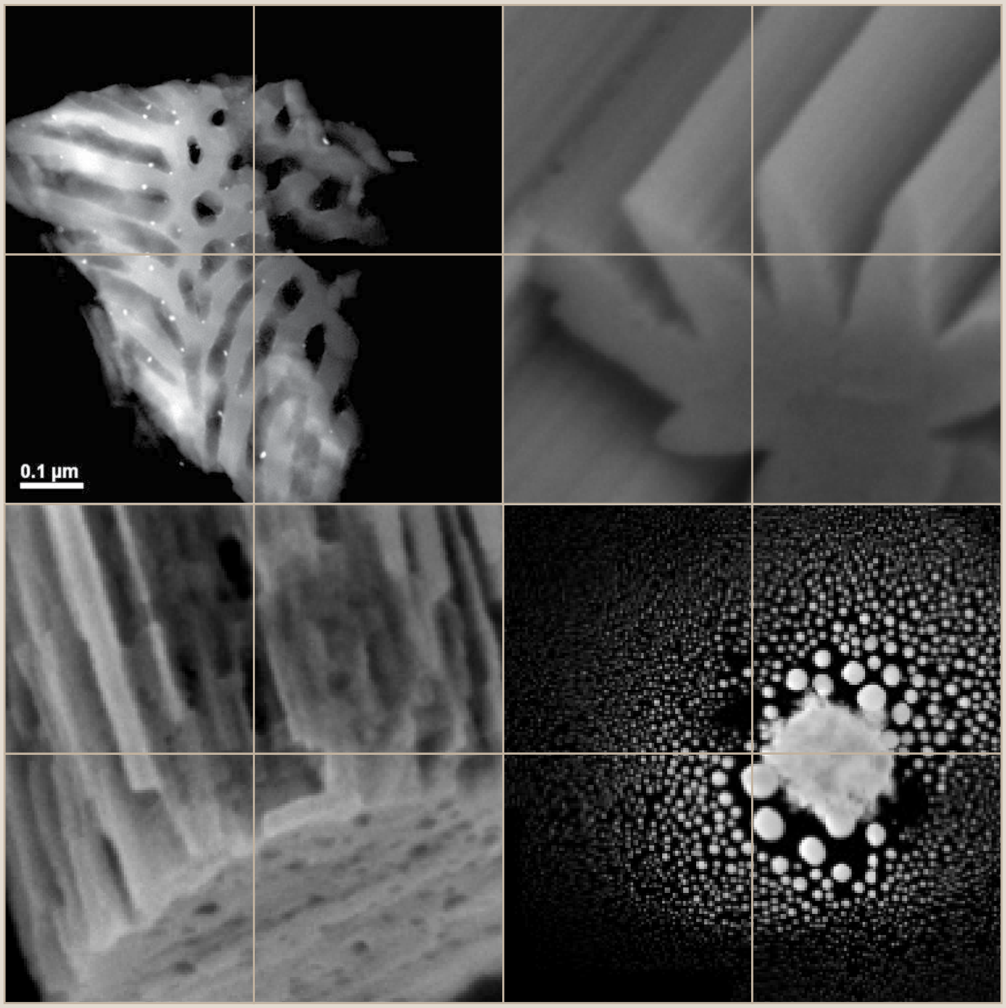
MULTIDISCIPLINARY PROGRAMS • CUTTING-EDGE RESEARCH

UNIVERSITY OF DELAWARE



Center for Catalytic Science and Technology

2010 Research Report

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

Dionisios G. Vlachos, Director
Center for Catalytic Science & Technology
University of Delaware
150 Academy Street
Newark, DE 19716-3119

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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

The Center for Catalytic Science and Technology (CCST) is one of the leading academic catalysis centers worldwide, and the quality and productivity of our research efforts continue to strengthen the center's tradition of excellence. Our successes during the past year are manifested in the number of federal and industrial grants, including the newly founded Catalysis Center for Energy Innovation (CCEI) by the Department of Energy (DOE), the number of publications and papers in high profile journals, the placement of alumni in academic and industrial positions and, as outlined on the home page of our Web site under "What's New in CCST," the awards won by our students and faculty.

CCST's strong institutional consortium continues to be a vital part of our center. We are grateful to the Eastman Chemical Company for sponsoring our 2010 Spring Seminar Series, an enriching series that featured distinguished seminar speakers who gave enlightening presentations. We webcast some of the seminars to members of our industrial consortium, and we plan further webcasting in the future to make additional seminars and Ph.D. theses defenses available.

We are pleased to welcome four new faculty members to CCST: **Michael Klein**, a University of Delaware (UD) alumnus and former faculty member, rejoins CCST as a professor in UD's Department of Chemical Engineering. Named the Dan Rich Chair of Energy, Mike is also director of

ASSOCIATE DIRECTOR

Mark A. Barteau
Chemical Engineering

EDUCATION
Ph.D., Stanford Univ.
M.S., Stanford Univ.
B.S., Washington Univ.

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

EDUCATION
Ph.D., Purdue Univ.
M.S., Purdue Univ.
B.S., Wayne State Univ.

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

EDUCATION
Ph.D., Univ. of Pittsburgh
B.S., Nanjing Univ.

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

EDUCATION
Ph.D., Harvard Univ.
A.M., Harvard Univ.
B.S., Univ. of Berkeley

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

ASSOCIATE DIRECTOR

Jochen A. Lauterbach
Chemical Engineering

EDUCATION
Ph.D., Free Univ. of Berlin
B.S., Univ. of Bayreuth

RESEARCH INTERESTS
High-throughput catalysis, fabrication of conducting polymer nanofilms, non-linear dynamics of catalytic reactions, and time-resolved IR spectroscopy of supported catalysts.

the University of Delaware Energy Institute (UDEI); **Joel Rosenthal** joins CCST as an assistant professor in the inorganic chemistry division of UD's Department of Chemistry and Biochemistry; **Don Watson** joins our center as an assistant professor in UD's Department of Chemistry and Biochemistry; **Feng Jiao** joins our university as an assistant professor in the Department of Chemical Engineering (see page 4 for more information about our new faculty).

Jochen Lauterbach, a faculty member in CCST since 2002, has joined the University of South Carolina as director of the Center of Economic Excellence in Strategic Approaches to the Production of Electricity from Coal. At a farewell reception honoring Jochen, we thanked him for his contributions both to CCST and to the Department of Chemical Engineering. We wish him much success in his future endeavors.

Adding to the excitement of the past year, we've also been busy setting up the infrastructure of our newly awarded CCEI, an Energy Frontier Research Center (EFRC) funded by the DOE. The scientific mission of CCEI is to develop novel heterogeneous catalysts for biomass conversion to chemicals, fuels, and electricity. New analytical equipment and renovated labs and office space needed in the Colburn Laboratory to accommodate the addition of support staff and researchers epitomize some of the changes that have taken place. Important scientific advances have already been achieved and many more are under way. We have established a number of strategic alliances with other centers and academic institutions, so the CCEI industrial consortium is off to a great start. You can find an overview of CCEI on pages 8-9 of this report. Additional information is available on the CCEI Web site [www.efrc.udel.edu].

CCST's annual research review will be on Thursday, October 7, 2010, at the Clayton Hall Conference Center in Newark, Delaware, and we invite you to join us. Registration and other information is available on our Web site [www.che.udel.edu/ccst/2010review.html].

Inside this report you will discover further evidence of CCST's continued success through the outstanding efforts of our faculty and students. We encourage you to contact us with questions or comments, and we hope you will visit our center either in person or via our Web site [www.che.udel.edu/ccst]. We look forward to continuing fruitful collaborations with each of you – our institutional partners, industrial sponsors and scientific colleagues. ✧

ASSOCIATE DIRECTOR

Raul F. Lobo

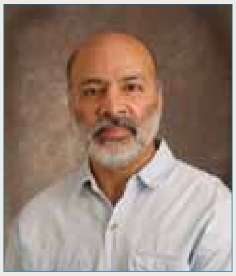
Chemical Engineering

EDUCATION

Ph.D., Cal. Inst. of Tech.
M.S., Cal. Inst. of Tech.
B.S., Univ. of Costa Rica

RESEARCH INTERESTS

Synthesis, characterization and discovery of novel microporous and mesoporous materials; structure property relationships in catalysts and adsorbents; novel photocatalysts preparation and characterization; redox processes and electron transfer in porous materials for applications in catalysis; biomass to chemical and fuels using heterogeneous catalysts.



S. Ismat Shah

Physics and Materials Science

EDUCATION

Ph.D., Univ. of Illinois at Urbana-Champaign
B.E., Univ. of Karachi

RESEARCH INTERESTS

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

Douglass F. Taber

Chemistry and Biochemistry

EDUCATION

Ph.D., Columbia Univ.
B.S., Stanford Univ.

RESEARCH INTERESTS

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

Andrew V. Teplyakov

Chemistry and Biochemistry

EDUCATION

Ph.D., Columbia Univ.
M.S., Columbia Univ.
B.S., Moscow State Univ.

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

EDUCATION

Ph.D., Univ. of California, Berkeley
B.S., Universität Hamburg

RESEARCH INTERESTS

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

New Faculty Members

Michael T. Klein has been named the Dan Rich Chair of Energy and director of the University of Delaware Energy Institute. Former faculty member and UD alumnus, he is an expert in chemical reaction engineering with special emphasis on the kinetics of complex systems. He has written over 200 research articles and has received numerous awards throughout his career including the R. H. Wilhelm Award in Chemical Reaction Engineering from the American Institute of Chemical Engineers, the National Science Foundation's Presidential Young Investigator Award, and the American Chemical Society's Delaware Valley Section Award. Michael served as dean of engineering at Rutgers University from 1998 to 2008.

Feng Jiao is joining the University of Delaware as an assistant professor in the Department of Chemical Engineering and as a faculty member in CCST, bringing his expertise on nanomaterials synthesis and applications on batteries, oxides, and solar fuels. Feng received his Ph.D. in chemistry from the University of St. Andrews in 2007. He was a postdoctoral associate at the Lawrence Berkeley National Laboratory prior to joining UD.

Joel Rosenthal joins CCST as an assistant professor in the inorganic chemistry division of UD's Department of Chemistry and Biochemistry. His research will focus on the development of catalytic systems for alternative energy capture and storage, including electrocatalysts for the reduction of CO_2 to energy rich fuels. Joel received his Ph.D. in inorganic chemistry from Massachusetts Institute of Technology in 2007 where he was also an NIH postdoctoral fellow from 2007 to 2010.

Donald A. Watson joins CCST as an assistant professor in UD's Department of Chemistry and Biochemistry. He will explore new transition metal catalysts for organic synthesis and energy storage. Don completed his Ph.D. in organic chemistry at University of California, Irvine in 2004. From 2004 to 2006, he was an NIH postdoctoral fellow at UC Berkeley. He then moved to the Massachusetts Institute of Technology to take a position as a postdoctoral associate, where he studied metal catalyzed processes for C-F bond formation before joining the UD faculty in July 2009.

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 non-proprietary 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

CCST Sponsors

ACS Petroleum Research Fund

Air Liquide

Army Research Laboratory

BASF

DARPA

The Dow Chemical Company

E. I. du Pont de Nemours and Co., Inc.

Eastman Chemical Company

ExxonMobil Research and Engineering Company

National Science Foundation

National Institute of Standards and Technology

Office of Naval Research

UOP LLC

U.S. Department of Energy

UTC Power

W.R. Grace & Co.

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.

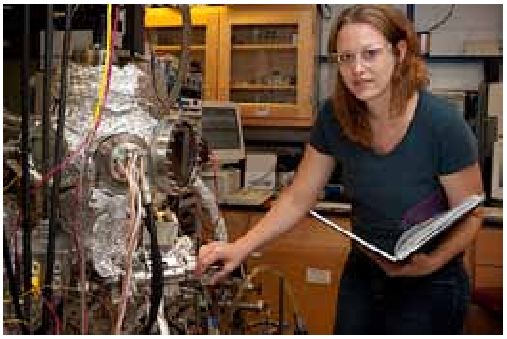
CCST's facilities and measurements are complemented with in-situ FTIR, XRD and EXAFS characterization at Brookhaven National Laboratories, activities led by Prof. Jingguang Chen.

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. A new 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.

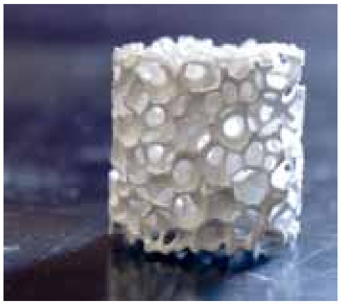
Surface Analysis Instruments

Fifteen 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), High Resolution Electron Energy Loss Spectroscopy (HREELS), FT-IR, Ellipsomicroscopy for Surface Imaging (EMSI), and Photoemission electron microscopy (PEEM).



Danielle Hansgen, a fourth year graduate student, is using a 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:

This laboratory houses three microbalance reactors which permit measurement of catalyst mass changes during reaction. These include a dual pan electrobalance, and a TEOM 1500 Inertial Mass Analyzer (Rupprecht and Patashnick, Inc.) configured to operate as a differential reactor with no dead volume or bypass.

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

Five 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.

High-Throughput Screening Laboratory

A 16-well reactor with temperature measurement and flow control for each reactor is available for high-throughput experiment. Attached to the reactor is an FTIR imaging set-up as truly parallel, quantitative high-throughput technique. It is used to study supported catalysts under realistic reaction conditions as well as under transient conditions (temporal resolution less than 2 seconds for the quantification of 16 reactor effluents).

> *“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)

Spectrometers

Solid State NMR Spectrometers:

The Department of Chemistry and Biochemistry along with CCST faculty have received a grant from NSF to purchase a new high-field solid-state NMR spectrometer that will be used, in part, for the investigation of heterogeneous catalysts. This instrument will be operational in 2011.

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:

This instrument is a new HP 8453 spectrophotometer with a single-beam, microprocessor-controlled collimating optics. A Labsphere RSA-HP53 diffuse reflectance and transmittance accessory for solids, turbid or strongly scattering samples is utilized for the study of heterogeneous catalysts.

