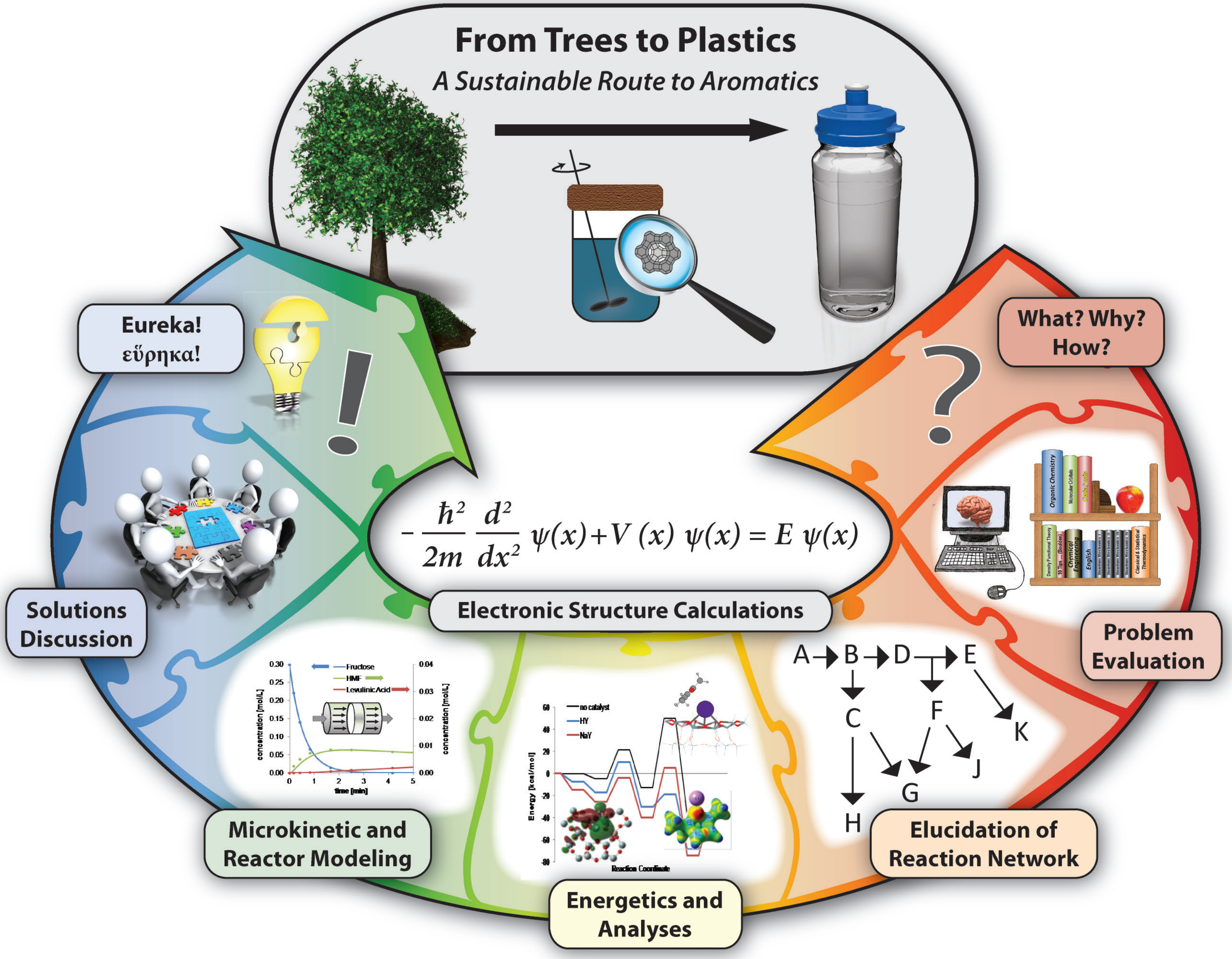
CENTER FOR CATALYTIC SCIENCE & TECHNOLOGY

RESEARCH REPORT
2013



Dare to be first.

UNIVERSITY OF DELAWARE

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FROM THE DIRECTOR

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Synthesis, characterization and discovery of novel microporous materials and structure property relationships in catalysts and adsorption.

Welcome to the 2013 edition of our annual report, a report that reflects the strength and dynamism of our research activities at the Center for Catalytic Science and Technology (CCST) in different areas of catalysis research.

CCST has had an extremely productive year with numerous interesting discoveries in catalysis and energy-related topics. For example, Joel Rosenthal, CCST faculty and assistant professor of Chemistry & Biochemistry, recently reported in the *Journal of the American Chemical Society* (JACS), the discovery of a bismuth-modified glassy-carbon electrode with excellent properties for the electrochemical conversion of CO_2 to CO on a variety of solvents. The devices have low overpotentials and high Faradaic efficiencies leading to excellent energy efficiency for CO production, comparable to what has been observed using expensive catalysts like silver or gold. Complementary to Rosenthal's findings, Feng Jiao, assistant professor of chemical and biomolecular engineering, also reported in JACS a discovery in electrocatalysis, in which he synthesized ordered mesoporous Mg-substituted Co_3O_4 spinels with crystalline walls. These materials produce a highly porous cobalt oxide with a significant amount of defects in the spinel structure. The materials have excellent properties for the oxygen evolution reaction from water using only earth-abundant materials and with excellent TOF per metal atom.

A different example is illustrated by an experimental and theoretical collaboration between Dionisios Vlachos and Jingguang Chen. They recently reported in *ChemSusChem* the discovery of molybdenum carbides as excellent catalysts for the selective hydrodeoxygenation of biomass-derived oxygenates to unsaturated hydrocarbons. This report highlights the great potential of molybdenum and tungsten carbides for the upgrading of oxygenates into fuels and more valuable chemical species. These three examples are just a few of the highlights that are described in this report. Donald Watson discovered a new catalyst for the silyl-Heck reaction for the coupling of vinyl and allylsilanes, Douglas Buttrey has made important strides in understanding the active site of the M1 catalyst for propane ammoxidation, etc. Our publication record reflects the high level of research activity at the Center and our commitment to maintain CCST as a leader in the development and understanding of catalysts that are of industrial and societal value.

This year has also brought some important changes in personnel to the CCST. I want to extend a welcome to Prof. Bingjun Xu, who joined Chemical and Biomolecular Engineering and CCST in August. Bingjun conducted his graduate studies with Profs. Cynthia Friend and Robert Madix in Chemistry at Harvard and just finished a postdoctoral fellowship with Prof. Mark Davis at Caltech. His research interests span from surface science to thermochemical cycles for energy conversion. I would also like to mention the departure of Prof. Jingguang Chen (to Columbia University) and Prof. Mark Barteau (to the University of Michigan) after many decades of extraordinary work for the CCST and the field of heterogeneous catalysis here at UD. Both are former directors of CCST and helped shape the culture of collaboration and industrial interactions that remain a hallmark of the Center to this day. We wish them well in their new career paths and look forward to continue to work with them collaboratively in the years to come.

Marguerite Mahoney has been the assistant to the Director for over four years, a position of incredible value to our students and faculty. She has supported CCST with incredible energy, ingenuity and enthusiasm. Beginning last year, Marguerite took the additional responsibility of assisting the University of Delaware Energy Institute (UDEI) and she has recently decided to focus her work at UDEI. Marguerite has been working with Rechilda (Chil) Alba, who will be the new assistant, to ensure a smooth transition. Please welcome Chil and meet her at the next Annual Review. I am sure Chil will carry on with our tradition of professionalism and service to students and faculty.

I invite you to read the report, maintain your contacts with CCST faculty, students and alumni and visit us for the upcoming 2013 Annual Research Review where many of the exciting findings described here and more will be presented.

With best regards,

RAUL LOBO
CCST Director

Industrial Sponsors Program

Our Industrial Sponsors Program embodies the principal mechanisms for industry-university cooperation as they have evolved over the Center's three decades of operation. The tangible benefits of such cooperation are many and include joint research programs, publications, and patents, as well as significant opportunities for support through established industry-university cooperative research funding mechanisms.

Benefits of Sponsorship

CCST sponsors benefit from the full portfolio of the Center's research activities including a number of programs designed to provide early access to nonproprietary research:

Access to CCST Facilities

- Sample analysis
- Discounted rates for experiments
- Use of CCST software

Faculty Expertise

- Consultation by CCST faculty

Recruitment

- Recruitment of outstanding students

Research Programs and Activities

- Invitation to the Center's annual research review at which the results of ongoing research programs are presented by center faculty and students
- Annual report of the Center's research activities and accomplishments

CCST Seminars

- Invitation to Center seminars by catalysis experts from around the world

CCST SPONSORS

- **Air Force Office of Scientific Research**
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- **Ashland Research Center**
- **E. I. du Pont de Nemours and Co., Inc.**
- **Eastman Chemical Company**
- **ExxonMobil Research and Engineering Company**
- **Imperium Aviation Fuels, LLC**
- **Johnson Matthey**
- **National Science Foundation**
- **National Institute of Standards and Technology**
- **U.S. Department of Energy**

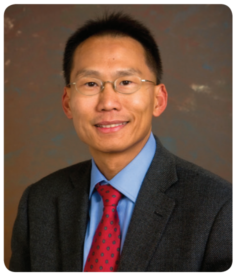
CENTER FACULTY

Douglas J. Buttrey

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Synthesis of complex oxides and alloys, composition-structure-property relationships in catalytic and electronic materials; high-resolution electron microscopy



Wilfred Chen

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

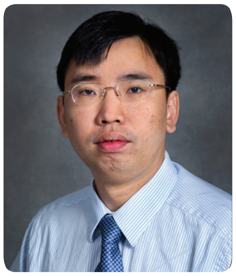
Cellular and metabolic engineering, synthetic biology for biofuel production, protein therapeutics, viral detection, drug discovery, protein purification.

Douglas J. Doren

Chemistry & Biochemistry

RESEARCH INTERESTS

Theoretical and computational methods with applications to materials science, surface science, catalysis and solvation



Feng Jiao

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Energy storage and conversion, advanced lithium-ion batteries, solar energy harvesting, and synthesis of nanostructure materials

Michael T. Klein

Chemical & Biomolecular Engineering

www.che.udel.edu/klein

RESEARCH INTERESTS

Chemical Reaction Engineering with special emphasis on the kinetics of complex systems

Raul F. Lobo

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

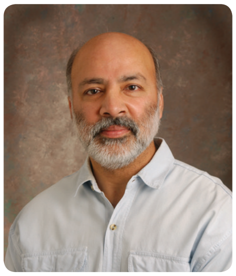
Synthesis, characterization and discovery of novel microporous materials, and structure property relationships in catalysts and adsorption.

Joel Rosenthal

Chemistry & Biochemistry

RESEARCH INTERESTS

Energy storage and conversion, solar energy harvesting, catalysis, electrochemistry, photochemistry, chemical detection arrays and inorganic synthesis.



