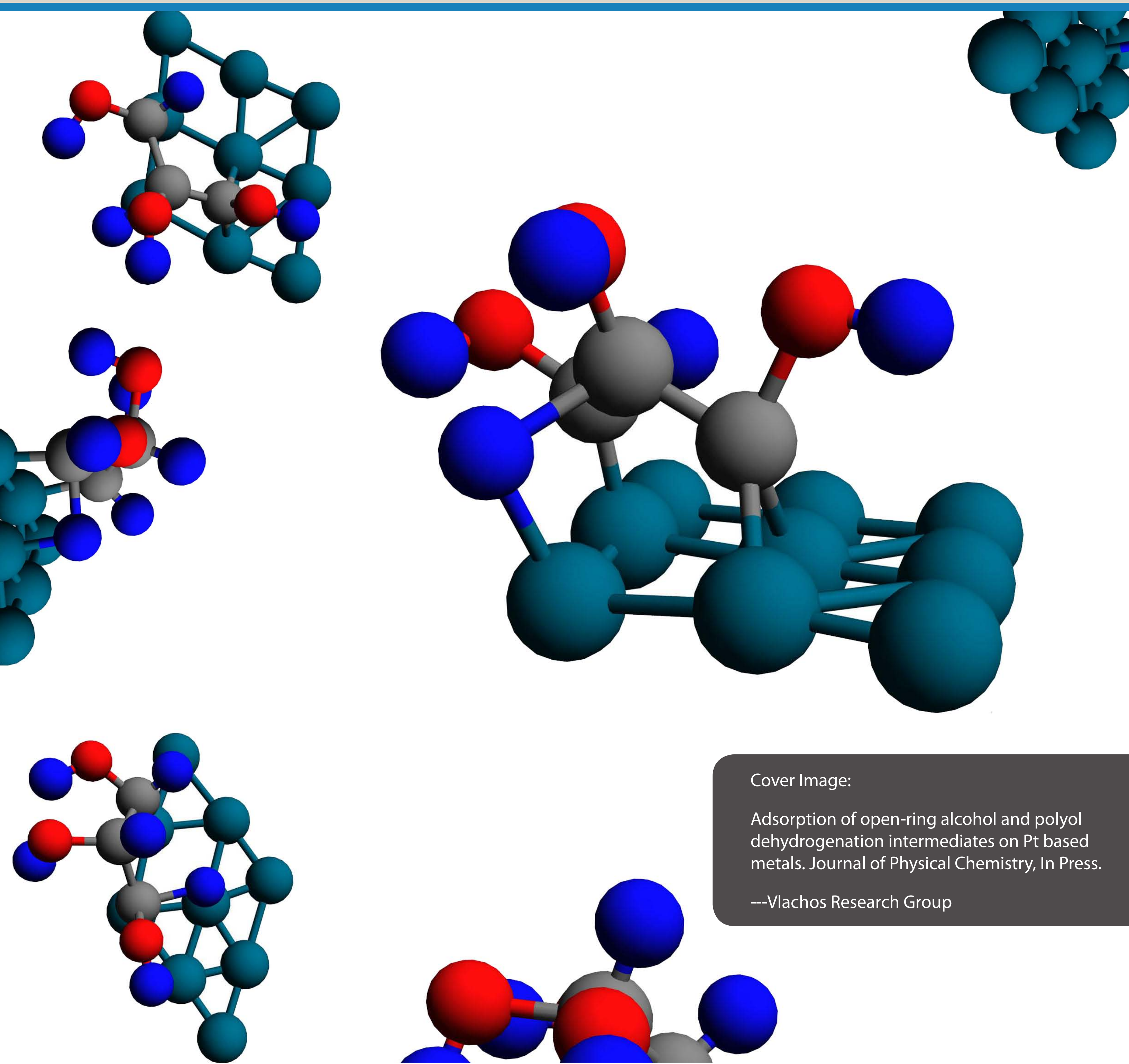
MULTIDISCIPLINARY PROGRAMS • CUTTING-EDGE RESEARCH



Cover Image:

Adsorption of open-ring alcohol and polyol dehydrogenation intermediates on Pt based metals. Journal of Physical Chemistry, In Press.

---Vlachos Research Group

CENTER FOR CATALYTIC SCIENCE AND TECHNOLOGY

2011 Research Report

Front cover:

Adsorption of open-ring alcohol and polyol dehydrogenation intermediates on Pt based metals. Journal of Physical Chemistry, In Press.

---Vlachos Research Group

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This publication is published annually by the University of Delaware Center for Catalytic Science & Technology. Please address inquiries to:

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150 Academy Street
Newark, DE 19716-3119

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2011

CCST RESEARCH REVIEW

Thursday, October 6, 2011

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FROM THE DIRECTOR

Dionisios G. Vlachos
Chemical Engineering

EDUCATION
Ph.D., Univ. of Minnesota
M.S., Univ. of Minnesota
B.S., National Technical Univ. of Athens

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

It's been another busy year in CCST, and I invite you to read all about our exciting research in the pages that follow. Our faculty, students and alumni continue the CCST tradition of excellence and have received numerous awards and distinctions. Among them are the 2011 Herman Pines Award in Catalysis (Jingguang Chen) and the AIChE Wilhelm Award in Chemical Reaction Engineering of the AIChE (Dion Vlachos). Mark Barteau was appointed co-chair of the Chemical Sciences Roundtable of the National Research Council and was named Fellow of the American Institute of Chemical Engineers (AIChE).

Richard F. Heck, the Willis F. Harrington Professor Emeritus at the University of Delaware (UD) and former CCST faculty member, was awarded the Nobel Prize in Chemistry for his discoveries of palladium catalysis for the construction of organic molecules. All of pharmaceutical chemistry and photolithography (the making of computer chips) depends on carbon bond formation. Heck's contribution was to make that bond catalytic, making large-scale industrial production affordable. The impact of that contribution has been profound. When DNA sequencing became important, Heck's chemistry made the coupling of organic dyes to the DNA bases possible. You can find all awards and descriptions on our website under "What's New in CCST" [www.che.udel.edu/ccst/index.html].

UD's Catalysis Center for Energy Innovation (CCEI) completed its second year in operation and published several exciting findings on biomass processing. CCEI is as an Energy Frontier Research Center funded by the Department of Energy. An overview of CCEI can be found on pages 8 & 9 of this report, and you can find more information in the CCEI newsletter available on the Center's website [www.efrc.udel.edu].

I would like to extend a warm welcome to our newest colleague, Yushan Yan, who joins both CCST and CCEI. Yushan joined the Department of Chemical Engineering at UD on July 1, 2011. Prior to joining UD, he was the Presidential Chair at the Chemical and Environmental Engineering Department at the University of California, Riverside. Yushan brings expertise in zeolite thin films as insulators for computer chips, corrosion-resistant coatings for aerospace alloys, and hydrophilic and antimicrobial coatings for water separation in space station, nanostructured fuel cell catalysts and membranes, alkaline fuel cells, and design, synthesis, and applications of nanoparticles, nanowires, and nanotubes.

I want to thank the Eastman Chemical Company for sponsoring our 2011 Spring Seminar Series that featured distinguished seminar speakers who gave enlightening presentations, and also for sponsoring the Eastman Chemical Award. The first was presented to Danielle Hansgen last year at CCST's annual research review for her work on developing novel bimetallic catalysts for ammonia decomposition. This year's award will be presented to Mike Salciccioli for his development of microkinetic models of biomass processing.

CCST's annual research review will be on Thursday, October 6, 2011, at the Clayton Hall Conference Center in Newark, Delaware, and we invite you to join us. Registration and other information is available on our website [www.che.udel.edu/ccst/2011review.html].

Last but not least, I want to welcome home Raul Lobo as he returns this summer from his one-year sabbatical at Berkeley. It gives me great pleasure to announce that Raul will be the new Director of CCST effective July 1, 2011. His appointment as director will enable us to jointly expand our industrial partnerships, and we plan to work closely together to continue the CCST traditions. I wish him much success and am confident that CCST will continue to grow under his leadership.

We encourage you to contact us with questions or comments, and we hope you will visit our Center either in person or via our website [www.che.udel.edu/ccst/]. We look forward to continuing fruitful collaborations with each of you – our institutional partners, industrial sponsors and scientific colleagues.

Dion Vlachos,
Director

CCST PARTNERS

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
- Access to pre-recorded seminars

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CENTER FACULTY

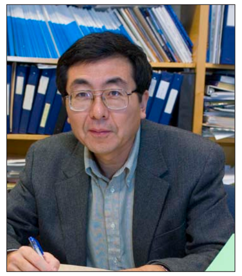
ASSOCIATE DIRECTOR

Mark A. Barteau
Chemical Engineering

RESEARCH INTERESTS
Surface science and catalysis by metal oxides and metals; selective oxidation; application of density functional theory to surface reactions; catalyst design; self-assembly of inorganic materials, scanning probe microcopies.

Douglas J. Buttrey
Chemical Engineering

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



ASSOCIATE DIRECTOR

Jingguang G. Chen
Chemical Engineering

RESEARCH INTERESTS
Synthesis and characterization of metal carbides and bimetallic alloys as novel catalytic and electrocatalytic materials for applications in environmental catalysis and fuel cells.

ASSOCIATE DIRECTOR

Douglas J. Doren
Chemistry and Biochemistry

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

Feng Jiao
Chemical Engineering

RESEARCH INTERESTS
Energy storage and conversion; lithium-ion batteries; photocatalysis; synthesis and characterization of nanostructure materials.

Michael T. Klein
Chemical Engineering

RESEARCH INTERESTS
Upgrading and conversion of renewable and fossil fuels; Chemical Reaction Engineering; Detailed kinetic modeling of complex reaction systems

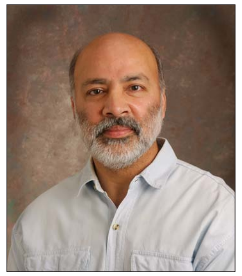
ASSOCIATE DIRECTOR

Raul F. Lobo
Chemical Engineering

RESEARCH INTERESTS
Synthesis and characterization of zeolites and other microporous materials, structure-property relationships in porous adsorbents and catalysts

Joel Rosenthal
Chemistry and Biochemistry

RESEARCH INTERESTS
Homogeneous catalysis and small molecule activation, electrocatalysis, photocatalysis, chemistry of consequence to renewable energy and molecular energy conversion



S. Ismat Shah
Physics and Materials Science

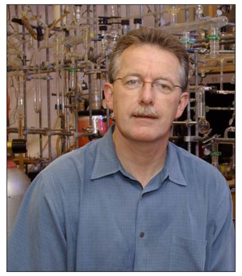
RESEARCH INTERESTS
Nanostructured materials synthesis via PVD and CVD processes with applications to environmental catalysis and energy generation.

Douglass F. Taber
Chemistry and Biochemistry

RESEARCH INTERESTS
Stereoselective synthesis of natural products, organometallic catalysis, computational organometallic chemistry.

Andrew V. Teplyakov
Chemistry and Biochemistry

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



ASSOCIATE DIRECTOR

Klaus H. Theopold
Chemistry and Biochemistry

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

Donald A. Watson
Chemistry and Biochemistry

RESEARCH INTERESTS
Transition-metal catalysis; organic synthesis; alternative energy chemistry

NEW FACULTY

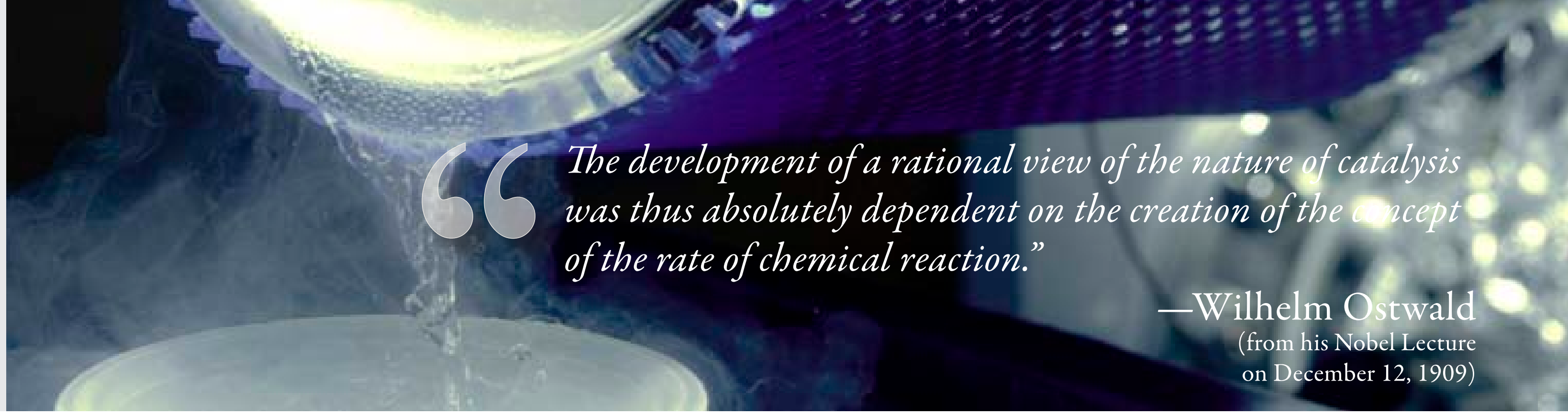
ASSOCIATE DIRECTOR

Professor Yushan Yan received his B. S. in Chemical Physics from the University of Science and Technology of China in 1988, and his Ph.D. in Chemical Engineering from the California Institute of Technology (Caltech) in 1997. He studied heterogeneous catalysis at the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences from 1988 to 1992 and zeolite membranes for his PhD thesis at Caltech from 1992 to 1996. He worked for AlliedSignal Inc. as a Senior Staff Engineer and Project Leader from 1996 to 1998 before joining the University of California at Riverside (UCR) as Assistant Professor. He was promoted to Associate Professor in 2002 and Professor in 2005. In 2006, he was selected as one of the five inaugural University Scholars at UCR. He was appointed Department Chair in 2008 and given the title of Presidential Chair in 2010. He joined the University of Delaware in July 2011. His research focuses on zeolite thin films for semiconductors and aerospace applications and new materials for fuel cells, energy storage and solar hydrogen generation. He received the Donald Breck Award in 2010 from the International Zeolite Association for his zeolite thin film research, and was awarded one of the 37 inaugural-round ARPA-E projects in 2009 from the Department of Energy for his hydroxide exchange membrane work. He is a Fellow of the American Association for the Advancement of Science. He has been an inventor of a large number of issued or pending patents. Several of his patents were licensed to form startup companies, e.g., NanoH2O, Full Cycle Energy, Zeolite Solution Materials (ZSM), and OH-Energy. He currently serves on the Scientific Advisory Board of NanoH2O. He is co-Founder of Full Cycle Energy, ZSM, and OH-Energy.

FACILITIES & CAPABILITIES

CCST has a wide array of equipment for preparation and advanced characterization of catalysts, kinetic measurements, as well as computational facilities and software for chemical and reaction engineering modeling.

CCST's facilities and measurements are complemented with in-situ FTIR, XRD and EXAFS characterization at Brookhaven National Laboratories, activities led by **Professor Jingguang Chen**.



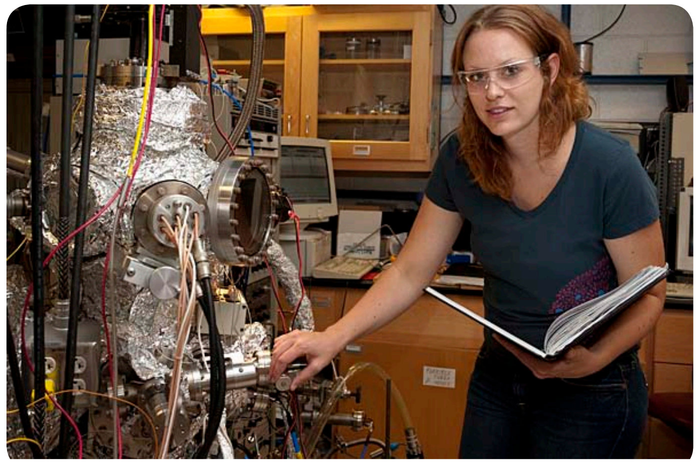
> *"The development of a rational view of the nature of catalysis was thus absolutely dependent on the creation of the concept of the rate of chemical reaction."*
>
> —Wilhelm Ostwald
> (from his Nobel Lecture
> on December 12, 1909)

XRAY DIFFRACTION

A Phillips X'Pert-MPD diffractometer has been added for the characterization of polycrystalline samples. The instrument is equipped with an attachment for the analysis of thin films. In addition, it has an environmental chamber to carry out variable temperature (77-750 K) and controlled atmosphere x-ray powder diffraction studies. An Anton-Paar SAXSess camera is used for small angle x-ray studies of catalysts and catalyst supports. A state-of-the-art Siemens single crystal diffractometer with a CCD detector is accessed through the Department of Chemistry and Biochemistry.

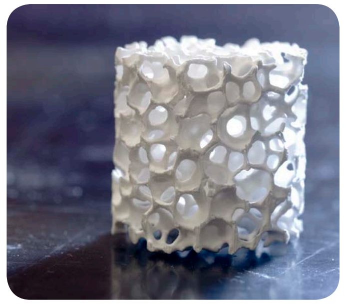
SURFACE ANALYSIS INSTRUMENTS

Three ultra-high vacuum surface analysis instruments are housed in the center. These instruments are all equipped for multiple electron spectroscopic techniques for determining surface composition, surface structure, and surface reaction chemistry. Techniques include Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), mass spectrometry, Temperature Programmed Desorption (TPD). X-ray and Ultraviolet Photoelectron Spectroscopies (XPS and UPS), Ion Scattering Spectroscopy (ISS) and High Resolution Electron Energy Loss Spectroscopy (HREELS).



Danielle Hansgen, a fourth year graduate student, is using an ultra high vacuum chamber to look at how adding a second metal to platinum changes the catalytic properties for the ammonia decomposition reaction.

REACTOR LABORATORIES



Microbalance Reactor Laboratories

We have six laboratory-scale plug-flow reactors for the evaluation of catalysts and determination of reaction rates. The reactors are assembled in a variety of configurations and are equipped with GC or GC/MS analysis systems. The reactors can be set up with gas or liquid feeds as needed.

We have fifteen stainless steel batch reactors for reactions in the liquid and liquid-gas phase with reaction volumes from 150 ml to 2 L. These units are assembled on demand as the research needs of the CCST evolve. In addition we have two photocatalytic reactors equipped with a GC and a IR spectrometer with a gas cell for product analysis.

Short Contact Time Reactors

Two reactor systems have been constructed for studying extremely fast and/or high temperature reaction systems. Catalyst contact times of milliseconds are routinely examined with reaction temperatures in excess of 1000°C. Short contact time reactions can be studied over both monolithic and standard supported catalysts with feasible contact times as short as 0.5 milliseconds over monolithic catalysts.

Vapor and Liquid Reactors

Flow and batch reactors operate at pressures ranging from a few torr to 5000 psi. These reactors are interfaced with GC, MS, HPLC, IR and GC/MS instruments for online product analysis.

SCANNING PROBE MICROSCOPES

Two Scanning Probe Microscopes with collective capability for air, liquid or vacuum operation, provide real space imaging of the atomic structure of surfaces by STM and AFM. These instruments facilitate study of the relation of the structure of modern catalytic materials to their surface reactivity. In addition, we have access to the microscopy facility in the College of Engineering that houses three AFM/STM instruments for surface characterization.

SPECTROMETERS

Solid State NMR Spectrometers

The Department of Chemistry and Biochemistry along with CCST faculty have received a grant from NSF to purchase two new high-field solid-state NMR spectrometers that will be used, in part, for the investigation of heterogeneous catalysts. This instrument will be operational in Spring 2012.