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 floating-point 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 Ene

UD receives single largest stimulus award to establish new to develop new technologies for converting grasses and tr

Parr reactor

Analytical equipment for measurement of biomass products

Bio-oil upgrade reactor

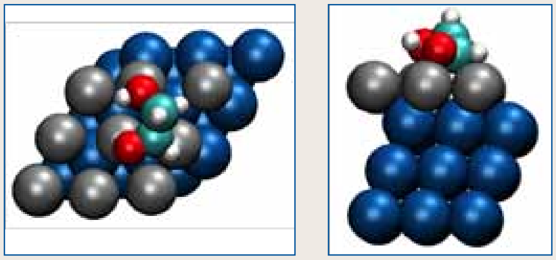
www.efrc.udel.edu

Under Department of Energy, Office of Basic Energy Sciences funding, CCST faculty and their collaborators, along with their students and postdocs, are developing new technologies and a fundamental understanding for the conversion of biomass derivatives and cellulose into added-value chemicals and fuels. One of the key challenges in the conversion of biomass-derived molecules is to control the C-C, C-O, C-H, and O-H bond scission, which will require fundamental understanding of reaction mechanisms using both theoretical and experimental methods.

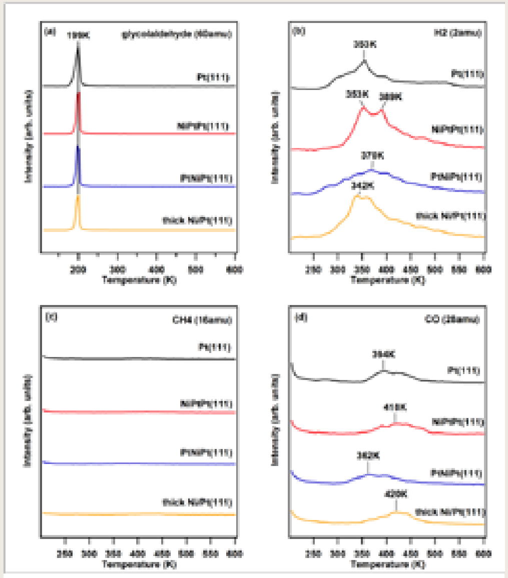
Set-up of the necessary infrastructure (reactors, analytical equipment) to study kinetics and perform catalyst screening and evaluation has been completed. Models complement experiments and enable rational model-based design of new catalysts.

TOPIC INVESTIGATED: Vapor phase and aqueous phase reforming of biomass derivatives (polyols, sugars, etc.) to syngas and hydrogen

KEY RESULTS: Through correlative quantum mechanical studies and fundamental surface science studies, this work entails development of concepts via experiments, characterization and modeling of selective C-C bond breaking and dehydrogenation of CHxOH.



Top and side views of adsorption geometry of glycolaldehyde on NiPtPt(111)



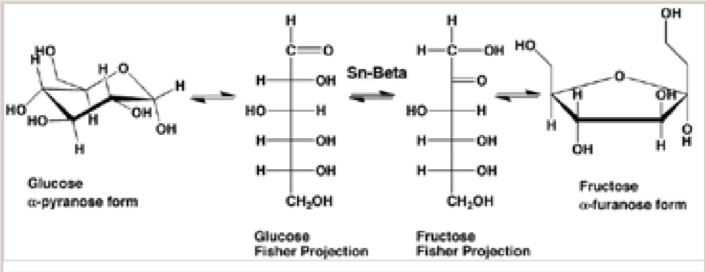
TPD spectra of (a) H_2, (b) CH_4, (c) CO, and (d) glycolaldehyde following 2L glycolaldehyde adsorption on Pt(111) and different Ni/Pt(111) surfaces

rgy Innovation

v Energy Frontier Research Center
ees into electricity and fuels

TOPIC INVESTIGATED: Conversion of biomass derivatives into added-value chemicals

KEY RESULTS: One class of compounds studied is sugars and furans. A novel Sn-Beta zeolite catalyst has been developed that enables the isomerization of glucose to fructose and the single pot conversion of biomass to HMF.

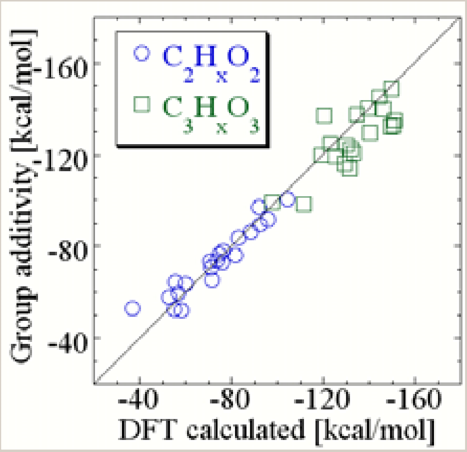


Isomerization of glucose to fructose

TOPIC INVESTIGATED: Development of semi-empirical group-additivity based methods to derive accurate thermochemistry on metal catalysts for complex model compounds for reforming and selective conversion of biomass derivatives to chemicals

KEY RESULTS: These methods extend prior gas-phase methods to surfaces and enable transferability between metals for rational catalyst design.

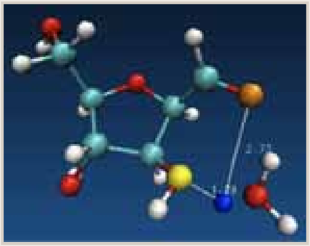
Comparison of DFT calculated enthalpy of formation (x-axis) of polyols adsorbates on platinum to estimated values derived through group additivity methods



TOPIC INVESTIGATED: Development of computational methods to understand biomass chemistry in aqueous phase

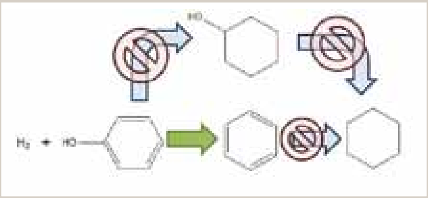
KEY RESULTS: These studies involve experimental and computational work of phase behavior in biphasic systems, equations of state in each phase, and kinetics of sugars and furans in various solvents.

Dehydration of fructose to HMF



TOPIC INVESTIGATED: Bio-oil upgrade using zeolites and other hierarchical multiscale materials to produce variable grade fuels

KEY RESULTS: Medium-pore zeolites were studied as catalysts to direct the formation of aromatic hydrocarbons during the catalytic fast pyrolysis of model compounds. The relationship between carbon yield to aromatics and micropore size suggests that the diameter of six-membered aromatic rings may be a key indicator of efficiency.



Hydrodeoxygenation of phenol shown along with the undesired aromatic hydrogenation reactions

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**

CONTACT INFORMATION

Phone:	(302) 831-4007
E-mail:	barteau@udel.edu
Web site:	www.che.udel.edu/barteau

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

J.C. Dellamorte, J.A. Lauterbach, M.A. Barteau, **"Palladium-Silver Bimetallic Catalysts with Improved Activity and Selectivity for Ethylene Epoxidation,"** *Applied Catalysis A: General* (accepted).

J.E. Rekoske, M.A. Barteau, **"Kinetics, Selectivity and Deactivation in the Aldol Condensation of Acetaldehyde on Anatase Titanium Dioxide,"** *Industrial and Engineering Chemistry Research* (accepted).

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).

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

J.C. Dellamorte, M.A. Barteau, J.A. Lauterbach, **"Opportunities for Catalyst Discovery and Development: Integrating Surface Science and Theory with High Throughput Methods,"** *Surface Science,* **603**, 1770 (2009).

A.C. Lukaski, M.A. Barteau, **"Investigation of Ethylene Oxide on Clean and Oxygen-Covered Ag(110) Surfaces,"** *Catalysis Letters,* **128**, 9 (2009).

J.C. Dellamorte, J.A. Lauterbach, M.A. Barteau, **"Promoter-Induced Morphological Changes of Ag Catalysts for Ethylene Epoxidation,"** *Industrial and Engineering Chemistry Research,* **48**, 5943 (2009).

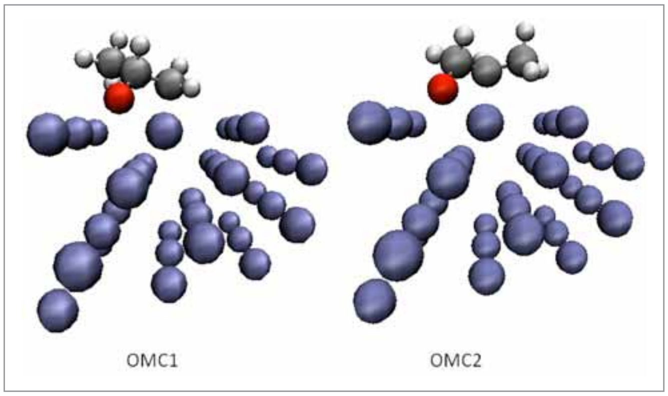
O. Skoplyak, M.A. Barteau, J.G. Chen, **"Comparison of H_2 Production from Ethanol and Ethylene Glycol on M/Pt(111) (M = Ni, Fe, Ti) Bimetallic Surfaces,"** *Catalysis Today,* **147**, 150 (2009).

EXPERIMENTAL AND THEORETICAL STUDIES OF PROPYLENE EPOXIDATION CATALYSTS

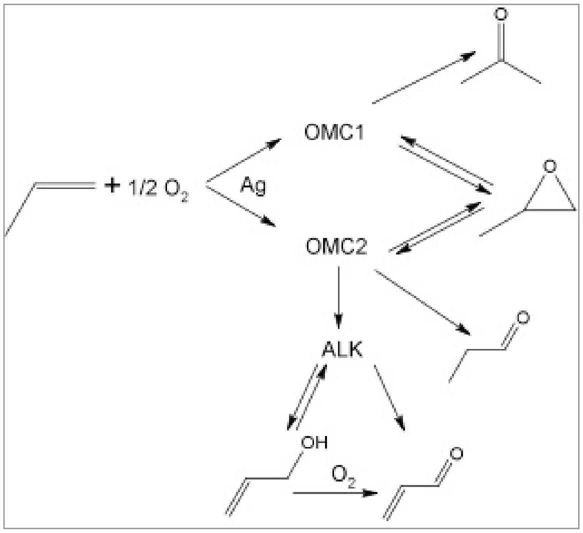
Faculty: Mark Barteau (Chemical Engineering)
Undergraduate Student: Marco Bedolla (Chemical Engineering)
Funding: U.S. Dept. of Energy, Basic Energy Sciences

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. All of these products, except for acrolein and allyl alcohol, are direct products of intramolecular rearrangement of the oxametallacycles. Based on literature data, it can be concluded that acrolein and allyl alcohol are formed by an allyl alkoxide species that results from the dehydrogenation of the oxametallacycle. The proposed reaction network is shown below. DFT calculations of the barriers for formation of different products demonstrate that these reaction channels also limit the selectivity of propylene epoxidation. Future studies will examine bimetallic and promoted catalysts that inhibit the formation of carbonyl-containing products from surface oxametallacycles. ✧



Oxametallacycle intermediates in the epoxidation of propylene



Proposed mechanism for the epoxidation of propylene

Douglas J. Buttrey

» **Professor of Chemical Engineering**

CONTACT INFORMATION

Phone: (302) 831-2034
E-mail: dbuttrey@udel.edu
Web site: www.che.udel.edu/buttrey

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).

W.D. Pyrz, D.A. Blom, R. Shiju, V.V. Guliants, T. Vogt, D.J. Buttrey, **"The Effect of Nb or Ta Substitution into the M1 Phase of the MoV(Nb,Ta)TeO Selective Oxidation Catalyst,"** *Catal. Today,* **142**, 320-328 (2009).

D.A. Blom, W.D. Pyrz, T. Vogt, D.J. Buttrey, **"Aberration-Corrected STEM Investigation of the M2 Phase of MoVNbTeO Selective Oxidation Catalyst,"** *J. Electron Microscopy,* **58**, 193-198 (2009, special issue on advanced electron microscopy in *Materials Physics*).

M. Sadakane, K. Yamagata, K. Kodato, K. Endo, K. Toriumi, Y. Ozawa, T. Ozeki, T. Nagai, Y. Matsui, N. Sakaguchi, W.D. Pyrz, D.J. Buttrey, W. Ueda, **"Synthesis of Orthorhombic Mo-V Based Oxides by Assembly of Pentagonal Mo_6O_{21} Polyoxometalate Building Blocks,"** *Angew. Chem. Int. Ed.,* **48**, 3782-3786 (2009, with frontispiece).

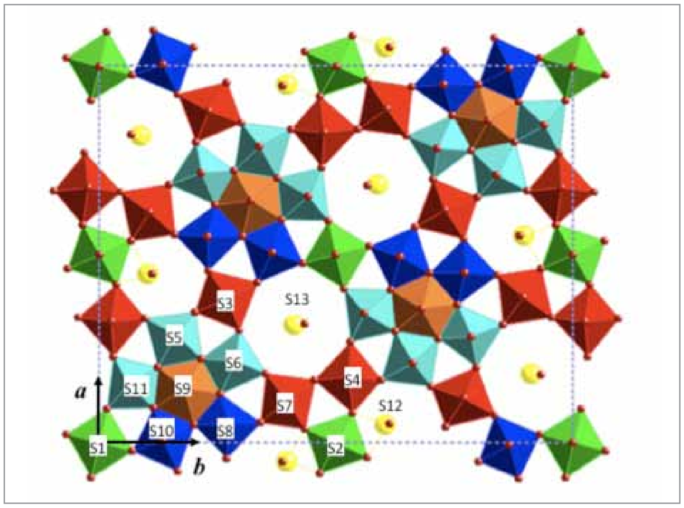
SYNTHESIS AND CHARACTERIZATION OF SINGLE PHASE M1 Mo-V-Nb-Te-O CATALYSTS FOR SELECTIVE OXIDATION AND AMMOXIDATION OF PROPANE

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

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. ✧

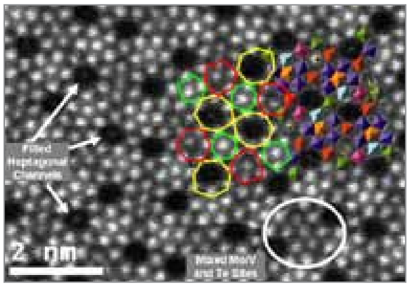


View (ab plane) of the new refined structure of M1 with 13 sites labeled. Color codes are as follows:
Red: (Mo^{6+})/Mo^{5+}/V^{4+}; Green: Mo^{5+}/V^{4+}; Blue: Mo^{6+}; Orange: Nb^{5+}; Cyan: Mo^{6+}/V^{5+}(trace); Yellow: Te^{4+}

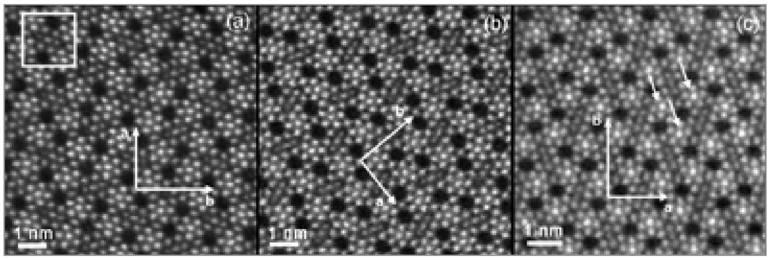
DIRECT STRUCTURE ANALYSIS OF COMPLEX Mo-V SUBOXIDES USING HIGH RESOLUTION SCANNING TRANSMISSION ELECTRON MICROSCOPY

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.

