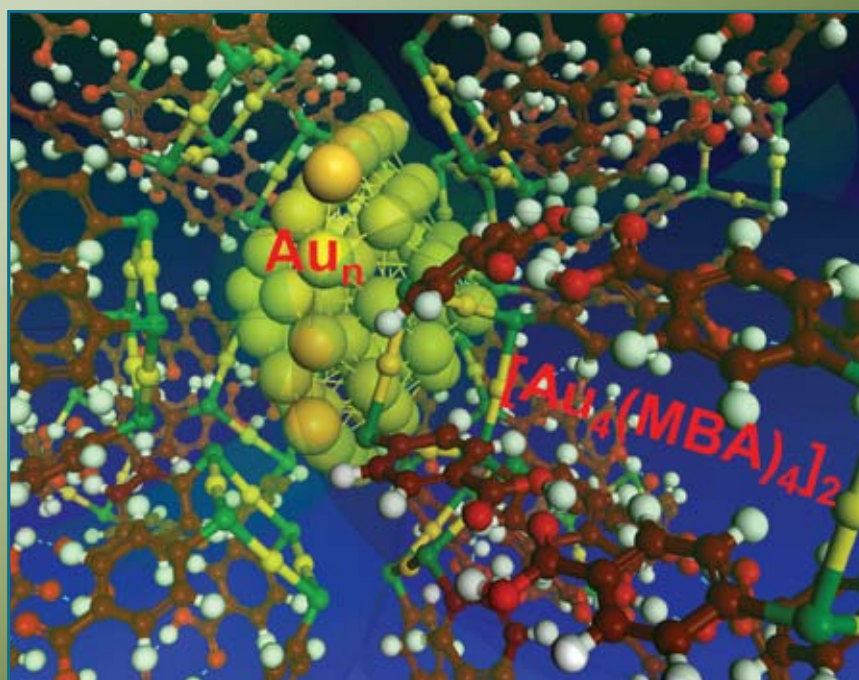


CCST

≡ Celebrating 30 years of research, education, and technology ≡

Center for Catalytic Science and Technology

2008 Research Report





From the Director:

Reflection of the past year

This past year has been a rewarding one for CCST with increased funding, over 80 journal publications, and many talks at national and international conferences. CCST faculty and students have won numerous awards. The quality and productivity of our research efforts continue to make CCST one of the leading academic catalysis centers worldwide.

Prof. Jingguang Chen stepped down from being the CCST director in December 2007. His leadership during the past nearly 8 years has been instrumental in taking the center to its current status. This year we launched the first issue of *CCST News*, our quarterly newsletter, with the hope of keeping sponsors, alumni, and friends abreast of recent CCST developments.

In addition to our traditional strength in surface science, heterogeneous and homogeneous catalysis, theoretical modeling, catalyst design, reactor design, and materials synthesis and characterization methods, many CCST faculty members are expanding their efforts in energy-related research. We are also more actively involved in the utilization and organization of the national synchrotron, neutron, and supercomputing facilities.

We hope you will find this report of the Center's activities informative and useful. We invite your questions, comments and visits, whether in person, by email, or via our website at [www.che.udel.edu/ccst]. We look forward to continuing fruitful collaborations with our industrial sponsors.

Thirty years of history

It has been 30 years since the center was dedicated in April 1978. The Center for Catalytic Science and Technology was formally established in 1977 following 9 years of catalysis research from a nucleus of faculty hired in the chemical engineering department around 1969. Arthur B. Metzner, then chairman of the department, was instrumental in supporting the idea of a center. The first director of CCST was Jim Katzer (later with Mobil Research and Development Company). Bruce Gates was one of the co-founders, and later one of the directors who brought a lot of energy and enthusiasm to CCST activities. Ken Bischoff was among the first group of faculty who significantly contributed to the CCST success over many years. George Schuit from Eindhoven joined in 1970 for a sabbatical year and came back regularly for succeeding years. He provided much of the expertise for catalysis. Al Stiles from DuPont in the role of a research professor brought in 42 years of industrial experience in the early 1970s that guided the group. The first generation of CCST faculty was later expanded by a vigorous group of young faculty including Mark Barteau, Cecil Dybowski, Hank Foley, Michael Klein, Doug Ridge from both the chemical engineering and chemistry and biochemistry departments. Other past CCST faculty include J. Bulkowski, H. Gold, S. Groh, D. Heck, H. Kwart, J. Olson, A. Rheingold, G. Schrader, R. Weber.

The industrial advisory council, led at first by Paul Weisz of Mobil, has always been instrumental in identifying opportunities for research and strengthening industry-CCST relations. Many industrial sponsors (12 in 1978-79 and 23 in 1981) have partnered over the years with CCST faculty. This has always been and continues to be an important avenue for funding, research ideas, education enhancement, and collaboration. With the change in funding and corporate strategies, CCST funding has also shifted from mainly (~70%) industrial in the first few years to mainly federal in the past few years. NSF and DOE have been instrumental in supporting CCST research.

Reflecting on the success of CCST over the past 30 years, education of graduate students and postdocs has always been central to the center's mission. Hundreds of CCST alumni are working around the globe. More than 70% of our alumni have found employment with CCST sponsors. A large fraction of our alumni have obtained academic positions and have been very successful.

The annual CCST expenditures (at the level of \$2.5 to \$3 million), the number of publications (over 80), the number of graduate students and postdocs (over 60), and the large number of attendees (over 100) in our annual symposia over the past few years (under the directorship of Jingguang Chen) speak to the vibrant environment of CCST and the continuous success of the center in the future.

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Air Liquide - Medal

Dr. Pascal Tromeur Division of Air Liquide Advanced Technologies
305 Water Street
Newport, DE 19804-2410

BASF

Dr. Friedbert Nees Catalysis Research & Development
101 Wood Avenue
Iselin, NJ 08830

The Dow Chemical Company

Dr. Daniel Trauth 1500 E. Lake Cook Road
Buffalo Grove, IL 60089

Eastman Chemical Company

Dr. Steven Perri P.O. Box 1972
Kingsport, TN 37662

Headwaters

Dr. Bing Zhou 1501 New York Avenue
Lawrenceville, NJ 08648

Lummus Technology – A CB&I Company

Dr. Anne Gaffney 1515 Broad Street
Bloomfield, NJ 07003-3096

Mitsubishi Chemical Corporation

Mr. Soichiro Yamada Petrochemicals Segment
1, Toho-cho, Yokkaichi, Mie
510-8530 Japan

Rohm & Haas Company

Dr. Michael Clark 727 Norristown Road
Spring House, PA 19477

UOP LLC

Dr. Simon Bare 25 East Algonquin Road
Des Plaines, IL 60016

UTC Power

Dr. Lesia Protsailo 195 Governor's Highway
South Windsor, CT 06074

W.L. Gore & Associates

Dr. Will Johnson 201 Airport Road
P.O. Box 1488
Elkton, MD 21922-1488

W.R. Grace & Co.