S. Ismat Shah

Materials Science & Engineering

RESEARCH INTERESTS

Nanostructured materials synthesis via PVD and CVD processes with applications to environmental catalysis and energy generation

Andrew V. Teplyakov

Chemistry & Biochemistry

RESEARCH INTERESTS

Experimental and computational surface and thin film chemistry, diffusion barriers, nucleation, growth, self-assembly, surface modification.

Klaus H. Theopold

Chemistry & Biochemistry

RESEARCH INTERESTS

Homogeneous catalysis, coordination polymerization of olefins, activation of dioxygen by novel oxidation catalysis

Dionisios G. Vlachos

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Multiscale simulation, reacting flows, reaction mechanism development, catalyst design, microreactors, portable power, energy, crystal growth, nanomaterials, zeolites, membranes, separations.

Donald A. Watson

Chemistry & Biochemistry

RESEARCH INTERESTS

Transition-metal catalysis; organic synthesis; alternative energy chemistry

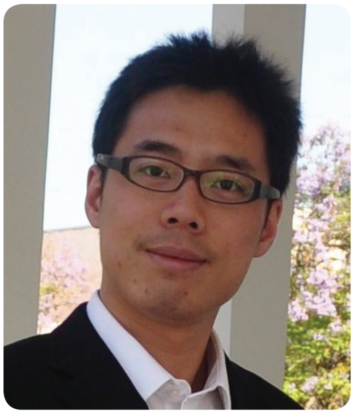
Yushan Yan

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

New materials for fuel cells, energy storage and solar hydrogen generation. Zeolite thin films for semiconductors and aerospace applications.

NEW FACULTY



Professor **Bingjun Xu** received his B.S. in Chemistry from Fudan University at Shanghai in 2004. He then stayed at Fudan University to pursue a Master's degree in heterogeneous catalysis during 2004-2007, working on synthesis and applications of solid acid catalysts for alkylation and dehydrogenation reactions. Upon finishing his Master thesis, he joined the Department of Chemistry and Chemical Biology at Harvard University as a graduate student. His graduate work focused on the mechanistic studies of gold surface mediated oxidative coupling reactions under ultrahigh vacuum conditions, employing a variety of surface sensitive reaction and spectroscopic techniques. He received the National Graduate Research Award of American Vacuum Society in 2011. After finishing his doctorate, he moved to the Department of Chemical Engineering at the California Institute of Technology for postdoctoral research, on thermochemical cycle for water splitting. He will join the Department of Chemical & Biomolecular Engineering at University of Delaware as Assistant Professor in the fall of 2013. His research will focus on efficient conversion of biomass to value-added chemicals, activation of alkanes and surface mediated electrochemical reactions for energy applications.

RECENT PUBLICATIONS

BUTTREY GROUP

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DOUGLAS J. BUTTREY

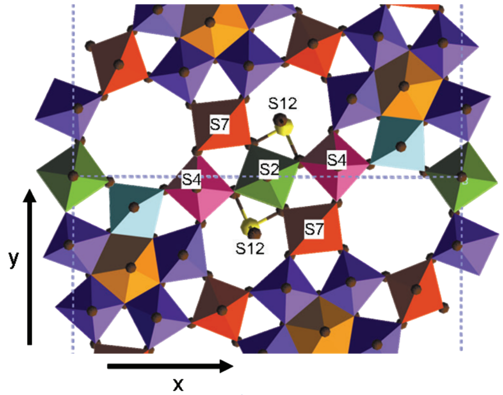
Synthetic Studies and Improved Structural Refinement of M1 Phase in Mo-V-Te-Nb-O Catalysts for Selective Oxidation and Ammoxidation of Propane

The Mo-V-Te-Nb-O mixed metal oxides are widely considered as the most efficient catalytic system for selective ammoxidation and oxidation of propane to acrylonitrile and acrylic acid, respectively. Two phases have been identified as the effective components: the orthorhombic M1 active phase and pseudo-hexagonal M2 promoter phase.

Two methods are often used for catalyst synthesis: the hydrothermal method and the slurry method. Both approaches involve mixing metal precursors in aqueous solutions as the first step. The former method requires the hydrothermal treatment of the resulting mixture in an autoclave, whereas in the slurry method, heat treatment (drying and calcination) is directly carried out after slurry formation. The hydrothermal method produces the M1 phase in a reasonably pure form without further purification. By contrast, the slurry method typically results in simultaneous formation of M1 and M2, though it has the benefit of implementation with comparative ease.

In addition to the M1 and M2 phases, a variety of minor impurities frequently accompany the desired phases. Since the impurities have simpler structures with smaller unit cells compared with the primary phases, these are often undetected. These may include $TeMo_5O_{16}$, V-substituted Mo_5O_{14}, Mo-substituted V_2O_5 and Te metal. The formation of $TeMo_5O_{16}$ is favored at relatively high slurry pH, whereas the formation of V-substituted Mo_5O_{14} is significantly affected by the heating rate of calcination. The formation of the V-substituted Mo_5O_{14} phase can be related to Te loss during the heat treatment. Mo-substituted V_2O_5 is always formed in small quantities when V is in excess, and can be removed by washing the product with concentrated hydrogen peroxide. In general, highly pure M1 can be produced by gently heating the precursor during calcination and washing the resulting product in hydrogen peroxide. An improved structural model of M1 has been developed using simultaneous Rietveld refinement of synchrotron and neutron diffraction data based on several improvements to the old model. These model improvements were motivated by feedback from aberration-corrected transmission electron microscopy. In addition, low-level impurity phases identified and included in the analysis.

The major part of the improvement results from the introduction of the Mo-substituted V_2O_5-type impurity phase. The improved refinement of the M1 model indicates that V preferentially occupies the linking sites (S1, S2, S3, S4, and S7 in Fig. 1) in the structure, consistent with the site contrast analysis based on previous HAADF imaging results. Bond valence sum results suggest that the oxidation state of V in the bulk contains significant 4+ valence, although it indicates that some linking sites (S3, S4, and S7 in Fig. 1) have a d^0/d^1 mixed configuration due to the presence of Mo^{6+}. These sites also showed intermediate level out-of-center distortion as compared to the typical severe distortion expected for d^0 sites with these elements. Based on electroneutrality considerations, it is apparent that the d^0 site concentration in sites S3, S4, and S7 closely matches the vanadium occupancy of these sites. Therefore, we believe that the vanadium in these sites is d^0 (V^{5+}) and the molybdenum is d1 (Mo^{5+}). It is and expected that surface V^{5+} species are needed in the active sites for propane activation.



Proposed active site

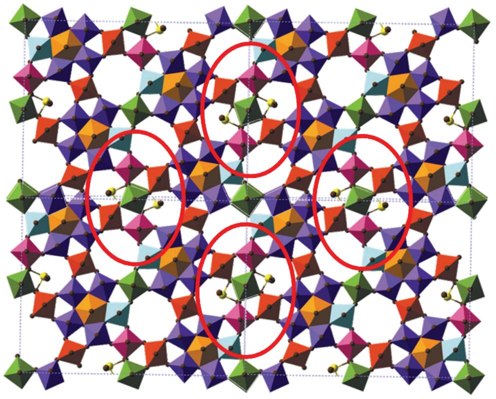


Fig. 1. [001] view (*ab* plane) of the new refined structure of M1 with 13 sites labeled, color codes are as follows: red: (Mo^{6+})/Mo^{5+}/V^{4+}, green: Mo^{5+}/V^{4+}, blue: Mo^{6+}, orange: Nb^{5+}, cyan: Mo^{6+}/V^{5+}(trace), yellow: Te^{4+}. –

Another important finding resulting from the improved refinement is the oxygens bridging the S2, S4, and S7 metal sites have anomalously large thermal parameters. Subsequent HAADF-STEM imaging experiments on the M1 phase have been performed to explore this further using a Protochips heating stage at Oak Ridge National Lab to observe the evolution of the structure with temperature. At 200°C, substantial thermal motion is evident among the active site metals producing some blurring in the image, whereas the pentagonal ring sites remain clear. Figure 2 shows the room temperature image (top) and the 200°C image (bottom). This is consistent with the large thermal parameters of active site oxygens observed in the room temperature refinement, and indicates that the active site is highly dynamic at elevated temperatures.

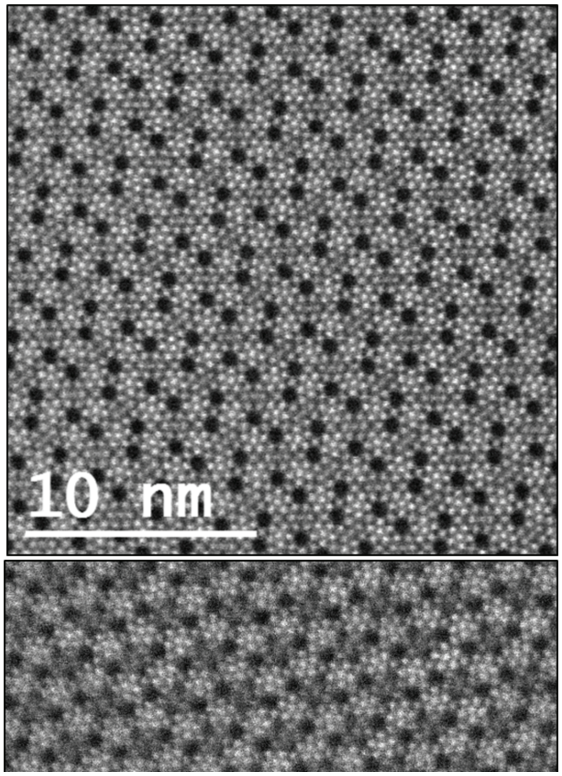


Figure 2. Aberration-corrected HADF-STEM images at ambient temperature (top) and at 200°C.

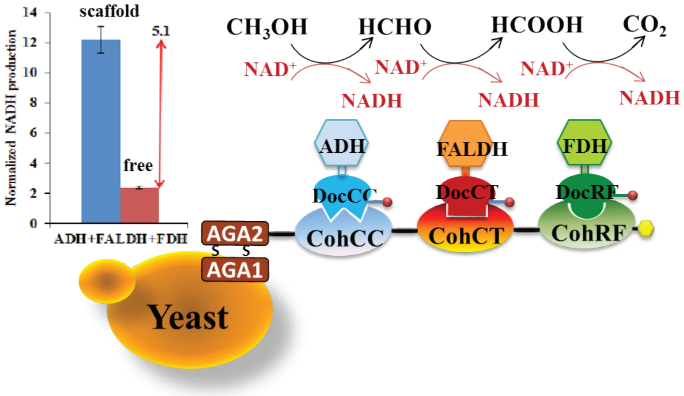
WILFRED CHEN

Functional assembly of a multi-enzyme methanol oxidation cascade on a surface-displayed trifunctional scaffold for enhanced NADH production

Current research efforts are focused on the engineering of protein scaffolds that can be used for biofuel production, disease diagnostic and treatment, drug discovery, and the environmentally-friendly biosynthesis. Another area of interest is the application of these scaffolds for biosensor development.