Fourier Transform Infrared Spectrometers

Five Fourier transform spectrometers are employed for catalyst characterization and reactant adsorption studies, using transmission, photoacoustic, and diffuse reflectance techniques.

UV/Visible Spectrometer

We have a UV/vis spectrometer from JASCO (model V-550) equipped with a diffuse reflectance cell for the analysis of powder and other solid samples.

COMPUTER FACILITIES AND MODELING SOFTWARE

The CCST computational facilities include 6 Beowulf clusters, all running CentOS Linux version 4.2 deployed with Warewulf. These clusters have a total of ~300 processors available for computation: 16 1.8 GHz Xeons, 44 2.4 GHz Xeons, 36 2.6 GHz Xeons, and 42 AMD Opteron 248 processors. Taken together, peak computational power is nearly a trillion floatingpoint operations per second (1 teraflops). These systems have a combined total disk storage capacity of 2 terabytes. The use of a single operating system over the clusters creates full binary compatibility between systems, which drastically reduces software development time. The newest of these clusters is using Ammasso RMDA Ethernet cards for extremely efficient parallel communications. The center also has several legacy systems - Silicon Graphics Solid Impact R10000 workstations (195 MHz, 64 bit microprocessor), and a Silicon Graphics Indigo XZ R4400 (150 MHz and 32 bit microprocessor).

Commercial software packages available on these machines include the Cerius and Insight II, ADF, Gaussian 98/03, Dacapo, Fluent, CHEMKIN, Matlab and Femlab. In-house software development ranges from simple reactor models to MPI based parallel molecular dynamics codes. Analysis of experimental data, such as Rietveld refinement of powder diffraction data and transmission electron microscopy simulations, is also done. To assist in-house software development we have the Portland Group Compiler Suite, Intel Fortran Compiler, Intel Math Kernel Library, and a wide range of scientific libraries, licensed under the GPL or a similar open-source license.

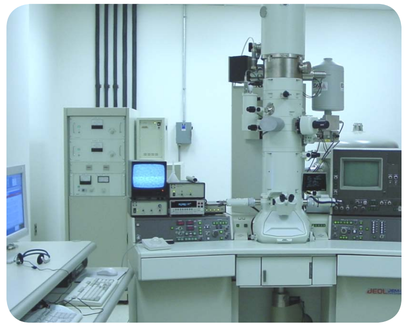
ADSORPTION INSTRUMENTS

We have added a new Micromeritics ASAP 2010 instrument to the CCST laboratories. The instrument can be used to measure adsorption capacities, surface areas, pore-size distributions at 77 K up to 300 K. We have also added an Altamira Instruments (Model AMI-200ip) for chemisorption, physisorption, and TPR measurements.

THERMOGRAVIMETRIC ANALYZER

A Cahn TGA 121 thermogravimetric analyzer is part of the Center's facilities (up to 1.5 g, 0.1 mg resolution). The instrument can be used for temperatures up to 1100°C, for adsorption capacity measurements, controlled atmosphere experiments, etc.

MICROSCOPES



The Electron Imaging Facility at University of Delaware includes two transmission electron microscopes (TEMs) and three scanning electron microscopes (SEMs) and provides the necessary infrastructure for carrying out TEM and SEM work. Scanning and high resolution transmission electron microscopy (STEM and HRTEM) are typically performed on a JEOL 2010F FasTEM field emission gun scanning transmission electron microscope (STEM). The nanoparticles size distribution and dispersion are measured using high angle annular dark field imaging. Energy dispersive spectroscopy (EDS) analysis in STEM mode is used to measure composition of individual nanoparticles.

CATALYSIS CENTER FOR ENERGY INNOVATION

UD receives single largest stimulus award to establish new Energy Frontier Research Center to develop new technologies for converting grasses and trees into electricity and fuels.

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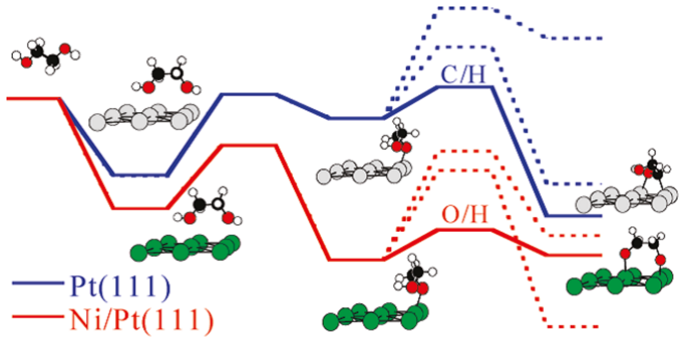
Theory and surface science experiments reveal the mechanisms of biomass decomposition on noble metal catalysts

Understanding the catalytic decomposition reaction pathways of biomass derived molecules can enable the design of more active and selective catalysts that facilitate the transformation of ligno-cellulosic biomass to fuels and chemicals. Toward this goal, researchers at the University of Delaware used a combination of quantum calculations and surface science experiments of isotopically labeled ethylene glycols to determine the decomposition pathways on Pt(111). Decomposition proceeds through initial O-H cleavage followed by C-H cleavage to form adsorbed glycolaldehyde. Additionally, several low activation barriers to carbon-carbon bond breaking exist in highly dehydrogenated surface intermediates. This implies that unlike hydrocarbons or mono-alcohols, the kinetically relevant steps in the decomposition of over-functionalized oxygenates may not be C-C cleavage. Finally, surface modification of Pt with Ni increases the rate of decomposition and alters the reaction pathway. This indicates that catalysts for biomass transformation to fuels and chemicals can be selectively tuned for desired bond breaking sequences.



Energetics of initial dehydrogenation reactions of ethylene glycol on Pt(111) and Ni/Pt(111) calculated via quantum mechanical calculations.

Relevant publication: Salciccioli, M., W. Yu, M.A. Barteau, J.G Chen, and D.G. Vlachos, Differentiation of O-H and C-H Bond Scission Mechanisms of Ethylene Glycol on Pt and Ni/Pt Using Theory and Isotopic Labeling Experiments. Journal of the American Chemical Society, 2011, 133(20), pp 7996-8004. http://pubs.acs.org/doi/abs/10.1021/ja201801t

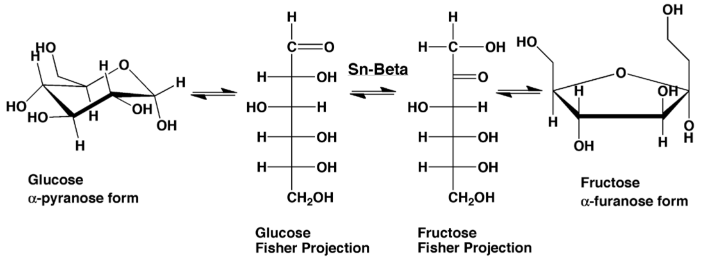
Research conducted by the Vlachos, Chen and Barteau groups at the University of Delaware.

New catalyst converts selectively biomass derived sugars to chemicals

A novel catalyst was developed to efficiently convert biomass derived sugars. This development can have unprecedented impact on the production of renewable chemicals and fuels. Interest in carbohydrate chemistry has been revitalized by the recent push to produce chemicals from biomass. A reaction of particular importance and difficulty is the isomerization of glucose to fructose, an intermediate step in the production of biofuels. Engineers at Caltech have shown that the use of Tin-Beta zeolites as catalysts for this reaction offers significant advantages over the traditional enzyme catalyst. This catalyst has been shown to be more stable than the enzyme catalysts, is unaffected by impurities that harm enzyme activity and is compatible with harsh environments, such as acidic solutions.

By coupling a dehydration reaction to the isomerization in hydrochloric acid solution, for instance, glucose was converted directly to 5-hydroxymethylfurfural (HMF) in high yields, proving Tin-Beta as an attractive catalyst for a one-pot process. The results are described in [1].

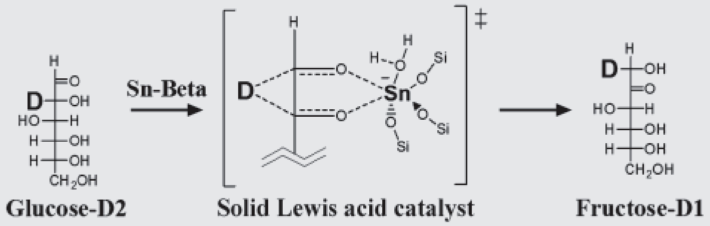
[1]. M. Moliner, Y. Román-Leshkov, and M. E. Davis, Proc. Nat. Acad. Sci. 107(14), 6164–6168 (2010); www.pnas.org/cgi/doi/10.1073/pnas.1002358107



Research conducted by the group of Mark Davis at Caltech

Functionality of a novel biomass conversion catalyst explained at the atomistic level

The core of catalytic chemistry research lies in understanding the role of a catalyst in a reaction. This understanding is crucial to the discovery of new materials leading to more energy efficient and benign chemical transformations. A critical reaction in utilization of the most abundant biomass ingredient, cellulose, is the conversion of glucose to fructose. Researchers at Caltech have now designed experiments to delineate the mechanism in this key chemical transformation catalyzed by a novel Sn-beta zeolite catalyst. The research team, under the supervision of Prof. Mark Davis, replaced the hydrogen atom attached to the C-2 carbon of the glucose molecule by a deuterium atom and performed the experiments with and without the Sn-beta catalyst in pure water. Nuclear magnetic resonance (NMR) experiments demonstrate the ability of the catalyst to facilitate the intramolecular hydrogen transfer from C-2 to C-1 and prove the first of this kind Lewis acid catalysis in water of biomass building blocks in stark contrast that Lewis acidity is generally suppressed by the presence of water. Given the fact that the Sn-beta catalyst is much more stable than the commercial enzymatic catalyst and active over a wide range of operating conditions, the findings of this work serve as a major milestone in developing catalysts for industrial scale biomass conversion process.



Isotopic labeling experiments reveal that an intra-hydride transfer rather than water mediated proton transfer convert abundant and inexpensive glucose to added-value fructose. In the transformation, the deuterium atom (D) shifts from the C-2 carbon in glucose to the C-1 carbon atom in fructose.

Relevant publication: Y. Román-Leshkov, M. Moliner, J. A. Labinger and M. E. Davis. Mechanism of glucose isomerization using a solid Lewis acid catalyst in water. Angew. Chem. Int. Ed. 2010, 49, 8954-8957.

This research was conducted by the group of Mark Davis at the California Institute of Technology.

Mark A. Barteau

» Senior Vice Provost for Research and Strategic Initiatives
» Robert L. Pigford Chair of Chemical Engineering
» Associate Director, Center for Catalytic Science and Technology
» Professor of Chemistry & Biochemistry

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EDUCATION

» Ph.D., Chemical Engineering – Stanford University (1981)

» M.S., Chemical Engineering – Stanford University (1977)

» B.S., Chemical Engineering – Washington University (1976)

RESEARCH INTERESTS

Surface science and catalysis by metal oxides and metals; selective oxidation; application of density functional theory to surface reactions; catalyst design; self-assembly of inorganic materials, scanning probe microcopies

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

» 2010: Fellow of the American Institute of Chemical Engineers

» 2010: Associate Editor, Topics in Chemical Engineering, Oxford University Press (since 1991)

» 2009: Giuseppe Parravano Award, Michigan Catalysis Society

» 2008: Named “One Hundred Engineers of the Modern Era” by the American Institute of Chemical Engineers

» 2006: National Academy of Engineering

RECENT PUBLICATIONS

M. Salciccioli, W. Yu, M. A. Barteau, J. G. Chen and D. G. Vlachos, “Differentiation of O-H and C-H Bond Scission Mechanisms of Ethylene Glycol on Pt and Ni/Pt Using Theory and Isotopic Labeling Experiments,” Journal of the American Chemical Society (2011).

J. C. Dellamorte, J. Lauterbach and M. A. Barteau, “Palladium-Silver Bimetallic Catalysts with Improved Activity and Selectivity for Ethylene Epoxidation,” Applied Catalysis A: General, 391, 281 (2011).

J. E. Rekoske and M. A. Barteau, “Kinetics, Selectivity and Deactivation in the Aldol Condensation of Acetaldehyde on Anatase Titanium Dioxide,” Industrial and Engineering Chemistry Research, 50, 41 (2011).

S. C. Chan and M. A. Barteau, “Physico-Chemical Effects on the Scale-up of Ag Photodeposition on TiO2 Nanoparticles,” Topics in Catalysis, 54, 378 (2011).

J. C. Dellamorte, J. Lauterbach and M. A. Barteau, “Effect of Preparation Conditions on Ag Catalysts for Ethylene Epoxidation,” Topics in Catalysis, 53, 13 (2010).

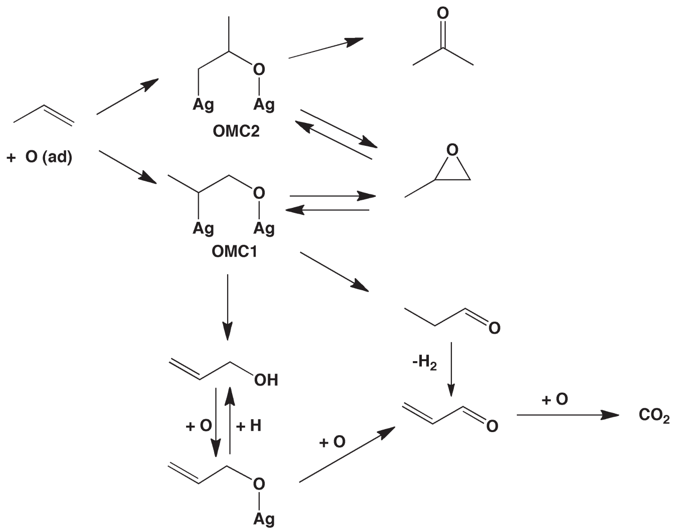
M. A. Barteau, “Reply to K. C. Waugh: “Comments on ‘Investigation of Ethylene Oxide on Clean and Oxygen-Covered Ag(110) Surfaces’”,” Catalysis Letters, 134, 5 (2010).

REACTION NETWORKS IN PROPYLENE EPOXIDATION CATALYSIS

Faculty: Mark Barteau, Raul Lobo (Chemical Engineering)
Postdoc: Apoorva Kulkarni (Chemical Engineering)
Undergraduate Student: Marco Bedolla (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences

We have previously demonstrated a variety of bimetallic catalysts that increase the selectivity of ethylene oxide formation relative to unpromoted silver catalysts. Drawing parallels from these successful catalysts, several silver-based catalysts were tested for propylene epoxidation performance. Cadmium, copper, cesium and rhenium were tested as promoters, but no catalyst achieved more than 5% selectivity at any conversion. While the competing combustion of propylene via allylic hydrogen abstraction is usually offered as the explanation for low propylene oxide (PO) selectivities, our studies of the reactions of PO shed new light on the sequential reaction processes that also diminish selectivity.

By examining the reaction of PO on silver catalysts under different conditions, a clearer picture of the reaction network has emerged. In the case of propylene oxidation or PO ring opening, two nearly energetically equivalent oxametallacycle structures are possible, as illustrated below. The product formation network must involve both oxametallacycle structures in order to explain the formation of acetone, propylene oxide, propanal, acrolein and allyl alcohol. Our reaction studies of PO ring opening under anaerobic conditions have shown that all of these products, except for acrolein, are direct products of intramolecular rearrangement of the oxametallacycles; acrolein is a secondary dehydrogenation product. Oxygen addition to the feed increases the conversion of PO somewhat, but we find no evidence for combustion of PO. In the presence of oxygen, allyl alcohol readily reacts on the surface of the catalyst to form acrolein, and CO_2 is generated primarily by acrolein oxidation. These results shed light on the network of reactions involving surface oxametallacycle intermediates that can influence the selectivity of propylene epoxidation with silver catalysts. In particular, they indicate that the design focus for improving PO selectivity should be on suppressing propylene combustion and on manipulating the branching reactions of surface oxametallacycles, rather than on sequential combustion of products.



Proposed reaction network for propylene epoxidation and decomposition over silver catalysts.

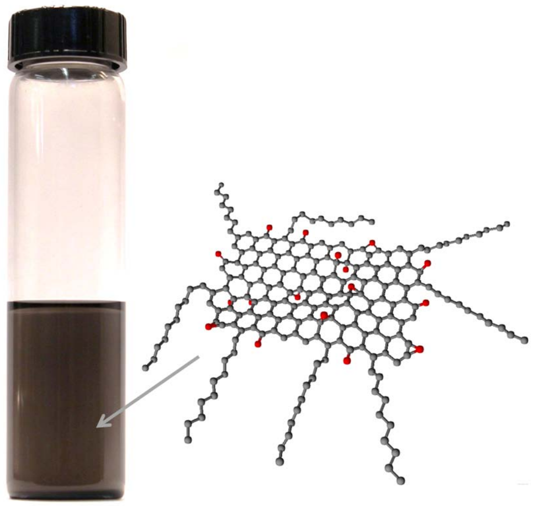
MULTIFUNCTIONAL COLLOIDAL NANOCATALYSTS FOR LIQUID FUEL COMBUSTION

Faculty: Mark Barteau (Chemical Engineering)
Visiting Researcher: Jean-Philippe Tessonnier (Chemical Engineering)
Collaborators: Ilhan A. Aksay, Daniel Dabbs (Chemical Engineering, Princeton University), Roberto Car, Annabella Selloni (Chemistry, Princeton University), Frederick L. Dryer (Mechanical & Aerospace Engineering, Princeton University), Bryan Eichhorn, Michael Zachariah (Chemistry & Biochemistry, University of Maryland), Jennifer Wilcox (Department of Energy Resources Engineering, Stanford University), Richard A. Yetter (Mechanical & Nuclear Engineering, Pennsylvania State University).
Funding: ARRA/AFOSR

Petroleum-based transportation fuels are constantly improved to increase fuel economy and released power. Most of the research carried out in this field consists in developing additives to enhance the ignition and combustion of the fuel, but also to help maintain the engine and prevent the formation of carbon build-up in the cylinders and on the valves. Other additives include corrosion inhibitors, antiknock agents, antioxidants, antistatic agents or fuel system icing inhibitors for example.

Although rarely investigated, nanocatalysts represent a particularly interesting class of additives. These nanomaterials are designed to increase the reaction rate and consequently the complete fuel combustion in very short residence times. Nanocatalysts are desired for high speed propulsion for which high energy release rates are required, but they are also expected to be beneficial for the combustion of gasoline and biofuels in conventional engines. The catalyst lowers the activation energy and consequently the ignition temperature. Thus, it decreases the amount of unburned hydrocarbons (HC) and soots in the exhaust gas, and lowers the operating temperature of the engine, which has a direct effect on the formation of harmful NO_x. In the case of biofuels, which in some cases may exhibit lower performance and/or lesser stability than fossil fuels, the addition of a catalyst might help them to perform satisfactorily.