Dr. Wu-Cheng Cheng 7500 Grace Drive
Columbia, MD 21044

Industrial Sponsors Program

The Center's 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.

Sponsorship

Participation in the Center Industrial Sponsors Program may be established or renewed annually via one of the following six options:

1. Grant of \$10,000 to CCST
2. Total grants to CCST faculty of \$30,000
3. Gifts-in-kind of \$30,000 or more
4. Full support of graduate student fellowship
5. Research contract
6. Joint industry-academic grant

The first four options above represent forms of unrestricted gifts and are subject to only nominal indirect costs. Research contracts may involve specific work statements, patent and publication terms, and are subject to standard University indirect cost rates.

Benefits to Sponsor

All industrial sponsors, regardless of the sponsorship mechanism chosen, can benefit from the full portfolio of Center research activities. The Center mounts a number of programs designed to provide early access to non-proprietary research results including:

- An annual research review at which the results of ongoing Center research programs are presented
- An annual report of the Center's research activities and accomplishments

Other benefits to our sponsoring companies include:

- Access to CCST facilities and faculty
- Interaction with CCST collaborators
- Recruitment of students
- Access to Center software



Research Grant	Funding Agency	Investigators
Experimental and Theoretical Studies of Surface Oxametallacycles-Connections to Heterogeneous Olefin Epoxidation	Department of Energy (3/06-3/09)	Mark Barteau
From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity	Department of Energy (9/03-9/09)	Mark Barteau, Doug Buttrey, Jingguang Chen, Jochen Lauterbach, Raul Lobo, Dion Vlachos
An Integrated Approach Toward Rational Nanocatalyst Design for Hydrogen Production	Department of Energy (9/05-8/08)	Doug Buttrey, Jochen Lauterbach, Dion Vlachos
Structure/Property Relationship in Metal Carbides and Bimetallic Alloys	Department of Energy (8/00-11/09)	Jingguang Chen
Dedicated Synchrotron Facilities for Catalysis	Department of Energy (9/05-8/11)	Jingguang Chen
Alternative Electrocatalysts	National Science Foundation (9/05-8/09)	Jingguang Chen
Catalyst Characterization Using Synchrotron Techniques	UOP (10/05-10/08)	Jingguang Chen
Catalyst Characterization	Lummus Tech. (3/07-8/08)	Jingguang Chen
Synthesis and Characterization of Electrocatalysts	UTC Power (12/07-12/08)	Jingguang Chen
Design of Bimetallic Catalysts	W.R. Grace & Co. (7/08-6/09)	Jingguang Chen
Tungsten Carbides as Cathode Materials	Department of Energy (1/07-12/09)	Jingguang Chen
Supercapacitors	Naval Research (1/08-12/10)	Jingguang Chen
Novel Photocatalysts With One- and Two-Dimensional Nanostructures	Department of Energy (9/07-8/10)	Doug Doren, Raul Lobo
Combined High-Throughput Spectroscopic and Modeling Approach to the Study of Heterogeneous Catalysts	National Science Foundation (4/04-4/08)	Jochen Lauterbach
High-Throughput Screening of Catalysts	Mitsubishi Chemicals (3/07-3/09)	Jochen Lauterbach
Solar Hydrogen IGERT	National Science Foundation (7/06-6/11)	Jochen Lauterbach, Christiana Honsberg, Thomas Beebe, Robert Opila, Suresh Advani
Unique Photo-Assisted Thermoelectric Materials and Devices	ATP (7/07-7/09)	Ismat Shah
Photocatalytic Degradation of PAH	NSF DMR (7/08-7/10)	Ismat Shah
Structural Investigation of Prostaglandin Conjugates (NIH MERIT Award)	GM 42056 (1993-2011)	Doug Taber
Structural Investigation of Prostaglandin Conjugates (National Institute of Health Research Grant)	GM 60287 (2000-2008)	Doug Taber
Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer	Department of Energy (9/06-8/09)	Klaus Theopold
Computationally Guided Design of Catalysts for Fluoroolefin Polymerization	National Science Foundation with DFG (8/06-7/09)	Klaus Theopold
Hierarchical Stochastic Algorithms for Materials Engineering	National Science Foundation (9/08-8/12)	Dion Vlachos
Hierarchical Multiscale Model-Based Process Engineering	National Science Foundation (3/07-2/10)	Dion Vlachos
Multiscale Modeling of Spatially Distributed Biological Systems	Department of Energy (8/05-8/08)	Dion Vlachos
Controlling Catalytic Microcombustors as Heat or Chemical Machines	National Science Foundation (8/07-7/10)	Dion Vlachos
Microchemical Technology for Future Energy Needs	National Science Foundation (8/07-8/10)	Dion Vlachos
Perovskite Buffer Layers for Compound Semiconductor Silicon Heteroepitaxy	National Science Foundation Career Award (2/03-2/09)	Brian Willis
Tunneling Spectroscopy for Nanofabricated Biochemical Sensors	National Science Foundation (6/06-6/09)	Brian Willis
Heteroepitaxy of Perovskite Oxide Layers on Si(100) by CVD	Intel Corporation (6/07-6/09)	Brian Willis
Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells	Department of Energy (6/07-6/10)	Brian Willis, Jingguang Chen
Next Generation Biochemical Sensors Based on Tunneling Spectroscopy	Department of Defense (2/08-2/11)	Brian Willis

» Meet the Faculty



Dionisios G. Vlachos, Director
Professor of Chemical Engineering

PhD – University of Minnesota (1992)
MS – University of Minnesota (1990)
BS – National Technical University of Athens, Greece (1987)

Contact Information:

(302) 831-2830
vlachos@udel.edu
www.che.udel.edu/vlachos

Research Interests:

Multiscale simulation, reacting flows, reaction mechanism development, microreactors, portable power, energy, crystal growth, nanomaterials, zeolites, membranes, separations, cellular engineering and cancer

Recent Awards/Research Accomplishments:

2007: George Piercy Distinguished Visiting Professor, Chemical Engineering and Materials Science Department, Univ. of Minnesota
2005-Present: Affiliated Member, Institute of Chemical Engineering and High Temperature Chemical Processes (ICE-HT) of FORTH (Foundation for Research and Technology, Hellas), Patras, Greece



Mark A. Barteau
Robert L. Pigford Chair of Chemical Engineering

PhD – Stanford University (1981)
MS – Stanford University (1977)
BS – Washington Univ. (1976)

Contact Information:

(302) 831-8905
barteau@udel.edu
www.che.udel.edu/barteau

Research Interests:

Surface science and catalysis by metal oxides and metals; acid-base catalysis; application of density functional theory to surface reactions; self-assembly of inorganic materials, scanning probe microscopies

Recent Awards/Research Accomplishments:

2008: Senior Vice Provost for Research and Strategic Initiatives, UD
2006: National Academy of Engineering
Associate Editor: Topics in Chemical Engineering, Oxford Univ. Press
Associate Editor: Journal of Vacuum Science and Technology A, American Vacuum Society



Douglas J. Buttrey
Professor of Chemical Engineering

PhD – Purdue University (1984)
MS – Purdue University (1978)
BS – Wayne State Univ. (1976)

Contact Information:

(302) 831-2034
dbuttrey@udel.edu
www.che.udel.edu/buttrey

Research Interests:

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

Recent Awards/Research Accomplishments:

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



Jingguang G. Chen
Claire D. LeClaire Professor of Chemical Engineering

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

Contact Information:

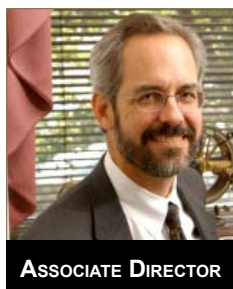
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Research Interests:

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

Recent Awards/Research Accomplishments:

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
2004-Present: Editorial Board: *Surface Science Reports*
2005-Present: Prof. of Chemistry (courtesy appointment), UD



Douglas J. Doren
Professor of Chemistry & Biochemistry

PhD – Harvard University (1986)
AM – Harvard University (1981)
BS – Univ. of Berkeley (1979)

Contact Information:

(302) 831-1070
doren@udel.edu
www.udel.edu/doren

Research Interests:

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

Recent Awards/Research Accomplishments:

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



Jochen A. Lauterbach
Professor of Chemical Engineering

PhD – Free University of Berlin (1994)
BS – University of Bayreuth (1992)

Contact Information:

(302) 831-6327
lauterba@udel.edu
www.che.udel.edu/lauterbach

Research Interests:

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

Recent Awards/Research Accomplishments:

- Discovered high activity catalysts for ammonia decomposition
- Designed selective catalysts for epoxidation
- Developed better after-treatment catalysts



Raul F. Lobo
Professor of Chemical Engineering

PhD – California Inst. of Technology (1995)
MS – California Inst. of Technology (1993)
BS – University of Costa Rica (1989)

Contact Information:

(302) 831-1261
lobo@udel.edu
www.che.udel.edu/lobo

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 in porous materials for applications in catalysis.

Recent Awards/Research Accomplishments:

- Found evidence for non-classical nucleation and crystal growth mechanisms in zeolite beta.
- Discovered the formation of O-O bonds from point defects (hydroxyl nests) in zeolites. These sites may lead to unexpected redox processes in parallel with desired catalytic processes at high temperatures.
- Reported a new mechanism for the decomposition of Brønsted acid sites in zeolites at high temperatures. The new decomposition pathway produces hydrogen gas and an oxidized site with a structure that remains to be determined. High temperature and oxidative conditions, such as those found in fluidized catalytic cracking, could lead to the formation of these new sites in FCC catalysts.
- Reported that ETS-10 microporous titanosilicates, doped with vanadium in the chains, have high photocatalytic activity for the decomposition of small hydrocarbons at room temperature.



S. Ismat Shah
Professor of Physics & Materials Science

PhD – University of Illinois at Urbana-Champaign (1986)
BE – University of Karachi, Pakistan, Bachelor of Engineering (1976)

Contact Information:

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ismat@udel.edu
www.udel.edu/mse/Faculty/Shah.htm

Research Interests:

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

Recent Awards/Research Accomplishments:

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

» Meet the Faculty



Douglass F. Taber

Professor of Chemistry & Biochemistry

PhD – Columbia University (1974)
BS – Stanford University (1970)

Contact Information:

(302) 831-2433
taberdf@udel.edu
valhalla.chem.udel.edu

Research Interests:

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

Recent Awards/Research Accomplishments:

- Development of new organic reactions for active natural products
- Invited speaker at ACS National Meeting (2006)
- Invited speaker at ACS Middle Atlantic Regional Meeting (2006)
- Invited speaker at Symposium, C-H Activation in Organic Synthesis (2007)



Andrew V. Teplyakov

Assoc. Prof. of Chemistry & Biochemistry

PhD – Columbia University (1997)
MS – Columbia University (1993)
BS – Moscow State University (1992)

Contact Information:

(302) 831-1969
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Research Interests:

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

Recent Awards/Research Accomplishments:

- 2008: Organizer of the Surface Science session at the EAS
- 2008: Research featured on the cover of *Langmuir*
- 2008: Invited Review, *Surface Science Report*
- 2007: Invited speaker, Gordon Research Conference on Chemical Reactions at Surfaces (Ventura, CA)
- 2007: Invited speaker, Eastern Analytical Symposium (Somerset, NJ)
- 2007: Invited speaker, 233rd National Meeting of the American Chemical Society (Chicago, IL)
- 2007: Invited Concept Paper, *Chemistry-A European Journal*



Klaus H. Theopold

Professor of Chemistry & Biochemistry

PhD – Univ. of California, Berkeley (1982)
BS – Universität Hamburg, Germany (1977)

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Research Interests:

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

Recent Awards/Research Accomplishments:

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



Brian G. Willis

Assistant Professor of Chemical Engineering

PhD – Massachusetts Institute of Technology (1999)
BS – Northwestern Univ., Illinois (1993)

Contact Information:

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Research Interests:

Experimental and computational chemistry investigations of surface reactions for nanoelectronics and energy applications, including atomic layer deposition processes

Recent Awards/Research Accomplishments:

- 2008: Patent application filed for "Method of Fabricating Monolithic Nanoscale Probes"
- 2008: Invited Speaker EAS
- 2008: Achieved epitaxial Sr/Si templates by ALD for oxide heteroepitaxy on silicon
- 2008: Demonstrated first reversible adsorption/desorption and detection with IETS in a monolithic nanoscopic tunnel junction
- 2007-2008: CNMS User Grant at Oak Ridge National Laboratory
- 2007: Nanotech Measurement Contest (sponsored by Keithley Instruments, Inc.)