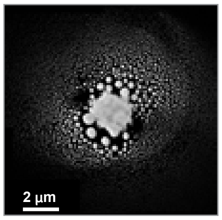
SYNTHESIS AND CHARACTERIZATION OF METALLIC AND BIMETALLIC NANOPARTICLES THROUGH ELECTRON MICROSCOPY

Faculty: Doug Buttrey, Dion Vlachos, Jochen Lauterbach (Chemical Engineering)

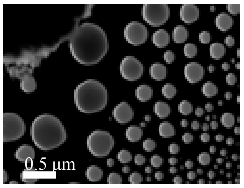
Collaborators: Jim Dumesic, Dante Simonetti, Edward Kunkes (Chemical & Biological Engineering, Univ. of Wisconsin); Thomas Vogt, Sangmoon Park (Chemistry & Biochemistry, University of South Carolina); Richard Crooks, Michael Weir (Chemistry & Biochemistry, University of Texas)
Graduate Students: William 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).

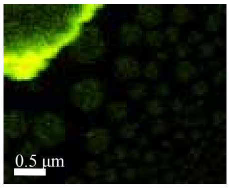
Our focus is the use of advanced TEM techniques for the characterization of both supported and unsupported catalysts. Our current research has been focused on a variety of nanoparticle and catalytic systems that include Ni-Bi alloys, Pt-Re supported catalysts, promoted Ru catalysts, and dendrimer encapsulated 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. ✧



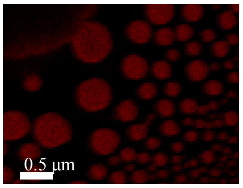
HAADF micrograph of a nano-particle field following an EBIF event



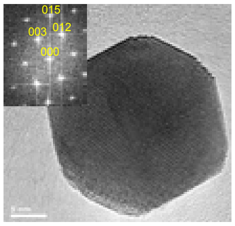
Typical HAADF image of nanoparticles following EBIF



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

» **Claire D. LeClaire Professor of Chemical Engineering**

» **Associate Director, Center for Catalytic Science and Technology**

» **Co-Director, Catalysis Center for Energy Innovation**

CONTACT INFORMATION

Phone: (302) 831-0642
E-mail: jgchen@udel.edu
Web site: www.che.udel.edu/chen

EDUCATION

Ph.D., Chemistry – University of Pittsburgh (1988)
B.S., Chemistry – Nanjing University (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

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
2005-Present: Professor of Chemistry (courtesy appointment), University of Delaware

RECENT PUBLICATIONS

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

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

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O. Skoplyak, M.A. Barteau, J.G. Chen, **“Comparison of H_2 Production from Ethanol and Ethylene Glycol on M/Pt(111) (M = Ni, Fe, Ti) Bimetallic Surfaces,”** *Catalysis Today,* **147**, 150-157 (2009).

A.M. Karim, V. Prasad, G.Mpourmpakis, W.W. Lonergan, A.I. Frenkel, J.G. Chen, D.G. Vlachos, **“Correlating Particle Size and Shape of Supported Ru/γ-Al_2O_3 with NH_3 Decomposition Activity,”** *J. Am. Chem. Soc.,* **131**, 12230-12239 (2009).

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STRUCTURE-PROPERTY RELATIONSHIP IN TRANSITION METAL CARBIDES

Faculty: Jingguang Chen (Chemical Engineering)
Graduate Students: Alan Stottlemyer, 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.

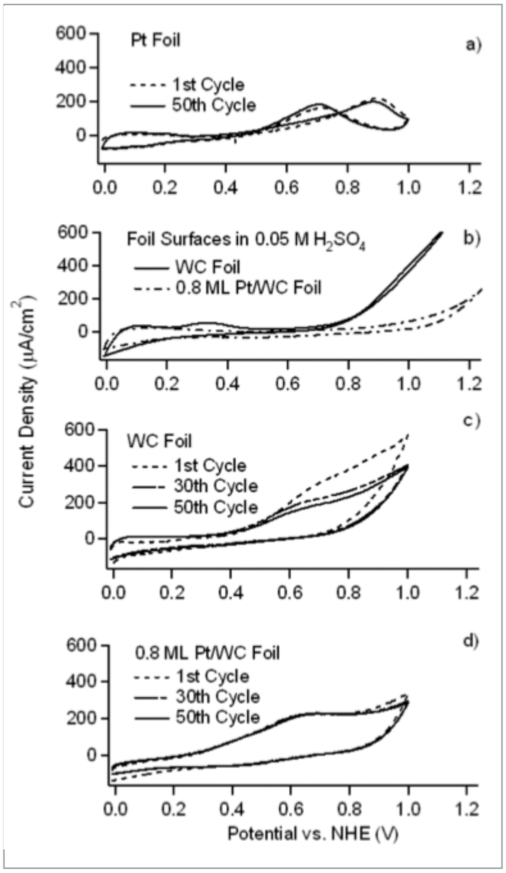
We have performed a series of surface science and catalytic investigations of the unique catalytic properties of TMCs. We have adopted three parallel experimental approaches: (1) to develop experimental procedures for the preparation of thin TMC films with desired electronic and structural properties; (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. ✧

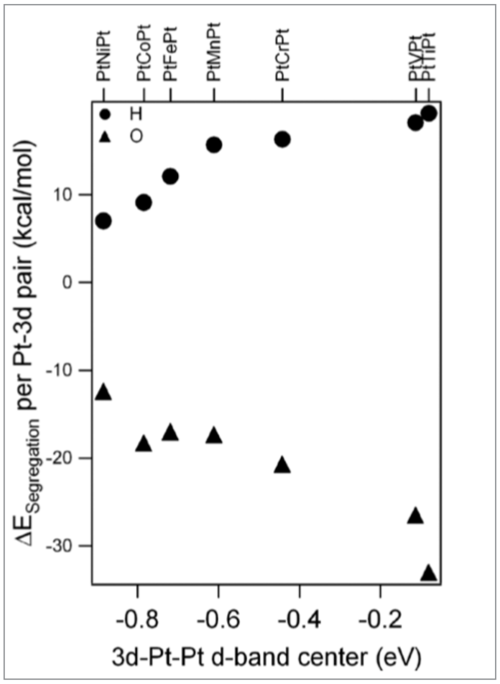


PHOTOELECTROCHEMICAL (PEC) DEVICES FOR WATER SPLITTING

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

The cathode reaction at PEC involves the reduction of H^+ to produce H_2. 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 H_2. 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, Beth Cheney, Jacob Weiner (Chemical Engineering)
Funding: U.S. 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.

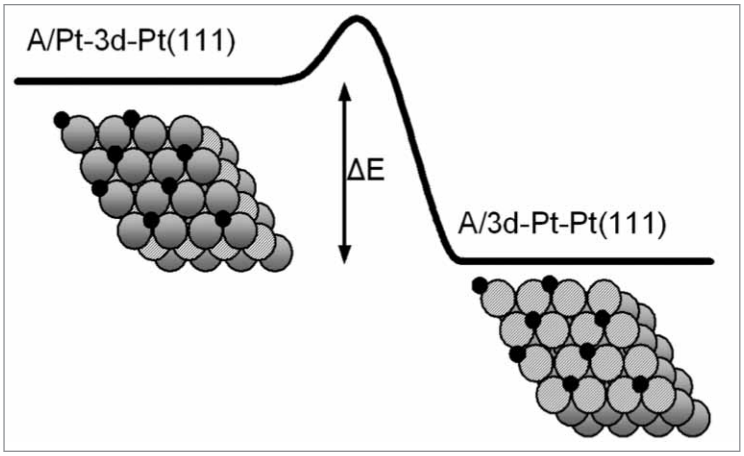
Our current studies in bimetallic catalysis include the selective hydrogenation of C=O and C=C bonds in unsaturated aldehydes, selective hydrogenation of acetylene in the presence of excess ethylene, and the production of hydrogen by selective reforming of oxygenates. The ultimate goal of these studies 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: Carl Menning, 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 electro-oxidation. 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

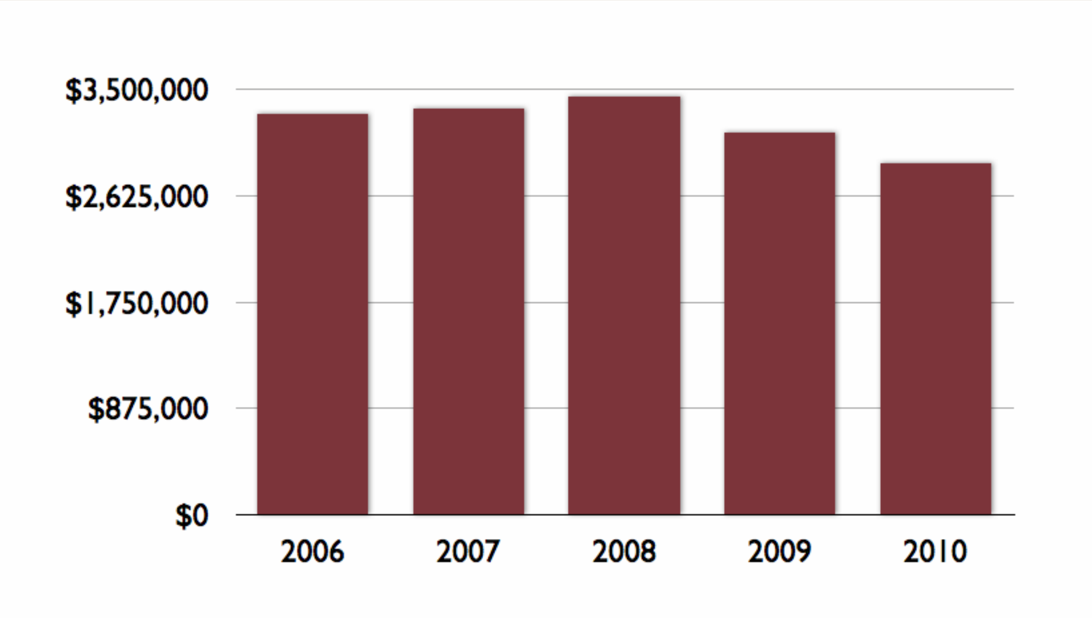
Faculty: Jingguang Chen (Chemical Engineering), Sergey Rykov (Visiting Professor)
Graduate Students: William Lonergan, Nebojsa Marinkovic, Adele Wang (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences

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.

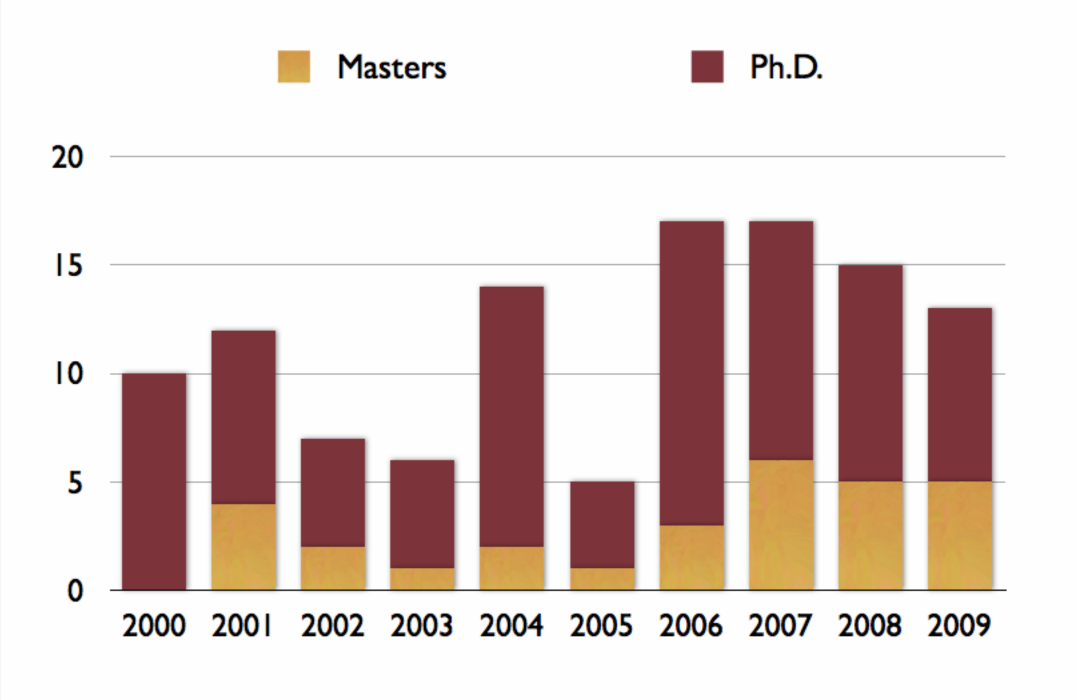
One example is the NEXAFS characterization of nanostructured carbon materials, which are produced by cesium-catalyzed structural rearrangement of amorphous carbon. We will also synthesize and characterize materials produced by doping transition metals onto the amorphous carbon or nanotube-like substrates. 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. ✧

Facts and Figures

Research Expenditures: 2006-2010



Degrees Awarded: 2000-2009



Douglas J. Doren

» **Associate Dean of Arts & Sciences**
» **Professor of Chemistry and Biochemistry**
» **Associate Director, Center for Catalytic Science and Technology**

CONTACT INFORMATION

Phone: (302) 831-1070
E-mail: doren@udel.edu
Web site: www.udel.edu/doren

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).