Nanocatalysts reported in the literature have shown significant improvements for the combustion of propellants or specialty fuels such as JP-5 or JP-10. They generally consist of organometallic precursors containing transition metals which decompose during the reaction to form catalyst nanoparticles. However, they have rarely been tested for conventional fuels. Our approach is to design nanohybrids composed of a metal oxide active phase and a functionalized graphene support. Graphene and functionalized graphene sheets (FGS) have been shown to have a great potential for electronics, polymer reinforcement, or energy storage (Li batteries, supercapacitors) for instance. One of our aims is to probe their potential for heterogeneous catalysis, either as catalyst or as catalyst support. FGS are at the border line between the molecule and the bulk material (as known in materials science). A sheet is made of a single layer of interconnected carbon atoms which propagates over several hundreds of nanometers to several microns. The FGS typically present many structural defects and a large amount of oxygen-containing functional groups bonded to the carbon network. We aim at controlling their surface chemistry to tune the catalytic activity of the active phase in a similar way as in homogeneous catalysis, while at the same time, these nanohybrids are expected to retain all the advantages of the heterogeneous catalyst (anchored active phase, easy separation). In this sense, FGS provide a unique chance for the design of single-site heterogeneous catalysts. In the present project, we used FGS derived from graphene oxide. The starting material still presents a fairly large amount of oxygen-containing groups on its surface (C/O=19). These groups are essential to



Suspension of modified FGS in toluene.

anchor the metal oxide active phase on the graphene surface and to prevent the formation of large aggregates which are undesired for this reaction. However, because of the polarity of the surface, these nanohybrids are solvated in polar solvents (alcohols, chloroform, etc.) but are poorly dispersed in non-polar hydrocarbons such as toluene or n-heptane. In addition, the decrease in the oxygen content in comparison to graphene oxide already leads to a partial re-stacking of the sheets along the c-axis, as observed by XRD. We therefore modified the surface by anchoring paraffinic chains in order to increase the solubility of the FGS in fuels and introduce a spacer that would prevent the sheets from re-stacking. The synthesized nanohybrids showed promising performance for the combustion of toluene, used as a model fuel. ❖

CCST LECTURE SERIES

Our 2011 Spring Seminar Series was sponsored by Eastman Chemical Company.

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JEFFREY MILLER
Argonne National Laboratory

Determination of CO, H_2 and H_2O Coverage by XANES on Pt and Au During Water Gas Shift Reaction: Experiment and DFT Modeling

FEBRUARY 23, 2011

LARRY CURTISS
Argonne National Laboratory

First Principles Studies of Nanoscale Effects on Catalytic Activity and Selectivity

MARCH 18, 2011

DAVID L. KING
Pacific Northwest National Laboratory

An Integrated System for Cleanup of Warm Syngas Generated by Coal or Biomass Gasification

APRIL 15, 2011

SUSANNAH SCOTT
University of California, Santa Barbara

Towards Non-flammable Polyolefins: Using Surface Chemistry and Catalysis to Design Composite Materials

AUGUST 15, 2011

TAKAHITO MOTEKI

"Synthesis of Pure Silica Sodalite from Layered Silicate Rub-15 by Topotactic Conversion and Its Unique Property"

Douglas J. Buttrey

» Professor of Chemical Engineering

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EDUCATION

- » Ph.D., Physical Chemistry – Purdue University (1984)
- » M.S., Biochemistry – Purdue University (1978)
- » B.S., Biology – Wayne State University (1976)

RESEARCH INTERESTS

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

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

- » Summer 2008: Visiting Professor, African University of Science and Technology, Abuja, Nigeria
- » Winter 2008: Visiting Professor, Catalysis Research Center, Hokkaido University, Sapporo, Japan

RECENT PUBLICATIONS

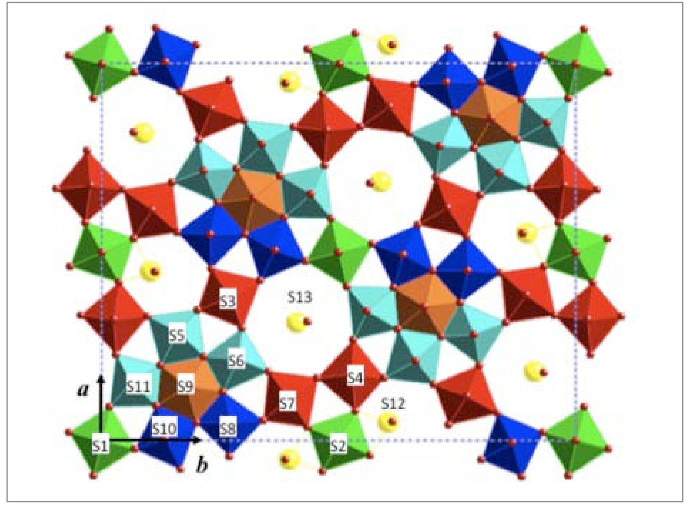
W.D. Pyrz, S. Park, D.A. Blom, D.J. Buttrey, T. Vogt, "High-Angle Annular Dark Field Scanning-Transmission Electron Microscopy (HAADF-STEM) Investigations of Bimetallic Nickel Bismuth Nanomaterials Created by Electron Beam Induced Fragmentation (EBIF)," J. Phys. Chem. C, 114(6), 2838-2543 (2010).

W.D. Pyrz, D.A. Blom, M. Sadakane, K. Kodato, W. Ueda, T. Vogt, D.J. Buttrey, "Atomic-Scale Investigation of Two-Component MoVO Complex Oxide Catalysts Using Aberration-Corrected High-Angle Annular Dark-Field Imaging," Chem. Mater., 22, 2033-2040 (2010).

W.D. Pyrz, D.A. Blom, M. Sadakane, K. Kodato, W. Ueda, T. Vogt, D.J. Buttrey, "Atomic-Level Imaging of MoVO Complex Oxide Phase Intergrowth, Grain Boundaries, and Defects Using HAADF-STEM," Proc. Natl. Acad. Sci., 107(14), 6152-6157 (2010).

SYNTHESIS AND CHARACTERIZATION OF SINGLE PHASE M1 MO-V-NB-TE-O CATALYSTS FOR SELECTIVE OXIDATION AND AMMOXIDATION OF PROPANE

Faculty: Doug Buttrey, Mark Barteau (Chemical Engineering)
Graduate Student: Xin Li (Chemical Engineering)



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+}

The Mo-V-Nb-Te-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 and pseudo-hexagonal M2, and M1 is generally accepted to be the key factor for propane activation.

Two methods are often used for catalyst synthesis: hydrothermal method and slurry method. Both ways have the mixing of metal precursors in aqueous solutions as the first step, while the former one requires the hydrothermal treatment in the autoclave to the resulting mixture, but in the slurry method heat treatment (drying and calcination) is directly followed once the slurry is formed. Hydrothermal method appears to be able to produce fairly pure M1 phase without further purification but slurry method is relatively easy in operation although simultaneous formation of M1 and M2 is often encountered.

In this work, we chose the slurry approach and focus on the synthesis and characterization of single phase M1 material in order to better understand the true crystal chemistry and intrinsic structure-property relationships. Several parameters have been investigated and it is found that besides M1 and M2, $TeMo_5O_{16}$, V-Mo_5O_{14}, and Mo-V_2O_5 are often formed as impurity phases. The formation of $TeMo_5O_{16}$ is favored at relatively high slurry pH, while the formation of V-Mo_5O_{14} is significantly affected by the heating rate of calcination. The formation of the Te-free V-Mo_5O_{14} phase can be related to Te loss during the heat treatment. Mo-V_2O_5 is always formed in small quantities when V in excess and can be removed by washing the product with concentrated hydrogen peroxide solution. In general, highly pure M1 can be produced by gently heating the precursor during calcination and washing the resulting product in hydrogen peroxide.

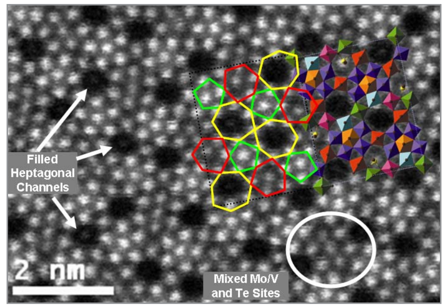
An improved structural model of M1 has been developed using simultaneous Rietveld refinement of synchrotron and neutron diffraction data together with several modifications to the old model. The major part of the improvement results from the introduction of a new Mo-containing V_2O_5-type impurity phase. The refinement results strongly suggest that V preferentially occupies the linking sites (S1, S2, S3, S4, and S7 in the figure) 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 is primarily 4+ and indicate that some linking sites (S3, S4, and S7 in the figure) might be 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 typical severe distortion for d^0 sites. The new model suggests a possible variation between the surface and the bulk where the transition between V^{5+} and V^{4+} can occur on surface to provide V^{5+} species which have been proposed to be the active sites for propane activation.

DIRECT STRUCTURE ANALYSIS OF COMPLEX MO-V SUBOXIDES USING HIGH RESOLUTION SCANNING TRANSMISSION ELECTRON MICROSCOPY

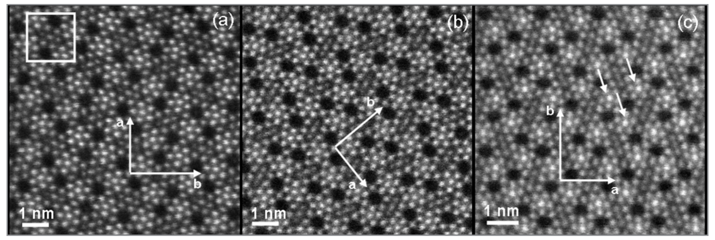
Faculty: Doug Buttrey (Chemical Engineering)
Collaborators: Thomas Vogt, Doug Blom (University of South Carolina NanoCenter)

Using high-resolution imaging in the scanning transmission electron microscope (HR-STEM), we have directly imaged the atomic framework of the complex of various substituted Mo-V-O bronze catalysts. In these images, we can directly measure fractional coordinates for the atomic columns and measure image contrast of each atomic column to estimate the local elemental occupancies. This is possible since the contrast in the image is related to the intensity of scattering from the elements present, and this scattering is roughly proportional to the square of the atomic number (Z). These catalysts are promising candidates for the selective oxidation and ammoxidation of propane to acrylic acid and acrylonitrile, respectively.

We believe that a detailed understanding of the underlying atomic framework may be an important key to understanding the mechanism behind the high activity and selectivity and may provide clues to the development of further catalytic improvements. Specifically, we have focused on the MoVNbTeO, MoVTaTeO, and MoVTeO formulations that possess a particularly active orthorhombic phase. Proposed structural details, determined from our previous studies using indirect scattering methods, were confirmed in direct space using the STEM imaging technique. In an atomically resolved STEM image of the Nb-containing sample (top right), it was possible to directly measure metal site coordinates and to estimate the composition of each atomic column based on the observed image contrast. This information was then used to build a structural model that showed good agreement with the model developed from the refinement of high-resolution x-ray and neutron powder diffraction data. By changing the synthetic technique from a slurry method to hydrothermal synthesis for the MoVTeNbO sample, it was possible to change the intercalation level of the heptagonal channel from partially occupied to vacant. By substitution or removal of elements, as shown in the figure below for the comparison of the MoVTeNbO to the MoVTaTeO and the MoVTeO catalyst, different elemental occupancies are observed. Close inspection of the contrast of the atomic columns in (c) reflects changes in the composition of the pentagonal ring centers (indicated by arrows); higher contrast is observed with Ta present than the same pentagonal center position in the MoVTeO and MoVNbTeO counterparts shown in (a) and (b) respectively. Interpretation of this contrast suggests that this position is preferentially occupied by Ta (Z=73) when present. By chemical analogy, it can be concluded that the pentagonal center in MoVNbTeO sample shown in (b) is occupied by Nb (Z=41). We can also estimate the distribution of both Mo, V, and Te based on this technique. This result is very promising for the structural characterization of unknown complex materials, since it provides a fast and reliable method for the development of starting models for subsequent Rietveld refinements.



HR-STEM image of the MoVTeNbO 'M1' catalyst. Included in the image are two renderings of our diffraction-based atomic model that are superimposed on top of the image showing good agreement. In the image, the heptagonal channels are occupied and the contrast varies from one atomic column to another, providing clues to the overall composition.



HR-STEM images of (a) MoVTeO (b) MoVNbTeO, and (c) MoVTaTeO 'M1' catalysts. The indicated a-b axes in each image show the orientation of a single unit cell within the image. The box shows a region within the MoVTeO catalyst that exhibits local contrast that differs from the other two catalysts suggesting compositional variation. The arrows in the MoVTaTeO catalyst indicate enhanced contrast that is indicative of Ta occupation in the pentagonal centers.

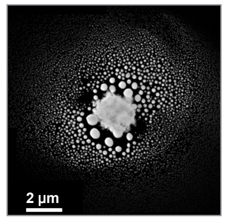
SYNTHESIS AND CHARACTERIZATION OF METALLIC AND BIMETALLIC NANOPARTICLES THROUGH ELECTRON MICROSCOPY

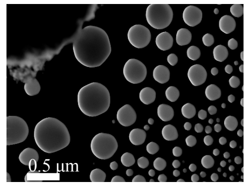
Faculty: Doug Buttrey, Dion Vlachos, Jochen Lauterbach (Chemical Engineering)
Collaborators: Jim Dumesic, Dante Simonetti, Edward Kunkes (Chemical & Biological Engineering, Univ. of Wisconsin); Thomas Vogt, Sangmoon Park (Chemistry & Biochemistry, University of South Carolina); Richard Crooks, Michael Weir (Chemistry & Biochemistry, University of Texas)
Graduate Students: William Pyrz, Hua Yang (Chemical Engineering)

Metallic and bimetallic nanomaterials have attracted significant interest recently due to their ability to provide enhancements to a variety of chemical processes. In addition to the effects of alloying, materials at small scales often exhibit physical and chemical properties that deviate from known bulk characteristics. Conventionally, catalyst design has been conducted through trial and error and successful catalysts are found through performance-based testing with little understanding of the true nature of the material. Recent efforts have been dedicated to understanding nanoparticle catalysts with emphasis on the properties of the metallic and bimetallic nanoparticles at the atomic scale. In the past several years, the superior spatial resolution provided by the transmission electron microscope (TEM) has improved the study of materials at the atomic level. For both supported and unsupported nanoparticles, TEM enables the investigation of atomic-level structure, composition, particle size, morphology, and particle polydispersity through advanced techniques such as high resolution imaging (HREM), high angle annular dark field imaging (HAADF), energy filtered imaging, and energy dispersive x-ray spectroscopy (EDS). Our focus is the use of advanced TEM techniques for the characterization of both supported and unsupported catalysts.

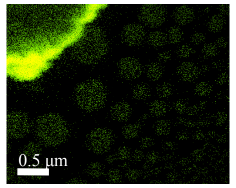
Our current research has been focused on a variety of nanoparticle and catalytic systems that include Ni-Bi alloys, Pt-Re supported catalysts, promoted Ru catalysts, and dendrimer encapsulated Pt and Au nanoparticles. In the Ni-Bi system, where applications include use as an alternative to lead-based solders and catalysts for synthesis of large diameter single-wall carbon nanotubes, we employ low temperature hydrothermal techniques to synthesize bimetallic Ni-Bi nanoparticles. The resulting product is a mixture of micron-sized NiBi, $NiBi_3$, and Bi particles. Under the electron beam in the TEM, we have shown that these alloy particles will undergo fragmentation and yield fields of bimetallic particles in a process we call electron beam-induced fragmentation (EBIF). The figure above shows a HAADF image and the figure below shows elemental maps (Ni K-edge and Bi M-edge) of a particle field after EBIF. The image shows particle sizes ranging from 1-500 nm and the elemental map confirms the formation of bimetallic nanoparticles. HREM imaging in the bottom figure shows that the nanoparticles are crystalline and FFT analysis shows the structure to be the rhombohedral lattice which is the same structure observed in pure Bi. ❖

HAADF micrograph of a nano-particle field following an EBIF event

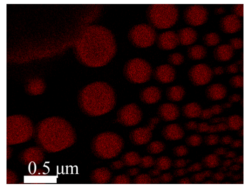




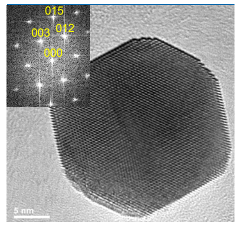
Typical HAADF image of nanoparticles following EBIF



Ni K edge x-ray map showing areas with Ni



Bi M edge x-ray map showing areas containing Bi



HREM image of a single Ni-Bi nanoparticle with the corresponding FFT image looking down the [100] zone axis

Jingguang G. Chen

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- » Associate Director, Center for Catalytic Science and Technology
- » Co-Director, Catalysis Center for Energy Innovation
- » Professor of Chemistry

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EDUCATION

- » PhD – Univ. of Pittsburgh (1988)
- » BS – Nanjing Univ., China (1982)

RESEARCH INTERESTS

Synthesis and characterization of metal carbides and bimetallic alloys as novel catalytic and electrocatalytic materials for applications in environmental catalysis and fuel cells. Determination of structure-property relationship on single crystal surfaces, PVD/CVD films, nanoparticles, and supported catalysts

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

- » 2011: Herman Pines Award in Catalysis, Chicago Catalysis Club
- » 2011: Excellence in Undergraduate Advising and Mentoring, UD
- » 2008: Excellence in Catalysis Award (New York Catalysis Society)
- » 2008: Fellow, American Vacuum Society
- » 2005-Present: Director-at-Large, North American Catalysis Society
- » 2005-Present: Principle Investigator, Synchrotron Catalysis Consortium

RECENT PUBLICATIONS

A.L. Stottlemyer, E.C. Weigert, and J.G. Chen, "Tungsten Carbides as Alternative Electrocatalysts: From Surface Science Studies to Fuel Cell Evaluation", Industrial & Engineering Chemistry Research, 50 (2011) 16-22.

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Q Lu, M.W. Lattanzi, K.M. Unruh, J.G. Chen, J.Q. Xiao, "High Energy and Power Density Supercapacitor Electrode Prepared from Monolithic NiO/Ni Nanocomposite", Angewandte Chemie International Edition (Journal Cover), 50 (2011) 6847-6850.

B.A. Cheney, J.A. Lauterbach and J.G. Chen, "Reverse Micelle Synthesis and Characterization of Pt/Ni Bimetallic Catalysts", Applied Catalysis A, 394 (2011) 41-47.

I.J. Hsu, D.A. Hansgen, B.E. McCandless, B.G. Willis and J.G. Chen, "Atomic Layer Deposition of Pt on Tungsten Monocarbide (WC) for the Oxygen Reduction Reaction", Journal of Physical Chemistry C, 115 (2011) 3709-3715.

H. Ren, D.A. Hansgen, T.G. Kelly, A.L. Stottlemyer and J.G. Chen, "Replacing Platinum with Tungsten Carbide (WC) for Reforming Reactions: Similarities in Ethanol Decomposition on Ni/Pt and Ni/WC Surfaces", ACS Catalysis, 1 (2011) 390-398.

T.G. Kelly, A.L. Stottlemyer, H. Ren and J.G. Chen, "Comparison of O-H, C-H and C-O Bond Scission Sequence of Methanol on Tungsten Carbide Surfaces Modified by Ni, Rh and Au", Journal of Physical Chemistry C, 115 (2011) 6644-6650.

M.P. Humbert, A.L. Stottlemyer, C.A. Menning, and J.G. Chen, "Bridging the Materials Gap between Single Crystal and Supported Catalysts Using Polycrystalline Ni/Pt Surfaces for Cyclohexene Hydrogenation", Journal of Catalysis, 280 (2011) 96-103.

J.P. Bosco, K. Sasaki, M. Sadakane, W. Ueda and J.G. Chen, "Synthesis and Characterization of Three-Dimensionally Ordered Macroporous (3DOM) Tungsten Carbide: Application to Direct Methanol Fuel Cells", Chemistry of Materials, 22 (2010) 966-973.

C.A. Menning and J.G. Chen, "Regenerating Pt-3d-Pt Model Electrocatalysts through Oxidation-Reduction Cycles Monitored at Atmospheric Pressure", Journal of Power Sources, 195 (2010) 3140-3144.