Enzymatic biofuel cells have significant advantages over conventional chemical fuel cells as since the enzymes are highly specific, and the devices can be operated under neutral pH and ambient temperature. However, they can be limited by low power densities, as most enzyme fuel cells employ only a single enzyme for partial fuel oxidation. A significant improvement in the current density can be achieved by using a multi-enzyme cascade capable of complete fuel oxidization. For example, methanol can be fully oxidized to CO_2 by three NAD+-dependent dehydrogenases, alcohol dehydrogenase (ADH), formaldehyde dehydrogenase (FALDH), and formate dehydrogenase (FDH) to provide six electrons to the anode rather than only two electrons based on a single-step oxidation.

We report a simple and low-cost strategy that allows the sequential and site-specific assembly of a dehydrogenase-based multi-enzyme cascade for methanol oxidation on the yeast surface using the high-affinity interactions between three orthogonal cohesin/dockerin pairs. The multi-enzyme cascade showed a five times higher NADH production rate than the non-complexed enzyme mixture, a result of efficient substrate channeling.



DOUGLAS DOREN

Theoretical Studies of Zinc-Gallium Oxonitride Visible Light Photocatalysts

Solid solutions of GaN and ZnO are a promising class of photocatalysts, capable of splitting water under visible-light irradiation. These materials have band gaps lower than either GaN or ZnO. We have examined two different forms of the zinc-gallium oxonitride (ZGON), the wurzite structure ($Ga_xZn_{x-1}N_xO_{x-1}$), and the spinel structure (Figure 1). This work has been done in collaboration with Professor Raul Lobo's group, which has provided the experimental studies to test our theoretical predictions. The structural and electronic properties have been studied using density-functional theory with the Linear Augmented Plane Wave (LAPW) method. A GGA+U approach is used to better describe the semicore 3d states of Ga and Zn and help improve band gap predictions, which are notoriously low in DFT calculations.

The wurzite structure calculations show that there exists a coupling between the N 2p and Zn 3d states, leading to a decreased band gap. The band gaps in the mixed metal oxonitrides are lower than either ZnO or GaN, thus allowing excitation by visible light. The trend in band gaps over the range of Zn concentrations ($0 \leq x \leq 1$) is consistent with experimental results. The expected band gap minimum corresponds to a high concentration of zinc ($x>0.6$) that cannot be synthesized by current approaches. We have calculated formation energies to understand the thermodynamic constraints on synthesis of these materials. Starting from ZnO and Ga_2O_3 in the presence of Ns at typical synthesis temperatures (1123 K), the heat of formation is negative up to x=0.6 (Figure 2). However, an alternative product distribution, with formation of Zn metal, becomes more favorable than oxonitride formation before x reaches 0.5 (Figure 2). This means that materials with high enough Zn-content to minimize the band gap cannot be synthesized with this approach.

One alternative synthesis is nitridation of sol-gel precursor, $ZnGa_2O_4$. Under low temperature synthesis conditions, an oxonitride with spinel structure is obtained. We have analyzed materials with low nitrogen and vacancy concentrations, $Zn_8Ga_{16}O_{29}N_2[V_O]$, with no transformation of the gallium atoms. We have explored the decrease in band gap from the pure precursor material (2.59 eV) to the ZGON (1.56 eV). We find that the addition of nitrogen creates new states at the top of the valence band, while the states at the bottom of the conduction band appear the same (Figure 3). Thus, we have concluded that these new states are leading to the decrease in band gap by raising the top of the valence band. We are working on examining other possible structures resulting from nitrogen substitutions and gallium transformations to confirm these findings. In addition, analogues with Al and Fe instead of Ga are being explored.

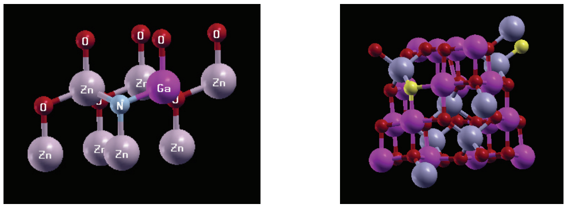


Figure 1 – Wurzite (a) and Spinel Structures (b)

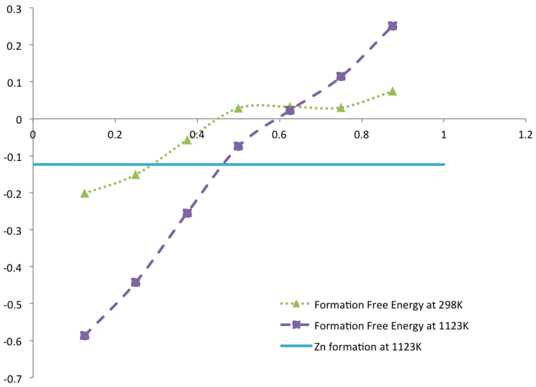


Figure 2 – The formation energy at 1123 K is negative for Zn content up to x=0.6. However, formation of Zn metal becomes favored below x=0.5, consistent with observed experimental limits on Zn concentrations.

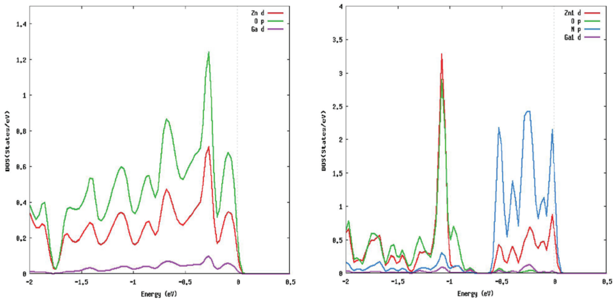


Figure 3. The Density of states of the pure spinel structure (a) and the nitrogen substituted structure (b) show new Zn d/ N p states formed at the top of the conduction band.

a. ZnGa2O4 b. Zn8Ga16O29N2[VO]

FENG JIAO

Photocatalytic Oxygen Evolution

Oxygen evolution from water using earth-abundant element based catalysts is crucial for mass solar fuel production. We recently synthesized a mesoporous cobalt oxide with an ultrahigh surface area (up to 250 m2 g-1) through Mg substitution in the mesoporous Co3O4 spinel, followed by a Mg-selective leaching process. Approximately one third of Mg cations were removed in the leaching process, resulting in a highly porous cobalt oxide with a significant amount of defects in the spinel structure. The activated mesoporous cobalt oxide exhibited high oxygen evolution activities in both the visible light driven [Ru(bpy)3]2+-persulfate system and the Ce4+/Ce3+ chemical water oxidation system. Under a strong acidic environment, a high turnover frequency (TOF) of ~2.2×10-3 s-1 per Co atom was achieved, which is more than twice of the TOFs of traditional hard-templated, mesoporous Co3O4. We also successfully extended the synthesis to other ordered mesoporous solids, such as Mn-doped Co3O4 and Ni-doped Co3O4.

MICHAEL T. KLEIN

Software Tools for the Construction of Detailed Kinetic Models

The worldwide energy transportation sector is almost entirely dependent on petroleum, a remarkable resource on which a highly sophisticated refining and vehicle infrastructure has grown. Given the capital value of the existing worldwide refining and transportation infrastructures, and the slow characteristic time for their change, it is likely that carbon-based resources, including unconventional feedstocks that will be upgraded for use with petroleum in the existing infrastructure, will be utilized for decades to come. Mathematical models of the chemistry of their upgrading and conversion will assist the commercial realization of these possibilities.

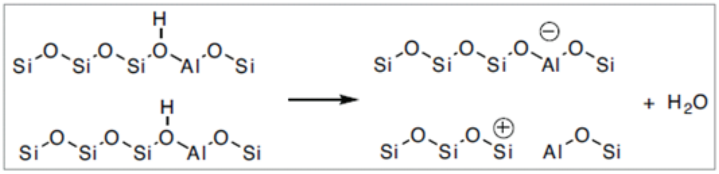
The considerable interest in molecule-based models of these chemistries is motivated by the need to predict both upstream and downstream properties. This is because the molecular composition is an optimal starting point for the prediction of mixture properties. The challenge of building these models is due to the staggering complexity of the complex reaction mixtures. There will often be thousands of potential molecular and intermediate (e.g., ions or radicals) species. Clearly, the use of the computer to not only solve but also formulate the model, would be helpful in that it would allow the modeler to focus on the basic chemistry, physics, and approximations of the model.

Our recent work has led to the development of an automated capability to model development. Statistical simulation of feedstock structure casts the modeling problem in molecular terms. Reactivity information is then organized in terms of quantitative linear free energy relationships. The model equations are then built and coded on the computer. Solution of this chemical reaction network, in the context of the chemical reactor, provides a prediction of the molecular composition, which is then organized into any desired commercially relevant outputs. Of particular note is the Attribute Reaction Model approach that is useful when the number of desired components in the molecular mixture is constrained by the practical limits of hardware and software.

RAUL F. LOBO

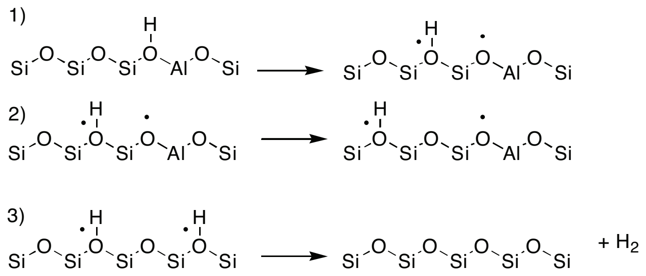
Redox Sites in Acid Zeolites

We study the chemistry of zeolites at high temperatures to determine the properties and structure of sites responsible for redox processes observed when organic molecules are adsorbed on the zeolite after heating. The model of Scheme 1 is generally accepted as the mechanism of zeolite dehydroxylation, and appears to be the dominant mechanism of dehydroxylation for zeolites with high aluminum content. However, in zeolites with low aluminum content, the Brønsted acid sites are isolated from each other and there is an energetic cost associated with the charge separation depicted in Scheme 1. We have recently investigated the dehydroxilation of high-silica H-zeolites using mass spectrometry-temperature programmed desorption (MS-TPD), and we have found that the main product is hydrogen gas. Moreover, the amount of hydrogen correlates with the amount of aluminum in the sample. We have repeated the experiment in other H-zeolites with similar results. These experiments show that Brønsted acid sites high-silica zeolites thermally decompose by a redox process, not by dehydration. This is a very unexpected result suggesting that some of what is believed to be acid catalysis at high temperatures in zeolites is in fact redox chemistry. Our group is trying to understand the potential role of the redox sites formed in the zeolite upon dehydrogenation in hydrocarbon catalysis. The understanding of redox processes in zeolites could help tailor future catalysts compositions to improve yield and selectivity in FCC catalysts.