Name	Advisor	Degree	Research Topic
Ali, Bakhtyar	Shah	PHYS	Nanocomposite Solar Cells
Bai, Sha	Taber	CHEM	Phosphonate Reagents for Aldehyde Homologation
Bao, Leijie	Shah	MSEG	High K Dielectric Thin Films
Bedenbaugh, John	Lauterbach	CHEG	Model Catalysts for High-Pressure Spectroscopic Investigations
Berry, James	Taber	CHEM	Rh-Mediated Amination of Esters
Bilbao, Danny	Lauterbach	CHEG	Non-Linear Dynamics of No + NH ₃ Reaction
Boppana, Venkata Bharat Ram	Lobo	CHEG	Novel Photocatalysts
Chan, Sze Chi (Joan)	Barteau	CHEG	Photochemistry and Photocatalysis of Oxide Nanoparticles
Chung, Kimberly	Buttrey	CHEG	Characterization of Complex Layered Nickelates
Collins, Stuart	Vlachos/Ogunnaik	CHEG	Multiscale Modeling of Diffusion-Reaction Processes
D'Addio, Elizabeth	Lauterbach	CHEG	Discovery of NH ₃ Decomposition Catalysts
Dellamorte, Joseph	Barteau/Lauterbach	CHEG	Investigation of Silver Catalyzed Olefin Epoxidation through Traditional & High-Throughput Techniques
DeMatteo, Peter	Taber	CHEM	Polycarbocycles from Alkenes
Douglass, Keith	Teplyakov	CHEM	Surface Passivation and Functionalization
Esposito, Daniel	Chen/Birkmire	CHEG	Photoelectrochemical Device for Water Splitting
Federici, Justin	Vlachos	CHEG	Microrreaction Technology for Portable Power Generation
Fickel, Dustin	Lobo	CHEG	Redox Sites in Zeolites
Gerstenhaber, David	Taber	CHEM	Enantiomerically-Pure Cyclohexenones from Epoxides
Goda, Amit	Chen/Barteau	CHEG	C-H Bond Activation by Bimetallic Surfaces
Guo, Pengfei	Taber	CHEM	One-Electron and Two-Electron Construction of Alkylated Quaternary Centers
Gupta, Rahul	Willis	CHEG	Electrode Strategies for Molecular Electronics Devices
Hansgen, Danielle	Vlachos/Chen	CHEG	Hydrogen Production from Alternative Fuels
Hassanain, Ghulam	Shah	PHYS	Nanomagnetism
Hould, Nathan	Lobo	CHEG	Zeolite Synthesis Mechanisms
Hsu, Irene	Willis	CHEG	Electrode Structure Effects in Molecular Devices
Humbert, Michael	Chen	CHEG	Synthesis and Evaluation of Electrocatalysts
Javadekar, Ashay	Barteau	CHEG	Mechanisms of Promoters in Olefin Epoxidation
Jove, Fernando	Theopold	CHEM	Small Molecule Activation with Iron Complexes
Leftwich, Timothy R.	Teplyakov	CHEM	Surface Chemistry on Silicon Surfaces and in Molecule Corrals
Li, Xin	Barteau/Buttrey	CHEG	Synthesis and Reactivity of Complex Bismuth Molybdates
Lonergan, William	Chen/Vlachos	CHEG	Synthesis and Characterization of Supported Catalysts
Lukaski, Adrienne	Barteau	CHEG	Olefin Epoxidation on Bimetallics
Madachik, Mark R.	Teplyakov	CHEM	Surface Self-Assembly and Co-Adsorption on Semiconductors
Mellinger, Zach	Chen	MSEG	Supercapacitors and Electrochemistry
Menning, Carl	Chen	CHEG	Bimetallic Cathode Electrocatalysts
Mettler, Matthew	Vlachos	CHEG	Process Intensification in Catalytic Reactors
Miao, Yinghong	Shah	MSEG	Quantum Dot Solar Cells
Monillas, Wesley	Theopold	CHEM	Small Molecule Activation with Chromium Complexes
Nash, Michael	Lobo/Doren	CHEG	Microporous Photocatalysts
Nelson, Christopher	Taber	CHEM	Applications of KH in Organic Synthesis
Paquette, Craig	Taber	CHEM	Synthesis of Mesembrine
Perrine, Kathryn A.	Teplyakov	CHEM	Photochemistry in Metal Deposition on Semiconductors
Pyrz, William D.	Buttrey/Lobo	CHEG	Characterization of Catalytic Materials Using Analytical & High-Resolution Electron Microscopy
Qiu, Tingzhu	Barteau	CHEG	Reactions of Multifunctional Reagents on Oxide Surfaces
Ren, Hui	Chen	CHEM	Bimetallic Catalysts
Rodriguez-Reyes, Juan Carlos	Teplyakov	CHEM	Diffusion Barriers and Interface Chemistry
Saliccioli, Michael	Vlachos	CHEG	Modeling and Experiments of Thermochemical Transformation of Biomass
Schmidt, Heather	Doren	CHEM	Doped Metal Oxides for Solar Fuel Production
Schulz, Meghan	Shah	MSEG	Nanostructured Oxides for Photochemical Reactions
Sheth, Ritesh	Taber	CHEM	Fe-Mediated Cyclohexenone Annulation
Shough, Anne Marie	Doren	CHEM	Photocatalytic Oxidation of Hydrocarbons in a Nanoporous Titanosilicate
Skliar, Dimitri	Willis	CHEG	Chemistry of Atomic Layer Deposition of SrTiO ₃
Skoplyak, Orest	Chen/Barteau	CHEG	Oxygenate Reactions on Bimetallic Surfaces
Stottlmyer, Alan	Chen	CHEG	Carbides as Alternative Electrocatalysts
Tian, Weiwei	Taber	CHEM	Synthesis of Sordaricin
Vijay, Rohit	Lauterbach	CHEG	Development of Novel High-Throughput Screening Techniques for Supported Catalyst Samples
Winski, David	Lauterbach	CHEG	Study of Catalytic Reactions Using Photo-Modulated Infrared Spectroscopy
Yang, Hua M.	Buttrey	CHEG	Advanced Characterization of Nanocatalysts for Ammonia Decomposition
Yessetepe, Emre	Shah	MSEG	Thermoelectric Nanocomposites
Young, John	Theopold	CHEM	Selective Ethylene Oligomerization Catalyzed by Chromium
Zhang, Xiaochun	Teplyakov	CHEM	Interface Chemistry of Biochemical Systems on Semiconductors

Alumni, Visiting Researchers & Postdocs

Postdoctoral Fellows & Visiting Researchers

Name	Advisor	Research Topic
Abbas, Manzar	Shah	Composite Nanostructures for Photovoltaics
Ahmed, Akhlaq	Shah	Co-Doped TiO ₂ ; Optical and Electronic Properties
Bourbakis, Yannis	Vlachos	First Principles Modeling of Catalyst Nanoparticle Synthesis and of Support Effects in Catalysis
Caratzoulas, Stavros	Vlachos	First Principles Simulations of Silicate Chemistry
Chakraborty, Purnendu	Vlachos	Multiscale Modeling of Membrane Dynamics
Chen, Ying	Vlachos	DFT and Microkinetic Modeling of Hydrocarbon Processing
Gunay, Ahmet	Theopold/Bartea	Heteropolyacid Catalysts
Guo, Peiming	Taber	New Catalysts for the Cyclocarbonylation of Alkenyl Cyclopropanes
Liu, Jianzhong	Doren	Ab Initio Thermodynamics of Aerosols and Proteins
Prasad, Vinay	Vlachos	Microkinetic Model-Based Design of Experiments and Catalysts
Rykov, Sergey	Chen	NEXAFS and Surface Spectroscopies
Scarpa, Andrea	Vlachos	Heat Regeneration Strategies in Chemical Reactors
Snively, Chris	Lauterbach	Development of Novel Spectroscopic Techniques
Stefanidis, George	Vlachos	Short Contact Time Multifunctional Reactors
Yamada, Soichiro	Lauterbach	High-Throughput Catalysis
Zhang, Changbin	Willis	Atomic Layer Deposition of Epitaxial Oxides