A.M. Shough, D.J. Doren, B. Ogunnaike, **"Transition Metal Substitution in ETS-10: DFT Calculations and a Simple Model for Electronic Structure Prediction,"** *Chem. Materials,* **21**, 1232 (2009).

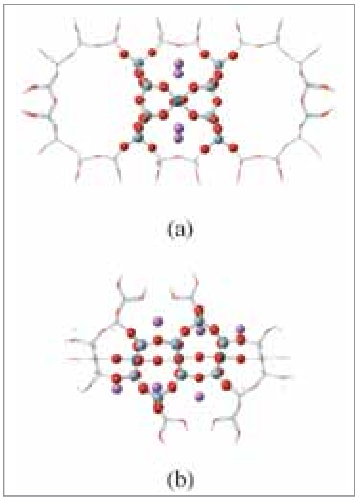
M.J. Nash, R.F. Lobo, D.J. Doren, **"Photocatalytic Oxidation of Ethylene by Ammonium Exchanged ETS-10 and AM-6,"** *Appl. Catalysis B-Environmental,* **88**, 232 (2009).

K. Ooms, T. Polenova, A.M. Shough, D.J. Doren, M.J. Nash, R.F. Lobo, **"Identification of Mixed Valence Vanadium in ETS-10 Using Electron Paramagnetic Resonance, V-51 Solid-State Nuclear Magnetic Resonance, and Density Functional Theory Studies,"** *J. Phys. Chem. C,* **113**, 10477 (2009).

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

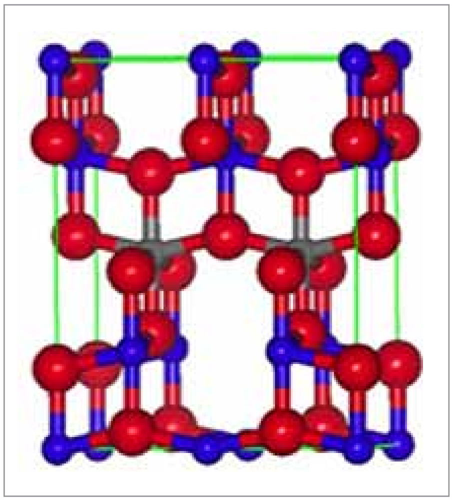
ETS-10 contains one-dimensional chains of TiO_6 octahedra within a nanoporous silicate framework (see figure on right). It is known to photocatalyze a variety of transformations of organic molecules. The structure and electronic properties can be controlled through synthesis, and this project is an effort 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 first-principles theoretical methods to study the material.



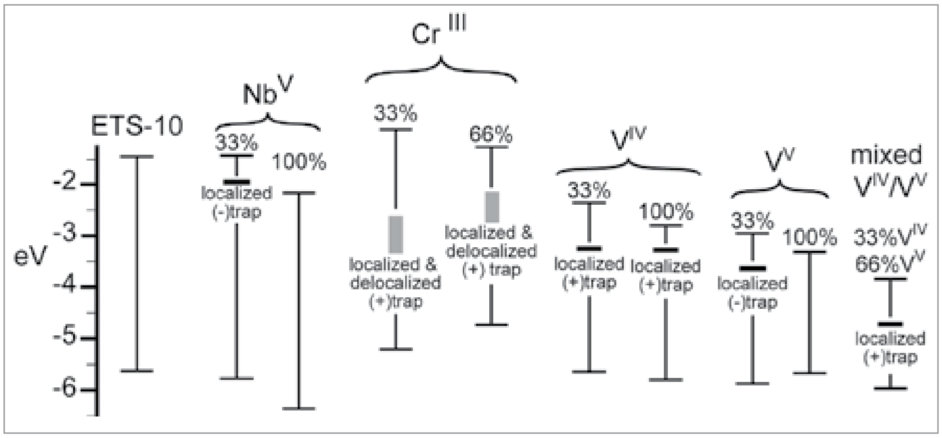
The structure of ETS-10 as viewed from the end (top) and the side (bottom) of the TiO_6 *chain. In our model, the atoms shown as spheres are treated with DFT, while the other atoms are included at the molecular mechanics level. In the bottom figure, some atoms are omitted for clarity.*

We have developed hybrid computational models that account for both the electronic properties of the TiO_6 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 TiO_6 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.

Jochen A. Lauterbach

» **Professor of Chemical Engineering**
» **Associate Director, Center for Catalytic Science and Technology**

CONTACT INFORMATION

Phone:	(803) 777-7904
E-mail:	lauteraj@cec.sc.edu
Web site:	www.che.sc.edu

EDUCATION

Ph.D., Physical Chemistry – Free University of Berlin (1994)
B.S., Technical Physics – University of Bayreuth (1992)

RESEARCH INTERESTS

High-throughput catalysis, fabrication of conducting polymer nanofilms, non-linear dynamics of catalytic reactions, and time-resolved IR spectroscopy of supported catalysts

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

Discovered high activity catalysts for ammonia decomposition; designed selective catalysts for epoxidation; developed better after-treatment catalysts
2008: Visiting Professor, Department of Physics, Dalhousie University, Canada

RECENT PUBLICATIONS

D. Bilbao, J.A. Lauterbach, **"Gas-Phase Coupling of Reactive Surfaces by Oscillating Reactant Clouds,"** *Journal of Catalysis,* **272(2)**, 309-314 (2010).

J.C. Dellamorte, J.A. Lauterbach, M.A. Barteau, **"Effect of Preparation Conditions on Ag Catalysts for Ethylene Epoxidation,"** *Topics in Catalysis,* **53(1)**, 13-18 (2010).

R. Vijay, H. Sakurai, C.M. Snively, J.A. Lauterbach, **"Mechanistic Investigation of Co Containing NOx Traps,"** *Topics in Catalysis,* **52(10)**, 1388-1399 (2009).

J.C. Dellamorte, J.A. Lauterbach, M.A. Barteau, **"Promoter-Induced Morphological Changes of Ag Catalysts for Ethylene Epoxidation,"** *Ind. Eng. Chem. Res.,* **48(13)**, 5943-5953 (2009).

J.C. Dellamorte, M.A. Barteau, J.A. Lauterbach, **"Opportunities for Catalyst Discovery and Development: Integrating Surface Science and Theory with High Throughput Methods,"** *Surface Science,* **603(10-12)**, 1770-1775 (2009, Special issue of *Surface Science* dedicated to Prof. Dr. Dr. h.c. mult. Gerhard Ertl, Nobel-Laureate in Chemistry 2007).

HIGH-THROUGHPUT ANALYSIS AND PREPARATION OF SUPPORTED CATALYSTS

Faculty: Jochen Lauterbach (Chemical Engineering)
Graduate Students: Elizabeth D'Addio, Beth Cheney (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences and NSF IGERT

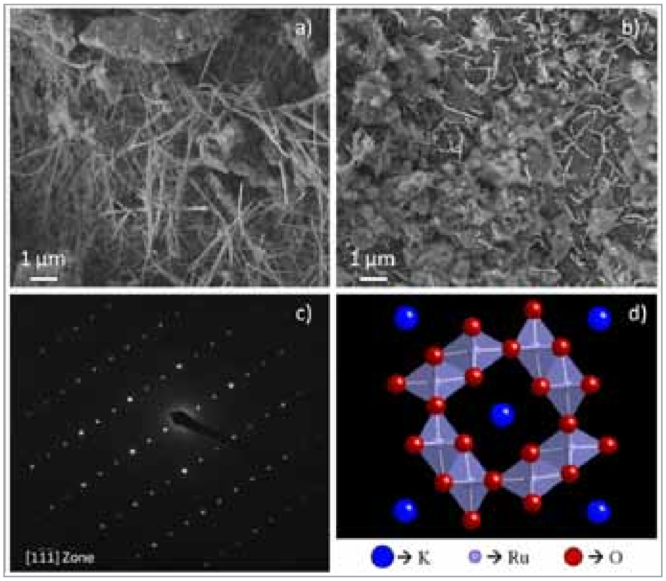
Historically, catalytic studies have been performed by testing a single catalyst formulation at a time. However, catalysts are very complex systems with compositional heterogeneity on both the nano- and mesoscales. Using a single reactor to systematically study hundreds to thousands of catalyst formulations in order to understand reaction behavior as a function of composition would require a prohibitive amount of time. Rising to the challenge of meeting this goal, combinatorial catalysis, or high-throughput screening, has opened new avenues for catalyst discovery and optimization. Several analytical approaches to high-throughput experimentation (HTE) have emerged for the rapid screening of catalyst activity. However, the true power of the combinatorial approach is realized with the ability to perform quantitative studies in parallel. Combining this methodology with modeling efforts and advanced characterization techniques can enhance our understanding of heterogeneously catalyzed reactions, accelerate discovery of novel catalyst formulations, and provide a framework for rational catalyst design. Novel high-throughput approaches are therefore needed to study catalytic reactions quantitatively, in parallel, and under both transient and steady state conditions. To answer this need, we have developed the application of

Fourier transform infrared (FTIR) imaging to quantify effluent composition from multiple reactors simultaneously with a sub-second time resolution. We are capable of testing on the order of hundreds of catalysts per month, taking into account important factors such as non-isothermal effects and transport limitations.

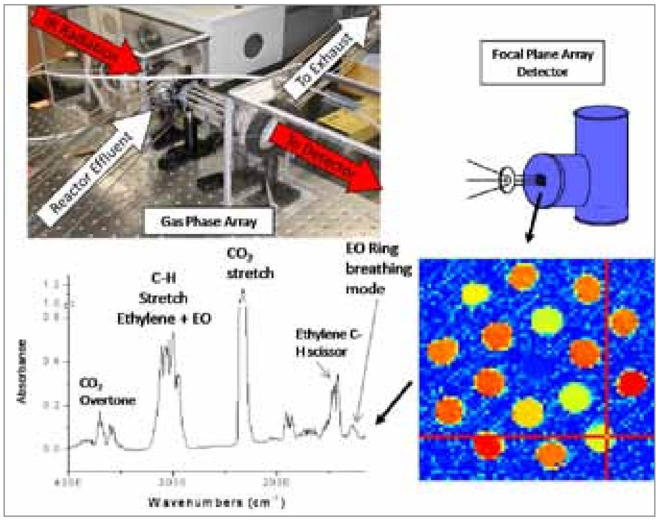
Our system routinely measures the effluent of 16 supported catalyst samples in ~1s. In order to perform these experiments, we employ FTIR imaging of the gas-phase exit streams of a 16 channel reactor. This technique combines the chemically rich information available from mid-infrared spectroscopy with the ability to acquire this information in a spatially resolved manner. A single data set consists of both spatial and spectral information, with each pixel containing a full IR spectrum. The end result is the ability to visualize the distribution of chemical species within complex systems.

Though the implementation of high throughput experimentation has widely expanded the capacity for testing catalysts, the vast parameter space associated with catalyst synthesis factors must be narrowed. Therefore, we implement statistical methods of design of experiments (DoE), which helps to guide experiments and extract the maximum amount of information in a systematic fashion. We have employed both screening designs and response surface designs to the optimization of active metal and promoter weight loadings, calcination times and temperatures, and reaction conditions, which has led to a considerable reduction in the number of experiments required, while preserving the quantity and quality of information obtained.

Currently, we explore the parameter space associated with ammonia decomposition catalysts. This chemistry is of interest because ammonia has been proposed as a chemical carrier of hydrogen for mobile alternative energy applications. However, high temperatures are currently required to attain a satisfactory ammonia conversion. This challenge necessitates rapid exploration of highly active novel catalytic materials for low temperature ammonia decomposition. The most active catalysts, potassium or rubidium promoted Ru, contained a unique “nanowhisker” morphology that we have identified using SEM and TEM techniques. The K-promoted catalysts formed single crystal hollandite (KRu_4O_8) after calcination. By varying preparation conditions, we have observed a consistent link between formation of hollandite and increased catalytic activity. Pure Hollandite crystals synthesized in our lab were active, but degraded after exposure to NH_3. Chemisorption experiments paired with microscopy of these catalysts at each stage of their lifetime suggest that the hollandite acts as a structural precursor to a highly dispersed Ru phase.



a) K-promoted Ru catalyst after calcination containing KRu_4O_8 Hollandite crystals; b) Hollandite degrades in reducing conditions to form highly dispersed Ru^0 phase; c) SAED image used to identify Hollandite on catalyst; d) [001] projection of KRu_4O_8.



FTIR Spectroscopic Imaging System; collimated beam of IR radiation interacts with 16 reactor effluents flowing through parallel, separate tubes that make up a sampling accessory called the gas phase array. Next, the focal plane array (FPA) detector, which is the infrared analog of a video camera, records the IR spectra as a function of both position and time. Each pixel of the image contains a full IR spectrum.

We also use the high throughput reactor system to explore the parameter space associated with microemulsion synthesis, or micelle/reverse micelle synthesis of catalyst nanoparticles. This technique can be utilized for increased control of particle size, a key parameter in heterogeneous catalysis for the achievement of specific surface sites, electronic properties, and structural characteristics leading to improved performance. Since its first successful implementation in the early 1980s, this synthesis technique has been used in the preparation of noble-metal catalysts, nanoparticles with highly controlled size distributions, bimetallic systems, and oxide-based materials. The solutions, which consist of a water phase, an oil phase, and a surfactant, enable the creation of nanosized reactors which provide the boundary for particle growth. The tunable parameters involved in micro-emulsion synthesis, such as water-to-surfactant ratio, nature of the surfactant, and nature of the reducing agent, allow for tailoring specific size and composition of bimetallics to hone the activity for a given chemistry.

We have explored several catalytic systems using this synthetic approach, including NOx storage and reduction catalysts (NSR) for automotive exhaust applications, ammonia decomposition for hydrogen storage applications, and ethylene epoxidation. For example, Co/Pt/Ba NSR catalysts were synthesized in this manner and compared to their incipient wetness counterparts in a high-throughput reactor system. The nanoparticles were also analyzed using electron microscopy and elemental analysis techniques.

For the ammonia decomposition reaction, Ru catalysts prepared using reverse micelles were shown to yield much higher conversions than their counterparts synthesized via incipient wetness impregnation.