Scheme 1: Dehydroxylation via heterolytic decomposition of Brønsted acid sites

A plausible path for the formation of hydrogen from BAS (Scheme 2) suggests that the product should lead to the formation of $[AlO_4]^0$ sites in the zeolite. Formally $[AlO_4]^0$ sites can more clearly be described as $[AlO_4/h]$, where h is a hole located (at low temperatures) on one of the oxygen atoms surrounding the aluminum—that is, one oxygen atom is oxidized to a formal oxidation state of 1–. This oxidized oxygen atom could be the source of the radical cations formed when organic molecules with low ionization potentials are adsorbed on acid zeolites.



Scheme 2: Proposed homolytic decomposition of Bronsted acid sites

In related research and in collaboration with Professor Doug Doren, we have found that zeolite silicalite-1 also desorbs hydrogen gas at high temperatures. This observation can be explained by a self-oxidation of the silica framework as depicted in Scheme 3. Again, we observe that oxygen atoms in the zeolite framework are changing their oxidation state from 2– to 1–, in this case, forming peroxo sites that we have also identified by UV/vis diffuse reflectance spectroscopy. The potential catalytic role of these sites remains unclear and we are currently studying the reactivity, and formation and decomposition of the peroxo sites to determine under what conditions they can affect the expected catalytic chemistry of other sites such as Brønsted acid sites.

Selective Carbon Dioxide and Hydrogen Zeolite Adsorbents

The efficient and selective capture of carbon dioxide from industrial flue gas streams is one of the most pressing issues facing the energy industry. Alkyl ammine-based separations are effective, but are also energetically inefficient leading to massive energy consumption. Adsorption on microporous adsorbents such as zeolites, MOFs, and carbon-based molecular sieves is a plausible alternative to alkyl ammine separations although an adsorbent with the desired high selectivity for CO_2 respect to N_2 and relatively low heats of adsorption for facile regeneration has not been discovered.

We have identified a new type of site in small pore zeolites selective for small molecules with negative electric quadrupole moments. CO_2 having a large quadrupole moment (-4.2 D Å, compared to nitrogen's -1.4 D Å) is a prime target for the design of new zeolite adsorbents using this new site as driver for adsorption. The properties of an adsorbent with this feature are shown in Figure 1, where the CO_2 and N_2 adsorption isotherms of H-SSZ-13 and Cu-SSZ-13 zeolites are displayed. The Cu-SSZ-13 zeolite is particularly selective at low pressures with an ideal selectivity higher than 15.

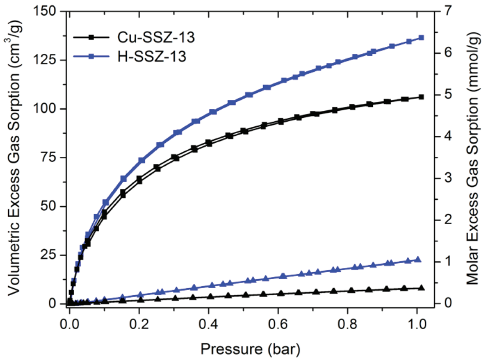


Figure 1. Adsorption/desorption isotherms of CO_2 and N_2 in H- and Cu-SSZ-13 zeolites at 298 K.

SSZ-13 is a small-pore zeolite with a three-dimensional pore system. It has a large microporous volume (~0.28 cc/g) and a simple structure with cations occupying exclusively, in Cu-SSZ-13, site I in the middle of the 6-ring windows (Figure 2). In collaboration with Craig Brown's group at NIST, we have conducted neutron powder diffraction measurements of CO_2 adsorbed on the Cu-SSZ-13 sample and we have found that the primary site for adsorption is not on the Cu sites, but the middle of the 8-ring window. The adsorption site can be observed in Figure 2 where the CO_2 molecule is located at the middle of the 8-ring window.

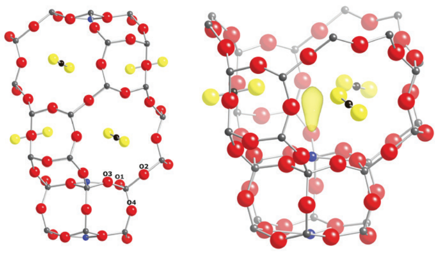


Figure 2. CO_2 adsorption site on Cu-SSZ-13 zeolite

The location of the CO_2 molecule on the 8-ring window, and not adsorbed on the Cu cation, is very unusual because in zeolites, physisorption of small molecules usually occurs at the extra-framework cations. The selective adsorption of CO_2 in the 8-ring, however, can be rationalized by a simple electrostatic model that considers the 8-ring zeolite window as a charged circular ring. A molecule with a large electric quadrupole moment, such as CO_2, interacts strongly with gradients in the electric field and at the plane of an 8-ring window there are, in fact, very strong gradients in the electric field. We are using these ideas to identify and test other zeolite materials for selective separation of CO2.

To selectively adsorb hydrogen molecules for hydrogen storage applications, we are taking advantage of the location of Cu atoms in zeolite SSZ-13 (above) and others that display cations on the pore surface. We are using the ability of Cu(I) ions to form medium-to-strong bonds with hydrogen molecules (and others species such as CO) to develop stable and selective adsorbents for these compounds. Ongoing investigations aim at maximizing adsorption capacity and selectivity using small-pore zeolites. This way we can take advantage of the pore size to protect the active sites against attack by larger molecules.

Hydrodeoxygenation of Pyrolysis Oil Model Compounds

Lignocellulosic biomass is a renewable source of carbon compounds that is a potential feedstock for fuel production. Fast pyrolysis is a promising platform for the conversion of solid biomass to organic liquids. Despite the similarity in molecular weight, the oxygen content of pyrolysis oil makes it acidic, viscous, and chemically unstable to be used as an effective fuel for internal combustion engines. Phenols derived from lignin are a major class of oxygenates found in pyrolysis oils, and contribute significantly to these undesirable properties. We are seeking for novel catalytic materials that are capable of converting these oxygenates to hydrocarbons in order to upgrade fast pyrolysis oils into cost-effective fuel additives.

Bifunctional supported metal catalysts are capable of deoxygenation via a combination of aromatic hydrogenation and acid-catalyzed dehydration. We have found that Pt/Al_2O_3 and Pt/SiO_2 catalysts can selectively produce toluene from m-cresol in the vapor phase at 533 K with modest H_2 pressure. A reaction network consisting of a pool of partially hydrogenated oxygenate intermediates most likely exist under reaction conditions. In this case, the dehydration of partially hydrogenated intermediates occurs quickly, and toluene can be produced preferentially to the fully saturated methylcyclohexane. However, if the rate of aromatic hydrogenation is increased relative to the rate of dehydration by increasing the H_2 pressure, the selectivity towards toluene decreases. Additionally, improving the rate of hydrogenation by using bimetallic PtNi and PtCo as a replacement for Pt also resulted in decreased selectivity to toluene. These results suggests that increasing the rate of HDO over these catalysts while maintaining selectivity to aromatics requires simultaneously improving the catalytic rate of both hydrogenation and dehydration reactions.

Recent density functional theory (DFT) calculations have indicated that strongly acidic sites can be generated by the formation of bimetallic particles between Pt and oxophilic metal promoters. In the presence of water, acidic hydroxyl groups are formed on partially reduced oxophilic metal species. The short diffusion distance between Pt sites and oxophilic metal-bound acid sites may be advantageous for the reaction rate and selectivity of hydrodeoxygenation. Since acid sites on Pt-Re bimetallic catalysts are generated by the oxophilic metals, activated carbon is a viable support material for these reactions. Initial investigations of the effect of Re- on Pt, Pd, and Ni catalysts show promising results for the hydrodeoxygenation of m-cresol using hydrogen to partially reduce the cresol prior to dehydration by the acid sites created by the oxophylic metal.

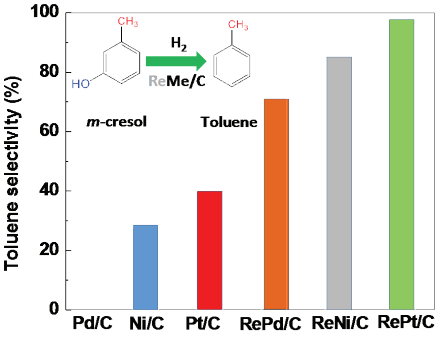
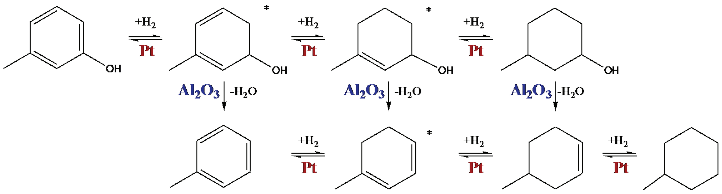


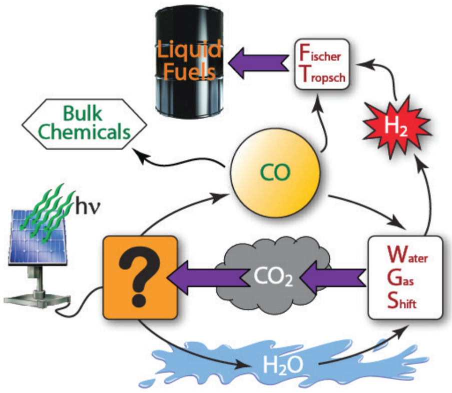
Figure 1: Selectivity of monometallic and Re-containing bimetallic catalysts for the production of toluene from m-cresol



Scheme 3: Proposed mechanism for the hydrodeoxygenation of m-cresol over bifunctional metal-acid catalysts.

JOEL ROSENTHAL

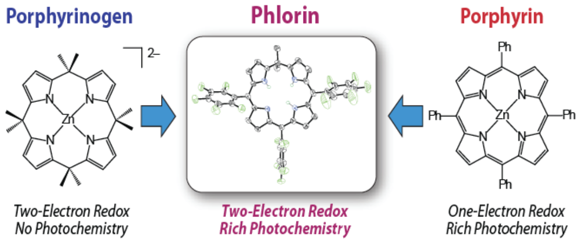
The widespread implementation of intermittent renewable energy sources such as solar and wind requires the efficient storage of electron equivalents. The development of methods to store energy via the generation of chemical fuels in a carbon-neutral fashion represents one strategy to address this issue. A major thrust of our research program is dedicated to the catalytic conversion of the greenhouse gas carbon dioxide to versatile, energy-rich species via energetically uphill chemical processes. We are particularly interested in the development of systems for the sequestration and reduction of carbon dioxide to generate value added species such as synthetic petroleum. One potential energy storage scheme that generates fuel from CO_2 is shown here.



Energy conversion and CO_2 remediation

We are synthesizing Ni and Pd complexes supported by carbene and nitrogen based ligands to promote this chemistry. Electrochemical and other mechanistic studies are elucidating the molecular design principles that drive efficient CO_2 activation. We are also investigating homologous systems, which incorporate hydrogen bonding functionalities to assist the activation of CO_2. Initial studies have shown that ditopic molecular clefts incorporating protonic functionalities can decrease the overall reorganization energy associated with formation of reduced CO_2 adducts and conversion to high-energy species. Our continuing work in this area is aimed at incorporating these molecular design principles into robust catalyst systems for liquid fuel production.