2006-2007 Alumni

Name	Advisor	Current Employer
Addo, Ernest	Shah	GE Solar
Baker, Colin	Shah	Air Force Research Laboratory
Beadle, Kendra	Chen/Willis	
BinTaleb, Abdulmalik	Theopold	SABIC (Saudi Arabia)
Bocharov, Semyon	Teplakov	Subsidiary of Schulmberger, Inc. (Kazan, Russia)
Buffone, Gerald	Theopold	Chipola College
Chung, Kimberly	Buttrey	
Cuadra, Amalia	Willis	Philadelphia School District
Deshmukh, Soumitra	Vlachos	Velocys
Enever, Michael	Bartea	Air Products
Fedeyko, Joseph	Lobo/Vlachos	Johnson Matthey
Frankowski, Kevin	Doren	University of Kansas
Frey, Jeffrey	Doren	University of Delaware
Goyal, Amita	Shah	University of Delaware
Guerin, Daniel	Shah	Naval Research Laboratories
Huang, Wei	Chen	Air Liquide
Kreisel, Kevin	Theopold	Postdoc, University of Wisconsin at Madison
Lopez, Liza	Bartea	DuPont
Ludwig, Jeffrey	Vlachos	ExxonMobil
Martinez-Inesta, Maria	Lobo	Faculty, Chemical Engineering, University of Puerto Rico of Mayagüez
Mayawala, Kapil	Vlachos/ Edwards	Novartis
McCormick, John	Chen	Rohm & Haas
McMillan, Noah	Lauterbach	Eastman Chemicals
Murillo, Luis	Chen	DuPont
Peddy, Mahitha Reddy	Theopold	
Pirolli, Laurent	Teplakov	Schlumberger, Inc.
Pradhan, Anshu	Shah	Novellus
Ren, Chelsea	Chen	Lummus Technology
Rimer, Jeff	Lobo/Vlachos	New York University
Shay, D.Travis	Theopold	Lyondell Chemical Corp.
Sikkander, Inthi	Taber	Albany Molecular
Snyder, Mark	Vlachos	University of Minnesota
Taluskie, Karen	Taber	Cambridge Isotopes
Vijay, Rohit	Lauterbach	ExxonMobil
Waite, Matthew	Shah	Faculty, Physics, West Chester University
Washburn, Seth	Lauterbach	ExxonMobil
Weigert, Erich	Chen	Johnson Matthey
Zellner, Michael	Chen	Los Alamos National Laboratory



Mark A. Barteau

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Jochen A. Lauterbach

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Raul F. Lobo

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(continued on page 12)

Redox Sites in Acid Zeolites

Faculty: Raul Lobo (Chemical Engineering)

Graduate Students: Dustin Fickel, Khalid Al-Majnoui (Chemical Engineering)

We study the chemistry of zeolites at high temperatures with the aim of determining the properties and structure of sites responsible for redox processes observed when organic molecules are adsorbed on the zeolite after heating. In particular, we have been investigating the thermal decomposition of zeolite Brønsted acid sites. The zeolite framework is composed of $[\text{SiO}_4]$ and $[\text{AlO}_4]^-$ tetrahedra, where the charge of the aluminum site is balanced by metal cations or protons (H^+) in the zeolite pores. The protons in zeolites coordinate to the framework to form Brønsted acid sites (BAS) $\text{Si}-\text{OH}-\text{Al}$. The OH group of the acid sites gives rise to an absorption band in the $3630\text{--}3660\text{ cm}^{-1}$ region of IR spectra and if a zeolite is heated above 873 K, the intensity of this vibration decreases until it disappears. This dehydroxylation of BAS has been assigned to the dehydration of two neighboring acid sites as described in Scheme 1 (on the next page), leading to Lewis acid sites believed to be important in the cracking of hydrocarbons at high-temperature.

The model of Scheme 1 is generally accepted and appears to be the dominant mechanism of dehydroxylation for zeolites with high aluminum content. However, in zeolites with low aluminum content—less than 10% with respect to silicon—the BAS are isolated from each and there is an energetic cost associated with the charge separation depicted in Scheme 1. We have recently investigated the dehydroxylation of high-silica H-zeolites using mass spectrometry-temperature programmed desorption (MS-TPD), and we have found that the main product is hydrogen gas. Figure 1 (on page 10) shows the MS-TPD of two samples of H-ZSM-5 heated stepwise to 250 °C, 525 °C and 750°C. During the third temperature ramp, mostly hydrogen is observed with only a small amount of water detected. 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 BAS of high-silica zeolites thermally decompose by a redox process, not by dehydration. This is a very unexpected result, and it is possible that some of what is believed to be acid catalysis at high temperatures in zeolites is, in fact, redox chemistry.

(continued on page 10)

Complex Transition Metal Oxides for Selective Oxidation

Faculty: Doug Buttrey (Chemical Engineering)

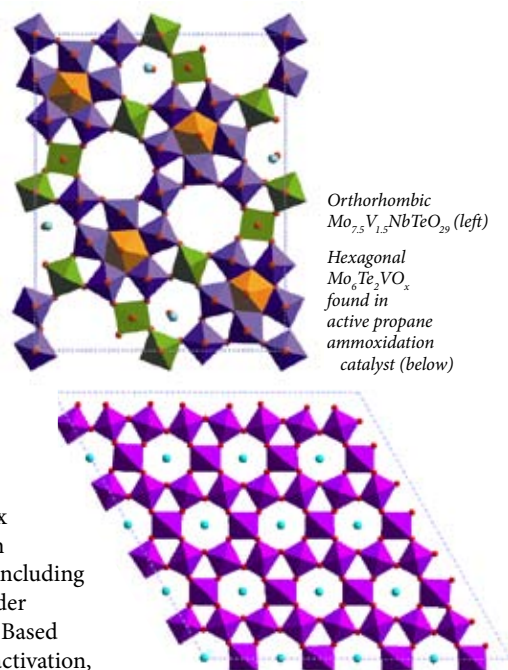
Graduate Student: William Pyrz (Chemical Engineering)

Highly selective, atom-efficient catalytic reactions are not only desired, but also mandatory in the petroleum and petrochemical industry. Since raw materials are increasingly becoming a proportion of the total end product cost, it is cost effective to preserve as much of the carbon from the feed material as possible. Any portion of the feed carbon lost or destroyed during catalytic reactions is waste product, usually unusable and often environmentally undesirable and expensive to dispose of. An example of atom-efficient catalytic reactions is selective oxidation of hydrocarbons in cases where the oxidation can be properly controlled. An approach used in obtaining desired selectivity is the application of the site isolation principle to the catalyst design. The principle states, in its simplest form, that surface oxygen, functional groups, or aggregates of functional groups must be spatially ordered on the catalyst surface in order to gain catalytic selectivity. Too much accessible oxygen in close proximity on the surface leads to complete combustion and waste.