Recent modeling studies for ethylene epoxidation have identified several bimetallic catalysts that would increase the selectivity toward ethylene oxide. However, efficient production of these bimetallics while maintaining a consistent particle size can be difficult. The reverse micelle technique provides a possible solution of providing tight size and concentration distributions for the validation of DFT and microkinetic modeling results.

The ultimate goal of our research approach, high-throughput and combinatorial-based research combined with modeling and advanced characterization, is to gain a complete understanding of each system studied, such that the intelligent design of novel catalytic materials with improved performance will be possible. ✧

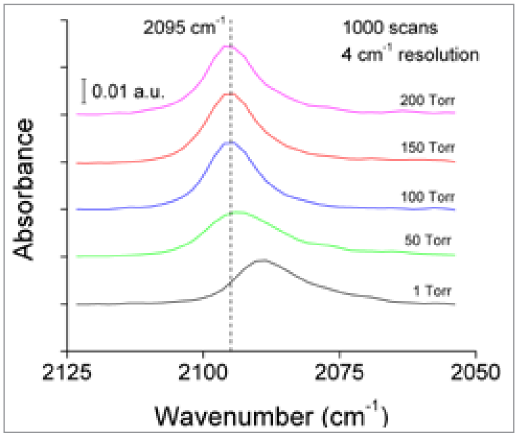
MODEL CATALYSTS FOR HIGH-PRESSURE SPECTROSCOPIC INVESTIGATIONS

Faculty: Jochen Lauterbach (Chemical Engineering)
Graduate Student: John Bedenbaugh (Chemical Engineering)
Funding: NSF-IGERT

Molecular-level catalytic investigations have traditionally been performed using model catalysts consisting of single crystal surfaces under ultra-high vacuum (UHV) conditions. However, discrepancies can exist between surface science observations in UHV conditions and industrial catalytic performance at higher pressures. For example, changes in the population of adsorption sites and variation in reaction mechanisms on catalyst surfaces have been observed as pressure increases above UHV conditions. This work addresses this pressure issue through the investigation of model catalytic systems over the range from UHV to atmospheric pressures.

In order to study catalytic systems above UHV conditions, investigative techniques capable of functioning in higher pressure environments without undue interference from gas phase molecules are required. To this end, a polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) system was constructed in our laboratory to enable analysis of surface adsorption behavior from UHV to near-ambient pressure conditions. This technique is capable of removing contributions from gas phase molecules to yield surface vibrational spectra. We have recently successfully demonstrated the ability to obtain surface spectra in the presence of near-ambient conditions in our laboratory.

In work currently being performed in our laboratory, we seek to explore surface adsorption behavior in higher pressure environments during simple reactions, such as CO oxidation and NH_3 decomposition. Studying adsorption behavior on a catalyst surface using vibrational spectroscopy yields information about the site a molecule is adsorbed on as well as the environment a molecule is in. The PM-IRAS technique is also capable of identifying the predominant adsorbates present in a system, potentially yielding information about reaction mechanisms. This work is motivated by trying to understand and correlate surface adsorption behavior at higher pressures with mechanistic information during reaction. ✧

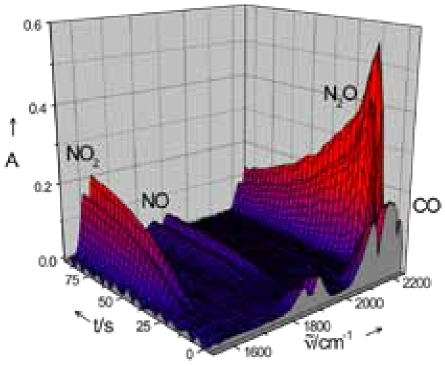


PM-IRAS study of the adsorption of CO on Pt(100) at 325 K for pressures from 1-200 Torr CO. A linear C-O stretch (~2090 cm^{-1}) was observed corresponding to CO adsorbed on atop sites. Frequency shift and peak sharpening of the adsorption band were observed at higher pressures. These results indicate higher CO coverages and peak band positions not achievable under UHV conditions.

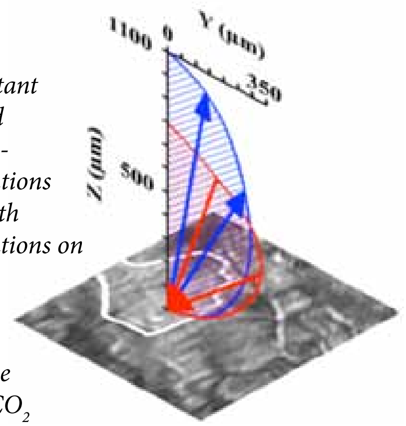
NON-LINEAR PHENOMENA IN HETEROGENEOUS CATALYSIS

Faculty: Jochen Lauterbach (Chemical Engineering)
Graduate Student: Danny Bilbao (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences

Catalyst operation and design in the chemical process industry have traditionally involved the use of simple mechanistic models to describe the dynamics of processes occurring on the catalyst surface. The Langmuir-Hinshelwood mechanism, for example, has enjoyed considerable application in the description of reaction mechanisms of most common industrial reactions. Simplifications in such descriptions are frequently made by practitioners, based on ideas of model reduction owing to the proper identification of the rate determining step, and/or the use of the steady state assumption to simplify matters. There are a number of simplifications made in this regard with respect to the behavior of the catalyst, as well as the role of dynamic behavior exhibited by the catalyst surface atoms. A priori, it is easy to see that transport of mass and energy (diffusion limited reactions or non-isothermal effects) can seriously invalidate all the above assumptions. Experimentally, however, it is possible to bypass these limitations, so that the kineticist can afford to make these assumptions in the use of simple dynamic models. More serious limitations to the above-simplified approach have come to light by virtue of the discovery of dynamic and spatial patterns on the surface of low index single crystal catalysts. The presence of non-linear phenomena like rate oscillations and patterns on crystal facets in supported catalysts is a confirmed fact. Clearly, simple Langmuir-Hinshelwood type models are inapplicable and will lead to serious errors in the extraction of the microkinetics from experimental data. A systematic and detailed effort is therefore needed to (a) increase our understanding of pattern formation, (b) improve existing models in terms of their rigor as well as the physics captured, and (c) come up with practical strategies to make the extraction of microkinetic information about rate processes from experimental data more reliable and accurate in the light of our understanding of pattern formation.



Transient spectra from fuel rich to fuel lean at 623 K for a nitrogen storage and reduction catalyst. The catalyst is 1.3 wt% Pt/ 9.0 wt% Fe/ 30 wt% Ba supported on γ-alumina. It can be seen that when O_2 *is introduced to the reactor (t~60 seconds), the CO is completely oxidized to* CO_2*, the* N_2O *band grows and decays and later (t=90 seconds) the* NO_2 *and NO bands appear.*



Angular reactant (CO-red) and product (CO_2*-blue) distributions associated with kinetic oscillations on a single grain (outlined in white) of a polycrystalline Pt foil. The* CO_2 *desorption distribution is slightly peaked towards the surface normal relative to the CO distribution which follows more closely a cos relation. Ultimately, the expanse of the CO adsorption distribution above a single grain will determine the spatial limits for the synchronization of activity on distant grains and in turn global catalyst performance. (*$p_{O2}=2.4x10^{-3}$ *mbar,* $p_{CO}=1.5x10^{-4}$ *mbar, T = 534 K)*

Experiments in our group are motivated by trying to understand and correlate spatio-temporal pattern formation with macroscopic behavior of the reaction rate. Photoemission electron microscopy (PEEM) and ellipsomicroscopy for surface imaging (EMSI) are used to follow, in real time, pattern formation on micron length scales. Using PEEM, spatiotemporal pattern formation can be observed in the 10^{-5} mbar pressure range. In an attempt to bridge the "pressure-gap," EMSI is used to follow pattern formation up to atmospheric pressure. The features of the nonlinear phenomena, observed in different pressure regimes, are markedly different. This is shown by comparison of various qualitative and quantitative features of spatio-temporal pattern formation as well as the dynamics of the macroscopic reaction rate.

In work currently being performed in our laboratory, we seek to explore the role of spatial coupling, via the gas-phase, in communicating local reactivity variations to distant locations on a surface. As a model system, we employ CO oxidation on polycrystalline Pt where, under particular conditions, individual grains exhibit self-sustained rate oscillations which are not necessarily synchronized across the surface, even under vacuum conditions. By locating these chemical oscillators on the surface using EMSI, while simultaneously monitoring the local gas-phase concentration using a scanning mass spectrometer, we are able to detect local variations in the gas-phase composition due to kinetic activity on individual catalyst grains. This analysis provides a more detailed picture of the surface/gas-phase interaction under reaction conditions, while allowing for the estimation of gas-phase coupling length scales which are crucial to the collective, global behavior of a catalytic system. ✧

Raul F. Lobo

» **Professor of Chemical Engineering**

» **Associate Director, Center for Catalytic Science and Technology**

CONTACT INFORMATION

Phone: (302) 831-1261
E-mail: lobo@udel.edu
Web site: www.udel.edu/lobo

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, characterization and discovery of novel microporous and mesoporous materials; structure property relationships in catalysts and adsorbents; novel photocatalysts preparation and characterization; redox processes and electron transfer in porous materials for applications in catalysis; biomass to chemical and fuels using heterogeneous catalysts

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

Found evidence for non-classical nucleation and crystal growth mechanisms in zeolite beta and developed synthesis to control particle size and composition of zeolite crystals; investigated small-pore Cu-exchanged zeolites for automotive deNOx applications and found materials more stable than Cu-ZSM-5; investigated the decomposition of Brønsted acid sites on Ga-zeolites showing that most sites decompose releasing hydrogen gas and producing a framework tetrahedral Ga and not extra-framework Ga; established that two kinds of redox sites can be form in H-zeolites by either low-temperature treatments in oxygen or high-temperature treatments in inert atmosphere; discovered a new photocatalyst containing zinc-gallium oxygen and nitrogen in the structure.

RECENT PUBLICATIONS

D.W. Fickel, A.M. Shough, D.J. Doren, R.F. Lobo, **"High-Temperature Dehydrogenation of Defective Silicalites,"** *Micropor. Mesopor. Mater.,* **129**, 156-163 (2010).

N.D. Hould, S. Kumar, M. Tsapatsis, V. Nikolakis, R.F. Lobo, **"Structure and Colloidal Stability of Nanosized Zeolite Beta Precursors,"** *Langmuir,* **26**, 1260-1270 (2010).

D.W. Fickel, R.F. Lobo, **"Copper Coordination in Cu-SSZ-13 and Cu-SSZ-16 Investigated by Variable-Temperature XRD,"** *J. Phys. Chem. C,* **114**, 1633-1640 (2010).

W. Huang, A. Li, R.F. Lobo, J.G. Chen, **"Effects of Zeolite Structure, Exchanged Cations and Bimetallic Formulations on the Selective Hydrogenation of Acetylene Over Zeolite-Supported Catalysis,"** *Cat. Lett.,* **130**, 380 (2009).

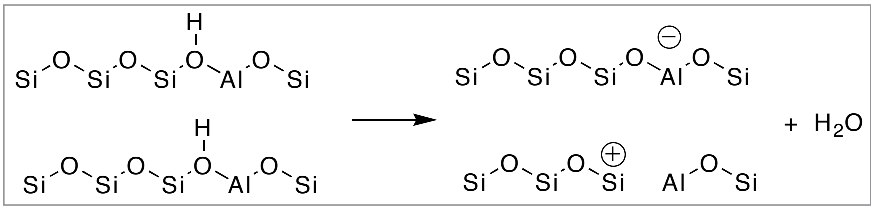
R.F. Lobo, A.E.C. Palmqvist, **"Nanostructures,"** *Curr. Op. Coll. Interface Sci.,* **14**, 225 (2009 – Editorial).

K. Ooms, T. Polenova, A.M. Shough, D.J. Doren, M.J. Nash, R.F. Lobo, **"Identification of Mixed Valence Vanadium in ETS-10 Using EPR, V51 NMR and DFT Studies,"** *J. Phys. Chem. C.,* **113**, 10477-10484 (2009).

M.J. Nash, R.F. Lobo, D.J. Doren, **"Photocataytic Oxidation of Ethylene by Ammonium Exchanged ETS-10 and AM-6,"** *Appl. Catal. B: Env.,* **88**, 232 (2009).