H. Ren, M.P. Humbert, C.A. Menning, J.G. Chen, Y. Shu, U. Singh, and W.-C. Cheng, "Inhibition of Coking and CO Poisoning of Pt Catalysts Surfaces by the Formation of Au/Pt Bimetallic Surfaces", Applied Catalysis A, 375 (2010) 303-309.

M.P. Humbert, C.A. Menning, and J.G. Chen, "Replacing Bulk Pt in Pt-Ni-Pt Bimetallic Structures with Tungsten Monocarbide (WC): Hydrogen Adsorption and Cyclohexene Hydrogenation on Pt-Ni-WC", Journal of Catalysis, 271 (2010) 132-139.

C.A. Menning, and J.G. Chen, "Theoretical Prediction and Experimental Verification of Stability of Pt-3d-Pt Subsurface Bimetallic Structures: From Single Crystal Surfaces to Polycrystalline Films", Topics in Catalysis, 53 (2010) 338-347.

W.W. Lonergan, D.G. Vlachos and J.G. Chen, "Correlating Extent of Ni-Pt Bond Formation with Low Temperature Hydrogenation of Benzene and 1,3-Butadiene over PtNi Bimetallic Catalysts", Journal of Catalysis, 271 (2010) 239-250.

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M.C. Weidman, D.V. Esposito and J.G. Chen, "The Electrochemical Properties of Tungsten and Tungsten Monocarbide (WC) Over Wide pH and Potential Ranges", Journal of Electrochemical Society, 157 (2010) F179-F188.

D.V. Esposito, S.T. Hunt, A.L. Stottlemyer, K.D. Dobson, B.E. McCandless, R.W. Birkmire and J.G. Chen, "Low-Cost Hydrogen Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide (WC) Substrates", Angewandte Chemie International Edition, 49 (2010) 9859-9862 (Journal Cover).

STRUCTURE-PROPERTY RELATIONSHIP IN TRANSITION METAL CARBIDES

Faculty: Jingguang Chen (Chemical Engineering)
Graduate Students: Dan Esposito (Chemical Engineering), Hui Ren (Chemistry)
Funding: U.S. Department of Energy, Basic Energy Sciences

The carbides of early transition metals (Groups IVB-VIB) are characterized by many unique and intriguing catalytic properties.It is now well established that, compared to their parent metals, TMCs often demonstrate catalytic advantages in activity, selectivity, and resistance to poisoning.

It has also been demonstrated that the catalytic performances of TMC are approaching or surpassing those of the more expensive Pt-Group metals (Pt, Pd, Ir, Rh and Ru), particularly in catalytic reactions involving the transformation of C-H bonds of hydrocarbons, such as in dehydrogenation, hydrogenation, hydrogenolysis, and isomerization reactions.

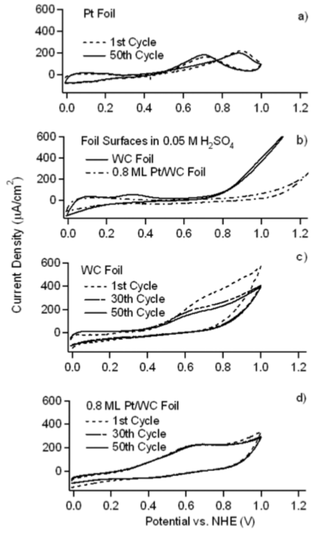
We have performed a series of surface science and catalytic investigations of the unique catalytic properties of TMCs. We have adopted three parallel experimental approaches: (1) to develop experimental procedures for the preparation of thin TMC films with desired electronic and structural properties; (2) to utilize a battery of surface science techniques to determine the correlation between electronic, structural and catalytic properties; and (3) to correlate the surface reactivities of the model TMC thin films to the catalytic properties of powder catalysts.

METAL CARBIDES AS ANODE ELECTROCATALYSTS AND CAPACITORS

Faculty: Jingguang Chen (Chemical Engineering)
Graduate Students: Thomas Kelly, Irene Hsu (Chemical Engineering), Zach Mellinger (Materials Science and Engineering)
Funding: NSF and Naval Research Lab

Currently the anode electrocatalysts in hydrogen and methanol fuel cells are the bimetallic alloys of Pt/Ru.However, the Pt/Ru electrocatalyst has two main disadvantages: its prohibitively high cost at the current catalyst loading and its susceptibility to poison by carbon monoxide (CO). Our research objective is to determine whether tungsten carbides can be used as alternative electrocatalysts that are less expensive and more CO-tolerant than Pt/Ru.Our research approaches involve the following parallel steps: (1) Mechanistic studies of the reactions of hydrogen, methanol, water and CO on well-characterized carbide and Pt/Ru single surfaces under UHV conditions; (2) using the surface science results as guidance to synthesize PVD and CVD films of carbide films with desirable structures; (3) evaluation of the PVD/CVD carbide films using electrochemical testing and spectroscopic techniques. We are also utilizing similar research approaches to introduce the carbide fuel cell functionality on the surfaces of composite materials to synthesize multi-functional composites.

Our recent results have revealed that molybdenum and tungsten carbides, in particular tungsten carbide in the WC phase, are promising catalysts for the electrooxidation of hydrogen and methanol. Furthermore, both surface science and electrochemical studies have demonstrated a synergistic effect by supporting submonomalyer coverages of Pt onto the WC substrate. Current studies are aimed at determining the stability and activity of WC and Pt/WC surfaces and thin films under in-situ conditions.



PHOTOELECTROCHEMICAL (PEC) DEVICES FOR WATER SPLITTING

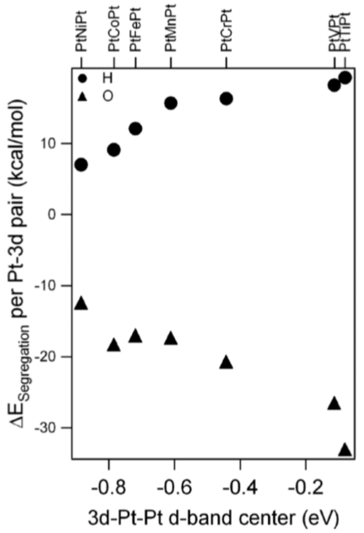
Faculty: Jingguang Chen (Chemical Engineering), Robert Birkmire (Institute of Energy Conversion)
Graduate Student: Dan Esposito, Yannick Kimmel, Robert Forest (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences

The cathode reaction at PEC involves the reduction of H+ to produce H2.Currently the most common cathode catalyst is Platinum (Pt).

Due to the high cost and limited supply of Pt, the utilization of large quantities of Pt will most likely hinder the commercialization of PEC.

We will attempt to solve this problem using two parallel approaches: (1) to reduce the loading of Pt by using Pt-based bimetallic alloys and (2) to replace Pt with alternative catalytic materials.Currently we are exploring the possibility of utilizing these carbide materials for the cathode reduction of H+ to produce H2.The cathode activity and stability of W and Mo carbides are being compared to those of Pt.We plan to employ a combination of in-situ electrochemical measurements and theoretical modeling to identify and synthesize carbide structures and compositions as alternative cathode catalysts in PEC.

Currently, we are also investigating the catalytic properties of TMC nanoparticles.The combined synthesis, characterization, and reactivity studies should help us determine the following two important properties of supported TMC: (a) What are the novel electronic and/or structural properties of the TMC nanoparticles and (b) at what particle dimension do the electronic and structural properties of TMC nanoparticles approach those of bulk TMC materials.



NOVEL PROPERTIES OF BIMETALLIC SURFACES AND SUPPORTED CATALYSTS

Faculty: Jingguang Chen, Dion Vlachos, Mark Barteau, Jochen Lauterbach (Chemical Engineering)
Graduate Students: Danielle Hansgen, William Lonergan, Weiting Yu, Jacob Weiner, Marc Porosoff (Chemical Engineering)
Funding: Department of Energy, Basic Energy Sciences and NSF IGERT

Bimetallic surfaces and catalysts, in particular with the metal overlayer at a monolayer-thickness, often show chemical activities that are different from the bulk materials.Our studies in bimetallic catalysis include experimental and theoretical efforts on well-characterized single crystal surfaces.

Using a combination of Temperature Programmed Desorption, High-Resolution Electron Energy Loss Spectroscopy, and Density Functional Theory (DFT) modeling, we have established a correlation between the unique chemical properties of Ni/Pt bimetallic surfaces to changes in the d-band center of surface Pt atoms.We have extended similar experimental and DFT modeling methods to investigate a wide range of bimetallic surfaces to determine a general correlation between the center and d-band and chemical properties.In addition to surface science studies, we also attempt to bridge the "materials gap" and "pressure gap" between model single crystal surfaces and realistic powder materials.We are currently synthesizing bimetallic catalysts on high surface area alumina supports and on zeolites.These bimetallic catalysts are evaluated using a combination of microreactor, transmission IR, and EXAFS under in-situ reaction conditions.

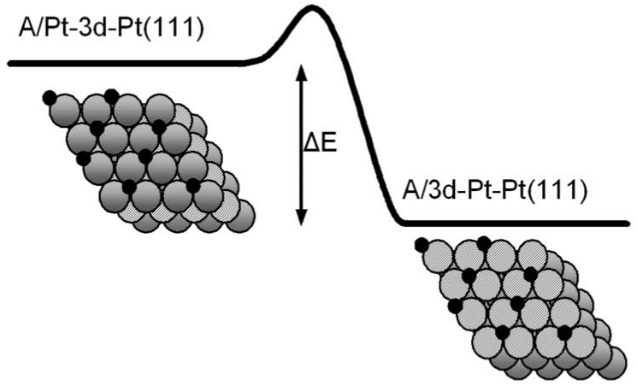
Our current studies in bimetallic catalysis include the selective hydrogenation of C=O and C=C bonds in unsaturated aldehydes, selective hydrogenation of acetylene in the presence of excess ethylene, and the production of hydrogen by selective reforming of oxygenates.The ultimate goal of these studies is to rationally design bimetallic catalysts with desired catalytic properties through a combination of surface science, DFT modeling, and reactor studies.

STABILITY OF PT AND PT-3D BIMETALLIC ELECTROCATALYSTS FOR FUEL CELLS

Faculty: Jingguang Chen (Chemical Engineering)
Graduate Students: Ke Xu, Weiting Yu (Chemical Engineering)
Funding: U. S. Department of Energy, EERE

One of the very important applications of Pt-3d bimetallic alloys is their utilization as the cathode electrocatalysts in hydrogen and methanol fuel cells.Typically the desirable cathode catalysts have the Pt-3d-Pt shell structure, with the 3d transition metal residing underneath the top-most Pt surface.Our recent surface science and DFT modeling results have indicated that the Pt-3d-Pt structure is not stable under oxygen-containing environment, such as under the operating conditions for the cathodic reduction of oxygen in PEM fuel cells.We have also determined the activation barriers for the oxygen-induced segregation of Ni (and Co) from the Pt-Ni-Pt (and Pt-Co-Pt) bimetallic structures.Our current studies are aimed at a systematic understanding of the stability of other Pt-3d-Pt structures and at finding ways to "anchor" the 3d metals to reduce the degree of segregation of 3d metals to the cathode surface.

Another stability issue in PEM fuel cells is the particle size of Pt. We are utilizing the e-beam deposition technique to prepare Pt particles with well-controlled particle size, which are subsequently tested for hydrogen and methanol electrooxidation.TEM, XRD and XPS are utilized to compare the particle size and surface compositions before and after the electrochemical measurements.Such comparison will provide important correlations between the particle size and electrocatalytic activity/stability.We will also utilize the e-beam deposition technique to synthesize Pt-3d-Pt thin films for cathode applications.



NEXAFS AND EXAFS CHARACTERIZATION OF CATALYTIC MATERIALS

Faculty: Jingguang Chen (Chemical Engineering), Sergey Rykov (Visiting Professor)
Graduate Student: William Lonergan, Nebojsa Marinkovic, Adele Wang (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences

Among the various characterization techniques, near-edge x-ray absorption fine structure (NEXAFS) is one of the most promising spectroscopies to provide fundamental understanding of the chemical and physical properties of inorganic compounds.In the past few years, we have carried out extensive and systematic NEXAFS investigations of different classes of inorganic compounds.NEXAFS is very sensitive to the local bonding environment, such as the number of d-electrons, spin configurations, ligand-field splitting, coordination numbers, local symmetries and crystal structures. These parameters are directly related to the electric, magnetic, and optical properties of transition metal compounds. Furthermore, NEXAFS studies are equally useful in the investigation of catalytic properties of inorganic compounds. Such studies are typically performed by correlating the catalytic performance of an inorganic compound with its electronic and structural properties, such as the oxidation state of the parent metal, the density of unoccupied states, and the local bonding geometries.The direct correlation of catalytic, electronic and structural properties often provides important information concerning the nature of the catalytic active sites, which potentially can be used as guidance for designing better catalysts.

Currently, we are utilizing NEXAFS to determine the electronic, structural and catalytic properties of a variety of novel inorganic materials.We are applying the NEXAFS technique to characterize a wide range of catalytic materials, including single crystal surfaces, PVD thin films, powder materials, and supported catalysts.

One example is the NEXAFS characterization of nanostructured carbon materials, which are produced by cesium-catalyzed structural rearrangement of amorphous carbon.We will also synthesize and characterize materials produced by doping transition metals onto the amorphous carbon or nanotube-like substrates.This approach might lead to the synthesis of supported transition metal carbides with novel structural and catalytic properties.Another example is the NEXAFS characterization of compositional and structural properties of thin film solar cells. ❖

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- » Associate Director, Center for Catalytic Science and Technology

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EDUCATION

- » Ph.D., Chemical Physics – Harvard University (1986)
- » A.M., Physics – Harvard University (1981)
- » B.S., Electrical Engineering and Computer Science – University of California, Berkeley (1979)

RESEARCH INTERESTS

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

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

- » 2007-Present: Associate Dean, UD College of Arts & Sciences
- » 2006-Present: Professor, UD Department of Physics & Astronomy (joint appointment)
- » 2001-Present: Professor, UD Department of Chemical Engineering (joint appointment)

RECENT PUBLICATIONS

O. Rahaman, A.C.T. van Duin, V.S. Bryantsev, J.E. Mueller, S.D. Solares, W.A. Goddard, D.J. Doren, "Development of a ReaxFF Reactive Force Field for Aqueous Chloride and Copper Chloride," J. Phys. Chem. A, 114, 3556 (2010).

D.W. Fickel, A.M. Shough, D.J. Doren, R.F. Lobo, "High-Temperature Dehydrogenation of Defective Silicalites," Microporous and Mesoporous Materials, 129, 156 (2010).

THEORETICAL STUDIES OF ZINC-GALLIUM OXONITRIDE VISIBLE LIGHT PHOTOCATALYSTS

Faculty: Doug Doren (Department of Chemistry and Biochemistry)
PhD Student: Heather Schmidt (Department of Chemistry and Biochemistry)

Solid solutions of GaN and ZnO are a promising class of photocatalysts, capable of splitting water under visible-light irradiation. The band gaps in the mixed metal oxonitrides are lower than either ZnO or GaN, thus allowing excitation by visible light. We have examined two different forms of the zinc-gallium oxonitride, the wurzite structure 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 ($Ga_xZn_{x-1}N_xO_{x-1}$) calculations show that there exists a coupling between the N 2p and Zn 3d states, leading to a decreased band gap. The trend in band gaps over the range of Zn concentrations ($0 \leq x \leq 1$) is consistent with experimental results (Figure 2). The expected band gap minimum corresponds to a high concentration of zinc that cannot be synthesized by current approaches. We have looked at formation energies to understand the thermodynamic constraints on synthesis of these materials. We have found the formation energy (relative to the experimental starting materials) becomes positive above about x=0.3, preventing synthesis of materials with high enough Zn-content to minimize the band gap (Figure 3). The effects of nitrogen pressure and use of other possible starting materials are currently being studied to identify routes for incorporating more Zn in the material.

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 spinel oxonitride (1.56 eV). We find that addition of nitrogen creates new states at the top of the valence band, while the states at bottom of the conduction band appear the same (Figure 4). 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. Thermodynamic studies similar to those done with the wurzite structures are also under way.

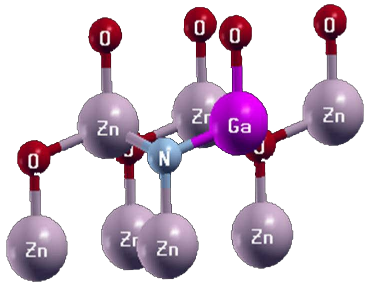


Figure 1 – Wurzite (a) and Spinel Structures (b)

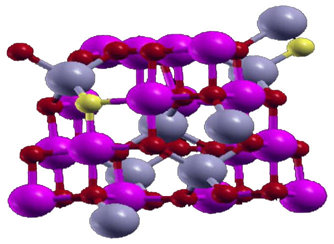


Figure 2 – The optimal band gap in $Ga_xZn_{x-1}N_xO_{x-1}$ is at a concentration around 0.7 however experimentally no structures with this Zn concentration have been made.

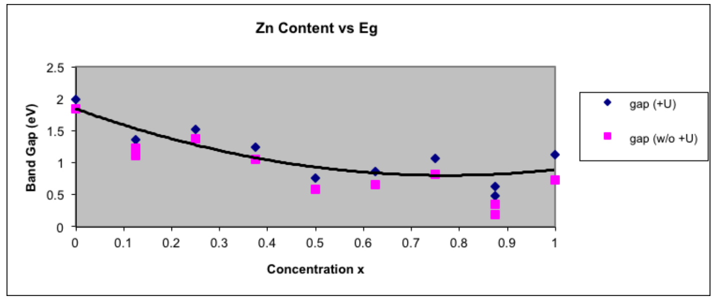


Figure 3 – The formation energy becomes positive after a Zn content of about 0.3 which is close to the limit seen experimentally.

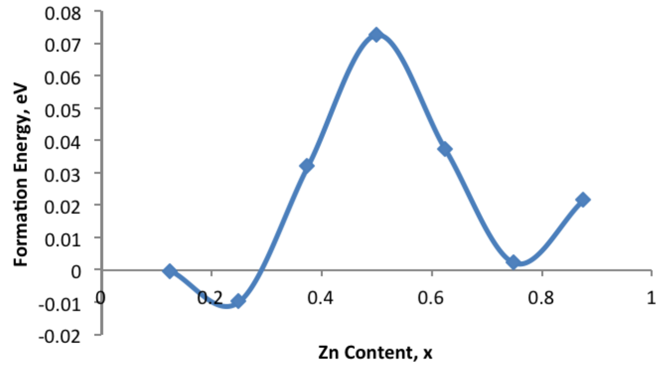
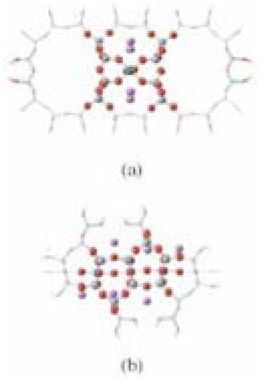


Figure 4 – The Density of states of the nitrogen substituted spinel structure ($Zn_8Ga_{16}O_{29}N_2[V_O]$) show new Zn d/ N p states (a) formed at the top of the conduction band while Zn d/O p states (b) around -1 eV are similar to the states seen in the pure $ZnGa_2O_4$.