Controlled site isolation should give us the opportunity to stop oxidation reactions at desired products instead of resulting in complete combustion. This is accomplished by controlling the accessible extent of oxidation at the local site. For example, we should be able to convert propane to propylene, isobutane to isobutylene, and ethyl benzene to styrene. All of these reactions are currently accomplished commercially by conventional catalytic dehydrogenation. However, dehydrogenation is equilibrium limited, requiring extensive recycle of unconverted feed material, and highly endothermic, requiring enormous amounts of energy to be supplied to the reactors. Conversely, controlled oxydehydrogenation and ammoxidation have no thermodynamic limitation (therefore, 100% product is theoretically possible with one pass) and they are exothermic, hence requiring no external heat input. It is well known that these reactions have great commercial importance in the petroleum and petrochemical industry, and an improvement in the efficiency would be highly desirable. Our approach provides a new and more energy-efficient pathway.

Bismuth molybdates have long been known as model mixed-metal oxide catalysts for selective oxidation and ammoxidation of olefins. In spite of the extensive literature relating to these materials, there has been relatively little attention paid to the evolution of structure and properties with variations in composition. The $\text{Bi}_2\text{O}_3\text{--MoO}_3$ phase diagram is rich with phases, of which only a few have been structurally refined. We have investigated the temperature dependence of some of the known phases and have solved structures of several unknown phases from x-ray and neutron diffraction data. Comparison of these structures and their temperature dependence may provide new insights on trends in catalytic performance.

A second system of interest for the selective ammoxidation/oxidation of propane is the complex mixed-metal molybdenum oxide systems. Our advanced characterization work has yielded insight on the structure and chemical composition of crystalline phases that are the major components in active catalyst materials (see figures on the right). High-throughput screening techniques (Symyx Technologies) have been used to prepare highly active Mo-V-(Nb,Ta)-Te-O propane ammoxidation catalysts as well as to isolate the nearly pure crystalline phases. A combination of TEM techniques including SAED, HR-TEM, EDS, and EELS, as well as various high-resolution synchrotron and neutron powder diffraction experiments has allowed us to characterize the crystal structure of each of these phases. Based on structural and compositional results, we have been able to propose likely active sites for alkane activation, hydrogen abstraction, and nitrogen insertion in the ammoxidation reaction mechanism.



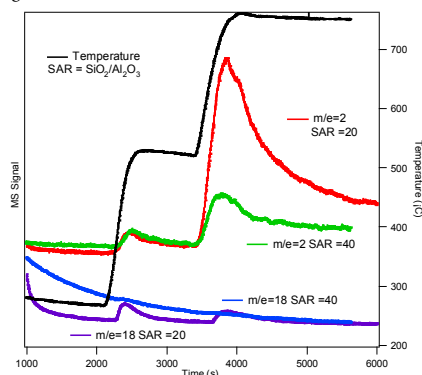
("Redox Sites in Acid Zeolites" continued from page 9)

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. Given that these materials are used to process literally millions of barrels of oil each day, even small improvements have a very substantial impact.

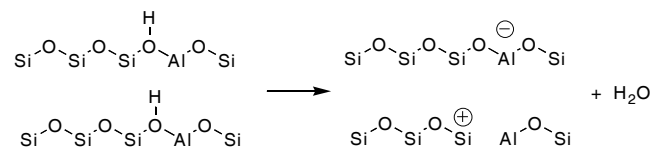
A plausible path for the formation of hydrogen from BAS (Scheme 2) suggests that the product should lead to the formation of $[\text{AlO}_4]^\circ$ sites in the zeolite. Formally $[\text{AlO}_4]^\circ$ sites can more clearly be described as $[\text{AlO}_4/h]^\circ$ where h is a hole located (at low temperatures) on one of the oxygen atoms surrounding the aluminum—that is, one oxygen atom is oxidized to a formal oxidation state of 1–. However, no evidence for the formation of these sites has been obtained as the samples are EPR silent. This could be due to further reaction of the sites to form species that have paired electrons or highly delocalized electrons.

In related research, we have found that samples of Silicalite-1 also desorb 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 peroxy 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 peroxy sites to determine under what conditions they can affect the expected catalytic chemistry of other sites such as Brønsted acid sites.

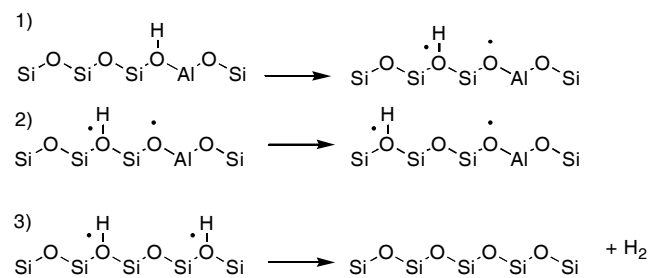
Figure 1



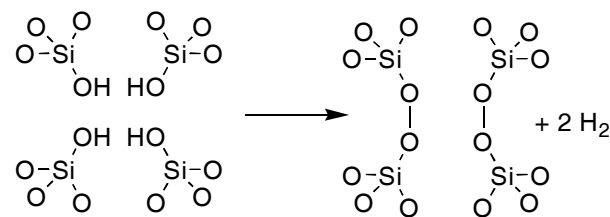
Scheme 1: Dehydroxylation via heterolytic decomposition of Brønsted acid sites



Scheme 2: Proposed homolytic decomposition of Brønsted acid sites



Scheme 3: Hydroxyl nest decomposition to form hydrogen gas and silylperoxy sites



Self-Assembly on Si(100) Surface and Molecular Electronics

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)

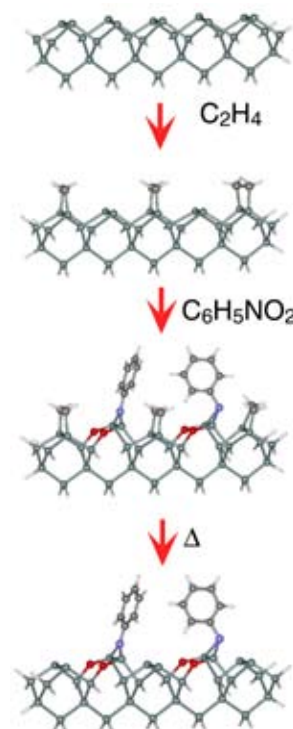
Collaborators: Tom Beebe, Doug Doren, Junghui Chen (Chemistry & Biochemistry), Robert Opila (Materials Science & Engineering), Brian Willis (Chemical Engineering)

Graduate Students: Timothy Leftwich, Mark Madachik, Xiaochun Zhang (Chemistry & Biochemistry)

Surface modification of silicon substrates is done with the purposes of understanding molecular assemblies of multifunctional molecules on silicon. The prototypical Si(100)-2x1 surface is used for chemical modification with cycloaddition schemes that deliver aromatic functional groups to this surface. As shown in the scheme on the right, this approach applied to the nitro-group delivers phenyl-groups attached to a nitrogen atom onto the Si(100) surface with high selectivity and can be used to space these groups based on the coadsorption with a site-blocker molecule, such as ethylene. Other silicon surface modifications include nitridation with ammonia that leads to surface groups of specific acidity, which can be used as high-temperature catalysts or as highly-stable support materials for high-temperature catalysts.