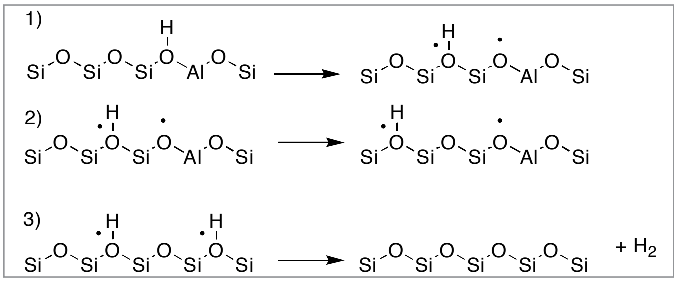
REDOX SITES IN ACID ZEOLITES

Faculty: Raul Lobo (Chemical Engineering)
Graduate Students: Dustin Fickel, Khalid Al-Majnouni (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences



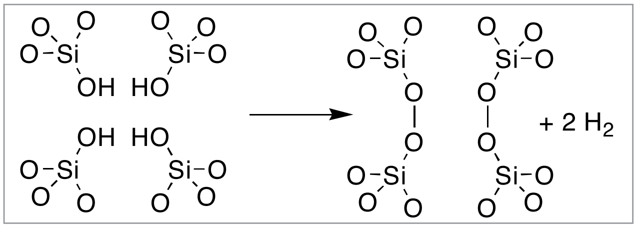
Scheme 1: Dehydroxylation via heterolytic decomposition of Brønsted acid sites

We study the chemistry of zeolites at high temperatures to determine the properties and structure of sites responsible for redox processes observed when organic molecules are adsorbed on the zeolite after heating. The model of Scheme 1 is generally accepted as the mechanism of zeolite dehydroxylation and appears to be the dominant mechanism of dehydroxylation for zeolites with high aluminum content. However, in zeolites with low aluminum content, the Brønsted acid sites are isolated from each 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 2: Proposed homolytic 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 3: Proposed homolytic decomposition of Brønsted acid sites

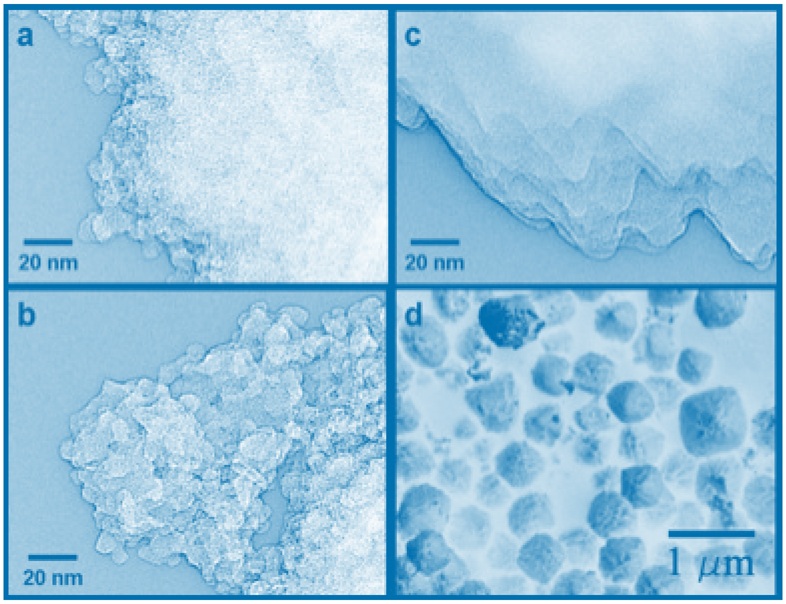
In related research and in collaboration with Professor Doug Doren, we have found that zeolite silicalite-1 also desorbs hydrogen gas at high temperatures. This observation can be explained by a self-oxidation of the silica framework as depicted in Scheme 3. Again, we observe that oxygen atoms in the 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. ✧

GROWTH MECHANISMS 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. ✧



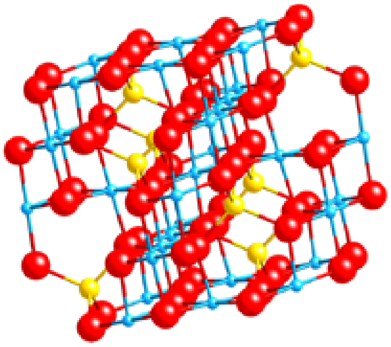
(a) and (b) show TEM images of the tertiary particles soon after they are first observed in the synthesis gel. These images show they are formed by the addition of smaller (secondary) units. Figures (c) and (d) also show that over time the morphology of the particles changes and reaches the well-known square pyramidal morphology usually observed for zeolite beta.

NOVEL PHOTOCATALYTIC MATERIALS

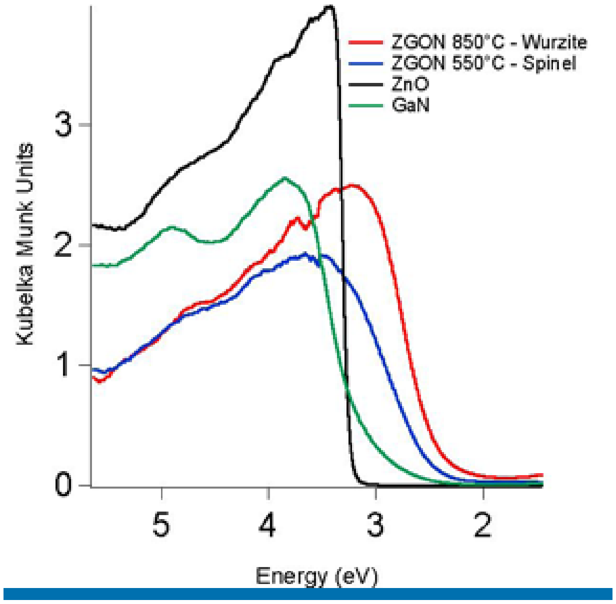
Faculty: Raul Lobo (Chemical Engineering)
Graduate Students: Bharat Boppana (Chemical Engineering), Heather Schmidt (Chemistry)
Funding: U.S. Department of Energy, Basic Energy Sciences

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.

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 (see figure on left).

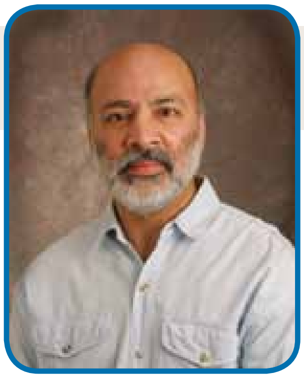


Spinel structure with metals in tetrahedral and octahedral coordination environments



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. ✧



S. Ismat Shah

» **Professor of Materials Science and Engineering**

» **Professor of Physics and Astronomy**

CONTACT INFORMATION

Phone:	(302) 831-1618
E-mail:	ismat@udel.edu
Web site:	www.mseg.udel.edu/research_faculty.html?fnid=4

EDUCATION

Ph.D., Materials Science and Engineering – University of Illinois at Urbana-Champaign (1986)
B.E., Metallurgical Engineering – Bachelor of Engineering (University of Karachi, Pakistan)

RESEARCH INTERESTS

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

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

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

G.H. Jaffari, A. Ceylan, C. Ni, S.I. Shah, **"Enhancement of Surface Spin Disorder in Hollow $NiFe_2O_4$ Nanoparticles,"** *J Appl. Phys.,* **107**, 1, doi:10.1063/1.3277041 (2010).

A.F. Khan, M. Mehmood, M. Aslam, S.I. Shah, **"Nanostructured Multilayer TiO_2–Ge Films with Quantum Confinement Effects for Photovoltaic Applications,"** *J Colloid and Interface Sci.,* **343**, 271, doi:10.1016/j.jcis.2009.11.045 (2010).

A.K. Rumaiz, J.C. Woicik, E. Cockayne, H.Y. Lin, G.H. Jaffari, S.I. Shah, **"Oxygen Vacancies in N Doped Anatase TiO_2: Experiment and First-Principles Calculations,"** *Appl. Phys. Lett.,* **95**, 1, doi:10.1063/1.3272272 (2009).

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B. Ali, L.R Shah, C. Ni, J.Q. Xiao, S.I. Shah, **"Interplay of Dopant, Defects and Electronic Structure in Driving Ferromagnetism in Co-Doped Oxides: TiO_2, CeO_2 and ZnO,"** *J. Phys.: Condens. Matter,* **21**, 456005, doi:10.1088/0953-8984/21/45/456005 (2009).

M. Coskun, G.H. Jaffari, S. Manzoor, M. Korkmaz, S.I. Shah, **"Synthesis and Magnetic Properties of Co–Cr_2O_3 Nanocomposites,"** *Journal of Magnetism and Magnetic Materials,* **322**, 13, 1731-1735 doi:10.1016/j.jmmm.2009.12.016 (2009).

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B. Ali, A.K. Rumaiz, A. Ozbay, E.R. Nowak, S.I. Shah, **"Influence of Oxygen Partial Pressure on Structural, Transport and Magnetic Properties of Co Doped TiO_2 Films,"** *Solid State Comm.,* **149**, 2210, doi:10.1016/j.ssc.2009.09.011 (2009).

O.A. Fouad, A.K. Rumaiz, S.I. Shah, **"Reactive Sputtering of Titanium in Ar/CH_4 Gas Mixture: Target Poisoning and Film Characteristics,"** *Thin Solid Films,* **517**, 5689, doi: 10.1016/j.tsf.2009.02.119 (2009).

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S.I. Shah, G.H. Jaffari, E. Yassitepe, B. Ali, **"Evaporation: Processes, Bulk Microstructures, and Mechanical Properties,"** Handbook of Thin Films, Ed. Peter Martin, John Wiley Publications, New York, doi:10.1016/B978-0-8155-2031-3.00004-1 (2009).

PHOTOELECTROCHEMICAL 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:

$$2p^+ + 2OH^- \rightarrow \tfrac{1}{2}O_2 + H_2O$$

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

$$2e^- + 2H_2O \rightarrow H_2 + 2OH^- \quad or \quad 2e^- + 2H^+ \rightarrow H_2$$

To improve the quantum conversion efficiency in a TiO_2-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 atomic-orbitals (OLCAO) and full-potential linearized augmented plane-wave (FLAPW) have revealed that upper valence band predominately consists of O2*p* states, whereas the conduction band consists mainly of Ti3*d* 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 TiO_2 lattice. The reported substitutional doping of cation and anion of TiO_2 catalysts have often been proven to improve the photocatalytic performance of TiO_2. Among all dopants reported, nitrogen doped TiO_2 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 $TiO_{2-x}N_x$ creates localized N2*p* 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 TiO_2 could introduce deep N2*p* states within the forbidden band. Although this significantly reduces the bandgap of TiO_2, 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 (O_2/H_2O) to promote the conduction band electron scavenging and prolonging the electron transfer kinetic. Thus, deep N2*p* 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, Fe_2O_3 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 TiO_2 and $SrTiO_3$. Although TiO_2 has lower band gap energy than that of $SrTiO_3$, it has been reported that $SrTiO_3$ yields one order higher quantum efficiency in photoelectrolysis comparing to TiO_2 electrode without additional voltage bias condition due to the lower electron mo-

(continued on page 39)

Douglass F. Taber

» **Professor of Chemistry and Biochemistry**

CONTACT INFORMATION

Phone:	(302) 831-2433
E-mail:	taberdf@udel.edu
Web site:	http://valhalla.chem.udel.edu

EDUCATION

Ph.D., Organic Chemistry – Columbia University (1974)
B.S., Chemistry – Stanford University (1970)

RESEARCH INTERESTS

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

AWARDS, HONORS & PROFESSIONAL ACTIVITIES

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

D.F. Taber, R.B. Sheth, W. Tian, **"Synthesis of (+)-Coronafacic Acid,"** *J. Org. Chem.*, **74**, 2433-2477 (2009).

D.F. Taber, C.M. Paquette, P.G. Reddy, **"One Carbon Homologation of Halides to Benzyl Ethers,"** *Tetrahedron Lett.*, **50**, 2462-2463 (2009).

D.F. Taber, P. Gu, **"Preparation of the Major Urinary Metabolite of (-)- Prostaglandin E2,"** *Tetrahedron*, **65**, 5904-5907 (2009).

D.F. Taber, P. Gu, R. Li, **"A Divergent Synthesis of the Δ13 9-Isofurans,"** *J. Org. Chem.*, **74**, 5516-5522 (2009).

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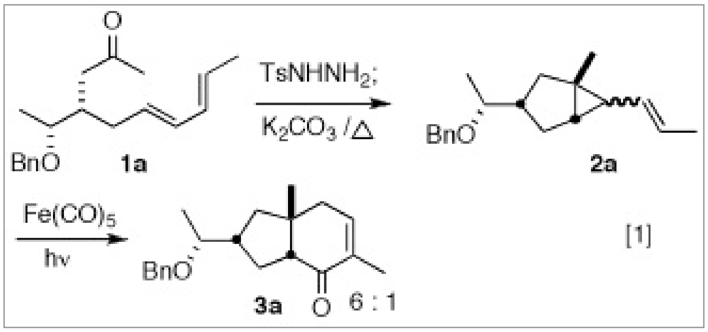
BICYCLIC CONSTRUCTION BY NET FE-MEDIATED [1 + 4 + 1] CYCLOADDITION

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

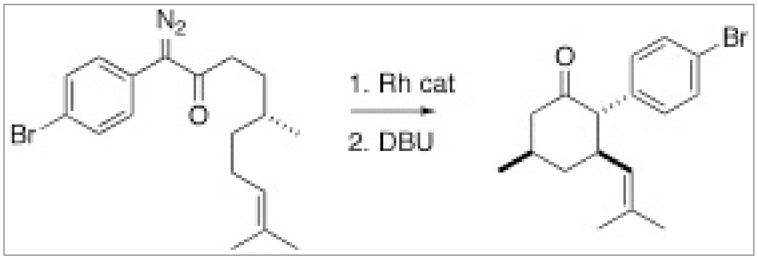
Carbocycles, as exemplified by calcitriol and taxol, can be potent drugs. Although computationally-driven lead generation often suggests potential new drug candidates that are polycarbocyclic, such candidates are usually not pursued, because of the assumption that a polycarbocyclic drug would be impractical 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)

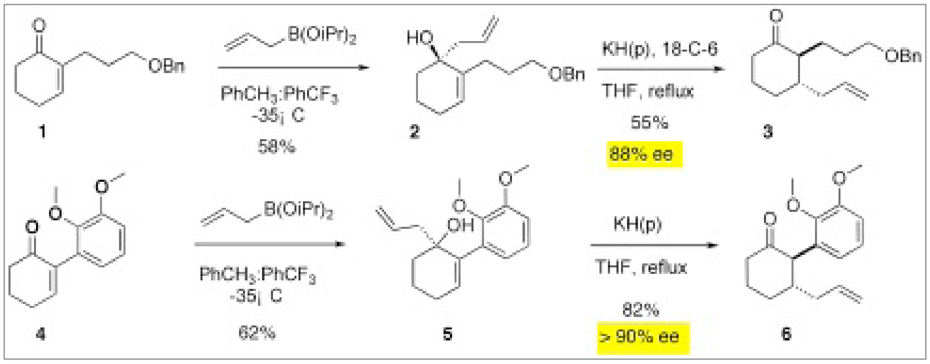
We have found that the Rh carbenes derived from α-diazo benzyl ketones are significantly more discriminating than are the Rh carbenes derived from β-ketoesters. When an electron rich C-H site is available six atoms away, cyclohexanone formation can dominate. This is in marked contrast to the cyclizations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



ASYMMETRIC ORGANOCATALYTIC CONJUGATE ALLYLATION OF CYCLIC ENONES

Faculty: Douglass F. Taber (Chemistry and Biochemistry)
Postdoctoral 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 α-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

» **Professor of Chemistry and Biochemistry**

CONTACT INFORMATION

Phone: (302) 831-1969
E-mail: andrewt@udel.edu
Web site: www.udel.edu/chem/teplyakov/andrew.html

EDUCATION

Ph.D., Chemistry – Columbia University (1997)
M.S., Chemistry – Columbia University (1993)
B.S., 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* (accepted for publication)
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

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

C. Dybowski, A. Teplyakov, **"Essential Data and Equations for a Course in Physical Chemistry,"** Pearson Publishing, ISBN-13: 978-0-558-30403-4; ISBN-10: 0-558-30403-6 (2009).

