments were designed when needed, the kinetic mechanism was identified and kinetic parameters were determined. The analysis included a critical analysis of the error structure of the $M(t)$ curves, where it was found that the error in $M(t)$ is heteroscedastic, i.e. the error depends of the magnitude of the measured value. This is the first time that a rigorous kinetic analysis has been done for olefin polymerization, where one can clearly identify mechanism, rate constants, error bounds on rate constants and most importantly what can and cannot be inferred from these kinetic experiments. The Discovery Informatics tools were needed to keep pace with the large number of models that needed to be analyzed for this catalyst system.

In order to unify the entire Ti data set with a single model, we have included the steric effects of the ligands by evaluating the solid angle available to the monomer for docking and assign the dominant energetic effect to the fraction of the counter ion binding energy (CIBE) that must be expended to move the anion away from the cation to allow access to the site by the monomer. The solid angles occupied by the two ligands (φ_1 and φ_2) and the CIBE were obtained via DFT calculations. The model equation for the propagation rate constant is postulated to be of a simple Arrhenius form with the angle dependent pre-factor

$$k_p = A4\pi \left\{ 1 - \sin^2\left(\frac{\varphi_1}{4}\right) - \sin^2\left(\frac{\varphi_2}{4}\right) - \theta \right\} \exp\left[-\frac{\alpha\text{CIBE}}{RT}\right] \quad (1)$$

The model has three fitting parameters (i) θ - the solid angle inaccessible to monomer which has not been explicitly accounted for by the ligand solid angles, including the solid angle occupied by the growing chain, (ii) α - a descriptor of the energy penalty (expressed as a fraction of CIBE) incurred when the counteranion is pushed away just far enough to enable monomer insertion ($0 < \alpha < 1$), and (3) A - a prefactor that scales the rate constant. Strictly speaking A should have an Arrhenius form also, but since the

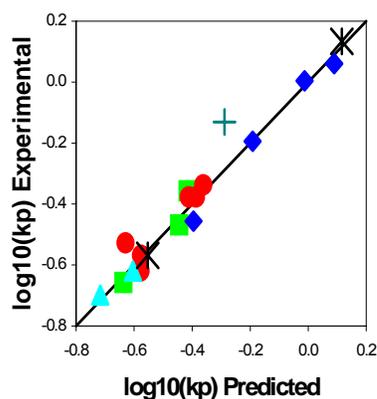


Fig. 2. Prediction of propagation rate $\alpha = 0.19$, $\theta = 0.127$. Cp 2,6 alkyl (■) - $A = 6.96 \times 10^3$; Cp* No 2,6-substituents (●) and Cp* 2,6 alkyl (◆) - $A = 2.47 \times 10^3$; Cp* OMe (▲) - $A = 1.27 \times 10^3$; Cp* 2,3,5,6-Ph and Cp* 2-benzyl (*) - $A = 0.062 \times 10^3$; 2-Cyclohexyl catalyst (+)

data being fitted were taken at a single temperature this is not necessary. The model predictions shown in Fig. 2 are quite encouraging. The values of A, given in the figure caption, were allowed to vary from one catalyst family to another. However, A changes only slightly, with the notable exception of the catalysts possessing a phenyl ring in the 2- position in the aryloxy ligand. The latter result indicates the presence of some new physics not captured by the simple CIBE and docking space descriptor set. Notwithstanding the need for more sophisticated models to capture increased ligand bonding complexity, this is the first predictive model with physical significance that can describe how one of the polymerization rate constants depends upon the structure of the catalyst. We are not aware of any other model with quantitative capabilities that is available in the literature.

Propane Aromatization over ZSM-5 Catalysts – We now have a 312 step, 38 reaction family, 25 parameter microkinetic model for propane aromatization of HZSM-5 [9]. The elementary kinetic steps include activation of alkanes via carbonium ion chemistry and subsequent, hydride transfer, dehydrogenation, olefin adsorption/desorption, oligomerization, β -scission, and cyclization. Data were obtained by measurement of methane, ethane, ethylene, propane, propylene, butane, butene, benzene, toluene and xylene in the effluent of fixed bed

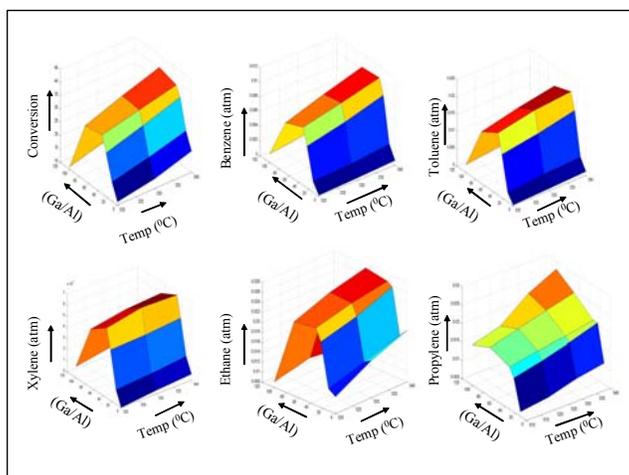


Fig. 3. Response to Ga loading at space time = 1.5 gcat-h/mol

reactors at different temperatures and space velocities. The modeling was strongly assisted by DFT calculations showing alkoxide intermediates, reactivities governed by carbenium ion-like transition states, detailed mechanisms for ring closure, and values for relative rates [4]. Of particular importance is the development of embedded cluster (i.e. QM/MM) calculations that include the long range effects of the lattice [7]. We are currently developing a data set that shows strong optima as a function of Ga/Al and Si/Al ratios for Ga promoted catalysts. Figure 3 shows the Ga dependence for Si/Al = 16. We are working on modeling this system, again

being guided by DFT which is predicting the importance of GaH^{2+} at Al–Al dual sites [8].

The Water Gas Shift Reaction – A newly designed and automated four reactor system that

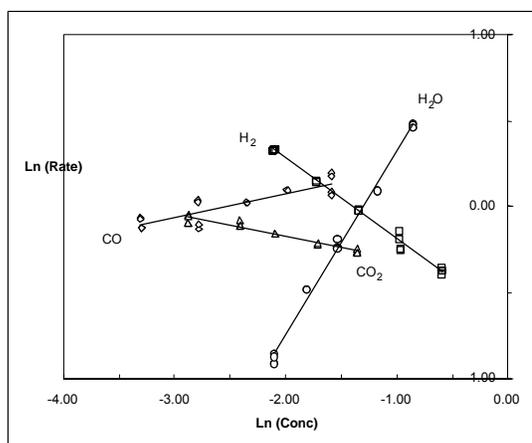


Fig. 4 Reaction orders for the water gas shift reaction on 1.6% Pt/Al₂O₃

can generate 64 data points per day has produced a benchmark data set for Ni, Pd and Pt. Studies of promoter oxides on Pd have shown their dramatic potential. La can increase the WGS rate by a factor of 30. The promoters can also lower the methanation rate by an order of magnitude. The fractional orders of reaction revealed by the benchmark data, as shown for Pt in Figure 4, suggest a high level of kinetic complexity even though the reaction is stoichiometrically simple. In modeling efforts so far, we have found even a relatively large number of data points insufficient to define all the constants needed for a complex sequence of elementary steps. Fractional orders imply adsorbed species, however, and we are

preparing to use fast FTIR and mass analysis to quantitate concentrations of surface intermediates to facilitate kinetic modeling.

A Multiplexed Rectilinear Ion Trap Mass Spectrometer for High-Throughput Analysis - A multi-channel mass spectrometer based on the rectilinear ion trap (RIT) mass analyzer was designed and constructed for simultaneous high-throughput analysis of multiple samples [10,12]. The instrument features four parallel ion source/mass analyzer/detector channels each housed in one quadrant of a specialized vacuum manifold, designed to minimize neutral cross-talk, and operated using a common set of modified commercial control electronics, including a single RF amplifier and transformer coil. This multiplexed mass spectrometer employs an array of four RITs ($x_0 = 5.0$ mm and $y_0 = 4.0$ mm, where x_0 and y_0 are the half-distances in the x and y dimensions, respectively).

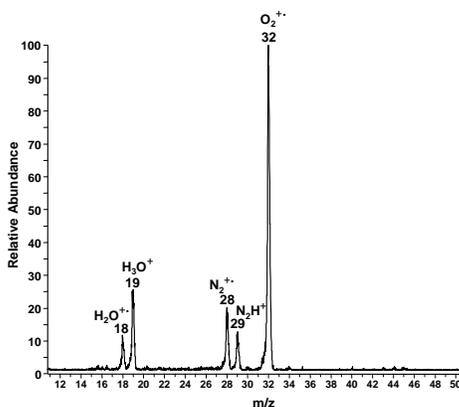


Fig. 5: Background mass spectrum from the multiplexed instrument

Mass spectra are acquired from four different samples simultaneously. The available mass/charge range is m/z 15 to 510 with excellent linearity of the mass calibration ($R^2 = 0.999999$). The peak width is less than m/z 0.3 at m/z 146, corresponding to a resolution of ~ 500 . Simultaneous MS/MS of ions due to four compounds (3-fluoroanisole, 4-fluoroanisole, 2-fluorobenzyl alcohol, 2,6-dimethyl-cyclohexanone) with the same nominal molecular radical cation but distinctive fragmentation patterns was demonstrated. Isolation and fragmentation efficiencies were $\sim 25\%$ and $\sim 75\%$, respectively, measured in the typical case of the molecular radical cation of acetophenone. Pre-acquisition differential data was obtained by real-time subtraction of the ion signals from two channels of the multiplexed mass spectrometer. The differential experiment offers proof-of-

principle for comparing mass spectra in high-throughput screening applications while reducing data storage requirements. The samples were introduced as vapors or gases into the ionization sources, usually through a leak valve. However, capillary introduction was also performed and produced a < 1 s total response profile (sum of rise and fall times) in the case of acetone. The background mass spectrum acquired from the multiplexed instrument contains peaks due to water (m/z 18 and 19), nitrogen (m/z 28 and 29), and oxygen (m/z 32) (See Fig. 5). The occurrence of ion-molecule reactions causes the relative intensity of these peaks to be dependent on the pressure inside of the ion trap and the ion storage time. For the data shown in Fig. 5, the pressure was 1.8×10^{-6} Torr and the ion storage time was < 5 ms before mass analysis. The peak intensity at m/z 32 (O_2^+) is greater than that at m/z 28 (N_2^+) due to charge transfer reactions. Given sufficient time and/or pressure, the dominant background peaks become m/z 19 (H_3O^+) and m/z 32.

Development of Informatics Tools – An e-lab notebook, searchable archival and relational databases, computational job sequencer, chemistry compiler, statistical tools for nonlinear parameter fitting and design of experiments for nonlinear systems, and a scaleable platform for 2D and 3D visualization of data are some of the informatics infrastructure that has been developed to drive all of these projects. These information management and analysis tools in concert with an advanced data visualization environment, an environment that enables the researcher to more effectively interact with data via the eye's high-bandwidth for information transfer, become increasingly important as our ability to generate both experimental and computational data and increasingly sophisticated models accelerates.

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Computational Studies of Structures, Basicities, Acidities, and Reactions of Group VIB Transition Metal Oxide Clusters and of NMR Chemical Shifts in Tungsten and Vanadium Oxides

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The structures and properties of group VIB transition metal oxide clusters, $(\text{MO}_3)_{1-6}$, were studied with density functional theory methods. Two types of clusters were investigated, the ring and the chain, with the ring being lower in energy. For $(\text{MO}_3)_6$, two additional conformations, the cage and the inverted cage, were studied. Normalized and differential clustering energies of the ring structures were calculated and were shown to vary with respect to the cluster size. Brønsted basicities and Lewis acidities based on a fluoride affinity scale were also calculated. These clusters are weak Brønsted bases with gas phase basicities comparable to those of H_2O and NH_3 . The clusters are, however, very strong Lewis acids and many of them are stronger than strong Lewis acids such as SbF_5 . Brønsted acidities of $\text{M}_6\text{O}_{19}\text{H}_2$ and $\text{M}_6\text{O}_{18}\text{FH}$ were calculated for Mo and W and these compounds were shown to be very strong acids in the gas phase. The electronic excitation energies of the clusters will be described and related to band gaps. The steps in oxidative dehydrogenation of CH_3OH on MO_3 and M_2O_6 will be described and the mechanisms contrasted. ^{51}V NMR chemical shifts have been calculated at the GIAO level for a wide range of vanadium oxides and used to explain a number of experimental results. The proton nmr chemical shifts for many $\text{M}_x\text{O}_y\text{H}_z$, $\text{M} = \text{Si}, \text{W}, \text{Mo}$ compounds including hydrogen bonded species have been calculated for comparison with experiment. We have studied the interaction of H_2O with OH groups on $\text{Si}(\text{OH})_4$, $\text{SiOH}(\text{OCH}_3)_3$, $\text{WO}_x(\text{OH})_y$, and $\text{WO}_x(\text{OH})_y(\text{OCH}_3)_z$ as a model for hydrogen bonding at potential catalytic sites. The results have been used to explain nmr analyses of atomic layer deposition.

Synthesis and Catalytic Chemistry of Yttrium and Lanthanide Metal Complexes

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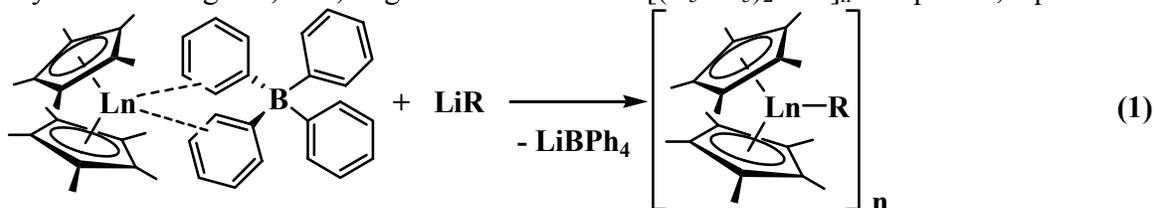
Goal

The objective of this research is to explore the fundamental synthetic and catalytic reactivity of complexes of yttrium and the lanthanide metals such that the unique chemistry available from the f elements can be utilized in energy related areas.

Recent Progress

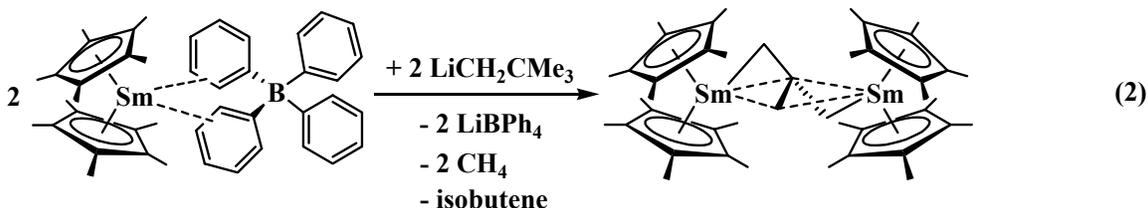
The research has focused on understanding two types of catalytic f element chemistry, both of which involve organometallic Group 13 compounds. The first is the lanthanide-based catalysis of the polymerization of dienes to high cis-1,4-polydienes, a reaction that generates synthetic rubber when the monomer is isoprene. This reaction is one of the most successful f element catalyses, but little is known about the mixed metal lanthanide aluminum chemistry that leads to the active catalyst. The second project involves the use of lanthanide complexes to regenerate boron hydride materials of potential use to provide hydrogen as a fuel in a future hydrogen economy.

One approach to these topics has employed bis(pentamethylcyclopentadienyl) lanthanide metallocenes as platforms for studying the chemistry of the reactive functionalities involved in these catalyses. In the course of this study, it was found that the $[(C_5Me_5)_2Ln][(\mu-Ph)_2BPh_2]$ complexes, which have a tetraphenylborate ligand loosely attached to a metallocene cation, $[(C_5Me_5)_2Ln]^{1+}$, are useful precursors to organometallic model compounds for these catalyses. The $[BPh_4]^{1-}$ anion is easily displaced by alkyl and aryl lithium reagents, LiR , to generate unsolvated $[(C_5Me_5)_2LnR]_n$ complexes, eq 1.



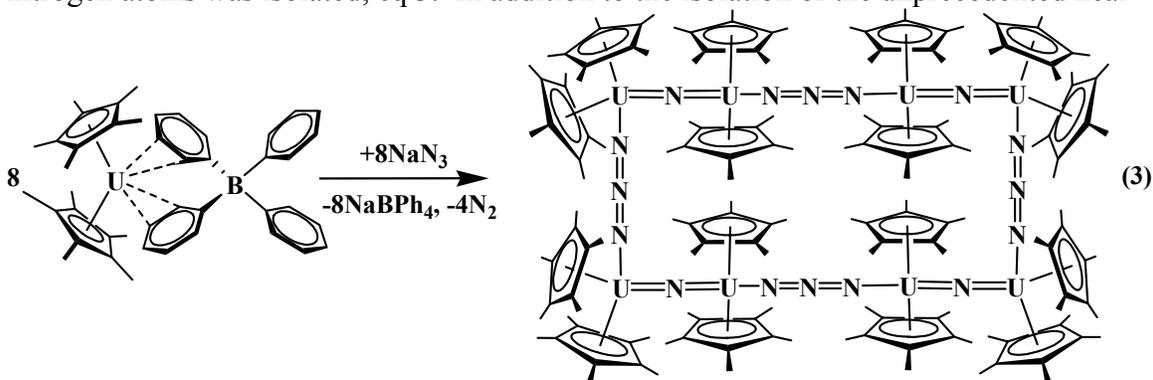
Since these unsolvated compounds are sterically unsaturated, they have high reactivity and have generated some spectacular results in C-H and C-C activation. In addition, the uranium version has led to the formation of some unprecedented nitride materials. Given the highly unusual nature of these results, we have pursued the fundamental aspects of this new chemistry along with the original topics. Two examples are described here.

The use of MeLi in eq 1 provided the first unsolvated $[(C_5Me_5)_2LnMe]_n$ complexes of the larger lanthanides. With $Ln = Sm$, the product is an asymmetrical trimer, $n = 3$, and is a highly reactive C-H activation reagent. When eq 1 was investigated with neopentyllithium, C-C activation was observed. Instead of the expected C_5 alkyl product, $[(C_5Me_5)_2Sm(CH_2CMe_3)]_n$, a C_4 product was isolated, the trimethylenemethane (TMM) complex, $[(C_5Me_5)_2Sm]_2[\mu-\eta^3:\eta^2-C(CH_2)_3]$, eq 2. This was the first planar and first



bridging TMM ligand isolated. Detailed modeling studies indicated that the complex is formed by a cascade of C-C and C-H activation reactions including β -alkyl elimination to make the $[(C_5Me_5)_2LnMe]_n$ complexes described above. The $[C(CH_2)_3]^{2-}$ ligand is formally a 6 electron donor that coincidentally has the same atomic composition as butadiene.

When the chemistry of the uranium analog, $[(C_5Me_5)_2U][(\mu-Ph)_2BPh_2]$, was investigated via eq 1 with NaN_3 , an unexpected complex containing a 24-atom ring of uranium and nitrogen atoms was isolated, eq 3. In addition to the isolation of the unprecedented near-



linear $U=N=U$ bridges, the synthesis shows that large nanometer scale complexes can be assembled with f elements. In the past it was thought that the f orbitals lacked the strong directional character necessary to form the rigid corners and edges of large molecular assemblies. Evidently, 5f element $(C_5Me_5)_2M$ metallocene units can generate these large supra-molecular arrays. This complex is also of interest because it is dense in uranium and nitrogen. This result also raises the possibility of a molecular precursor approach to uranium nitride, UN, a possible future nuclear fuel that must be prepared in highly purified form. Since molecular species with such uranium nitride skeletons were previously unknown, this option was not previously viable. Although these $[(C_5Me_5)_2M][(\mu-Ph)_2BPh_2]$ -based results move the project in a new direction, this is a topic of interest to the Department of Energy and is being pursued. This result represents a good example of how funding for basic science can make contributions more broadly in the field.

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Nanocluster Catalysts Formation and Stabilization Fundamental Studies

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Goals

One primary goal of our DOE-funded program is to determine which stabilizers and other factors are best for the formation, stabilization and catalytic activity of transition-metal nanoclusters. A second goal is to continue our mechanistic studies of the nucleation, growth and agglomeration of catalytically active transition-metal nanoclusters. A third goal is to exploit nanoclusters in interesting catalytic reactions. Each of these goals is central to the rational advancement of nanoclusters in catalysis.

Recent Progress

(1) *Nanocluster Stabilization Fundamental Studies.* We made considerable progress in this area this past year based on Lisa Starkey-Ott's Ph.D. thesis work. First, we wrote the first review of transition-metal nanocluster stabilizers.¹ Next, using the 5 criteria method developed by our group in 2002, we were able to systematically evaluate for the first time five solvents, six polymers, three ionic liquids,² and three halides for their ability to control the formation, and allow the subsequent stabilization, of prototype Ir(0)_n nanoclusters. We found that that (i) surface-adsorbed anions and (ii) high dielectric constant (ϵ) solvents are the most important factors for the formation and stabilization of transition-metal nanoclusters,³ results consistent with DLVO theory of colloidal stability. Interestingly, somewhat surprisingly, but importantly, we also discovered that even traditionally weakly coordinating anions such as BF₄⁻ contribute significant stability to nanoclusters in high ϵ solvents. Simple BF₄⁻ in propylene carbonate rivals the stability imparted by better known, but more complex (and to some extent unnecessary), classic stabilizers such as poly(vinylpyrrolidone).

(2) *Fundamental Studies of Nanocluster Formation and Agglomeration.* Our two 2005 publications^{4,5} (mentioned as in-press in last years' report) promise to become classics in that they detail, for the first time, the more complete, 4-step mechanism for transition-metal nanocluster nucleation, growth (autocatalytic surface growth), bimolecular agglomeration and now also the novel step of autocatalytic agglomeration between smaller nanoclusters and larger bulk metal particles. There is no other work in the world that currently rivals our nanocluster mechanism of formation studies, the reason being that only we have figured out how to perform routinely high-precision kinetic studies of nanocluster formation. Building on this work, we are developing a quantitative kinetic method to rank nanocluster stabilizers based on their rate constants of agglomeration

(using both the 3-step mechanism developed by our group in 2004 and the 4-step mechanism described in 2005).

(3) *Nanocluster Catalysis Studies.* Our Ir(0)_n nanocluster, acid-assisted catalysis of neat acetone hydrogenation (mentioned as in-press in last year's report) appeared in 2005. It is *the best current catalyst* for the *room temperature, high activity, and highly selective* hydrogenation of acetone at 22 °C and 40 psig H₂ pressure to give 95% 2-propanol and 5% diisopropyl ether, all at 100% conversion with 16,400 demonstrated total catalytic turnovers.⁶

Lisa Starkey-Ott in the PI's group also completed an interesting paper probing the effects of added ionic liquid (IL) on acetone hydrogenation catalysis. The impetus for this study was the report by others that our identical [(1,5-COD)IrCl]₂ precatalyst provided acetone hydrogenation in ILs, but at much slower rates if temperature, pressure and catalyst concentrations are taken into account. Lisa's careful studies revealed that added IL serves primarily *to poison* both the precatalyst and the nanocluster catalyst at room temperature and 40 psig H₂ pressure.⁷ Additionally, this investigation probes the historically vexing "Is it homogeneous or heterogeneous catalysis?" question, our results revealing that a *bulk metal catalyst*, and not the claimed nanoclusters, are very likely the active species in the literature report of acetone hydrogenation catalysis in IL at higher temperatures, pressures and catalyst concentration.

Lastly, an in-press article distinguishes between homogeneous Pt(II) and heterogeneous Pt(0)_n hydrogenation catalysis when beginning with either Pt(1,5-COD)Cl₂ or Pt(1,5-COD)(CH₃)₂.⁸ The implication of heterogeneous catalysis clarifies observations made over 30 years ago questioning the nature of the true catalyst when beginning from these Pt precursors.

DOE Interest

Nanoclusters are metal particle catalysts closely analogous to the supported-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. Nanoparticles are also expected to have their own, unique reactivity as now demonstrated.

Future Plans

In the coming year, in addition to finishing up for publication the rest of the papers connected to Lisa Starkey-Ott's Ph.D. thesis, we plan to begin more detailed studies of nanocluster nucleation phenomena, since control of nucleation is a key to reliable, controlled nanocluster syntheses. Such studies—all of a fundamental nature—continue to be possible only due to our DOE grant support, funding for which we remain most grateful.

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7. "Are Imidazolium-Based Ionic Liquids a Preferred Medium and Stabilizer for $\text{Ir}(0)_n$ Nanocluster Catalysts? The Case of Acetone Hydrogenation" Starkey Ott, L.; Campbell, S.; Seddon, K. R.; Finke, R. G. Manuscript in preparation.
8. "Is it Homogeneous Pt(II) or Heterogeneous $\text{Pt}(0)_n$ Catalysis? Evidence that $\text{Pt}(1,5\text{-COD})\text{Cl}_2$ and $\text{Pt}(1,5\text{-COD})(\text{CH}_3)_2$ plus H_2 form Heterogeneous, Nanocluster plus Bulk-Metal Pt(0) Hydrogenation Catalysts." Finney, E. E.; Finke, R. G. *Inorg. Chem. Acta* **2006**, in press.

Studies Relevant to Catalytic Activation of Small Molecules

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Current Graduate Students: Chosu Khin, Gerald Macala, Dale Rimmer, John Garcia

Undergraduate Students: Brian Elder, Viktoriya Stepanyan

Collaborators: Dr. Tigran Kurtikyan, Armenian Academic of Sciences; Prof. Alexei Iretskii, Lake Superior State University (Michigan); Dr. Ivan Lorkovic, Raytheon Corp.

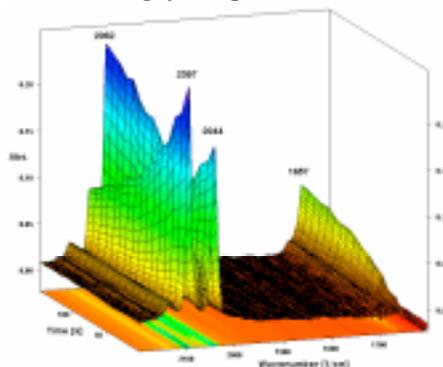
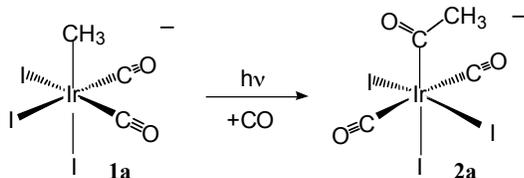
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Goal(s):

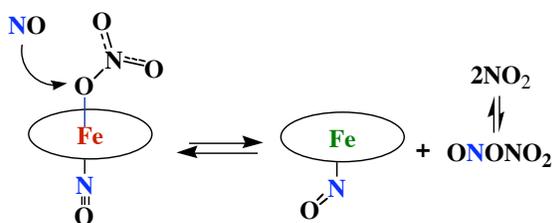
Application of quantitative techniques including time-resolved spectroscopy to elucidate fundamental mechanisms of transition metal catalyzed reactions of small molecules such as carbon monoxide carbonylations of various substrates and halogen or nitrogen oxide mediation in selective oxidations of others.

Recent Progress:

Carbonylation reactions: *Studies of Intermediates Relevant to Iridium-Catalyzed Methanol Carbonylation:* For some time we have had an interest in the applications of flash photolysis coupled to time-resolved infrared detection (TRIR) for the investigation of reactive intermediates in catalytic carbonylation mechanisms (*Coord. Chem. Rev.* 2003). We have recently extended such TRIR studies to probe intermediates relevant to iridium catalyzed carbonylation of CH₃OH to acetic acid. In the course of this study, the unprecedented photo-induced CO migratory insertion illustrated in eq. 1 was observed (temporal IR spectral changes shown in the figure). This result suggests that facile migratory insertion to form acyl Ir(III) complexes is strongly dependent on the orientation of other ligands relative to the methyl- and carbonyl groups participating directly in formation of the acyl group (Volpe *IC* 2006).



Nitrogen oxides as redox mediators: *Reactions of free and coordinated NO_x species.* This study is concerned with the quantitative reaction chemistry of NO_x species and the metal complexes LM-NO_x with various substrates. Studies to date have focused on systems where M is iron, manganese or copper, and L is a polydentate ligand such as porphyrin or salen. The longer-term goal is to use metal NO_x species to mediate the activation of dioxygen for the selective oxidation of such substrates. One feature of these systems has been the complexity of the interconversions between various NO_x that are promoted by the metal centers, an issue not only of importance to the catalysis chemistry but also to the roles of these species in biological media (*JIB* 05). In this context, over the past several years we have had the good fortune to collaborate with Dr. Tigran Kurtikyan of the Armenian Academy of Sciences, who is especially skilled in using optical and IR spectroscopy to characterize reactive intermediates formed in sublimed layers of metallo porphyrins and the reactions of these species at different temperatures. This technique has proved especially effective in examining the complex interactions and transformations of metallo porphyrins with various NO_x. For example, with this technique we were able to demonstrate the reversible interplay shown in eq. 1 (*JACS* 05). This methodology will also allow use to introduce other reactants and to study oxygen transfer mechanisms involving coordinated NO_x in detail.



DOE Interest:

Chemical catalysis has a huge impact on the US and world economies, and the discovery of systems having greater efficiency and selectivity or capable of previously unachievable transformations remains an intellectual challenge of strategic importance. Understanding the fundamental molecular pathways that define catalysis dynamics, thermodynamics and mechanisms remains essential for the design and optimization of efficient and environmentally friendly applications of energy and chemical feedstocks.

Ongoing and Future Studies:

Carbonylations: Our future investigations in this area will focus on time-resolved optical and IR spectral studies of metal-based organometallic radicals that may be relevant in proposed carbonylation mechanisms. While we have demonstrated dramatic effects of photolysis-induced radical formation on the dynamics of metal carbonyl intermediates (mss in preparation), it has been difficult to characterize directly the metal acyl radicals implicated as intermediates in catalytically relevant systems such as proposed for alkene hydrocarboxylation on molybdenum carbonyls with iodide promoters.

Nitrogen oxide systems. We will continue the reactivity studies of various metalloporphyrin complexes in sublimed layers given that these have already provided important insight into the interconversions involving coordinated NO_x. These have been coupled and compared to flash photolysis and stopped-flow spectrophotometric kinetics

investigations in solutions as well as DFT computations of expected intermediates. We are also examining potential stoichiometric and catalytic oxidations of model substrates mediated by NO_x complexes of various iron, copper, manganese and ruthenium platforms. In this context, we are also turning our attention to aqueous soluble systems.

Partial oxidations of hydrocarbons: We plan to continue investigating key steps in a halogen mediated process for the partial oxidation of alkanes (Zhou...*Chem. Commun.* **2003**). These studies include attempts to improve procedures for catalytic halogenations of alkanes and probes of halocarbon reactions with soluble metal oxo complexes and model MO_x model solids. Characterizing such mechanisms will contribute to understanding the metathesis chemistry of these complexes as well as analogous processes such as the metal oxide catalyzed halocarbon transformations of potential interest with regard to environmental remediation.

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DE-AC06-76RLO 1830

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**An Energy-Based Approach to Molecular and Interfacial Catalyst Development:
Thermochemistry, Kinetics and Theory of Catalytic Transformations**

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Goal

Demonstrate that an approach based on an understanding of the thermodynamics of the elementary reactions of hydrogen transfer can lead to the rational development of new catalysts. The fundamental reactions of hydride, proton, and hydrogen atom transfer are ubiquitous in catalytic reactions. Knowledge of the factors controlling the energetics of these reactions and the ability to predict the energetics of these reactions will enable rational approaches to catalyst development.

Recent Progress

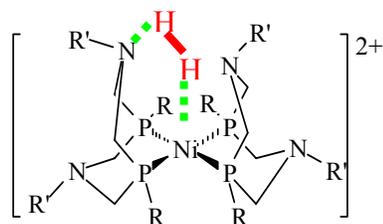
Experimental and theoretical determination of M-H and S-H bond energies: Experimental and theoretical methods have been used to determine the heterolytic and homolytic bond dissociation free energies (BDFEs) or enthalpies for a wide range M-H and S-H bonds of transition metal hydride complexes and for organic and organometallic compounds containing S-H and C-H bonds (see list of publications). These values permit the determination of the relative energies of potential and actual intermediates in catalytic cycles.

Linear Free energy correlations: A linear free energy relationship has been found between S-H bond strengths (from 70-91 kcal/mol) and rates of hydrogen atom transfer to the benzyl radical from organic and organometallic thiol groups (10^4 - 10^7 M⁻¹s⁻¹). Theoretical studies established MS-H bonds from 30-90 kcal/mol. Radical reactivity Mo-H, Mo-SH, FeS-H, Pt-H, Os-H, Rh-H, Ir-H, and Ru-H bonds has been measured. Rate constants can be used to predict homolytic BDEs and vice versa. Similar free energy correlations have also been developed between redox potentials of transition metal complexes containing diphosphine ligands and the acidity, hydricity, and homolytic BDFEs of the corresponding hydrides.

Factors determining the energetics of fundamental reactions: Combined structural and thermodynamic studies have been used to determine the effect of metal, ligand substituents, and ligand structure on the energetics of hydrogen atom, proton, electron, and hydride transfer reactions. For example, the hydride donor ability of [HM(diphosphine)₂]⁺ (where M = Ni, Pd, Pt) complexes is strongly dependent on the natural bite angle (NBA) of the diphosphine ligand - varying by 20 kcal/mol as the NBA changes by 33°. In contrast, the homolytic bond dissociation free energy and the pK_a values are insensitive to this structural change. EXAFS studies are being used to correlate solution structures with these parameters.

Applications to catalysis: New homolytic thermochemistry of MoSH groups allows the prediction of hydrogenation rates for MoS clusters in thermal hydrogenolysis reactions.

Thermochemical data gained here has been used to develop molecular catalysts for the electrochemical production and oxidation of H₂. These catalysts include MoS dimers that operate at very low overpotentials for the production of H₂ and the nickel-based diphosphine complex shown in the structure below. The thermodynamic studies described above allow the relative energies of all of the intermediates in the catalytic cycle to be determined, and this information has been used to guide the design of this catalyst, which has an activity for H₂ production approaching that of the hydrogenase enzymes. This information has also been used to guide the design of catalysts for the reverse process, the oxidation of H₂.



DOE Interest

Knowledge of the energetics of hydride, proton, and hydrogen atom transfer permits the determination of the relative energies of intermediates in catalytic cycles. This information can be used to guide the design of new catalysts as illustrated by the development of new nickel-based molecular catalysts for H₂ production and oxidation with very high activities. This approach is general and can provide a powerful new tool for predicting and controlling the energies of catalytic intermediates, a significant step toward understanding how to design catalysts to control catalytic activity and selectivity.

Future Plans

Experimental and theoretical efforts will continue to determine the kinetics and thermodynamics of the fundamental reactions of hydride, proton, and hydrogen atom transfer for a variety of transition metal hydrides and MS-H compounds. This data will be used to develop semi-empirical models for predicting these thermodynamic properties. These models will make use of ligand additivity relationships, linear free energy relationship, and empirical relationships that exist between different structures and supported by theory. These models will in turn be used to construct energy profiles for catalytic reactions. These energy profiles or maps will be used to guide the development of first row transition metal catalysts for H₂ oxidation and production that equal or exceed the performance of hydrogenase enzymes.

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Co-PI: Valentin Gogonea

Modulation of the electronic properties of tetrahydrobiopterin cofactor by the protein electric field

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Abstract

The electronic structure of the neutral, cation and anion forms of (6R)-5,6,7,8-tetrahydrobiopterin (BH₄, a key cofactor in the electron transfer to P₄₅₀ heme of nitric oxide synthase, NOS), has been calculated in gas phase, solution (dielectric and explicit water) and NOS environment using the density functional theory (B3LYP/6-31+G(d,p)), and the ionization potential (IP) and electron affinity (EA) of the cofactor have been derived in these chemical environments. It was found that (i) the electronic structure of BH₄ is very susceptible to the presence of an external electric field, and (ii) conformational changes of BH₄ structure alone do not affect its electronic structure significantly. In gas phase, water and protein environment the neutral BH₄ is the most stable species, while in dielectric the anion becomes the most stable species. In protein environment the IP of BH₄ is about half that in gas phase and its EA is about five times lower than in gas phase. The computational results indicate that changes in the external electric field due to protein dynamics may lead to configurations that have the BH₄ ion as stable as, or more stable than, the neutral form, making BH₄ to act as a molecular switch in the electron transfer to heme.

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

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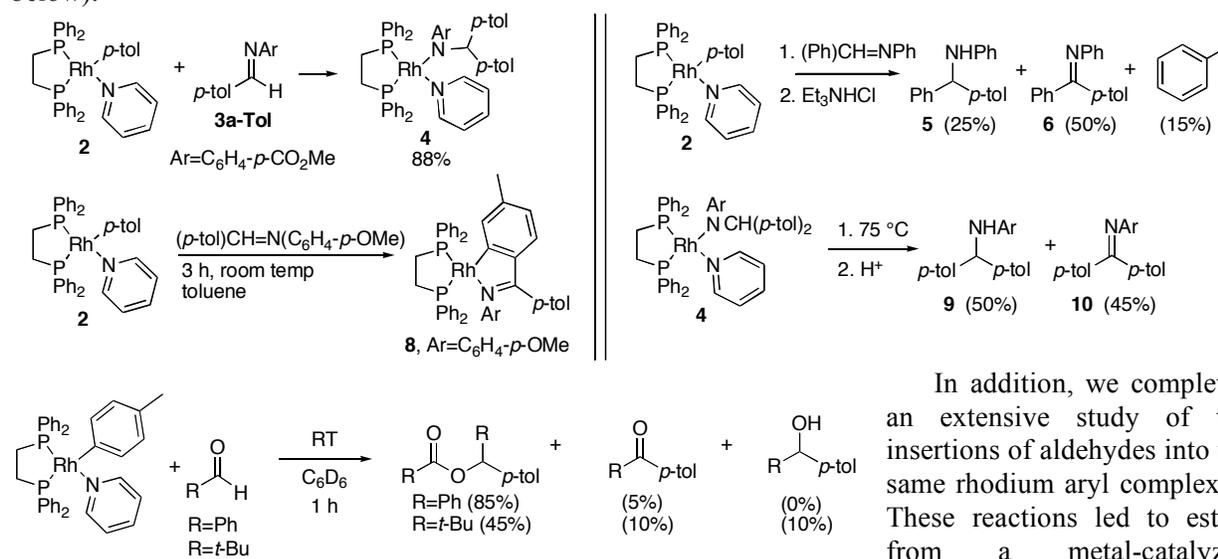
Goals

The 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

Since 2004, we have revealed several new types of insertion reactions of transition metal complexes involving amido and alkoxo complexes as reactant or product. In addition, we have published the first oxidative addition of ammonia to form a monomeric transition metal hydrido amido complex and have begun to delineate the factors that favor this structure over a tautomeric ammonia complex.

Insertions of Aldehydes and Imines. During 2004, we published work on the first insertion of an imine into an isolated late transition metal organometallic complex. These reactions were based on our previous studies of the insertions of aldehydes into related organometallic complexes. To observe the insertion of imines, we prepare complexes with a labile dative ligand, such as the pyridine in the complex at the top left of the scheme below. This arylrhodium complex reacted with imines to form amido complexes. In some cases the amido complexes were stable, but in other cases the amido complexes underwent processes, such as cyclometalation to form the metallacycle shown at the bottom right or β -H elimination to form the ketimine and the amine from subsequent reduction of the imine (right of scheme below).

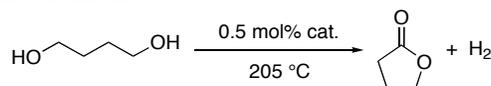


In addition, we completed an extensive study of the insertions of aldehydes into the same rhodium aryl complexes. These reactions led to esters from a metal-catalyzed

Tischenko reaction of the ketone that results from insertion of the aldehyde and β -hydrogen elimination from the resulting alkoxide.

Practical synthesis of γ -butyrolactone from butanediol. We also reported a highly efficient ruthenium catalyst for the oxidative cyclization of butanediol to γ -butyrolactone. Although ruthenium-catalyzed oxidative cyclizations of diols are known with acetone as hydrogen acceptor,⁸⁴ this acceptor and the need to separate this acceptor and the accompanying alcohol from the final product makes the cost of the process too high to displace the current method to produce γ -butyrolactone. However, a high-yield reaction with high turnover numbers (ca 10,000) without a hydrogen acceptor would likely comprise a next generation of technology to produce this material. We found a catalyst that meets these goals (see Table 1).

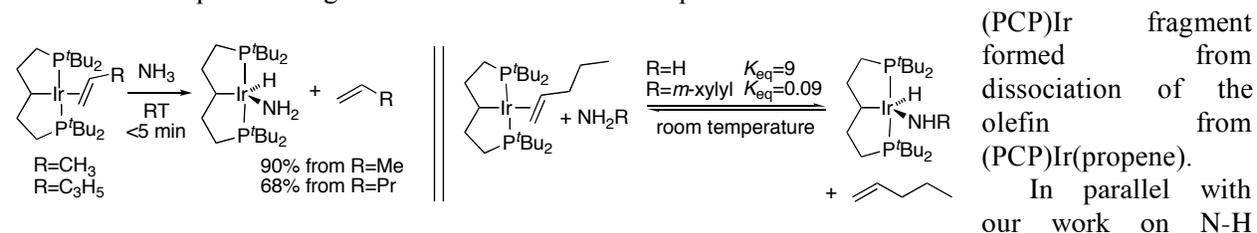
Table 1. Conversion of 1,4-butanediol to γ -butyrolactone catalyzed by complexes that likely react by outer-sphere hydrogen transfer mechanisms.^a



Entry	Catalyst	Time	Ratio (diol: GBL) ^b	
1	Shvo dimer	12 h	13: 87	
2	Shvo amide analog	10 h	77: 1	
3	<i>trans</i> -RuHCl(tmen)(BINAP)	10 h	7:67	
4	(DPPF)RuCl ₂ (eda)	10 h	31: 69	
5	(DIOP)RuCl ₂ (eda)	10 h	0: 97	
6	(PPh ₃) ₂ RuCl ₂ (eda)	10 h	19:91	
7	(PMe ₃) ₂ RuCl ₂ (eda)	10 h	0: 99	

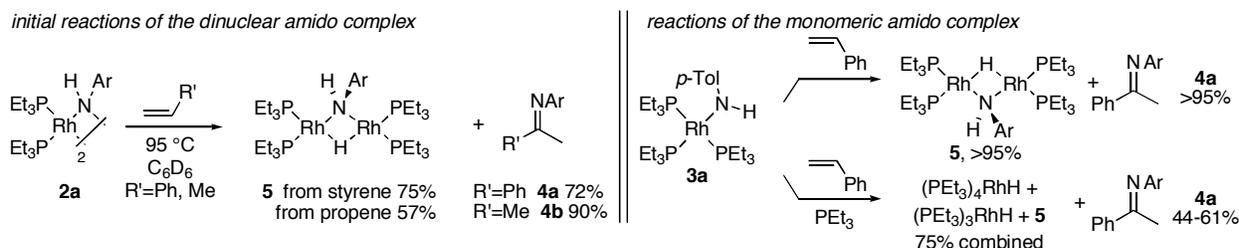
^a Reaction conditions: catalyst 0.005 mmol and 1.1 mmol of 1,4-butanediol were heated at 205 °C for 10-12 h in a capped vial; ^b Ratios determined by GC. When the sum of the values is less than 100%, other products were observed in the GC trace. eda=ethylenediamine, tmen = tetramethylethylenediamine.

Oxidative Addition of Ammonia. In 2005, we reported the oxidative addition of ammonia to form a stable, monomeric amido hydride complex. We had previously shown that the reaction of ammonia with a (PCP)Ir fragment containing an aromatic backbone simply formed the ammonia complex (PCP)Ir(NH₃). To favor the oxidative addition, we prepared a complex with a more electron-donating pincer ligand with an aliphatic backbone. Reaction of the propene or pentene complex of this fragment (PCP)Ir(CH₂=CHR) with ammonia formed a stable, monomeric amido hydride complex by oxidative addition. Isotopic labeling and kinetic studies of this process showed that ammonia reacted with the

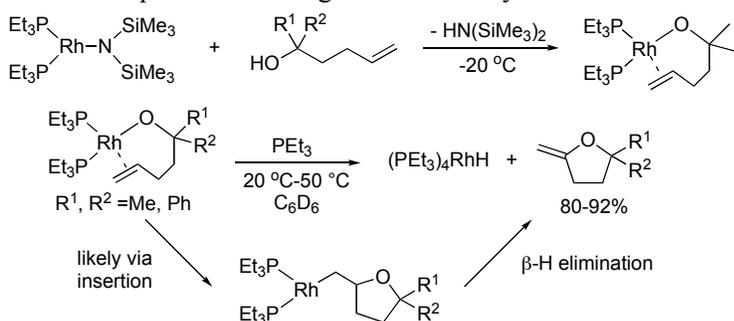


activation, we have sought to develop transition metal amido complexes that would insert unactivated olefins into the M-N bond. Several years ago we first found that the simple rhodium amide [(Et₃P)₂Rh(NHPh)]₂ reacted with styrene and propene to transfer the amido group from the metal to the olefin. This reaction formed imine and the dinuclear rhodium hydride [(PEt₃)₂Rh(m-H)(m-NHAr)Rh(PEt₃)₂]. More recently we found that the analogous monomer [Rh(PEt₃)₃(NHAr)] reacts with

the same olefins to give the same imine and rhodium products. Of course, the kinetic behavior of the monomers is simpler, and for this reason we focused our recent studies on the reactions of this monomer. All data pointed to a mechanism involving migratory insertion of the olefin into the M-N bond.



With these results in hand, we sought to extend the insertion processes to the reactions of rhodium alkoxo complexes. Although we have not yet observed intermolecular insertions, we have recently shown



that a rhodium alkoxo complex with a pendant olefin binds the olefin to form a species with an alkoxo complex cis to a coordinated olefin. This complex was characterized at $-20\text{ }^{\circ}\text{C}$. Upon warming to room temperature, this complex forms the rhodium hydride and 2,2-dimethylmethylene tetrahydrofuran, most likely by insertion of the olefin, followed by β -hydrogen elimination to

form the final products.

Future Studies. Our work for the near future involves further work on the mechanism of the N-H activation of ammonia, development of systems for the activation of alkylamines, and determination of the structural features of the pincer ligand needed to observe the oxidative addition of ammonia. In addition, we will study the insertions of olefins into metal amido and alkoxo complexes of rhodium with different ancillary ligands and will extend these insertion processes to other square-planar d^8 systems and will probe insertions into d^6 Rh(III) systems.

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DE-FG02-04ER15599

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CATALYSIS SCIENCE INITIATIVE: Supported Molecular Catalysts: Synthesis, In-Situ Characterization and Performance

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Goals

For more than a century, catalysis by solid surfaces (heterogeneous catalysis) has made possible technological breakthroughs and stimulated new fields, exemplified by surface science. Solid catalysts offer decisive technological advantages over liquids and gases, being noncorrosive, easily separated from fluid products, and applicable at high temperatures to overcome limitations of thermodynamics and kinetics of the reactions. However, almost all solid catalysts suffer from the disadvantage of being unselective, because the intrinsic nonuniformity of their surfaces implies active sites with a spectrum of reactivities. Elucidation of the structures and reactivities of these sites is challenging because they are small, dispersed, and nonuniform.