PHOTOCATALYSIS IN ETS-10, A NANOSTRUCTURED TITANOSILICATE

Faculty: Doug Doren (Chemistry & Biochemistry)
Graduate Student: Anne Marie Shough (Chemistry & Biochemistry)
Funding: U.S. Department of Energy

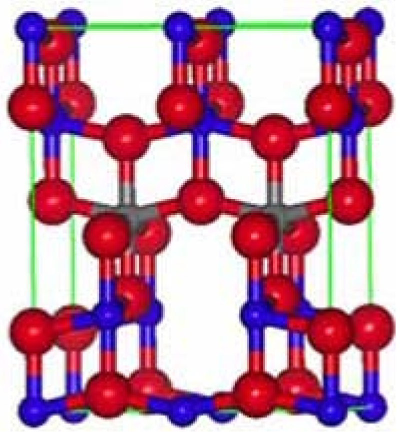
ETS-10 contains one-dimensional chains of TiO6 octahedra within a nanoporous silicate framework (see figure below). It is known to photocatalyze a variety of transformations of organic molecules. The structure and electronic properties can be controlled through synthesis, and this project is an effort to understand how this flexibility can be used to improve photocatalytic activity. This is a collaboration with the Lobo group, where experimental studies are being pursued while we are using firstprinciples theoretical methods to study the material.



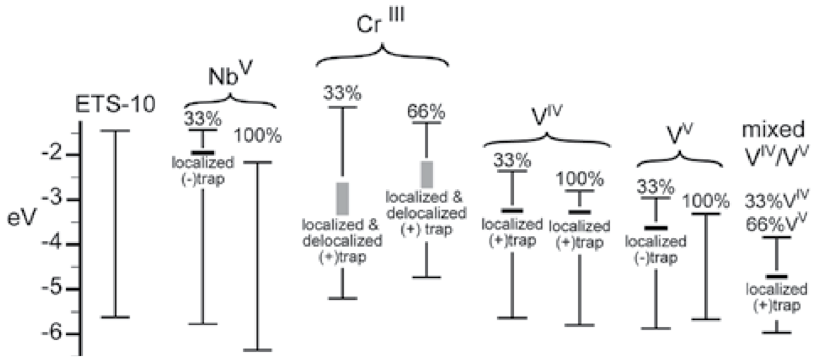
The structure of ETS-10 as viewed from the end (top) and the side (bottom) of the TiO6 chain. In our model, the atoms shown as spheres are treated with DFT, while the other atoms are included at the molecular mechanics level. In the bottom figure, some atoms are omitted for clarity

We have developed hybrid computational models that account for both the electronic properties of the TiO6 chains (using density functional theory) and the silicate framework (using molecular mechanics). Initial work was focused on the effect of substituting V for Ti in the TiO6 chains, since this is known experimentally to reduce the optical bandgap and allow absorption in the visible. We can predict the energetically favorable sites for substitution, the relative stability of V+4 and V+5 in each site, and the effect of doping on the electronic states of the material. We find that vanadium doping creates new states that allow visible light to cause transitions that do not exist in the undoped material. This has been observed experimentally, and we have been able to identify which of these transitions correspond to catalytically active excitations. The effects of substituting a number of other transition metals (Cr, Fe, Nb) have been explored, and these can shift the positions of the valence and/or conduction band, though not as effective as V in reducing the band gap (see figure below). We are currently using the results of these first-principles calculations to develop a simple model that can predict the effect that transition metal substitutions (including combinations of different metals) are likely to have on the electronic energies in this system.

This model will be used to guide choices of other materials to study with valence and conduction band positions chosen to permit specific redox reactions. ❖



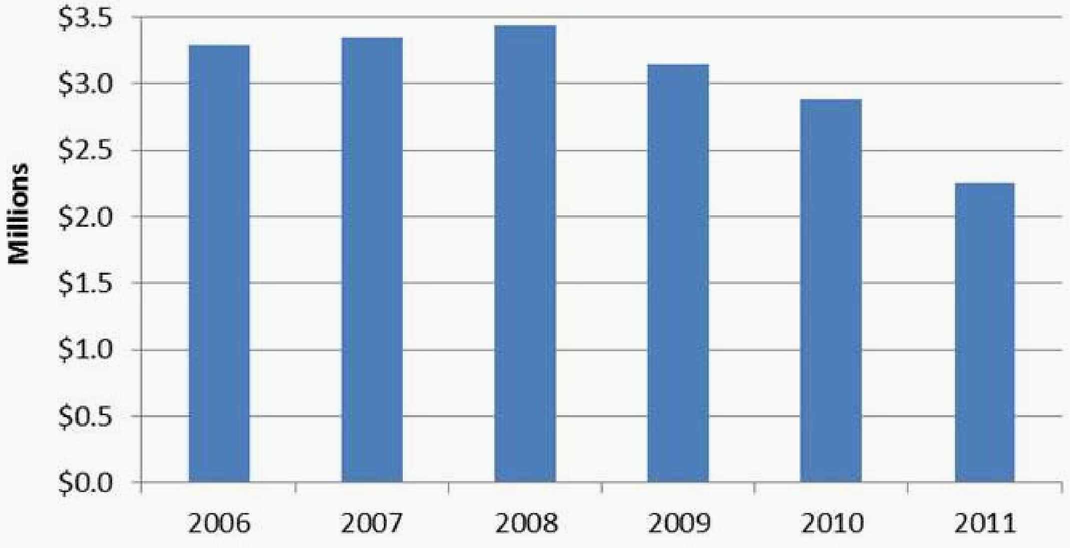
Model of Cr-doped anatase with an oxygen vacancy. The vacancy is required for charge neutrality, but the magnetic coupling between the Cr d-electrons depends on the relative positions of the Cr atoms and the vacancy.



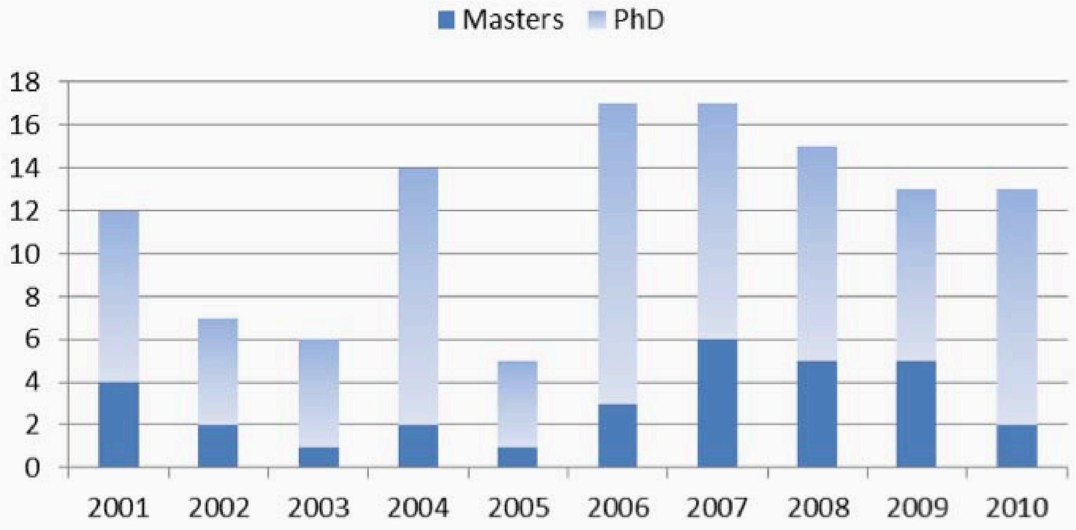
Comparison of energies of valence and conduction band edges, band gaps and midgap states for ETS-10 and derivatives with various transition metals substituted for Ti. Model of Cr-doped anatase with an oxygen vacancy. The vacancy is required for charge neutrality, but the magnetic coupling between the Cr d-electrons depends on the relative positions of the Cr atoms and the vacancy.

FACTS AND FIGURES

RESEARCH EXPENDITURES 2006-2011



DEGREES AWARDED 2001-2010



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EDUCATION

- » B.S., Chemistry - Fudan University
- » Ph.D., Chemistry - University of St. Andrews
- » Solar Energy, Postdoc - Lawrence Berkeley National Laboratory

RESEARCH INTERESTS

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

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

- » Material Research Society Graduate Student Award 2008
- » Electrochemical Society 2007 Student Research Award of the Battery Division

RECENT PUBLICATIONS

Boppana, V. B. R. & Jiao, F. Nanostructured MnO_2: an efficient and robust water oxidation catalyst. Chemical Communications, in press.

Jiao, F. &Frei, H. Nanostructured cobalt and manganese oxide clusters as efficient water oxidation catalysts. Energy & Environmental Science 3, 1018-1027 (2010).

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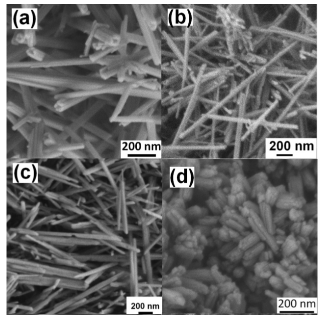
NANOSTRUCTURED MNO_2: AN EFFICIENT AND ROBUST WATER OXIDATION CATALYST

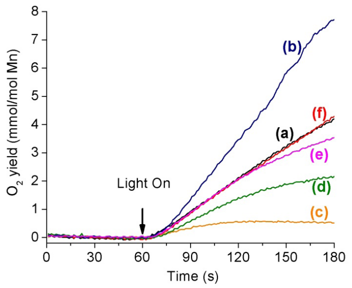
Faculty: Feng Jiao (Chemical Engineering)
Graduate Student: Venkata Bharat Ram Boppana (Chemical Engineering)

Water oxidation is a critical reaction for solar fuel production from abundant sources, e.g. CO_2 and water. In the past few years, we reported the first examples of cobalt and manganese oxide nanoclusters inside mesoporous silica supports as efficient and robust oxygen evolution catalysts driven by visible light. Both catalysts exhibited high O_2 yields per second compared with their micron sized counterparts, however it is still unclear that the high activity is mainly due to their much larger geometrical surface area or other effects, e.g. morphologies and crystal structures.

Recently, we have successfully synthesized nanostructured MnO_2 with different morphologies and polymorphs and systematically investigated their photocatalytic properties in water evolution reaction. All materials exhibit excellent water oxidation activity under visible light by using $Ru(bpy)_3^{2+}$ as sensitizer and $Na_2S_2O_8$ as sacrificial electron acceptor. One important observation is that irrespective of their morphologies and crystalline structures, most of the manganese dioxides exhibit a similar TOF per surface Mn. This finding provides us guidance for further developing new generation water oxidation catalyst: the morphology and crystal structure have negligible effect on water oxidation activity of MnO_2 catalysts, while large surface area will significantly enhance their activity. ❖



SEM images for as-synthesized (a) α-MnO_2 nanotubes, (b) α-MnO_2 nanowires, (c) β-MnO_2 nanowires, (d) α-MnO_2 nanoparticles.



Oxygen evolution results for (a) as-synthesized α-MnO_2 nanotubes, (b) α-MnO_2 nanowires, (c) α-MnO_2 nanoparticles, (d) β-MnO_2 nanowires, (e) ground α-MnO_2 nanotubes, and (f) acid-treated α-MnO_2 nanotubes.

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EDUCATION

- » Sc.D. -- Massachusetts Institute of Technology (1981)
- » B.Ch.E. -- University of Delaware (1977)

RESEARCH INTERESTS

Upgrading and conversion of renewable and fossil fuels; Chemical Reaction Engineering; Detailed kinetic modeling of complex reaction systems

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

- » 2008 R. H. Wilhelm Award in Chemical Reaction Engineering, AIChE
- » Editor-in-Chief, Energy and Fuels, January 2002 – present
- » Board of Governors Professor of Chemical Engineering, Rutgers University, 1998-2010
- » Chair, International Advisory Board, Curtin Centre for Advanced Energy Science and Engineering, Curtin University of Technology, Australia
- » Participation in Chinese Government "Plan 111"
- » "Top 100" author in citations in Industrial and Engineering Chemistry
- » Blue-Green Seminar, University of Michigan and Michigan State University, 10/14/2004
- » Advisory Board Member, CUNY Department of Chemical Engineering
- » Associate Editor, Energy and Fuels, January 1992-2001
- » Consulting Editor, AIChE J., January 1992-2002

RECENT PUBLICATIONS

Hou, Z., Bennett, C. A., Klein, M. T. and P. S. Virk, Approaches and Software Tools for Modeling Lignin Pyrolysis, Energy Fuels, 2010, 24 (1), pp 58-67.

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MOLECULAR LEVEL KINETIC MODELING OF UPGRADING AND REFINING PROCESSES FOR COMPLEX FEEDSTOCKS INCLUDING BIOMASS

Faculty: Michael Klein (Chemical Engineering)
Postdoc: Craig Bennett
Graduate Students: Zhen Hou, Brian Moreno (Chemical Engineering)

As the world presses forward into a future of dwindling traditional petroleum resources, alternative energy sources, such as biomass, must be presently considered. Although alternative conversion options exist, it is unlikely that the energy industry will walk away from trillions of dollars of existing refinery infrastructure. Whereas traditional oil processing has benefited from numerous decades of knowledge and understanding, biomass conversion is still in its infancy. Therefore, it is important to study and understand the processing and properties of these oxygen hetero-atom rich feedstocks as they are converted into synthetic oils, and ultimately fuels. One such method of obtaining an understanding of alternative feedstock processing and property prediction is to model the kinetics at a molecular level.

Our research has centered on the development of the Kinetic Modeler's Toolkit (KMT) for the past few decades. KMT provides the ability: to predict molecular concentrations for feeds based on bulk property measurements (CME: Composition Model Editor); to automatically construct and analyze large scale reaction networks based on simple chemistry rule selections (NetGen: Network Generator & INGen: Interactive Network Generator); and to tune rate parameters, edit rate laws, and run "what if" processing scenarios (KME: Kinetic Model Editor). In addition, recent developments have focused on Attribute Reaction Modeling (ARM) wherein the reaction centers (or attributes) of macromolecules, such as resid, or bio-polymers like lignin, are independently considered and reacted. Statistical renormalization reconstructs the products based on the juxtaposition of the independent product attributes.

The inclusion of oxygen hetero-atoms into our library of acid, metal, and radical based refinery chemistries has become a research priority. Upon completion, our KMT suite will become a major contribution to the world of modeling biomass conversion and upgrading. ❖

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EDUCATION

- » Ph.D., Chemical Engineering – California Institute of Technology (1995)
- » A.M., Chemical Engineering – California Institute of Technology (1993)
- » B.S., Chemical Engineering – University of Costa Rica (1989)

RESEARCH INTERESTS

Synthesis and characterization of zeolites and other microporous materials, structure-property relationships in porous adsorbents and catalysts

RECENT PUBLICATIONS

Korhonen, S.T., Fickel, D.W., Lobo, R.F., Weckhuisen, B.M., Beale, A.M.,"Isolated Cu^{2+} ions: active sites for the selective catalytic reduction of NO", *Chem. Comm.*, **2011** *47* 800-802.

Fickel, D.W., D'Addio, E., Lauterbach, J.A., Lobo, R.F., "The ammonia selective catalytic reduction activity of copper-exchanged small-pore zeolites", *Appl. Cat. B-Env.* **2011** *102*, 441-448.

Hould, N.D.; Foster, A.; Lobo, R.F., "Zeolite Beta Mechanism of Nucleation and Growth", *Micropor. Mesopor. Mater*., **2011**, *142*, 104-115.

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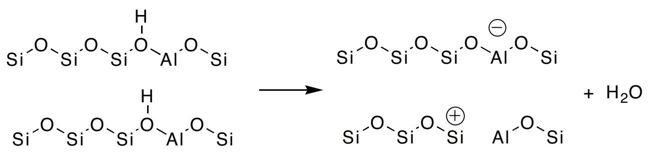
Foster, A.; **Lobo, R.F.**; "Identifying Reaction Intermediates and Catalytic Active Sites through in-situ Characterization Techniques", *Chem. Soc. Revs.,* **2010**, *39*, 4783.

REDOX SITES IN ACID ZEOLITES

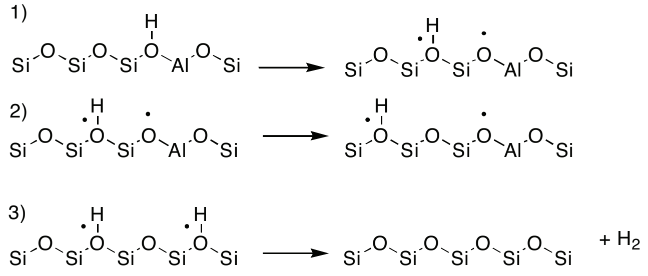
Faculty: Raul Lobo (Chemical Engineering)
Graduate Students: Jan Ho Yun (Chemical Engineering)
Funding: National Science Foundation

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 aluminumcontent. However, in zeolites with low aluminum content,the Brønsted acid sites are isolated from each 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.



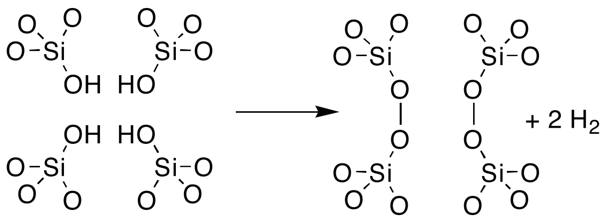
Scheme 1: Dehydroxylation via heterolytic decomposition of Brønsted acid sites

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 $[AlO_4/h]_0$ 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 Brønsted 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, 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. [2]



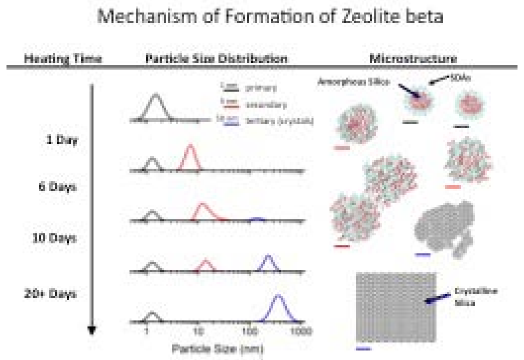
Scheme 3: Proposed homolytic decomposition of Brønsted acid

GROWTH MEC HANISMS OF ZEOLITE CATALYSTS

Faculty: Raul Lobo (Chemical Engineering)
Graduate Student: Nathan Hould (Chemical Engineering)
Funding: National Institute of Standards and Technology

High-silica zeolites are a prototypical example of materials that self-assemble from mixtures of inorganic and organic moieties. This complex mixture evolves from an 'amorphous gel' into a highly organized hybrid crystalline material, where an inorganic host framework surrounds an organic guest or structure-directing agent. Much effort has been devoted to understanding the nucleation and growth mechanisms of these materials and in particular a model system—the so-called clear gel synthesis of silicalite (siliceous ZSM-5) using tetrapropylammonium hydroxide (TPA OH) as structure director—has been closely examined. The most general finding has been that before the observation of any crystals, the silica-TPAOH-water mixture rapidly microsegregates forming two metastable phases: a *continuous* water-rich phase containing most of the water, a fraction of the TPAOH and a small amount of silica, and a *discontinuous* silica-rich phase that is observed in the form of nanoparticles of ~3-5 nm. The nanoparticles' role before and during crystal growth remains unclear.

We have recently investigated the synthesis of zeolite beta, another important industrial zeolite catalyst that can be prepared through nanoparticle precursors as zeolite ZSM-5. Compared to ZSM-5, zeolite beta is prepared using tetraethylammonium as the structure director and the synthesis gel must contain some aluminum in addition to silicon for successful zeolite beta formation. We also find that initially silica nanoparticles (~5 nm) form spontaneously at room temperature, but upon heating, these primary nanoparticles aggregate into secondary nanoparticles (20-30 nm in diameter). After six days, these secondary nanoparticles start to form tertiary nanoparticles (300 nm) that have the structure of zeolite beta (by XRD). The tertiary particles separated early from solution are clearly formed from subunits that are identical in size to the secondary particles. These subunits have also the structure of zeolite beta. It seems that zeolite beta initially forms by the selective aggregation of the secondary particles that have changed over time into zeolite beta. These studies show that the population of secondary particles consists of units that change structurally over time at different rates. As they change structurally, colloidal interparticle forces also change and the small fraction of secondary particles that eventually form the crystals of zeolite beta aggregate selectively forming the observed tertiary particle population. Aluminum is essential for particle aggregation, and without it, the secondary particles do not progress to form the structure of zeolite beta.