Currently investigated are reactions of cyclocondensation with H-terminated silicon substrates and nanostructures of silicon on highly oriented pyrolytic graphite.

Other projects of the Teplyakov group involve collaborative efforts with the groups from Hunter College in New York on the properties of polyoxometallic systems and a group of Professor George W. Flynn from Columbia University in New York on properties of carbonaceous surfaces.



Photocatalysis in Doped TiO_2 Nanoparticles

Faculty: Doug Doren (Chemistry & Biochemistry)

Graduate Student: Yushan Wang (Physics)

This project concerns the effects of dopants on the electronic structure of TiO_2 nanoparticles. Our first-principles theoretical studies are designed to support experimental work done in the Barteau, Chen and Shah groups at Delaware. TiO_2 nanoparticles have the anatase structure and can be controllably doped with a range of cationic or anionic substituents. Experiments have shown that the band gap decreases when particles are doped with N (substituting for O) or Nd (substituting for Ti). This allows excitation of electrons by visible light, and the particles demonstrate enhanced photocatalytic behavior. We have used density functional theory to determine the origins of the band gap reduction. As shown in Figure 1, substituting N for O creates new states at the top of the valence band, while substituting Nd for Ti creates new states at the bottom of the conduction band. For both dopants, the band gap is reduced because the new states intrude into the gap of the pure material while being coupled to the bulk states. This behavior is specific to these elements: theoretical studies of several other transition metal dopants predict that they either produce states in the band gap that are not coupled to the delocalized band states, or the additional states they create lie within the TiO_2 bands so that the gap is not reduced. We have now explored the effects of a range of different transition metal substituents, including V, Cr and Co (see Figure 2). These have some interesting properties as dilute magnetic semiconductors and find that magnetic properties are enhanced by coupling of metal-d electrons through oxygen vacancy sites.

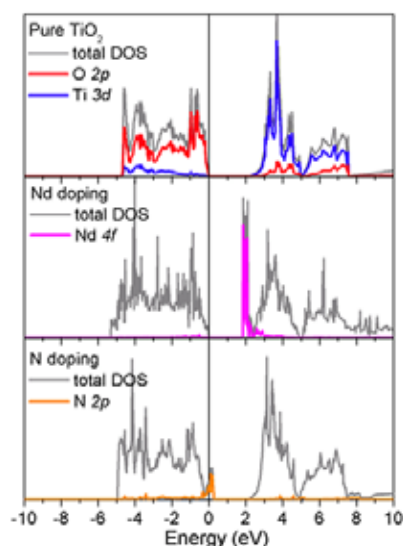


Figure 1: Density of electronic states in pure TiO_2 (anatase) and in anatase doped with Nd and N. Dopant levels in these calculations are at the 4 atom percent level, while experimental dopant levels are about 1 atom percent.

Photocatalysis in ETS-10, A Nanostructured Titanosilicate

Faculty: Doug Doren (Chemistry & Biochemistry)

Graduate Student: Anne Marie Shough (Chemistry & Biochemistry)

ETS-10 contains one-dimensional chains of TiO_6 octahedra within a nanoporous silicate framework (see Figure 3). 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. 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 4). 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.

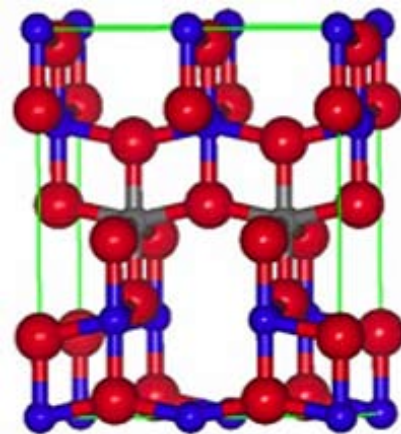


Figure 2: Model of Cr-doped anatase with an oxygen vacancy. The vacancy is required for charge neutrality, but the magnetic coupling between the Cr d electrons depends on the relative positions of the Cr atoms and the vacancy

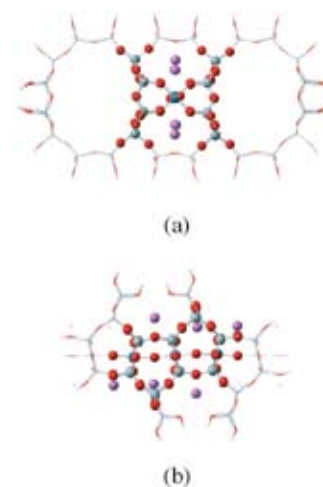


Figure 3: The structure of ETS-10 as viewed from the end (top) and the side (bottom) of the TiO_6 chain. In our model the atoms shown as spheres are treated with DFT, while the other atoms are included at the molecular mechanics level. In the bottom figure, some atoms are omitted for clarity.

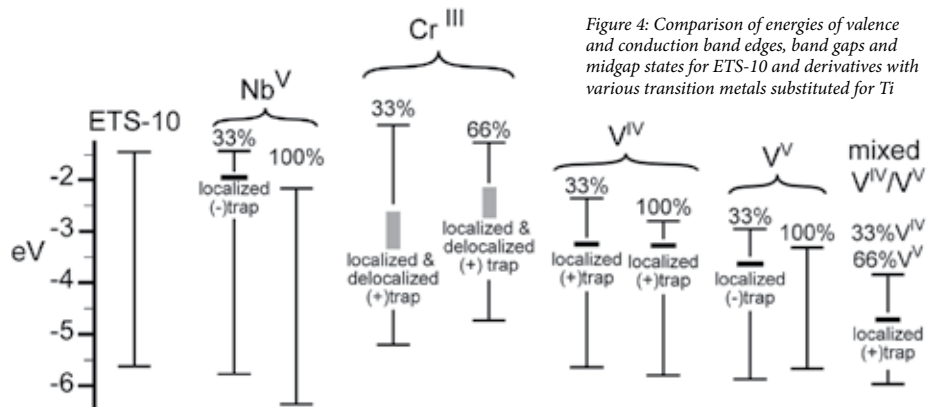


Figure 4: Comparison of energies of valence and conduction band edges, band gaps and midgap states for ETS-10 and derivatives with various transition metals substituted for Ti