Development of New Molecular Scaffolds for Multielectron Photochemistry



Evolution of the Phlorin macrocycle

In developing a research program centered on the molecular chemistry of renewable energy, we are pursuing new catalysts for the direct photochemical production of energy rich species such as H_2 from H_2O or hydrohalic acids. Accordingly, we are designing new porphyrinoid architectures that are capable of engendering a multielectron reactivity. This represents a major advancement over typical porphyrin architectures, which only allow for single electron reactivity. Through rational design, we seek to overcome the kinetic barriers of small-molecule activation while driving energy-storing endothermic reactions via the direct input of solar energy.

We have designed a new porphyrinoid macrocycle that is a hybrid cousin of the porphyrinogen and porphyrin. This new architecture is known as a Phlorin and we have shown that it is capable of supporting a complex multielectron redox chemistry while maintaining the rich photochemical properties intrinsic to most porphyrinoids. In addition to being able to recognize several different anionic species, the Phlorin is a suitable platform for binding of transition metal centers including cobalt and zinc. Current work is aimed at promoting energy-storing catalytic processes using these systems.

S. ISMAT SHAH

Role of Oxygen Pressure in Nitrogen and Carbon co-doped TiO_2 Thin Films Prepared by Pulsed Laser Deposition Technique

Photo activity under sunlight is the main interest since the Sun's energy is free. When the photons with energy higher than the band gap of TiO_2 hit the material, they create electron-hole pairs. The electrons and the holes can be used for reducing metal ions and oxidation of organic chemicals, respectively. Another application is to generate solar hydrogen by using semiconductor TiO_2 photoanode material in photoelectrochemical cells. The similar process applies but the holes are used for oxidization of water to create H+ ions and O_2 gas. Meanwhile, the electrons are used to reduce H+ ions at the platinum cathode to form H_2 gas. Therefore, the process is provides a clean way to produce H_2 gas. The focus of this study is to increase the efficiency of the photoactivity of the TiO_2 semiconductor by sensitizing it to the visible spectrum.

The two phases of TiO_2, anatase and rutile, are of interest due to their photocatalytic properties. Although the anatase phase has a slightly wider band gap (3.2 eV) than the rutile phase (3.0 eV), it is more efficient in terms of photocatalytic activities (Sclafani, Palmisano, & Davi, 1991; Vidal, Herrero, Romero, Sanchez, & Sanchez, 1994). Rutile phase, however, is thermodynamically more stable in the bulk form. The peak in solar spectrum is in the visible region; around 500 nm. TiO_2, on the other hand absorbs light mostly in the UV part of the spectrum; below 387 nm (anatase) – 413 nm (rutile). Having mixed anatase and rutile phases may enhance the photocatalytic activity due to having a range of energy band gap (3.2 and 3.0 eV) to enhance photon absorption efficiency. Also, according to Zhang et al., phase junction formed between the surface anatase nanoparticles and the surface rutile particles is the main reason for a better photocatalytic activity (Zhang, Xu, Feng, Li, & Li, 2008).

Substitution of N doping with O in TiO_2 matrix was discussed in another study and the direct relation between oxygen vacancies and N doping was shown (Ruzybayev, Yassitepe, Ali, Bhatti, & Shah, n.d.). In the same study, we showed that N and C co-doped TiO_2 films reduced the band gap remarkably which resulted in absorption of the most of the visible portion of the solar spectrum, including the 500 nm region. N has a valency of three, while C has a valency of four. Under oxygen deficient conditions, N either substitutes with O in the form of N^{-3}, or does not substitute O but stays in the lattice interstitially. On the other hand, C can substitute with either O in the form of C^{-4} or Ti in the form of C^{+4}. Substitution with O is favored under oxygen deficient conditions along with O vacancies. Under oxygen-rich conditions, C is more favored to substitute with Ti and/or take lattice interstitial positions (Valentin, Pacchioni, Selloni, & Cozzi, 2005).

The goal of this study is to obtain the optimum mixture of anatase and rutile phases of TiO_2 by changing the reactive O_2 gas pressure during the deposition. Undoped and N and C co-doped samples were prepared and the overall effect of N and C co-doping and varying O_2 gas pressure was investigated. The results showed that crystallinity can be controlled, and mixed phases with sufficient doping samples absorb light starting from 550 nm.

Reactive pulsed laser deposition method (Lin et al., 2008) was used to prepare undoped TiO_2 and N and C co-doped TiO_2 thin films. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-Vis spectroscopy were used to study the structural, chemical, and optical properties of the samples. Samples are identified as:

Table 1. Sample labeling

			Oxygen Pressure		
			4 mTorr	**50 mTorr**	**100 mTorr**
Undoped TiO_2	Target	**00**	00-004	00-050	00-100
$TiO_{1.9}N_{0.05}C_{0.05}$		**05**	05-004	05-050	05-100
$TiO_{1.8}N_{0.10}C_{0.10}$		**10**	10-004	10-050	10-100

XRD results are summarized in figure 1 showing the role of O_2 pressure on the crystal structure of undoped and co-doped TiO_2. 50 mTorr O_2 gas pressure, 10-050 sample, has the best mixture of anatase and rutile and the higher dopant concentrations. Higher oxygen partial pressure reduces the oxygen concentration in the parent material leading to a higher incorporation of the dopants which makes the higher c/a anatase unstable and the anatase – rutile transformation is promoted.

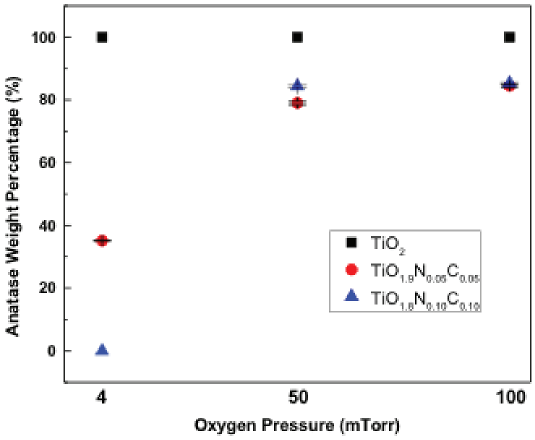


Fig. 1 Anatase weight percentage calculated by using A(101) and R(110) main reflection peaks.

XPS further clarifies the role of oxygen pressure in type of doping. C1s core level scans were collected and adventitious carbon peak at 284.6 eV was used for calibration of all regions. After the calibrations, the N1s core level region was investigated. In figure 3, undoped samples contain neither substitutional nor interstitial N doping. Also, as expected, substitutional N doping is favored under an oxygen deficient environment (4 mTorr O2) and interstitial N doping is favored under an oxygen rich environment (100 mTorr).

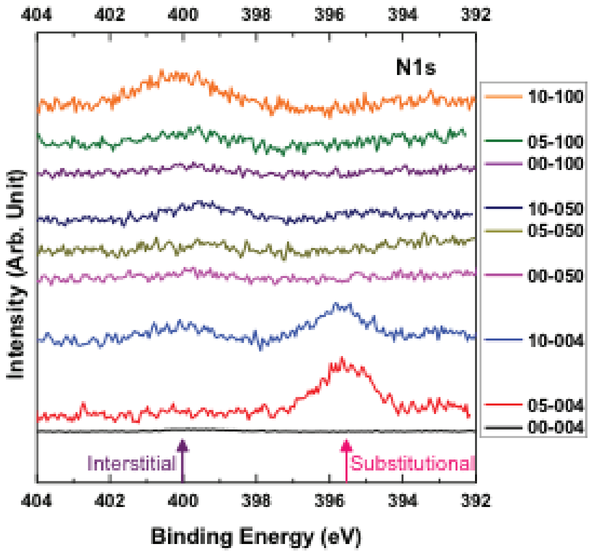


Fig. 2.

XPS N1s region scans.

UV-Vis DRS measurements were carried out to determine the absorbance of each sample. Undoped TiO_2 and $TiO_{1.9}N_{0.05}C_{0.05}$ target samples had an absorbance starting around 375 nm, which corresponds to the anatase band gap (387 nm) due to none or very low N and C co-doping conditions. Only samples prepared by using $TiO_{1.8}N_{0.10}C_{0.10}$ target showed significant change, as seen in figure 3. Since 10-050 has the best mixture of anatase and rutile phases among all samples, and higher doping concentrations relative to the samples prepared by other targets, it shows the most of the absorbance of the spectrum starting from 550 nm which lies around the main peak of the solar spectrum. The absorbance behavior of 10-004 is due to the oxygen vacancies.

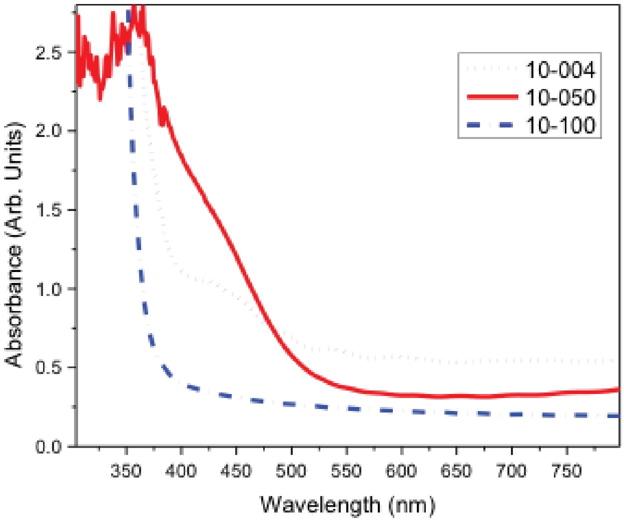


Fig. 3. UV-Vis DRS absorbance plot for $TiO_{1.8}N_{0.10}C_{0.10}$ target. The visible absorption starting from 550 nm is the best at 10-050 sample.