In contrast, catalysis in solution (homogeneous catalysis), although generally lacking the aforementioned advantages of heterogeneous catalysis, is economically attractive when the catalysts are highly selective; selectivity is associated with the uniformity of the molecular catalytic species. Such uniformity also pertains to atoms and ions in the gas phase, which catalyze reactions without the constraints of solvents or surfaces. Gas-phase species may be more active than conventional catalysts, but, because of their low densities and difficulty of separation from products, they are not well suited to applications. If it were possible to realize supported analogues of gas-phase catalysts, the advantages would include both selectivity and the aforementioned advantages of solid catalysts generally—and also the opportunity for incisive theoretical modeling. Supported molecular catalysts offer the technological advantages of solid catalysts generally—and the additional advantage of allowing incisive characterization of well-defined surface species, provided that they can be synthesized to be nearly uniform.

Recent Progress

We have prepared a uniform supported catalyst from the precursor $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$ and a crystalline (dealuminated Y zeolite) support. The ethylene ligands exhibit uniform fluxionality, as in a true molecular species, as shown by ^{13}C MAS NMR spectra. The incisiveness of the characterization of these species rivals that of molecular catalysts in solution. The natural-abundance ethylene ligands introduced synthetically are easily and completely exchanged by either ^2H - or ^{13}C - labeled ethylene, as verified by IR and NMR spectroscopy, respectively. The sites catalyze ethylene hydrogenation.

We emphasize the lack of a Rh–Rh contribution in the EXAFS data, consistent with the presence of exclusively mononuclear rhodium. The experimental Rh–O coordination number is 2.2 ± 0.4 , representing the coordination of Rh to the zeolite framework. The Rh–O distance is 2.19 Å, consistent with previously reported distances for rhodium complexes bonded to oxide supports. The Rh–C coordination number was determined to be approximately 3.9, consistent with 2 ethylenes π -bonded to Rh. The EXAFS (average) Rh–C bond length (2.09 Å) is close to the XRD values for the precursor $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$ (2.13, 2.14 Å). The Rh–Al coordination number was determined to be 0.4, but this contribution could be determined only tentatively, as the error bound is high. The Rh–Al distance found

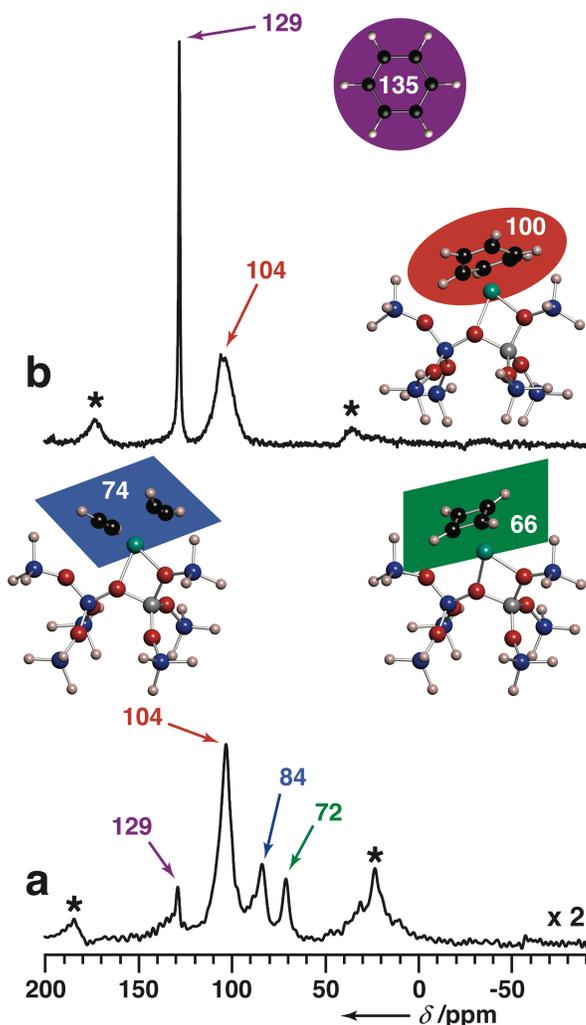
by EXAFS spectroscopy was 2.92 Å (cf. the calculated value, 2.89). The active site of the zeolite-supported rhodium catalyst was represented as a structure optimized at B3LYP using appropriate basis sets and a cluster model of a zeolite anion site; the model matches the EXAFS data within error.

^{13}C MAS NMR spectra decisively demonstrate that the supported rhodium complex indeed has intact π -bonded ethylene ligands and that no other carbonaceous species were introduced by the ethylene- $^{13}\text{C}_2$ exchange procedure. Most important, by acquiring ^{13}C MAS NMR spectra of the supported complex over a range of temperatures, we observed a temperature dependence of the line width similar to that reported by other workers for a crystalline sample of the precursor complex. The ^{13}C resonance of the π -bonded ethylene ligands is broadened as a result of a conflict of ^1H - ^{13}C dipolar decoupling and random anisotropic reorientation of the ^1H - ^{13}C bond vector. When these two dynamical processes occur on the same time scale *for all spin-pairs in the sample*, the carbon resonance is broadened in its entirety—and correspondingly no signal was observed for our sample at temperatures near room temperature with a 27-kHz proton dipolar decoupling field. If the metal sites of our zeolite-supported rhodium catalyst were structurally diverse, this diversity would map into a distribution of rotational barriers for the ethylene ligands, and some of the sites would yield sharp ^{13}C components at each temperature investigated—as we have verified by using another, less uniform, support (MgO). The rotational barrier for ethylene ligands in our supported complex is sensitive to both electronic and steric interactions. The result that all ethylene ligands in the catalyst have a common rotational barrier is powerful evidence that we have synthesized a supported rhodium complex that has a degree of structural uniformity characteristic of crystalline complexes and solution species.

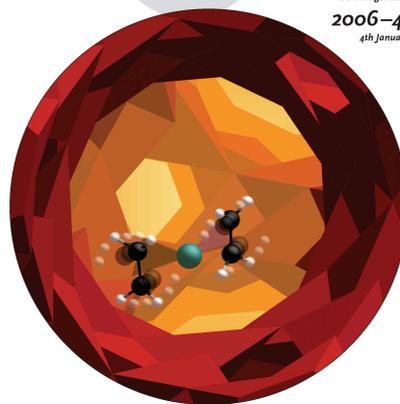
The ethylene ligands in the zeolite-supported complex exchange readily with acetylene, which undergoes cyclotrimerization in a catalytic cycle on the rhodium centers. The catalyst has been characterized spectroscopically, even while functioning at realistic pressures and temperatures, and by modeling by electronic structure methods based on density functional theory. Shown below are two ^{13}C MAS NMR spectra. The lower spectrum was obtained after loading acetylene- $^{13}\text{C}_2$ onto a sample of the supported molecular catalyst. Observed are signals assigned to the bis-acetylene complex and the benzene complex as well as a cyclobutadiene complex that exists as a spectator in equilibrium with the pathway between reactants and products. The upper NMR spectrum shows that the benzene complex of the supported metal cation is formed directly by exchange of benzene- $^{13}\text{C}_6$ for ethylenes. We are concluding a detailed investigation of this catalytic cycle based on comprehensive spectroscopic measurements and theoretical modeling.

DOE Interest:

Catalysts consisting of nearly uniform (molecular) structures on solid supports offer the advantages of solids (ease of separation from products, lack of corrosion) combined with the advantages of molecular catalysts in solution, including high selectivities. These catalysts mark a significant step toward the subtlety and selectivity of nature's catalysts, the enzymes. Supported molecular catalysts have already found important industrial applications, exemplified by the metallocenes used for alkene polymerization. This class of catalyst—of interest because precisely synthesized samples can be so highly uniform and subject to such incisive characterization—also offers compelling opportunities for fundamental investigations that will propel the rapid advancement of catalysis science. These catalysts are stimulating collaborations between experimentalists and theorists; between synthesis, characterization, and performance experts; and between those whose roots are in molecular chemistry, surface chemistry, and materials science.



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Serine Octamers and Homochirality

R. C. Cook and S. C. Nierlich

Enantioselective α -Fluorination

P. M. P. Ma

Organic Chemistry in Water

J. M. Lindeman and F. Anderson

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Future Plans:

We plan to investigate well-defined cationic rhenium clusters on oxide supports, characterizing them with the spectroscopy and theoretical methods mentioned above as well as for hydrocarbon conversion catalysis at high temperatures. We are also extending the work to iridium catalysts.

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**Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes
Through Tailored Nanostructures.**

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Project Start Date: 9/15/03 (* = current)

Project Goal

The overarching goal of this program is to lay the scientific foundations for a new class of heterogeneous catalysts in which materials with nanoscale structuring are utilized to control the flow of reactants to and products from optimized reaction sites and, to the extent possible, to control the flow of energy released in the surface reactions.

Bartels focus in this project is on the investigation and characterization of (a) the dynamic behavior of adsorbates on metal surfaces as a foundation for the development of methods that enhance catalytic activity of supported nanoparticles by steering the diffusion of reactants towards active centers; (b) Substrate-mediated adsorbate excitation and adsorbate-adsorbate excitation transfer that induce/influence relevant surfaces reactions.

DOE Interest

Catalytic reactions have great importance for a broad range of industrial and environmental processes including e.g. catalytic CO oxidation in exhaust systems, 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.

Research Plan and Results

Our vision of a new class of catalysts calls for substrate structures that guide the motion of adsorbates towards catalytically active sites. Realistic catalysts generally consist only to a small fraction of the material to which the catalytic activity is attributed, the remainder being support

and a matrix/binder. This renders efficient transport of the reactants to the active sites an issue with great potential impact.

Guiding Surface Diffusion by Adsorbate-Substrate and Adsorbate-Adsorbate Interactions

In this context, we performed fundamental investigations on a) how the interactions between adsorbate and substrate can guide surface diffusion and b) how interactions with neighboring adsorbates modify surface mobility. Both of these research efforts were conducted on a Cu(111) surface, which offers a top layer of sixfold symmetry (threefold symmetry, if the second layer is included). fcc(111) surfaces are the equilibrium surfaces of many metals (Ag, Au, Cu, Pd, etc.), which renders the hexagonal (111) motif the one most commonly expressed in metallic micro- and nanoparticles. Generally, hexagonal surfaces are regarded as exhibiting the highest symmetry for crystalline media. They are also among the least reactive, which renders transport across them towards sites of greater activity (e.g., step-edges, other surface irregularities, and regions of different composition) even more important.

Surfaces of lower symmetry are known to guide the diffusion of adsorbates along their structural features (e.g., atomic rows on (110) surfaces, step-edges on regularly stepped surfaces, etc.). STM investigations have been tremendously useful in both elucidating and quantifying the details of such processes. Our investigations have shown that similar 1-dimensional guidance can be achieved on the hexagonal fcc(111) surface despite the *absence of structural differences along the three equivalent in-plane directions*. The origin of this guidance effect is completely different from the familiar influence of the inherent surface anisotropy. It arises from the detailed molecule/surface interaction. We demonstrated this effect using a molecule, 9,10-diacetylthioanthracene (DTA), that we designed for this purpose. We found that when deposited on a Cu(111) substrate a DTA molecule diffuses exclusively along the direction in which it is initially aligned. This behavior amounts to a breaking the substrate symmetry. It converts a 2D random walk into a 1D phenomenon. The guiding principle in the design of the DTA molecule was the transfer of the concept of bipedal locomotion (i.e., walking) to the scale of individual molecules. In particular, we could show that if adsorbate-substrate interactions require at least one of a molecule's substrate linkers be attached to the surface at all times, guiding of the molecule's diffusive motion can be achieved (Fig. 1). The novelty of this guided diffusion process earned the findings widespread attention in the scientific community, including mentioning in C&EN news and as one of the 25 'Physics Top Stories for 2005'.

We also addressed the diffusion and reaction of smaller molecules. In this case our interest was to understand distinctive changes in the rates induced by *local changes in the chemical or structural environment of a molecule*. These investigations also included both theoretical and experimental components. The theoretical component was based on the use of Density Functional Theory calculations for a wide range of surface configurations. For example, PI Rahman calculated the barriers for successive abstraction of all hydrogen atoms from ammonia adsorbed at a variety of sites on nickel and palladium surfaces.

On the experimental side, we explored the impact of intermolecular interactions on the surface dynamics in the model system CO/Cu(111). It is generally understood that higher adsorbate coverages lead to

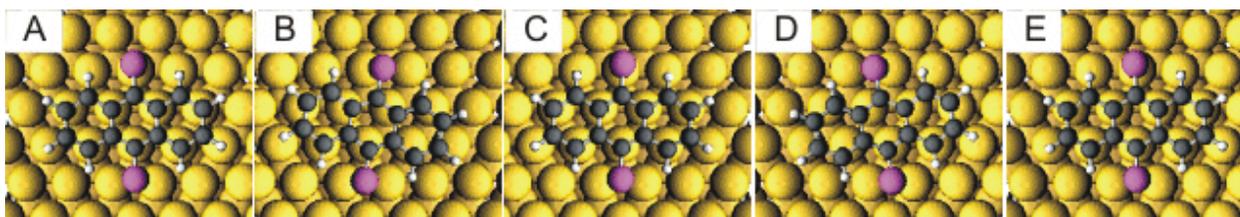


Fig. 1 Molecular configurations during the linear diffusion of DTA on a Cu(111) surface. At any instant either one of the sulfur (purple) substrate linkers is outside a favorable hollow site or the ring system as a whole is misaligned with the substrate.

higher diffusion rates because the diffusion barrier is related to the adsorption energy, which typically decreases with increasing adsorbate coverage. In the literature there is, however, very little direct quantitative evidence to support this view point. The exception are experiments of repeated local

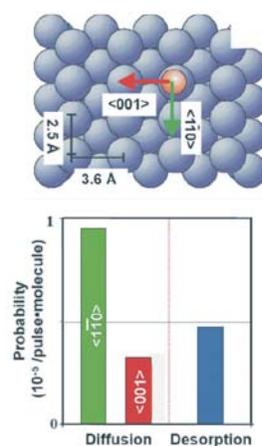


Fig. 3 Distribution of CO reactions following femtosecond substrate heating for the CO/Cu(110) system. The different reactions observed are associated with a wide range of activation barriers.

photodesorption of surfaces and LEEM/PEEM measurements of reaction fronts, which have somewhat limited spatial resolution. We performed STM measurements in which we created local coverage gradients by means of tip-based desorption of CO molecules from a completely covered substrate. By following the diffusion of molecules back into the depleted region, we could measure the surface diffusivity as a function of local coverage. We found that the diffusivity increases by more than a factor of 3 as the coverage increases from the low-coverage limit of isolated molecules (Fig. 2). This finding underscores the impact of the local environment on surface dynamic processes. To probe the intermolecular interactions at the core of this phenomenon, we investigated how the diffusive motion of pairs of CO molecules differs from that of the isolated species. As in literature investigations of Cu/Cu(111) and CO/Pd(111), we found that certain separations for the two partners are preferred. Unlike the earlier studies, we examined diffusive motion as a function of the intermolecular separation. From such data, variations of the adsorption potential and of the diffusion barriers between different adsites can be obtained (Fig. 2) that have a statistical error of $\leq 1\%$ of the total diffusion barrier (i.e., in the sub-meV range for the case of CO/Cu(111)). Data from this investigation can be used to model the acceleration of surface diffusion with increasing coverage up to the point at which collective adsorbate interactions are not well reproduced by a linear combination of pair interactions.

Adsorbate and Energy-Flow Dynamics following Ultrafast Substrate Excitation

The experimental work described above proceeded at cryogenic temperatures in order to limit the diffusion rate of the reactants to a regime compatible with the seconds scanning rate of our STM. Under realistic catalytic conditions, in which the reactant thermal energy is sufficient to induce the chemical transformation of reactants to products, diffusion (with its very low barrier) is expected to be an extremely rapid phenomenon – so rapid that adsorbates cannot be traced by STM. At cryogenic temperatures the branching ratio between diffusion and high-energy processes is very much to the disfavor of the latter and even extensive STM investigations are generally not able to observe chemical transformation of reactants unless other sources of excitation (e.g. the tunneling current) are used. To circumvent this problem, we developed a technique based on alternated imaging of a surface area by STM and femtosecond optical excitation. Although the experiments are conceptually straightforward, success would not have been possible without a combination of the STM-expertise of PI Bartels (e.g. development of dedicated control circuitry to interface the laser and to prevent adverse effects of tip illumination) and the expertise of PI Heinz in optically driven surface processes.

Application of ultra-short high-energy laser pulses at photon energies that are non-resonant to adsorbate transitions does generally not cause adsorbate reactions directly. The photons are rather absorbed by the electrons of the substrate surface, which causes their effective temperature to rise dramatically during a

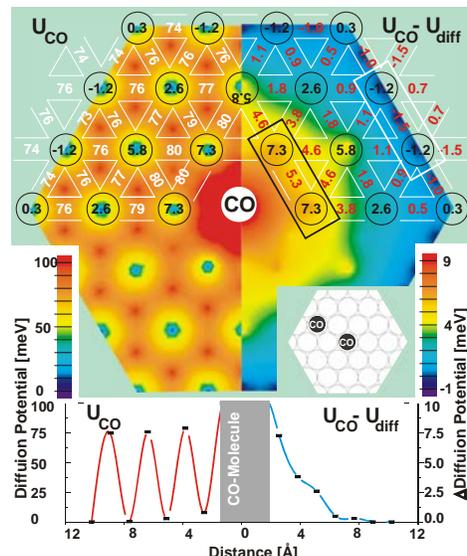
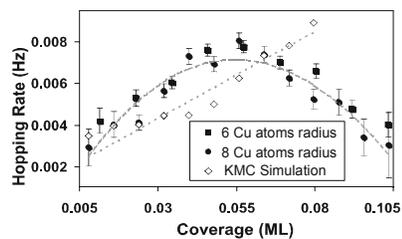


Fig. 2 (top) Variations of CO/Cu(111) diffusivity in dependence on the local coverage; (bottom) The diffusion potential of a CO molecule in the vicinity of another one located at the center of the plot (right) and its variation from the unperturbed potential (left). All values in meV.

short transient until they are able to dissipate the deposited energy via diffusion into the bulk and via coupling to the phononic/vibrational degrees of freedom of the substrate and of adsorbed atoms/molecules. Our measurements for the CO/Cu(110) system showed that under such conditions the rates of desorption and of diffusion along and across the substrate atomic rows are similar (Fig. 3). This is in marked contrast to STM experiments in thermal equilibrium, where only diffusion along the row is observed. Observation of a ratio of the rates for desorption and diffusion of ≈ 10 despite the fact that the barrier for CO-desorption is ≈ 5 times higher than that for diffusion, indicates that (a) a very high excitation level of the adsorbates is reached and (b) that these experiments can provide data on the effectiveness of the energy flow dynamics between different adsorbate modes, the substrate electronic bath and its phononic bath. We wish to explore these phenomena further, experimentally and theoretically. It is also noteworthy that the thermal transient of the substrate electrons is at the same time so brief and so intensive, that energetic surface reactions can occur without being obscured by a massive number of diffusion events.

Results with Minor or No Direct Involvement of Bartels

Binary Nanoparticle Superlattices: So far, we focused on combining two *different* types of nanoparticles with the goal of obtaining potentially valuable neighbor-neighbor interactions on the nanoscale. Very little is known about the collective properties of any multicomponent superlattice and there are literally only a few reports in the literature so far. Collaborators O'Brien and Murray are leaders in the materials discovery process and believe that this new class of materials presents opportunities in the rational design of new catalysts.

Catalytic Growth of Carbon Nanotubes: During the current grant period, PI O'Brien has developed advanced CVD growth capabilities. The method can produce single-walled nanotubes with lengths up to the centimeter scale. These nanotubes are highly oriented spatially and their origin is defined by the placement of the catalyst. This allowed high-precision optical investigation of their properties by PI Heinz.

Theoretical Investigation of Nanoparticle Surfaces: Traditional first principles calculations are based on “zero-temperature” and “zero-pressure” techniques, while real catalysts work at finite temperature and in contact with a gas-phase environment at ambient pressure. As shown recently for of RuO₂, exchange of chemical species with the environment causes dramatic modifications of the surface structure, composition and geometry, that in turn change the mechanism of the catalytic reaction fundamentally. We develop *ab initio* thermodynamics approaches capable of treating nanoparticle surface in equilibrium with a gas phase environment.

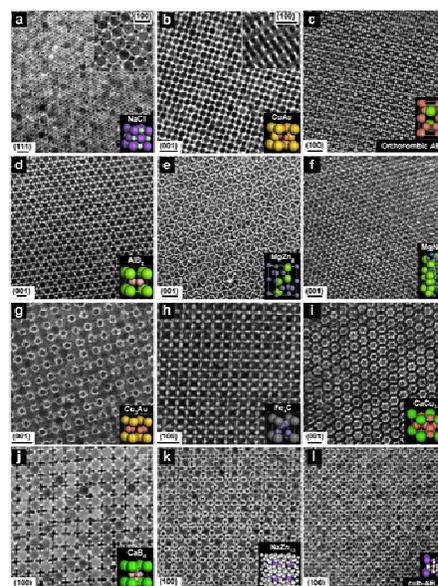


Fig. 4 TEM images of the characteristic projections of the binary superlattices, self-assembled from different nanoparticles, and modeled unit cells of the corresponding three-dimensional structures.

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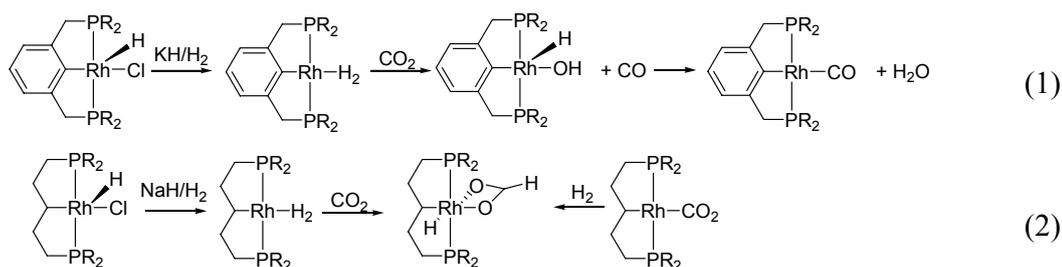
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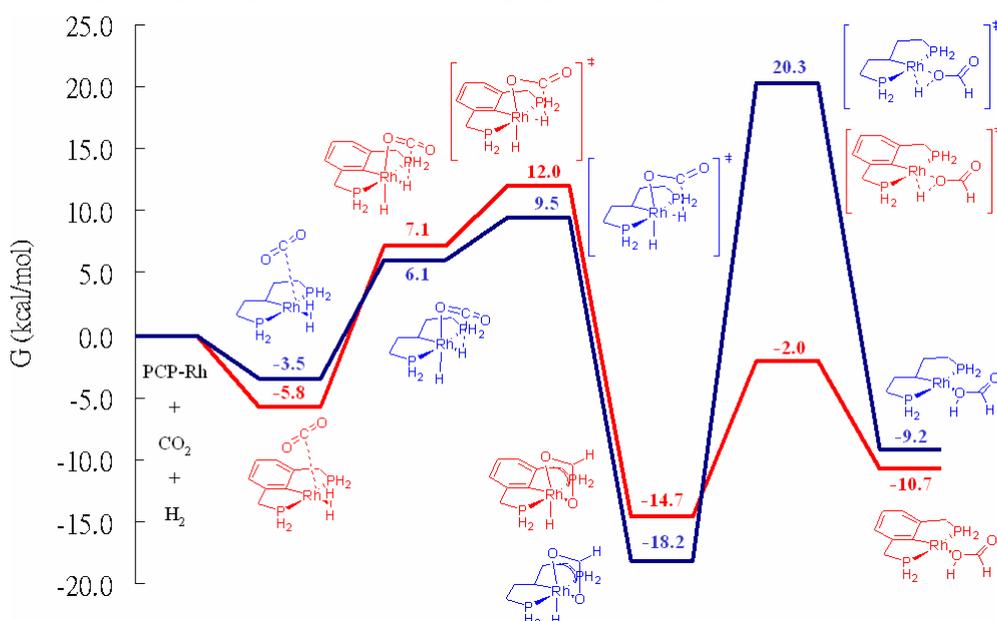
Mechanistic Study on Rh-mediated Reverse Water-Gas Shift Reactions: Insights For CO₂ Reduction

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Two types of PCP-Rhodium complexes exhibit different reactivities in the hydrogenation of carbon dioxide (Eq 1 & 2, R = t-butyl). In Eq. 1, the Rh-carbon monoxide (CO) complex is the final product, while in Eq. 2, the reaction ceases at the hydridorhodium formate complex.



We used theoretical calculations to model and examine the proposed mechanisms for these reactions. We have investigated possible pathways involving the formation of rhodium dihydride and hydridorhodium formate species as important intermediates in reaction 1, which were supported by our experimental observations. Although the dihydrogen complexes are more stable than the corresponding dihydride complexes, the reduction of CO₂ has to proceed through the dihydride structures. The major difference in the reactivities of these two PCP-Rh complexes is the energy barrier of the reductive elimination of formic acid from the hydridorhodium formate complex. We hypothesize that this is an essential step for the next decarbonylation reaction which leads to the formation of a Rh-CO product. The molecular structure of the Rh-CO product was elucidated by a single crystal X-ray crystallographic analysis.



This work is supported by the Photochemistry and Radiation Research Program of the Office of Basic Energy Sciences.

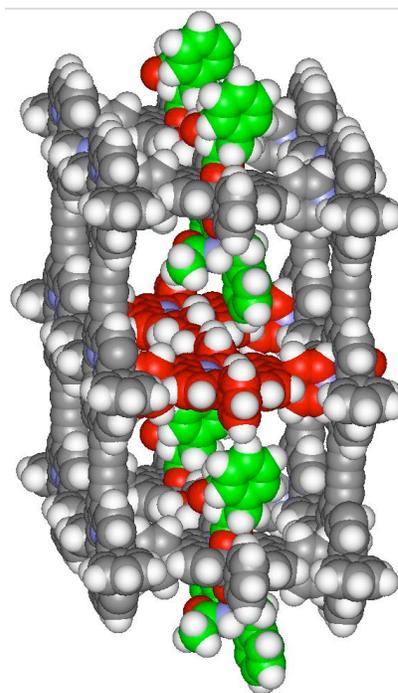
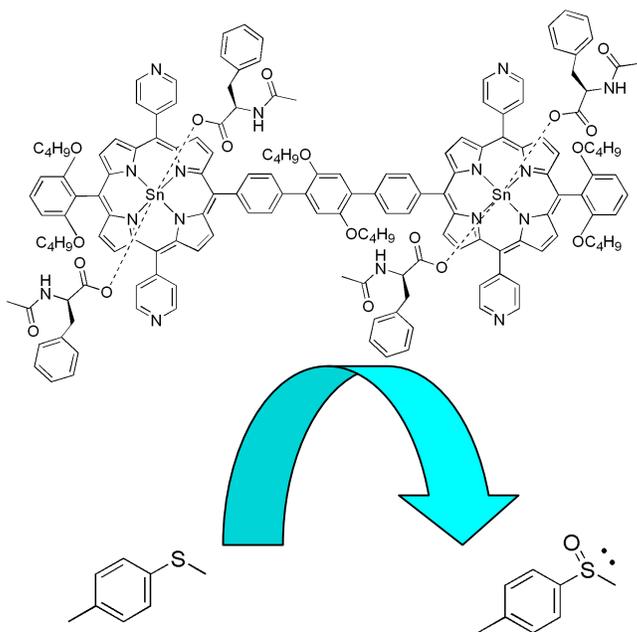
Bio-inspired Supramolecular Assemblies for Oxidative Catalysis

Contact: J. T. Hupp or S. T. Nguyen, Dept. of Chemistry and Institute for Catalysis in Energy Processes, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208; phone: (847)491-3504 or (847)467-3347; Email: j_hupp@northwestern.edu or stn@northwestern.edu

Supramolecular assemblies are assemblies constructed from molecules rather than atoms as building blocks. Typically, the assemblies obtained are thermodynamic structures. Often their stability comes from marshalling multiple weak interactions in a highly reinforcing way. This allows for a modular approach to catalyst assembly and testing. Furthermore, it yields structures that spontaneously reassemble when disrupted. Supramolecular chemistry has attracted the attention of catalytic chemists because of its potential for bringing together cooperative catalytic sites, stabilizing potent reaction centers, and creating architectures that elicit reaction selectivity.

We have used directed assembly approaches to coordination chemistry to obtain catalytically competent supramolecular assemblies in high synthetic yield. Many of these spontaneously form in a single step. The active sites are reminiscent of those found in certain metalloenzymes. The most elaborate assemblies attain their complexity and high functionality through a combination of cooperative binding, coordinative orthogonality, and sterically programmed self-sorting behavior. Characterization of the structures of assemblies in reaction environments has been done via solution-phase X-ray scattering and molecular diffraction.

This poster will focus mainly on assemblies designed to catalyze oxidation reactions in size-selective and enantioselective fashion. Shown below is a self-assembling 18-porphyrin structure featuring manganese active sites and amino-acid-defined chiral cavities. A related poster describes selective oxidation catalysts based on permanently microporous metal-organic frameworks.



Basic Principles that Govern the Interaction of Organometallic Catalysts with Supports – The Science of Immobilized Molecular Catalysts

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Goal

Immobilized organometallic catalysts, in principle, can give high rates and selectivities like homogeneous catalysts with the ease of separation enjoyed by heterogeneous catalysts. However, the science of immobilized organometallics has not been developed because the field lies at the interface between the homogeneous and heterogeneous catalysis communities. By assembling an interdisciplinary research team that can probe all aspects of immobilized organometallic catalyst design, the entire reacting system can be considered, where the transition metal complex, the complex-support interface and the properties of the support can all be considered simultaneously from both experimental and theoretical points of view. Researchers at Georgia Tech and the University of Virginia are studying metal pincer and N-heterocyclic carbene complexes as catalysts for basic feedstock and building block reactions (i.e. carbon-carbon bond formations, dehydrogenations, etc.) and metal salen complexes (as catalysts for enantioselective reactions) immobilized on polymeric, silica and nanoparticle supports. Using these model systems, the fundamental principles that can be used to understand and design future classes of immobilized organometallic catalysts will be elucidated.

DOE Interest

The work performed in this program elucidates fundamental principles important in the design of immobilized catalysts. These catalysts have the potential of being very active and selective while being easy to separate for the reaction medium. All of these aspects provide a substantial energy advantage in chemical processing.

Recent Progress (2005-present)

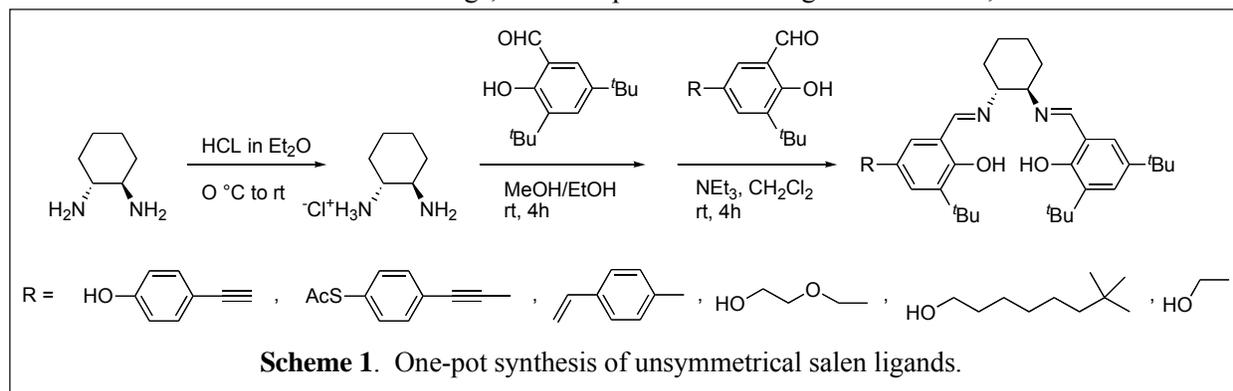
Over the last twelve months, efforts have focused on developing immobilized, asymmetric salen complexes on a number of supports. The salen ligand was chosen as a target for immobilization due to the myriad different asymmetric reactions it can promote using a wide variety of metals. A key aspect of our program is elucidating how metal salen complexes should be immobilized to obtain optimal catalytic properties. In particular, we hypothesize that different immobilization strategies will be required for the two broad classes of reactions that metal salen complexes catalyze – (i) reactions that involve a single metal center vs. (ii) reactions that are bimolecular in metal complex.

Despite a large number of literature reports on attempts to immobilize Jacobsen's salen catalysts, highly active and selective, *recyclable* salen systems have not been fully realized to date for many reactions. In most studies, the activities and selectivities of the supported catalysts were significantly lower than their homogeneous counterparts. There are a wide variety of hypotheses about why they do not behave as well as the homogeneous analogue including a lack of rotational or translational degrees of freedom, or inaccessibility of the catalytically active sites to the substrates. Furthermore, in previous studies, the recyclability of the supported catalysts turned out to be a major challenge. Often, the catalytic activities and/or selectivities drop significantly when the catalysts were reused. Therefore, to date, no detailed studies have conclusively shown what the cause of the poor performance is and what potential catalyst designs can alleviate these problems.

The supported salen complexes that have been investigated during the last 12 months are active catalysts for the asymmetric epoxidation (AE) of olefins (Mn – salen) and the hydrolytic kinetic resolution of terminal epoxides (Co – salen). In this case, AE represents a reaction that requires only a single metal complex, whereas HKR requires two. In the case of the asymmetric epoxidation, the Mn(III)

complex is oxidized to Mn(V) by a single oxygen source such as a peroxide and the Mn(V) species is responsible for the epoxidation of the olefin, whereby the manganese is reduced back to Mn(III). The most common deactivation pathway for this system is the dimerization of a Mn(III)- and a Mn(V)-complex resulting in an *oxo*-bridged Mn(IV)-O-Mn(IV) species. For this reason it has been proposed that a highly active Mn-Salen epoxidation catalyst can best be realized by immobilizing the complex in such a way that a perfect site isolation of all catalytic moieties is guaranteed. The mechanism of the hydrolytic kinetic resolution, on the other hand, is believed to involve a cooperative bimetallic pathway, with one cobalt activating the epoxide while a second metal site activates the nucleophile (water). In this case, a system allowing an easy interaction of the two metal centers is desired, whereas a system with site-isolated catalytic centers should be less selective. Because of the very different mechanistic paths of AE and HKR, we proposed that, once design principles for the synthesis and activity of supported catalysts for these two reactions have been worked out, the development of supported salen catalysts for myriad other reactions should be straightforward, as the reactions will fall into one of the two classes of salen reactions discussed above.

One hurdle we had to overcome early on in our studies was the large-scale synthesis of *monofunctionalized* salen catalysts. Whereas the vast majority of preparative and catalytic studies on this family of compounds have been dedicated to salen ligands with C₂-symmetry, recent studies have demonstrated that unsymmetrical salen ligands, where the term unsymmetrical describes two distinct substituents on the two aromatic rings, hold important advantages. However, at the start of our



studies, the synthesis of unsymmetrical salens was difficult and low yielding. We developed a practical one-pot synthesis of enantiopure unsymmetrical salen ligands (outlined in Scheme 1), using a 1:1:1 molar ratio of a chiral diamine and two different salicylaldehydes. We demonstrated the utility of this one-pot approach by synthesizing a variety of monofunctionalized salen ligands containing different linkers ranging from rigid phenylene ethynyls to alkyl chains and ethylene glycol-based linkers. In all cases, the new synthetic protocol can readily be performed in good yields (60–85%) on the multigram scale with good tolerance toward various functional groups.⁷

After the development of a straight-forward synthesis of monofunctionalized salen ligands, we focused on the synthesis, characterization, computational description, and catalytic evaluation of supported metal salen complexes. First, we prepared a series of salen-based monomers that are norbornene or styrene-based and can be polymerized either via free radical polymerization or ring-opening metathesis polymerization (ROMP) to yield salen-containing homo and co-polymers.^{6-8, 17}

For evaluation of the poly(norbornene)-based Mn-Salen complexes as asymmetric epoxidation catalysts, we chose styrene, 1,2-dihydronaphthalene, and *cis*- β -methyl styrene as substrates, representing a terminal, a cyclic and a *cis*-disubstituted, non-cyclic olefin. Kinetic studies of the catalytic reactions demonstrated the high activities of the polymer-supported salen systems with quantitative conversion using four mol-% Mn after 150-300 seconds. The epoxidations of styrene and *cis*- β -methyl styrene were as fast as the control experiments using the original non-supported Jacobsen complex. All copolymers had catalytic activities that were higher than and enantioselectivities equal to their homopolymer analogues. This superiority of the copolymers may be associated with better good site-isolation of the manganese centers (*vide supra*).⁸

In parallel with this experimental study, a theoretical characterization of the Mn-Salen was also carried out. Numerous theoretical studies over the past decade have sought to elucidate the electronic properties that give rise to the stereochemical control afforded by the Mn-Salen system. Despite a large number of theoretical studies, extracting definitive conclusions from theory has proven challenging. Due to the difference in the description of these systems afforded by the two most commonly used theoretical approaches, we undertook a high-level theoretical study to benchmark the performance of each of these methods for this challenging system.

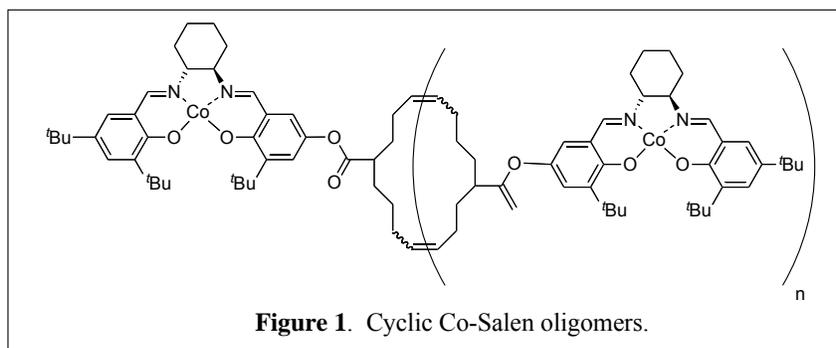
Using robust multi-reference theoretical approaches, we have examined¹¹ many of the low-lying electronic states of oxo-Mn-Salen, several of which have not been explored previously. The model system and geometry employed was taken from work by Ivanic *et al.*. State-averaged complete active-space self-consistent field (SA-CASSCF)/6-31G* wavefunctions were obtained both with a 12 electron in 11 orbital active space as well as an 8 electron in 7 orbital active space. Our highest-quality results, including corrections for finite basis and relativistic effects, indicated the ground spin state to be a closed-shell singlet, followed by a pair of low-lying triplet states at slightly more than 3 kcal mol⁻¹. A pair of nearly degenerate open-shell singlet states, 2¹A and 3¹A, lie around 35 kcal mol⁻¹ followed by the high-spin 1⁵A state at a little more than 40 kcal mol⁻¹. The presence of a second, low-lying triplet state nearly isoelectronic with the singlet and the other triplet has not been discussed previously. The proximity of so many states may result in highly complex potential energy surfaces involving conical intersections and avoided crossing effects, which may complicate reaction mechanisms for Mn-Salen catalysis. Through detailed analysis of the CI expansion from CASSCF calculations, we have demonstrated the multi-reference character of this system. These results suggest that much care should be taken in theoretical studies of Mn-Salen systems when applying more “black box” computational methods like density functional theory or single-reference wavefunction methods.

Three different polymer/oligomer supports were studied for the Co-Salen catalyzed HKR (norbornene, styrene, cyclooctene-based monomers). The catalytic performance of the poly(norbornene)-based cobalt complexes was studied in the hydrolytic kinetic resolution (HKR) of racemic epichlorohydrin (ECH).⁸ Using either the homopolymer or the two copolymers, the (R) epoxide was fully converted after five hours to its corresponding diol, leaving pure (S) epoxide in the reaction mixture in above 99% enantiomeric excess. After this time period, 55% of the racemic mixture was converted indicating selectivities similar to the original Jacobsen CoOAc catalyst (53% conversion, >99% ee under solvent-free conditions). Unlike, the homogeneous Jacobsen Co-Salen catalyst, our poly(norbornene) Co-Salen catalysts could be easily removed from the reaction mixture, demonstrating the possibility of facile metal removal from the products. Furthermore, the polymeric Co-Salen catalysts were recycled with retention of their outstanding selectivities.⁸

All the poly(styrene)-supported catalysts were also highly reactive and enantioselective for the HKR of epichlorohydrin.⁶ Copolymer-based supported catalysts showed the most desired catalytic performances. In this case, the best supported catalysts were more active and equally selective compared to the original Jacobsen catalyst (99% ee at 55% conversion). The soluble poly(styrene)-supported catalysts were recovered by precipitation after the catalytic reactions and were recycled three times to afford almost identical enantiomeric excesses as the first run, with slightly reduced reaction rates.⁶ These results demonstrated that the poly(styrene)-based catalysts were slightly higher in activity than their poly(norbornene)-based analogues. We attributed this enhanced activity to an increase in polymer backbone flexibility (enabling enhanced formation of the bimetallic transition state), which was proposed as one of the key hypotheses in the original proposal.

To further enhance the polymer backbone flexibility, we synthesized poly(1-octene)-based supported Co complexes that were expected to be highly flexible and to have a random coil conformation in solution.¹⁷ Interestingly, the ruthenium-based olefin metathesis resulted in the formation of larger ring cycles (cyclic oligomers) rather than high polymer. MALDI-TOF and NMR spectroscopies provided unambiguous insights into the structures of these oligomers at a molecular level. The oligo(cyclooctene)-supported Co-Salen complexes were examined for their catalytic efficiency in the HKR of terminal epoxides. For most epoxides, an exceptionally low catalyst loading of 0.01 mol% was employed. In all cases, enantiomeric excesses above 99% were observed within several hours and isolated yields (crude conversions measured by GC or HPLC were usually approximately 5% higher) of 43-48% were

obtained.¹⁷ At the same catalyst loading, the unsupported Co-Salen catalyst developed by Jacobsen showed no catalytic activity, demonstrating the superiority of our cyclic catalyst. We attributed this high activity to the close proximity of two Co-centers in our cyclic oligomers, *i.e.* an increase in local molarity of the cobalt centers that enhanced the formation of a bimetallic transition state, in contrast to the high dilution of the small molecule Jacobsen system catalyst. The effect of concentration of the new polymeric catalyst on the rate



of the reaction was also studied. As the catalyst concentration was doubled, the conversion of epichlorohydrin at short reaction times also doubled. Thus, the rate was directly proportional to catalyst loading, unlike the reaction with Jacobsen's catalyst. *It is noteworthy that the oligo(cyclooctene)-supported Co-Salen complexes are the most active and selective unsymmetrically functionalized catalysts developed to date. Catalyst loadings as low as 0.01 mol% can be used with complete conversions within several hours for a variety of epoxides.*

After establishing the activities and selectivities of these novel catalysts, we carried out preliminary recycling studies on the homogeneous Jacobsen's Co-Salen catalyst without intermediate regeneration with acetic acid. The R,R-Jacobsen Co-Salen catalyst (0.5 mol%) was utilized in the HKR of epichlorohydrin (10 mmol) with water (0.7 eq.). Under these reaction conditions, a conversion of 54 % and an ee of 100 % could be obtained in about four hours. The catalyst was recycled up to four times by evaporating the reaction products from the previous run under vacuum. However, the reaction rate decreased significantly with each cycle. This was hypothesized to be due to the reduction of Co(III) to Co(II) during the HKR reaction. Therefore we studied the state of the metal using UV-Vis and XANES spectroscopy. Using UV-vis spectra of the Jacobsen Co(II)salen catalyst (inactive) and Jacobsen Co(III)salen catalyst (active) before and after the catalytic reaction, we established that the mechanism of catalyst deactivation is not due to cobalt reduction.

We also performed preliminary X-ray absorption spectroscopy on Jacobsen's homogeneous as well as the oligo(1-octene)-based Co-Salen catalysts to probe the effect of immobilization of Co-Salen and the change in oxidation state of the Co metal center during the HKR reaction (X10-C at NSLS, Brookhaven National Lab). The Co K-edge (7709 eV) spectra of various Co-Salen complexes were collected at room temperature in both fluorescence and transmission modes. The normalized XANES spectra of immobilized Co-Salen catalysts resembled the homogeneous Jacobsen Co-Salen catalysts in their respective oxidation states, indicating efficient immobilization of the Co-Salen ligand onto the polymeric support. The XANES spectra can clearly distinguish the Co-Salen complexes in +2 and +3 oxidation states since there is a pre-edge peak at about 2.1 eV followed by a peak at ~19.2 eV above the edge energy in Co(III) salen catalysts, whereas a pre-edge peak at about 6.6 eV followed by a peak at ~17.7 eV above the edge energy is present in Co(II) salen catalysts. With these distinguishing features of Co-Salen catalysts in two different oxidation states, we measured the *in-situ* XANES spectra of Jacobsen's Co-Salen catalyst under the HKR reaction conditions. A pre-edge peak at about 2.1 eV above the edge was found in the XANES spectra in every case, which is a characteristic feature of the Co metal center in +3 oxidation state. These results are consistent with the UV-Vis results discussed earlier, which indicated very little reduction of the Co(III) to Co(II) during the HKR of epichlorohydrin. The intensity of the peak at 19.2 eV above the edge energy was found to increase with time. We do not yet know how to account for this feature.

In parallel with these experimental studies, molecular models of poly(norbornene) and mesoporous silica supports were developed. An accurate model of mesoporous silicates is required before the behavior of catalysts in their mesopores can be modeled due to the sensitivity of the catalyst behavior to the interaction of the tethered catalyst with walls of these mesopores. We developed models of both

MCM-41 and SBA-15 hexagonal mesoporous materials.^{3, 5, 13} The SBA-15 materials are being investigated in the experimental portion of this work and the MCM-41 material served as a reasonable model material on which to initiate this model development because it was not complicated by the presence of micropores that traverse the interstitial space in between the mesopores. The MCM-41 model was able to reproduce many experimental results germane to their use as hosts for tethered metal complexes including pore size, surface area, adsorption behavior, etc. Our detailed molecular model was able to reproduce the atomic structure of the interstitial silica in between the pores (as determined by WAXD) and the surface density of hydroxyls in the mesopores. This protocol was also used to produce a model of SBA-15 mesoporous silicate. Given the more compelling evidence for the existence of micropores in the interstitial space of SBA-15, such micropores were included in the model of SBA-15. A model with such micropores (model 1) was compared to a similar model with no micropores (model 2) and a simpler model that was lacking the appropriate level of amorphousness in the interstitial space (model 3). The best model (model 1) is pictured in Figure 2 along with a Connolly surface map of the micropores therein.

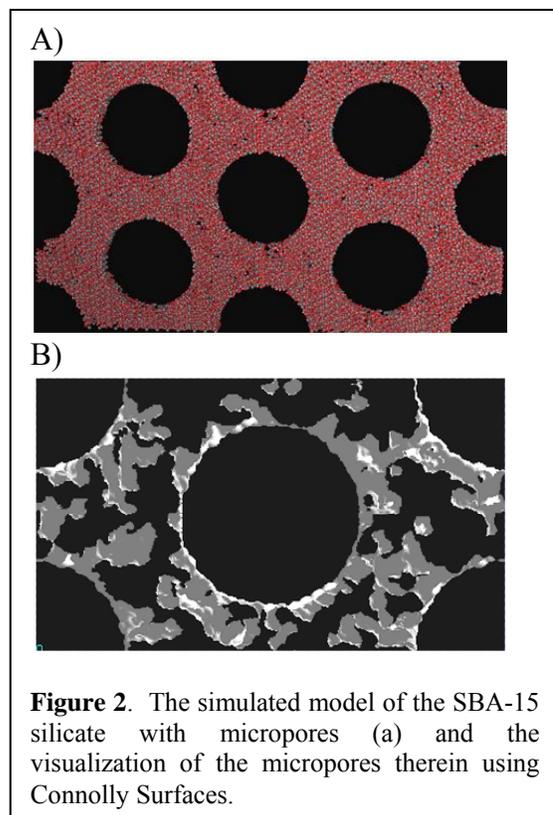


Figure 2. The simulated model of the SBA-15 silicate with micropores (a) and the visualization of the micropores therein using Connolly Surfaces.