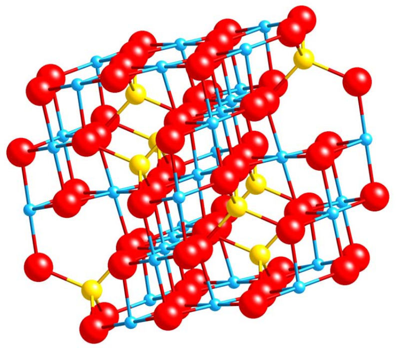


This schematic illustrates our main findings. Zeolite beta is formed by aggregation of secondary particles upon restructuring into the zeolite beta crystal form from an initially amorphous primary nanoparticle. See Hould and Lobo, Langmuir, 2010 for more details.

NOVEL PHOTOCATALYTIC MATERIALS

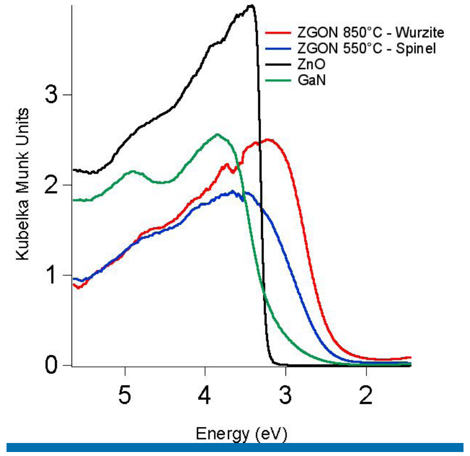
Faculty: Raul Lobo (Chemical Engineering)
Graduate Students: Bharat Boppana (Chemical Engineering), Heather Schmidt (Chemistry)
Funding: U.S. Department of Energy, Basic Energy Sciences

We are synthesizing new photocatalytic materials for the partial and total oxidation of volatile organic compounds using oxygen at low temperatures. Our aim is to develop materials that can use effectively a portion of the visible light of the electromagnetic radiation spectrum to induce electron-hole pair formation. Our approach starts with metal oxide wide bandgap semiconductors (such as TiO_2 or ZnO) and engineers the bandgap by the incorporation of metals of higher oxidation state *and* nitrogen into the solid structure. For instance, starting with ZnO, Ga_{III} and N_{3-} can be isomorphously substituted for ZnO. The effect of such substitution is to increase the energy level of the valence band without much change in the position of the conduction band. The overall effect is to decrease the *effective* bandgap facilitating the formation of electron-hole pairs using visible light.



Spinel structure with metals in tetrahedral and octahedral coordination environments

Our contribution has centered on the use of novel precursor materials that increase the range of compositions (Zn/ Ga ratios) that can be prepared as oxy-nitrides. Using sol-gel techniques we have prepared Zn/Ga mixed oxide precursor materials that have led to two important discoveries. At low temperatures (less than 550°C), we have prepared a new phase of zinc-gallium oxy-nitrides with a spinel structure (see figure above). In these materials of base composition $ZnGa_2O_4$ the reaction with ammonia leads to $ZnGa_2O_{4-1.5x}N_x$ with a dramatic change in the bandgap (see figure on left). Using sol-gel precursors and higher reaction temperatures, we have been able to prepare zinc-gallium oxy-nitrides with zinc contents near 30% approaching the optimum composition that has been predicted by theory to minimize the bandgap.



UV/vis diffuse reflectance spectra of ZnO and Zn/Ga oxinitrides (Zn/Ga = 1/2) treated in ammonia atmosphere at various temperatures

To systematically improve materials properties and understand the mechanistic differences between the oxy-nitride solid solutions and the parent oxides, we are collaborating with Professor Doug Doren's group to develop theoretical descriptions of these materials. Related work on transition metal substitutions ETS-10, described separately in this report, has shown how a combination of theory and experiment can establish a guide for "engineering" more reactive, yet photostable, materials for photocatalysis. For the zinc gallium oxy-nitrides, we are using density functional theory methods to understand how composition and crystal structure affect the bandgap. These methods are also being used to understand the thermodynamics of nitrogen substitution, and how synthesis conditions can be used to control the range of compositions that are thermodynamically accessible. This theoretical work will help to direct synthesis studies toward the materials with optimal band gaps and provide a guide to the conditions needed to reach the desired targets. ❖

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EDUCATION

» Ph.D., Inorganic Chemistry – Massachusetts Institute of Technology (2007)

» B.S. *summa cum laude* with honors, New York University (2001)

RESEARCH INTERESTS

Molecular chemistry of consequence to renewable energy, multielectron redox catalysis and small molecule activation. We hold expertise in the areas of organic and inorganic synthesis, organometallic chemistry, electrochemistry, photochemistry and catalysis.

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

» 2011 - ORAU Ralph E. Powe Junior Faculty Enhancement Award

» 2007-10 - Ruth L. Kirschstein NIH Postdoctoral Fellow

» 2007 - ACS Division of Inorganic Chemistry – Young Investigator Award

RECENT PUBLICATIONS

Joel Rosenthal, Alexander B. Nepomnyashchii, Julia Kozhukh, Allen J. Bard and Stephen J. Lippard, "Synthesis, Photophysics, Electrochemistry and Electrogenerated Chemiluminescence of a Homologous set of BODIPY Appended Bipyridine Derivatives" *J. Phys. Chem. C* 2011 In Press.

Joel Rosenthal and Stephen J. Lippard, "Direct Detection of Nitroxyl in Aqueous Solution using a Tripodal Copper(II) BODIPY Complex" *J. Am. Chem. Soc.* 2010, *132*, 5536-5537.

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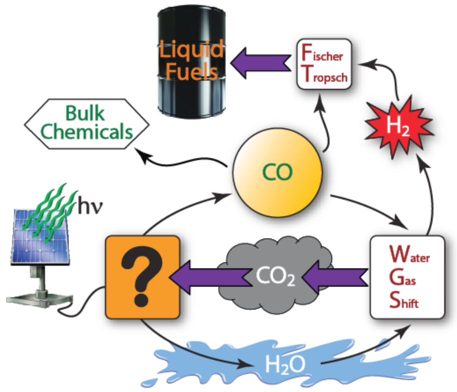
RENEWABLE CONVERSION OF CARBON DIOXIDE TO LIQUID FUELS

Faculty: Joel Rosenthal (Chemistry and Biochemistry)
Postdoc: Piyal Ariyananda
Graduate Students: John Dimeglio, Eric Guardino, Tian Qiu (Chemistry and Biochemistry)
Funding: UD Research Foundation, American Chemical Society PRF

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 CO2 is shown here.

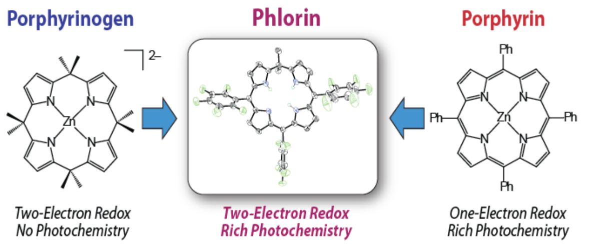


Energy conversion and CO_2 remediation

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

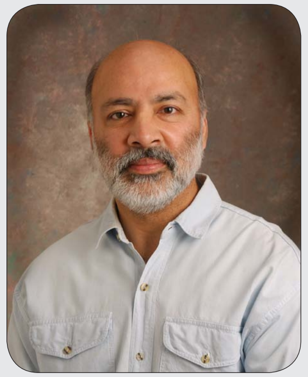
Faculty: Joel Rosenthal (Chemistry and Biochemistry)
Graduate Students: Allen Pistner (Chemistry and Biochemistry)



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 H2 from H2O 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

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- » Professor of Physics and Astronomy

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EDUCATION

- » PhD, Materials Science and Engineering - University of Illinois at Urbana-Champaign (1986)
- » BE, Metallurgical Engineering – University of Karachi, Pakistan, Bachelor of Engineering (1976)

RESEARCH INTERESTS:

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

RECENT AWARDS/ACCOMPLISHMENTS

- » 2007: Excellence in Teaching Award, UD College of Engineering
- » 2007-Present: Member Board of Directors, Society of Vacuum Coaters
- » 2003-Present: Chair, Education Committee, Society of Vacuum Coaters

RECENT PUBLICATIONS

Stabilization of surface spin glass behavior in core-shell Fe67Co33-CoFe2O4 nanoparticles, G. Hassnain Jaffari, S. Rizwan Ali, S. K. Hasanain, G Güntherodt, and, S. Ismat Shah, J. Appl. Phys. 108, 63921 (2010) doi:10.1063/1.3478738.

Defect induced ferromagnetism in carbon-doped ZnO thin films, Sadaf Akbar, S.K. Hasanain, Manzar Abbas, S. Ozcan, B. Ali, S. Ismat Shah, Solid State Comm. 17, 151 (2011) doi:10.1016/j.ssc.2010.10.035.

A new route for the synthesis of CuIn0.5Ga0.5Se2 powder for solar cell applications Emre Yassitepe, Zaki Khalifa, G. Hassnain Jaffari, Chuen-Shii Chou, Sonia Zulfiqar, Muhammad Ilyas Sarwar and Syed Ismat Shah, Powder Technology 201 (2010) 27–31

Synthesis, morphology and properties of self-assembled nanostructured aramid and polystyrene blends, S. Shabbir, S. Zulfiqar, S. Ismat Shah, Z. Sarwar, I Muhammad, J Physical Chem. B. Accepted for Publication (2010)

Hydrogen generation under visible light using nitrogen doped titania anodes, H. Lin, A. K. Rumaiz, M. Schulz, C. P. Huang, and S. Ismat Shah, J Appl. Phys. 107, 1 (2010) doi:10.1016/j.powtec.2010.02.034

Enhancement of surface spin disorder in hollow NiFe2O4 nanoparticles, G. Hassnain Jaffari, Abdullah Ceylan, C. Ni, and S. Ismat Shah, J Appl. Phys. 107, 1 (2010) doi:10.1063/1.3277041

PHOTOELECTROC HEMICAL SPLITTING OF WATER USING N:TIO$_2$ ANODE

Faculty: Ismat Shah (Physics and Materials Science)

The principle of photocatalytic reaction in colloidal systems is to oxidize the electron rich solutes (i.e. soluble organic compounds), through either a direct hole oxidation or an indirect oxidation, by hydroxyl radical generated at the valence band. In such a reaction scheme, photoexcited electrons are scavenged mainly by dissolved oxygen molecules to complete the electron transfer cycle. Clearly, this leads to a waste of photogenerated electrons.

We use such a photocatalytic system to produce hydrogen from water; hydrogen being one of the most promising sustainable energy resources. For water electrolysis in a semiconductor particulate system, the energy of the conduction band edge must be higher than the upper water stability limit $E(H^+/H_2)$ on the absolute energy scale. This, in fact, is a difficult requirement to meet in a particulate system without appropriate energy alignment between Fermi energy of soluble species and valence/conduction band edges of the semiconductor photocatalyst.

Fujishima and Honda first reported photocurrent generation using TiO_2 semiconductor electrodes in 1972. Their attempt showed the feasibility of conversion of photon energy into chemical energy (H_2) without wasting of photo-induced electron excitation in photocatalytic systems. The photoelectrochemical (PEC) system consists of a photoelectrode and a counter electrode. When electron-hole pairs are generated due to efficient photo excitation, the holes created on the anode will oxidize adsorbed OH_- and discharge the O_2 via an oxidation reaction:

$$2p_{+} + 2OH_{-} \rightarrow ½O_2 + H_2O$$

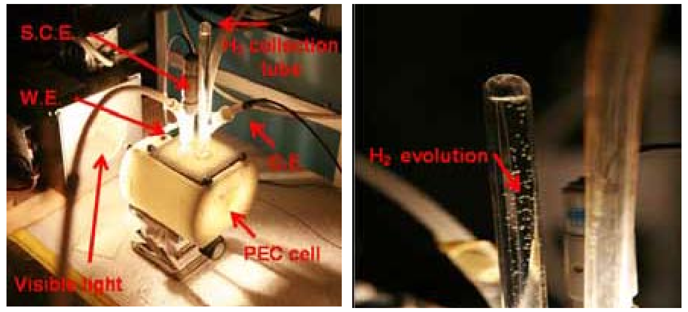
Simultaneously, the photo-excited electrons migrate to the cathode through external circuit and generate H_2 via a reduction reaction:

$$2e_{-} + 2H_2O \rightarrow H_2 + 2OH_{-} \text{ or } 2e_{-} + 2H_{+} \rightarrow H_2$$

To improve the quantum conversion efficiency in a TiO2-based PEC system, the most efficient approach is to reduce the bandgap of the semiconductor. Theoretical studies based on first-principles orthogonalized linear-combinations of atomicorbitals (OLCAO) and full-potential linearized augmented plane-wave (FLAPW) have revealed that upper valence band predominately consists of O2p states, whereas the conduction band consists mainly of Ti3d states. In principle, if energy states could be introduced within this forbidden energy band, considerable reduction in the bandgap could be obtained. Therefore, quantum efficiency is enhanced by an increase in the visible light photon absorption. The most promising method to approach this goal is to dope the impurities into TiO2 lattice. The reported substitutional doping of cation and anion of TiO2 catalysts have often been proven to improve the photocatalytic performance of TiO2. Among all dopants reported, nitrogen doped TiO2 is consistently recognized as one of the most visible light sensitive photocatalysts, both theoretically and experimentally. The density of states (DOS) calculation based on spin restricted local density approximation (LDA) from Asahi predicted that substitutionally doped TiO2-xNx creates localized N2p states just above the valence band edge. This results in a mild reduction in band gap (~0.3 eV) and red shifts the optical absorption edge around 100 nm beyond the UV light region. Asahi also showed that the interstitial and mixture of substitutional and interstitial N doped TiO2 could introduce deep N2p states within the forbidden band. Although this significantly reduces the bandgap of TiO2, it also encourages the rate of recombination and reduces the charge carrier mobility, which could be a hindering effect for photocatalysis. For the soluble organic removal in a colloidal suspension system, the oxidative power not only depends on how low the valence band edge is in absolute energy scale, but it also requires the energy of the conduction band edge to be higher than the bottom of water stability limit (O2/H2O) to promote the conduction band electron scavenging and prolonging the electron transfer kinetic. Thus, deep N2p localized states created by interstitial doping may give a detrimental effect to photocatalysis.

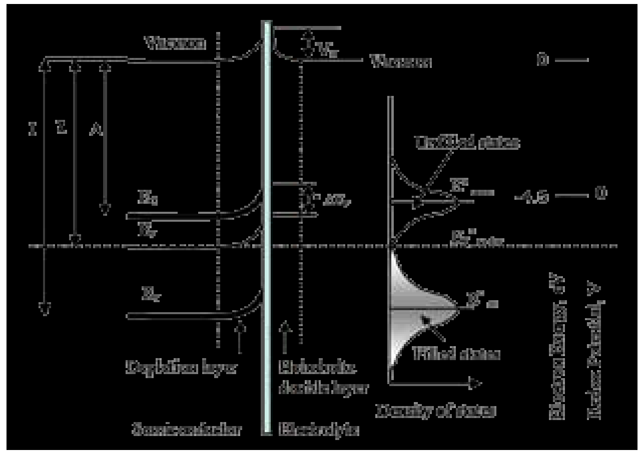
To optimize the water splitting performance in a PEC system, the semiconductor photoanode is required to have its valence band edge positioned below the lower water stability limit. Several semiconductors that meet this requirement have been reported. Among these materials, Fe2O3 has the lowest band gap (Eg = 2.3 eV). However, it is unstable in aqueous environments due to corrosion problem.

The most commonly used semiconductor oxide for the PEC application have been reported to be TiO2 and SrTiO3. Although TiO2 has lower band gap energy than that of SrTiO3, it has been reported that SrTiO3 yields one order higher quantum efficiency in photoelectrolysis comparing to TiO2 electrode without additional voltage bias condition due to the lower electron mo- bility in TiO2, which is caused by band bending.



A photoelectrochemical cell using N:TiO_2 as the anode

The characteristic energy positions [(e.g. Fermi energy E_F, conduction and valence band edges (E_C and E_V)] of a semiconductor material are most commonly expressed on the absolute vacuum energy scale (AVS). However, electrochemistry usually positions the redox couple energy of a specific element with respect to the normal hydrogen electrode (NHE). The absolute vacuum energy scale has been reported to be offset by -4.5 eV from the redox energy of a normal hydrogen electrode at 25 $_o$C. The figure below is a schematic energy diagram of an n-type semiconductor/electrolyte interface (a good example of the TiO_2/solution junction system). From the figure, we can see both valence and conduction band edges bend upward from its flat band potential due to the presence of depletion region (Schottky barrier), which in turn, gives a plausible effect if a reduction reaction is desired, but a hindering effect when oxidation reaction is wanted. The direction of electron flow in a semiconductor/liquid junction PEC system is dictated by the relative energy position between the semiconductor band edges (E_C and E_V) and the Fermi energy of the redox couple species ($E_{F\ o\ redox}$) at the solid/liquid interface. Hence, the greater difference between the Fermi energy of the redox couple and energy at valence band edge, the higher driving force for promoting oxidation process is created. Hence, using an electron rich electron donor rather than direction oxidation of water molecular is another approach to enhance the performance of PEC system.



Energy band diagram of the interface between an n-type semi-conductor surface and an electrolyte

For reduction reaction (hydrogen evolution), a catalyst with higher redox potential is normally preferred as cathode material. Platinum [$E(Pt_{2+}/Pt)$ = 1.19 V v.s. NHE] is the most commonly used material in PEC system. However, the energy difference between redox potential of cathode material and upper water stability limit (H_+/H_2) is fixed at constant pH value. Thus, the only way to enlarge the driving force for the reduction reaction (H_2 generation) is to apply a forward biased potential between the working electrode and counter electrode. By applying a forward or reversed biased potential, the magnitude of band bending and the direction of electron injection can be maneuvered, yielding a high resolution energy-band tunability. The energy alignment between redox species and band edges of semiconductor electrode can be achieved by controlling type and concentration of dopant, material of cathode and photoanode substrate, types of reactant, and direction/magnitude of bias voltage in PEC systems.

There are two main factors that affect the quantum conversion efficiency of PEC systems:

1. Band gap of the semiconductor material, which governs the amount of the photon that can be utilized through photoexcitation process. The reduction of semiconductor band gap can be done by doping of impurities that creates impurity electronic states within its intrinsic forbidden band and reduces its effective band gap.

2. Relative energy positions between the redox species and Fermi energy or band edge energy of electrodes. This dictates the direction of electron flow and determines the performance of PEC system.

We have used an N doped TiO_2 thin film anode to allow broader photon spectrum harvesting. Using this electrode, a photoelectrochemical cell is fabricated, shown in the figure above. Although the successful operation of the cell for H generation can be seen in the figure under a visible light source, the cell is currently being evaluated for its performance efficiency. ❖

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EDUCATION

» Ph.D., Organic Chemistry – Columbia University (1974)

» B.S., Chemistry – Stanford University (1970)

RESEARC H INTERESTS

Stereoselective synthesis of natural products, organometallic catalysis, computational organometallic chemistry

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

» 2011: Invite d speaker, Fifth International Symposium "The Chemistry of Aliphatic Diazo Compounds: Advances and Outlook" (St. Petersburg, Russia)

» Development of new organic reactions for biologically active natural products

» 2010: Invited speaker, 1st Annual World Congress of Catalytic Asymmetric Synthesis (Beijing)

» 2010: Invited speaker, American Chemical Society National Meeting (Boston)

» 2010: Speaker, Pacifichem (Honolulu)

RECENT PUBLICATIONS

Taber, D. F.; Nelson, C. G. Aliphatic C-H to C-C conversion: Synthesis of (-)-Cameroonan-7 -ol. J. Org. Chem. 76: 1874 (2011).