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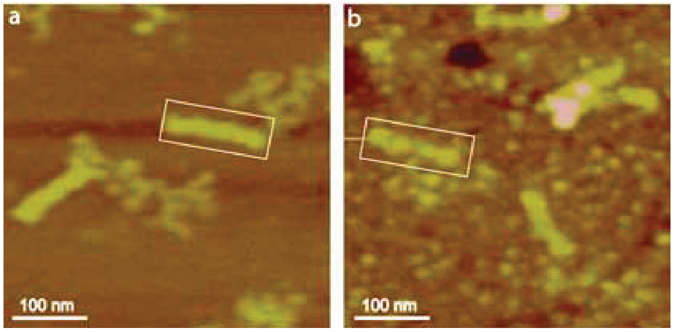
ANDREW V. TEPLYAKOV

Covalently Attached Macromolecules on Semiconductor surfaces

We have used C60 Buckminster fullerenes as spectroscopic and microscopic probes to establish the covalent nature of their binding to appropriately terminated self-assembled monolayers on silicon. We have investigated this chemistry using multiple spectroscopic and microscopic techniques and have verified the formation of a covalent link using computational investigation of core level energy shifts in N 1s spectral region and vibrational signatures of covalently bonded fullerenes. Current studies, as illustrated in the figure below, focus on shape-restricted DNA molecules covalently bonded to SAMcovered Si(111) single crystal surface. These DNA structures are designed by the research group of our collaborator, Professor Junghuei Chen (Department of Chemistry and Biochemistry, University of Delaware). We have successfully bonded triangular and rectangular DNA molecules to the self-assembled monolayers on silicon, confirmed that they are bonded covalently, and analyzed their apparent height. The plan for further development of this research direction in the future includes design of the 3D structures using DNA molecules for preferential binding to the semiconductor surface on one side of the structure, design of the covalently linked scaffolds with specific biochemical binding sites located within the Debye length from the interface, and testing the sensing capabilities of a device based on this approach, as well as ultimately designing a biosensor based on these studies . [2]



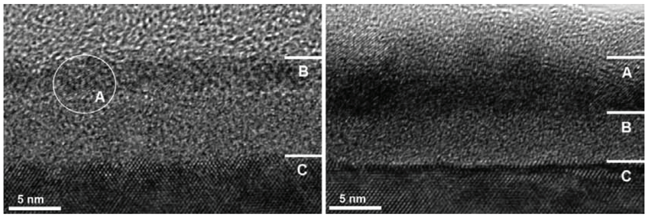
AFM images of (a) the rectangular DNA molecules with thiol linkers on mica (b) the rectangular DNA molecules with thiol linkers on SSMCC modified amineterminated Si(111)

Chemical Modification of Semiconductor surfaces

Semiconductor substrates are widely used in many applications. Multiple practical uses involving these materials require the ability to tune their physical (bandgap, electron mobility) and chemical (functionalization, passivation) properties to adjust those to a specific application. The goal of this research direction is to develop new strategies for manipulating the surface properties of semiconductor materials in a controlled way. Our expertise allows us to selectively tune the chemical and physical properties of semiconductor surfaces by an appropriate choice of elemental or III-V semiconductor, or by chemical modification. Our approach focuses on chemical passivation, on molecular switches and on the use of a variety of functionalized self-assembled monolayers. The findings of these investigations will be relevant for future applications in molecular and nanoelectronics, sensing, and solar energy conversion. Because of its interdisciplinary nature, selected topics from this work have become a team effort within the Integrative Graduate Education and Research Traineeship Program at the University of Delaware entitled "Sustainable Energy from Solar Hydrogen." In addition to surface modification, this project also focuses on the potential modification schemes and uses of graphenes. A major part of the effort is directed towards understanding reactivity and catalytic properties of surface silicon nitride sites with specifically designed basicity. [2]

Thin Solid Films for Microelectronics

The main goal of this project is to develop molecular-level understanding, control, and predict chemical reactions relevant for the formation and properties of complex ultrathin diffusion barrier films on semiconductor substrates. The current technologies dictate that the thickness of diffusion barriers will approach just a few nanometers within the next 15 years, as estimated by the International Technology Roadmap for Semiconductors. Therefore, questions of scaling the physical properties of the films enter a qualitatively new era: these properties now have to be analyzed and understood at the atomic level. The key objective of this project is to promote desired surface chemical reactions for clean Ta- and Ti-based film deposition, while preventing impurity incorporation (C, O, F) at the interfaces formed during this process. Our group employs thermal and photochemical methods to achieve this control. The structure of these amorphous or polycrystalline films presents many challenges. Our group has developed a novel approach to understand their properties. It combines a newly established experimental strategy with novel computational models designed recently in our laboratory to investigate local interactions in these complex systems. As summarized in the figure above, we can deposit a predominantly amorphous Ti-based film and alter its surface properties by nitridation with ammonia. The surface chemisty of the film can be reversibly tuned by chemical methods. Modern deposition and characterization techniques designed for and tested on Ti-based films will be further applied to investigate the poorly characterized Ta-, Hf-, and W-based materials. With the new deposition precursor molecules becoming available, this project will rely on the materials that are currently predicted to be suitable as diffusion barriers and branch into novel materials.



Cross-sectional TEM micrograph of a TiNC film before (left) and after (right) NH_3 post-annealing. The TiNC film is composed of crystalline nanostructures (A) embedded in an amorphous matrix (B)deposited onto a single crystalline silicon substrate (C). Upon post-annealing, the top layers of the film are mostly polycrystalline (A) and the inner portion of the film (B) remains amorphous. Crystallization in the top layers is attributed to the nitridation of the TiNC film to form TiN.

KLAUS H. THEOPOLD

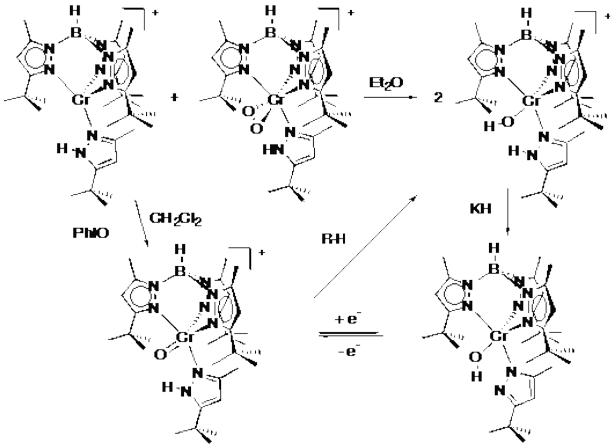
Small Molecule Activation with Sterically Hindered Tris(pyrazolyl)borate Metal Complexes

Chromium Dioxygen Complexes: We have prepared a series of chromium(III) superoxide complexes via binding of O_2 to coordinatively unsaturated chromium(II) precursors. These complexes are the first structurally characterized representatives of their kind [i.e. chromium(III) superoxide complexes], and they all adopt the rare "side-on" binding mode of superoxide that we first discovered in TptBu.MeCo(O_2).

Dioxygen Activation: Reaction of the dioxygen complexes with their precursors results in splitting of the O-O bond and the formation of reactive chromium(IV) oxo intermediates. Avoiding all hydrogen atom donors in the reaction of [TptBu.MeCr(pz'H)] BARF with PhIO has allowed the isolation and full characterization of [TptBu.MeCr(O)(pz'H)]BARF. The redox chemistry of the latter was investigated in collaboration with Prof. D.H. Evans, in order to estimate the affinity of the oxo complex for a hydrogen atom.

Hydrocarbon Activation: [TptBu.MeCr(O)(pz'H)]BARF reacts with organic molecules containing weak C-H bonds ($D_{C\text{-}H}$ <90 kcal/mol) by hydrogen atom abstraction to yield the chromium(III) hydroxide [TptBu.MeCr(OH)(pz'H)]BARF. Activation parameters and isotope effects for several reactions have been determined. For example, the kinetic isotope effect for the hydrogen atom abstraction from 9,10-dihdroanthracene at 293 K is $k_H/k_D = 25.2$.

Determination of the temperature dependencies of the H- and D-abstraction reactions revealed large differences ($\Delta E_0 = 6.7(8)$ kcal/mol and $A_H/A_D = 2.7 \times 10^{-4}$). These values indicate a significant contribution of quantum mechanical tunneling to the hydrogen atom transfer. H-atom tunneling has been invoked for several oxidation enzymes, and this small molecule reaction provides a valuable model system for the study of H-atom tunneling.

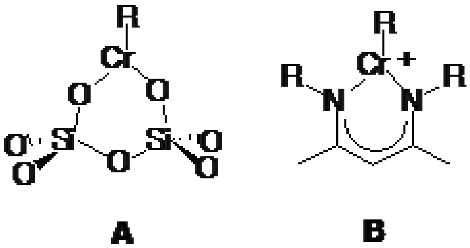


Cobalt Imido Complexes: Our investigation of cobalt dioxygen chemistry has yielded evidence for the intermediacy of the terminal cobalt oxo species $Tp_{tBu.Me}Co{=}O$ in several reactions; however, this compound is apparently too reactive for even spectroscopic detection. We have thus pursued the chemistry of isoelectronic imido complexes, $Tp_{tBu.Me}Co{=}NR$, as chemical models. For example, reaction of $Tp_{tBu.Me}Co(N_2)$ with Me_3SiN_3 yielded a cobalt(III) amido species resulting from hydrogen atom abstraction from the ligand by the inferred imido complex $Tp_{tBu.Me}Co{=}NSiMe_3$.

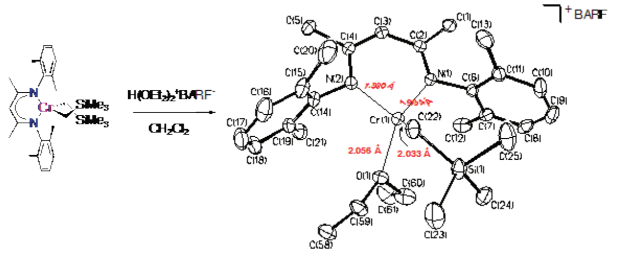
Stable Cobalt Imido Complexes: To our surprise, tertiary alkyl azides (e.g. R=tBu, Ad) have produced isolable cobalt(III) imido complexes. However, the thermal reactivity of these compounds also includes the functionalization of ligand C-H bonds. The mechanism of this C-H activation and the exact nature of the unusual products are currently under investigation.

Homogeneous Models for Chromium Polymerization Catalysts

Chromium Alkyls: We are constructing a homogeneous model system for the Phillips catalysts for ethylene polymerization (i.e. inorganic Cr/SiO_2, see *A* in the figure below). To mimic the coordinatively unsaturated chromium on a hard oxide support, we have chosen N, N'-disubstituted diketiminate ligands [“(R)2nacnac”, as in B], i.e. bidentate nitrogen ligands that confer variable steric protection upon the chromium.



We have prepared a series of neutral and cationic chromium alkyls supported by $(Ar)_2$nacnac ligands (Ar=Ph, 2,6-Me_2Ph, 2,6-$^iPr_2$Ph). These paramagnetic complexes feature chromium in a range of formal oxidation states (II–V). Structurally characterized cationic Cr(III) alkyls of the general type $[(Ar)_2nacnacCr(R)(OEt_2)]^+BARF$ (Ar=2,6-Me_2Ph, 2,6-$^iPr_2$Ph; R=Me, CH_2SiMe_3) catalyze the polymerization of ethylene and the copolymerization of ethylene with α-olefins in the absence of any cocatalysts.



Extraordinarily low polydispersities (M_w/M_n=1.1-1.4) provide evidence for "living" polymerization catalysis, and the polymer microstructure of polyethylene produced with sterically encumbered $[(2,6\text{-}_i\text{Pr}_2\text{Ph})_2\text{nacanac Cr(OEt}_2\text{)Me]BARF}$ shows evidence for "chain walking."