Summary

Three new classes of supported metal-Salen complexes have been prepared: (i) poly(norbornene) homo and copolymers, (ii) poly(styrene) homo and copolymers, and (iii) cyclic oligo(cyclooctene)s. The key results of studies of these catalysts are:

- 1) Catalytic activity and selectivity track well with polymer flexibility, with the cyclooctene system representing the most active and selective Co-Salen catalyst for the HKR of *rac*-epichlorohydrin. Based on these results, flexibility is deemed to be a key metric in supported catalysts that operate by a bimetallic transition state, involving two metal complexes.
- 2) The supported catalysts are recoverable and reusable with identical selectivities, although some degradation in activity is noted. In the literature, this loss of activity upon recycle has been hypothesized to be due to reduction of the active Co(III) species to Co(II). Our spectroscopic results indicate that this is not the primary cause of deactivation in these systems with epichlorohydrin.
- 3) Theoretical descriptions of Mn-Salen complexes that rely on HF or DFT approaches may miss important subtleties in the electronic structure of this complex that may affect chemical reactivity.
- 4) Several new models for the hexagonal mesoporous silicas MCM-41 and SBA-15 were developed that reproduce: (i) experimental and literature small angle *and* wide angle XRD patterns, (ii) experimental pore volumes, surface areas and microporosity, (iii) literature adsorption isotherms, and (iv) experimental and literature TEM images.

Furthermore, the key results not detailed in this abstract were obtained over the past 12 months:

- 1) Supported or soluble Pd(II) Pincer complexes are only precatalysts in Heck couplings.
- 2) Ru(II), Pd(II) and Pd(0) complexes of the polymer-supported N-heterocyclic carbene ligands HC were prepared and used as catalysts for olefin metathesis, Heck, Suzuki and Sonogashira couplings¹⁸.

- 3) An optimal method for modeling the dynamics of the cyclopentane ring was developed¹⁵ and this allowed for the creation of models of the various forms of poly(norbornene). The impact of side-chains and backbone structure on the conformation of the polymer was elucidated.
- 4) One-pot multistep catalytic reaction sequences can be promoted using magnetic nanoparticle-supported catalysts in tandem with traditional gravimetrically recovered catalysts¹⁰.

Publications 2005-2006 (PIs underlined)

- 1) "Evidence that SCS Pincer Pd(II) Complexes are only Precatalysts in Heck Catalysis and the Implications for Recycle and Reuse." K. Yu, W. Sommer, J. Richardson, M. Weck and C. W. Jones, *Advanced Synthesis and Catalysis* **2005**, 347, 161-171.
- 2) "Investigations into the Stability of Immobilized Pd^{II} Pincer Complexes During Heck Catalysis." W. Sommer, K. Yu, J. S. Sears, Y. Ji, X. Zheng, R. J. Davis, C. D. Sherrill, C. W. Jones and M. Weck, *Organometallics* **2005**, 24, 4351-4361.
- 3) "A Model for the Structure of MCM-41 Incorporating Surface Roughness." C. Sonwane, C. W. Jones and P. J. Ludovice, *Journal of Physical Chemistry B*. **2005**, 109, 23395-23404.
- 4) "Investigations of Pd Leaching from Supported Pd Catalysts during the Heck Reaction." Y. Ji, S. Jain and R. J. Davis, *Journal of Physical Chemistry B*. **2005**, 109, 17232-17238.
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- 8) "A Modular Approach for Supported Monofunctionalized Salen Catalysts" M. Holbach and M. Weck, *Journal of Organic Chemistry* **2006**, 71, 1825-1836.
- 9) "On the Nature of the Active Species in Palladium Catalyzed Mizoroki-Heck and Suzuki-Miyaura Couplings – Homogeneous or Heterogeneous Catalysis, A Critical Review." N. T. S. Phan, M. Van Der Sluys and C. W. Jones, *Advanced Synthesis and Catalysis* **2006**, 348, 609-679. Cover Article.
- 10) "Expanding the Utility of Multi-Step Reaction Networks via Catalyst Compartmentation and Recovery." N. T. S. Phan, C. S. Gill, J. V. Nguyen, Z. J. Zhang and C. W. Jones *Angewandte Chemie International Edition* **2006**, 45, 2209-2212.
- 11) "The Electronic Structure of oxo-Mn(salen): Single- and Multi-Reference Approaches," J. S. Sears and C. D. Sherrill, *Journal of Chemical Physics* **2006**, in press.
- 12) "Poly(vinylpyridine) Quadrapure TU as Selective Poisons for Soluble Catalytic Species in Coupling Reactions – Application to Polymer Entrapped Palladium." J. M. Richardson and C. W. Jones, *Advanced Synthesis and Catalysis*, **2006**, submitted.
- 13) "A Structural Model for SBA-15 Mesoporous Silica" C. Sonwane, J. Richardson, C. W. Jones and P. J. Ludovice, *Microporous and Mesoporous Materials*, **2006**, submitted.
- 14) "Highly Accessible Catalytic Sites on Recyclable Organosilane-Functionalized Magnetic Nanoparticles." N. T. S. Phan and C. W. Jones, *Journal of Molecular Catalysis A. Chemical*, **2006**, in press.
- 15) "The Importance of Symplectic MD Algorithms in the Dynamics of Cyclopentane" A. Swann, P.J. Mucha and P.J. Ludovice, *Journal of Computational Chemistry*, **2006**, submitted.
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Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds

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Goals and Objectives

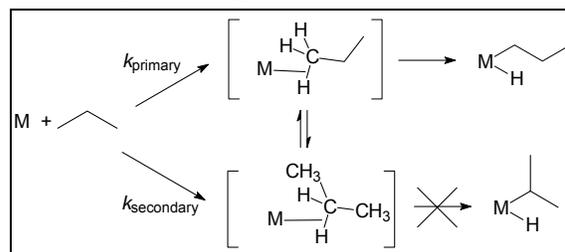
This project has as its overall goal improvement in the intelligent use of our energy resources, specifically petroleum derived products. This goal requires the development of new routes for the manipulation of C-H and C-C bonds, with transfer of the new technology to industry. During the second year of the current 3 year project period, our research has focused on the following specific goals: (1) fundamental studies of C-H bond cleavage reactions in functionalized substrates using trispyrazolylboraterhodium complexes, (2) discovery of new carbon-carbon bond cleavage reactions, (3) catalytic C-H and C-C bond functionalization, and (4) carbon-fluorine bond activation.

Significant Recent Achievements and Results

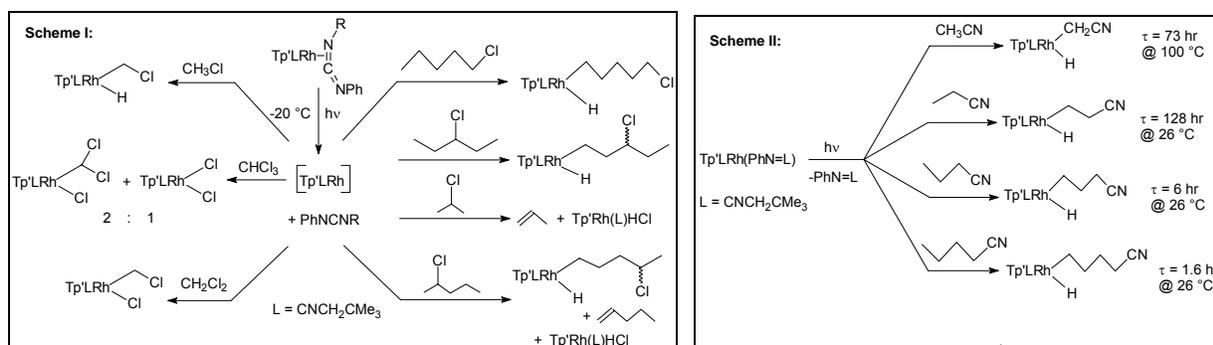
The accomplishments of the current year include: (1) we have successfully measured and quantitatively modeled the processes available to metal alkyl hydride complexes in a trispyrazolylborate-rhodium complex; (2) we have preliminary results that measure *for the first time* the selectivity for a metal fragment binding to methyl vs methylene groups in a linear hydrocarbon; (3) we have examined the selectivity for C-H vs. C-Cl bond cleavage in chloroalkanes, including chloromethane, and determined kinetic selectivities; (4) we have examined C-H activation in alkylnitriles and established their stabilities; (5) we have cleaved C-C bonds in a variety of aryl-acetylenes, expanding tremendously the breadth of C-C cleavage; (6) we have investigated C-CN cleavage in 2-methyl-3-butenenitrile using Ni(0) as it compares to the DuPont adiponitrile process; (7) we have investigated C-F cleavage using Cp*₂HfH₂ for comparison to our earlier Zr work.

Our poster will focus on two of our current areas of research:

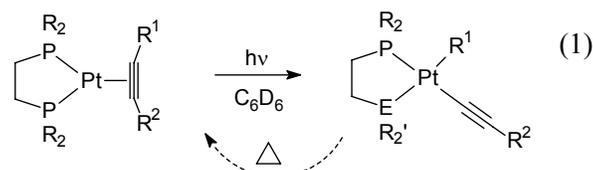
C-H Bond Activation: With our trispyrazolylborate rhodium system, we have been able to determine the relative rates at which C-H bond of an alkane first binds to the Tp'RhL fragment. The execution of this experiment is not completely obvious, as reaction of the fragment with any linear hydrocarbon only gives a single product, the n-alkyl hydride. One cannot determine how the alkane initially bound if a single product is observed. We have performed competition experiments with pentane and propane that allow one to determine alkane binding selectivities. This analysis shows that *a methylene group binds 1.5× faster than a methyl group.*



We have also examined activation of several chloroalkanes (Scheme I). *A 100% preference for C-H activation of a terminal methyl group over a C-Cl bond is observed.* With chloromethane, only C-H cleavage is seen. A competition between chloromethane and methane shows a 2.5× preference for C-H activation of chloromethane. We have also examined activation of several cyanoalkanes (Scheme II). *A 100% preference for C-H activation of a terminal methyl group is observed.* Curiously, these adducts show remarkable stability towards reductive elimination, an effect that appears to be attributable to the inductive electron-withdrawing power of the cyano group.



C–C Bond Activation: We have investigated a series of P-P and P-N chelates of group 10 metals for activity in C-C bond activation. The platinum complexes proved to be the easiest to synthesize and study, since the adducts are fairly stable. The strategy was to use a source of Pt(0) in the presence of the P-P chelate and an alkyne, to isolate the complex, and then to look at reactions of the complex. With diphenylacetylene, the preparation of the adduct was straightforward and allowed comparison of the P-P chelate with the P-N chelate. While the P-P chelated complex showed *no reactivity* with added diphenylacetylene even after heating, the P-N chelated complex reacted at room temperature to give a metallacyclopentadiene complex. Further comparative reaction studies of this system showed that the phenyl-alkyne C-C triple bond can be made to undergo oxidative addition (eq 1)! This reaction has now been examined for a wide variety of aryl and alkyl alkynes, including $\text{C}_2(\text{C}_6\text{F}_5)_2$, $\text{C}_2(\text{C}_6\text{H}_3\text{Me}_2)_2$, $\text{C}_6\text{H}_5\text{CCvinyl}$, and $\text{C}_6\text{H}_5\text{CCBu}^1$.



In addition, we are studying the C-CN cleavage in 2-methyl-3-butenitrile (Scheme III), an isomerization that is key to the DuPont adiponitrile process. The selectivity is found to have strong temperature and solvent effect. We are also engaged in DFT calculations of C-CN bond cleavage reactions of benzonitrile at the Ni(dippe) fragment. These show a remarkable feature in the transition state for C-CN cleavage in which the C–CN bond has rotated by 90° relative to the NiP_2 plane (Figure 1).

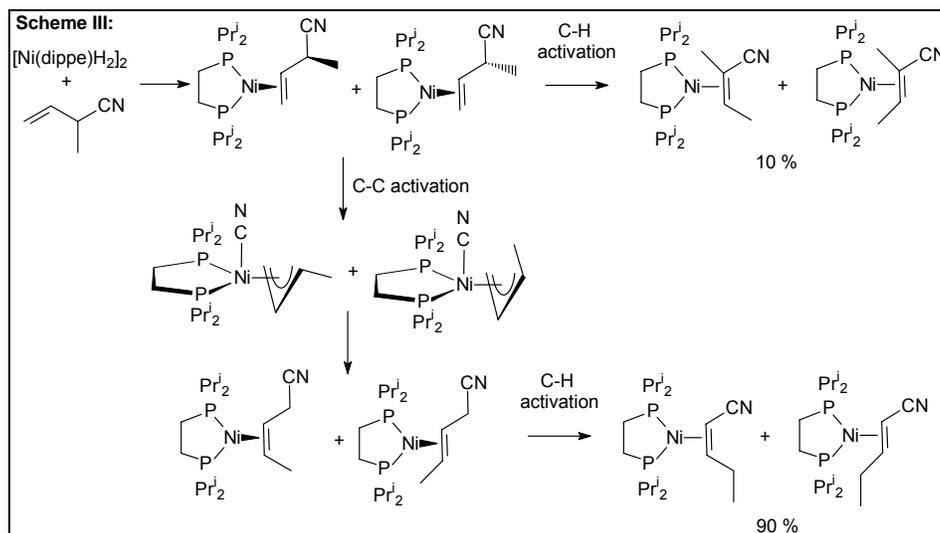
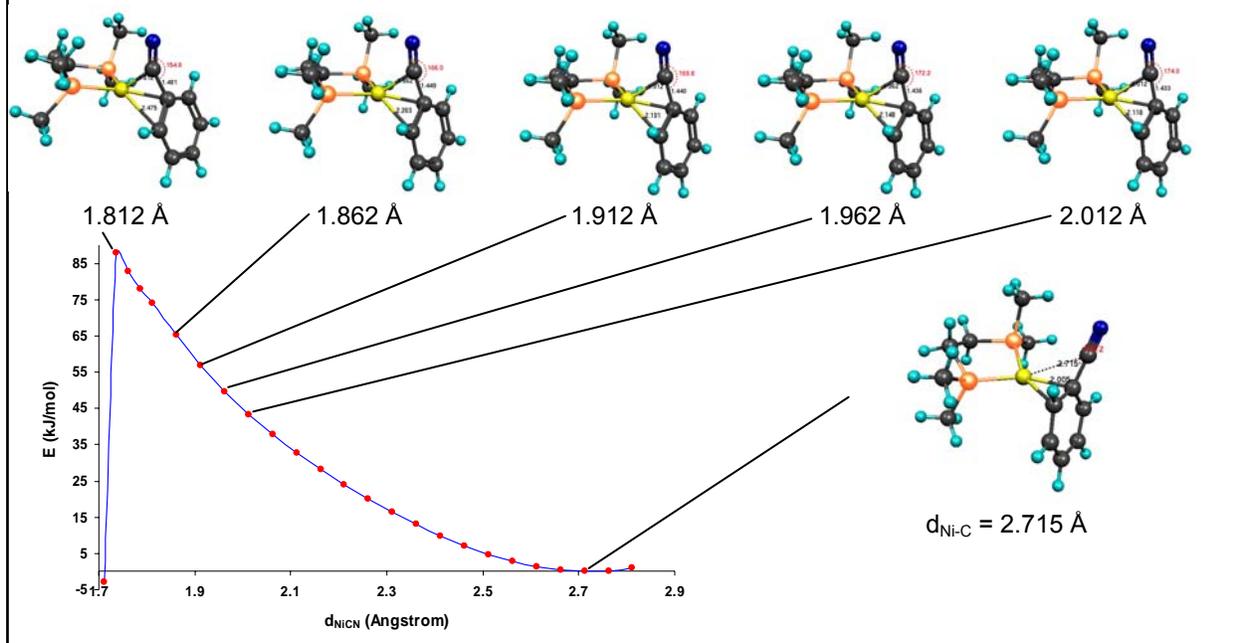


Figure 1. Modeling the C-CN Cleavage Transition State: constrain Ni-C distance to decrease



Extended Impact on Science, Technology, and Society

The work done here demonstrates that homogeneous transition metal compounds can break a variety of *strong* carbon-element bonds, including C-H, C-C, and C-F. These studies show that *direct processes* for conversion of hydrocarbons to value-added products are feasible, and that the scope for these new processes can include the strongest of bonds to carbon. The ability to manipulate C-C bonds in hydrocarbons offers the very useful advantage of being able to become independent of a single hydrocarbon source for the production of our organic specialty chemicals and fuels.

Future Plans

This coming year, our research will focus on the items presented in our proposal where we have had success. These include: (1) carbon-carbon bond cleavage reactions, (2) fundamental studies of C-H bond cleavage reactions of trispyrazolylboraterhodium complexes, (3) C-C cleavage in nitriles. We have made progress in each of these areas over the past year, and will continue our studies in these areas.

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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 developing strategies for the synthesis of functionalized polyolefins 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 can polymerize or copolymerize *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 "polar" monomers are $\text{CH}_2=\text{CHX}$ compounds, such as vinyl chloride (VC), acrylonitrile (AN) and vinyl ethers, in which the functional group is directly bonded to the olefin. These monomers are polymerized by radical or ionic mechanisms, but control of polymer composition and structure in such reactions is limited compared to what is possible through catalyst tuning 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 VC/ α -olefin copolymers (plasticizer-free, flexible PVC-type materials) or styrene/VC 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 to identify and understand the chemical issues that underlie this challenge.

We studied the reactions of VC with Ti, Zr, Fe, Co, Ni and Pd single-site catalysts. Two important reaction channels were observed. First, certain catalysts initiate radical VC polymerization 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 $\text{Cp}^*\text{TiCl}_3/\text{MAO}$, $(\text{C}_5\text{R}_5)_2\text{ZrR}^+$ in the presence of trace O_2 , and 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 VC insertion and β -Cl elimination of L_nMR active species to produce L_nMCl species and $CH_2=CHR$. This process terminates chain growth after a single VC insertion, is fast for both early and late metal L_nMR species, and is the main obstacle to insertion polymerization of VC. However, deuterium labeling experiments show that several mechanisms are operative for these reactions and provide hints to how a successful catalyst might be developed. For example, (di-imine) PdR^+ catalysts undergo 2,1 VC insertion to produce (di-imine) $PdCHClCH_2R^+$ species, which undergo chain walking and *syn*- β -Cl elimination. This result suggests that non-chain-walking late metal catalysts may be good candidates for VC copolymerization.

We studied the reactions of Pd-based catalysts with AN and olefin/AN mixtures. Cationic " L_2PdMe^+ " active species form N-bound AN adducts that rearrange to the pi-bound isomers and undergo 2,1 insertion to yield $L_2Pd\{CH(CN)Et\}^+$. These alpha-cyano alkyls form $[L_2Pd\{CH(CN)Et\}]_n^{n+}$ ($n = 1-3$) aggregates in which the Pd units are linked by PdCHEtCN---Pd bridges. Further AN or olefin insertion is strongly inhibited by the tendency of $L_2Pd\{CH(CN)CH_2R\}^+$ species to aggregate, which competes with monomer coordination, and by the low insertion reactivity of $L_2Pd\{CH(CN)CH_2R\}(substrate)^+$ species, which results from the presence of the electron-withdrawing alpha cyano group. At high temperature, AN acts as a chain transfer agent in ethylene polymerization via 2,1-insertion into L_nMR followed by beta-H elimination, to produce PE- $CH_2CH_2CH=CHCN$ end groups and L_2PdH^+ species that start new chains.

We studied two catalyst that were claimed to polymerize AN by insertion mechanisms: Cy_3PCuMe (**1**) and $(bipy)_2FeEt_2$ (**2**). **1** undergoes reversible ligand redistribution at low temperature in solution to form the tight ion-pair $[Cu(PCy_3)_2][CuMe_2]$ (**3**). The structure of **3** was assigned based on (i) the stoichiometry of the **1=3** equilibrium, (ii) the observation of a triplet for the PCy_3 C1 ^{13}C NMR resonance due to virtual coupling to two ^{31}P nuclei, and (iii) reverse synthesis of **1** by combining separately generated $Cu(PCy_3)_2^+$ and $CuMe_2^-$ ions. Complex **1**, free PCy_3 , and $(bipy)_2FeEt_2$ (**2**) each initiate AN polymerization. In each case, the poly-AN contains branches that are characteristic of an anionic polymerization mechanism. The major initiator in AN polymerization by **1** is PCy_3 , which is liberated from **1**. A transient iron hydride complex is proposed to initiate AN polymerization by **2**.

Vinyl-ethers ($CH_2=CHOR$) are attractive potential polar comonomers for olefin polymerization because their steric and electronic properties can be tuned. Earlier studies showed that L_nMR^+ species can initiate cationic polymerization of alkyl vinyl ethers. We found that this process can be completely suppressed by control of reaction conditions, tailoring of the vinyl ether structure, and proper selection of catalyst. Initial studies show that under such conditions, olefin/vinyl-ether insertion copolymerization is possible.

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. Our work is providing insights to the specific chemical challenges that must be met to achieve this goal.

Future Plans

We are pursuing the following themes:

(i) We are designing catalysts that are inherently highly reactive 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 isotopically-labeled VCs to determine the detailed mechanisms of "net 1-2 insertion/ β -Cl elimination" reactions.

(iii) We are exploring "multifunctional" catalysts that contain flexible arrays of pendant Lewis acids, Lewis bases, charged moieties, or hydrogen-bond donors and acceptors in the second coordination sphere. These systems are 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.

(iv) We are studying the reactions of metal catalysts with olefins and vinyl ethers, for which initial studies indicate copolymerization is possible.

Publications (2004 - 06)

- (1) "Electron-Deficient Group 4 Metal Complexes of Sulfur-Bridged Dialkoxide Ligands: Synthesis, Structure, and Polymerization Activity Studies." Lavanant, L.; Silvestru, A.; Faucheux, A.; Toupet, L.; Jordan, R. F.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 5604-5619.
- (2) "Theoretical Studies of Cycloaddition Reactions of Cationic Aluminum β -Diketiminato Alkyl Complexes with Alkenes and Alkynes." Ariafard, A.; Lin, Z.; Jordan, R. F. *Organometallics* **2005**, *24*, 5140-5146.
- (3) "Unusual Reactivity of Tris(pyrazolyl)borate Zirconium Benzyl Complexes." Lee, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 9384-9385.
- (4) "The Exploration of Neutral Azoligand-Based Grubbs Type Palladium(II) Complex as Potential Catalyst for the Copolymerization of Ethylene with Acrylonitrile. A Theoretical Study Based on Density Functional Theory." Yang, S.-Y.; Szabo, M. J.; Michalak, A.; Weiss, T.; Piers, W. E.; Jordan, R. F.; Ziegler, T. *Organometallics* **2005**, *24*, 1242-1251.
- (5) "Acrylonitrile Insertion Reactions of Cationic Palladium Alkyl Complexes." Wu, F.; Foley, S. R.; Burns, C. T.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 1841-1853.
- (6) "Polar Copolymerization by a Pd-Diimine Based Catalyst. Influence of Catalyst Charge and Polar Substituent on Catalyst Poisoning and Polymerization Activity. A Density Functional Theory Study." Szabo, M. J.; Jordan, R. F.; Michalak, A.; Piers, W. E.; Weiss, T.; Yang, S.-Y.; Ziegler, T. *Organometallics* **2004**, *23*, 5565-5572.
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- (8) "Acrylonitrile Polymerization by Cy_3PCuMe and $(Bipy)_2FeEt_2$." Schaper, F.; Foley, S. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 2114-2124.
- (9) "Generation and Insertion Reactivity of Cationic Palladium Complexes that Contain Halogenated Alkyl Ligands." Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600-609.

Direct Epoxidations Using Molecular Oxygen

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Collaborators: Constantine A. Stewart, Richard P. Muller (Sandia National Labs)

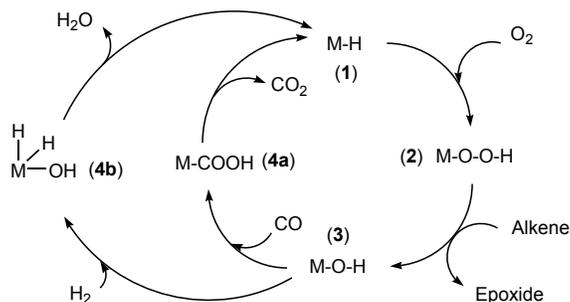
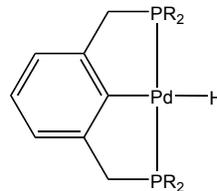
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Goal

We are interested in utilizing homogeneous catalysts with molecular oxygen to examine epoxidation reactions that cannot be catalyzed by known heterogeneous systems. While attractive, efficient routes to these organic epoxides will be the major synthetic focus, the fundamental mechanistic understanding of oxidation chemistry gained in our studies will be of significant value to DOE's interest in using molecular oxygen in partial oxidation catalysis.

Recent Progress

Identification of Route. We have only recently been funded (starting January, 2006) to examine direct epoxidation of alkenes using molecular oxygen as the oxidant. We have begun investigating the proposed catalytic routes shown below. Reaction of a metal hydride with dioxygen would convert it to a metal hydroperoxide. The hydroperoxide complex can directly epoxidize the alkene substrate, and then the resulting metal hydroxide can be converted back to the hydride with the use of reagents such as CO or H₂ gas. While initial preparations and reactions of salen-metal complexes of Co, Fe, Pd, and Pt have not led to promising results, our early results with phosphine-pincer complexes indicate the potential viability of this approach.

**Proposed Catalytic Cycles for Making Epoxides****Example of Pincer/Pd-H**

Initial Results. With seed funding provided by the Sandia National Laboratories LDRD Program we have prepared various (PCP)Pd-H complexes to evaluate as possible catalysts. Using the (*t*-Bu)₂P- derivative we have recently observed the first unequivocal insertion of O₂ into a Pd-H bond. We have structurally characterized the resulting

hydroperoxide species (PCP)Pd-OOH, and have shown that the insertion appears not to proceed via a radical chain pathway. Preliminary experiments have also been carried out on the remaining steps of the cycles shown in the scheme above. Remarkably, each step has been demonstrated with the (PCP)Pd system, albeit side-reactions and complications are evident. Mechanistic studies of these model reactions followed by and ligand/metal modification will allow for the optimization of these reaction steps.

DOE Interest

Significant reduction of energy usage in industrial-scale catalytic processes goes to the heart of the interests of DOE. As well, elimination of reaction steps in multi-step routes in order to prepare functionalized products is also of importance. More effective atom-efficient reactions providing less waste is also desired, particularly when combined with these other interests. Using molecular O₂ as the oxidation source can impact both the economic and environmental issues in a positive manner. We feel our research program underway meets all of these challenges. However, we also feel that the fundamental knowledge that we generate, knowledge that can be applied as well towards other important DOE-sponsored project areas, is the real work product to emerge from our studies. Recent "DOE Workshops on Catalysis" have emphasized the overwhelming importance of improved partial oxidation processes.

Future Plans

We are just beginning this study and building on our promising initial results, there are many research directions to pursue. Having completed a detailed mechanistic study on the first step of the cycle (oxygen insertion into the Pd-H bond) and having demonstrated the viability of the subsequent steps, we are anxious to examine these later steps in more detail. We are also attempting to examine the intimate mechanism of the insertion reaction of O₂ into (PCP)Pd-H theoretically in a collaboration with Richard P. Muller from Sandia National Laboratories.

We will be considering the optimization of the metal/ligand combination employed in this chemistry. The range of substituents on the PCP-pincer ligand will be explored, with both steric effects to block potential formation of inactive dinuclear species, and electronic factors to allow for more facile conversion of the entire catalytic cycle probed in order to produce an ideal system. We are also preparing analogous NCN pincer complexes of Rh and Ir. As the solubility of O₂ is of critical importance and is much higher in fluorocarbon solvents, we are preparing fluorous-tailed derivatives of the PCP-Pd complexes to increase their solubilities in these solvent systems. An added benefit is that the overall process will be safer on either the laboratory or larger scale. Finally, in order to demonstrate that the entire cycle is catalytic we must integrate all the individual steps into a single system which will produce epoxides using molecular oxygen.

Publications (2006)

- M.C. Denney, N.A. Smythe, K.L. Cetto, M. Denney, R.A. Kemp, and K.I. Goldberg, "Insertion of Molecular Oxygen into a Palladium(II) Hydride Bond", *J. Amer. Chem. Soc.* 128 (2006) 2508-2509.

Transition Metal-Mediated Reactions of Small Molecules

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The main purpose of the work is to study chemical binding and splitting of sigma bonds (H-H, C-H, etc) on transition metal complexes to provide groundwork for the design of new catalysts to for example convert abundant methane and biomass to useful fuels. The work will involve synthesis of new electrophilic metal complexes and dihydrogen complexes, particularly for heterolytic splitting of H₂ and its microscopic reverse, formation of H₂, on transition metal centers. New methodologies for biomimetic hydrogen production via modeling hydrogenase enzymes with iron catalytic sites are also being designed. These electrophilic iron catalysts may also be useful for deuteration of organic compounds via heterolysis of deuterium gas. Use of multifunctional phosphonium ligands in catalysts is also being explored.

Recent Progress

Synthesis of complexes containing phosphonium ligands for potential use as catalysts. We have extended our studies of phosphonium complexes as multifunctional catalysts by investigating diaminophosphonium ([PN₂]⁺) complexes of nickel. By utilizing the bulky Ni(0) starting material, NiL₃ (L = P(O-*o*-tolyl)₃), we have been able to characterize both monomeric [(L)₂Ni-PN₂] complexes as well as nickel dimers containing bridging phosphonium moieties (Fig. 1). By adjusting the stoichiometry of the [PN₂]⁺ to NiL₃ we have established the formation of the first, to our knowledge, bis-phosphonium metal complex [Ni(PN₂)₂(L)]²⁺.

Investigation of the electronic donating ability of phosphonium ligands were examined by the use of a slightly modified ligand, [PN₂*], where unsaturation is introduced into the ligand backbone. When the phosphonium chloride (Cl-PN₂*) is reacted with NiL₃, one observes oxidation addition of the P-Cl bond and generation of a Ni(II)-Ni(II) dimer with bridging phosphonium ligands (Fig. 2). This [PN₂*]⁺ to [PN₂*]⁻ demonstrates the ability of these ligands to oxidize first-row transition metals.

In an attempt to synthesize a homoleptic Ni-(PN₂)_x complex, Ni(cod)₂ was reacted with multiple equivalents of Cl-PN₂. Whereas, in most cases, the products of these reactions were unstable, reaction with the bulky mesityl-substituted Cl-PN₂ gave black crystals. X-Ray analysis revealed an interesting dimeric structure with bridging phosphonium ligands (Fig. 3). However, the geometry observed in this complex differed from what was expected. Instead of having a completely symmetric structure, or a structure in which each phosphonium ligand was oriented towards a different nickel center, the structure showed that both phosphonium ligands were oriented towards the same metal center. Calculations are currently underway to explain the electronic structure of this unusual complex.

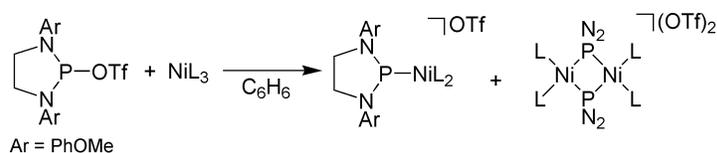


Figure 1: Reaction of [PN₂][OTf] with NiL₃

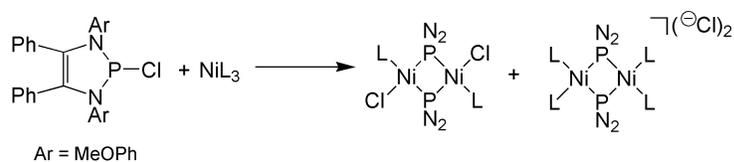


Figure 2: Reaction of Cl-PN₂* with NiL₃

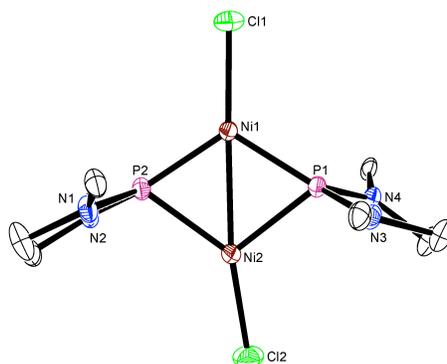
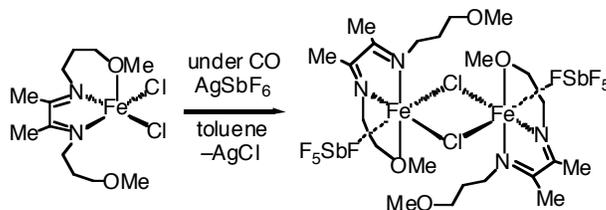


Figure 3: [Ni(Cl)(PN₂)₂]₂ structure, mesityl groups omitted for clarity.

Iron-diimine Complexes. Investigations relating to modeling enzymatic-type heterolytic splitting of H₂ were carried out on iron complexes containing tetradentate diimine ligands with hemilabile sidearms. Attempts to prepare octahedral Fe^{II} complexes containing a CO ligand that favors molecular binding and heterolysis of H₂ in both organometallic complexes and hydrogenase enzymes led instead to unexpected rejection of binding of the normally strong CO ligand.



Weakly-coordinating anions such as SbF₆⁻ were found to interact with the high-spin Fe center in lieu of Fe-CO binding. Computations showed that addition of CO to a *high-spin* Fe-diimine complex is strongly influenced by spin effects and is essentially thermoneutral, i.e. spin crossover to a low-spin CO adduct is disfavored thermodynamically here rather than kinetically. The ligand field strengths are critical: the diimine complexes do not bind CO but analogues containing diphosphines with strong ligand fields bind CO tightly and also coordinate H₂. It thus appears that Nature utilizes the unusual cyanide ligands in hydrogenases to increase ligand field strength to ensure a vital low-spin configuration for the di-iron active site to maintain its CO ligands. The calculations are useful in understanding and predicting whether spin crossover on ligand addition is disfavored thermodynamically or kinetically (e.g. “spin block”).

Deuteration of organic compounds. Acidic dihydrogen complexes of cationic bis(diphos)ruthenium complexes were investigated as catalysts for the deuteration of acetone under an atmosphere of D₂ gas. Stoichiometric partial deuteration was observed but was not catalytic apparently because acetone coordinated too strongly to the catalyst and tied up the D₂ binding site.

DOE Interest

Energy security is currently of the highest concern and hydrogen is of course the fuel of most future promise. Both hydrogen production and storage are critical problems for developing a hydrogen economy, and transition metal catalysts will surely play a crucial role here. Reversible molecular binding of H₂ (one or *more* H₂ ligands)

and heterolytic splitting of the strong H–H bond (and its microscopic reverse) are key systems for study here. Development of catalysts with base metals such as iron are also of critical importance, and Nature has used iron for eons in the active sites of enzymes and can provide biomimetic inspiration here. Hydrogenase enzymes contain highly organometallic dinuclear Fe centers with CO/CN ligands and carry out sophisticated inorganic chemistry in bimodally producing hydrogen and converting it to electrical energy (as in fuel cells). Design of new ligand systems that model and fine-tune catalytic conversions electronically and stereochemically is the strength of homogeneous catalysis and will be vital here. Inexpensive iron catalysts may also be useful for facilitating chemical transformations such as deuteration of organic compounds using deuterium gas split heterolytically. Importantly many of the lessons learned in activation of the H–H bond may directly apply to activation of other sigma bonds such as C–H, Si–H, and B–H important in for example conversion of methane to liquid fuels. In most such cases $M(\eta^2\text{-H-X})$ sigma complexes, even as transients, play an important role in electrophilic activation of alkanes, silanes, and boranes.

Future Plans

Electrophilic complexes for coordination and heterolytic activation of X-H sigma bonds will continue to be synthesized by e.g. protonation of low-coordinate metal aryls under H_2 to produce hydrogen-rich species such as $[\text{MH}_x(\text{H}_2)_y]^{n+}$. Protonation of homoleptic anionic polyhydrides such as $[\text{FeH}_6]^{4-}$ with acids with low-coordinating anions will be examined in order to determine if such complexes with *multiple* dihydrogen ligands will be stable. Novel media and conditions such as ionic liquids and high pressures would be employed for these and related studies of alkane C–H bond activation on metal complexes. There is great potential for new science to emerge from such studies since other molecules of high interest such as methane could bind to these lightly-bound metal centers and undergo catalytic transformations. Methods for biomimetic photochemical production of hydrogen fuel based on combining photochemical metal-complex receptors with iron complexes that model hydrogenase enzymes are also being conceptualized on this important problem that addresses energy security. Expansion of research done with electrophilic phosphonium ligands, as well as phosphonium analogs of B, C, Ge and Sn, will be investigated. These electrophilic ligands will be reacted with transition metal complexes and analyzed for periodic trends that may be observed. Additional research will be carried out on N-heterocyclic carbene (NHC) assisted addition of these ligands to transition metal centers, creating potentially active X-H activation catalysts. Preliminary results suggest that addition of NHC's to the electrophilic phosphonium ligands, and analogs, assists in addition of the ligands to transition metals, whereas little or different reactivity may be observed without addition of the NHC.

We will continue to investigate heterolytic splitting of D_2 gas on cationic metal- H_2 complexes for syntheses of deuterated organics such as acetone- d_6 via isotopic exchange. Acidic metal- H_2 complexes that exchange with D_2 gas will be the catalyst and will be tested by dissolution in acetone- d_6 under H_2 and observing protonation of the methyl groups by NMR. Simple aquo complexes such as $[\text{M}(\text{H}_2\text{O})_6][\text{BF}_4]_2$ ($\text{M} = \text{Fe}, \text{Ru}$) will be studied for catalytic activity since an aquo-dihydrogen complex $[\text{Ru}(\text{H}_2\text{O})_5(\text{H}_2)][\text{BF}_4]_2$ is known in the literature, and the H_2 ligand is acidic and exchanges with protons from water.

Publications 2004-2006

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Catalyst Structures Determined by *Operando* EXAFS Spectroscopy

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Solution phase EXAFS spectroscopy collected under catalytic reaction conditions was used to characterize the organometallic species produced. These results have shown that previously reported nanoparticulate metal catalysts are predominately four-metal-atom clusters under catalytic conditions, which only after the reaction transform into metallic particles. The results are presented along with solution-phase EXAFS of unstable intermediates germane to catalytic cycles.

**Cluster-Expanded Solids:
A Strategy for Assembling Functional Porous Materials**

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Goal

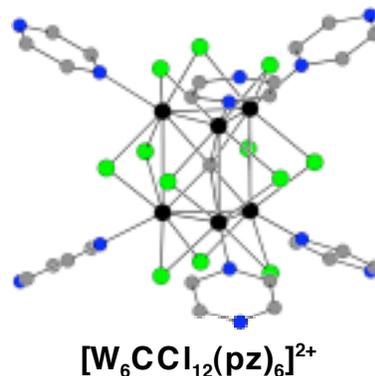
The intention of the research is to explore the use of molecular precursors in the assembly of microporous coordination solids that function as sieves, sensors, or catalysts.

Recent Progress

Cyano-Bridged Frameworks Incorporating $[\text{Zr}_6\text{BCl}_{12}]^{2+}$ Cluster Cores. The reaction between $[\text{Zr}_6\text{BCl}_{18}]^{4+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ in aqueous solution, leads to the immediate precipitation of the cluster-expanded Prussian blue analogue $(\text{Et}_4\text{N})[\text{Zr}_6\text{BCl}_{12}][\text{Cr}(\text{CN})_6] \cdot \text{Et}_4\text{NCl} \cdot 3\text{H}_2\text{O}$. The cubic Prussian blue type structure of this compound was confirmed via Rietveld profile analysis of X-ray powder diffraction data, and magnetization measurements reveal the onset of long-range magnetic ordering at 2 K.

Trigonal Prismatic Cluster Building Units. Simultaneous reduction of WCl_6 and CCl_4 with bismuth metal at 450 °C, leads, upon work-up, to the carbon-centered trigonal prismatic cluster $[\text{W}_6\text{CCl}_{18}]^{2-}$. Cyclic voltammetry experiments performed on solutions containing this cluster show that it possesses five chemically-accessible redox states. Related reactions incorporating NaN_3 in place of CCl_4 led to the analogous nitrogen-centered cluster $[\text{W}_6\text{NCl}_{18}]^{2-}$, enabling access to even more reduced electron counts. Substitution of the outer chloride ligands in clusters of this type has led to species such as $[\text{W}_6\text{CCl}_{12}(\text{CF}_6\text{SO}_3)_6]^{2-}$, $[\text{W}_6\text{CCl}_{12}\text{I}_6]^{2-}$, $[\text{W}_6\text{CCl}_{12}(\text{DMF})_6]^{2+}$, and $[\text{W}_6\text{CCl}_{12}(\text{py})_6]^{2+}$, with significant variation in the associated electrochemical behavior. The kinetics of ligand self-exchange in solvated clusters has been studied by ^1H NMR spectroscopy, as have the effects of adding a catalytic amount of reductant on the substitution rates. In addition, we have prepared a series of cluster units with terminal ligands capable of bridge formation, for use in assembling porous framework solids: $[\text{W}_6\text{CCl}_{12}(\text{CN})_6]^{3-}$, $[\text{W}_6\text{CCl}_{12}(\text{pz})_6]^{2+}$, $[\text{W}_6\text{CCl}_{12}(4,4'\text{-bpy})_6]^{2+}$, and $[\text{W}_6\text{CCl}_{12}(4\text{-CNpy})_6]^{2+}$.

Homoleptic Trimethylsilylacetylide Complexes. Reactions between simple transition metal salts and LiCCSiMe_3 have been shown to generate three new octahedral complexes: $[\text{Cr}(\text{CCSiMe}_3)_6]^{3-}$, $[\text{Fe}(\text{CCSiMe}_3)_6]^{4-}$, and $[\text{Co}(\text{CCSiMe}_3)_6]^{3-}$. Characterization of these molecules has enabled us to



establish the ligand field strength of trimethylsilylacetylide as lying just below methyl in the spectrochemical series.

Microporous Magnets for Magnetic Separations. We have continued our work on developing high-temperature microporous ferro- and ferrimagnets of potential utility for performing magnetic separations. Recent studies have focused on $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ and $\text{Cr}_3[\text{Cr}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$, two of the highest-ordering ferrimagnetic Prussian blue analogues known. It was found that both materials can be dehydrated by heating at 75 °C under dynamic vacuum for 24 h, leaving the metal-cyanide framework intact. Gas uptake measurements showed the resulting solids to be porous, with BET surface areas of 370 m^2/g and 650 m^2/g , respectively. Moreover, magnetic susceptibility measurements performed on $\text{CsNi}[\text{Cr}(\text{CN})_6]$ indicated an ordering temperature of 65 K, the highest ordering temperature yet observed for a microporous magnet. Future work will focus on probing the utility of these and related, higher-ordering materials in magnetic separations, specifically, determining if the magnetic field can enhance the adsorption of dioxygen over dinitrogen.

Prussian Blue Analogues Incorporating $[\text{Co}(\text{CN})_5]^{3-}$ as O_2 -Selective Adsorbents. We have also investigated the selective binding of dioxygen to $[\text{Co}(\text{CN})_5]^{3-}$ complexes for use in separating dioxygen from air. While molecular salts such as $\text{Li}_3[\text{Co}(\text{CN})_5] \cdot 2\text{DMF}$ can show a large dioxygen uptake at 25 °C, the kinetics of adsorption are slow and the material slowly decomposes over several hundred cycles. We have attempted to overcome these problems by incorporating $[\text{Co}(\text{CN})_5]^{3-}$ within rigid, porous extended solids of the type $\text{M}_3[\text{Co}(\text{CN})_5]_2$, which display the Prussian blue structure. Thus far, we have measured the dioxygen sorption properties of $\text{M}_3[\text{Co}(\text{CN})_5]_2$ ($\text{M} = \text{Co}, \text{Cu}, \text{Zn}$). While all three compounds have similar surface area and pore volume, $\text{Zn}_3[\text{Co}(\text{CN})_5]_2$ reversibly adsorbs 8 cm^3/g of O_2 at 25 °C and 900 torr, while $\text{Co}_3[\text{Co}(\text{CN})_5]_2$ irreversibly adsorbs 10 cm^3/g of O_2 and $\text{Cu}_3[\text{Co}(\text{CN})_5]_2$ adsorbs less than 1 cm^3/g of O_2 under the same conditions. This suggests that the strength of dioxygen binding can be tuned by varying the counter ion. Future work will focus on measuring the adsorption kinetics and stability of these materials, as well as maximizing the dioxygen uptake.

DOE Interest

The new microporous materials resulting from these studies may be of utility in a range of applications, including molecular sieving, detection of volatile organic compounds, ion exchange, and heterogeneous catalysis.

Future Plans

New Cluster Building Units for Synthesis of a Microporous Magnet. Our efforts to produce molecular cluster building units capable of delivering strong magnetic coupling with surrounding metal ions will continue. The goal here is to generate solids with ordering temperatures at or above room temperature for use in performing magnetic separations (e.g., for the noncryogenic separation of dioxygen from dinitrogen). New targets of particular interest here include the clusters $[\text{Gd}_6\text{CCl}_{18}]^{9-}$, $[\text{Re}_{6-n}\text{Mo}_n\text{Q}_8(\text{CN})_6]^{(4+n)-}$, $[\text{M}_6\text{Q}_8(\text{CN})_6]^{n-}$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}$), and $[\text{B}_6(\text{CN})_6]^{1-}$. In addition, we have begun to explore the possibility of producing related actinide-based clusters.

Characterization of Photomagnetic Solids. The photomagnetic properties of porous solids incorporating $[\text{Re}(\text{CN})_7]^{3-}$ and $[\text{Re}(\text{CN})_8]^{3-}$ will be further characterized, with the intention of developing potential sensing applications.

Synthesis of Acetylenediide-Bridged Solids. The new trimethylsilylacetylide complexes obtained recently will be used in coupling reactions intended to produce unprecedented frameworks featuring acetylenediide bridges.

Reactivity of Porous Frameworks Incorporating Coordinatively-Unsaturated Metal Sites. Attempts will be made to exploit the coordinatively-unsaturated metal sites within dehydrated cluster-expanded Prussian blue solids for heterogeneous catalysis. The reactivity of several new microporous metal-organic frameworks with exposed metal coordination sites will also be investigated. Preliminary work on a highly-porous sodalite-type phase has shown that two-coordinate Mn^{2+} guest cations can activate O_2 to generate terminal Mn^{IV} -oxo units. The possibility of utilizing such materials as catalysts for epoxide formation will be explored.

Publications (2005-2006)

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5. "Determination of ^{77}Se - ^{77}Se and ^{77}Se - ^{13}C J -Coupling Parameters for the Selenocyanide Clusters $[Re_5OsSe_8(CN)_6]^{3-}$ and $[Re_4Os_2Se_8(CN)_6]^{2-}$ " Ramaswamy, K.; Tulskey, E. G.; Long, J. R.; Kao, J. L.-F.; Hayes, S. E. *Inorg. Chem.*, submitted.

Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis and Homogeneous Models

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Goals

The goals of this project are to elucidate, model, and exploit pathways by which organometallic molecules undergo chemisorptive activation and dramatic reactivity enhancements on metal oxide surfaces. These processes connect directly to the efficiency of real-world, large-scale industrial processes and the capability to produce cleaner, greener, more environmentally acceptable products. The research combines organometallic synthesis, surface chemistry and catalysis with computational modeling, and involves collaboration with industrial scientists. Specific objectives of the past year were: 1) Understand organometallic molecule chemisorption on “super Brønsted acid” oxides and nanoparticles, 2) Synthesize/characterize mononuclear and polynuclear homogeneous models for the chemisorbed catalytic species, 3) Characterize the thermochemistry, structures, molecular dynamics, and catalytic properties of these species, 4) Model computationally the catalytic properties.