T.R. Leftwich, A.V. Teplyakov, **"Chemical Manipulation of Multifunctional Hydrocarbons on Silicon Surfaces,"** *Surf. Sci. Rep.,* **63**, 1-71 (2008, Invited review).

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

J.C.F. Rodríguez-Reyes, C. Ni, H.P. Bui, T.P. Beebe Jr., A.V. Teplyakov, **"Reversible Tuning of the Surface Chemical Reactivity of Titanium Nitride and Nitride-Carbide Diffusion Barrier Thin Films,"** *Chem. Mater.,* **21(21)**, 5163-5169 (2009).

M.R. Madachik, A.V. Teplyakov, **"Coadsorption of Ethylene and Nitrobenzene on Si(100)-2x1: Towards Surface Patterning at the Molecular Level,"** *J. Phys Chem. C,* **113**, 18270-18275 (2009).

X. Zhang, I.H. Antonopoulos, S. Kumar, J. Chen, A.V. Teplyakov, **"Tuning the Geometry of Shape-Restricted DNA Molecules on the Functionalized Si(111),"** *Appl. Surf. Sci.,* **256**, 815-818 (2009, in press).

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K.A. Perrine, T.R. Leftwich, C. Weiland, M.R. Madachik, R.L. Opila, A.V. Teplyakov, **"Reactions of Aromatic Bifunctional Molecules on Silicon Surfaces: Nitrosobenzene and Nitrobenzene,"** *J. Phys. Chem. C,* **113(16)**, 6643–6653 (2009).

COVALENTLY ATTACHED MACROMOLECULES ON SEMICONDUCTOR SUBSTRATES

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)

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

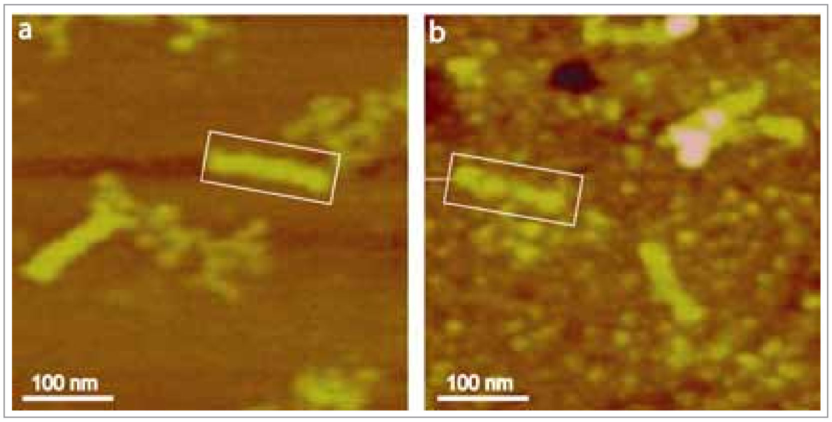
We have used C_{60} Buckminster fullerenes as spectroscopic and microscopic probes to establish the covalent nature of their binding to appropriately terminated self-assembled monolayers on silicon. We have investigated this chemistry using multiple spectroscopic and microscopic techniques and have verified 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 SAM-covered 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. ✧

CHEMICAL MODIFICATION OF SEMICONDUCTOR MATERIALS

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)

Collaborators: Robert Opila (Materials Science & Engineering), George Flynn (Chemistry, Columbia University)
Graduate Students: Timothy Leftwich, Keith Douglass, Mark Madachik (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. ✧

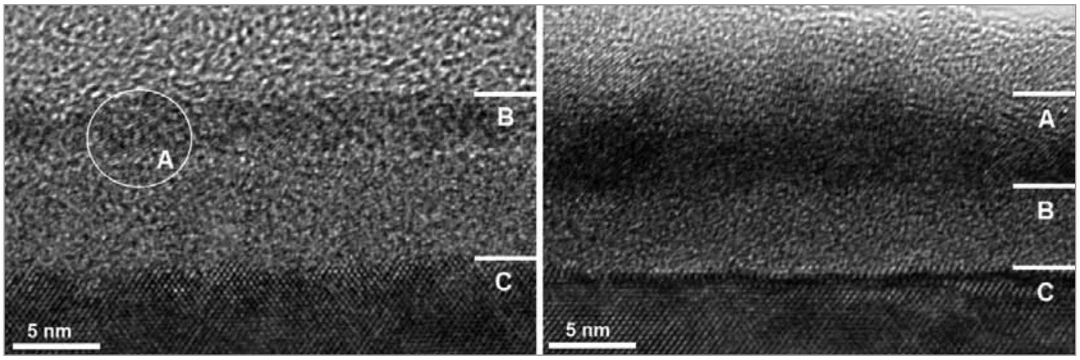


AFM images of (a) the rectangular DNA molecules with thiol linkers on mica (b) the rectangular DNA molecules with thiol linkers on SSMCC modified amine-terminated Si(111)

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 Connecticut)
Graduate Students: Kathryn Perrine, Juan Carlos Rodrígues-Reyes, Keith Douglas, Jia-Ming Lin (Chemistry & Biochemistry)
Funding: NSF



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

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 ultra-thin 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, the 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 both rely on the materials that are currently predicted to be suitable as diffusion barriers and branch into novel materials. ✧

PHOTOELECTROCHEMICAL SPLITTING OF WATER USING N:TiO$_2$ ANODE

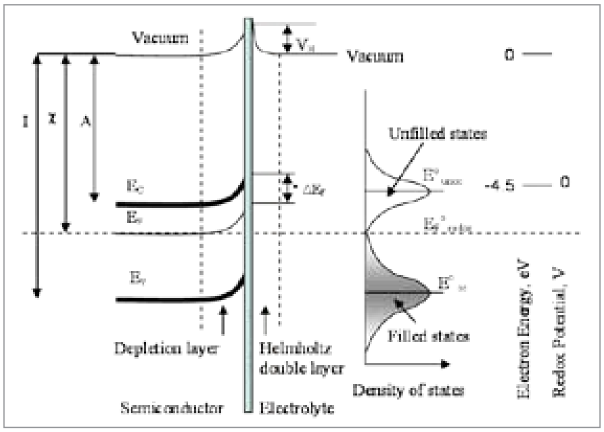
Faculty: Ismat Shah (Physics and Materials Science)

(continued from page 33)

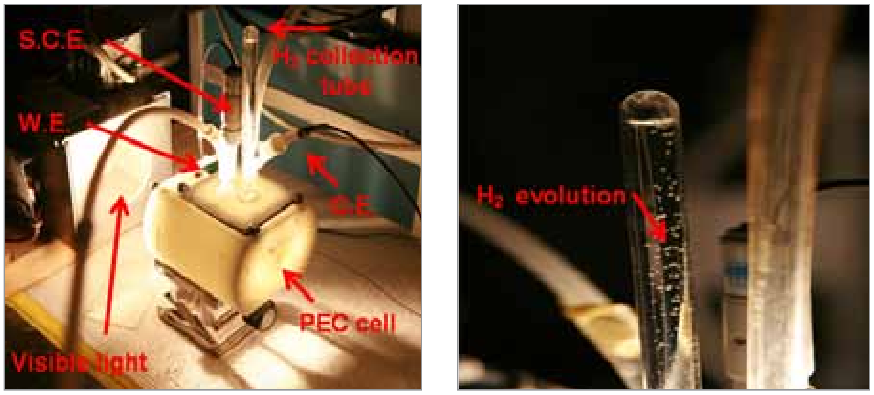
bility in TiO$_2$, which is caused by band bending.

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 °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.

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.



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

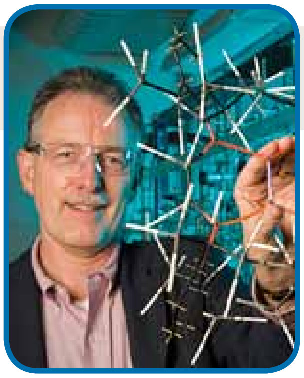


A photoelectrochemical cell using N:TiO$_2$ as the anode

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. ✧



Klaus H. Theopold

- **Professor and Chair of Chemistry and Biochemistry**
- **Associate Director, Center for Catalytic Science and Technology**

CONTACT INFORMATION

Phone: (302) 831-1546
E-mail: theopold@udel.edu
Web site: www.udel.edu/theopold/boss.html

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).

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

W.H. Monillas, G.P.A. Yap, K.H. Theopold, **"Synthesis and Structural Characterization of bis(μ2-Iodo)-bis(diethyl ether)-(N-N'-(bis(2,6-diisopropylphenyl)pentane-2,4-diketiminato)-lithium-chromium, a Cr(II) (β-diketiminato) Complex with a Coordinated LiI Salt,"** *J. Chem. Crystallogr.,* **39**, 377 (2009). (Erratum, *J. Chem. Crystallogr.*, 39, 544, 2009)

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W.H. Monillas, G.P.A. Yap, K.H. Theopold, **"Synthesis and Structure of (TMEDA)Cr(I)(2)(THF) and [(N,N-DMEDA)(2)CrI] I,"** *J. Chem. Crystallogr.,* **39**, 842 (2009).

J.F. Young, G.P.A. Yap, K.H. Theopold, **"2,4-Pentane N,N'-Bis(2,6-Diisopropylphenyl) Ketiminato Cobalt (II) (trimethylsilyl) Methylene,"** *J. Chem. Crystallogr.,* **39**, 846 (2009). (Erratum, *J. Chem. Crystallogr.*, 409, 85, 2010).

W.H. Monillas, G.P.A Yap, **"Synthesis and Structure of Chromium(II) Complexes Supported by Both a β-Diketiminate and an Amidinate Ligand,"** *J. Chem. Crystallogr.,* **39**, 849 (2009).

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

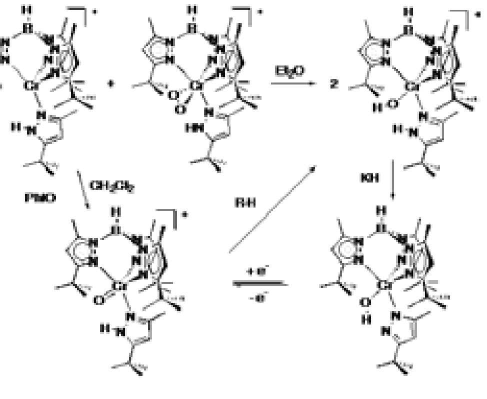
Chromium Dioxygen Complexes: We have prepared a series of chromium(III) superoxide complexes via binding of O_2 to coordinatively unsaturated chromium(II) precursors. These complexes are the first structurally characterized representatives of their kind [i.e. chromium(III) superoxide complexes], and 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 $Tp^{tBu.Me}Co{=}O$ in several reactions; however, this compound is apparently too reactive for even spectroscopic detection.



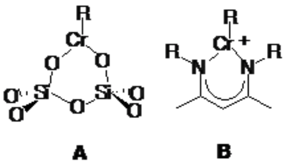
We have thus pursued the chemistry of isoelectronic imido complexes, $Tp^{tBu.Me}Co{=}NR$, as chemical models. For example, reaction of $Tp^{tBu.Me}Co(N_2)$ with Me_3SiN_3 yielded a cobalt(III) amido species resulting from hydrogen atom abstraction from the ligand by the inferred imido complex $Tp^{tBu.Me}Co{=}NSiMe_3$.

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

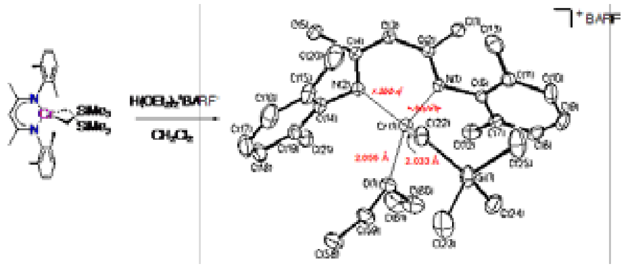
HOMOGENEOUS MODELS FOR CHROMIUM POLYMERIZATION CATALYSTS

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 on the right). To mimic the coordinatively unsaturated chromium on a hard oxide support, we have chosen N, N'-disubstituted diketiminate ligands ["$(R)_2$nacnac", as in *B*], i.e. bidentate nitrogen ligands that confer variable steric protection upon the chromium.



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



Extraordinarily low polydispersities (M_w/M_n=1.1-1.4) provide evidence for "living" polymerization catalysis, and the polymer microstructure of polyethylene produced with sterically encumbered $[(2,6\text{-}^iPr_2Ph)_2\text{nacnac Cr}(OEt_2)Me]$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)Me_2 on a zeolite (MCM-22) and characterized the resulting olefin polymerization catalysts by a variety of spectroscopic methods. ✧

Dionisios G. Vlachos

- » **Director, Catalysis Center for Energy Innovation**
- » **Director, Center for Catalytic Science & Technology**
- » **Elizabeth Inez Kelley Professor of Chemical Engineering**

CONTACT INFORMATION

Phone: (302) 831-2830
E-mail: vlachos@udel.edu
Web site: www.udel.edu/vlachos

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

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

D.G. Vlachos, 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 part of the plenary lecture).

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N. Kaisare, G.D. Stefanidis, D.G. Vlachos, **“Millisecond Production of Hydrogen from Alternative, High Hydrogen Density Fuels in a Cocurrent Multifunctional Microreactor,”** *Ind. Eng. Chem. Res.*, **48**, 1749-1760 (2009).

G. Mpourmpakis, D.G. Vlachos, **"The Effects of the MgO Support and Alkali Doping on the CO Interaction with Au,"** *Journal Phys. Chem. C,"* **113**, 7329-7335 (2009).

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W. Hauptmann, M. Votsmeier, J. Gieshoff, D.G. Vlachos, A. Drochner, H. Vogel, **"A Fast Approach to Predictive Models: NO-Oxidation in Exhaust Gas Aftertreatment Systems,"** *Topics in Catalysis,* **52(13-20)**, 1925-1928 (2009).