Supported Polymerization Catalysts: Taking our earlier work on cyclopentadienyl chromium alkyls, which serve as models for the Union Carbide catalyst, one step closer to the actual heterogeneous catalyst, we have fixed Cp*Cr(py)Me2 on a zeolite (MCM- 22) and characterized the resulting olefin polymerization catalysts by a variety of spectroscopic methods. [2]

DIONISIOS G. VLACHOS

Predictive, Hierarchical Multiscale Microkinetic Modeling

In our group we develop 'elementary' like reaction mechanisms for catalytic reactions. We use a hierarchical, multiscale approach to construct reaction mechanisms that capitalizes on the power of DFT, molecular modeling, and CFD but only on an as needed basis (on demand). Hierarchical modeling means that we employ simple and inexpensive tools first to identify the 'key' steps of a process and then apply higher level, more expensive tools only for the few key steps. This approach combines the predictive power of high-level theory with the computational efficiency of lower level semi-empirical methods. We develop detailed reaction mechanisms for a variety of processes on metals, carbides, and oxides. Examples include:

- Catalytic combustion of hydrogen, carbon monoxide, and hydrocarbons
- Water-gas shift
- Selective oxidation of carbon monoxide in the presence of hydrogen
- Reforming (steam, dry, and autothermal) of natural gas and biomass
- Partial oxidation and steam reforming at short contact times for syngas and hydrogen production
- Hydrogenation of alkenes and dehydrogenation of alkanes
- Oxidative dehydrogenation of alkanes to olefins
- Ammonia decomposition for hydrogen production
- Biomass hydrogenation, dehydration, isomerization, reforming
- JP-8 catalytic combustion and reforming

An example of the predictive capability of a detailed microkinetic model is depicted in Figure 1. The power of our hierarchical multiscale approach is that we develop predictive reaction mechanisms that can describe multiple experiments from UHV conditions to high pressures (pressure gap) and from single crystals to industrial catalysts (materials gap) over a wide range of operating conditions. Our close collaboration with industry is essential in developing reaction mechanisms of practical interest. Due to the hierarchical approach, we can develop mechanisms in short periods of time and improve important parameters with higher-level theory only when needed.

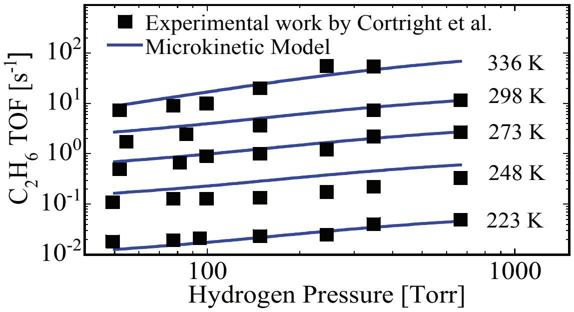


Figure 1. Comparison of experimental data (points) and simulations using our newly developed full microkinetic model (lines) for ethylene hydrogenation and ethane hydrogenolysis on Pt-based catalysts.

First-principle-based Semi-empirical Methods for Thermochemistry and Kinetics

First-principle simulation of biomass processing is hindered by the sheer size of biomass derivatives and the associated computational cost of quantum codes. Researchers at Delaware developed a new framework for estimating thermochemistry of oxygenated species and rate constants on transition metals that drastically reduces the expense involved in kinetic modeling of biomass catalytic processing. This methodology allows for an inexpensive screening of a reaction mechanism which can be followed by refinement of sensitive mechanistic parameters via a limited number of (expensive) quantum calculations. The framework has been applied to ethylene glycol and glycerol decomposition chemistry on platinum to reveal interesting reactivity trends. It has been found that initial C-H bond scission reactions in the mechanism are rate controlling, whereas C-C bond cleavage is expected to be fast under typical thermal decomposition conditions. The oxygenate surface intermediate heat of formations calculated via group additivity are compared to those via DFT for ethylene glycol and glycerol decomposition intermediates in Figure 2.

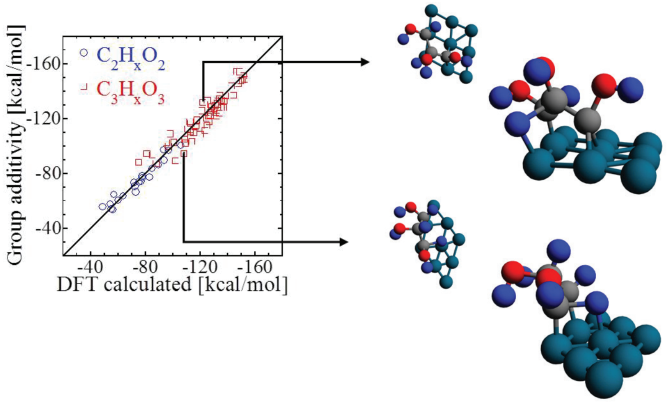


Figure 2. Parity graph comparing first-principle density functional theory (DFT) calculations to first-principle-based semi-empirical, excel-based group additivity values along with snapshots of structures of oxygenated species on Pt manifesting the multi-dentate nature of binding of these adsorbates.

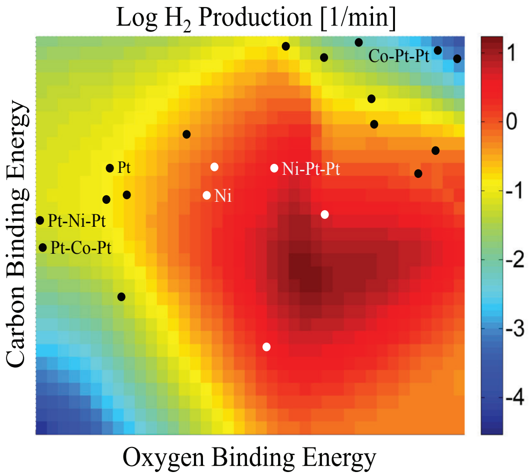


Figure 3 Example of predicted volcano mountain projected to two-dimensions for identification of optimal catalysts for reforming of biomass vs. element heats of adsorption. The labeled points indicate the performance of known catalysts and the unlabeled ones indicate predicted materials under testing.

Computational-driven Design of Catalysts

Quantum-based rational catalyst design, while promising, is far from becoming a reality for complex reaction systems. Furthermore, what initially appears as a very active catalyst may be unsuitable due to reactor scale (e.g., heat/mass transfer, hot spots) effects. Our thesis is that development of a hierarchical multiscale theoretical framework can be invaluable in the course of catalyst design by gathering and extracting kinetic and catalyst information from quantitative experiments and characterization data and integrating it multiscale modeling that links from the quantum to the macroscopic, processing scales. By developing such models for many catalysts, we create libraries of kinetics models that we subsequently use for catalyst design. An example of catalyst design is shown in Figure 3.

Biomass Processing

We carry out experiments and develop models to understand and predict biomass processing. Processes under investigation include:

» Reforming
» Selective hydrogenation
» Dehydration
» Isomerization
» Hydrodeoxygenation
» Pyrolysis

Our work focuses on both biomass depolymerization to obtain bio-oil as well as bio-oil upgrade. In pyrolysis, our aim is to design a micropyrolyzer to obtain intrinsic kinetics of biomass pyrolysis. The experimental efforts are complemented with computational studies. In bio-oil upgrade, our interest is in screening experimentally and computationally novel materials for the selective conversion of bio-oil to gasoline, diesel, and jet fuels. In addition, we study the selective conversion of sugars to chemicals and fuels. An example entails the conversion of starch to glucose to fructose and to 5-hydroxymethyl furfural. The experimental studies are combined with modeling where we employ a variety of multiscale methods ranging from ab initio quantum chemistry calculations with implicit solvation, to hybrid quantum mechanics/molecular mechanics (QM/MM) and ab initio Molecular Dynamics free energy calculations, with explicit solvation. An example is shown in Figure 4.

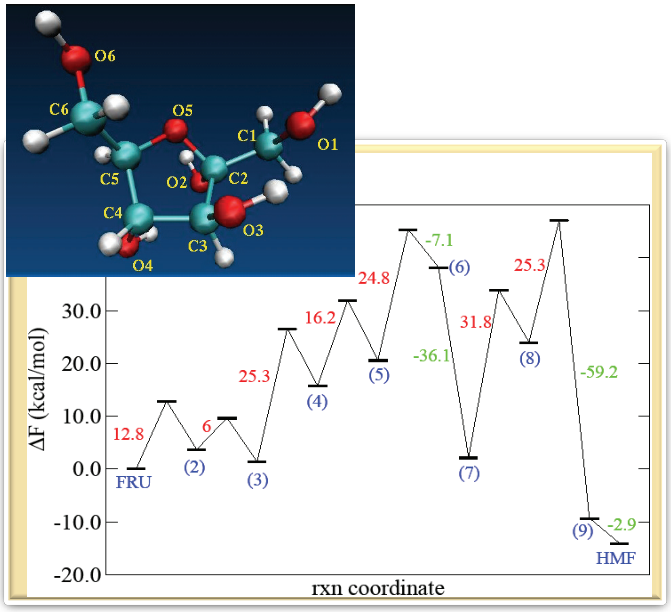
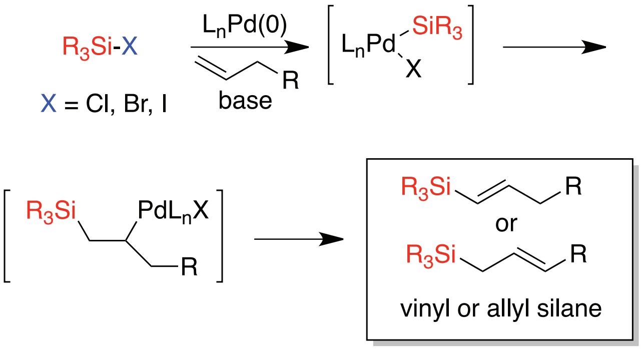


Figure 4. Free energy of the elementary steps of fructose dehydration to HMF predicted using quantum mechanics/molecular mechanics molecular dynamics simulations. Schematic shows a ball and stick view of fructose.

DONALD A. WATSON

Our research program is broadly focused on the development of transition metal catalysts for applications in organic synthesis and alternative energy. Due to the importance of complex organic molecules in biology, medicine, agrochemical and material science, we are developing catalytic methods that allow high-value organic molecules to be prepared from inexpensive and abundant starting materials. We are particularly interested in inventing new reactions for the stereocontrolled introduction of heteroatoms, such as silicon and nitrogen, in rapid fashion. We are also employing principles of catalyst design and organometallic catalysis to prepare novel materials for use as catalysts in alternative fuel preparation and energy storage. Two projects currently under investigation are summarized below.