Recent Progress

In the past effort period, we focused on three primary areas: 1) Synthesis and characterization of the single-site organometallic species produced by chemisorption of early transition metal hydrocarbyls on highly Brønsted acidic metal oxides, 2) Understanding catalyst-cocatalyst structure and their interplay in single-site homogeneous polymerization catalyst function, 3) Using quantum chemical studies of single-site polymerization catalysts to understand the role of cocatalyst and solvation. A brief account of each activity is given below.

1. The Significance of Catalyst-Cocatalyst Ion-Pairing on Structure, Activity, and Selectivity of Single-Site Polymerization Catalysts

The solution structures of the metallocene homogeneous polymerization catalyst ion-pairs $[\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**1**), $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**2**), $[(\text{Me}_2\text{SiCp}_2)\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**3**), $[\text{Me}_2\text{C}(\text{Fluorenyl})(\text{Cp})\text{ZrMe}]^+[\text{FPBA}]^-$ (FPBA = tris(2,2',2''-nonafluorobiphenyl)fluoroaluminate) (**4**), $[\text{rac-Et}(\text{Indenyl})_2\text{ZrMe}]^+[\text{FPBA}]^-$ (**5**), $[(\text{Me}_5\text{Cp})_2\text{ThMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**6**), $[(\text{Me}_2\text{SiCp}_2)\text{Zr}(\text{Me})(\text{THF})]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**7**), $[(\text{Me}_2\text{SiCp}_2)\text{Zr}(\text{Me})(\text{PPh}_3)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**8**), $[(\text{Me}_2\text{SiCp}_2)\text{Zr}(\text{Me})(\text{THF})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**9**), $[(\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{Zr}(\text{Me})(\text{solvent}))]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (solvent = benzene, toluene) (**10**), $[(\text{Cp}_2\text{ZrMe})_2(\mu\text{-Me})]^+[\text{MePBB}]^-$ (PBB = tris(2,2',2''-nonafluorobiphenyl)borane) (**11**), and $[(\text{Cp}_2\text{Zr})_2(\mu\text{-CH}_2)(\mu\text{-Me})]^+[\text{MePBB}]^-$ (**12**), having the counteranion in the inner (**1**, **3**, **4**, **5**, and **6**) or outer (**7**, **8**, **9**, **10**, **11**, and **12**) coordination sphere, have been investigated for the first time in solvents with low relative permittivity such as benzene or toluene by a battery of 1-D and 2-D NMR techniques. It is found that the

average interionic solution structures of the inner sphere contact ion-pairs are similar to those in the solid state crystal structures with the anion B-Me (**1**, **3**) or Al-F (**5**) vectors oriented toward the free zirconium coordination site. The HOESY spectrum of complex **6** is also in agreement with the reported solid-state structure. In contrast, in outer sphere contact ion-pairs **7**, **8**, **9**, and **10**, the anion is located far from the Zr-Me⁺ center and much nearer to the Me₂Si bridge than in **3**. PGSE NMR and cryoscopy measurements as a function of concentration (0.1-5.0 mM) indicate that the tendency to form aggregates of nuclearity higher than simple ion-pairs is dependent on whether the anion is in the inner or outer coordination sphere of the metallocenium cation. Complexes **2**, **3**, **4**, **5**, and **6** show no evidence of aggregation up to 5 mM (well above concentrations typically used in catalysis) or at the limit of saturated solutions (complexes **3** and **6**), while concentration-dependent behavior is observed for complexes **7**, **8**, **10**, and **11**. These outer sphere ion-pairs begin to exhibit significant evidence for ion-quadruples in solutions having concentrations greater than 0.5 mM with the tendency to aggregate being a function of metal ligation and anion structure. Above 2 mM, compound **8** exists as higher aggregates that are probably responsible for the loss of interionic structural specificity.

The thermodynamic and structural characteristics of Al(C₆F₅)₃-derived vs. B(C₆F₅)₃-derived group 4 metallocenium ion pairs are quantified. Reaction of 1.0 equiv. of B(C₆F₅)₃ or 1.0 or 2.0 equiv. of Al(C₆F₅)₃ with *rac*-C₂H₄(η⁵-Ind)₂Zr(CH₃)₂ (*rac*-(EBI)Zr(CH₃)₂) yields *rac*-(EBI)Zr(CH₃)⁺H₃CB(C₆F₅)₃⁻ (**1a**), *rac*-(EBI)Zr(CH₃)⁺H₃CAI(C₆F₅)₃⁻ (**1b**), and *rac*-(EBI)Zr²⁺[H₃CAI(C₆F₅)₃]₂⁻ (**1c**), respectively. X-ray crystallographic analysis of **1b** indicates the H₃CAI(C₆F₅)₃⁻ anion coordinates to the metal center via a bridging methyl in a manner similar to B(C₆F₅)₃-derived metallocenium ion pairs. However, the Zr-(CH₃)_{bridging} and Al-(CH₃)_{bridging} bond lengths of **1b** (2.506(3) Å and 2.024(3) Å, respectively) indicate the methyl group is less completely abstracted than for typical B(C₆F₅)₃-derived ion pairs. Ion pair formation enthalpies (ΔH_{ipf}) determined by isoperibol solution calorimetry in toluene from the neutral precursors are -21.9(6) kcal mol⁻¹ (**1a**), -14.0(15) kcal mol⁻¹ (**1b**), and -2.1(1) kcal mol⁻¹ (**1b**→**1c**), indicating Al(C₆F₅)₃ to have significantly less methide affinity than B(C₆F₅)₃. Analogous experiments with Me₂Si(η⁵-Me₄C₅)(*t*-BuN)Ti(CH₃)₂ indicate a similar trend. Furthermore, kinetic parameters for ion pair epimerization by cocatalyst exchange (ce) and anion exchange (ae), determined by line-broadening in VT NMR spectra over the range 25 – 75 °C, are ΔH_{ce}[‡] = 22(1) kcal mol⁻¹, ΔS_{ce}[‡] = 8.2(4) e.u., ΔH_{ae}[‡] = 14(2) kcal mol⁻¹, and ΔS_{ae}[‡] = -15(2) for **1a**. Line broadening for **1b** is not detectable until just below the temperature where decomposition becomes significant (~75-80 °C), but estimation of the activation parameters at 72 °C gives ΔH_{ce}[‡] = 22 kcal mol⁻¹ and ΔH_{ae}[‡] = 16 kcal mol⁻¹, consistent with the bridging methide being more strongly bound to the zirconocenium center than for **1a**.

In related work, A series of mononuclear and polynuclear trityl perfluoroarylborate, -aluminate, and -gallate reagents, potential cocatalysts/activators for metallocene-mediated olefin polymerization have been synthesized via fluoride abstraction from trityl fluoride (Ph₃CF) by the organo-Lewis acid reagents B(C₆F₅)₃ (**1**), B(*o*-C₆F₅C₆F₄)₃ (**2**), and Al(C₆F₅)₃ (**3**), by derivitization of Ph₃C⁺FAl(*o*-C₆F₅C₆F₄)₃⁻ (**4**), and by reaction of trityl fluoride with *in-situ* generated Ga(C₆F₅)₃ (**5**). Reaction of trityl fluoride with tris(perfluoroaryl)boranes **1** and **2** yields trityl tris(perfluoroaryl)fluoroborates Ph₃C⁺FB(C₆F₅)₃⁻ (**6**) and Ph₃C⁺FB(*o*-C₆F₅C₆F₄)₃⁻ (**7**), respectively. Three trityl tris(perfluorophenyl)fluoroaluminates (Ph₃C⁺)_xF_x[Al(C₆F₅)₃]_y^{-x} (x = 1, y = 1, **8**; x = 1, y = 2, **9**; x = 2, y = 3, **10**) can be isolated from reaction of trityl fluoride with tris(perfluoroaryl)alane **3** in appropriate molar ratios. Reaction of trityl tris(perfluoroaryl)fluoroaluminate **4** with **3** affords the asymmetric fluoro-bridged trityl bis[tris(perfluoroaryl)]aluminate Ph₃C⁺(C₆F₅)₃AlFAl(*o*-C₆F₅C₆F₄)₃⁻ (**11**), while reaction of trityl halides Ph₃CCl and Ph₃CBr with **3** gives the corresponding trityl tris(perfluorophenyl)haloaluminates Ph₃C⁺XAl(C₆F₅)₃⁻ (X = Cl, **12**; X = Br, **13**). Isolable, symmetric fluoro-bridged trityl bis[tris(perfluoroaryl)]gallate Ph₃C⁺F[Ga(C₆F₅)₃]₂⁻ (**14**) is derived from a "one pot" reaction of trityl fluoride with Ga(C₆F₅)₃, generated *in situ* from **4** + Ga(CH₃)₃. Of these new species, compounds **7** and **10-14** were characterized by single-crystal X-ray diffraction. Trityl salts **6** – **13** react with C₅-symmetric metallocene precatalyst Me₂C(Cp)(Flu)ZrMe₂ (**15**; Cp = C₅H₄; Flu = C₁₃H₈, fluorenyl) to form isolable

ion-pair complexes or characterizable mixtures. Species **6** reacts with **15** to generate known ion-pair $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrMe}^+ \text{MeB}(\text{C}_6\text{F}_5)_3^-$ (**16**), and reaction of **7** with **15** gives fluoro-bridged dimeric diastereomers $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrMe}]_2(\mu\text{-F})^+ \text{FB}(o\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$ (**17**). Trityl tris(perfluorophenyl-fluoroaluminates **8**, **9**, and **10** all react with **15** to afford mixtures of $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrMe}^+ \text{FAl}(\text{C}_6\text{F}_5)_3^-$ (**18**) and diastereomeric $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrMe}]_2(\mu\text{-Me})^+ (\text{C}_6\text{F}_5)_3\text{AlFAl}(\text{C}_6\text{F}_5)_3^-$ (**19**). Asymmetric species **11** cleanly affords diastereomeric $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrMe}]_2(\mu\text{-Me})^+ (\text{C}_6\text{F}_5)_3\text{AlFAl}(o\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3^-$ (**20**) in reaction with metallocene **15**. Adducts of **12** and **13** with metallocene **15** afford decomposition products $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}(\text{C}_6\text{F}_5)$ (**21**) and $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{Zr}(\mu\text{-Br})]_2^{2+} [\text{Al}(\text{C}_6\text{F}_5)_4]_2^{2-}$ (**22**), respectively. Complexes **17** - **22** were characterized by single-crystal X-ray diffraction.

2. Metal Hydrocarbyl Chemisorption on Sulfated Metal Oxide Surfaces

In this area, we previously showed that electrophilic zirconium alkyls are created in very high coverages by protonolysis of group 4-alkyl bonds and that these adsorbate species exhibit very high activity for arene and olefin hydrogenation as well as olefin polymerization. The benzene hydrogenation rate exceeds that of any catalyst yet discovered. The kinetics and mechanism of these catalytic processes were characterized in detail, revealing that ~ 95% of the surface Zr species are catalytically significant--very unusual for any heterogeneous catalyst. We have now expanded this investigation to other sulfated metal oxides. The sulfated metal oxides (SMOs) sulfated stannia (SnS), sulfated iron oxide (FeS), and sulfated titanium dioxide (TiS) have been synthesized as support materials / cocatalysts for supported homogeneous Ziegler-Natta olefin polymerization and hydrogenation catalysts. Powder X-ray diffraction shows that SnS forms in the cassiterite phase, FeS forms in the alpha phase and TiS forms in the anatase phase. ^{13}C CPMAS NMR spectroscopic analysis of $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_5)_2$ / SMO chemisorption shows that cationic zirconocenium species are formed along with varying amounts of catalytically-inactive μ -oxo ($\text{Cp}_2\text{Zr}(\text{CH}_3)_2\text{O}$ -surface) species, depending on the support material. Ethylene polymerization data with the supported catalysts show that polymerization activity is dependent on both ligand precursor ($(\text{Zr}(\text{CH}_2\text{Ph})_4 > \text{Cp}^*\text{ZrMe}_3$) and support material (SnS > FeS > TiS). Catalysts are also active for benzene hydrogenation and are readily separable from liquid phase products using physical or, in the case of FeS, magnetic techniques. In an investigation at the interface of heterogeneous and homogeneous catalysis, sulfated tin oxide nanoparticles with crystallite sizes of ~5 nm were synthesized and used as effective supports for homogeneous zirconium hydrocarbyl olefin polymerization and arene hydrogenation catalysts. It is found by CPMAS ^{13}C NMR that electrophilic cationic adsorbate structures are formed on chemisorption/activation and that hydrogenation and polymerization activities are comparable to those of the bulk supports. EXAFS studies of several ZrS and AlS supported systems are underway in collaboration with Dr. Jeremy Kropf (Argonne National Laboratory); in the case of $\text{Cp}^*\text{ZrMe}_3/\text{ALS}$, in which ~ 95% of the Zr sites are catalytically active, it appears that the $\text{Cp}^*\text{ZrMe}_2^+$ cation essentially “floats” above the AlS^- anion with very weak ion pairing.

3. Theoretical Studies

The stereochemical aspects of olefin polymerization processes mediated by the C_1 -symmetric constrained geometry catalyst $\text{H}_2\text{Si}(\text{ind})(\text{tBuN})\text{TiCH}_3^+$ (ind = indenyl), including the role of the cocatalyst have been analyzed using DFT techniques. The energetics of catalyst activation are first analyzed and compared to experiment. The energetics of heterolytic ion pair separation are next scrutinized and the effects of solvent environments assessed. The calculated thermodynamic profiles for ethylene insertion at $\text{H}_2\text{Si}(\text{ind})(\text{tBuN})\text{TiCH}_3^+$ illustrate that the kinetics of insertion processes at the $\text{H}_2\text{Si}(\text{ind})(\text{tBuN})\text{TiR}^+$ cation can be analyzed in terms of SCF potential energies. We next compared the energetic profile of ethylene insertion at the naked $\text{H}_2\text{Si}(\text{ind})(\text{tBuN})\text{TiCH}_3^+$ cation with that at the related ion pair adducts to understand counterion influence. It is seen that the presence of the counterion, although affecting the overall catalytic activity, does not significantly influence the stereochemical properties of the catalyst and, hence, the

polymer microtacticity. Moreover, the second ethylene insertion at $\text{H}_2\text{Si}(\text{ind})(^t\text{BuN})\text{Ti}-(^n\text{C}_3\text{H}_7)^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$ has been analyzed to evaluate counteranion influence on the ethylene propagation barrier. There is evidence that the propagation transition state is energetically comparable to the first insertion transition state and that the solvent has negligible effects on the energetic profile. These findings allow analysis of the propylene insertion process within the less computationally demanding “naked cation” approach. Thus, monomer enchainment at $\text{H}_2\text{Si}(\text{ind})(^t\text{BuN})\text{TiR}^+$ is analyzed for $\text{H}_2\text{Si}(\text{ind})(^t\text{BuN})\text{TiCH}_3^+$ + propylene (first insertion) and for $\text{H}_2\text{Si}(\text{ind})(^t\text{BuN})\text{Ti}(\text{C}_4\text{H}_6)^+$ + propylene (second insertion). Data describing the first insertion highlight the sterically-dominated regioselection properties of the system. In particular, activation energies show that the olefin insertion regiochemistry is predominantly 1,2 (primary), while the second insertion similarly reflects the catalyst stereochemical properties, with steric effects introduced by the growing chain (mimicked by an isobutyl group) preferentially favoring insertion pathways, that afford isotactically enriched polymers.

DOE Interest

The catalyst syntheses, mechanistic studies, and product characterization activities that are the central part of this project relate directly to the efficiency, selectivity, and “greenness” of real-world industrial catalytic processes that are practiced on a huge scale and to the ability of these processes to produce cleaner, more environmentally acceptable products. These multifaceted, highly interdisciplinary projects provide ideal training for young scientists needed as part of a highly skilled U.S. technical workforce.

Future Plans

We plan to continue our efforts in all three of the above areas. In the area of novel supports for molecule-based catalysts, EXAFS studies on adsorbate structure have begun in collaboration with Dr. Jeremy Kropf of ANL. Systems with virtually 100% active sites present a unique opportunity. We also plan to expand our studies to other types of highly Brønsted acidic supports, to use polymerization reactivity probes of the ion-pairing “tightness,” and to explore tandem supported catalytic processes in which cascade processes are turned on by virtue of the close proximity of the catalytic sites on the surface. This will be compared with results in solution on homogeneous model structures. In the area of ion-pairing studies, we plan to investigate cocatalyst-selectivity effects in other systems where ion-pairing might be intimately connected with enchainment selectivity. In the theoretical arena, we will explore whether double-layer effects at oxide surfaces may loosen ion-pairing, hence produce the enhanced reactivities observed. We will also investigate the effects of ion-pairing on enchainment stereochemistry.

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Inorganic-Organic Molecules and Solids with Nanometer-Sized Pores

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Goal

We are constructing porous inorganic-organic hybrid molecules and solids that contain coordinatively unsaturated metal centers.

Recent Progress

We have prepared extended-solid and molecular porous materials based on multifunctional β -diketone ligands, and studied their host-guest chemistry.

1. Extended solids

We initially studied supramolecular porous solids derived from $M(\text{Pyac})_2$ (see Figure 1) or $M(\text{Pyac})_3$. These are formed when the $M(\text{Pyac})_n$ building block reacts with a second metal ion M' (e.g. Ag, Cd, Hg). Although these reactions produce solids with pores in the 15-21 Å range, many of them are unstable under guest exchange. We believe this is because it is difficult for more than four pyridine moieties to assemble around one M' . Indeed, there are very few examples of simple homoleptic pyridine complexes $M'(\text{py})_n$ with $n > 4$. The result is that the nets we have assembled contain either 3 or 4 pyridine moieties at each M' , and almost none of these are 3D nets.

In order to prepare 3D solids using this approach, we needed a ligand L that produces stable homoleptic complexes $M'L_6$ (or $M'L_5$) in high yield. We believe the most promising such ligand is an isocyanide: $M'(\text{CNR})_6$ complexes are known to have high stability for many d^6 ions (e.g. Cr^0 , Mn^I , Fe^{II} , Re^I). Therefore, we needed to prepare a bifunctional isocyanide- β -diketone ligand; our target has been the phenyl isocyanide derivative CNphacH (see Figure 2). We have synthesized this ligand, and we are studying two strategies (see Figure 3, top of next page) for using it to assemble 3D solids.

(A), initial complexation of β -diketone moiety: We explored this route first, because synthesis of isocyanides (via dehydration of formamides) requires reactive reagents such as POCl_3 , and these react with β -diketones. Therefore, we complexed the β -diketone moieties before dehydration. This route for the synthesis of $(\text{CNphac})_2\text{Cu}$ is illustrated in Figure 4. The isocyanide moieties in $(\text{CNphac})_2\text{Cu}$ are still available for complexation to other metals, such as Au.

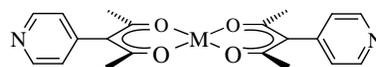


Figure 1. The “rod”-shaped building block $M(\text{Pyac})_2$.

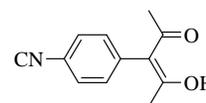


Figure 2. The isocyanide- β -diketone CNphacH .

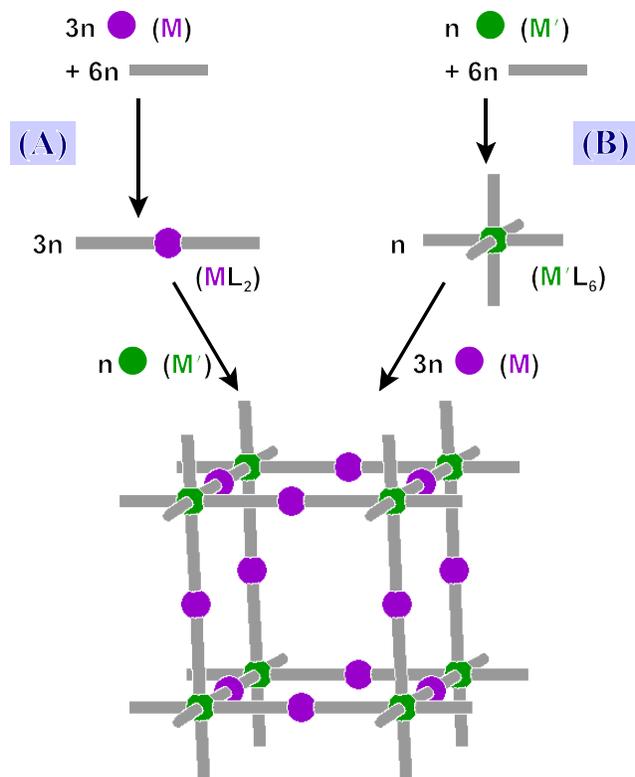


Figure 3. Schematic illustration of two routes (labeled **(A)** and **(B)**) for assembling porous 3D solids “ $M'M_3L_6$ ” with a ReO_3 -type structure, from metals M and M' . The isocyano- β -diketone bridging ligand is represented by — .

2. Molecular materials

New work in this area utilizes the *m*- and *o*-phenylenebis(β -diketone) ligands shown in Figures 5 and 6. We previously reported the surprising result that *m*-PBAH₂ forms a *molecular square* on reaction with Cu^{2+} , not the expected hexagon. This host binds C_{60} and C_{70} efficiently. We have now explored reactions with σ -binding guest molecules. For example, 4,4'-bipyridine binds both internally and externally at the same time, producing a polymeric system (shown in

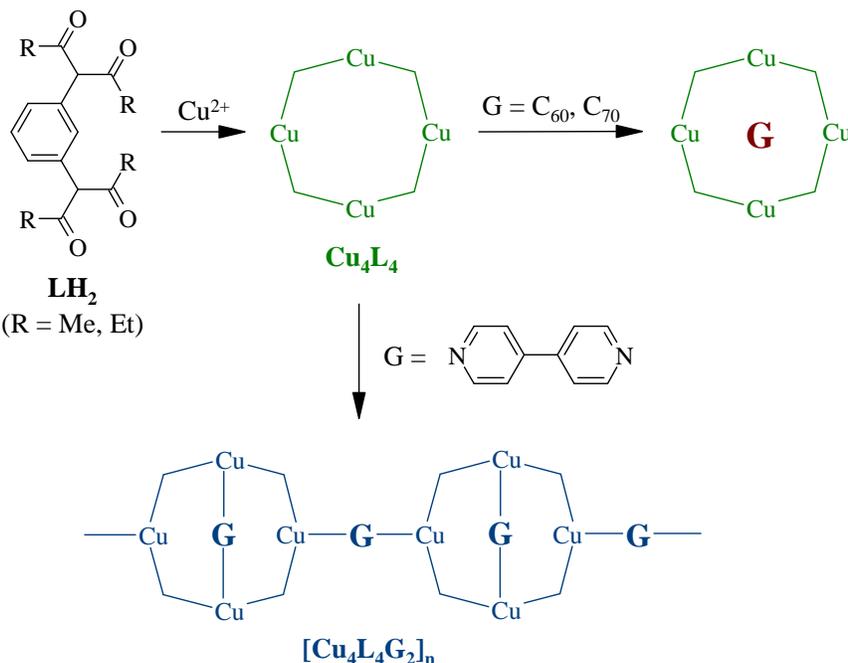


Figure 5. The *m*-disubstituted ligands L form *molecular-square* complexes Cu_4L_4 ($Cu \cdots Cu \sim 14 \text{ \AA}$). These bind C_{60} and C_{70} via π interactions, and amines such as 4,4'-bpy in a σ fashion.

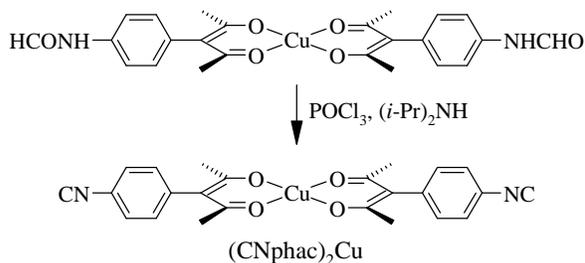


Figure 4. Final step in the synthesis of the isocyanide- β -diketone complex $(CNphac)_2Cu$.

(B), initial complexation of isocyanide moiety: This is more complicated, because the free $CNphacH$ ligand cannot be prepared directly (as outlined above). However, it can be prepared from $(CNphac)_2Zn$. We are now studying the properties of this unique hard/soft bifunctional ligand by reaction with d^6 metals.

Whether route **(A)** or route **(B)** is preferable, the final goal is the preparation of 3D porous extended solids such as $M'M_3L_6$ (see Figure 3).

blue in Figure 5).

The *ortho* isomer was expected to produce triangular M_3L_3 complexes. However, the product is again unexpected, dimeric $Cu_2(o-PBA)_2$, as shown in Figure 6. This material is green in solution, like most of our other supramolecular Cu(II) complexes, but it forms crystals that are either blue-purple or orange, depending on the solvent of crystallization. We are studying the structure of these crystalline materials, because the color changes appear to be inducible in the solid state and may therefore lead to sensor applications.

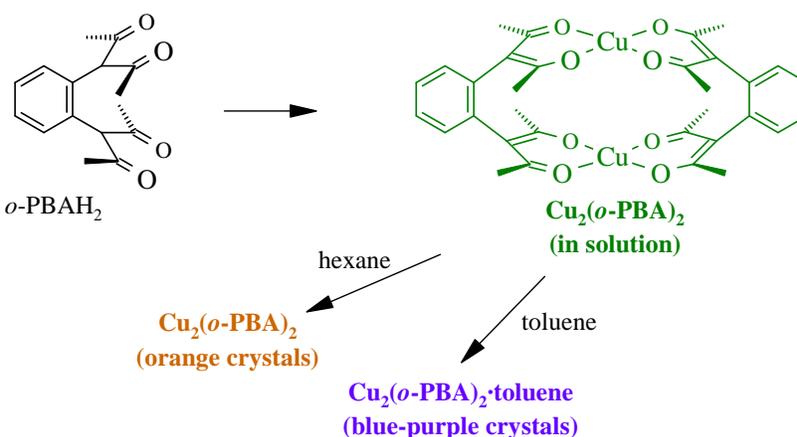


Figure 6. The ligand *o*-PBAH₂ forms a *dimer*, not the expected trimer, whose color is very sensitive to solvent/crystal environment.

DOE Interest

We expect to use the approaches outlined here to prepare new porous molecules and solids that expose reactive metal sites to the interiors of enclosed cavities and channels. Possible applications of the resulting materials include sensors, thin-film membranes for separations, and catalysts, all of which may derive improved selectivity from the placement of the active metal sites inside the cavities.

Future Plans

For the extended-solid species, we are now working toward porous materials that have both exposed M sites and the ability to exchange guest molecules while maintaining structural integrity. We are also exploring new techniques for preparing and interconverting our supramolecular materials, and approaches for incorporating catalytic sites into the structures.

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(Three others in preparation/submitted)

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CATALYSIS SCIENCE INITIATIVE: Principles of Selective O₂-Based Oxidation by Optimal (Binuclear) Catalytic Sites

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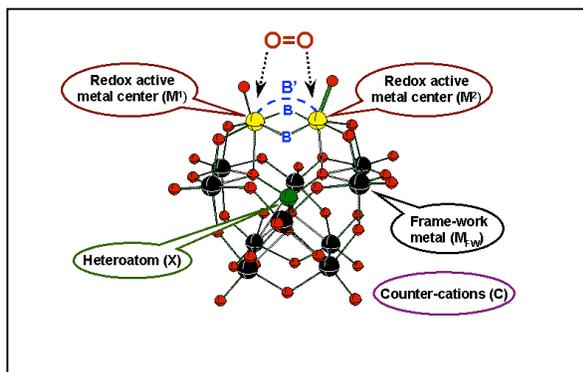
Goal. The goal of this project is to develop a combined experimental and theoretical approach to enable molecular-level understanding of the mechanisms of selective (non-radical), reductant-free, O₂-based oxidation of organic substrates catalyzed by polyoxometalates (POMs) with di-metal active sites, virtually the only synthetic compounds capable of this chemistry. The objectives of this integrated effort have entailed clarification of the structural, solution and catalytic properties of one of the few purported catalysts for selective O₂-based oxidations of organic substrates, the polyoxometalate (POM) of formula $[\text{X}M^1M^2(\text{OH})_2(\text{M}_{\text{FW}})_{10}\text{O}_{38}]^{n-}$, where M^1 and $M^2 = \text{Fe}$. In addition, the structural and electronic properties of the di-iron complex and others this class where $M_{\text{FW}} = \text{Mo}$ and W ; M^1 and $M^2 = \text{Ru}, \text{Mn}, \text{Cu}, \text{Co}, \text{Mo}$ and W , and $\text{X} = \text{B}, \text{P}, \text{Si}, \text{Al}, \text{Co}$ and Zn and the relationships between these properties and catalytic activity are sought.

DOE Interest. The proposed research addresses the selective (non-radical) oxidation of organic substrates by O₂ catalyzed by bimetal centers. The design and realization of catalysts capable of such transformations remains a monumental challenge and has occupied some of the most capable investigators for years. This program addresses key issues in depth on metal oxide cluster anions (polyoxometalates or “POMs”) substituted with two adjacent d-electron-containing redox-active metals not only for their intellectual significance and potential practical importance, but also because they provide a foundation for developing and exploring broadly applicable principles central to designing optimal synthetic catalysts and understanding related catalytic biological processes (such as those catalyzed by intensely investigated enzymes methane monooxygenase (MMO) and ribonucleotide reductase (RNR)). One reaction (of several) the goals of this effort address that would have a major impact on energy transportation and utilization is the selective O₂-based oxidation of methane (96% of natural gas) to methanol, a process that has yet to be achieved satisfactorily by a non-biological catalyst.

Research Plan. This grant targets a deeper understanding of the structural, electronic and dynamic factors underlying the design of catalysts for selective reductant-free O₂-based (or air-based) oxidations. It aims to establish the factors that control reactivity (rates, selectivities and catalyst stabilities) in such processes. To address the high expectations and goals of this program we proposed a highly integrated experimental and computational approach. The generic highly alterable binuclear-active-site POM structure (family of complexes), $[\text{X}(M^1M^2\text{OH})_2(\text{M}_{\text{FW}})_{10}\text{O}_{38}]^{n-}$ ($M^1M^2\mathbf{1}$) is illustrated in Figure 1. We proposed to systematically alter many key structural components of $M^1M^2\mathbf{1}$, while all the other structural components are kept

constant. For each POM, the experimental and theoretical parameters that are simultaneously the most insightful were targeted.

Figure 1. Graphical overview of the central integrated experimental-computational thrust of the program as exemplified by one of the 3 multi-component POM catalysts, $[\alpha\text{-X}(\text{M}^1\text{M}^2\text{OH}_2)_2(\text{H}_2\text{O})\text{W}_{10}\text{O}_{38}]^{6-}$ (**1**). All the following key parameters impacting reactivity could (and most successfully have been) altered and the consequences addressed experimentally and computationally. Parameters: M^1 and $\text{M}^2 = \text{Fe}$, Mn , Cu , Co , Ru , Cr , etc.; $\text{B} = \text{O}$, OH ; $\text{B}' = \text{acetate}$, etc.; $\text{M}_{\text{FW}} = \text{W}$ and/or Mo ; $\text{X} = \text{P}$, Si , Al , Zn , B , Co , etc.; $\text{C} = \text{Li}^+$, Na^+ , K^+ , R_4N^+ , biological cations, chiral cations, etc.



The single biggest determinant of reactivity is likely the proximal and potentially interacting d-electron-containing metals M^1 and M^2 . Our results bear this out (see below). The identity of both the in-plane (oxo or hydroxo) and/or other ligands bridging M^1 and M^2 (B and B' , respectively) are dictated in part by the identity of M^1 and M^2 . At the same time, these ligands can also be altered systematically because the four bonds to M^1 and M^2 from the $[\alpha\text{-Keggin}]$ POM unit are chelating and fairly robust. The main “framework” metals of the POM (M_{FW}) can be varied, too. Finally, the heteroatoms, X , and counterions, C , can be (and have been) altered.

In addition to these compositional parameters, the redox potentials and characteristic reactivity of each POM is targeted. The catalytic activity of the POMs for oxygenation of the important model substrates cyclohexene, cyclohexane, tetrahydrothiophene and/or *p*-chlorophenol was targeted and has been assessed. Key steps and reactions we study include: binding of dioxygen to the ($\text{M}^1_{\text{red}}\text{M}^2_{\text{red}}$) subunit; reactions of the resultant oxygen adduct, (M^1M^2)(O_2), with select substrates; O-O bond cleavage to form the reactive intermediates (M^1M^2)(O)₂; and reactions of these species with select substrates.

The detailed mechanisms of these processes are of core importance to this program because this information not only is of considerable fundamental value and insight in its own right, but also provides the reliable information needed to interpret the results from the sophisticated computational assessments of these mechanisms we have been conducting in parallel with the experimental work.

Recent Progress

Comprehensive studies of olefin epoxidation in organic solvents by O_2 catalyzed by $[\alpha\text{-SiFe}_2\text{W}_{10}\text{O}_{38}(\text{H}_2\text{O})_2]^{6-}$ (**1**) (the much-discussed system recently reported by Mizuno et al.) revealed that this catalytic epoxidation chemistry proceeds predominantly *via* the radical-chain autoxidation. The intact POM is only minimally involved. As a consequence, the focus of our research with this and related catalytic POM families shifted to aqueous solutions.

Attempts to grow crystals of $[\alpha\text{-SiFe}_2\text{W}_{10}\text{O}_{38}(\text{H}_2\text{O})_2]^{6-}$ (**1**) from aqueous solutions resulted in isolation of several new multi-iron-containing POMs, which are possible by-products or intermediates in the synthesis of **1** itself. For example, a new Fe(III) tungstosilicate derivative, $\text{K}_7[(\text{CH}_3)_2(\text{NH}_2)]_8([\alpha\text{-SiW}_{10}\text{O}_{36})_3\text{Fe}_6(\text{OH})_9(\text{H}_2\text{O})_6]\cdot 31\text{H}_2\text{O}$ (**2**) was isolated and comprehensively characterized. Polyanion **2** can be viewed as trigonal (trilobal) arrangement of three $\{\alpha\text{-SiW}_{10}\}$ polyanion units connected by an electrophilic $[\text{Fe}_6(\text{OH})_9(\text{H}_2\text{O})_6]^{9+}$ central core. Interestingly, **2** can be viewed alternatively as the first member of a new class of POM catalysts (activity

addressed below) in which a cluster of redox active proximal d-electron metals are stabilized by multiple POM ligands. Such clusters have frequently been discussed in the literature but realizing such structures that have reasonable stability, particularly in the optimal green solvent, water, has been problematical. In contrast to **1**, the iron atoms of the Fe₂ centers are no longer bonded to the oxygens of the internal heteroatom (Si in this case). The presence of this “out-of-pocket” {SiM₂W₁₀} structural motif has only been observed in one other structurally characterized POM, a dichromium(III) α -derivative. The trimeric like complex, **2**, isomerizes to different di-iron-containing POMs depending on the experimental conditions. For example, a new POM, $[\alpha(3,12)\text{-SiFe}_2\text{W}_{10}\text{O}_{36}(\text{OH})_2(\text{H}_2\text{O})\text{Cl}]^{5-}$ (**3**) has been synthesized and thoroughly characterized (the numbers 3 and 12 indicate the positions of Fe centers according to IUPAC numbering scheme). POMs of the Keggin structural class are the most common, they now appears in thousands of publications, and they constitute the main component of several catalytic processes commercialized in recent years. POM **3** represents a number of firsts including a dimeric metal-substituted α -Keggin compound that is disorder-free in the solid state. The X-ray crystallographic structure determination of **2** and **3** and other POMs of importance to this program has lead to a finding that could be of considerable and general value given the large number of papers and many groups studying POM-based catalysts. It is impossible to grow disorder-free crystals of α Keggin complexes substituted with one or more d-electron transition metal centers, the centers that are largely responsible for myriad catalytic activities in model studies and commercialized catalysts alike. However, in this DOE program we have obtained eight disorder-free X-ray structures of substituted α or β Keggin isomers (4 published or in submission and 4 more to be submitted in manuscripts shortly) and all are disorder free facilitating identification of the catalytically important terminal ligands on the d-electron metal centers. Thus use of α or β isomers in POM catalysis research is recommended.

The ability of **2** and other new complexes recently prepared in this program, to catalyze the selective aerobic (air as oxidant with no external reductant) oxidations was examined in some detail. Aerobic epoxidation (organic solutions) and 2-mercaptoethanol (RSH) oxidation (aqueous solutions) have been reported. Neither **2** or **3** is active in epoxidation. However, **2** is a highly active catalyst for thiol oxidation (hundreds of turnovers to the desired disulfide product realized using ambient air in an hour or two). The reaction kinetics of 2-mercaptoethanol oxidation reveal, among other noteworthy features, that the catalytically active species forms during the isomerization of **2**. These studies are consistent with dissociation of a $(\alpha\text{-SiW}_{10}\text{O}_{36})^{8-}$ unit from trimer, **2**, to generate an active $[(\alpha\text{-SiW}_{10}\text{O}_{36})_2\text{Fe}_6(\text{OH})_9]^{7-}$ unit. The dissociated $(\alpha\text{-SiW}_{10}\text{O}_{36})^{8-}$ isomerizes to $(\beta\text{-SiW}_{10}\text{O}_{36})^{8-}$, which in its turn reacts with catalytically active species rendering them inactive. This mechanism is supported by multiple lines of evidence, including, for example inhibition of catalysis by alkali metal cations and by $\alpha\text{-SiW}_{10}$ as well as kinetic modeling (fitting considerable data to various mechanisms).

A recent publication in *Science* prompted an investigation of another celebrated selective and “green” catalytic oxidation result, namely that $[(\alpha\text{-SiW}_{10}\text{O}_{36})]^{8-}$, the POM from which the adjacent di-d-electron-substituted POMs (henceforth “ α -M₂-Keggin” POMs) above are made, catalyzes fast and extremely selective H₂O₂-based alkene epoxidation. Our calculations indicate that the reported structure of the $[(\alpha\text{-SiW}_{10}\text{O}_{36}\text{H}_4)]^{4-}$ catalyst (two terminal aqua and two oxo ligands) is actually “ $[(\text{SiO}_4)\text{W}_{10}\text{O}_{28}(\text{OH})_4]^{4-}$ ”, a structure with four terminal hydroxo ligands. This result in consistent with a careful analysis of the reported X-ray structure in the *Science* article and also with defensible acidity values. Based on our theoretical and experimental studies (kinetics and product distributions in H₂O₂-based cyclooctene epoxidation), a reaction mechanism for these epoxidations involving initial generation of hydroperoxy (W-OOH) species and a water molecule followed by O-O bond cleavage in W-OOH and epoxide formation is proposed. Importantly, a

proximal counter cation significantly reduces the rate-limiting barrier and is key to this environmentally attractive epoxidation chemistry.

Computational studies of the Fe, Ru, Tc, Mo and Rh derivatives of $[(\text{SiO}_4)\text{M}_2(\text{OH})_2\text{W}_{10}\text{O}_{32}]^{4-}$, as well as $[(\text{XO}_4)\text{Ru}_2(\text{OH})_2\text{W}_{10}\text{O}_{32}]^{4-}$, with X = Al, Si, P and S show that, except M = Mo, the “closed” isomer is energetically more favorable than “open” one. The M-M interaction is strong only for M = Mo and Ru. These data clearly show that the heteroatom, X, in the di-Ru substituted β -Keggin POMs, $[(\text{X}^{\text{n+}}\text{O}_4)\text{Ru}_2(\text{OH})_2(\text{M}_{\text{FW}})_{10}\text{O}_{32}]^{(8-\text{n})-}$, for X = Al^{III} (**4**), Si^{IV} (**5**), P^V (**6**) and S^{VI} (**7**), where M_{FW} = Mo and W, is crucial in defining the lower-lying electronic states of the system, which in turn, likely impact reactivity to a considerable degree. For the electropositive X = Al^{III} (**4**), the ground state is ¹A₁, while for the more electronegative X = S^{VI} (**7**) the ground state is the high-spin ⁷B₁ state. Thus, X can function as a “internal switch” for defining the ground electronic states and, consequently, the reactivity of the β -M₂-Keggin POMs. Interestingly, in M_{FW} = Mo-systems, the dependence of the energy gap between the high-spin and low-spin states as the central atom, X, varies is less pronounced than in M_{FW} = W systems. For purposes of experimental verification the computationally predicted β -[(SiO₄)Ru₂(OH)₂(OH)₂W₁₀O₃₂]⁴⁻ was prepared and characterized.

In the course of our research, we developed two additional and fundamentally new classes of POM complexes, which, like the β -M₂-Keggin complexes, contain active centers that are proximal to and interacting with other metal centers of the POM unit. Significantly, both classes of complex facilitate O₂-based organic oxidation reactions: (1) giant POMs that contain multiple one-electron-reduced metal centers (d¹ Mo(V) and V(IV) centers) and (2) late-transition metal oxo (LTMO) compounds. The terminal metal oxo unit in these latter complexes has been the object of considerable discussion in the literature and at conferences for 40 years and there have been commensurate (but failed) experimental efforts over this period to prepare these species (occupied π^* and π^* antibonding M=O orbitals render the M=O unit intrinsically unstable). Despite the computational challenges, we have obtained evidence that appropriate POM ligands stabilize LTMO species in part by stabilizing occupied metal-oxo unit $\pi^*[\text{M}(\text{d}_{\text{xz,yz}})\text{-O}(\text{p}_{\text{x,y}})]$ antibonding orbitals. These POMs share several structural, electronic, and reactivity features in common with redox active metal oxide supports, such as TiO₂ and CeO₂, that are present in myriad oxidation catalysts including several commercial ones. Since late-2004 the team has prepared and thoroughly characterized LTMO species of the work-horse elements for catalysis, and catalytic oxidation in particular (Pt, Pd and Au). We believe we have also made a Ag-oxo complex but this will remain speculative until additional data have been collected and reproduced. Figure 2 summarizes four structurally distinct LTMO complexes that have been characterized to a degree that is commensurate with their unprecedented status: multiple elemental analyses from two companies, X-ray structure determinations at liquid He temperature, corroborating neutron diffraction studies (with Tom Koetzle, Art Schultz and Paula Piccoli at Argonne NL) and/or EXAFS (with Britt Hedman, Keith Hodgson, and Elena Slonkina at Stanford and SSRL), 5K optical spectra (with Martin Kirk at the U. of New Mexico) and ¹⁷O NMR which located the noble-metal oxo oxygen in the expected chemical shift range. All these data are consistent with diamagnetic d⁶ Pt(IV)-oxo, Pd(IV)-oxo centers and even more remarkable d⁸ Au(III)-oxo centers.

The tetra-*n*-butylammonium (TBA) and other organic-solvent soluble salts of the LTMO complexes have been made. Significantly, the Au-oxo complex in Figure 2C produces a different (and unusual) distribution of products in cyclohexene oxidation (*c*-C₆H₁₂, O₂ in CH₃CN) compared to that from a autoxidation (LTMO-free) control reaction (*c*-C₆H₁₂, O₂ in CH₃CN alone or in the presence of radical initiators). Informative stoichiometric oxo transfer reactions from Au^{III}-oxo and the isostructural Pd^{IV}-oxo complexes to organic substrates using ¹⁷O NMR have been conducted. Protocols for enriching several LTMO compounds in ¹⁷O from H₂¹⁷O following

by purification were developed, and ^{17}O NMR experiments under Ar established that the oxo oxygen on Au or Pd is selectively transferred to organic substrates (alkenes, phosphines, phosphites and sulfides have been examined thus far).

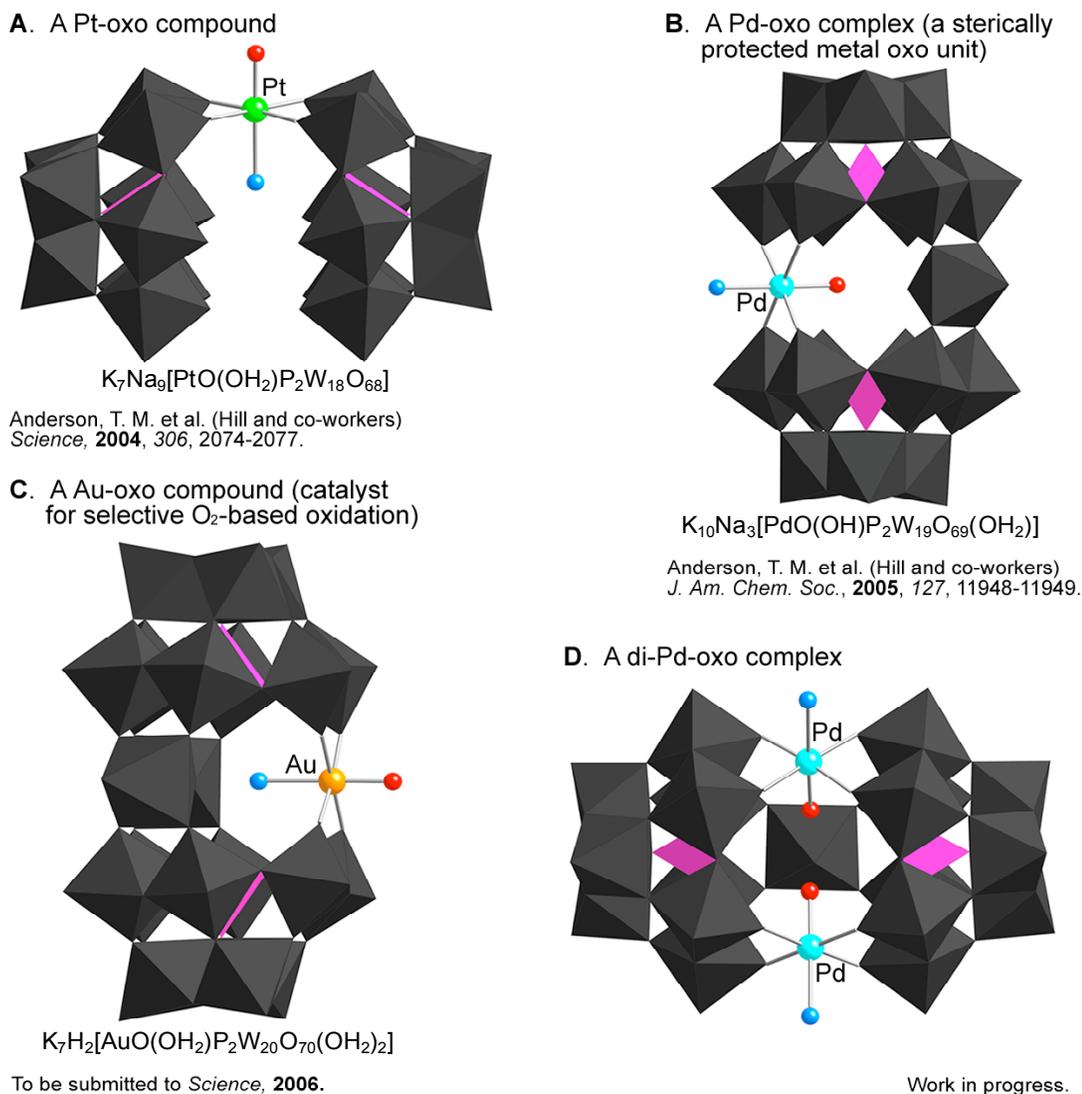


Figure 2. Late-transition-metal oxo (LTMO) compounds. X-ray and/or neutron diffraction structures are shown in combined polyhedral and ball-and-stick notation. In polyhedral notation the octahedra represent MO_6 units and the tetrahedra represent XO_4 units, with $\text{M} = \text{W}$ and $\text{X} = \text{P}$ in these cases; the M or X atoms are at the centers of the polyhedra and oxygens are the vertices. Color code: W, charcoal grey; P, pink; oxo, red; H_2O or OH, dark blue; Pt, green; Pd, light blue; Au, gold. Three different metal-oxide ligand systems are involved: two separate PW_9 ligands in the case of A, and a single POM unit ligand in the other cases.