Huang, H.; Nelson, C. G.; Taber, D. F. Potassium hydride in paraffin: a useful base for Williamson ether synthesis. Tetrahedron Lett. 51: 3545-3546 (2010).

Taber, D. F.; Guo, P.; Pirnot, M. T. Conjugate addition of lithiated methyl pyridines to enones. J. Org. Chem. 75: 5737-5739 (2010).

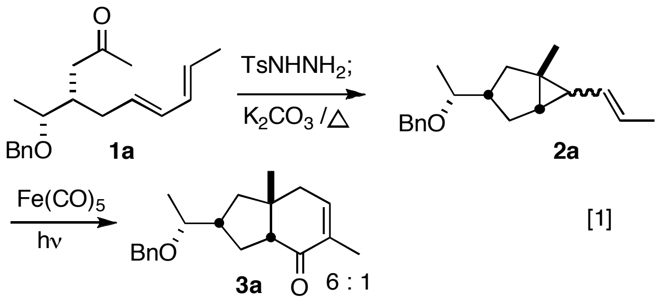
Taber, D. F.; Guo, P.; Guo, N. Intramolecular [1+4+1] cycloaddition: Establishment of the method. J. Am. Chem. Soc 132: 11179-11182 (2010).

Taber, D. F.; Straney, P. J. The Synthesis of laurolactam from cyclododecanone via a Beckmann rearrangement. J. Chem. Educ. 87: 1392, 2010.

BICYCLIC CONSTRUCTION BY NET FE-MEDIATED [1 + 4 + 1] CYCLOADDITION

Faculty: Douglass F. Taber (Chemistry and Biochemistry)
PhD Student: Pengfei Guo (Chemistry and Biochemistry)

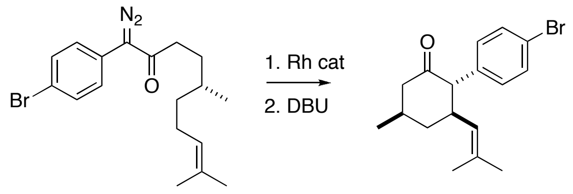
Carbocycles, as exemplified by calcitriol and taxol, can be potent drugs. Although computationally-driven lead generation often suggests potential new drug candidates that are polycarbocyclic, such candidates are usually not pursued, because of the assumption that a polycarbocyclic drug would be impractical to manufacture. We report a simple two-step route to the enantiomerically-pure carbobicyclic scaffold 3a from the acyclic ketone 1a.



CYCLOHEXANONES BY RH-CATALYZED INTRAMOLCULAR C-H INSERTION

Faculty: Douglass F. Taber (Chemistry and Biochemistry)
Postdoctoral Student: Peiming Gu (Chemistry and Biochemistry)

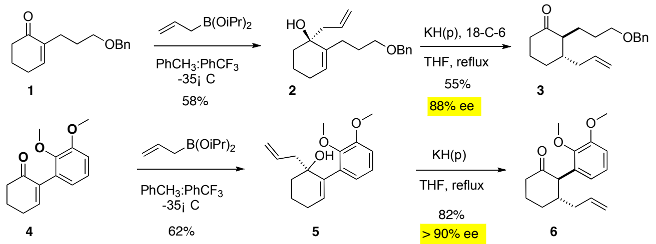
We have found that the Rh carbenes derived from α-diazo benzyl ketones are significantly more discriminating than are the Rh carbenes derived from β-ketoesters. When an electron rich C-H site is available six atoms away, cyclohexanone formation can dominate. This is in marked contrast to the cyclizations of α-diazo β-ketoesters, that consistently deliver cyclopentanone products.



ASYMMETRIC ORGANOCATALYTIC CONJUGATE ALLYLATION OF CYCLIC ENONES

Faculty: Douglass F. Taber (Chemistry and Biochemistry)
PhD Student: David Gerstenhaber (Chemistry and Biochemistry)

Several procedures have been put forward in recent years for enantioselective conjugate addition to prochiral cyclic enones. To date, however, no method has been published that is effective with an -alkyl cyclic enone such as **1** It occurred to us that enantioselective 1,2-allylation followed by KH-mediated oxy-Cope rearrangement could offer a solution to this problem. In our hands, the current most effective catalyst for the allylation is 3,3'-dibromo binol, introduced by Schaus for the enantioselective allylation of aromatic ketones. ❖



Andrew V. Teplyakov

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EDUCATION

- » PhD, Chemistry – Columbia University (1997)
- » MS, Chemistry – Columbia University (1993)
- » BS, Chemistry – Moscow State University (1992)

RESEARCH INTERESTS

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

AWARDS, HONORS, & PROFESSIONAL ACTIVITIES

- » 2010: Invited review, Chemical Society Reviews
- » 2010: Organizer of the Surface Science Session at the EAS
- » 2009: Invited speaker, Eastern Analytical Symposium, Somerset, NJ
- » 2009: Invited speaker, 56th International Symposium and Exhibition of the American Vacuum Society (San Jose, CA)
- » 2008: Research on dehydrative cyclocondensation reactions on hydrogen-terminated Si(100) and Si(111) highlighted in Chemical and Engineering News

RECENT PUBLICATIONS

Bent, S. F.; Kachian, J. S.; Rodríguez-Reyes, J. C. F. and Teplyakov, A. V. Tuning the reactivity of semiconductor surfaces by functionalization with amines of different basicity. PNAS 2011, 108(3), 956-960.

Perrine, K. A., Rodríguez-Reyes, J. C. F. and Teplyakov, A. V. Simulating the reactivity of disordered surface of the TiCN thin film. J. Phys. Chem. C, accepted, DOI: 10.1021/jp203294d.

K.A. Perrine, A.V. Teplyakov, "Reactivity of Selectively Terminated Single Crystal Silicon Surfaces," Chem. Soc. Rev., DOI: 10.1039/B822965C (2010).

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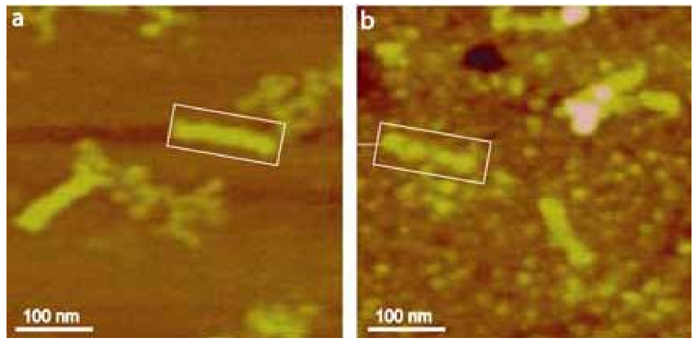
K.A. Perrine, A.V. Teplyakov, "Metallic Nanostructure Formation Limited by the Surface Hydrogen on Silicon," Langmuir, DOI: 10.1021/la100269m (2010).

COVALENTLY ATTAC HED MACROMOLECULES ON SEMICONDUCTOR SURFACES

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)
Collaborators: Junghuey Chen, Thomas P. Beebe Jr. (Chemistry and Biochemistry), Sylvain Cloutier (Electrical and Computer Engineering)
Graduate Students: Yue Liu, Xiaochun Zhang, Timothy Miller, Fangyuan Tian (Chemistry & Biochemistry)
Funding: NSF

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 in 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

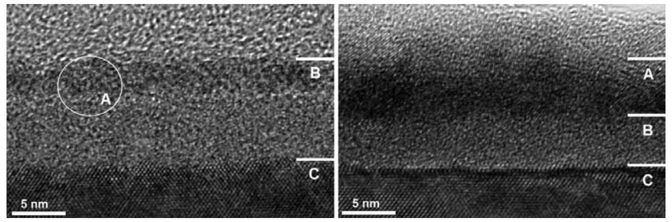
Faculty: Andrew Teplyakov (Chemistry & Biochemistry)
Collaborators: Robert Opila (Materials Science & Engineering), George Flynn (Chemistry, Columbia University)
Graduate Students: Fangyuan Tian, Jia-Ming Lin, Sam Kung (Chemistry & Biochemistry)
Funding: NSF, ACS-PRF

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]

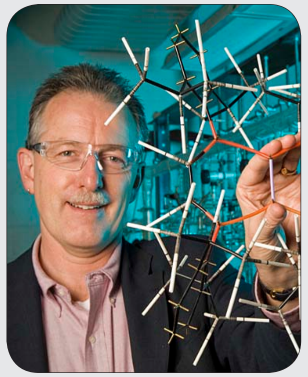
THIN SOLID FILMS FOR MICROELECTRONICS

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)
Collaborators: Robert Opila (Materials Science & Engineering), Chaoying Ni (Chemical Engineering), Thomas P. Beebe Jr. (Chemisty & Biochemistry), Steven Brown (Chemistry & Biochemistry), Brian Willis (Chemical Engineering, University of Connectiut)
Graduate Students: Jia-Ming Lin, Jia Gao (Chemistry & Biochemistry)
Funding: NSF

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) NH3 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

- Professor and Chair of Chemistry and Biochemistry
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EDUCATION

- Ph.D., Inorganic Chemistry – University of California, Berkeley (1982)
- Vordiplom, Chemistry Universität Hamburg (1977)

RESEARCH INTERESTS

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

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

- 2007-present: Chair, Department of Chemistry and Biochemistry
- 2004: JSPS Invitation Fellowship, Japan Society for the Promotion of Science

RECENT PUBLICATIONS

F.A. Jové, C. Pariya, M. Scoblete, G.P.A. Yap, K.H. Theopold, "A Family of Four-Coordinate Iron(II) Complexes Bearing the Sterically Hindered Tris(pyrazolyl)borato Ligand [TptBu,Me]," Chem. Eur. J. (In press).

J.F. Young, L.A. MacAdams, G.P.A. Yap, K.H. Theopold, "The Synthesis, Characterization, and Alkylation of Nacnac Chromium Triflate Derivatives," Inorg. Chim. Acta (In press).

W.H. Monillas, T.C. Bazzzoli, G.P.A Yap, K.H. Theopold, "Synthesis and Structure of bis(β-Diketiminate) Chromium(II) Complexes," J. Chem. Crystallogr., 40, 67 (2010).

A. Gunay, K.H. Theopold, "C-H Bond Activations by Metal Oxo Complexes," Chem. Rev., 110, 1060 (2010).

C. Puttnual, L.A. MacAdams, K.H. Theopold, "β-Diketiminate Supported Vanadium and Chromium Chloride Complexes," Inorg. Synth., 35, 30 (2010).

SMALL MOLECULE ACTIVATION WITH STERICALLY HINDERED TRIS (PYRAZOLYL)BORATE METAL COMPLEXES

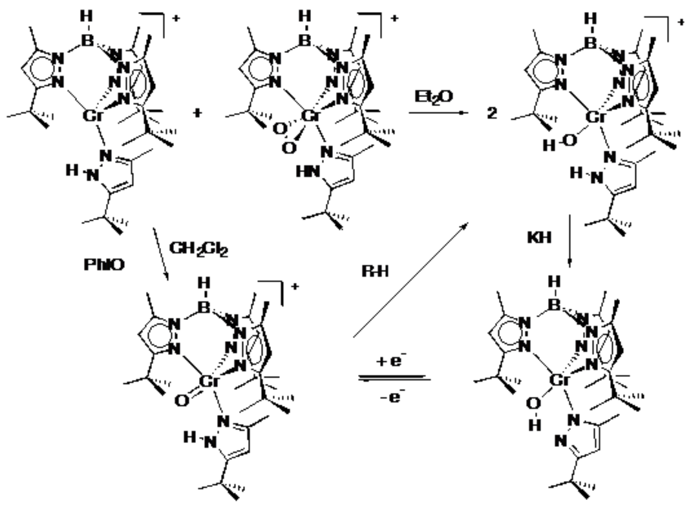
Faculty: Klaus Theopold (Chemistry & Biochemistry)
Postdoc: Ahmet Gunay (Chemistry & Biochemistry)
Graduate Students: Eric Sirianni, Fang Dai (Chemistry & Biochemistry)
Funding: U.S. Department of Energy

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.



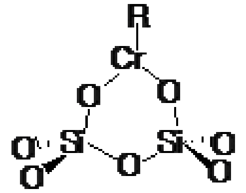
Cobalt Imido Complexes: Our investigation of cobalt dioxygen chemistry has yielded evidence for the intermediacy of the terminal cobalt oxo species Tp$_{\mathrm{tBu.\,Me}}$Co=O in several reactions; however, this compound is apparently too reactive for even spectroscopic detection. We have thus pursued the chemistry of isoelectronic imido complexes, Tp$_{\mathrm{tBu.Me}}$Co=NR, as chemical models. For example, reaction of Tp$_{\mathrm{tBu.Me}}$Co(N$_2$) with Me$_3$SiN$_3$ yielded a cobalt(III) amido species resulting from hydrogen atom abstraction from the ligand by the inferred imido complex Tp$_{\mathrm{tBu.Me}}$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.

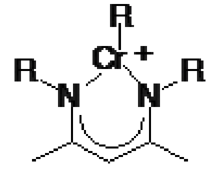
HOMOGENEOUS MODELS FOR CHROMIUM POLYMERIZATION CATALYSTS

Faculty: Klaus Theopold (Chemistry & Biochemistry)
Graduate Students: John Young, Jingmei Shen (Chemistry & Biochemistry)
Funding: NSF

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.

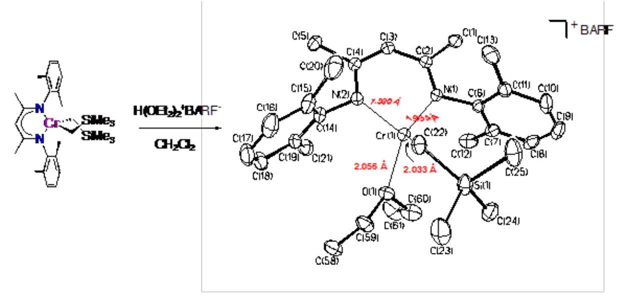


A



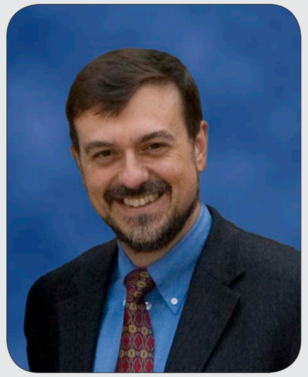
B

We have prepared a series of neutral and cationic chromium alkyls supported by (Ar)$_2$nacnac ligands (Ar=Ph, 2,6-Me$_2$Ph, 2,6-$_i$Pr$_2$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)$_2$nacnacCr(R)(OEt$_2$)]$_+$BARF (Ar=2,6-Me$_2$Ph, 2,6-$_i$Pr$_2$Ph; R=Me, CH$_2$SiMe$_3$) 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-$_i$Pr$_2$Ph)$_2$nacanac Cr(OEt$_2$)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

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- Director, Center for Catalytic Science & Technology
- Elizabeth Inez Kelley Professor of Chemical Engineering

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EDUCATION

- Ph.D., Chemical Engineering and Materials Science – University of Minnesota (1992)
- M.S., Chemical Engineering and Materials Science – University of Minnesota (1990)
- B.S., Chemical Engineering – National Technical University of Athens (1987)

RESEARCH INTERESTS

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

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

- 2011 AIChE R.H. Wilhelm Award in Chemical Reaction Engineering
- 2009: Fellow of the American Association for the Advancement of Science
- 2009: Top 100 Engineers, International Biographical Centre
- 2009: Elizabeth Inez Kelley Professorship of Chemical Engineering, University of Delaware
- 2007: George Piercy Distinguished Visiting Professor, Chemical Engineering & Materials Science Dept., University of Minnesota

RECENT PUBLICATIONS

K. Bijjula and D. G. Vlachos, Catalytic ignition and autothermal combustion of JP-8 over a Pt/γ-Al2O3 catalyst, Proc. Comb. Inst. 33, 1801–1807 (2011).

M. Salciccioli, Y. Chen, and D. G. Vlachos, Microkinetic modeling and reduced rate expressions of ethylene hydrogenation and ethane hydrogenolysis on platinum, Ind. Eng. Chem. Res. 50, 28–40 (2011).

M. S. Mettler, G. D. Stefanidis and D. G. Vlachos, Enhancing stability in parallel plate microreactor stacks for syngas production, Chem. Eng. Sci. 66, 1051–1059 (2011).

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W. Hauptmann, M. Votsmeier, H. Vogel, and D. G. Vlachos, Modeling the simultaneous oxidation of CO and H2 on Pt - Promoting effect of H2 on the CO-light-off, Appl. Cat. A: General 397, 174–182 (2011).

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Z. Ulissi, V. Prasad, and D. G. Vlachos, Effect of multiscale model uncertainty on identification of optimal catalyst properties, J. Catal., Accepted (2011).

D. G. Vlachos and S. Caratzoulas, The roles of catalysis and reaction engineering in overcoming the energy and the environment crisis, Chem. Eng. Sci. 65, 18–29(2010), Invited as plenary lecture.

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V. Papavassiliou, P. Pacouloute, K. T. Wu, R. Drnevich, D. Vlachos, J. Hemmings, and L. Bonnel, Catalytic Partial Oxidation Pilot Plant Study, Ind. Eng. Chem. Res. 49(1), 94–103 (2010).

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W. W. Lonergan, D. G. Vlachos, and J. G. Chen, Correlating extent of Pt–Ni bond formation with low-temperature hydrogenation of benzene and 1,3-butadiene over supported Pt/Ni bimetallic catalysts, J. Catal. 271(2), 239-250 (2010).

G. Mpourmpakis, A. N. Andriotis, and D. G. Vlachos, Identification of Descriptors for the CO Interaction with Metal Nanoparticles, NanoLetters 10, 1041-1045 (2010).

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M. Salciccioli, Y. Chen, and D. G. Vlachos, DFT derived group additivity and linear scaling methods for prediction of oxygenate stability on metal catalysts: Adsorption of open-ring alcohol and polyol dehydrogenation intermediates on Pt based metals, J. Phys. Chem. C 114, 20155–20166 (2010).

H. Y. Wang, M. Stamatakis, D. A. Hansgen, S. Caratzoulas, and D. G. Vlachos, Understanding mixing of Ni and Pt in the Ni/Pt(111) bimetallic catalyst via molecular simulation and experiments, J. Chem. Phys. 133, 224503 pg. 1-11 (2010).

K. Radhakrishnan, A. Halasz, D. G. Vlachos, and J. S. Edwards, Quantitative understanding of cell signaling: The importance of membrane organization, Curr. Opinion Biotech. 21(5), 677-682 (2010).

PREDICTIVE, HIERARCHICAL MULTISCALE MICROKINETIC MODELING

Faculty: Dion Vlachos (Chemical Engineering),
Postdocs: Ying Chen, N. Peela (Chemical Engineering)
Graduate Students: D. Hansgen, M. Salciccioli, J. Sutton, S. Edie, M. Christiansen, J. Weiner, S. Tacchino (Chemical Engineering)

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.