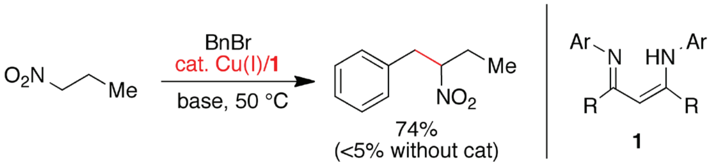
In the first project, we have begun to investigate the possibility of efficient silyl-Heck reactions. Many reactions are now known that employ the oxidative addition of a carbon-halide bond to a low-valent metal, most commonly palladium. Notable examples include the Heck, Suzuki, and Buchwald-Hartwig reactions. These transformations, along with the many related protocols, provide powerful methods for the construction of a vast array of complex organic molecules. In contrast, however, synthetic reactions involving the oxidative addition of heteroatom-halide bonds with low-valent metals have been much less explored. In this light, we have begun to develop a silyl-variant of the Heck reaction, involving the palladium catalyzed coupling of a silylhalide and an alkene. The products from these reactions are vinyl and allyl silanes, both of which are important compounds and useful nucleophiles in organic synthesis (Scheme 1). Very recently, we have shown that the proposed processes can be carried out under very mild reaction conditions in high yield, and we expect to publish on our initial results in the near future.



Scheme 1. Development of Silyl-Heck Reaction for the Preparation of Unsaturated Organosilanes.

In the second project, we have become interested in developing new reactions of nitroalkanes. Nitroalkanes are important building blocks used to assemble complex organic frameworks. These compounds, and the nitronate anions derived from them, participate in a broad range of carbon-carbon (C–C) bond-forming reactions, including additions to aldehydes, ketones and Michael acceptors, as well as palladium catalyzed allylation and arylation reactions. In contrast, however, efficient C–C bond formation via C-alkylation of nitroalkanes with simple alkyl electrophiles remains a challenging problem in organic synthesis. Instead of alkylating at carbon, nitronate anions typically react with alkyl electrophiles at oxygen. Although several systems have been developed to overcome this inherent selectivity, all of them have significant drawbacks (such as harsh conditions and highly toxic or specialized reagents) that limit their use in preparative organic synthesis. The development of an operationally simple method to C-alkylate nitroalkanes using simple alkyl electrophiles would allow facile access to complex nitroalkanes, which in turn can be used to prepare high-value amines and carbonyl compounds and are versatile intermediates in a variety of reactions in synthetic chemistry.

Recently, we have discovered that catalysts employing inexpensive Cu(I) salts and readily accessible 1,3-diketimine ligands promote the C-alkylation of nitroalkanes with benzyl bromide in high yield (Scheme 2). Our initial investigation examined the coupling of benzyl bromide and 1-nitropropane. In the absence of catalyst, benzaldehyde (resulting from O-alkylation) is observed as the major product. With 20 mol% catalyst, 3-nitro-1-phenyl butane is obtained in 74% yield. Notably, catalyst systems based upon other metals and/or ligands have thus far proven much less effective. We are in the final stages of catalyst optimization and are beginning to explore the generality of the method; initial experiments suggest that the reaction will exhibit good functional group tolerance. We expect this new catalytic method will allow facile preparation of a variety of classes of biologically active compounds that are widely used in medicine and biology.



Scheme 2. Discovery of Copper Catalyst for C-Benzylation of Nitroalkanes.

YUSHAN YAN

Nanostructured Materials for Energy, Environment, and Electronics

Zeolite thin films: Zeolites are a class of crystalline oxides that have uniform and molecular-sized pores (3 to 12 Å). Although natural zeolites were first discovered in 1756, significant commercial development did not begin until the 1950s when synthetic zeolites with high purity and controlled chemical composition became available. Since then, major commercial applications of zeolites have been developed for catalysis, adsorption, and ion exchange, mostly using zeolites in powder or power composite form. Researchers have investigated zeolite thin films within the last 20 years, but mostly for applications as separation membranes and membrane reactors. We were the first to propose, study, and demonstrate that zeolite thin films can have new, diverse, and economically significant applications that others had not previously considered. These new applications include zeolite thin films as insulators for computer chips, corrosion resistant coatings for aerospace aluminum alloys, hydrophilic and antimicrobial coatings for water separation in space. We have also explored zeolite coatings and polymer zeolite composite membranes for biomedical, antifouling, biofuel purification, fuel cell and seawater desalination applications.

Catalysts and membranes for fuel cells, energy storage and solar hydrogen

Fuel cells have been considered promising for powering vehicles, homes, and portable electronic devices. Their widespread commercial use, however, hinges on our ability to reduce their cost and improve their durability. We have developed new concepts for catalysts and membranes to drastically reduce cost and increase the durability of polymer electrolyte fuel cells. We were the first to improve the platinum nanoparticle utilization through in situ electro-deposition of platinum on carbon nanotubes directly grown on carbon paper. We were the first to propose, study, and demonstrate that platinum nanotubes can have much improved durability and activity over the platinum nanoparticles supported on carbon. We were also the first to propose, study, and demonstrate that quaternary phosphonium based hydroxide exchange membranes can have much improved conductivity and durability over the conventional quaternary ammonium based membranes. We have also proposed that the new HEMs and catalysts are also promising in electrolyzers and flow batteries for storage of solar and wind electricity, and for solar hydrogen generation.

Donald Watson Wins NSF Award

Donald Watson, an assistant professor and organic chemist in UD's Department of Chemistry and Biochemistry, has received the NSF Career and Cottrell Scholar Awards. His research focuses on the development of new reactions that enable the synthesis of complex organic molecules.

Part of the Watson Research Group's effort has been dedicated to creating new methods to prepare organosilanes. His interest in developing new routes to such compounds stems from their extreme utility and widespread applications in drug synthesis, agrochemical synthesis, and material science.

The NSF Career Award funds Watson to examine new ways to construct vinyl and allyl silanes using simple alkene starting materials.

This Silyl-Heck Reaction, as he has termed it, is a very simple method to prepare these two types of important organosilanes.

In the new method, his group adds silicon to unfunctionalized, alkenes, which are cheap and widely available.

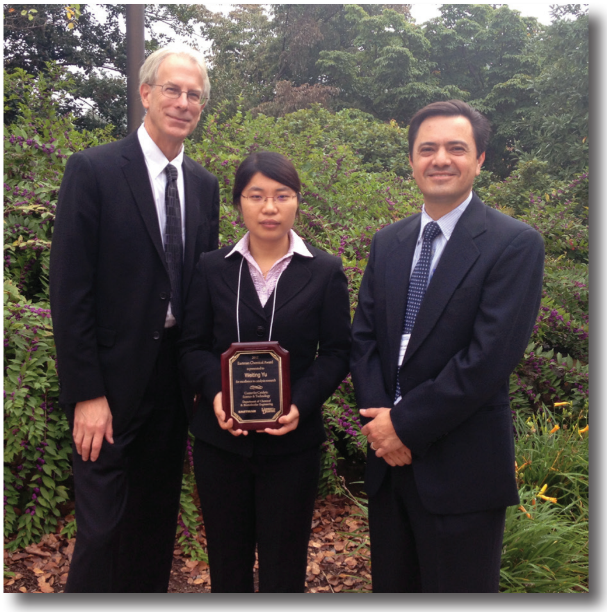
The research builds off the Nobel Prize-winning work of UD's Richard Heck, Willis F. Harrington Professor Emeritus of Chemistry and Biochemistry, whose pioneering developments of reactions to form carbon-carbon bonds through palladium catalysis enabled chemists to make molecules as complex as those created by nature itself.

2013 Eastman Chemical Student Award

Nima Nikbin is the recipient of the 2013 Eastman Chemical Student Award. Nima's work deals with the applications of quantum chemical calculations and theoretical chemistry to the analysis of catalysis problems of biomass derived molecules. He has investigated the difficult problem of understanding the molecular basis for catalytic activity and selectivity in the liquid phase for molecules as complex as fructose. This award recognizes his research accomplishments and the breath of his research activities. As a result of this award, Nima will give a summary of recent research results at the next CCST Annual Research Review and will receive a plaque and a gift at the Annual Review.

Yushan Yan, Among 66 Selected to Share in Energy Technology Funding

Professor Yushan Yan has received a new grant from the ARPA-e program from the Department of Energy for a total of $793,000. This Advanced Research Projects Agency- Energy (ARPA-E) program seeks to support science and technology with the potential to produce game-changing breakthroughs in energy technology, form the foundation of new industries and have large commercial impact. Professor Yan's proposal is one of only 66 proposals funded by the ARPA-e program. Professor Yan's group has developed a new concept in flow batteries, a device that is used to store electrical energy when there is surplus production, and to deliver this energy efficiently and rapidly when it is needed. The discoveries of the Yan's group should allow efficient electricity storage needed to cope with the intrinsic irregularity of renewable wind and solar electricity generation.



Weiting Yu is the recipient of the **2012 Eastman Chemical Student Award.** Pictured right is Raul Lobo and Guy Steinmetz on left.

CCST Faculty HIGHLIGHTS

Douglas J. Buttrey

- Scientific Committee for the 7th World Congress on Oxidation Catalysis, Saint Louis, MO, 2013
- Keynote Speaker for the 7th World Congress on Oxidation Catalysis, Saint Louis, MO, 2013
- 2012 Purdue Chemistry Outstanding Alumni Award
- Winter 2012: Visiting Professor, African University of Science and Technology, Abuja Nigeria

Wilfred Chen

- Biotechnology Progress Award for Excellence in Biological Engineering Publication, 2012

Michael T. Klein

- Peter H. Given Lectureship in Coal Science, February, 2013
- Member of the AspenTech Academy, 2012-present
- Editor-in-Chief, Energy and Fuels, January 2002-present

Joel Rosenthal

- DuPont Young Professor Award, 2012

S. Ismat Shah

- Madhuri and Jagdish N. Sheth International Alumni Award for Exceptional Achievement, University of Illinois, 2013.
- Society of Vacuum Coaters, Mentor Award, 2012
- COMSATS Visiting Scholar Award (CIIT Islamabad, Pakistan), Spring 2012.
- TUBITAK Visiting Scholar Award (Hacettepe University, Turkey), Summer 2012.

Andrew V. Teplyakov

- Feature article: Tian, F. and Teplyakov, A. V. Silicon surface functionalization targeting Si-N linkages. Langmuir 2013, 29(1), 13-28. Invited Feature Article, Image featured on the cover of the journal.
- Received the American Chemical Society Delaware Section Award, 2012.

Donald Watson

- 2013 NSF CAREER Award
- 2013 Cottrell Scholar Award

Yushan Yan

- Outstanding Alumni Lecture, Dalian Institute of Chemical Physics, Chinese Academy of Sciences
- Distinguished Engineering Professor, University of Delaware
- Donald Breck Award, International Zeolite Association
- Presidential Chair, University of California
- Fellow, American Association for the Advancement of Science
- ChangJiang Professor (Visiting at Zhejiang University), Chinese Ministry of Education
- University Scholar (inaugural), University of California, Riverside
- Overseas Young Investigator, Chinese Academy of Sciences

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- Dr. Raul F. Lobo – UD Department of Chemical & Biomolecular Engineering
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