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8. Quiñero, D.; Morokuma, K.; Geletii, Y. V.; Hill, C. L.; Musaev, D. G. "A Density Functional Study of Geometry and Electronic Structures of $[(SiO_4)(M^{III})_2(OH)_2W_{10}O_{32}]^{4-}$," $M = Mo, Ru$ and Rh . *J. Mol. Catal.* **2006**, in press.
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The following invited mini-review will be completed shortly:

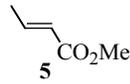
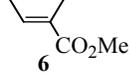
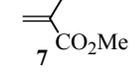
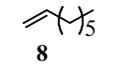
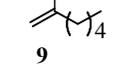
Hill, C. L. Anderson, T. M.; Cao, R.; Geletii, Y. V.; Fang, X.; Musaev, D. G.; Morokuma, K.; Kirk, M. "Terminal Metal Oxo Complexes of the Noble Metals. Structural, Electronic and Catalytic Properties of these Long-Sought Species", Special Issue of *Comptes Rendus Chimie* (French National Academy of Sciences) on Homogeneous and Biomimetic Oxidation-Reduction Catalysis, Reedijk, J., Ed.; 2006.

Catalytic Applications of H• Transfer from Transition-Metal Hydride Complexes

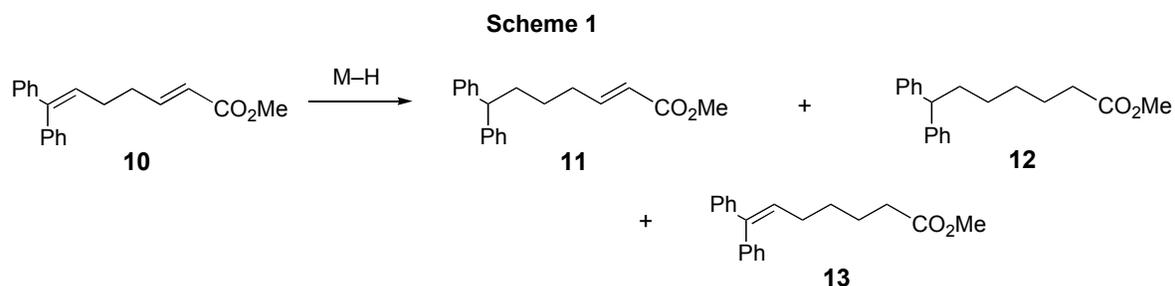
Students: Jongwook Choi, Deborah Smith, Mary Pulling, Marcos Arribas-Layton
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The rate constants k_H for hydrogen atom transfer from $\text{CpCr}(\text{CO})_3\text{H}$ to the olefins below have been determined from the observed rates of H/D isotope exchange, or hydrogenation, or both. The substituents on the olefin have a large impact on these values. Phenyl-substituted olefins accept H• more readily than do carbomethoxy-substituted alkenes; carbomethoxy-substituted olefins accept H• more readily than do alkyl-substituted olefins. Additional methyl or phenyl substituents on the incipient radical center increase k_H by stabilizing the radical being generated. A methyl substituent on the carbon receiving the H• reduces k_H significantly.

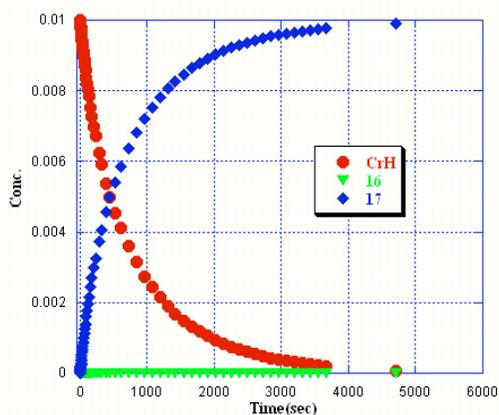
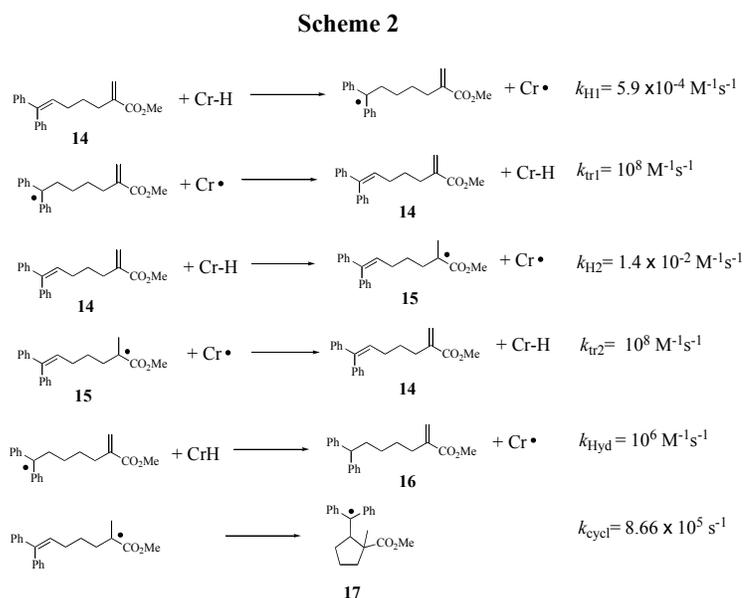
Rate Constants for H• transfer from $\text{CpCr}(\text{CO})_3\text{H}$ to Various Olefins at 50°C

Olefin	k_H ($\times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$)	Olefin	k_H ($\times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$)
	0.59		$< 3.2 \times 10^{-4}$
	460		$\approx 1.2 \times 10^{-2}$
	79		14
	15.8		$< 1.1 \times 10^{-4}$
			$\approx 3.2 \times 10^{-3}$

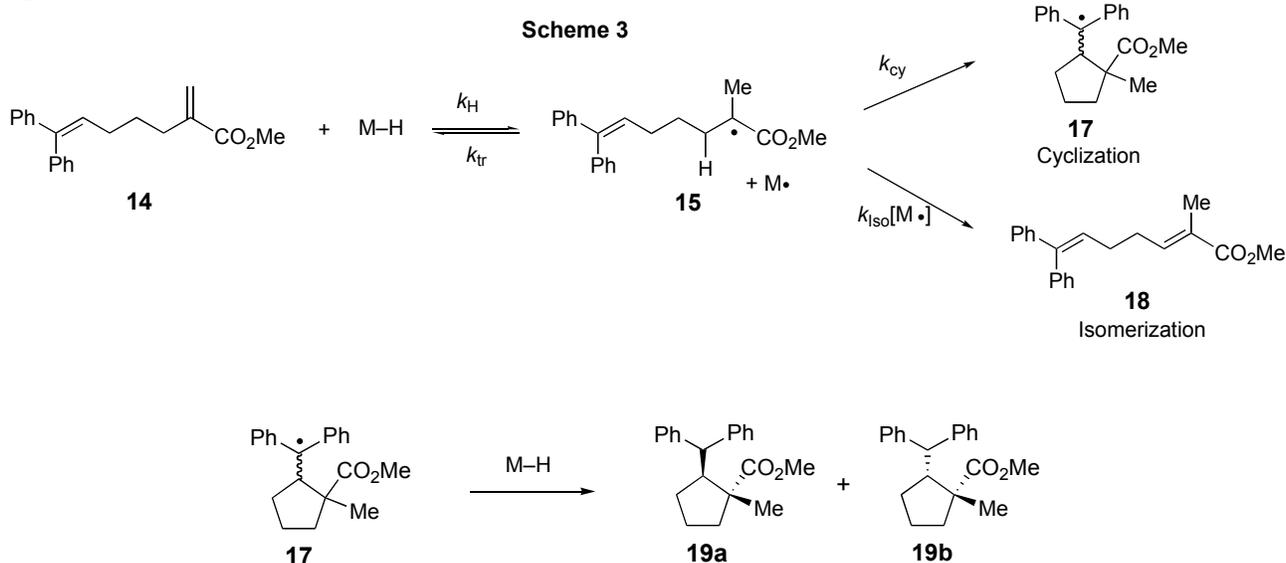
These data explain the outcome of our initial attempt to use H• transfer from $\text{CpCr}(\text{CO})_3\text{H}$ to induce a radical cyclization. The diphenyl substituents on the left-hand double bond in **10** would ensure the rapid cyclization of a carbomethoxy-substituted radical. However, experiments with **10** and $\text{CpCr}(\text{CO})_3\text{H}$ afforded no cyclization but small amounts of the hydrogenation product **11**. The more reactive hydride $\text{HCo}(\text{CO})_4$ provided a 45:45:10 ratio of the hydrogenation products **11**, **12**, and **13** in Scheme 1. (We assume that the relative reactivities of various olefins toward $\text{HCo}(\text{CO})_4$ are the same as their relative reactivities toward $\text{CpCr}(\text{CO})_3\text{H}$.) These results indicate that H• is preferentially transferred to the diphenyl-substituted double bond, consistent with the k_H values for model substrates **1** and **5** in the Table. The formation of the minor product **13** does imply that there is some H• transfer to the carbomethoxy-substituted double bond.



We therefore redesigned the cyclization substrate to take advantage of the relative rates of $H\cdot$ transfer to olefins **1–9** (see Table above). The carbomethoxy-substituted double bond will become the preferred $H\cdot$ recipient if we replace it with an exo methylene, as $H\cdot$ transfer to the methacrylate **7** is faster than $H\cdot$ transfer to **1**. Indeed, simulation of the reaction between **14** and $CpCr(CO)_3H$ (Scheme 2) at $50\text{ }^\circ C$, using our k_H values for **1** and **5**, the literature value for k_{cycl} , and estimates for k_{tr} and k_{hyd} ($10^8\text{ M}^{-1}s^{-1}$ and $10^6\text{ M}^{-1}s^{-1}$, respectively), suggested that most $H\cdot$ transfer to **14** would lead to cyclization, and that the reaction would be complete within an hour.



However, treatment of substrate **14** with $\text{CpCr}(\text{CO})_3\text{H}$ gave principally the isomerization product **18** (see Scheme 3). We surmised that the undesired **18** arose from the presence of adventitious $\text{CpCr}(\text{CO})_3\cdot$ at the beginning of the reaction, as an impurity in the $\text{CpCr}(\text{CO})_3\text{H}$. (More $\text{CpCr}(\text{CO})_3\cdot$ is formed by the hydrogenation reactions.) We hoped that performing the reaction under H_2 would keep the $\text{CpCr}(\text{CO})_3\cdot$ from persisting in solution by converting it back to $\text{CpCr}(\text{CO})_3\text{H}$.



To test this hypothesis we treated substrate **14** with $\text{CpCr}(\text{CO})_3\text{H}$ under 80 psi H_2 at room temperature. Isomerization was effectively suppressed. After four days the cyclization products **19** were obtained in good yield, along with small amounts of hydrogenation byproducts. The major diastereomer of **19**, **19a**, has been isolated.

DOE Interest. Such radical-mediated carbon–carbon-bond forming reactions have many synthetic applications, but are traditionally carried out with the stoichiometric use of Bu_3SnH — and the toxicity of that reagent has limited the industrial use of this chemistry. Our reaction is not only **tin free** but **catalytic**.

Future Plans. A new substrate with geminal substitution on the carbon backbone has been synthesized to take advantage of the Thorpe-Ingold effect. The cyclization rate should be accelerated and the formation of hydrogenation and isomerization products should be suppressed.

Publications in 2004-2006:

Anson, C. E.; Sheppard, N.; Pearman, R.; Moss, J.; Stöbel, P.; Koch, S.; Norton, J.R. A vibrational study of the diosmacyclobutene complex $\text{Os}_2(\text{CO})_8(\mu_2-\eta^1, \eta^1-\text{C}_2\text{H}_2)$: The use of organometallic complexes as vibrational models for chemisorbed ethyne. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1070–1076.

Tang, L.-H.; Norton, J.R. Effect of Steric Congestion on the Activity of Chromium and Molybdenum Metalloradicals as Chain Transfer Catalysts during MMA Polymerization. *Macromolecules* **2004**, *37*, 241–243.

Three additional publications are in draft form.

Synthesis, Directed Assembly, and Local Probe Measurements of Dipolar, Organic Nanostructures

Students: Chaya Ben-Porat, George Tulevski, Mark Bushey, Dr. Thuc-Quyen Nguyen, and Dana Horoszewski

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Goal

To develop methods to grow individual wires that are attached to metal surfaces and measure their properties locally.

Recent Progress

Individual Catalyst Sites for Molecular Wire Growth

Increasingly the DOE project is working toward catalytic methods to growth molecular wires that are structurally and electronically contacted to metal surfaces. We recently found that carbene precursors such as diazoalkanes react with clean ruthenium surfaces to yield monolayers of carbenes on metal surfaces. We are interested in using these methods to grow molecular scale wires through the ring opening reactions shown below in Figure 1.

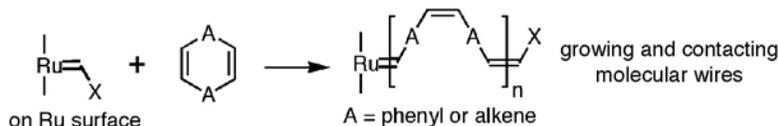


Figure 3. A scheme to grow molecular wires from individual catalyst sites on a ruthenium surface.

We have recently shown that these surfaces are able to initiate the olefin metathesis reaction. The system investigated is shown in Figure 2 below. Monolayers can be generated through reaction with the appropriate diazoalkanes and then interconverted by reaction with olefins. We can detect the products of the surface reactions with IR, XPS, and scanned probe measurements as well as the byproducts of the reaction by GC/MS (shown in Figure 2).

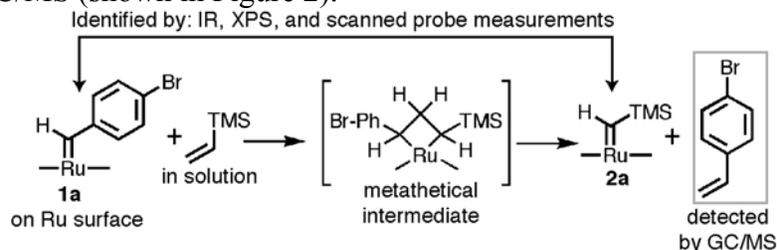


Figure 2. A surface metathesis reaction.

To study these reactions in detail we have developed a new method for the synthesis of nanocrystals of ruthenium that are coated with carbenes. These particles are able to initiate olefin metathesis. We can follow the kinetics of these reactions using GC/MS and NMR.

DOE Interest

These studies are significant because they could provide a deeper understanding of how polar properties emerge and propagate on the nanoscale. Moreover, these columnar structures provide a mechanism to convert electrical energy to mechanical energy at extremely small length-scales. For the electrical measurements, the potential outcomes for these experiments are unprecedented, providing a deeper understanding of how charge is delocalized in low dimensional organic nanostructures and as a general method to use catalysis to create molecular electronics devices.

Future Plans

Our future plans are in measuring the conductivity of the wires grown in situ from the ruthenium surfaces through ring opening metathesis polymerization.

Publications

- (1) “Self-Assembly and Electronics of Dipolar Linear Acenes”, Q. Miao, M. Lefenfeld, C. Kloc, T. Seagrist, and C. Nuckolls, *Adv. Mater.*, **2005**, *17*, 407–412.
- (2) “Attaching Organic Semiconductors to Gate Oxides: In Situ Assembly of Monolayer Field Effect Transistors”, G. S. Tulevski, Q. Miao, M. Fukuto, R. Abram, B. Ocko, R. Pindak, M. Steigerwald, C. Kagan, and C. Nuckolls, *J. Am. Chem. Soc.*, **2004**, *126*, 15048–15050.
- (3) “Formation of Catalytic Metal-Molecule Contacts”, G. S. Tulevski, M. B. Myers, M. Hybertsen, M. Steigerwald, and C. Nuckolls, *Science*, **2005**, *309*, 591–594.
 - News of the Week in *Chemical and Engineering News*, **2005**, *83*, 9.
- (4) “Molecular Wires from Contorted Aromatics”, S. Xiao, M. Myers, Q. Miao, S. Sanaur, K. Pang, M. L. Steigerwald, and C. Nuckolls, *Angew. Chem.*, **2005**, *44*, 7390–7394.
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- (6) “Organization of Acenes with a Cruciform Assembly Motif”, Q. Miao, X. Chi, S. Xiao, R. Zeiss, M. Lefenfeld, C. Kloc, T. Siegrist, M. Steigerwald, and C. Nuckolls, *J. Am. Chem. Soc.* **2006**, *128*, 1340–1345.
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- (8) “Chemoresponsive Monolayer Transistors”, X. Guo, M. Myers, M. Lefenfeld, R. Steiner, J. T. Yardley, P. Kim, and C. Nuckolls, *Proc. Nat. Acad. Sci (USA)*, submitted.
- (9) “Integrating Sites for Polymer Growth into Ruthenium Particles”, F. Ren, M. Carnes, M. Steigerwald, and C. Nuckolls, in preparation.
- (10) “STM Imaging of Self-Assembled Helical Nanostructures”, T.-Q. Nguyen, R. Martel, A. Carlsen, P. Avouris, M. L. Bushey, L. E. Brus, and C. Nuckolls, *in preparation*.
- (11) “Organization of Acenes with a Cruciform Assembly Motif”, Q. Miao, X. Chi, S. Xiao, R. Zeiss, M. Lefenfeld, C. Kloc, T. Siegrist, M. Steigerwald, and C. Nuckolls, *submitted*.
- (12) “A Catalytic Path to Ohmic Contact in Metal-Molecule Junctions”, G. S. Tulevski, M. B. Myers, M. Hybertsen, M. Steigerwald, and C. Nuckolls, *submitted*.
- (13) “Electric Fields on Oxidized Silicon Surfaces: Static Polarization of PbSe Nanocrystals”, C. Ben-Porat, O. Cherniavskaya, L. Brus and K.-S. Cho and C. B. Murray, *J. Phys. Chem. B.*, *accepted for publication*.
- (14) “Large Dipole Moments in One Dimensional Organic Nanostructures Composed of Substituted Arenes as Measured by Dielectric Impedance Spectroscopy”, J. H. Dickerson, M. L. Bushey, S. Banerjee, T.-Q. Nguyen, C. Nuckolls, and I. P. Herman, *submitted*.
- (15) “Molecular Interactions in One-Dimensional Organic Nanostructures”, T.-Q. Nguyen, R. Martel, P. Avouris, M. L. Bushey, C. Nuckolls, and L. Brus, *J. Am. Chem. Soc.*, **2004**, *126*, 5234–5442.

- (16) “Dimeric π -stacks on Gold using Three Dimensional Lock-and-Key Receptors,” G. S. Tulevski, M. L. Bushey, J. L. Kosky, S. J. Toshihiro-Ruter, and C. Nuckolls, *Angew. Chem. Int. Ed.*, **2004**, *43*, 1836–1839..
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- (20) “Synthesis, Self-Assembly, and Electro-optic Switching of One-Dimensional Nanostructures from New Crowded Aromatic,” M. L. Bushey, T.-Q. Nguyen, and C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 8264–8269.

Negative Thermal Expansion of γ -Alumina-Supported Pt Catalysts

Joo Kang, Laurent Menard, Duane Johnson, Ralph Nuzzo (UIUC)

DE-FG02- 03ER15476

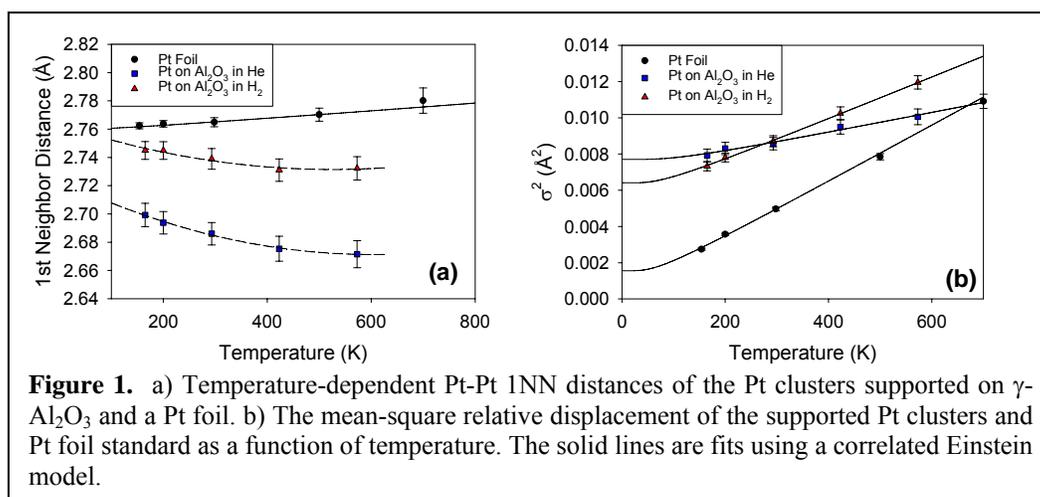
Anatoly Frenkel (Yeshiva University)

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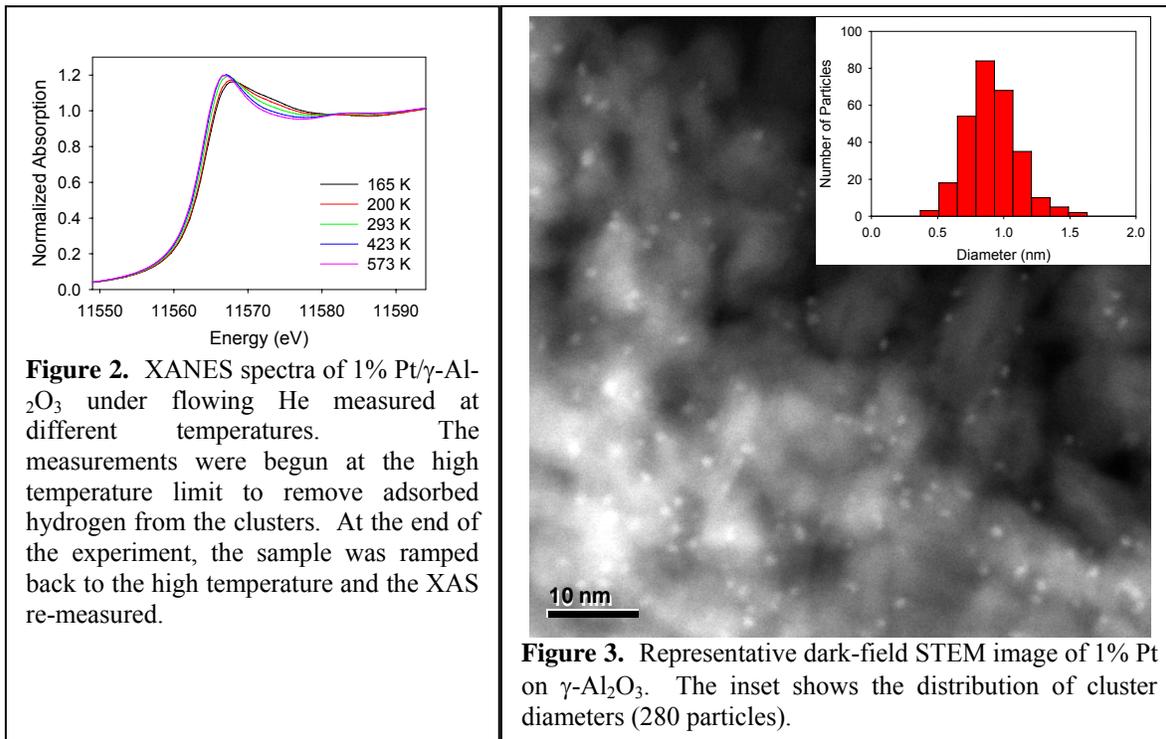
Judith Yang (University of Pittsburgh)

DE-FG02- 03ER15475

Despite extensive research efforts seeking to elucidate the origins of the catalytic properties of oxide-supported and promoted metal cluster catalysts, fundamental understandings of their properties and mechanisms of operation remain far from complete. This arises in part from the considerable structural complexity of heterogeneous catalysts, as well as the sensitivity of their activity to: mechanistic impacts related to surface area, porosity, and defect sites; “quantum size effects;” and physico-chemical effects of the oxide support itself on the electronic structure of the cluster. We show here using STEM and x-ray absorption spectroscopy (EXAFS and XANES) that the support/cluster interactions in a Pt on γ -alumina catalyst (a system used to produce essentially all liquid hydrocarbon fuels) results in the surprising behavior of negative thermal expansion (NTE) – the contraction of the Pt-Pt bonding distances with increasing temperature, over temperatures ranging from 165 to 573 K (Figure 1a). Negative thermal expansion is uncharacteristic of close-packed metals (and the majority of materials) in their bulk form because the anharmonicity of the interatomic potential results in a greater mean interatomic distance at higher temperatures. Our EXAFS/XANES data (Figures 1,2) suggest that the NTE results as a consequence of electronic effects mediated by the temperature-dependence of the metal-support interactions, bonding involving charge transfer between the support and the Pt cluster. We find that there is a clear effect of temperature on the XANES spectra (Figure 2); the qualitative changes seen are consistent with aspects of previous studies on the impact of H_2 adsorption and support effects on Pt clusters (i.e. the shift in the edge energy, decrease in white line intensity, and white line broadening).



Quantitative, atom-counting STEM measurements were also performed on the supported Pt clusters to determine their shape and average size on a per atom basis (Figure 3).



Our systematic study of the EXAFS Debye-Waller factors in all samples reveals enhanced anharmonicity of the Pt-Pt pair vibrations and the non-Gaussian nature of the effective Pt-Pt pair potential. We model the Pt-Pt vibrational amplitude σ^2 as a sum of three terms:

$$\sigma^2(T) = \sigma_{st}^2 + \sigma_E^2(T) + \sigma_{CT}^2(T),$$

where σ_{st}^2 is the static, temperature-independent disorder (due to the surface and interface disorder), $\sigma_E^2(T)$ is the temperature-dependent Pt-Pt bond vibration amplitude which can be modeled using quasi-harmonic Einstein approximation, and $\sigma_{CT}^2(T)$ is a contribution to the total bond length disorder due to the temperature-dependent support-particle charge transfer. By studying temperature dependent EXAFS data, these effects can be deconvoluted. This study advances an understanding of the interplay between structural and electronic properties in systems relevant to heterogeneous catalysis and a new form of mesoscopic structural behavior in an important form of nanoscale matter.

Nanocatalysts: Synthesis, Properties, and Mechanisms

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Collaborators: David R. Mullins, Edward W. Hagaman, Stephen J. Pennycook, Viviane Schwartz, Sergey Rashkeev, Andrew Lupini

Postdocs: Haoguo Zhu, Jason Clark

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6201

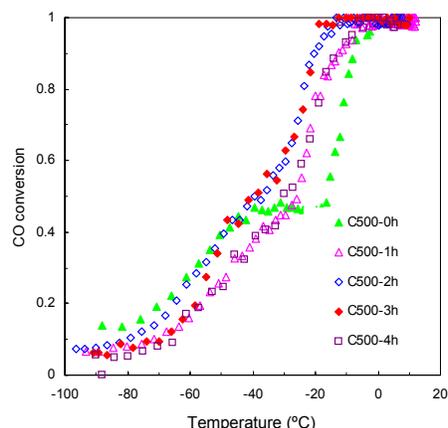
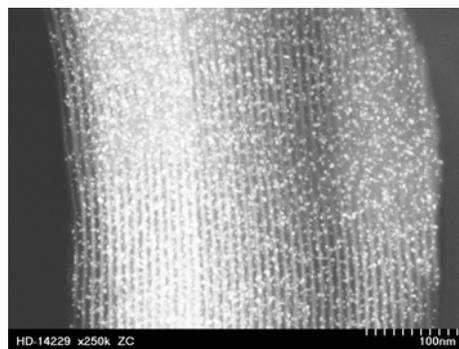
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Goal

Au is striking as a catalytic material because Au catalysts exhibit a pronounced sensitivity to particle size. Our goal is to understand the factors which control catalytic reactivity on supported Au nanoparticles. Our approach incorporates novel synthetic techniques to prepare nanostructured Au catalysts with high selectivity and activity, characterization techniques to study the relations between structure and reactivity, and computational work to enhance our understanding of the catalytic interactions.

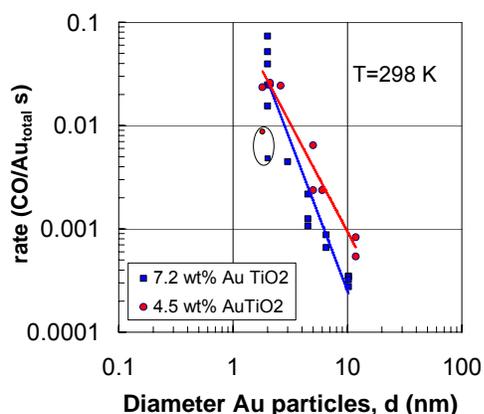
Recent Progress

We have developed several synthesis methodologies for the preparation of Au catalysts on tailored non-porous and mesoporous supports. Periodic mesoporous silicas are potential candidates as scaffolds to synthesize supported Au nanocrystals with controlled size and shape. The control over both size and shape of metal particles is exceedingly important for Au catalysts. Although the deposition-precipitation (DP) method using HAuCl_4 can be used to prepare gold nanoparticles on titanium oxide substrates, it is difficult to deposit gold nanoparticles ($<30 \text{ \AA}$) on silica materials with this methodology, because of the low isoelectric point (IEP) of SiO_2 . We have explored a strategy to overcome the low IEP of silica-based materials by the introduction of a high-IEP oxide component into silica materials *via* surface sol-gel process (SSP) modification or by the corresponding gas phase synthesis, atomic layer deposition (ALD). Recently, we have explored a novel efficient method using a gold cationic complex precursor $[\text{Au}(\text{en})_2]^{3+}$ (en =ethylenediamine) *via* a wet chemical process. The gold cationic precursor was immobilized on negatively charged surfaces of silica by a unique DP method that makes use of the deprotonation reaction of ethylenediamine ligands. Applying this method to Au deposition on SBA-15 leads to uniform Au particles of 2.9 nm dispersed in the 7 nm pores of the SiO_2 (micrograph). After activation, the resulting mesoporous catalyst is highly active for CO oxidation, much superior to silica-supported Au catalysts previously prepared by various solution techniques. It is also highly resistant to sintering (see Fig) because of the stabilization of Au nanoparticle inside mesopores. The pH of the gold precursor solution during synthesis plays a key role in determining the catalytic activity through the regulation of $[\text{Au}(\text{en})_2]^{3+}$ deprotonation reaction and the surface interaction of silica with the gold precursor. This new DP methodology for gold catalysts opens up a new avenue to



deposit gold precursors on low-IEP supports.

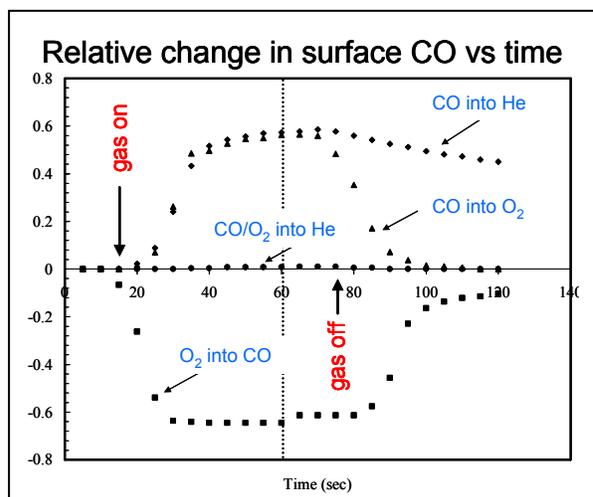
The size dependence of activity in gold catalysts was examined experimentally to better understand the origin of the size dependence. Extended x-ray absorption fine structure was used to determine mean particle size and a flow reactor was used to assess activity of the catalysts for CO oxidation as a function of temperature. A sequence of calcination steps was used to systematically increase the mean Au particle



size while repeated measurements of the activity were conducted. In this way the size dependence can be obtained in a single catalyst to avoid differences due to variations in support, synthesis conditions, Au loading or incidental impurities. Two Au catalysts with different Au loadings were prepared on TiO₂ by deposition precipitation and each used for the measurements. For Au particles with mean particles size, d , in the range of 2 to 10 nm, the measured TOF at 298 K varies as $d^{-1.9 \pm 0.2}$ and $d^{-1.1 \pm 0.2}$ for a 7.2 wt % and 4.5 wt % Au / TiO₂ (P25) catalysts, respectively. Variation between samples emphasizes the conclusion that the activity is sensitive to many factors which may mask the true structure dependence. It is concluded that the observed decrease in activity as particle sizes grow larger than 2 nm is controlled

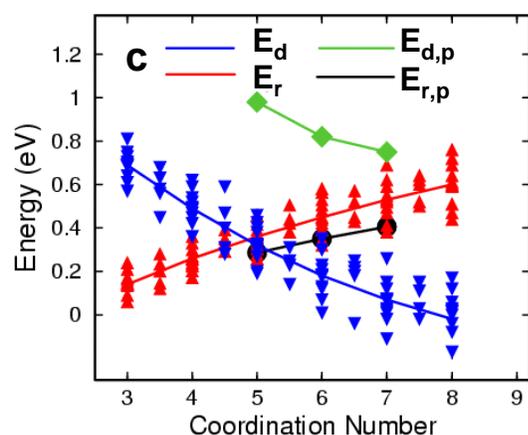
by the population of low coordinate sites, rather than size dependent changes in overall electronic structure of the nanoparticle. No evidence is found for a maximum in activity at small particle size in the 2-10 nm size range studied, However, a decrease in activity for much smaller particle sizes is expected from published work that shows loss of activity for Au clusters with less than 7 atoms.

Transient studies on the oxidation of CO over Au/TiO₂ and other supported Au catalysts have been performed using a zero dead volume reactor with gas switching/pulsing. A time-resolved fast scanning FTIR monitors surface changes while a quadrupole mass spectrometer continuously monitors reaction products. Using this *in operando* approach, it has been possible to probe the elementary steps in the CO oxidation reaction. Controlled switching between the reactants, alone or mixed, permitted analysis of adsorption and desorption rates and the competition between reactants for surface sites. Two types of carbonates (bidentate, monodentate) and carboxylates were observed and their formation on the TiO₂ support was shown to be catalyzed by Au particles. These species were not associated with rapid formation of CO₂. Instead a surface species of CO₂ was demonstrated to have a relatively long residence time and to desorb slowly with respect to its rapid formation by surface oxidation of CO. Gas switching experiments (see figure) show that pre-adsorption of O₂ does not interfere with subsequent CO uptake nor does CO pre-adsorption interfere with O₂ uptake. Surface CO oxidation during flow of reactant mixture (CO/O₂) is so fast that adsorbed CO is not observed, although adsorbed CO₂ is evident. Further experiments are planned to determine how mechanistic details vary between different catalyst formulations and under different reaction conditions. Such results will help clarify observed support effects, the impact of Au particle size variation and the role of water in the mechanism.



To learn more about how nanostructure affects CO oxidation, first-principles calculations were performed for Au clusters supported on a TiO₂ slab terminated by non-polar surfaces. The clusters and the top surface layers were fully relaxed. Gold (or Pt) clusters containing from 5 to 35 atoms, were deposited and relaxed on the TiO₂. Many different ensembles were constructed and optimized. Minimum reaction paths for the CO+O₂ oxidation reactions were found using the nudged-elastic-band method. For statistical analysis of the CO and O₂ binding energies and the reaction barriers, at least 8 different configurations were used for each coordination number of the Au atoms to which the oxygen molecule was attached.

We find that at least one substrate O vacancy is needed to anchor Au particles. Given the same number of oxygen vacancies we find no significant differences between Au bonded to anatase (101) and rutile (110) surfaces. The adsorption of O₂ and CO molecules was optimized at various sites and the binding energies and reaction barriers were calculated. On virtually all Au particles, O₂ adsorbs as a molecule. Adjacent O₂ and CO molecules react to produce CO₂, which desorbs, leaving a bonded O atom. Upon adsorption, the neighboring Au-Au bonds are weakened making the rotation and stretching needed for the reaction less energetically costly. The figure shows computed reaction barriers (E_r) and O₂ desorption energies (E_d) as



a function of the coordination number, n , of the Au atoms that are bonded to the O₂ molecule. Results for several cluster sizes and structures are included. The most striking result for Au nanoparticles is the crossing of the E_r and E_d curves. Reaction is favorable at sites with average coordination $n < 5$, when $E_r < E_d$, i.e., the time for the reaction to occur is shorter than the residence time of the adsorbed O₂ molecule. At perimeter sites, O₂ molecules bind strongly in a bridging bond between Au and Ti cations ($E_{d,p}$). At this site catalytic activity is favored even with $n = 6$ or 7 because the bridge bond to the substrate helps weaken the O-O bond. Reaction barriers on the perimeter ($E_{r,p}$) also decrease with decreasing coordination.

DOE interest

New catalysts are needed to achieve incremental or revolutionary improvements in technologies related to emission control, fuel cells and hydrogen utilization. This work provides a research basis for preparing, testing and understanding catalysts with potential application in these technologies.

Future Plans

The controlled synthesis of interfacial layers and new methods for Au deposition will be extended to manipulate nanoscopic architectures of catalytic reaction centers. Activity and stability of layered catalysts vary widely depending upon the support. The adsorption of reactants and products on the functionalized catalysts will be studied by FTIR and pulsed reaction to determine how it is influenced by support variation and to determine mechanistically the effects of variation in the support upon the activity of Au catalysts. The activity and selectivity of Au catalysts for reactions other than CO oxidation will be explored, including selective and total oxidation of methanol. A key question is whether variation in activity and selectivity is described primarily by growth in Au particle size or if support-metal interactions play a crucial role.

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Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

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Goals

The specific objectives and research goals of the research performed during the previous grant period have been to obtain information that is relevant to transition metal mediated transformations of organic substrates. Such studies are of importance due to the fact that vast quantities of organic materials are available from natural resources but their full potential is yet to be realized because of synthetic difficulties. Specific issues that were addressed during the course of this research included: (i) the role of molybdenum in hydrodesulfurization chemistry, (ii) haptotropic shifts involving the reaction of η^6 -arene complexes with H_2 and associated equilibrium isotope effects, and (iii) the synthesis of aqua-dihydride complexes of molybdenum and tungsten of potential relevance to green chemistry.

Research Plan and Progress**1. Ansa Molybdenocene Complexes in Modeling Hydrodesulfurization**

Hydrodesulfurization (HDS) is the largest volume and most important industrial catalytic application of transition metals and is the process by which sulfur containing impurities are removed from crude petroleum feedstocks and fuels. For this reason, we have initiated a series of studies directed towards activating thiophene by molybdenum compounds and have reported the first example of thiophene C–S bond cleavage by molybdenum, namely cleavage of the C–S bond of thiophene by the *ansa* molybdenocene dihydride complex $[Me_2Si(C_5Me_4)_2]MoH_2$. The observation of C–S bond cleavage is significant because the corresponding reaction of Cp_2MoH_2 yields a thienyl–hydride complex *via* cleavage of the a C–H bond. In order to explain this difference in reactivity, we have performed DFT calculations to establish the relative energies of the various C–H and C–S bond cleavage products and also the corresponding η^1 -S–thiophene adduct. These calculations indicate that the product of C–S bond cleavage is more stable than both (i) the thienyl–hydride resulting from C–H bond cleavage and (ii) the η^1 -thiophene adduct. The calculations also demonstrate that the *ansa* bridge confers stability to the metallathiacycle relative to the thienyl–hydride and thereby provide a thermodynamic explanation for the different reactivities of Cp_2MoH_2 and $[Me_2Si(C_5Me_4)_2]MoH_2$ towards thiophene.

2. Haptotropic Shifts of Arene Ligands: Origin of The Naphthalene and Anthracene Effects

Haptotropic shifts play important roles in the transition metal catalyzed transformations of polycyclic aromatic compounds. For example, facile ring–slippage has also been proposed to account for the increased lability of naphthalene compared to that of benzene in metal–arene complexes, a phenomenon referred to as the “naphthalene effect”. However, despite the many observations that naphthalene is more readily displaced than benzene, there are no experimental studies that quantify the influence of ring fusion on a well-defined reversible η^6/η^4 haptotropic shift. For this reason, we have investigated the reactivity of the η^6 -benzene, η^6 -naphthalene, and η^6 -anthracene compounds (η^6 -PhH)Mo(PMe₃)₃,

$(\eta^6\text{-NpH})\text{Mo}(\text{PMe}_3)_3$, and $(\eta^6\text{-AnH})\text{Mo}(\text{PMe}_3)_3$ towards H_2 . These studies indicate that ring fusion to an arene (*i*) promotes the oxidative addition of H_2 to a metal center *via* facilitating an η^6 to η^4 haptotropic shift, and also (*ii*) promotes hydrogenation of the arene.

The more facile displacement of naphthalene and anthracene from a metal center, compared to that of benzene, has previously been rationalized in terms of the loss of resonance energy upon folding the arene from the planar geometry to the bent geometry in the proposed $[(\eta^4\text{-ArH})\text{M}]$ intermediate. However, DFT calculations indicate that the ability to ring-slip is *not* determined by a loss of resonance energy. Rather, the variation in overall thermodynamics correlates well with changes predicted by consideration of $\text{Mo}-(\eta^6\text{-ArH})$ and $\text{Mo}-(\eta^4\text{-ArH})$ bond energies. Specifically, the intrinsic “snap” $\text{Mo}-(\eta^6\text{-ArH})$ BDEs *decrease* in the sequence benzene ($67.1 \text{ kcal mol}^{-1}$) > naphthalene ($62.2 \text{ kcal mol}^{-1}$) \approx anthracene ($64.0 \text{ kcal mol}^{-1}$), whereas the $\text{Mo}-(\eta^4\text{-ArH})$ BDEs exhibit the opposite trend and *increase* in the sequence benzene ($64.4 \text{ kcal mol}^{-1}$) < naphthalene ($77.5 \text{ kcal mol}^{-1}$) < anthracene ($82.1 \text{ kcal mol}^{-1}$). As a result of these opposing trends, of which the latter is dominant, the oxidative addition of H_2 becomes more exothermic in the sequence benzene < naphthalene < anthracene.

A knowledge of metal-hydrogen BDEs is central to understanding and predicting reaction pathways involving H_2 , but such values are rather limited. For this reason, we sought to determine the average Mo-H BDE for $(\eta^4\text{-AnH})\text{Mo}(\text{PMe}_3)_3\text{H}_2$ *via* the temperature dependence of the equilibrium constant (K) for oxidative addition of H_2 to $(\eta^6\text{-AnH})\text{Mo}(\text{PMe}_3)_3$, from which a value of $59.1 \text{ kcal mol}^{-1}$ was obtained. In addition to measuring the Mo-H BDE, we have also determined the equilibrium isotope effect (EIE) for oxidative addition of H_2 and D_2 to $(\eta^6\text{-AnH})\text{Mo}(\text{PMe}_3)_3$ because a knowledge of EIEs is essential for interpreting kinetic isotope effects associated with multistep reactions. Most interestingly, and in contrast to previous reports pertaining to the EIE for oxidative addition of H_2 and D_2 to a single metal center, the EIE for oxidative addition of H_2 and D_2 to $(\eta^6\text{-AnH})\text{Mo}(\text{PMe}_3)_3$ is *normal* over virtually the entire temperature range ($30 - 90^\circ\text{C}$) measured. DFT calculations demonstrated that the origin of this unusual result is the existence of low energy Mo-H stretches for $(\eta^4\text{-AnH})\text{Mo}(\text{PMe}_3)_3\text{H}_2$.

3. Aqua-Hydride Complexes of Molybdenum and Tungsten

Hydride and organometallic complexes that are stable to water are of considerable relevance with respect to aqueous phase organometallic chemistry and its application to green chemistry. However, aqua and hydride ligands represent unusual combinations because hydride derivatives are typically thermodynamically unstable with respect to hydrolysis to yield either hydroxo or oxo complexes. Of relevance to this area, we have synthesized aqua-dihydride complexes of molybdenum and tungsten, namely $\text{M}(\text{PMe}_3)_3(\kappa^1\text{-O}_2\text{CR})_2(\text{OH}_2)\text{H}_2$ ($\text{M} = \text{Mo}, \text{W}$), and have thereby demonstrated that such aqua-dihydride complexes may be isolated.

DOE Interest

The mission of the Catalysis and Chemical Transformations program of the Department of Energy is to support basic research to understand the chemical aspects of catalysis because “Catalysts are crucial to energy conservation in creating new, less-energy-demanding routes for the production of basic chemical feedstocks and value-added chemicals. Catalysts are also indispensable for processing and manufacturing fuels that are a primary means of energy storage.” Our research focuses on several issues pertaining to catalysis that belong to the above mission, such as hydrodesulfurization and hydrogenation.

Future Plans

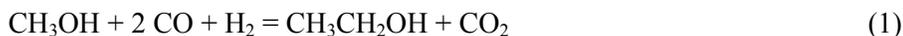
The principal objectives of the research to be performed in the next budget period will be to use calixarene and sulfur-derivatized calixarene ligands to synthesize molybdenum compounds with oxo and sulfur-rich coordination environments that are intended to mimic aspects of heterogeneous catalysts, such as hydrodesulfurization and hydrodenitrogenation catalysts.

Publications Citing DOE Support

1. “Kinetic and Equilibrium Deuterium Isotope Effects for C–H Bond Reductive Elimination and Oxidative Addition Reactions Involving the *Ansa*–Tungstenocene Methyl–Hydride Complex $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$ ” by Kevin E. Janak, David G. Churchill, and Gerard Parkin, in *Activation and Functionalization of C–H Bonds, ACS Symposium Series* **2004**, 885, 86-104.
2. “Molybdenocene Trihydride Complexes: Influence of a $[\text{Me}_2\text{Si}]$ *Ansa* Bridge on Classical versus Nonclassical Nature, Stability with Respect to Elimination of Dihydrogen, and Acidity” by Kevin E. Janak, Jun Ho Shin, and Gerard Parkin, *J. Am. Chem. Soc.* **2004**, 126, 13054-13070.
3. “Theoretical Investigation of the Metal-Metal Interaction in Dimolybdenum Complexes with Bridging Hydride and Methyl Ligands” by Mu-Hyun Baik, Richard A. Friesner and Gerard Parkin, *Polyhedron* **2004**, 23, 2879-2900.
4. “Chiral *Ansa* Zirconocene Compounds with $[\text{Me}_2\text{Si}]$ and $[\text{Me}_4\text{Si}_2]$ Bridges and with *t*-Butyl Ring Substituents: Synthesis and Structural Characterization of the *Racemo* Complexes *rac*- $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_2-2,4-\text{Bu}^t_2)_2]\text{ZrCl}_2$ and *rac*- $[\text{Me}_4\text{Si}_2(\text{C}_5\text{H}_2-2,4-\text{Bu}^t_2)_2]\text{ZrCl}_2$ ” by Cary E. Zachmanoglou, Jonathan G. Melnick, Brian M. Bridgewater, David G. Churchill, and Gerard Parkin *Organometallics* **2004**, 24, 603-611.
5. “*Ansa*–Titanocene Pyrrolyl Complexes: The Synthesis and Structural Characterization of $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Ti}(\text{NC}_4\text{H}_4)\text{X}$ (X = H, Me, Cl and NC_4H_4) and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{Me}_3\text{CH}_2)]\text{Ti}(\text{NC}_4\text{H}_4)$ ” by Hyosun Lee, Jeffrey B. Bonanno, Brian M. Bridgewater, David G. Churchill, and Gerard Parkin, *Polyhedron* **2005**, 24, 1356-1365.
6. “Synthesis and Structural Characterization of $\text{M}(\text{PMe}_3)_3(\text{O}_2\text{CR})_2(\text{OH}_2)\text{H}_2$ (M = Mo, W): Aqua–Hydride Complexes of Molybdenum and Tungsten” by Guang Zhu and Gerard Parkin, *Inorg. Chem.* **2005**, 44, 9637-9639.
7. “Carbon–Hydrogen *versus* Carbon–Chalcogen Bond Cleavage of Furan, Thiophene and Selenophene by *Ansa* Molybdenocene Complexes” by David G. Churchill, Brian M. Bridgewater, Guang Zhu, Keliang Pang, and Gerard Parkin, *Polyhedron* **2006**, 25, 499-512.
8. “Hydride, Halide, Methyl, Carbonyl, and Chalcogenido Derivatives of Permethylmolybdenocene” by Jun Ho Shin, David G. Churchill, Brian M. Bridgewater, Keliang Pang, and Gerard Parkin, *Inorg. Chim. Acta* in press.
9. “Oxidative Addition of Dihydrogen to $(\eta^6\text{-Arene})\text{Mo}(\text{PMe}_3)_3$ Complexes: Origin of The Naphthalene and Anthracene Effects” by Guang Zhu, Kevin E. Janak, Joshua S. Figueroa, and Gerard Parkin, *J. Am. Chem. Soc. ASAP*.
10. “A Normal Equilibrium Isotope Effect For Oxidative Addition of H_2 to $(\eta^6\text{-Anthracene})\text{Mo}(\text{PMe}_3)_3$ ” by Guang Zhu, Kevin E. Janak and Gerard Parkin, *Chem. Commun.* Submitted.

selective homogeneous catalytic ethanol synthesis chemistry discovered in the Fluid Catalysis Program under BES/Chemical Sciences funding.