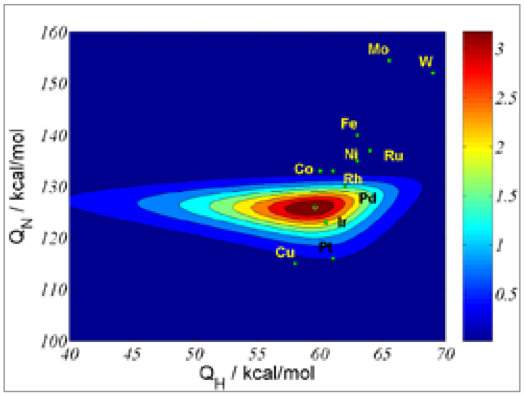
A.M. Karim, V. Prasad, G.Mpourmpakis, W.W. Lonergan, A.I. Frenkel, J.G. Chen, D.G. Vlachos, **"Correlating Particle Size and Shape of Supported Ru/γ-Al_2O_3 with NH_3 Decomposition Activity,"** *J. Am. Chem. Soc.,* **131**, 12230-12239 (2009).

MODEL-BASED DESIGN OF EXPERIMENTS AND CATALYSTS

Faculty: Dion Vlachos (Chemical Engineering), Vinay Prasad (Visiting Faculty), Matteo Maestri (Visiting Scholar)
Postdocs: Ayman Karim, Yiannis Mpourmpakis, Ying Chen (Chemical Engineering)
Graduate Students: Danielle Hansgen, Justin Federici, Michael Salciccioli (Chemical Engineering)
Undergrad Students: Zachary Ulissi, Anshu Arya (Chemical Engineering)
Funding: NSF-CBET

Experiments are typically carried out at certain conditions, and it is often found that only a small number of kinetic parameters are important (active) under those conditions. A natural question is whether one could design experiments based on a model, rather than statistical design, in order to increase the number of active model parameters and the accuracy of parameter estimation from data. We have developed a theoretical framework that enables us to increase the information content of models in order to use them reliably for catalyst and process optimization. In particular, a global search in experimentally feasible parameter space is conducted on the computer, using a Monte Carlo global search algorithm. At each point in parameter space, a reactor simulation is run using the current detailed kinetic model along with a local sensitivity analysis of experimentally measured responses with respect to kinetic parameters. Our objective is to identify suitable combinations of experimental variables that sensitize the maximum number of kinetic steps.

DFT-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 with 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 the figure below. ✧



Example of predicted volcano mountain projected to two-dimensions for identification of optimal catalysts for ammonia decomposition to hydrogen: ammonia conversion (normalized scale) vs. element heats of adsorption (kcal/mol). The elements indicate the performance of known catalysts.

RATIONAL STRATEGIES FOR NANOMATERIALS DESIGN

Faculty: Dion Vlachos, Raul Lobo (Chemical Engineering), Michael Tsapatsis (Univ. of Minnesota), Stavros Caratzoulas (Visiting Researcher)
Graduate Student: Khalid Al-Majnouni (Chemical Engineering)
Funding: NSF-NIRT

The demand for subnanometer control for nanomaterial fabrication and applications has refocused attention on microporous materials (e.g., zeolites). Their ordered crystalline microstructure and finely tuned nanometer-sized pores, coupled with well-established techniques for fabricating thin, oriented films, make them attractive for a wide range of current and future applications. Despite decades of research leveraging microporous materials for catalytic (e.g., hydrocarbon cracking, shape-selective catalysis) and non-catalytic applications (e.g., pressure swing adsorption, gas separation), rational design of new microporous films and fine tailoring of current materials demands a comprehensive understanding of these materials over a wide range of scales. Research in our group is focused on development of a comprehensive, fundamental understanding of zeolites and nanomaterial applications. This requires a multifaceted, multiscale approach involving research on understanding and controlling:

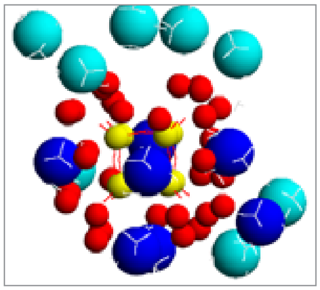
- Silica phase behavior and self-assembly of nanoparticle zeolite precursors
- Nucleation and mechanisms of zeolite growth
- Zeolite particle morphology
- Growth and preferential thin film (membrane) orientation
- Multiscale modeling of diffusion, separation, and reaction of interacting guest molecules in zeolite thin films under non-equilibrium conditions
- Non-destructive characterization of polycrystalline zeolite thin films
- Multiscale modeling of quantum dot formation

We employ an integrated experimental (e.g., SAXS, SANS, DLS, FTIR, TGA, SEM, XRD, fluorescence confocal optical microscopy) and theoretical (e.g., molecular dynamics, kinetic Monte Carlo, hierarchical parameterization techniques, continuum mesoscopic theories) approach to elucidate critical understanding at each scale. ✧

THERMODYNAMIC AND KINETICS OF NANOZEOLITIC PRECURSOR FORMATION

Faculty: Dion Vlachos, Stavros Caratzoulas, Raul Lobo (Chemical Engineering), Michael Tsapatsis (University of Minnesota)
Graduate Student: Khalid Al-Majnouni (Chemical Engineering)
Funding: NSF-NIRT

We employ a variety of tools, such as classical chemical equilibria, population balances, surface complexation models, the Poisson-Boltzmann equation, and molecular dynamics to unravel the thermodynamic driving force for nanoparticle formation and the kinetics of nanoparticle formation. Furthermore, we study nucleation of zeolites and the role of templates (organic and inorganic cations) on nanoparticle stabilization. A snapshot from a molecular dynamics simulation investigating templating effects is shown in the figure below. ✧



Snapshot from molecular dynamics simulation. The silica octamer in the center gets decorated by cations (tetramethyl ammonium cation), which expel water molecules from the bridged Si-O-Si oxygens protecting nanoparticles from hydrolysis.

HIERARCHICAL MULTISCALE MICROKINETIC MODEL DEVELOPMENT

Faculty: Dion Vlachos (Chemical Engineering), Vinay Prasad (Visiting Faculty), Matteo Maestri (Visiting Scholar)
Postdocs: Ayman Karim, Yiannis Mpourmpakis, Ying Chen (Chemical Engineering)
Graduate Students: Danielle Hansgen, Justin Federici, Michael Salciccioli (Chemical Engineering)
Undergrad Students: Zachary Ulissi, Anshu Arya (Chemical Engineering)
Funding: DOE-Hydrogen, NSF-CBET

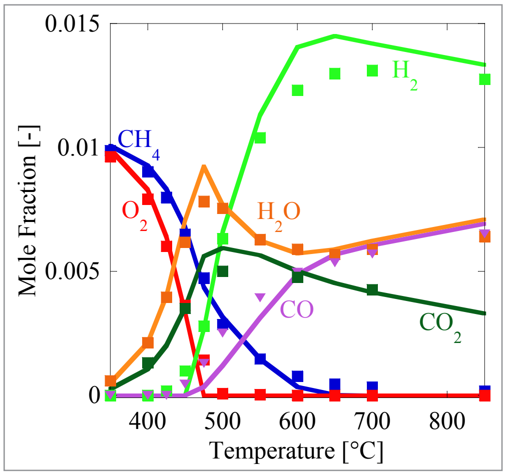
Predictive mathematical modeling based on fundamental fluid mechanics, multicomponent transport, and detailed chemistry is an invaluable tool in guiding experiments and reactor optimization. While computational fluid dynamics (CFD) simulators are commonplace, detailed reaction mechanisms are generally lacking for most important industrial processes. One approach for mechanism development is to extract all parameters from experimental data. The other is to do it based on quantum mechanical density functional theory (DFT). Both approaches have serious limitations.

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 noble metals 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)
- Partial oxidation and steam reforming at short contact times for syngas production
- Hydrogenation of alkenes and dehydrogenation of alkanes
- Oxidative dehydrogenation of alkanes to olefins
- Ammonia decomposition for hydrogen production

An example of the predictive capability of a detailed microkinetic model is depicted in the figure below. 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. ✧

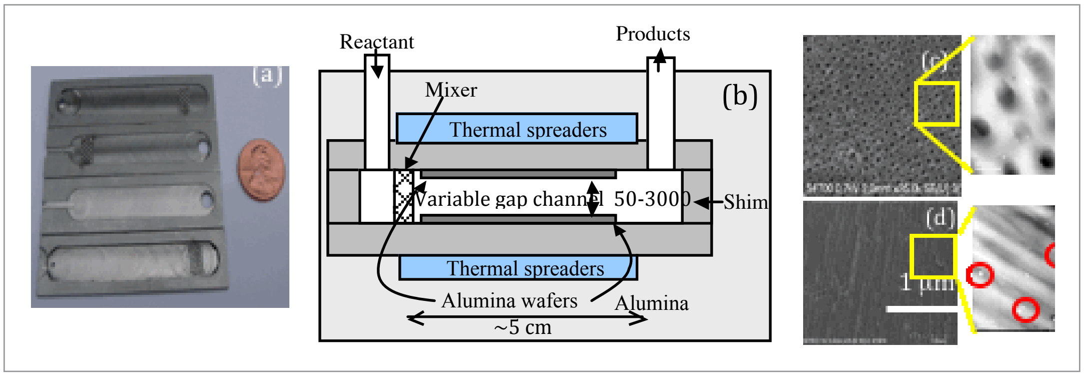


Comparison of experimental data (points) and simulations using our newly developed full microkinetic model (lines) for methane partial oxidation on Rh/Al_2O_3 catalysts

PROCESS INTENSIFICATION IN MULTIFUNCTIONAL MICROCHEMICAL SYSTEMS

Faculty: Dion Vlachos (Chemical Engineering), Erich Wetzel (U.S. Army Research Laboratory)
Postdoc: George Stefanidis (Chemical Engineering)
Graduate Students: Justin Federici, Matthew Mettler (Chemical Engineering)
Undergrad Student: Megan Zagrobelny (Chemical Engineering)
Funding: NSF-CBET

Future energy production will most probably happen at much smaller scales in a decentralized fashion. Since cost escalates with reduction of plant size, it is important to intensify processes. In order to achieve this, we employ microreactors whose transport rates are much faster than their large-scale counterparts. In addition, we impart multifunctionality in these microsystems, for example, by integrating endothermic and exothermic reactions via fast heat transfer through a separating wall to further intensify the system. As another example, we study catalytic membrane reactors. Our work employs multiscale modeling that builds on reduced kinetic models derived from fundamental microkinetic models along with computational fluid dynamics (CFD) simulations. In addition, we fabricate tunable microreactors with variable surface area, wall conductivity, surface to volume ratio, and no moveable parts for various energy generation applications. Processes of interest include partial oxidation, steam and dry reforming, autothermal reforming, dehydrogenation, hydrogenation, and ammonia decomposition for hydrogen production for fuel cells. Furthermore, we develop guidelines for fast ignition, optimal packing and statistic mixer structures, thermal management (e.g., recuperative and regenerative heat integration, such as reverse flow), and optimum operation of microreactors. In a related project, microreactors are coupled with thermoelectric elements to produce electricity in the Watt range or to produce compact reformers. ✧

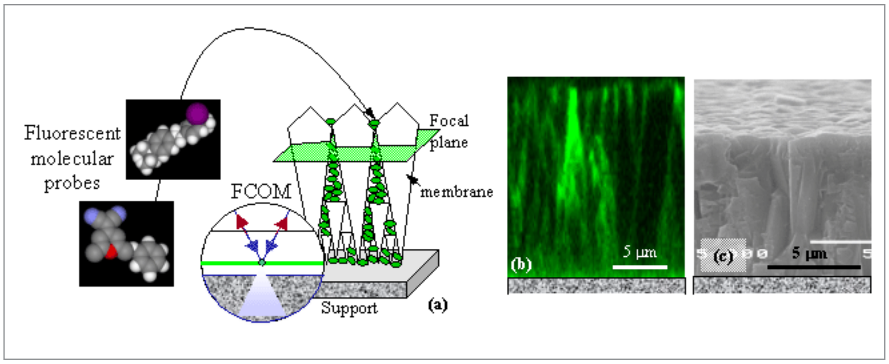


(a) Photograph of and (b) schematic side view (not to scale for ease of visualization) of a composite wall, tunable microreactor.
(c) Scanning electron micrograph (SEM) of a porous anodized alumina wafer ~75 μm thick (top view). The pores' diameter is ~50 nm.
(d) SEM of pores running across the wafer. Catalyst is deposited within the wafer via dip-coating. Pt nanoparticles are indicated at the right-most TEM images (red circles) at the pore mouth, but mainly within the pores, and are confirmed by elemental analysis. Micromixers 27 are also embedded.

NON-DESTRUCTIVE CHARACTERIZATION OF POLYCRYSTALLINE MICROPOROUS THIN FILMS

Faculty: Dion Vlachos, Raul Lobo (Chemical Engineering), Michael Tsapatsis (University of Minnesota), Stavros Caratzoulas (Visiting Researcher)
Graduate Student: Khalid Al-Majnouni (Chemical Engineering)
Funding: NSF-NIRT

A challenge in the development of theory and detailed simulation of diffusion through microporous thin films has been the prediction of permeation performance for real membranes that exhibit permeation anomalies (e.g., unexpectedly low selectivities and deviations from single-crystal theory). This underscores the need for quantitative characterization of microporous membrane polycrystallinity. Fluorescence confocal optical microscopy (FCOM) studies involving selective adsorption of dye molecules in polycrystalline features have highlighted the extent of this polycrystallinity in zeolite membranes. An example is shown in the figure on the right. Quantitative interpretation of FCOM images, however, has remained relatively elusive. Consequently, we are developing new experimental and image analysis protocols to more quantitatively characterize confocal images of dye-saturated zeolite membranes. ✧



(a) Non-destructive fluorescence confocal optical microscopy (FCOM) imaging of zeolite membranes (e.g., silicalite-1, NaX) with fluorescent dyes selectively adsorbed in non-zeolitic pathways characterizes (b) membrane polycrystallinity comparable to that observed via (c) SEM. Images shown here are for c-oriented silicalite-1 membranes.

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Front cover: Advanced characterization images of catalytic materials

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www.che.udel.edu/ccst

Center for Catalytic Science & Technology
University of Delaware
150 Academy Street
Newark, DE 19716-3119
Phone: (302) 831-8056
Fax: (302) 831-2085