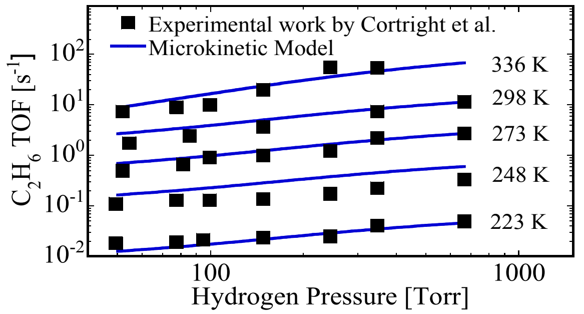

Figure 1. Comparison of experimental data (points) and simulations using our newly developed full microkinetic model (lines) for ethylene hydrogenation and ethane hydrogenolysis on Pt-based catalysts.

FIRST-PRINCIPLE-BASED SEMI-EMPIRICAL METHODS FOR THERMOCHEMISTRY AND KINETICS

Faculty: Dion Vlachos (Chemical Engineering),
Postdocs: Ying Chen (Chemical Engineering)
Graduate Students: Michael Salciccioli, J. Sutton, S. Edie (Chemical Engineering)

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.

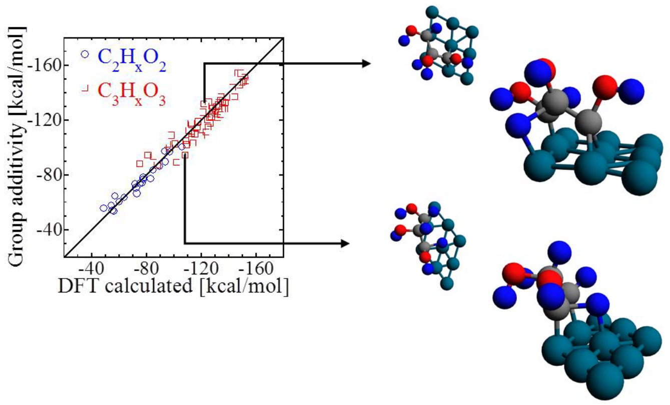

Figure 2. Parity graph comparing first-principle density functional theory (DFT) calculations to first-principle-based semi-empirical, excel-based group additivity values along with snapshots of structures of oxygenated species on Pt manifesting the multi-dentate nature of binding of these adsorbates.

COMPUTATIONAL-DRIVEN DESIGN OF CATALYSTS

Faculty: Dion Vlachos, J.G. Chen (Chemical Engineering),
Graduate Students: D. Hansgen, M. Salciccioli, J. Sutton (Chemical Engineering)

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.

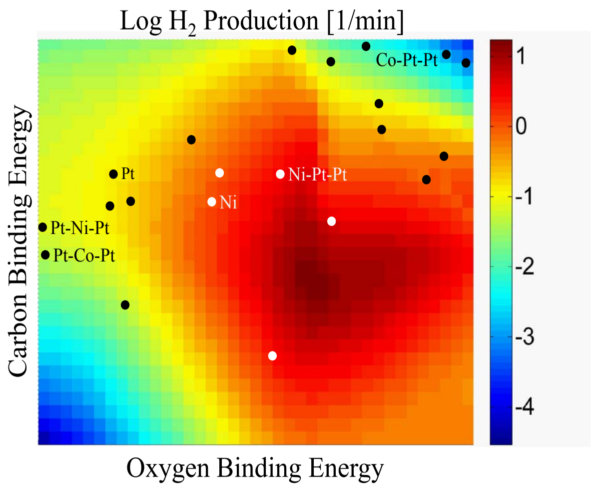

Figure 3 Example of predicted volcano mountain projected to two-dimensions for identification of optimal catalysts for reforming of biomass vs. element heats of adsorption. The labeled points indicate the performance of known catalysts and the unlabeled ones indicate predicted materials under testing.

BIOMASS PROCESSING

Faculty: Dion Vlachos (Chemical Engineering)
UD co-PIs: J. G. Chen, V. Nikolakis, S. Caratzoulas, W. Deng, S. Sandler, R. Lobo (Chemical Engineering), D. Doren (Chemistry and Biochemistry)
UMass co-PIs: P. Dauenhauer, G. Huber (Chemical Engineering)
Postdocs: Y. Chen, S. Mushrif, Y. Huang (Chemical Engineering)
Graduate Students: M. Mettler, S. Tupy, V. Choudhary, V. Vorotnikov, T. Courtney, N. Nikbin, D. Swift (Chemical Engineering)

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. ❖

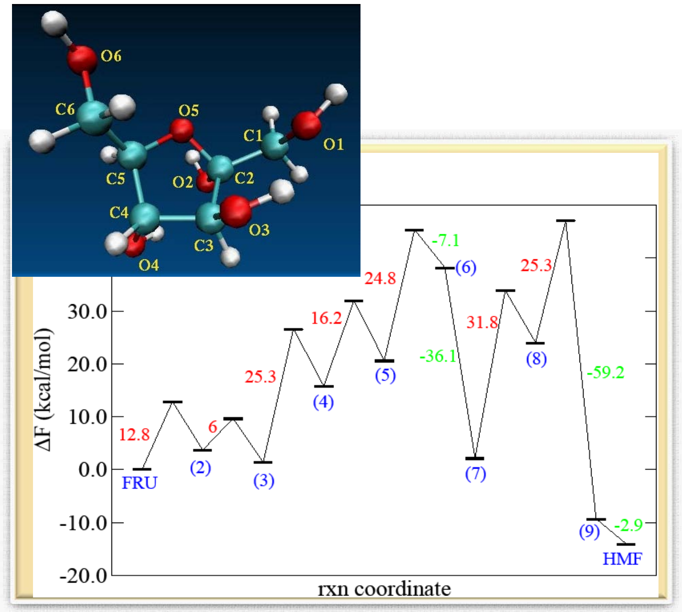

Figure 4. Free energy of the elementary steps of fructose dehydration to HMF predicted using quantum mechanics/molecular mechanics molecular dynamics simulations. Schematic shows a ball and stick view of fructose.

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EDUCATION

- » B.S., 1998, University of California, San Diego
- » PhD, 2004, University of California, Irvine

RESEARCH INTERESTS

Transition-metal catalysis; organic synthesis; alternative energy chemistry

HONORS, AWARDS & PROFESSIONAL ACTIVITIES

- » 2009 Faculty Appointment University of Delaware
- » 2004 Ruth L. Kirschstein National Research Service Award
- » 2003 University of California Regents Dissertation Fellowship, UCI
- » 2001 Pharmacia Graduate Research Fellowship

RECENT PUBLICATIONS

Watson, D. A. *Selected Diastereoselective Reactions: Heck Type Cyclizations.* In *Comprehensive Chirality*; Carreira, E. and Yamamoto, H., Eds.; Elsevier, New York, *in press*.

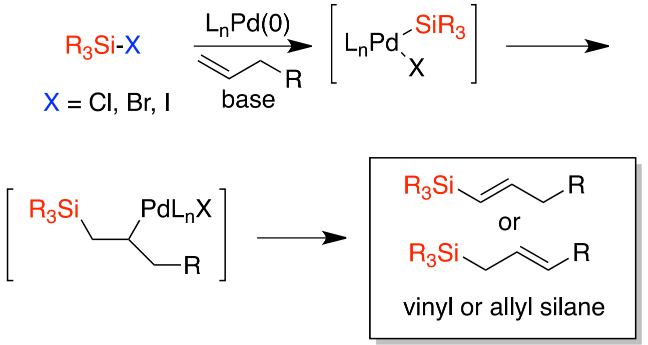
Shen, X.; Jones, G. O.; Watson, D. A.; Bhayana, B.; Buchwald, S. L. "Enantioselective Synthesis of Axially Chiral Biaryls by the Pd-Catalyzed Suzuki-Miyaura Reaction: Substrate Scope and Quantum Mechanical Investigations" *J. Am. Chem. Soc.*, **2010**, *132*, 11278-11287.

Cho, E. J.; Senecal, T. D.; Kinzel, T.; Zhang, Y.; Watson, D. A.; Buchwald, S. L. "The Palladium-Catalyzed Trifluoromethylation of Aryl Chlorides" *Science* **2010**, 328 (5986) 1679-1681.

Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; Garcia-Fortanet, J.; Kinzel, T.; Buchwald, S. L. "Formation of ArF from LPdAr(F): Catalytic Conversion of Aryl Triflates to Aryl Fluorides" *Science* **2009**, 325 (5948) 1661-1664.

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.

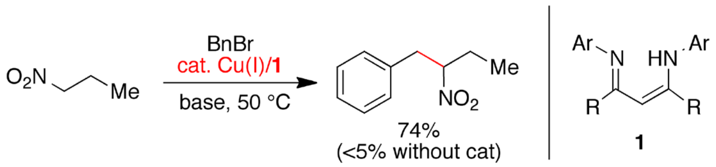
In the first project, we have begun to investigate the possibility of efficient silyl-Heck reactions. Many reactions are now known that employ the oxidative addition of a carbon-halide bond to a low-valent metal, most commonly palladium. Notable examples include the Heck, Suzuki, and Buchwald-Hartwig 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.

FACULTY & STUDENT HIGHLIGHTS 2011

DION VLACHOS IS APPOINTED EXECUTIVE EDITOR OF CHEMICAL ENGINEERING SCIENCE

Effective August 1, 2011, Dion Vlachos has been appointed executive editor of Chemical Engineering Science for Reaction Engineering, Catalysis and Materials Processing. The journal publishes papers on the fundamentals of chemical engineering, including applications of biology, chemistry, and physics.

CCST FACULTY, KLEIN, SELECTED ACS FELLOW

Michael T. Klein from the University of Delaware College of Engineering, has been selected as 2011 American Chemical Society (ACS) Fellow.

ACS is the world's largest scientific society. The fellows program, established in 2008, recognizes members "for outstanding achievements in and contributions to science, the profession and the society." More than 350 ACS members from academe, industry and government have been distinguished with this honor.

Michael T. Klein, director of the UD Energy Institute, Dan Rich Chair in Energy and professor of chemical engineering, is an expert in chemical reaction engineering, with a special emphasis on the kinetics of complex systems.

CCST FACULTY: JIAO AND ROSENTHAL, RECEIVE UDRF GRANTS

Electrocatalytic Reduction of Carbon Dioxide to Chemical Fuels. Concerns over greenhouse gas emissions and climate change are propelling research forward on renewable energy. Joel Rosenthal, assistant professor of chemistry and biochemistry, will explore the development of nickel and palladium electrocatalysts that will freely give away electrons when they react with carbon dioxide, thus chemically reducing the greenhouse gas into energy-rich carbon monoxide or methanol fuels.

Novel Nanoporous Cathode Material for Lithium-ion Batteries. Feng Jiao, an assistant professor of chemical engineering, is working to develop novel cathode materials to boost the energy storage of lithium-ion batteries, which are used in items ranging from laptops to electric cars. He is exploring a new synthetic method, ionothermal synthesis, for preparing lithium manganese phosphates with 3D nanoporous structures. The material's porosity would enable the removal and re-insertion of lithium ions from/into the 3D channels at high current density

DION VLACHOS WINS 2011 AMERICAN INSTITUTE OF CHEMICAL ENGINEERING'S R.H. WILHELM AWARD

Dion Vlachos, director of the Catalysis Center for Energy Innovation and Elizabeth Inez Kelley Professor of Chemical Engineering at UD, has won the 2011 American Institute of Chemical Engineering's (AIChE) R.H. Wilhelm Award in chemical reaction engineering. Sponsored by ExxonMobil Research and Engineering Company, the honor recognizes Vlachos' pioneering work on multiscale modeling and application to development, design and interpretation of catalytic reaction mechanisms, rational materials design and renewable energy. Vlachos will receive the award at the AIChE annual meeting in October.

FORMER CCST PROFESSOR, RICHARD HECK, RECEIVES NOBEL PRIZE

Richard F. Heck, the Willis F. Harrington Professor Emeritus at the University of Delaware, has been awarded the Nobel Prize in Chemistry. Heck, 79, was honored alongside fellow researchers Akira Suzuki, 80, of Hokkaido University in Sapporo, Japan, and Ei-Ichi Negishi, 75, of Purdue University, "for palladium-catalyzed cross couplings in organic synthesis." They will share a $1.5 million award.

The Nobel Prize in Chemistry was announced by the Royal Swedish Academy of Sciences during a press conference held this morning in Stockholm. The Nobel laureates are scheduled to present their lectures December 8, 2010.

According to the Nobel statement, the scientists were honored for discovering "more efficient ways of linking carbon atoms together to build the complex molecules that are improving our everyday lives."

"This is a tremendous accomplishment for Prof. Heck and his colleagues, acknowledging the development of a tremendously sophisticated tool that will aid scientists to make potential cancer drugs and medicines," UD Provost Tom Apple said.

Douglas Taber, professor in the Department of Chemistry and Biochemistry who has known Heck as a colleague since 1982, explained the importance of his work, saying, "All of pharmaceutical chemistry and photolithography, the making of computer chips, depends on carbon bond formation. His [Heck's] contribution was to make that bond catalytic in the expensive metal, making large-scale industrial production affordable. When DNA sequencing became important, Heck chemistry made the coupling of organic dyes to the DNA bases possible."

MICHAEL SALCICCIOLI RECEIVES 2011 KOKES AWARD FOR THE 22ND NORTH AMERICAN CATALYSIS SOCIETY (NACS) MEETING

Grad student Michael Salciccioli is a recipient of the 2011 Kokes Award for the 22nd North American Catalysis Society (NACS) meeting in Detroit, MI, in June 2011.

The Richard J. Kokes Travel Award program of NACS aims to encourage undergraduate and graduate students to attend and participate in this biennial conference. It provides funding for the conference registration fee, hotel accommodations, and a travel allowance.

This award is sponsored by the North American Catalysis Society and the local Michigan Catalysis Society.

PROFESSOR JINGGUANG CHEN, CLAIRE D. LECLAIRE PROFESSOR, RECEIVES 2011 HERMAN PINES AWARD IN CATALYSIS

Jingguang Chen, Claire D. LeClaire Professor of Chemical Engineering at the University of Delaware, is a world leader in surface science studies of carbide and bimetallic catalysts.

Catalysts increase the rate of chemical reactions. Bimetallic catalysts are formed by combining atoms of two metals. The result is a unique metal with physical, chemical and electronic properties unlike either parent metal.

Chen's work has shortened long standing materials and pressure gaps critical in converting fundamental science to industrial practice using a unique combination of surface science, theoretical modeling, catalysis and in-situ reactor studies, leading to the development of novel concepts and catalytic materials for a wide range of chemical reactions.

In particular, his research group revolutionized understanding and design of bimetallic and carbide surfaces and their applications to technologies ranging from catalysts to fuel cells.

On May 19, Chen will receive the 2011 Herman Pines Award in Catalysis at the 2011 Catalysis Club of Chicago Spring Symposium in Naperville,Ill. Given annually, the award recognizes an individual with significant contributions to catalysis in either fundamental research or industrial processes.

DOUGLASS F. TABER, PROFESSOR OF CHEMISTRY AND BIOCHEMISTRY, CHOSEN AS THE 2011 ALLAN R. DAY AWARD RECIPIENT

Douglass F. Taber, professor of chemistry and biochemistry at the University of Delaware, has been chosen as the 2011 recipient of the Allan R. Day Award from the Philadelphia Organic Chemists' Club.

Taber will be presented the award at the club's Oct. 27 meeting, when he will also deliver a research seminar to the audience. The award recognizes his contributions to the development of new methods for organic synthesis and the application of those methods in the total synthesis of

Taber earned his doctorate in organic chemistry at Columbia University and has been a member of the UD faculty since 1982.

The award is given in memory of Allan R. Day, who taught chemistry at the University of Pennsylvania for more than 40 years, becoming professor emeritus in 1968.

CCST STUDENT RECEIVES EASTMAN CHEMICAL AWARD

Congratulations to Mike Salciccioli who has been selected as the recipient of the 2011 Eastman Chemical Award. Mike is in his 4th year working with Dr. Dion Vlachos. The presentation of the award will take place during our annual symposium on October 6, 2011 at Clayton Hall.

CCST RESEARCHERS PUBLISH FINDINGS IN NATURE CHEMISTRY

A team of chemical engineering researchers at the University of Delaware has developed a computational framework for screening potential bimetallic catalysts. The finding was published online in Nature Chemistry on April 25.

The paper, "Using First Principles to Predict Bimetallic Catalysts for the Ammonia Decomposition Reaction," was authored by Danielle Hansgen, a fourth-year doctoral candidate, and her advisers, Dion Vlachos, Elizabeth Inez Kelley Professor, and Jingguang Chen, Claire D. LeClaire Professor.

Chen explains that the decomposition reaction is critical to the use of ammonia as a hydrogen storage medium for applications such as fuel cells that require an extremely pure form of hydrogen. Ruthenium has proven to be an effective catalyst for breaking ammonia down into its constituents, nitrogen and hydrogen, but as a rare metal, it is scarce and expensive.

"Ruthenium is the best single element for this reaction," Chen says, "but since it's not a viable option for large-scale commercialization, we began to look at combinations of two metals that are more abundant to see if we could achieve similar results."

To narrow the pairs of metals for consideration, the researchers first examined the characteristics that make ruthenium so effective. They developed a chemical descriptor of the bond -- it had to be strong enough to decompose ammonium but weak enough to allow for complete catalysis and leave a clean surface -- and then validated that descriptor using an appropriate bimetallic catalyst.

That pair -- nickel and platinum -- proved to be an effective "guinea pig" for the experimental work, but it is still too expensive for broad use. However, with the descriptor validated, the researchers now have a framework for examining other bimetallic catalysts that use more plentiful elements.

Vlachos points out that the same principles could be applied to search for cheaper catalysts for other reactions, including the selective oxidation of carbon monoxide for hydrogen purification and hydrogenation of hydrocarbons.

Both faculty members give full credit for the work to Hansgen, with Vlachos providing support on the computational and Chen on the experimental side.

The research was carried out under UD's Center for Catalytic Science and Technology. ---Article by Diane Kukich

CCST STUDENT RECEIVES EASTMAN CHEMICAL AWARD

Congratulations to Danielle Hansgen who received the 2010 Eastman Chemical Award in October 2010 during the CCST Review. Danielle has since completed her doctoral degree (with Dr. Jingguang Chen and Dr. Dionisios Vlachos) and is now working at INTEL.

Congratulations as well to the winner of the 2011 Eastman Chemical Award, Michael Salciccioli for his work on development of microkinetic models of biomass processing. The presentation of the award will take place during our annual symposium on October 6, 2011 at Clayton Hall. Michael is advised by Professor Dionisios Vlachos.

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CCST's advisory board provides feedback on past accomplishments and suggestions on future research directions. We extend our sincere appreciation to our industrial board members for their time and help in this important endeavor.

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- » **Dr. Mark A. Barteau** – UD Department of Chemical Engineering
- » **Dr. Jingguang G. Chen** – UD Department of Chemical Engineering
- » **Dr. Wu-Cheng Cheng** – W.R. Grace & Co.
- » **Dr. Douglas J. Doren** – UD Department of Chemistry and Biochemistry
- » **Dr. Raul F. Lobo** – UD Department of Chemical Engineering
- » **Dr. Friedbert Nees** – BASF
- » **Dr. Carmo J. Pereira** – E. I. du Pont de Nemours and Co., Inc.
- » **Dr. Guy Steinmetz** – Eastman Chemical Company
- » **Dr. José Santiesteban** – ExxonMobil Research and Engineering Company
- » **Dr. Pavol Pranda** – Air Liquide
- » **Dr. Lesia Protsailo** – UTC Power
- » **Dr. Klaus H. Theopold** – UD Department of Chemistry and Biochemistry
- » **Dr. Daniel Trauth** – The Dow Chemical Company
- » **Dr. Dionisios G. Vlachos** – UD Department of Chemical Engineering

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