The catalytic cycle for an early version of this chemistry is shown in Fig. 1. Unlike the conventional $\text{HCo}(\text{CO})_4$ catalyzed homologation process first reported by Wender, et al, that carbonylates methanol to a mixture of water and higher alcohols in a proposed carbonium ion mechanism, the new catalytic chemistry depicted in Fig.1 produces ethanol in a selective $\text{S}_{\text{N}}2$ process without the coproduction of significant amounts of either water or higher alcohols. The $\text{HFe}(\text{CO})_4^-$ catalyzed reaction occurs in the temperature range of 180-220 °C at pressures ($3\text{CO} + \text{H}_2$) near 300 atm in accord with stoichiometry of Eqn. 1.



The rate determining step in the catalytic reaction (nucleophilic attack of $\text{HFe}(\text{CO})_4^-$ on $(\text{CH}_3)_4\text{N}^+$) was selected for separate study and in 1-methyl-2-pyrrolidinone solvent was determined to have an enthalpy and entropy of activation of 44 kcal/mol and +17 eu, respectively. The catalytic approach used for the original iron based catalyst works well with a variety of metal carbonyls, some of which function especially well in combination with each other. Our future activities are focused on the mechanism of synergistic effects in the improved heterobimetallic catalysts.

DOE Interest

a. In catalytic ethanol synthesis

Our research on homogeneous carbonylation chemistry produced a selective catalytic ethanol synthesis route that is timely in today's energy circumstances. Our recent work and planned future activities on this system are aimed at uncovering the mechanism of an interesting and unusual heterobimetallic synergistic catalytic effect in this system wherein a mixture of iron and manganese carbonyl ions was demonstrated to be more active than either of the complexes when used separately. We believe that understanding of such synergistic effects is important because this knowledge might lead to new possibilities for catalyst design.

b. In related activities

In earlier high-pressure kinetic studies, the Fluid Catalysis Program demonstrated the first mononuclear catalyst for homogeneous carbon monoxide hydrogenation and determined the rate law and the currently accepted mechanism for the $\text{HCo}(\text{CO})_4$ catalyzed reaction (see F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Sixth Edition, 1999, p. 1253). More recently, in research aimed at experimental and theoretical parameterization of the reaction coordinates of this mechanistically important reaction, it conducted kinetic measurements on homogeneous catalytic carbon monoxide hydrogenation, in situ, in an NMR probe for the first time. Also, supercritical carbon monoxide was used as a gas-like reaction medium (to aid in the theoretical calculations) for the first time in homogeneous CO hydrogenation.

This program pioneered the use of homogeneous catalysts in supercritical fluids and invented supercritical hydroformylation catalysis. To conduct in situ spectroscopic studies of supercritical and other high-pressure industrial process chemistry, it developed the toroid-pressure probe, the R&D 100 Award winning toroid-cavity imager, and most recently, a magic-angle-spinning toroid-cavity probe that imparts the high sensitivity and imaging capability of toroids to high-resolution solid-state NMR spectroscopy. This program recently reported the first high-pressure NMR characterization of reverse micelles in supercritical carbon dioxide.

Future Research

In earlier work we had shown that $\text{Co}_2(\text{CO})_8$ catalyzes the hydrogenation of $\text{Mn}_2(\text{CO})_{10}$ by forming a rapidly hydrogenated heterobimetallic species, $(\text{CO})_5\text{MnCo}(\text{CO})_4$, which quickly reached equilibrium concentrations under the reaction conditions and could be observed in the solutions at high pressures using both ^{55}Mn and ^{59}Co NMR spectroscopy. In solutions containing both carbonyls, the catalytic effect is due to the fact that the two step process of forming the mixed heterobimetallic dimer and its hydrogenation to form $\text{HMn}(\text{CO})_5$ is faster than the direct reaction of hydrogen with $\text{Mn}_2(\text{CO})_{10}$. Hydrogenation of the mixed dimer also produces $\text{HCo}(\text{CO})_4$, which reversibly loses hydrogen to produce $\text{Co}_2(\text{CO})_8$, thereby regenerating the catalyst. We suspect that chemistry of this sort is responsible for the heterobimetallic synergistic catalyst effect observed in the mixed $\text{HFe}(\text{CO})_4/\text{Mn}(\text{CO})_5$ ethanol synthesis system. We will test this hypothesis by searching for mixed metallic intermediates and examining their fate kinetically using operando spectroscopic methods at high pressures and temperatures.

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Oc Hee Han, Seen Ae Chae, Rex E. Gerald II, Robert J. Klingler, Jerome W. Rathke, and Klaus Woelk, "Hybrid Coil NMR Detector," *J. Kor. Mag. Reson. Soc.*, submitted for publication.

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R. E. Gerald II, R. J. Klingler, and J. W. Rathke, "Nuclear Magnetic Resonance Imaging Apparatus," US Patent # 6,674,283 issued January 6, 2004

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R. E. Gerald II, J. Sanchez, and J. W. Rathke, "Video Toroid Cavity Imager," US Patent # 6,774,635 issued August 10, 2004

R. E. Gerald II and J. W. Rathke, "Passively Shimmied Principal Detector Element for Toroid Cavity Detector NMR Probes," US Patent # 6,788,064 issued September 7, 2004

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Supramolecular Ensembles with Functionality: Organometallic Cyanocages

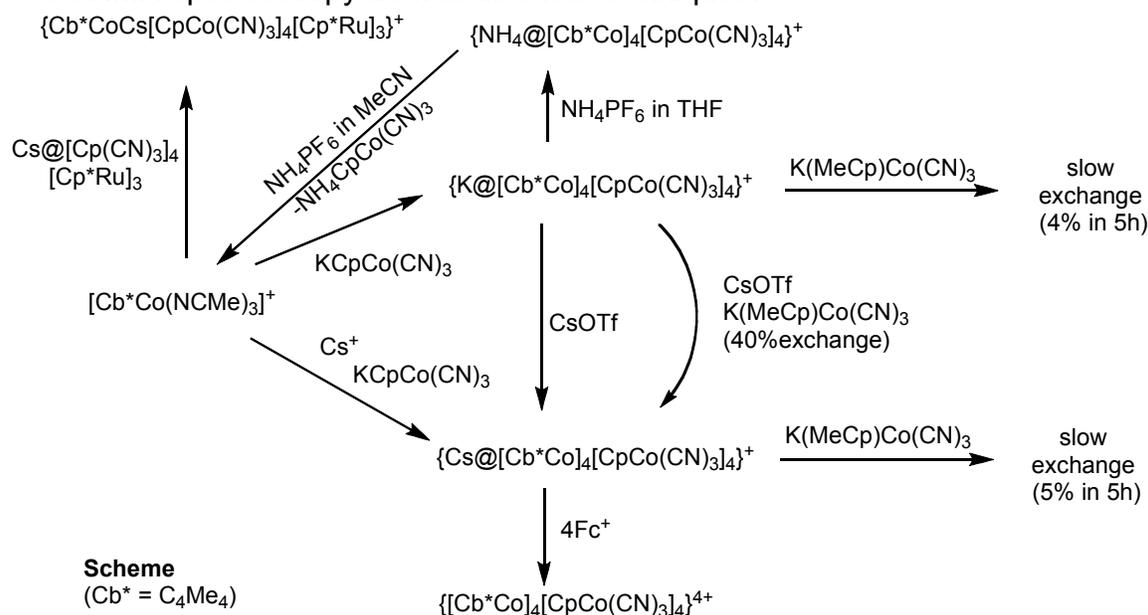
Students: Julie Boyer, Zachariah Heiden, Haijun Yao
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Goal

Develop new classes of supramolecules as supports, separation agents, and catalysts. Investigate the reactions of small molecules with metal-ligand ensembles as these processes relate to energy producing technologies.

Recent Progress

Electro-active Cyanometallate Boxes: The rigidity of cyanometallate cages enables selective host-guest behavior, which is conceptually relevant to the separation of radioactive $^{137}\text{Cs}^+$ from solutions containing excess K^+ . The complementation of these supramolecular systems with redox behavior is topical, e.g. Plenio described a ferrocene-modified cryptand that exhibits a 80 mV difference when complexed to K^+ vs Cs^+ and a bis(calix[4]diquinone) sequestrant displays a 60 V difference for its K^+ vs Cs^+ derivative. For this project, we use of the Cb^*Co^+ fragment ($\text{Cb}^* = \eta^4\text{-C}_4\text{Me}_4$) for the construction of electro-active cages. Condensation of $[\text{N}(\text{PPh}_3)_2][\text{CpCo}(\text{CN})_3]$ and $[\text{Cb}^*\text{Co}(\text{NCMe})_3]\text{PF}_6$ in the presence of K^+ gives the deep purple salt $\{\text{K}[\text{Cb}^*\text{Co}]_4[\text{CpCo}(\text{CN})_3]_4\}\text{PF}_6$, $[\text{KCo}_8]\text{PF}_6$. The analogous heterometallic cage $\{\text{K}[\text{Cp}^*\text{Rh}(\text{CN})_3]_4[\text{Cb}^*\text{Co}]_4\}\text{PF}_6$ ($[\text{KRh}_4\text{Co}_4]^+$) was also prepared. These species readily bind Cs^+ as indicated by ^{133}Cs NMR spectroscopy as well as other techniques.



Chemical oxidation of MeCN solutions of $[MCo_8]^+$ ($M = K, Cs$) with four equiv of $FcPF_6$ liberates the free alkali metal ion, producing $[Co_8]^{4+}$. The oxidation-induced dissociation of Cs^+ from $[CsCo_8]^+$ is chemically reversed using $CsOTf/Cp_2Co$. Cation recognition by $[Co_8]$ and $[Rh_4Co_4]$ cages were investigated electrochemically. $\Delta E_{1/2}$ for K^+ vs Cs^+ can be further amplified using non-polar solvents and larger, less coordinating electrolytes. Dichloroethane solutions with $NBu_4B(C_6H_3-3,5-(CF_3)_2)_4$ electrolyte displayed a 180 mV difference between $[KCo_8]^+$ (-0.69 V vs. Cp_2Fe) and $[CsCo_8]^+$ (-0.51 V, vs. Cp_2Fe).

Cyanometallates with Lewis Acidic Sites: A series of molecular boxes have been prepared wherein the box is robust but one vertex bears kinetically labile sites. Two simple examples are $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3[MNCMe]\}PF_6$ ($M = Ag, Cu$) wherein the MeCN ligands can be displaced by many ligands. Still more interesting are $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3[M(NCMe)_3]\}^{2+}$ ($M = Ni, Fe$). These species appear to serve a building blocks to still larger supramolecules. Similarly, $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(PPh_3)_2X\}^z$ cages were generated, with $X = H, Cl,$ and MeCN. These are the first low-symmetry (C_s) cyanometallate boxes, as indicated by NMR spectroscopy. The catalytic properties of these species is under study.

New Cyanometallate Building Blocks: The preparation of series of Ru-CN compounds is intended to uncover new classes of ensembles that will be reactive toward small molecules. Representative target include $[Ru(CN)_n(PPh_3)_{5/6-n}]^{(n-2)-}$. The higher cyanides have been prepared, where ensemble formation is precluded, and current focus is on the di- and tricyanides. Surprisingly little research has been conducted on other catalytically relevant metal centers, e.g. the Rh(I)-CN- PPh_3 and Pt(0)-CN- PPh_3 systems.

Cage Assembly Pathways: Experiments continue to examine the “design rules” underpinning the formation of cyanometallate cages. Of particular interest is the dependence of cage assembly pathways on initial conditions. For example, one can prepare two distinct cages with the formula $[Cp^*Rh(CN)_x]_n^{z+}$ where $x = 1.5$ ($n = 6, z = 3$) or 1.7 ($n = 7, z = 2$). Depending on how the cage is nucleated, assembly proceeds in a manner that preserves the ordering of the Rh-CN-Rh linkages and the open structure or proceeds with disordered CN ligands and produces more condensed structures.

DOE Interest

Our program aims at three aspects of the DOE program: discovery of new compositions relevant to small molecule separations, remediation of radio-wastes, and multimetallic arrays relevant to catalysis, especially H_2 processing. The separation of Cs^+ and related heavy elements is an important component of radio-waste processing. This technology must be underpinned by basic research aimed at uncovering novel ion binding models that could define new host-guest interactions or which could define the fundamental interactions responsible for ion selectivity. Second, collections of metal centers behave in ways that single

metals cannot. These cages can form three-dimensional structures that bind substrates in unusual ways leading to selective sequestration or conversion of substrates. A traditional means of linking metals involves cyanide, but this approach has been little explored in the context of organometallic chemistry. The ultimate goal of this work is to develop hybrid inorganic-organic containers that shape-selectively bind molecules for conversion into useful products.

Future Plans

- Develop design rules leading to ordered multimetallic arrays using cyano-building blocks.
- Prepare planar multi-metallic arrays using cyanide and analogues for use as building blocks to nanostructured catalysts and separation agents.
- Using cyanide or other multiply bonded ligands, develop new motifs for H₂ activation and oxidation.

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- "Bis[(1,4,7,10,13,16-hexaoxacyclooctadecane)potassium] carbonyltricyanorhodate(I) acetonitrile solvate" Whaley, C. M.; Rauchfuss, T. B.; Wilson, S. R. *Acta Cryst. C.* **2005**, E61, m1918–m1919.
- "Organo-Tricyanoborates as Tectons: Illustrative Coordination Polymers Based on Copper (I) Derivatives" Yao, H.; Kuhlman, M. L.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2005**, *44*, 6256-6264.
- "Competing H-H, S-S, and M-M Bond Formation in the "Shape-Shifting" Cluster [Ru₄S₃(arene)₄]²⁺" Kuhlman, M. L.; Rauchfuss, T. B. *Angew. Chem. Int. Ed.* **2004**, *43*, 6742-5.
- "Condensation of [Ru₃S₂(cymene)₃]²⁺ with Sulfide to Give the Dendritic Cluster [Ru₉S₈(cymene)₆]²⁺" Kuhlman, M. L.; Rauchfuss, T. B. *Organometallics*, **2004**, *23*, 5085-87.
- "Structural and Mechanistic Studies on Ion Insertion into the Molecular Box [CpCo(CN)₃]₄[Cp*Ru]₄" Ramesh, M.; Rauchfuss, T. B. *J. Organometal. Chem.* **2004**, *689*, 1425-30.
- "Synthesis and Characterization of the Hexagonal Prismatic Cage {THFC[PhB(CN)₃]₆[Cp*Rh]₆]⁶⁺" Kuhlman, M. L.; Yao, H.; Rauchfuss, T. B. *Chem. Commun.* **2004**, 1370-1.
- "Hybrid Cluster-Cages Formed via Cyanometallate Condensation: CsCo₄Ru₆S₂(CN)₁₂, Co₄Ru₉S₆(CN)₉, and Rh₄Ru₉S₆(CN)₉ Frameworks" Kuhlman, M. L.; Rauchfuss, T. B. *Inorg. Chem.* **2004**, *43*, 430-435.
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In Situ SAXS Studies of Polymer-Clay Nanocomposites

(Nanoporous Silicate Catalyst Design – FWP 54510)

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Abstract

Because membranes in general are important to catalysis and because adding polymer can change drastically the characteristics of layer silicate clay supports, an investigation into whether the characteristics of polymer-clay nanocomposite films (PCNs) can lead to unique metal nanocluster morphology was initiated. Self-supporting, transparent films were obtained upon slowly evaporating aqueous mixtures of synthetic silica-hectorite, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, and polyethylene oxide (PEO). The films were reduced under H_2 at 120-150°C. XRD showed development of Pt(0) peaks upon reduction; a lineshape analysis showed particles from 3.8 nm to 7.5 nm depending upon processing conditions. These values were confirmed by TEM, and a high dispersion of the metal throughout the matrix is evident. The spherical Pt(0) nanoparticles are dispersed primarily within the external polymeric matrix. An in situ SAXS study of the reduction process has been performed. Under an inert, non-reducing atmosphere, the shape of the scattering curve for the Pt(II)-containing film does not change as the temperature is raised from 30°C to 150°C. Under H_2 , however, the shape of the scattering curves visually changes between 100-120°C, presumably as the Pt(II) ions reduce and coalesce. Two structural levels are needed to fit these curves using the general unified fit equation, with two subsequent R_g values. One of the R_g values corresponds to a diameter of 4.8-5.1 nm. Since this value correlates to those determined via XRD and TEM, it is assumed to arise from the reduced Pt(0) nanoparticles that form in situ during reduction. This experiment demonstrated that SAXS alone (without anomalous methods) can be used to follow the growth of a metal nanoparticle in situ. A similar study was also carried out using the grazing incidence SAXS method. This served to show that studies on the surfaces of PCN films are possible. The GISAXS data were acquired as the temperature was raised, and horizontal cuts at $q_z = 0.34 \text{ \AA}^{-1}$ were taken. From these data, the R_g 's were calculated and plotted vs. temperature. The data reveal that, at low wt% Pt, the nanoparticles reach and maintain a maximum size (2.9-3.4 nm). At high loadings, however, the nanoparticles continue to coalesce past 200°C. For the low loading samples, in PCNs with less polymer (PEO:clay = 1.0) the Pt(0) nanoparticles are larger at 3.4 nm, while with more polymer present (PEO:clay = 1.2), the sizes reach only 2.9 nm. This suggests that there can be control over particle size depending upon certain synthetic parameters.

High Temperature Chemistry of Aromatic Hydrocarbons

Students: Bancu, M.; Donovan, P.; Hill, T.; Jackson, E.; Peng, L.; Tsefrikas, V.; Xue, X.

Collaborators: de Meijere, A.; Petrukhina, M. A.; Hoffmann, R.; Duncan, M. A.; Rabinovitz, M.; Parish, C.; Lovas, F. J.; McMahon, R. J.; Grabow, J.-U.; Mack, J.; Kuczkowski, R. L.; Nakamura, E.; Märk, T. D.; Hopf, H.; Tykwinski, R. R.

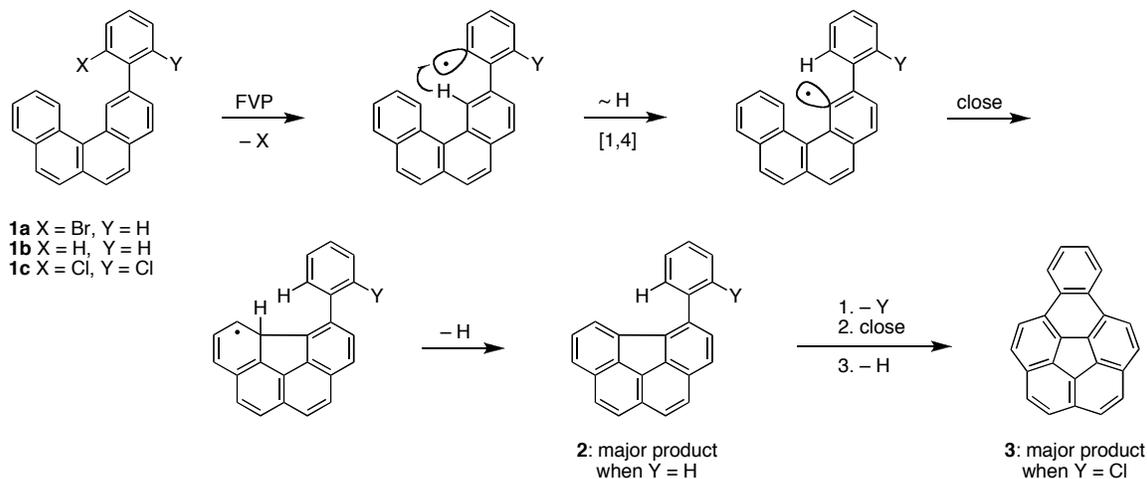
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Goal

The primary goal of this research is to uncover all the principal reaction channels available to polycyclic aromatic hydrocarbons (PAHs) at high temperatures in the gas phase and to establish the factors that determine which channels will be followed in varying circumstances. New structure-property relationships for PAHs are also studied.

Recent Progress

Translocations of hydrogen atoms in a 1,4-manner from the 2-position in biphenyl or larger biaryl radicals to the 2'-position have not previously been reported. Judging from the calculated free energy of activation, however, one would expect this rearrangement to occur quite readily at flame temperatures. To demonstrate the feasibility of the 2 → 2' hydrogen translocation at high temperatures in the gas phase, we have synthesized the brominated hydrocarbon **1a** and subjected it to flash vacuum pyrolysis (FVP). As expected (see scheme), hydrocarbon **2** was formed as the major product, presumably by the pathway shown, which involves a 1,4-translocation of hydrogen. Control experiments with the same starting material that lacks the bromine atom (**1b**) confirm that very little 5-membered ring closure occurs without the orchestrated generation of a radical intermediate to trigger the cascade of bonding changes.



In light of these results, we explored the use of a hydrogen 1,4-translocation rearrangement to initiate a double cyclization sequence from FVP of **1c**. The outcome of this experiment constituted a short new synthesis of benzocorannulene (**3**), a bowl-shaped C₂₄H₁₂ fullerene subunit.

Details concerning this representative project can be found in publication no. 11. Results from other projects can be found in the other publications listed.

DOE Interest

An understanding of the fundamental molecular transformations, rearrangements, and interconversions of PAHs at high temperatures in the gas phase, as revealed by careful studies on small, well-designed, molecular systems, provides insights into the underlying chemistry of many important processes that are more complex, such as the generation of energy by the combustion of fossil fuels, the uncatalyzed gasification and liquefaction of coal, the production of fullerenes in fuel-rich flames, and the formation of soot and carcinogenic pollutants in smoke. The rational control of any of these processes, whether it be the optimization of a desirable process or the minimization of an undesirable one, requires a clear knowledge of the basic chemistry that governs the fate of the species involved.

Future Plans

Experiments designed to increase our understanding of thermal cyclodehydrogenation reactions are now occupying much of our attention. In fuel-rich flames, the fusion of simple hydrocarbons into highly condensed, carbon-rich products such as fullerenes, soot particles, and discrete PAHs (*e.g.*, the carcinogenic benzo[*a*]pyrene) is accompanied by the loss of many hydrogen atoms. Though the exact sequence of events leading to these products is not known in detail, much of the hydrogen is almost certainly lost in conjunction with the generation of new rings by *intramolecular* C–C bond formation (“cyclodehydrogenation”). Surprisingly little is known about the mechanism(s) of these ubiquitous high temperature transformations. Experimental studies are virtually nonexistent, and very little computational work has been published on such reactions.

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- 3) “Dicyclobuta[*de,ij*]naphthalene and Dicyclopenta[*cd,gh*]pentalene,” Macaluso, M.; Parish, C.; Hoffmann, R.; Scott, L. T. *J. Org. Chem.* **2004**, *69*, 8093-8100.
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- 5) "Unprecedented Complexation of Two Transition Metals to the Concave Surface of a Geodesic Polyarene: {[Rh₂(O₂CCF₃)₄]₃(Dibenzo[a,g]corannulene)₂}," Petrukhina, M. A.; Andreini, K. W.; Tsefrikas, V. M.; Scott, L. T. *Organomet.* **2005**, *24*, 1394-1397.
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CATALYSIS SCIENCE INITIATIVE: Design of heterogeneous catalysts for the low temperature metathesis of unfunctionalized and functionalized olefins

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Postdoctoral fellows: Naseem Ramsayhe, Swarup Chattopadhyay

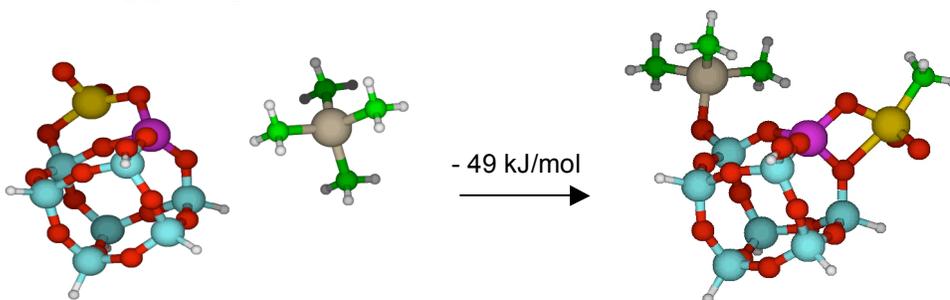
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Goals

Supported Re oxide catalysts show particular promise in large-scale olefin metathesis, because they are active at much lower temperatures and are more functional group-tolerant than catalysts based on oxides of either Mo or W. These properties make them potentially useful in liquid phase reactions involving biorenewable feedstocks, such as seed oils. One goal of our project is to create fundamental knowledge about how the active sites form spontaneously in the metal oxide precursors, and how they are deactivated, particularly in the presence of promoters (alkyltin compounds) and poisons (functionalized olefins). This knowledge will be used to design catalysts with increased metathesis activity, better long-term stability and higher functional group tolerance.

Recent Progress

Role of the SnMe₄ promoter. The well-known Re₂O₇/Al₂O₃ catalyst performs metathesis of functionalized olefins in the presence of an alkyltin promoter. We showed previously, by computational analysis and experiment, that one of the effects of the SnMe₄ promoter is the *in situ* formation of CH₃ReO₃. We have evaluated the activities of SnMe₄-promoted Re₂O₇/Al₂O₃ and CH₃ReO₃/SiO₂-Al₂O₃ for the homometathesis of propylene under identical reaction conditions. The reactivities of the catalysts prepared by either the heterogeneous or the organometallic grafting route are identical. Thus we infer that the active site on the SnMe₄-promoted Re₂O₇/Al₂O₃ catalyst, *Scheme 1*, is the same as that formed during grafting of CH₃ReO₃.



Scheme 1. The reaction of a grafted perrhenate with SnMe₄, to give grafted trimethyltin and grafted MeReO₃, is energetically favorable. Silica-alumina is modeled with an aluminosilsesquioxane monosilanol cube. Color scheme: Re (yellow), Al (purple), Si (blue), O (red), C (green), H (white).

We investigated the fate of SnMe_4 by ^{119}Sn MAS NMR and Sn K-edge EXAFS (not shown). Both revealed only the presence of $\equiv\text{SiOSnMe}_3$ sites. We also observed methane evolution upon treatment of silica-alumina with SnMe_4 . The SnMe_4 promoter therefore has two roles: (1) it generates CH_3ReO_3 *in situ* by displacing the surface perrhenates (*Scheme 1*); and (2) it caps the remaining surface hydroxyl sites that cause side-reactions of the olefins. Neither of these roles requires a direct interaction between Sn and Re in the active site. Consequently, we reasoned that it should be possible to reproduce the effect of the Sn promoter with other reagents that do not preclude catalyst regeneration (as the alkyltin reagents do). *In situ* generation of CH_3ReO_3 was accomplished by treating a perrhenate catalyst with AlMe_3 , which methylates Re and caps the hydroxyl sites. The resulting catalyst was active for propylene metathesis at 0°C .

Characterization of the supported organometallic catalyst. CH_3ReO_3 is not itself a catalyst for olefin metathesis. Understanding the nature of the CH_3ReO_3 -solid oxide interaction is the first step towards explaining how heterogeneous rhenium-based catalysts acquire their unique metathesis activity, since the oxide acts not only as a support but also as a catalyst activator. The dramatic effect of the support in our propylene homometathesis benchmarking reaction is shown in *Figure 1*.

We investigated the nature of the CH_3ReO_3 sites on silica-alumina using a combination of spectroscopic and computational analyses. Two ^{13}C signals appear at high Re loading, *Figure 2*. The site responsible for the peak at ca. 20 ppm is also seen on dehydrated silica,

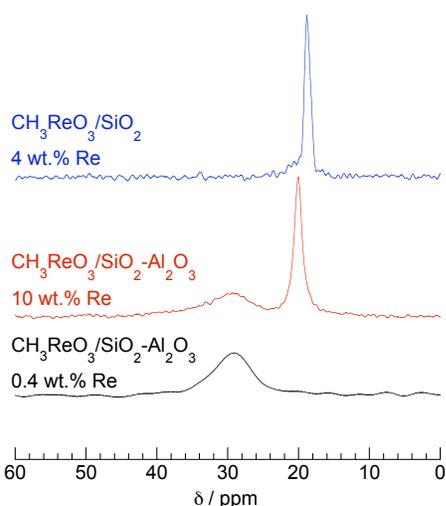


Figure 2. ^{13}C CPMAS spectra for $^{13}\text{CH}_3\text{ReO}_3$ grafted onto dehydrated silica and silica-alumina.

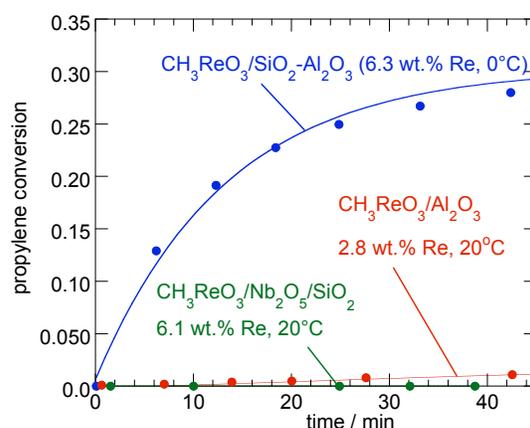


Figure 1. Rate of propylene homometathesis for CH_3ReO_3 on different oxide supports. Reactions were performed in a batch reactor with 10 mg catalyst at the specific temperature. Conversion is defined as $2\text{P}_{\text{C}_2\text{H}_4}/\text{P}_{\text{C}_3\text{H}_6,0}$.

which yields an inactive catalyst. In contrast, the spectrum of CH_3ReO_3 on dehydrated silica-alumina at low Re loading (< 1 wt.% Re) consists of a single peak at ca. 32 ppm, corresponding to reasonably uniform sites. This material is also the most active catalyst. By inference, the peak at 32 ppm represents the metathesis active site(s).

The molecular-level structure of the active species in the ‘single-site’ material was elucidated by EXAFS at the Re L_3 edge, *Figure 3*. The spectrum shows clear evidence for a well-defined association of CH_3ReO_3 with Al sites on the silica-alumina surface. The curve-fit, *Table 1*, shows that Re is five-coordinate. The $\text{Re}=\text{O}$ group interacts with an $\text{Al}-\text{O}_s$ group on the silica-alumina surface via *two* Lewis acid-base interactions ($\text{Re}\leftarrow\text{O}$ and $\text{O}_s\rightarrow\text{Al}$).

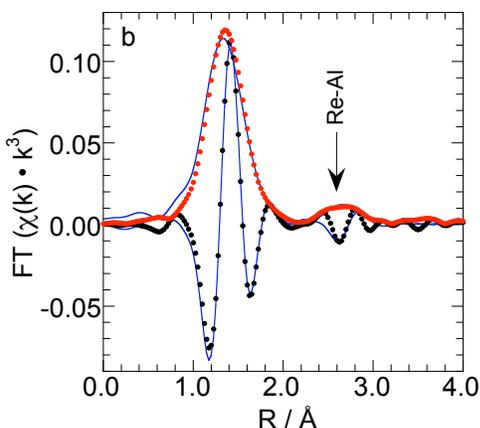


Figure 3. EXAFS data (red/black) and curve fit (blue) for CH_3ReO_3 on silica-alumina (1.3 wt.% Re).

path	EXAFS curve-fit			DFT-calculated distance
	N	R (Å)	σ^2 (Å ²)	(Å)
Re=O	2	1.69	0.0012	1.678, 1.681
Re=OAI	1	1.79	0.0016	1.789
Re-C	1	2.07	0.0012	2.096
Re-O _{support}	1	2.13	0.0056	2.172
Re-Al	1	3.06	0.0054	3.044

Table 1. Comparison of EXAFS path lengths (Å) for CH_3ReO_3 grafted onto dehydrated silica-alumina, with DFT-calculated bond distances for CH_3ReO_3 grafted onto an aluminosilsesquioxane cube.

Insight into the origin of Lewis acidity in silica-alumina. Quantitative ^{27}Al MAS NMR gave no direct insight into the nature of the Lewis acid site that binds and activates the catalyst. Over 90% of the signal disappeared when the silica-alumina was dehydrated, and was not restored upon grafting CH_3ReO_3 at any loading. Consequently, we inferred that the required Lewis acid sites are likely to be distorted from tetrahedral geometry.

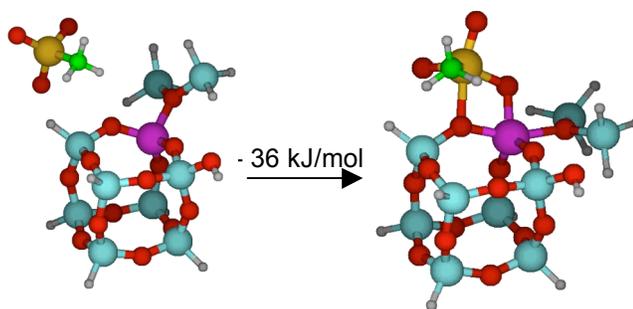


Figure 4. DFT-calculated reaction energies and structures for the interaction between a siloxane-capped aluminosilsesquioxane monosilanol cube and CH_3ReO_3 .

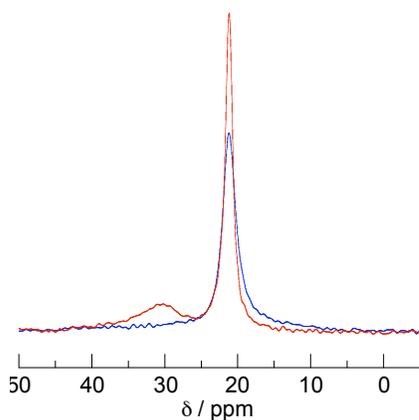


Figure 5. Single-pulse ^{13}C MAS NMR spectra for CH_3ReO_3 on silica-alumina (10 wt% Re), recorded under MAS conditions (12 kHz, red line); and static conditions (blue line), with the same number of scans.

Table 1 shows the agreement between the independently-developed EXAFS and DFT model parameters for both Lewis acid-base interactions ($\text{Re} \leftarrow \text{O}$ and $\text{O}_s \rightarrow \text{Al}$). The Lewis acidity of silica-alumina therefore originates in the distortion of the four-coordinate Al sites upon dehydration. These sites appear to become five-coordinate upon interaction with a Lewis base.

Insight into the origin of site multiplicity in supported Re catalysts. Alternatives to the most favorable grafting site, Figure 4, explain the nature of the inactive CH_3ReO_3 sites on silica-alumina. Maximum metathesis activity occurs at ca. 1 wt.% Re, with no increase for loadings up to 10 wt% Re. The presence of a ^{13}C CPMAS NMR signal at 20 ppm is associated with the inactive sites. This signal is surprisingly narrow for a solid-state NMR spectrum, suggesting that these sites possess high mobility. Indeed, much of this signal persists even under static (non-spinning) conditions, Figure 5. Yet the species responsible for this signal interacts strongly enough with the silica-alumina surface to resist desorption under dynamic vacuum (10^{-4} Torr) at room temperature.

Hydrogen-bonding is clearly evident in the FTIR spectrum of grafted CH_3ReO_3 at these loadings. DFT calculations showed that CH_3ReO_3 forms a stable adduct with the aluminosilsesquioxane cube by hydrogen-bonding via an oxo ligand to the silanol corner, *Figure 6a*. The acidity of the silanol (and hence the strength of the hydrogen-bond to CH_3ReO_3 , is very sensitive to the coordination environment at the neighboring Al. Thus the presence of CH_3ReO_3 coordinated to Al renders the adjacent silanol acidic enough to form a very strong hydrogen-bonding interaction, *Figure 6b*. H-bonded CH_3ReO_3 is not desorbed until 80°C (10^{-4} Torr).

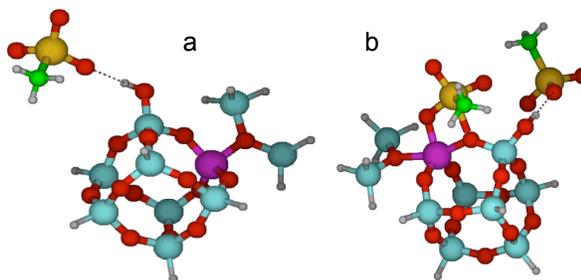


Figure 6. DFT-calculated structures for CH_3ReO_3 hydrogen-bonded to silica-alumina.

Metathesis rate law and selectivity.

Kinetic studies of the metathesis reaction were undertaken using propylene homometathesis as a convenient standard with which to compare different catalyst formulations. The rate is described very simply by a single parameter, k_1 , in reversible pseudo-second-order kinetics, eq 1:

$$P(t) = P_{eq} + 2P_{eq}(P_0 - P_{eq}) / (2P_{eq} - P_0 + P_0 e^{\frac{2k_1 t \cdot P_0 P_{eq}}{(P_0 - P_{eq})}}) \quad (1)$$

where $P(t)$ is the partial pressure of propene at time t ; P_0 is its initial partial pressure; P_{eq} is its equilibrium partial pressure; and k_1 is the forward rate constant (with $k_{-1} = k_1/K$ as the reverse rate constant). Capping the surface hydroxyls with hexamethyldisilazane, $(\text{Me}_3\text{Si})_2\text{NH}$, prior to adsorption of the catalyst resulted in *no change in metathesis activity*. This is reasonable in view of our finding that the catalyst is activated by its grafting onto Lewis acid sites. However, the capped catalyst does show *increased metathesis selectivity*. Furthermore, the capped catalyst shows *no deactivation* in subsequent additions of propylene, *Figure 7*. By comparison, the uncapped catalyst deactivates strongly between additions of substrate, just like the heterogeneous $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ system.

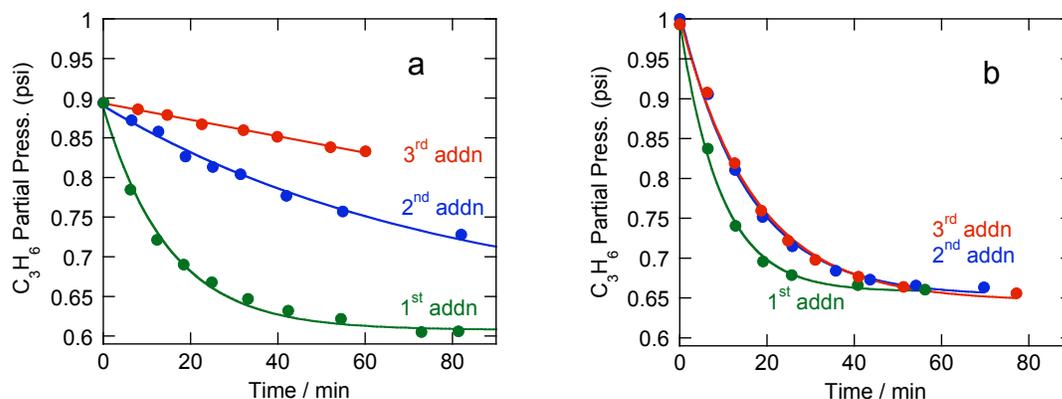


Figure 7. Effect of silanol capping on deactivation of CH_3ReO_3 /silica-alumina catalyst during three sequential additions of propylene: (a) uncapped catalyst, showing severe deactivation; (b) capped catalyst, showing no deactivation after the second addition.

Future Plans

We plan to pursue preliminary kinetic studies on the rates of metathesis of functionalized olefins and the poisoning effects of various non-olefinic substrates containing functional groups. In particular, activity for ethenolysis of internal olefins is desirable.

Our computational investigations of possible mechanisms of active site formation in supported Re catalysts have shown that neither tautomerization of $\text{CH}_3\text{Re(VII)}$ nor aldehyde extrusion from a rhenaoxetane are viable carbene-forming mechanisms. We have shifted our attention to Re(V) active sites, which may be formed in situ from Re(VII) and appear to be more reasonable candidates as carbene precursors. We are attempting to prepare and characterize the reactivity of supported organorhenium(V) sites directly, to complement our computational studies. The lower-valent active sites will also be probed for their activity in catalytic olefination reactions with carbonyl compounds.

We are also investigating the role of Lewis acidity and basicity of the activating support oxide on initiation of metathesis. Substitution of Al by B and Ga and variation of the support synthesis method will be used to explore and optimize the interactions leading to activation.

Publications acknowledging this grant (2004-2006)

Moses, A. W.; Ramsahye, N. A.; Eckert, J.; Scott, S. L. "Evidence for Spontaneous Tautomerization of Methyltrioxorhenium Supported on Silica-alumina", manuscript in preparation.

Deguns, E. W.; Taha, Z. A.; Scott, S. L. "Ring-forming reactions in the deposition of TiCl_4 on silica", manuscript in preparation.

Scott, S. L.; Eckert, J.; Chmelka, B. F.; Moses, A. W.; Leifeste, H. D.; Ramsahye, N. A.; Chattopadhyay, S.; Raab, C. "Supported Re Catalysts for Metathesis of Functionalized Olefins", *Catal. Org. React.*, accepted for publication.

Moses, A. W.; Ramsahye, N. A.; Raab, C.; Leifeste, H. D.; Chattopadhyay, S.; Chmelka, B. F.; Eckert, J.; Scott, S. L. "Methyltrioxorhenium Interactions with Lewis Acid Sites of an Amorphous Silica-Alumina", *Organometallics* **2006**, ASAP Article.

Taha, Z. A.; Deguns, E. W.; Chattopadhyay, S.; Scott, S. L. "Formation of Digallium Sites in the Reaction of Trimethylgallium with Silica", *Organometallics* **2006**, *25*, 1891-1899.

Deguns, E. W. "Reactions of Titanium, Vanadium, Aluminum and Gallium Complexes with Silica", Ph.D. Thesis, University of California, Santa Barbara, 2006.

Leifeste, H. D. "Kinetic Studies of Metathesis Reactions Catalyzed by Supported Methyltrioxorhenium", M.Sc. Thesis, University of California, Santa Barbara, 2005.

Title: Transition Metal Mediated Transformations of Small Molecules

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Megan Majcher, David K. Newsham, Yiyong Hong

Goals and Objectives

Catalytic polymer synthesis by metal compounds is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The theme of the proposed research is the design of new metal-based systems for the synthesis of novel classes of polymers. In the process, we hope to address key questions concerning the steps involved in such polymerization reactions.

Significant Recent Achievements and Results

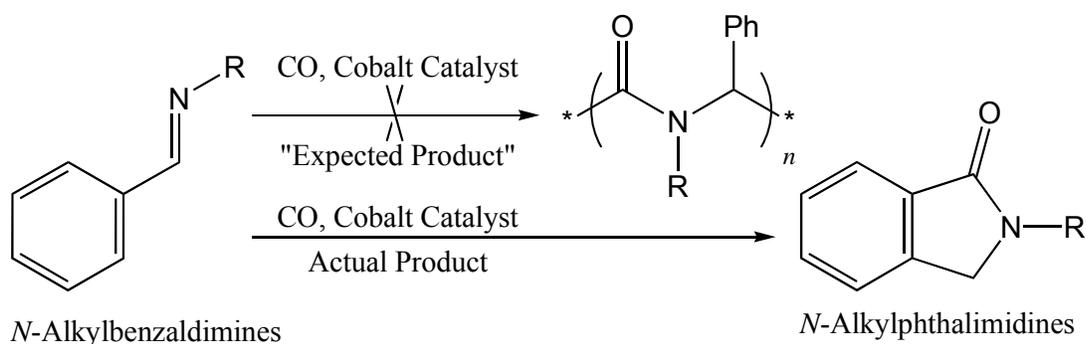
Below we briefly summarize some of our recent research achievements. Further details can be found in the publications listed at the end.

A significant fraction of the work during the current grant period has been devoted to catalytic systems for (A) the homopolymerization of functionalized norbornene derivatives and (B) the copolymerization of simple alkenes and norbornene derivatives with acrylate monomers. A new palladium-based catalyst was found for the vinyl addition polymerization of norbornene derivatives, including those with pendant oxygen functionalities. For norbornene, a polymerization rate of 1000 tons norbornene/mol Pd•hour was observed at 25°C. However, the polymerization rate was found to decrease for norbornene derivatives with pendant functionalities. *Endo*-substituted norbornenes are polymerized more slowly than their corresponding *exo* isomers. The size of the substituent plays a role. However, the coordinating ability of the functionality plays an even bigger role in attenuating polymerization than its size. The formation of chelates upon the coordination of the *endo*-functionalized norbornene is responsible, in part, for the observed decrease in polymerization rate. A further and, even greater, reason for the diminution of activity of *both* the *endo* and the *exo*-functionalized isomers is simply the coordination of the functionality to the metal center.

A copper-mediated mild procedure for the synthesis of random copolymers of acrylates with 1-alkenes, ranging from ethene to 1-decene, as well as norbornene derivatives, has been discovered. Copolymers with greater than 20 mol% incorporation of the 1-alkene are formed.

The system is *living*, thereby allowing the synthesis of novel block terpolymers of acrylates with 1-alkenes and/or norbornenes by the sequential addition of the latter monomers.

Finally, in the course of our search for a metal-catalyzed system for the alternating copolymerization of imines with carbon monoxide, we have uncovered a cobalt-catalyzed system for the conversion of *N*-alkylbenzaldimines to *N*-alkylphthalimidines through tandem C-H activation and cyclocarbonylation.



Future Plans

During the upcoming year we intend to follow, for the most part, the lines of research outlined in the most recent proposal. This will involve investigations of metal-mediated processes for the synthesis of polymers and copolymers. The principal goal of the proposed research will be the design of new systems for the formation of polymers with interesting architectures. The research will focus on two specific areas: (A) metal-mediated homo and copolymerization of polar vinyl monomers with non-polar alkenes and norbornene derivatives, and (B) metal-catalyzed polypeptide synthesis through alternating copolymerization of imines with carbon monoxide.

Impact on Science and Technologies of Relevance to DOE

Catalytic polymer synthesis by metal compounds is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. Indeed, several high-volume commercial polymers are only accessible through metal-mediated routes. Hence, the achievement of a fundamental understanding of all aspects of such catalysis is an important goal. The Technology Vision 2020 report also cites the importance of developing new catalysts for customizing polymer properties. The theme of our research is the design of new metal-based catalytic systems for the synthesis of novel classes of polymers. For example, the copolymerization of functionalized vinyl monomers with non-polar alkenes remains an area of great interest in synthetic polymer chemistry, because the addition of functionalities to a polymer which is otherwise non-polar can greatly enhance the range of attainable properties. One particular area of interest is the homopolymerization of norbornene derivatives and their copolymerization with acrylates to form materials suitable for deep UV photolithography.

Publications Based on DOE Grant (2004-present)

1. "The Addition Polymerization of Functionalized Norbornenes: The Effect of Size, Stereochemistry and Coordinating Ability of the Substituent," Jeffrey K. Funk, Cecily E. Andes, and Ayusman Sen, *Organometallics*, **2004**, *23*, 1680.
2. "Living/Controlled Copolymerization of Acrylates with Non-activated Alkenes," Shengsheng Liu and Ayusman Sen, *J. Polym. Sci., A: Polym. Chem.*, **2004**, *42*, 6175.
3. "The Reaction of Palladium(1,5-cyclooctadiene)(Alkyl)(Chloride) with Norbornene Derivatives: Relevance to Metal-Catalyzed Addition Polymerization of Functionalized Norbornenes," Myeongsoon Kang and Ayusman Sen, *Organometallics*, **2004**, *23*, 5396.
4. "Metal-Mediated Polymerization of Acrylates: Relevance of Radical Traps?" Megan Nagel, Walter F. Paxton, Ayusman Sen, Lev Zakharov, and Arnold L. Rheingold, *Macromolecules*, **2004**, *37*, 9305.
5. "Swelling Behavior of a New Crosslinked Poly(allylamine) Hydrogel and Selective Hydrogenation Catalyzed by a Palladium-Gel Conjugate," Yiyong Hong and Ayusman Sen, *Polym. Mater. Sci. Eng.*, **2005**, *93*, 518.
6. "Living/Controlled Copolymerization of Polar Vinyl Monomers with Non-activated Alkenes," Ayusman Sen and Sachin Borkar, *Polym. Prepr. - Am. Chem. Soc., Div. Polym. Chem.*, **2005**, *46(2)*, 284.
7. "Novel Fluoroalkene-Methyl Acrylate Copolymers by Atom Transfer Radical Polymerization," Sachin Borkar and Ayusman Sen, *Macromolecules*, **2005**, *38*, 3029.
8. "Neutral N-O Chelated Palladium(II) Complexes: Syntheses, Characterization, and Reactivity," Myeongsoon Kang and Ayusman Sen, *Organometallics*, **2005**, *24*, 3508.
9. "Catalytic Carbonylation of 4-Penten-1-ol to ϵ -Caprolactone and Oligocaprolactone," Jeffrey K. Funk, David K. Newsham, David N. Goldstein, Shengsheng Liu, and Ayusman Sen, *J. Mol. Cat. A: Chemical*, **2005**, *239*, 185.
10. "Cobalt Catalyzed Carbonylation of N-alkylbenzaldimines to N-alkylphthalimidines: Tandem C-H Activation and Cyclocarbonylation," Jeffrey K. Funk, Hemant Yennawar, and Ayusman Sen, *Helvetica Chim. Acta*, **2006**, in press.

Alkene Oxidation with Platinum Oxo Complexes and Gold Cluster Complexes as Models for Supported Gold Cluster Catalysts

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 Students: Endre (Andy) Szuromi

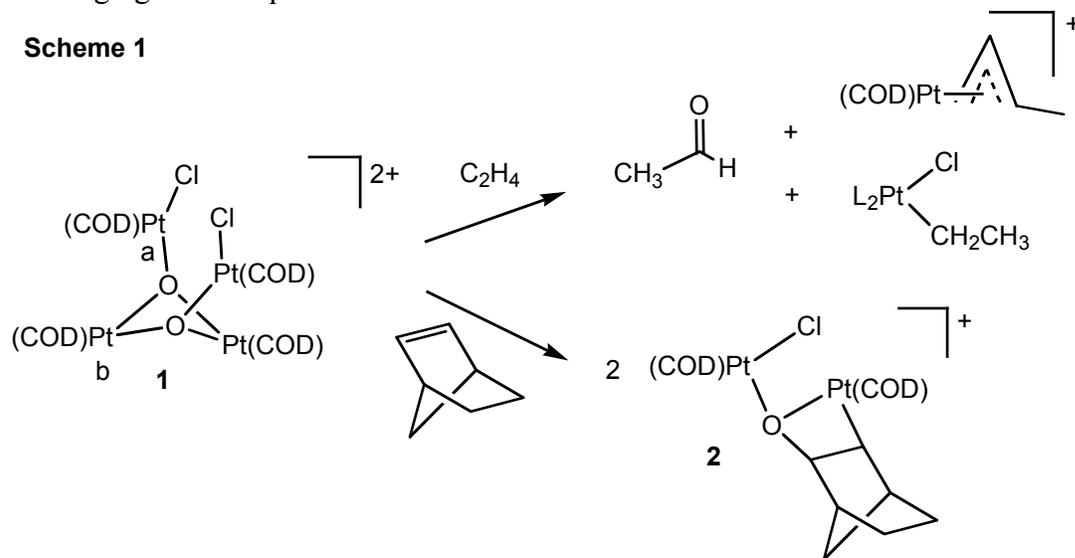
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Goals

1) Understand the factors in late transition metal oxo complex reactions with alkenes and other unsaturated substrates and 2) improve understanding of supported gold cluster catalysts by the preparation and study of gold complexes and gold cluster complexes containing Au-M (M = Al, Ga, Si, Ge, Ti) and Au-O bonds.

Recent Progress

Alkene oxidation chemistry. Despite a general prejudice toward terminal oxo complexes as the only reactive species in oxidation chemistry we reported the novel alkene oxidation chemistry of bridging oxo complex **1** shown in Scheme 1.



Further investigation of the chemistry of platinaoxetane **2** revealed the unexpected alkene exchange reactions shown in Scheme 2. A kinetic investigation of the exchange between platinaoxetanes **2** and **3** revealed it to be catalyzed by $(COD)Pt(OTf)_2$, Ag^+ , and BF_3 giving vital clues to how late transition metal oxo complexes can oxidize alkenes, a long sought goal of this project.

DOE Interest

The improved understanding of the chemistry of metal oxo complexes and gold cluster complexes that will be gained by studying the reactivity and formation of the above complexes will increase our fundamental understanding of critical interactions in important catalytic processes. The benefits could be many, including increased efficiency, new processes, and less pollution.

Future Plans

We will continue our work on the platinum alkene oxidation chemistry with the goal of determining key species in the catalytic processes and the factors that make the (COD)Pt system so far unique in alkene oxidation chemistry.

Publications (2004-present)

“Acidities of Platinum(II) m-Hydroxo Complexes Bearing Diphosphine Ligands” Anandhi, U.; Sharp, P. R. *Inorg. Chem.* **2004**, *43*(21), 6780-6785. DOI: [10.1021/ic049463m](https://doi.org/10.1021/ic049463m)

“A Gallium Coated Gold Cluster” Anandhi, U.; Sharp, P. R. *Angew. Chem. Intl. Ed.* **2004**, *43*(45), 6128-6131. DOI: [10.1002/anie.200461295](https://doi.org/10.1002/anie.200461295)

“Palladium-Gold Oxo Complexes” Singh, A.; Sharp, P. R. *Dalton Trans.* **2005**, 2080-2081. DOI: [10.1039/b504808g](https://doi.org/10.1039/b504808g)

“Alkene Coupling through Triflic Acid Elimination on Pt” Szuromi, E.; Sharp, P. R. *Organometallic*, **2006**, *25*(3), 558-559. DOI: [10.1021/om0507631](https://doi.org/10.1021/om0507631)

“Pt(II) and Pd(II) Dibenzo[a,e]cyclooctatetraene (DBCOT) Oxo and Halide Complexes: Comparison to 1,5-COD Analogs” Singh, A.; Sharp, P. R. *Organometallics*, **2006**, *25*(3), 678-683. DOI: [10.1021/om050713w](https://doi.org/10.1021/om050713w)

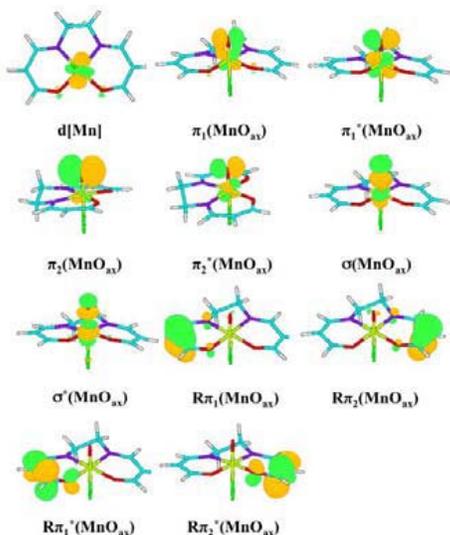
“Gold(I) Complexes Containing Au-Ge Bonds” Anandhi, U.; Sharp, P. R. *Inorg. Chim. Acta*, in press. Invited contribution to a special edition in honor of M. Mingos.

Theoretical Investigations of Metal-Salen Catalysts

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School of Chemistry and Biochemistry
Georgia Institute of Technology*

Schiff-base complexes of transition metals have seen numerous applications in transition metal catalysis, with one of the most prominent being the chiral manganese salen catalysts originally employed by Katsuki and Jacobsen for the asymmetric epoxidation of terminal olefins. A number of theoretical studies over the past decade have sought to elucidate the electronic properties that give rise to the stereochemical control afforded by the Mn(salen) system, including extensive work by Musaev, Morokuma, and co-workers¹ and by Cavallo and Jacobsen.² Despite this, definitive conclusions from theory have proven challenging. Other researchers have pointed to major qualitative discrepancies in the description of the epoxidation reaction from two of the most commonly employed density functionals.^{2d}

Using multi-reference wavefunction-based approaches we have explored³ many of the low-lying electronic states of an oxo-Mn(salen) model system, several of which have not been explored previously, using the geometry and model system of Ivanic and co-workers.⁴ Large complete-active-space self-consistent-field (CASSCF) computations have been performed in pursuit of an accurate ordering of the relevant electronic states. Basis set and relativistic effects have been considered. For the geometry considered, our best results indicate the ground spin state to be the closed-shell singlet state, followed closely by a pair of low-lying triplet states.



CASSCF/6-31G* natural orbitals for the 1⁵A state of oxo-Mn-Salen

Further, we have explored the existence of multiple solutions to the Hartree-Fock (HF) and Kohn-Sham density functional theory (KS DFT) equations. Wavefunction stability analysis was performed by diagonalization of the molecular-orbital Hessian. The HF results are shown to be qualitatively incorrect for the relative energies of the states

considered and the existence of multiple solutions to the HF equations is established. Although the popular density functionals such as B3LYP and BP86 are superior to the HF results in that they provide a more physical description of the relative energies and do not exhibit the multiple solutions, they give inconsistent answers regarding the ordering of the lowest singlet and triplet states as well as greatly underestimate the singlet-quintet gap. Definitive conclusions remain elusive as to what functional, if any, is capable of describing the Mn(salen) catalyzed olefin epoxidation to high accuracy. To determine the applicability of DFT methods to the investigation of Mn(salen) asymmetric epoxidation reactions as well as other metal-salen catalyzed transformations, we are currently extending our efforts to other model systems as well as other metals. We will briefly mention some of these, including Co(salen) and Ru(salen) model systems. The conclusions from this systematic study will serve to guide the future theoretical investigation of numerous metal-salen catalyzed transformations.

Support from the DOE BES Catalysis Program (DE-FG02-03ER15459, C. W. Jones, PI; M. Weck, P. Ludovice, C. D. Sherrill, R. J. Davis, co-PI's) is gratefully acknowledged.

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Stereomodulated Degenerative Transfer Living Ziegler-Natta Polymerization of Propene

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Manipulation of polymer microstructure through catalyst ligand modifications has provided a wealth of new polypropene-based materials, ranging from stiff elastomers to elastomers. The standard ‘one catalyst – one material’ approach, however, does have practical limitations for either fine-tuning physical properties through minor adjustments about a given microstructure, or for accessing a completely different microstructure altogether. This poster will focus on our ability to prepare an almost infinite variety of new polypropene microstructures through the living polymerization of propene that can be achieved using the single preinitiator, $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrMe}_2[\text{N}(\text{Et})\text{C}(\text{Me})\text{N}(\text{t-Bu})]$, in combination with the borate activator, $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$. More specifically, by simply adjusting stoichiometry, the ability to fine-tune microstructures from between being highly isotactic to completely atactic will be demonstrated, as well as, the ability to prepare the first well-defined examples of stereogradient polypropene and a broad range of different isotactic-atactic stereoblock polypropene elastomers through programmed stereomodulated living propene polymerization.

Mechanisms of Organometallic Copper Oxidase Reactions

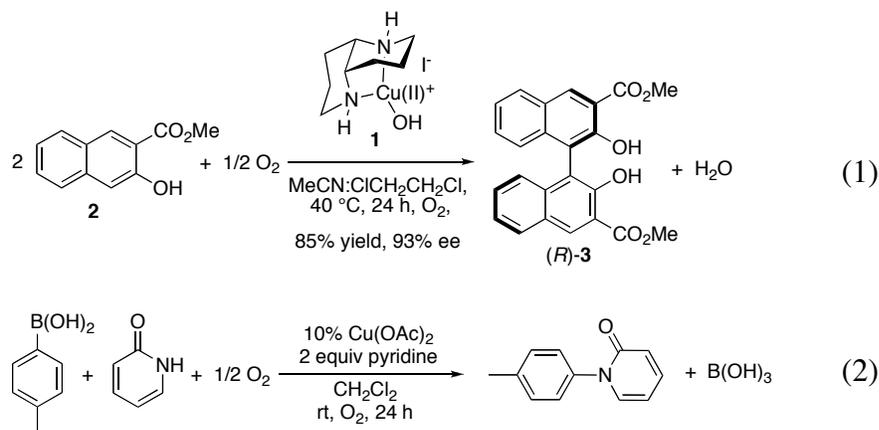
Students: Amanda E. King, Lauren M. Huffman, Xuan Ye
 Collaborators: Thomas C. Brunold (UW-Madison)
 Marisa C. Kozlowski (Penn – Funding: NSF CHE-0094187)
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Goal

Elucidate the mechanisms of copper-catalyzed aerobic oxidative C–C and C–X coupling reactions and investigate fundamental organometallic and inorganic transformations relevant to catalytic turnover. Insights into the catalytic mechanisms of these reactions have important implications for the development of new aerobic oxidation reactions.

Recent Progress

This recently initiated project focuses on two valuable transformations in organic chemistry: asymmetric oxidative C–C coupling of naphthol substrates (eq 1) and oxidative C–N coupling between amines (or related nitrogen nucleophiles) and organoboron reagents (eq 2). In contrast to many other copper-catalyzed oxidation reactions that promote heteroatom-transfer to an organic substrate from oxene or nitrene precursors, these reactions employ molecular oxygen as a terminal oxidant to achieve Cu-mediated oxidative coupling of two reduced organic substrates. The ability of copper to undergo facile one-electron chemistry raises fundamental questions concerning the mechanism of these two-electron oxidation reactions that employ a four-electron oxidant.



Our preliminary studies of these reactions have focused on kinetic characterization of the catalytic reactions. For example, in collaboration with Prof. Marisa Kozlowski and Brian Hewgley (Penn), we have investigated the oxidative biaryl coupling reaction by monitoring the reaction progress via chromatography (GC, HPLC) and gas-uptake methods (Figure 1). The reaction can be initiated either with a Cu^I or Cu^{II} form of the catalyst, and in both cases a "burst" phase is observed. These results, together with the initial-rate dependence on individual

components of the reaction reveal that the reaction does not proceed by a simple two-stage ("ping-pong") oxidase mechanism observed in many homogeneous Pd-catalyzed aerobic oxidation reactions and enzymatic Cu-oxidase reactions.

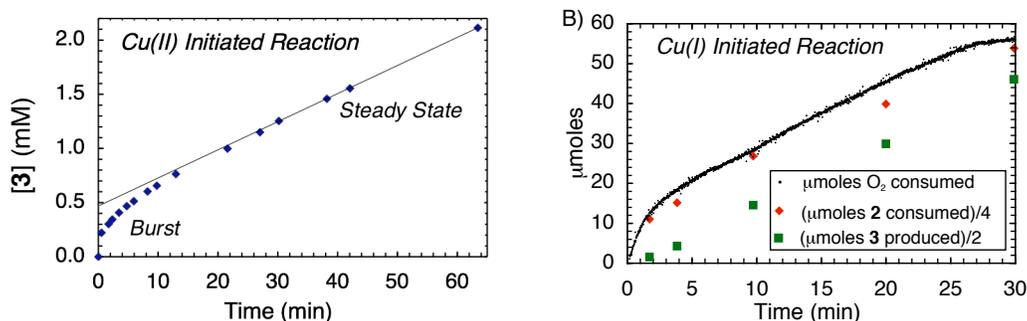


Figure 1. A) Kinetic time-course for product **3** formation in the oxidative biaryl coupling reaction with catalyst **1** from HPLC data. Conditions: **[2]** = 94 mM, **[1]** = 2 mM, atmospheric O₂, MeCN, 40 °C, internal std: [4-biphenyl phenyl ether] = 23 mM. B) Kinetic time-course for the oxidative biaryl coupling reaction with the Cu^I catalyst [LCu^I(I)]. (●) actual O₂ uptake; (◆) μmoles **2** consumed divided by 4; (■) μmoles **3** formed divided by 2. Conditions: **[2]** = 151 mM, **[4]** = 10 mM, pO₂ = 840 Torr, [4-Biphenyl phenyl ether] = 42 mM, 6 mL MeCN, 40 °C. Concentrations of **2** and **3** determined by GC.

DOE Interest

The selective oxidation of organic molecules, ideally with molecular oxygen as the oxidant, is of critical significance for the efficient use of hydrocarbon feedstocks. Moreover, insights gained from this work should reveal conceptual links between fundamental studies of metalloenzymes and model systems and the development of synthetically useful aerobic oxidation reactions.

Future Plans

Mechanistic characterization of these catalytic reactions will employ kinetic methods, such as those mentioned above, together with computational and spectroscopic methods (e.g., EPR spectroscopy in collaboration with Prof. Thomas Brunold). In addition, efforts will be made to probe the fundamental reaction steps associated with the catalytic processes.

Publications Acknowledging DOE Support

Hewgley, J. B.; Stahl, S. S.; Kozlowski, M. C. **2006**, *submitted for publication*. "Mechanistic Study of a Synthetic Copper Oxidase Reaction for Asymmetric Biaryl Coupling and Evidence Against a Ping-Pong Mechanism"

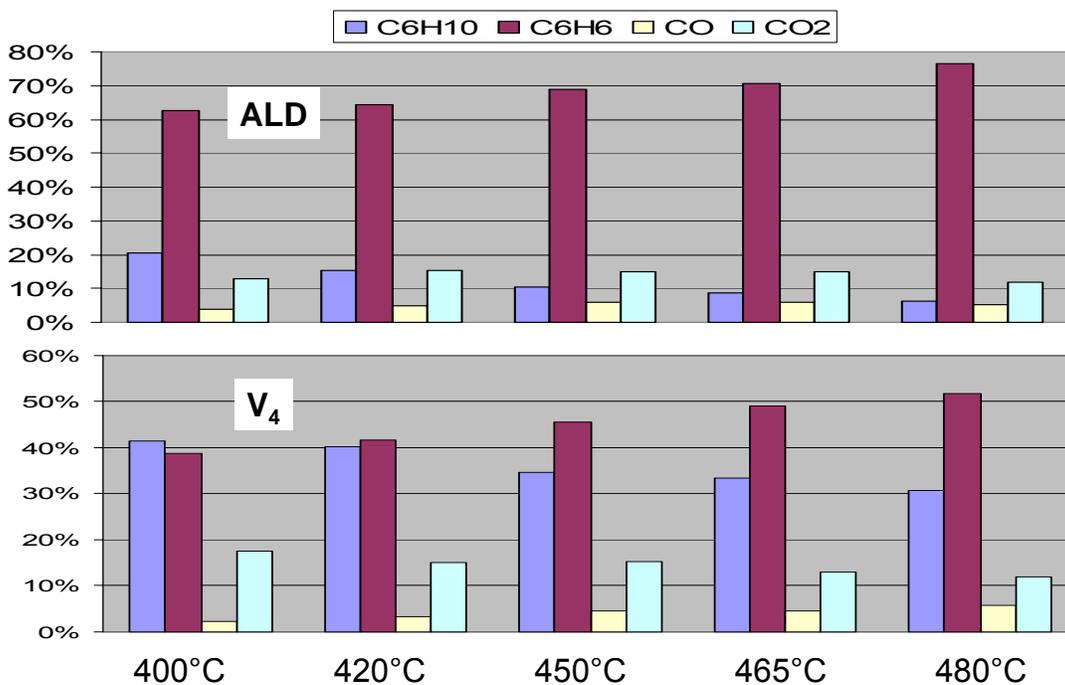
Activity and Selectivity of Vanadium Oxide Catalysts Supported on Nanostructured Membranes

ANL: J. Elam, P. Zapol, L. Curtiss, C. Marshall, M. Pellin

NU: L. Broadbelt, H. Kung, M. Kung, T. Marks, R. Snurr, and P. Stair

The oxidative dehydrogenation of cyclohexane to cyclohexene and benzene was studied over vanadium oxide catalysts supported on nanostructured membranes. The supported vanadyl species were prepared by three different methods: conventional wet impregnation, atomic layer deposition and impregnation with organometallic precursors with well-defined nuclearity. The reaction was studied at a series of temperatures, and the specific activity, kinetic parameters, and selectivity were compared. The vanadium oxide catalysts prepared using a V_4 organometallic precursor exhibited remarkably high specific activity and selectivity to the olefin product. This behavior can be explained by the structural requirements of over oxidation to form benzene.

Selectivity Comparison: 1 ML ALD and 0.4 ML V_4 VOX



KC-03-04-01
DE-FG02-03ER15457

Peter C. Stair (Argonne National Lab)
Peter C. Stair (Northwestern University)

Institute for Catalysis in Energy Processes (ICEP)

Additional PIs:

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NU: M. Bedzyk, L. Broadbelt, V. Dravid, D. Ellis, J.-F. Gaillard, F. Geiger, K. Gray, M. Hersam, J. Hupp, H. Kung, M. Kung, L. Marks, T. Marks, S. Nguyen, K. Poeppelemeier, W. Sachtler, R. Snurr, R. Van Duyne, E. Weitz

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Goals :

The overall scientific goals of ICEP are to understand at the molecular level catalytic and photocatalytic transformations relevant to energy harvesting, storage, and utilization and to further the discovery and development of highly efficient catalytic and photocatalytic processes. ICEP is organized into three (3) subtasks:

1. *Model Catalytic and Photocatalytic Systems*: The overall goal of this subtask is to develop fundamental, atomic level understanding of the relationship between catalytic chemistry and the surface atomic structure and electronic properties of the catalyst. The components of this subtask include:

- Synthesis of model catalytic materials for oxidation and photocatalysis.
- Catalyst surface structure determination by electron and x-ray diffraction.
- Catalyst surface structure by scanning probe microscopy.
- Surface science of catalytic chemistry.
- In-situ catalytic chemistry by Raman and SFG spectroscopy.
- Theory.

2. *Nanostructured Membrane Catalysis*: The overall goal of this subtask is to develop fundamental understanding of the relationship between catalyst structure at the nanoscale and the resulting catalytic chemistry. The components of this subtask include:

- Synthesis of highly uniform, nanostructured membranes.
- Synthesis of catalytic components.
- Catalytic testing.
- Structural and chemical characterization.
- Theory and modeling.

3. *Catalytic and Photocatalytic Chemical Transformations*: The overall goals of this subtask are to achieve a fundamental understanding of factors that influence elementary catalytic and photocatalytic reaction steps and to advance the development of highly

effective catalytic and photocatalytic systems. The catalytic and photocatalytic chemistry will continue to focus in the near term on selective oxidation but will evolve toward hydrogen production and CO₂ utilization. The components of this subtask include:

- Novel synthesis of catalytic and photocatalytic phases.
- Catalyst and photocatalyst testing and reaction studies.
- In-situ characterization of elementary reactions.
- Theory and modeling.

DOE Interest :

The understanding and control of reactions catalyzed on solid surfaces *at the molecular-level* is a “grand challenge” for 21st Century catalysis science. We expect that the fundamental results of this research will provide structure-function relationships between catalytically active sites and the chemical reactions they catalyze that are at the heart of this challenge. This project brings together a team of university and national laboratory researchers who develop methods for the design and synthesis of active catalytic sites at the atomic scale and tailored support structures at the nanometer scale, diverse spectroscopy, microscopy, and x-ray scattering techniques for detailed characterization (both ex-situ and in-situ) of catalyst structure and dynamics, elucidation of catalytic reaction mechanisms, and theory applied to catalytic processes.

Research plan:

Model Catalytic and Photocatalytic Systems: Understanding surface structure and bonding, how they depend on surface chemical reactions, and how they influence catalysis and photocatalysis are the central themes of this subtask. If the surface structure of a given oxide or supported cluster could be predicted this would have an enormous impact upon our understanding of numerous chemical processes. The objective of this subtask is to address this outstanding experimental and theoretical problem for oxide surfaces and supported atoms and clusters. To tackle this problem we target critical and difficult theoretical challenges such as *ab-initio* predictions of multicomponent-oxide surface free energies, the structure of supported clusters, and reaction pathways. Experimental challenges include synthesizing well-defined oxide and supported cluster systems, determining surface structure as a function of environmental or reactive conditions, and evaluating the relationship between surface structure and specific chemical properties.

Nanostructured Membrane Catalysis: A particularly interesting concept for a catalyst topology is the nanostructured membrane depicted in **Fig. 1**. Conceptually, the membrane consists of an assembly of identical pores having nanometer dimensions that span a flow reactor so as to produce an array of nanoreactors. With this assembly, each reagent molecule must traverse an identical pore and, ideally, each diffusion path can be engineered through control over the pore diameter, wall composition, and length. This results in more uniform (and controllable) contact times than are possible with a conventional fixed bed catalyst. Moreover, if the pore diameter could be adjusted to atomic dimensions, then reagent-size control similar to a zeolite would be possible. By coating the pore walls one might imagine controlling reagent flow through hydrophilic or hydrophobic interactions as shown in the bottom of **Fig. 1**. In principle, this chemical

gradient might be used to enhance the removal of products and reduce the chance of additional, unwanted reactions. With a sufficiently large number of pores in the array, it might be possible to form one catalytically active particle in each pore and still have

- **Uniform Pores**
 - Nanoreactor Array
- **Contact Control**
 - Identical Diffusion Paths
 - Contact Time Control
- **Reagent Size Control**
 - Pore-size Selection
- **Site Isolation**
 - One Particle in Each Pore
 - No Sintering
- **Sequenced Sites**
 - Sequence Particles Along Pore

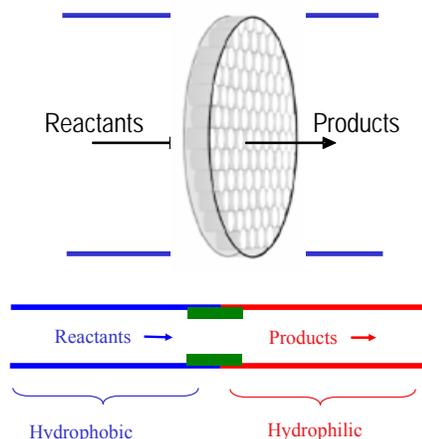


Figure 1 Schematic diagram of a nanostructured membrane topology

enough catalytic material for practical applications or fundamental studies. If only one particle resides in each pore, then sintering would be virtually eliminated. Finally, since reagents flow preferentially in one direction through this structure, there exists the potential to sequence different catalytic sites along each pore.

Nanostructured membranes, fabricated by a combination of anodic aluminum oxidation (AAO) and atomic layer deposition (ALD) possess most, if not all, the features of the ideal nanostructured membrane topology. They offer novel catalyst environments which: 1) provide larger, controllable pore sizes than conventional mesoporous materials (for containing large clusters or arrays of catalyst sites, for efficient in-diffusion of large/elaborate molecular precursors or feedstock molecules, and for out-diffusion of large/elaborate product molecules), 2) permit tailoring of channel size and wall composition by ALD, 3) constrain catalyst mobility, thus hindering agglomeration, and 4) control flow of reagents in, out, and through the catalyst structure.

Catalytic and Photocatalytic Chemical Transformations: The projects in this subtask are categorized according to whether the processes are catalytic or photocatalytic. Studies of catalytic transformations are inspired by both highly selective, biological monooxygenase systems and newly discovered Au catalysts. The catalytic systems to be studied include derivatives of oxo-metal complexes of vanadium, iron, and copper, and modified Au catalysts. These systems will be thoroughly characterized with emphasis on the mode of oxygen activation, redox properties, hydrocarbon oxidation mechanisms, and the effect of the active site environment. The objective is to conduct a coordinated program to understand the activation and reaction of an oxygen molecule in relevant systems, including oxometal complexes of differing nuclearity and Au catalysts, by thoroughly elucidating the pathways and energetics of oxidation reactions on these catalysts, especially the reaction of each of the two oxygen atoms. The objectives are to obtain an understanding of how oxygen activation and reaction depends on the active sites and their environment.

The central hypothesis of the research on photocatalysis is that the chemical reactivity of photocatalytic active sites for CO₂ reduction can be tuned by careful selection and manipulation of the metal center and its surroundings. This will be tested in two systems, TiO₂ nanocomposites and metal-oxo bridged centers in mesoporous

materials that undergo light initiated metal to metal charge transfer (MMCT) chemistry. The first focus is on the *nano-scale structured environment* where highly active photocatalytic centers are created at solid-solid interfaces, altering the coordination environment of the lattice metal cations. Recent evidence indicates that mixed phase titania displays high photocatalytic activity due to interfacial or adlineation sites, the identity of which is likely to be tetrahedrally coordinated Ti^{4+} sites. The effects of *molecular scale manipulations* will be tested using a wide array of light-absorbing MMCT complexes, highly dispersed in mesoporous materials with varying pore size.

Representative Recent Results:

The structure of two model supported catalyst systems, $\text{VO}_x/\alpha\text{-Fe}_2\text{O}_3(0001)$ and $\text{WO}_x/\alpha\text{-TiO}_2(110)$, have been studied by XPS and AFM and by XSW imaging analysis under an atmospheric pressure ambient. The rearrangement of V and W cations has been observed under oxidation and reduction processing.

$\text{VO}_x/\alpha\text{-Fe}_2\text{O}_3(0001)$

The *in-situ* x-ray analysis of $\text{VO}_x/\alpha\text{-Fe}_2\text{O}_3(0001)$ took place in a custom designed surface scattering and spectroscopy instrument, located at the APS DND-CAT 5ID-C station. This system was studied as a function of V coverage (0.5 and 1.0 ML) and V oxidation state (V^{3+} and V^{5+}), i.e. the vanadium was present as an oxo-species. Oxidation was induced by RT exposure to atomic oxygen from a UHV thermal gas cracker. In brief, the XSW data shows that oxidation causes the V average adsorption height to increase by 0.6 Å. XPS shows that this same process causes the V oxidation state to change from 3+ to 5+. This combined XSW-XPS study agrees with the picture in which the added oxygen atom forms a double bond with the V taking an electron from the back-bond and making the V more weakly bound to the substrate surface oxygen. The XSW image (not shown) shows that there are in fact two V sites that are laterally aligned with the two symmetry non-equivalent Fe bulk-like sites.

$\text{WO}_x/\text{TiO}_2(110)$

A sub-monolayer tungsten-oxide catalyst was prepared on fully hydroxylated $\alpha\text{-TiO}_2(110)$ using the atomic layer deposition (ALD) method. Using XSW analysis, the 3D tungsten atom density distribution was derived. As shown in **Fig. 2**, the surface tungsten atoms occupy two non-equivalent high symmetry sites, atop and bridge sites with respect to underlying oxygen atom layer, with equal probabilities. These XSW measurements of ALD heterolayer growth clearly show for the first time that ALD conformal layers can be highly coherent with the substrate lattice. The dehydration of tungsten oxide via thermal oxidation moved the tungsten atoms inward by 0.7 Å. Removal of the coordinated water molecule between supported tungsten oxides and substrate can explain this lowering of adsorption height.

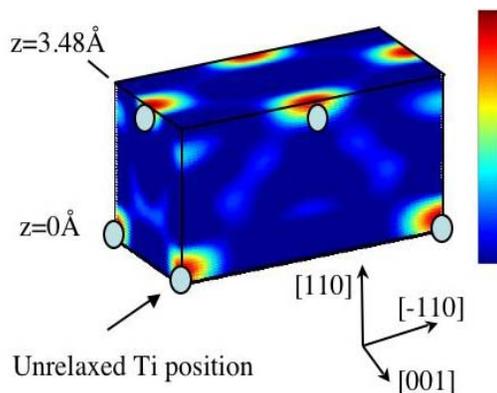


Figure 2: 3D W atomic density map generated by the summation of several TiO_2 (hkl) XSW measured Fourier components. Open circles denote ideal bulk-like Ti sites at height of 0 and 3.25 Å

Nanostructured membrane frameworks that approach the ideal characteristics described above have been fabricated at Argonne National Laboratory and Northwestern University using a combination of electrochemical, anodic aluminum oxidation (AAO) and atomic layer deposition (ALD). Binary ALD reaction sequences have been developed to deposit a wide variety of materials including oxides, nitrides, sulfides and metals. Because gas transport into mesoporous and microporous materials is diffusion-limited; surfaces at the entrance to the AAO membrane will receive reactant exposures that are $\sim 10^3$ larger than the interior surface. Despite this, ALD has a demonstrated ability to coat mesoporous

materials uniformly^{18, 19} including AAO.²⁰ An example of pore diameter control and uniformity with ALD coated AAO is depicted in Fig. 3.

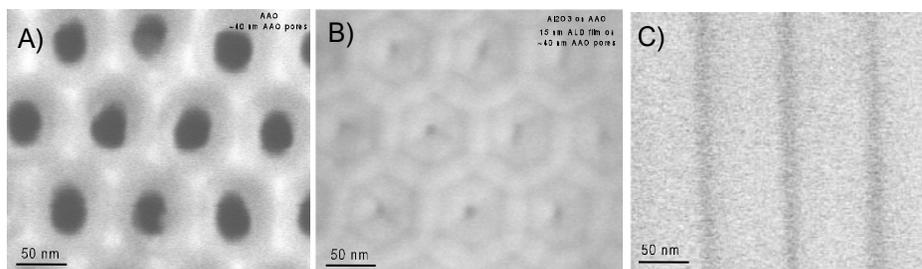
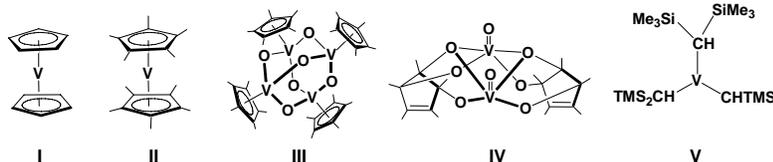


Figure 3 A) Plan view SEM image of surface of the original 40 nm AAO material. B) Plan view SEM image of the surface of the 40 nm AAO material coated with 15 nm of alumina. C) Cross sectional view of 40 nm AAO material coated with 15 nm of alumina taken from the center of the AAO membrane (note that the coating is uniform despite the high aspect ratio)

To understand issues involving the active site, a number of organovanadium complexes **I-IV** were synthesized as precursors to vanadium oxide of varied nuclearity, anchored on alumina surfaces and AAO membranes, and characterized using spectroscopic techniques. Chemisorption of organovanadium complexes **I-III** on dehydroxylated alumina led to evolution of cyclopentadiene, suggesting protonolysis of metal-cyclopentadienyl linkages by the surface OH groups. These complexes were also used as vanadium precursors for AAO-supported vanadia catalysts. The exact nature of the species anchored on these surfaces is still under investigation using a variety of physiochemical techniques. Atomic layer deposition techniques were also used to deposit vanadium oxides using $(C_5Me_5)_2V$ (**II**) as the precursor. Steady growth at 0.03 nm/cycle was observed for V_2O_5 .

The use of more reactive and volatile organovanadium ALD precursors is under further investigation.



Charge separation in pure and mixed phase TiO_2 photocatalysts was studied using EPR spectroscopy in order to explore the role rutile plays in enhancing the photoactivity of P25. While previous work regards rutile as a passive electron sink hindering recombination in anatase, our findings detail very different phenomena: The rapid electron transfer from rutile to anatase. The results suggest that there is a morphology of nanoclusters containing rutile crystallites interwoven with anatase crystallites creating a solid-solid interface across which photoexcited electrons are transferred from rutile to lower energy anatase lattice trapping sites. Thus, rutile acts as an antenna to extend the photoresponse of the mixed phase catalyst into the visible light region and its association

with anatase in a preferred nanostructured arrangement results in spatial separation of the charge carriers and hindered recombination. Anatase then serves to activate rutile, and the solid-solid interface between the nanoparticles of the two materials creates catalytic “hot spots” or adlineation sites. We identified an *interfacial*, tetrahedrally coordinated Ti^{4+} site as an electron trapping site that is intrinsic to P25 and is not observed in the pure phase materials.

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Microporous and Mesoporous Nano-Sized Transition Metal Oxides: Preparation, Characterization and Application.

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Collaborators: Katie Carrado (Argonne), Joe DiCarlo (Yardney), Jon Hanson (Brookhaven), Dave Mullins (Oak Ridge), Alex Navrotsky (UC Davis).

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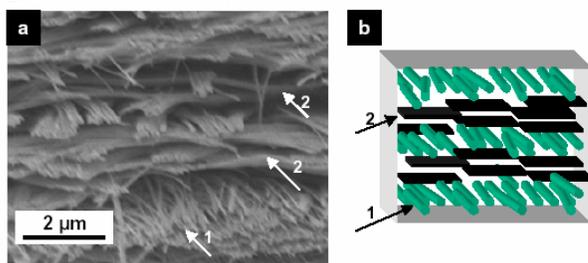
web page: <http://web.uconn.edu/chemistry/SuibGroup/suibg.html>

Goals To prepare aqueous colloids of nano-size (10 Å to 1000 Å) porous manganese oxides as precursors for various OMS systems; to prepare novel doped octahedral molecular sieve (OMS) and octahedral layer (OL) structures via aqueous colloidal routes; to understand factors that control size and shape of porous nano-size oxides; to fully characterize physical and chemical properties of the above-mentioned systems; to use porous metal oxides for selective oxidations, shape selective oxidations, and chiral oxidations; to explore new potential applications of these systems in secondary non-aqueous rechargeable batteries, and as membranes.

Recent Progress

Unique Morphologies

Fig. 1, Porous OMS paper.



A major focus has been the control of size and shape of porous transition metal oxides. Various morphologies have been prepared including stars, multipods, helices, flowers, hollow spheres, and inorganic dendrites. Some paper membrane materials have been prepared that have aligned rods that are at 90° to rods in alternate

layers as shown in Fig. 1. These materials have been used in selective oxidations and relationships among yield, selectivity, activity and morphology have been studied.

New Materials

New materials have been produced by isomorphous substitution of porous OMS and OL. Iron framework materials have led to unique magnetic properties with ferromagnetic behavior at elevated temperature. Both high V⁵⁺ and low Cu²⁺ framework substitutions have been done. Novel pores such as 1x2x3x1x2x3 slit like pore systems have been produced. Intercalated lithium OMS and OL materials have been used for secondary rechargeable battery materials. Several synchrotron and neutron characterization experiments are being done to study location and structure of ions in these systems and oxidations states of these mixed valent systems. *In situ* X-ray and small angle neutron scattering studies are done to study synthetic intermediates.

Oxidation Catalysis

Several organic substrates have been used for selective oxidations using OMS and OL catalysts. Alcohol oxidations, styrene oxidation, electrocatalytic oxidation of styrene, alkylation, hydrogen generation, and amination reactions have been shown to occur over OMS. Kinetic isotope experiments have been done to obtain mechanistic information.

DOE Interest

Fundamental knowledge in the areas of synthesis, new characterization methods, structural analysis, mixed valency, electron transfer, magnetic behavior, conductivity, catalysis, and photocatalysis has been obtained in our studies of OMS and OL materials. The novelty of porous

semi-conducting molecular sieves has allowed fundamental studies of effects of electron transfer in such systems. High resolution spectroscopic and microscopic characterization studies have led to an excellent understanding of many of the fundamental structural and electronic features of these systems. Catalytic studies have led to correlations of activity/selectivity, shape selectivity, and redox or electron transfer capability. Unique features of our systems include the unusual hollowness of MnO₂ materials; the myriad of morphologies available in these systems (helices, nano-ropes, nano-wires, nano-lines, nano-patterns, nano-spheres); variety of tunnel structures (1x1/1x2, 2x2, 3x3, 2x4, 3x5); excellent conductivity; ease of ion-exchange; transformations to alternate structures while preserving the macro-morphologies of wires, lines, and patterns; outstanding selectivity and activity in selective oxidations; and excellent adsorption properties. Helices or wires with such variation in length and diameter, as well as the uniquely high permeability and porosity are novel. Porous thin films are important for sensors, optical coatings, membranes, and in catalysis. Novel battery and sensor systems have been designed that are functional and low cost. Catalytic oxidations and condensations are the focus of our catalysis studies. The unique combination of availability of many structural types, good electrical properties, high permeability, and high porosity is rare.

Future Plans

Our major efforts continue to be focused on the aerobic catalytic oxidation of alcohols. We have been studying the kinetics of such reactions and finding ways to enhance activity, which in most cases can be as high as 100%. We are also trying to extend this work to chiral alcohols. Catalytic shape selective oxidations (selective, not total) are a major goal of this work.

In the area of synthesis of new materials, we are preparing nanosize manganese oxide layered materials of various morphologies and surface areas. We are continuing nano-film work with protein/manganese oxide layers for catalytic studies such as the conversion of styrene to styrene oxide is one such reaction. Framework doping with iron has produced ferromagnetic materials and these are looked at with magnetic susceptibility studies.

The colloidal preparations have led to a new family of materials that have unique morphologies and properties. Porous, helices, wires, thin films and nano-patterns of manganese oxide have been synthesized. These systems offer outstanding porosity, versatility for preparation of new materials, and many new applications. We are continuing to prepare such systems and are trying to understand their mechanisms of formation. We have made headway in making similar manganese oxide colloids solely from aqueous solutions and also in the preparation of a variety of transition metal nano-lines and nano-patterns.

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Polycyclic Aromatic Hydrocarbons with Curved Surfaces: Buckybowls.

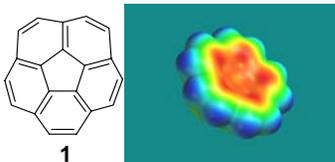
Personnel Praveen Bachavala (graduate student)
Renata Sygula (part-time research associate)

Collaborators Robert J. Angelici (Iowa State University and Ames Laboratory)

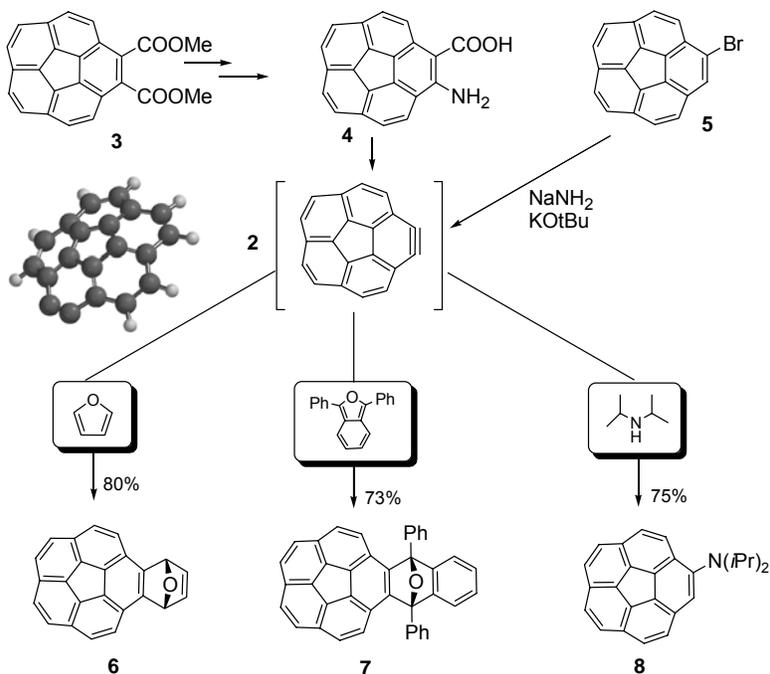
Contact A. Sygula, Department of Chemistry, MSU, Mail Stop 9573, Mississippi State, MS 39762; asygula@chemistry.msstate.edu; (662) 325.7612

Goal

The major goal of this project is development of synthetic procedures leading to curved-surface Polycyclic Aromatic Hydrocarbons (PAHs) Buckybowls structurally related to fullerenes. Practical, solution-based synthetic methods are of premium importance and significant progress in that area has been made in part due to this DOE sponsored program. We continue to aim at the preparation and characterization of novel buckybowls with an emphasis on the synthesis of larger systems starting from corannulene (**1**).

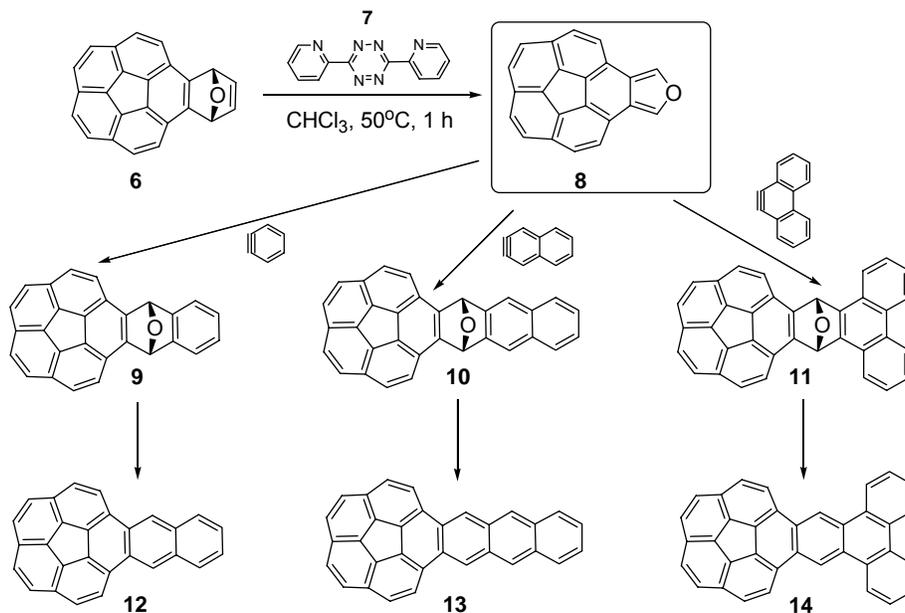
**Recent Progress**

Corannulyne – a nonplanar Benzynes. An aryne derived from corannulene (1,2-dehydro



-corannulene or corannulyne, **2**) represents an attractive possibility since it opens a number of synthetic routes leading to syntheses of larger systems with corannulene subunits. Subsequently, we pursued the formation of corannulyne by the “classical” anthranilic acid route starting from dimethyl 1,2-corannulenedicarboxylate (**3**), synthesized previously in our laboratory. However, our numerous attempts failed to develop a synthetically useful procedure for **4**. Therefore we turned our attention to alternative methods of benzyne generation starting from easily accessible bromocorannulene **5**. We learned that treatment of **5** with an excess of sodium amide/potassium *tert*butoxide in THF at room temperature in presence of trapping agents leads to the formation of addition products **6** – **8** with respectable yields of 70 – 80%, presumably through a formation of corannulyne **2**. In addition to significant synthetic potential of **2**, it represents the first reported example of bowl-shaped aryne, as evidenced by our computation studies which predict **2** to have similar curvature and bowl-to-bowl inversion barrier as the parent **1**. Theory also predicts that corannulyne is slightly more stable (therefore less reactive) than benzyne.

Corannulenoisofuran. Availability of corannulyne and its potential reactions with dienes opens numerous possibilities for the syntheses of large systems with corannulene subunits. Quite recently we succeeded in synthesis of an *isofurane* with corannulene framework, using **6** as a starting material. Thus, treatment of **6** with commercially available tetrazine **7** in chloroform produces corannulenoisofuran **8**, another potential



synthon for syntheses of large corannulene-containing systems through its reactions with activated dienophiles, including triple bonds and benzyne. *Isobenzofurans* have been proven as excellent dienes and their synthetic applications are well documented in literature. Several *isofurans* are too reactive to be isolated and are generated *in situ*. In contrast, **8** seems to be quite stable as a solid, although its solutions in organic solvents slowly decompose when exposed to air and/or light. We are currently exploring chemistry of corannulenoisofuran. We have found that **8** cleanly reacts with benzyne

like 1,2-didehydrobenzene, 2,3- didehydronaphthalene and 9,10- didehydrophenanthrene to produce adducts **9** - **11** in good yields. Moreover, these adducts can easily be deoxygenated by standard methods giving hydrocarbons **12** – **14**, respectively, which represent a nice “marriage” of buckybowls with planar PAHs.

DOE Interest

Buckybowls represent a novel class of PAHs with interesting properties which have not yet been fully explored. We hope that the recent progress in synthetic methodologies leading to these large molecular architectures will spark more vigorous research in the area of material sciences of these systems (a “Molecules to Materials” approach). Aside of their structural novelty buckybowls offer several potential applications such as: acting as “lithium sponges” due to their proven affinity to alkali metals; they often form porous solids due to the imperfect packing of nonplanar molecules, thus can be consider as potential gas-storage materials; the curvature of the carbon networks introduces a novel factor in molecular recognition and complex formation (Molecular Clips and Tweezers), etc.

Future Plans

We will continue to explore the synthetic opportunities afforded by the availability of both aryne **2** and isofuran **8**. Several reactions of **2** with dienes like furans will be explored hopefully leading to large systems which structural and physical properties will be studied. Similarly, **8** offers very interesting possibilities of making nanometric sized PAH systems with embedded corannulene units, as demonstrated above by the test reactions with simple arynes.

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Small Molecule Activation with Sterically Hindered Tris(pyrazolyl)borate Metal Complexes

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Goal

To advance the understanding of the coordination and activation of small molecules (O₂, N₂, etc.) by metal complexes, and to investigate the mechanisms of 'proton coupled electron transfer' (PCET) to reactive inorganic complexes.

Recent Progress

Cobalt Imido Complexes: Our interest in the chemistry of cobalt imido complexes of the type $\text{Tp}^{\text{R,R'}}\text{Co}=\text{NR}$ stems from their isoelectronic relationship to the elusive $\text{Tp}^{\text{tBu,Me}}\text{Co}=\text{O}$. We have postulated the formation of the latter as a reactive intermediate in the activation of O₂ and N₂O by various $\text{Tp}^{\text{tBu,Me}}\text{Co}$ complexes. To our knowledge no terminal cobalt oxo complex has ever been isolated.

Addition of one equivalent of alkyl azide (RN₃, R = Me, Et, ^tBu, Ad) to a THF solutions of $\text{Tp}^{\text{tBu,Me}}\text{Co}(\text{N}_2)$ at room temperature afforded a series of imido complexes $\text{Tp}^{\text{tBu,Me}}\text{Co}=\text{NR}$, which have all been structurally characterized; the representative molecular structure of $\text{Tp}^{\text{tBu,Me}}\text{Co}=\text{NAd}$ (**1**) is shown in Figure 1.

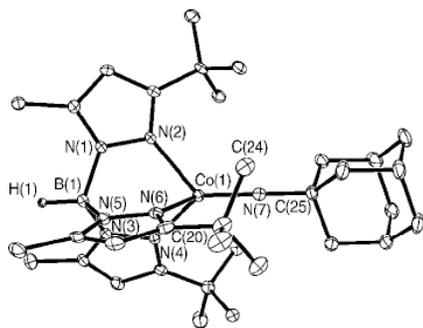


Figure 1. The molecular structure of **1** (thermal ellipsoids set at 30 % probability). Selected interatomic distances [Å] and angles [°]: Co(1)-N(7) 1.655(2), Co(1)-N(2) 2.051(2), Co(1)-N(4) 2.038(2), Co(1)-N(6) 2.049(2); Co(1)-N(7)-C(25) 178.3(2), N(2)-Co(1)-N(4) 89.54(8), N(2)-Co(1)-N(6), 88.10(8), N(4)-Co(1)-N(6) 90.09(9).

The paramagnetic nature of the d⁶ ion in this Co^{III} complex distinguishes it from the few other known cobalt(III) imido complexes, all of which are diamagnetic low spin molecules. Considering the typical d-orbital splitting of a TpCoX fragment under C_{3v} symmetry, we have suggested a $1e^4a^12e^1$ (d⁶, S = 1) electronic configuration for **1**. We wondered whether the difference in the electronic structure would affect the reactivity of **1**. Most interesting is its thermal decomposition, as it parallels the reactivity of the unstable intermediates $\text{Tp}^{\text{tBu,Me}}\text{Co}=\text{NTMS}$ and $\text{Tp}^{\text{tBu,Me}}\text{Co}=\text{O}$.

This reaction was discovered upon heating **1** to 40°C for 10 days in the presence of ethylene (1 atm), aiming for aziridination; however, the ethylene merely served to reversibly trap the reaction product as an ethylene complex, and product **3** can also be prepared in the absence of ethylene. Its molecular structure is shown in Figure 2.

There are several possible mechanisms for the transformation of **1** into **3**, but based on various related observations, we favor PCET, followed by collapse of the resulting alkyl radical onto the amido ligand (Co-N(H)Ad) thus generated. In view of our experience with other H transfer reactions (see e. g. Cr chemistry below), we wondered about a possible tunneling contribution to this reaction. Consequently we have measured the kinetic isotope effect (KIE) of the reaction using **1-d₀** and **1-d₂₇** (containing perdeuterated *tert*-butyl groups).

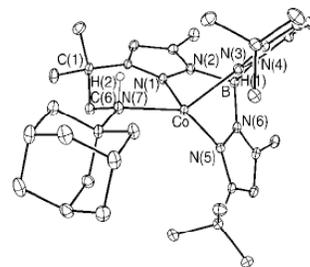


Figure 2. The molecular structure of **3** (thermal ellipsoids set at 30 % probability). Selected interatomic distances [Å] and angles [°]: Co-N(7) 2.1675(14), Co-N(1) 2.0284(13), Co-N(3) 2.1068(13), Co-N(5) 2.0771(14), C(6)-N(7) 1.501(2), N(7)-C(25) 1.5517(2); N(1)-Co-N(3) 90.99(5), N(1)-Co-N(5) 92.69(5), N(1)-Co-N(7) 89.12(5), N(3)-Co-N(5) 86.46(5), N(3)-Co-N(7) 133.41(5), N(5)-Co-N(7) 140.08(5), Co-N(7)-C(6) 107.61(10), Co-N(7)-C(25) 128.08(10) C(6)-N(7)-C(25) 112.20(12).

To our surprise, we obtained values of k_H/k_D ranging from 1.22 (at 303K) to 1.35 (at 363), i. e. very small effects. We have also determined an intramolecular KIE, using selectively labeled **1-d₉** (each *tert*-butyl group being $-C(CH_3)_2(CD_3)$) The KIE obtained by product analysis (1.25 at 333 K) is consistent with the small values obtained in the intermolecular experiment. The mechanistic implication of these small isotope effects are presently unclear. We plan to carry out calculations to identify the transition state for the reaction. If nothing else, these results show that our understanding of this class of reactions (whether it be named PCET, H-atom transfer, or C-H activation) is far from complete.

Hydrogen atom tunneling: The abstraction of hydrogen atoms from organic molecules by metal oxo complexes is an archetypical reaction in oxidation catalysis and bioinorganic chemistry. Moving the lightest of all atoms, hydrogen transfer reactions occasionally exhibit experimental evidence of involving quantum mechanical tunneling. The circumstances that favor tunneling and the question whether the latter can be facilitated – e. g. in the evolution of an enzyme – are subjects of current interest.

The reaction of $[Tp^{t-Bu,Me}Cr(O)(pz'H)]BARF$ (**2**) with 9,10-dihydroanthracene (DHA) in methylene chloride rapidly and essentially quantitatively produced $[Tp^{t-Bu,Me}Cr(OH)(pz'H)]BARF$ and anthracene. Kinetic isotope effect measurements using 9,9,10,10-tetradeuterioanthracene (DHA-d₄, 99.6 %D) showed $k_H/k_D(303K) = 19.1$ and $k_H/k_D(293K) = 25.2$. While these kinetic isotope effects certainly imply C-H(D) bond breaking in the rate determining step, their values are unusually large. H/D kinetic isotope effects substantially in excess of 7-9 are often considered an indication of a tunneling contribution, although this is not a sufficient condition by itself. Two further criteria used to support hydrogen atom tunneling are i) a difference in the activation enthalpy of the H and D transfer that is larger than the difference in the zero point energies of the bonds broken ($\Delta(\Delta H^\ddagger) > 1.2$ kcal/mol), and ii) a significant difference in the pre-exponential factors resulting from an Arrhenius analysis ($A_H/A_D < 0.7$). Therefore we have determined the activation parameters for the reactions of **1** with DHA and DHA-d₄.

Figure 3 shows Eyring plots for both reactions, and lists the activation parameters derived from both Eyring and Arrhenius analyses of the temperature dependencies of the rate constants. It is readily apparent that the two additional tests for quantum mechanical tunneling are met. Indeed, the deviations are extreme; thus the case for tunneling of the hydrogen atom is unambiguous. The observation of H-atom tunneling in this PCET is reminiscent of similar results in our earlier cobalt dioxygen chemistry.

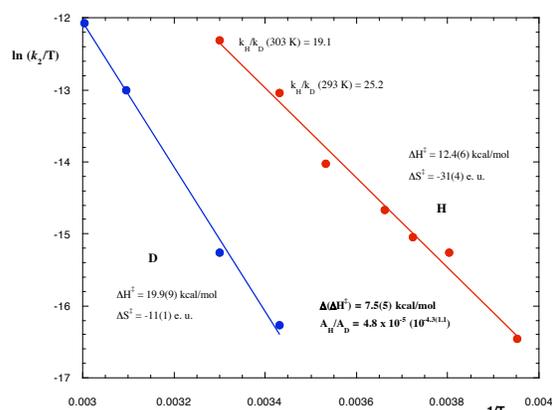


Figure 3. Activation parameters for the abstraction of H or D from dihydroanthracene.

These small molecule studies serve as models for biological systems, which are now acknowledged to exhibit tunneling components in many hydrogen transfer reactions. However, note the stark contrast to the cobalt imido chemistry described above. The circumstances that lead to hydrogen tunneling and/or its expression in unusually large isotope effects are not clear cut. Further studies of PCET reactions are necessary to elucidate these factors; they will be part of our future work.

Tris(pyrazolyl)borate Iron chemistry: The prevalence of iron in oxidation enzymes and the position of this element between chromium and cobalt has prompted us to initiate an exploration of $\text{Tp}^{\text{tBu.Me}}\text{Fe}$ chemistry. We have optimized conditions for the preparation of $[\text{Tp}^{\text{tBu.Me}}\text{Fe}(\text{OEt}_2)]\text{BARF}$ and $\text{Tp}^{\text{tBu.Me}}\text{Fe}(\text{CO})$. In fact, reduction of $\text{Tp}^{\text{tBu.Me}}\text{FeI}$ under N_2 yields a sensitive purple material that exhibits a characteristic $\nu_{\text{N}=\text{N}}$ at 1968 cm^{-1} ($\text{Tp}^{\text{tBu.Me}}\text{Fe}(\text{N}_2)?$). These substitutionally labile Fe(II) and Fe(I) precursors react with O_2 and oxo and imido synthons ($\text{PhI}=\text{O}$, $\text{PhI}=\text{NTs}$, AdN_3) to yield new iron complexes. Full characterization of these compounds and an investigation of their reactivities will be part of the future work.

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Bradford B. Wayland

Catalytic Hydrogenation of Carbon Monoxide and Hydrocarbon Oxidations

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Primary Objectives

Central objectives of this program encompass the development of new strategies and catalyst materials that activate CO, H₂, CH₄, C₂H₄, O₂ and related substrates relevant to the conversion of carbon monoxide, alkanes and alkenes to organic oxygenates. One of the primary objectives is the design and synthesis of metal complexes that manifest reactivity patterns associated with potential pathways for the hydrogenation of carbon monoxide. Particular emphasis is placed on developing metal systems that react with CO to produce metallo-formyl (M-CHO), dimetal ketone (M-C(O)-M), and dimetal dionyl (M-C(O)-C(O)-M) complexes which are implicated in pathways for CO hydrogenation. Hydrocarbon oxidations using molecular oxygen encompass major objectives in methane activation and functionalization as well as regioselective hydration and oxidation of alkenes. Another broad goal and recurring theme is to establish and grow the thermodynamic data base for a wide scope of organo-metal transformations in a range of reaction media.

Recent Progress

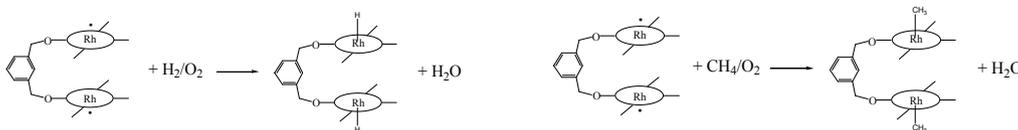
I. Tethered Diporphyrin Dimetal Complexes for Reactions where Two Metal Sites Occur in the Transition State: The initial objective was to prepare bimetallo-radical complexes by tethering two porphyrins together to increase the rates of metalloradical substrate reactions that involve two metalloradicals in the transition state. Our longer range goals are to apply tethered bimetallo species to advance a series of objectives including dioxygen homolysis, CO reductive coupling, and carbene coupling.

A. Tethered Diporphyrins: A series of tethered diporphyrin ligands were designed specifically to improve the rates for rhodium(II) porphyrin reactions with substrates such as methane where two metallo-radicals occur in the transition state. The essential design feature needed to accomplish this objective is to have the appropriate length and flexibility of the tethering unit which permits the two metal centers to reach the required transition state for the intramolecular substrate reaction. Steric demands for the individual porphyrin units are varied to preclude or permit intra and intermolecular M-M bonding. These features have been incorporated into a set of diporphyrin ligands by linking two porphyrin units with a series of diether spacers. One example diporphyrin ligand with a *m*-xylyl diether tether has been utilized in a series of applications.

B. Kinetic-mechanistic and Equilibrium Thermodynamics Studies for Reactions of $\cdot Rh(m\text{-xylyl})Rh\cdot$ with H₂ and CH₃R Substrates: Facile alkane hydrocarbon reactions with kinetic and thermodynamic preference for CH₄ reaction over that for other

alkanes and CH₃OH along with complete exclusion of aromatic C-H bond reactions is currently a unique set of selectivity features for rhodium (II) porphyrins. These reaction characteristics result from the combined structural and electronic features of the substrate, metal complex, and transition state. The favorable selectivity features for this system justify the continuing effort to enhance reaction rates and selectivity further and to explore strategies for alkane functionalization for the metalloradical activation pathway.

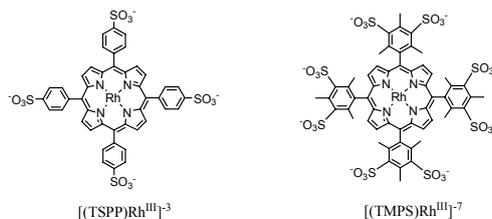
C. Dioxygen Reaction of \cdot Rh(*m*-xylyl)Rh \cdot : The dirhodium(II) tethered diporphyrin (\cdot Rh(*m*-xylyl)Rh \cdot) reacts in benzene with oxygen to form 1 : 1 and 2 : 1 superoxo complexes. Dioxygen pressure dependence for the mole fraction averaged ¹HNMR shift associated with rapid O₂ exchange is used in determining equilibrium constants of 1.5×10^4 and 7.4×10^3 for the 1 : 1 and 2 : 1 dioxygen adducts respectively. Reaction of O₂ and an excess of H₂ with \cdot Rh(*m*-xylyl)Rh \cdot produces catalytic formation of water and the dihydride complex as the final rhodium porphyrin species. Reaction of O₂ and CH₄ with \cdot Rh(*m*-xylyl)Rh \cdot produces a stoichiometric quantity of water and the dimethyl complex.



The pathways for these dioxygen substrate reactions are a current focus of interest.

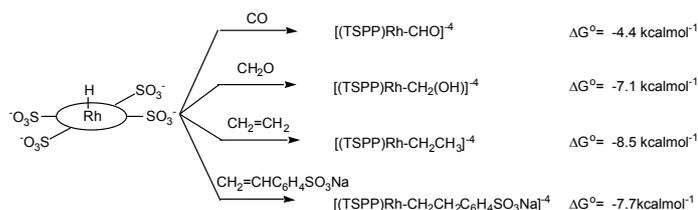
II. Reactivity and Thermodynamic Studies of Rhodium Porphyrin Substrate

Reactions in Aqueous Solution: Current interest in converting organometallic processes from organic to aqueous media has stimulated us to direct our attention toward evaluating the scope of organometallic reactions and thermodynamic parameters for rhodium porphyrin species in water. Sulfonation of tetraphenyl porphyrin (H₂TPP) and tetramesityl porphyrin (H₂TMP) provides a convenient source for a set of water soluble porphyrins (H₂TSP, H₂TMPS) that have distinctly different steric requirements.



A. Substrate Reactions of (TSP)Rh-H with CO, RCHO and CH₂=CHR in Water:

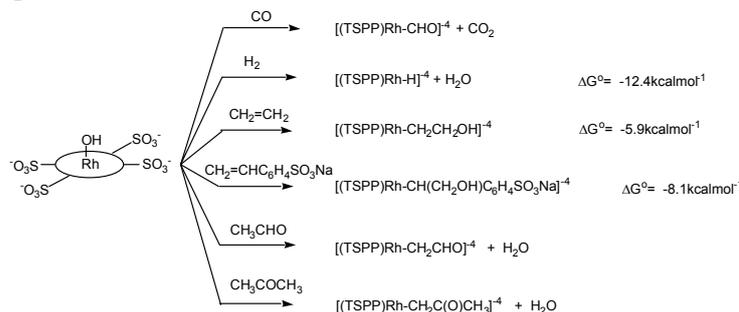
Each of the (por)Rh-H reactions with unsaturated substrates that were first observed in organic media have now been observed to have analogous reactions in water. Reactions of (TSP)Rh-H with CO, aldehydes and olefins that produce formyl, α -hydroxyalkyl and alkyl derivatives are summarized in Scheme 1. The hydride complex $[(\text{TSP})\text{Rh}-\text{H}]^{-4}$ heterolytically dissociates as a weak acid in water ($K_a = 8.0 \times 10^{-8}$). Substrate reactions are very fast in water compared to benzene which is ascribed to the presence of ionic reaction pathways in water.



Scheme 1: Reactivity patterns of $[(\text{TSPP})\text{Rh-H}]^{4-}$ in water ($\Delta G^\circ(298\text{K})$)

B. Substrate Reactions of (TSPP)Rh-OH with CO, H₂, RCHO and CH₂=CHR:

Reactions of a Rh-OH unit with a series of substrates in water are currently being evaluated for comparison with Rh-H reactions and as a route for olefin oxidations.



Scheme 2: Reactions of (TSPP)Rh-OH with CO, H₂, olefins, aldehydes and ketones in water

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Preparation of Supported Au Nanocatalysts from Au₁₃ Cluster Precursors

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DE-FG02- 03ER15476

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DE-FG02- 03ER15475

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DE-FG02- 03ER15477

The structure of Au heterogeneous catalysts on the anatase form of TiO₂ has been characterized by high resolution electron microscopy (HREM) and quantitative Z-contrast scanning transmission electron microscopy (STEM). These materials are prepared by deposition of highly monodisperse Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₄ (8-Å diameter) ligand-protected clusters on anatase, followed by reaction with ozone or an oxidative thermal treatment to remove the ligands. The materials obtained differ markedly in each case. The HAADF-STEM images (Figure 1) show that the thermally-treated materials (Fig. 1a) grow to a much larger size [2.7 ± 0.6 nm, average number of Au atoms/particle: 324 ± 264 atoms] than the ozone-treated samples (Fig. 1b) [1.2 ± 0.5 nm, 40 ± 49 atoms]. It was found that subsequent thermal treatments of the ozone-derived supported nanoparticles at 673 K in air (Fig. 1c) did not induce additional growth [1.5 ± 0.4 nm, 46 ± 34 atoms], indicating that sintering is strongly impacted by the particle/support interactions developed by the ozone-based low-temperature ligand removal step.

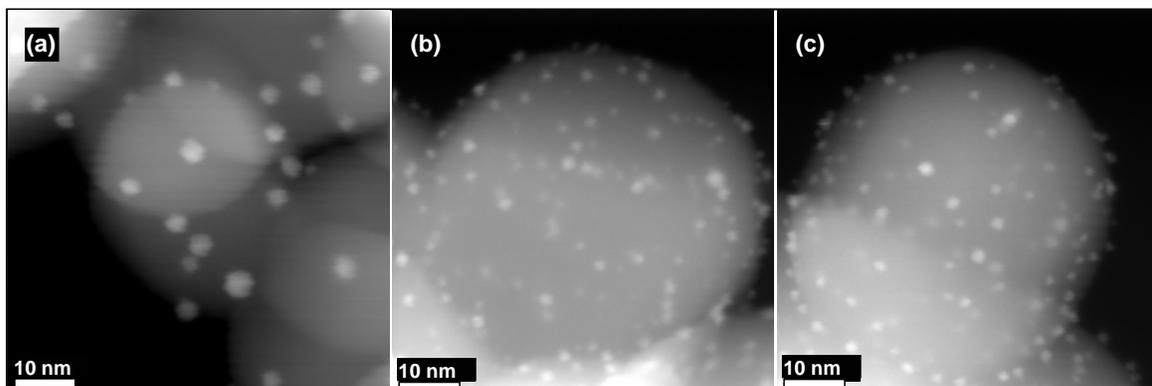


Figure 1. Representative HAADF-STEM images of (a) nanoparticles after thermal treatment, (b) nanoparticles after ozone treatment, and (c) nanoparticles after ozone treatment followed by calcination.

The shape of the supported Au particles prepared using either method of ligand removal was determined using both HREM (Figure 2) and the atom count-diameter relationship determined on a per particle basis in the quantitative STEM measurements (Figure 3). For the thermal treatment at 673 K in air, the supported particles are found to adopt a nearly spherical geometry. The atom count-diameter profile of 100 particles (Fig. 3a) shows that the distribution of particles actually lies slightly to the right of the spherical model (modeled as a cuboctahedron) which indicates some flattening. The HREM images (Fig. 2a) are consistent with this and show some truncation of the Au nanoparticles with typical aspect ratios (particle height/diameter) of 0.85. The smaller supported nanoparticles prepared using the ozone ligand-removal assume a more oblate geometry, consistent with a hemispherical shape (modeled as a truncated cuboctahedron) as evidenced in both the HREM image (Fig. 2b) and the HAADF-STEM results (Fig. 3b). These particles are resistant to further growth even up to temperatures of 673 K in air. Although the average diameter of these particles does increase slightly upon this thermal treatment, there is no

concomitant increase in the number of Au atoms in the nanoparticles which indicates particle flattening and not particle sintering. This is illustrated in Figure 3c where it is evident that the distribution of particle atom counts as a function of diameter lies slightly below the hemispherical model line. This is in contrast to the material after ozone treatment but prior to thermal treatment in which the data are symmetrically scattered around the hemispherical line. These latter effects are of particular interest for Au catalysis in which small, thermally-stable particles with large area nanoparticle/support interfaces are indicated to have the highest activity.

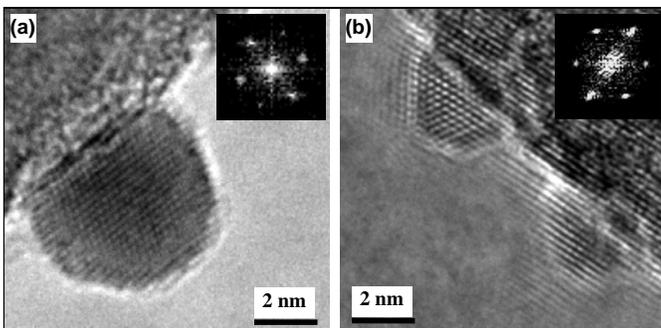


Figure 2. HREM images of a Au nanoparticles on TiO₂ support after ligand removal by (a) thermal treatment and (b) ozone treatment. The insets are the Fourier transforms of the Au particles, indicating face-centered cubic structure.

In order to develop a better understanding of the impacts of nanoparticle size and support effects on catalytic activity, it is desirable to develop synthesis protocols that are broadly applicable to a large number of supports such that the catalysts are impacted by the same chemistries during preparation. In this context, the facile deposition of Au₁₃ ligand-protected clusters has also been demonstrated on Al₂O₃ and C black. Following ozone treatment, supported particles with average diameters of 1.9 nm were observed on both of these supports. Interestingly, a similar protocol using mesoporous SiO₂ (SBA-15) resulted in nanoparticles, and in some instances nanowires, with critical dimensions that were determined by the diameter of the pores in SiO₂ (~8 nm).

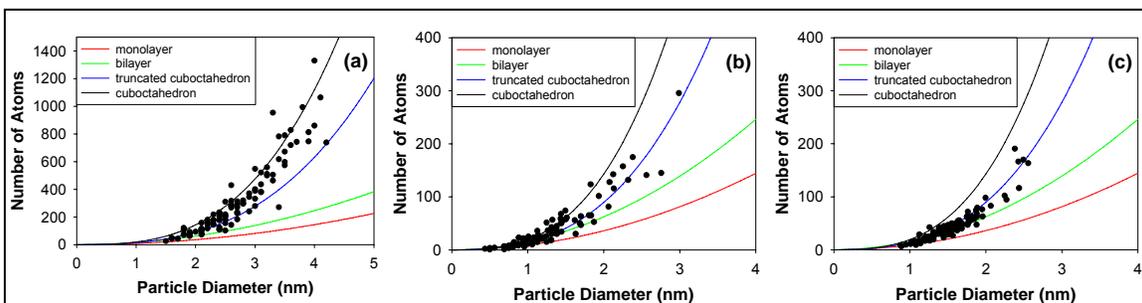


Figure 3. Number of atoms in the Au nanoparticles plotted as a function of nanoparticle size for (a) nanoparticles after thermal treatment, (b) nanoparticles after ozone treatment, and (c) nanoparticles after ozone treatment followed by calcination.

DEFG02-03ER15476

Judith Yang (U. Pittsburgh)

CATALYSIS SCIENCE INITIATIVE: The Reactivity and Structural Dynamics of Supported Metal Nanoclusters Using Electron Microscopy, *in situ* X-Ray Spectroscopy, Electronic Structure Theories, and Molecular Dynamics Simulations.

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Goals:

The research plan of work will have two programmatic foci: 1) We will center on the continued development of state of the art tools (electron microscopy, X-ray absorption fine-structure (XAFS) spectroscopy and first principles theories) for characterizing the structural dynamics of nanoscale materials important in heterogeneous catalysis. 2) We will develop a directed set of applications, ones in which the collaborating team of investigators will exploit recently developed tools to fully investigate the properties of metal-based nanoscale materials explicitly chosen for their utility in catalysis and advanced energy conversion systems:

- The monodispersed, supported Pt nanoclusters (where we have recently observed negative thermal expansion effect) and their alloys with Rh and Ir;
- The Au nanocluster catalysts supported on TiO₂ where atomic level correlations between cluster structures and size-dependent perturbations of electronic structure generate novel forms of reactivity unique to the nanoscale size regime;
- Novel alloy systems that our recent work has shown function as extremely efficient anode catalysts in direct oxidation fuel cells—an effort that will bring our novel characterization methods to bear on an energy system of great current interest that exploits heterogeneous catalytic processes involving solid-liquid interfaces.

DOE Interest:

Obtaining fundamental atomistic understanding of the structural dynamics of nanoscale catalyst materials, especially as they operate in real catalytic environments, represents an important grand challenge—one whose redress is needed to support progress in energy-related missions of the Department of Energy. Such understanding is required in order to

overcome the main limitation in many important heterogeneous catalytic processes. This goal serves as both 1) the focus of the tool development part of this effort and as 2) the application of these tools to reforming catalyst systems, delivering more than 5 billion gallons of hydrocarbon fuels, using the test case of Pt/ γ -Al₂O₃.

Research Plan:

During the previous grant period, we developed the suite of inter-related tools for nanocatalyst structure analysis: experimental (electron microscopy, X-ray absorption spectroscopy) and theoretical (density functional theory-based). There still remain very crucial needs that must be addressed before full 3-D atomic level descriptions of the structures and dynamics of catalytic materials can be developed in ways that are relevant to their use in real processes.

The highest priority on our list of such needs is systematic investigation of Negative Thermal Expansion (NTE) that we recently observed in Pt/ γ -Al₂O₃ clusters (Figure 1) – the totally unexpected effect in closed packed structures.

This observation has broad implications for heterogeneous catalysis, since the impacts on energetics it suggests must also bear on catalytic activity as well. We will investigate and compare the roles of the metal-support charge transfer and metal-support bond length disorder on the NTE. We believe this is a general effect relevant to bonding interactions of Pt with this support, even in cases where larger cluster sizes would serve to obscure signatures of support-mediated NTE under a larger, more bulk-like response.

As part of our systematic investigation of metal-support and metal-adsorbate interactions, we will employ new instrumental capacities that we have recently contributed to this effort. Due to several recent investments made in electron microscopy and XAS research infrastructure in 2005-2006 by members of our team (Yang – a JEM2100F instrument at U. Pittsburgh, new developments in tomography, Nuzzo – a VG-STEM and JEOL 2200F, with monochromator and aberration-corrected lens, microscopes at UIUC, Frenkel – establishment of the Synchrotron Catalysis Consortium facilities at Brookhaven Lab with capabilities for time-resolved (1s) XAFS), our new capabilities will allow us, for the first time, to carry out direct structural investigation (using the combination of electron microscopy and XAFS) of metal-support interfaces.

We will extend current methods that enable DFT-based calculations to identify low-energy structures, utilizing a rapid-selection protocol that appears to be well suited to applications involving supported nanoscale materials. In particular, we will investigate passivation effects on the clusters (from, e.g., H and OH) or due to the support chemistry that result from processing. Moreover, due to processing, defects are found on the support that interact with the nanoclusters and alter their structure and properties. We will look at these critical combination effects for the microstructure and morphology of supported metal clusters – which may be responsible for the recently observed negative thermal expansion effect. In general, we will connect rigorously and quantitatively the observed properties to details of the processing and surface and interface effects.

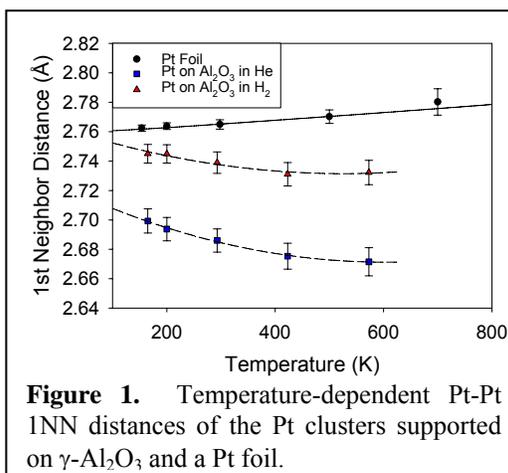


Figure 1. Temperature-dependent Pt-Pt 1NN distances of the Pt clusters supported on γ -Al₂O₃ and a Pt foil.

Recent Progress:

We recently studied the preparation of Au on TiO₂ heterogeneous catalysts by deposition of highly monodisperse Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₄ (8-Å diameter) ligand-protected clusters on anatase, followed by reaction with ozone or an oxidative thermal treatment to remove the ligands and expose catalytic surface sites. The materials obtained differ based on the ligand-removal technique employed. For the thermal treatment at 673 K in air, the supported particles grow to an average size of 2.7 nm (±0.6 nm) in diameter and are found to adopt a spherical geometry. Particle growth is greatly inhibited when ozone is used to remove the ligands (average diameter 1.2±0.5 nm). These particles assume a more oblate geometry, consistent with a truncated hemispherical shape. It was found that subsequent thermal treatments of the ozone-derived supported nanoparticles at 673 K in air did not induce additional growth, indicating that sintering is strongly impacted by the particle/support interactions developed by the ozone-based low-temperature ligand removal step. Furthermore, the method of catalyst preparation via Au cluster precursors treated with ozone is broadly applicable to a variety of substrates (an advantage over the current benchmark deposition-precipitation method). We have demonstrated the preparation of Au nanoparticles on Al₂O₃, carbon black, and mesoporous SiO₂ using this general approach.

Structural relaxation of nanoparticles as studied by EXAFS

In the mixed-ligand Au₁₃ nanoparticles (Fig. 2 a,b), the EXAFS analysis revealed the presence of an icosahedral strain of ca. 2.5% as compared to the 5% strain predicted geometrically. This strain relaxation is correlated with and can be understood in terms of the ligand bonding that terminate the cluster's surface. Obtaining such levels of structural understanding, however, is only possible if the synthetic protocols used deliver samples that are comprised of extremely monodispersed nanoparticles, a condition where it becomes possible to use EXAFS to discriminate intra vs. inter particle disorder (where the latter arises as a result of size-dependent atomic bond-length relaxation).

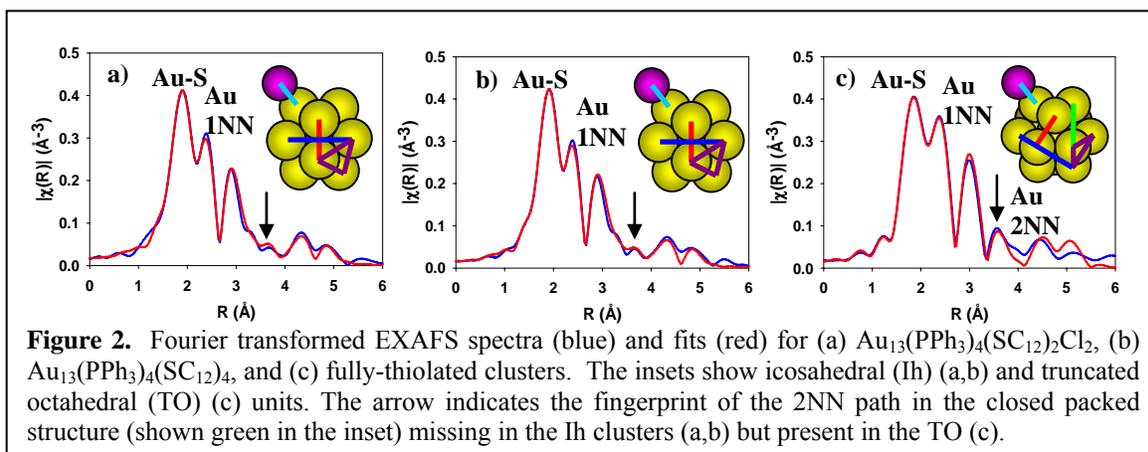


Figure 2. Fourier transformed EXAFS spectra (blue) and fits (red) for (a) Au₁₃(PPh₃)₄(SC₁₂)₂Cl₂, (b) Au₁₃(PPh₃)₄(SC₁₂)₄, and (c) fully-thiolated clusters. The insets show icosahedral (Ih) (a,b) and truncated octahedral (TO) (c) units. The arrow indicates the fingerprint of the 2NN path in the closed packed structure (shown green in the inset) missing in the Ih clusters (a,b) but present in the TO (c).

In general, structural relaxations in nanoclusters (e.g., contractions of metal-metal bond lengths) occur due to the large number of non-bulk like atoms. The data in Figure 3 illustrate this point in greater detail, highlighting our recent EXAFS measurements made on a series of rigorously characterized Pt catalysts supported on γ -Al₂O₃. The data show the strong size dependent scaling of the average first-shell Pt-Pt bonding distances found in these samples. These distances are plotted here in terms of the 1NN coordination number measured by EXAFS, a parameter that correlates with both the particle's shape and diameter (which can be independently obtained by microscopy for monodispersed clusters). The sample with the smallest Pt particles (0.9 nm)

consisted of a highly homogeneous sample of Pt₁₅ clusters (HAADF-STEM). The EXAFS data illustrate that size effects, in this case, elicit strong contractions of the metal-metal bonding distances—a structural relaxation that also develops a correlated and significant degree of interatomic disorder in the catalytic clusters. These relaxations can be partially lifted by H₂ which dissociates and passivates the surface bonds of the clusters.

Morphology and structural relaxation of nanoparticles studied by theory

The microstructure and morphology of supported metal clusters largely determine the catalytic activity and selectivity, as well as observed structural properties such as bond distributions. Using careful applications of density functional theory (DFT) methods, we have studied the morphology of a Pt₃₇ supported on carbon with(out) hydrogen (H) passivation, which is highly relevant to nanocluster processing. We find that a Pt₃₇ cluster without H has a morphological change driven by a shear instability in which (100) facets distort to (111) to lower surface energy, as found from the adsorption energetics of H on Pt (100) and (111) facets. In fact this shear instability is a remnant of that found in semi-infinite bulk Pt in which the (100) surface is unstable to formation of (111) facets. With H passivation, however, the sheared structure is automatically reversed to the truncated cuboctahedral (TC) structure found under processing condition, which included H₂ anneal; moreover, the average first nearest neighbor Pt-Pt bond length increases by 3%, which agrees very well with our experiments, as does the bond distributions and disorder [2]. Such calculations are sensitive to the molecules used for passivation and the supports used, which is the focus of our near term efforts. In addition, we have detailed the origin of bond distribution and bond disorder within metallic Pt and mixed Ru-Pt nanoparticles that were observed experimentally [10]. In addition we have shown critical errors that are implicit to most standard DFT calculations that produce incorrect ground states for mid transition-metal clusters [14].

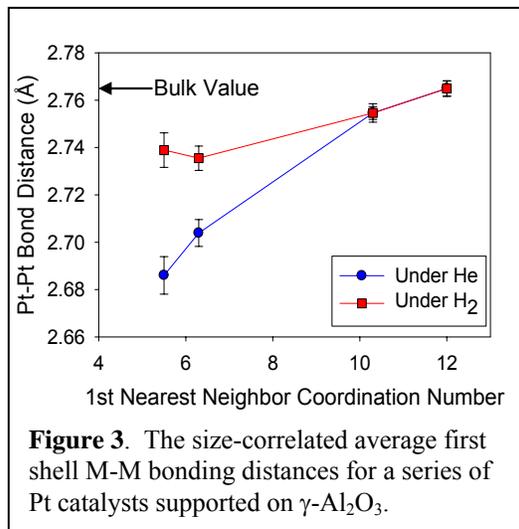


Figure 3. The size-correlated average first shell M-M bonding distances for a series of Pt catalysts supported on γ -Al₂O₃.

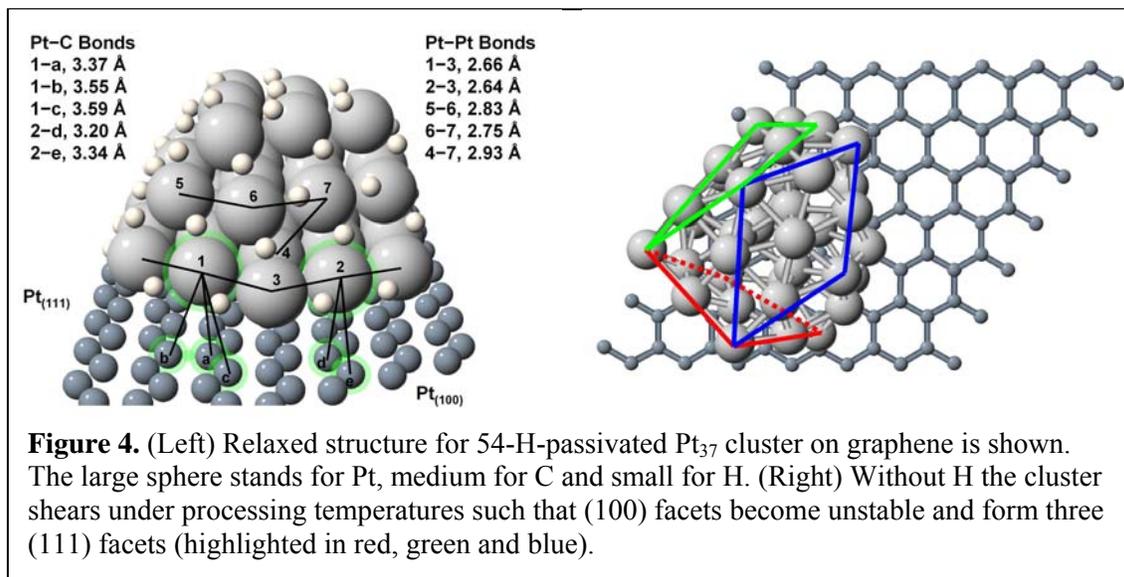


Figure 4. (Left) Relaxed structure for 54-H-passivated Pt₃₇ cluster on graphene is shown. The large sphere stands for Pt, medium for C and small for H. (Right) Without H the cluster shears under processing temperatures such that (100) facets become unstable and form three (111) facets (highlighted in red, green and blue).

Publications (acknowledging DOE support):

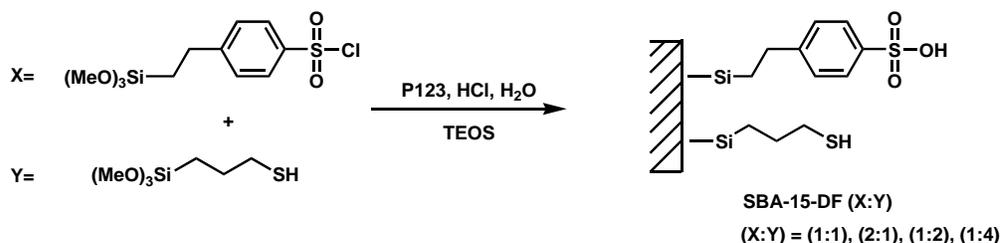
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It is very clear from this data that the thiol is the cause of the enhancements seen in the rate and selectivity in this reaction. Even very small amounts of thiol cause tremendous increases in the reaction rate and favors the formation of BPA over the o,p' isomer.

Based on these observations, we pursued a solid material that was functionalized with thiol and sulfonic acid groups. Using a modified one-pot procedure for the synthesis of SBA-15, we were able to incorporate various ratios of sulfonic acid to thiol on mesoporous SBA-15 (Scheme 1).

Scheme 1. Thiol/Sulfonic acid functionalized SBA-15.



These materials were then characterized by many characterization methods available for organically functionalized materials including ^{13}C solid state NMR, ^{29}Si solid state NMR, XRD analysis, N₂ adsorption, TGA analysis, elemental analysis, Ellman's titration to determine thiol content, and acid titration through NaCl exchange to determine sulfonic acid content. We then used these materials to catalyze the reaction to form Bisphenol A and the results are presented in Table 2.

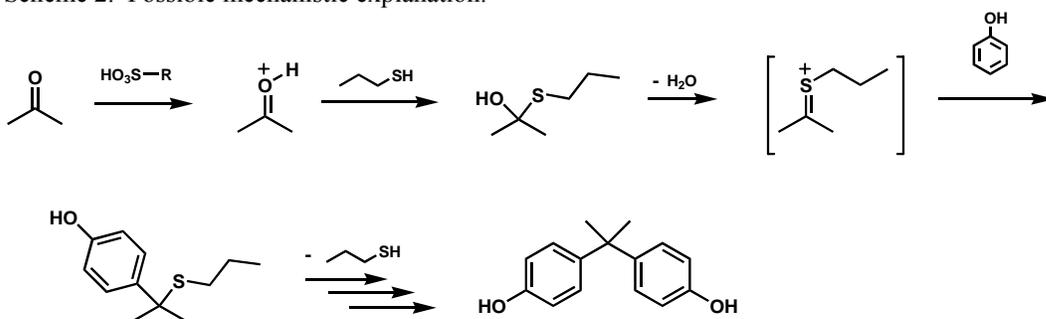
Table 2. Heterogeneous catalysis with mixed thiol/sulfonic acid catalysts.

Entry	Catalyst (eq)	Ratio (acid:SH)	% BPA	% o,p'	p,p' : o,p'	PSY
1	SBA-15-DF (1:1)	1:1	70.6	4.0	17.3:1	74.6
2	SBA-15-DF (2:1)	2:1	60.0	5.0	12.0:1	65.0
3	SBA-15-DF (1:2)	1:2	78.0	3.9	19.8:1	81.9
4	SBA-15-DF (1:4)	1:4	71.3	4.4	16.3:1	75.7
5	Phys. Mix.	1:1	14.6	4.9	3.0:1	19.5
6	pTSA	—	20.5	5.1	3.99:1	25.6
7	+	1:1	25.6	5.7	4.5:1	31.3
8	pTSA +	1:1	29.5	7.2	4.1:1	36.7

Reaction conditions: 3.5 eq phenol, 1.0 eq acetone, 0.01 eq sulfonic acid, 100°C, 24 hours
 Yields determined by HPLC quantification of BPA and o,p' isomer production. Conversion calculated based on acetone as limiting reagent. Per site yield calculated per sulfonic acid site. pTSA = para-toluenesulfonic acid. Entry 5 is a physical mixture of SBA-propyl-SH and SBA-SO₃H in a 1:1 ratio.

As is clearly indicated by entries 1-4, these materials with varying ratios of sulfonic acids and thiol give rise to large enhancements in selectivity and reaction rate, some higher than the best homogeneous cases. The most telling is entry 5, which was done with a physical mixture of the two functional groups on separate supports, where there is almost no enhancement in selectivity or rate when the two functional groups are isolated. This is indicative of a cooperative effect that involves both functional groups giving rise to increased conversion and selectivity. We have proposed the mechanism below in Scheme 2 to rationalize these observations. This mechanism involves the acetone first being activated by the acid and then the nucleophilic thiol attacking the carbonyl to give an activated charged sulfur intermediate. This intermediate is more reactive towards nucleophiles (hence causing rate increases) and the aliphatic chain of the thiol is positioned where it would impart a steric influence on the approach of phenol, potentially affecting selectivity as well.

Scheme 2. Possible mechanistic explanation.



Towards this end, we have investigated the steric influence of the thiol (Table 3). The steric nature of the thiol clearly has a dramatic effect on conversion and selectivity. Although this is not direct proof of the proposed mechanism, it does suggest that the thiol does interact with the site of phenol addition to affect selectivity.

Table 3. Steric effect of thiol on reaction.

Entry	Catalyst (eq)	Additive (eq)	Conv.		p,p' : o,p'	PSY
			BPA (%)	o,p (%)		
1	(0.01)	(0.01)	8.8	5.7	1.5:1	14.5
2	(0.01)	(0.01)	45.3	6.4	7.1:1	51.7
3	SBA-15 (0.01)	(0.01)	2.9	1.0	2.8:1	3.9
4	SBA-15 (0.01)	(0.01)	12.7	1.1	11.1:1	13.8

Reaction conditions: 3.5 eq phenol, 1.0 eq acetone, 0.01 eq sulfonic acid, 100°C, 24 hours
 Yields determined by HPLC quantification of BPA and o,p isomer production. Conversion calculated based on acetone as limiting reagent. Per site yield calculated per sulfonic acid site.

Presentations:

Design of Hybrid Organic-Inorganic Materials for Heterogeneous Catalysis. Oral Presentation, E-MRS conference, Strasbourg, France. June 3rd, 2005.

Design of Hybrid Organic-Inorganic Materials for Heterogeneous Catalysis. Poster Presentation, ICCOSS conference, UCLA, Los Angeles, CA. July 6th, 2005.

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Publications:

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