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Photoelectrochemical Splitting of Water Using N:TiO₂ Anode

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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 photo-generated 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 TiO₂ semiconductor electrodes in 1972. Their attempt showed the feasibility of conversion of photon energy into chemical energy (H₂) without wasting of photo-induced electron excitation in photocatalytic systems. The photoelectrochemical system (PEC) 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 O₂ via an oxidation reaction: $2p^+ + 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O$

Simultaneously, the photo-excited electrons migrate to the cathode through external circuit and generate H₂ via a reduction reaction: $2e^- + 2H_2O \rightarrow H_2 + 2OH^-$ or $2e^- + 2H^+ \rightarrow H_2$

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

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

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

The characteristic energy positions [e.g. Fermi energy E_F, conduction and valance 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 redox energy at normal hydrogen electrode scale at temperature of 25°C. Figure 1 is a schematic energy diagram of an n-type semiconductor/electrolyte interface (a good example of the TiO₂/solution junction system). From the figure, we can see both valance 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 redox}^o) at the solid/liquid interface. Hence, the greater difference between the Fermi energy of the redox couple and energy at valance 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.

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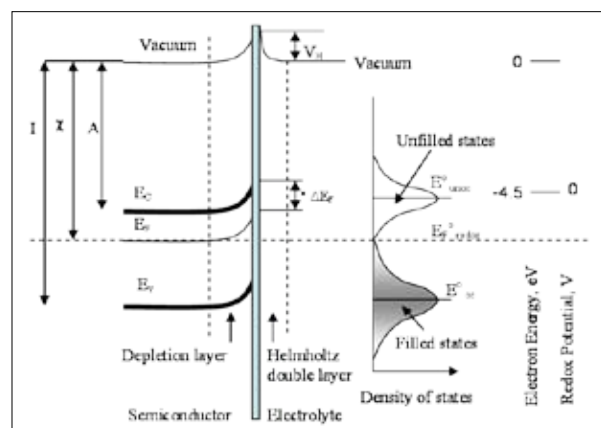


Figure 1: Energy band diagram of the interface between an n-type semi-conductor surface and an electrolyte

TiO₂ Nanoparticle Catalysis and Photocatalysis

Faculty: Mark Barteau (Chemical Engineering)

Graduate Student: Sze Chi (Joan) Chan (Chemical Eng.)

Heterogeneous photocatalysis based on TiO₂ has been the focal point of numerous investigations in recent years because of the chemical stability of this material and its nontoxicity, and because of the potential for the total destruction of organic compounds in polluted air and wastewater. The band gap (E_g) of TiO₂ anatase is ~3.2 eV, which corresponds to only a limited portion (3-4%) of the solar spectrum. This relatively large band gap has significantly limited more widespread application, particularly to indoor situations. Various methods have been suggested to enhance the efficiency of the photocatalytic process involving TiO₂ under visible light irradiation, including doping, functionalization of the surface with metallic particles, and reduction of particle size to nanoscale.

The present work demonstrates the advantages of combining high resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field (HAADF) techniques for direct visualization of the reactivity of submicron and nanoscale photocatalysts. The photocatalytic reduction of Ag salts to metallic Ag on the surfaces of TiO₂ particles was used to probe the spatial distribution of photoreactive sites on the sub-micrometer-scale and nanoscale TiO₂ particle surfaces. The size, spatial distribution, and the wavelength dependence of the Ag nanoparticles photodeposition on the TiO₂ surfaces were quantified by analysis of the HRTEM and HAADF images. To further extend our study, we also investigated the photodeposition of Au nanoparticles on TiO₂ surfaces. Currently, we are focusing on scaling up the Ag photodeposition on TiO₂ nanoparticles. Ag/TiO₂ nanoparticles obtained from the scaled-up process were characterized by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and HAADF. This study provides new insights into the particle size distribution, surface structures, and other physical properties of potential relevance to the catalytic performance of Ag and Au nanoclusters supported on TiO₂. The use of gold in catalyst application is attracting increasing attention. It has been shown that gold nanoparticles with sizes below 5 nm exhibit unique catalytic properties for CO oxidation, the water gas shift reaction, and epoxidation of propylene, despite the inert character of gold. Information obtained from this study, therefore, will be of benefit in developing devices and techniques based on TiO₂ nanoparticles and TiO₂-supported metal nanoparticles as, from the HRTEM and HAADF results, we have been able to produce high loadings of uniform Au nanoparticles by photodeposition on TiO₂ nanoparticles.

Selective Oxidation of Propylene to Acrolein Over Bi-V-Mo-O and Bi-V-Nb-Mo-O Catalysts

Faculty: Mark Barteau, Doug Buttrey (Chemical Engineering)

Graduate Student: Xin Li (Chemical Engineering)

Selective oxidation catalysis produces about 25% of the most important organic chemicals and intermediates. One example is selective oxidizing propylene to acrolein over bismuth molybdate-based multicomponent catalysts. Significant research efforts have been carried out aimed at replacing propylene with the more abundant and less expensive propane. Based on extensive studies already done, particularly on Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9} for ammoxidation of propane to acrylonitrile, it is believed that V⁺⁵ is the key element for paraffin activation and Nb helps improve the selectivity. Previous work in our group showed that adding a limited amount of V to β -Bi₂Mo₂O₉ increased the activity for propylene oxidation, but not for propane. The objective of this research is to explore structure-activity relationships of Bi-V-Mo-O and Bi-V-Nb-Mo-O catalysts for propylene oxidation, in order to develop an improved catalyst system for selective oxidation of propane or other paraffin feedstocks.

Two groups of catalysts: BiV_xMo_{1-x}O_{4.5-x/2} and BiV_xNb_yMo_{1-x-y}O_{4.5-x/2-y/2} were synthesized with nominal compositions by coprecipitation methods derived from β -Bi₂Mo₂O₉ with various x and y values. Reaction studies in a fixed-bed reactor showed that for Bi-V-Mo-O catalysts, adding small amounts of V improves the activity by facilitating the oxygen availability. Specifically, activity increases with adding V up to x=0.05, around which the approximate solubility limit is reached. Beyond this limit (x=0.0625), low conversions were obtained. For Bi-V-Nb-Mo-O catalysts, when x+y=0.06 (above the approximate solubility limit), activity is also relatively low compared to Bi-V-Mo-O catalysts. XRD data showed that for both groups of samples, new phases formed when the approximate solubility limit was exceeded, which could be related to the drop in performance. Also when x+y=0.06, XRD peaks with odd k values were reduced significantly, indicating a new phase that possibly maintains the β structure but with b parameter halved (β variant phase).

Rational Strategies for Nanomaterials Design

Faculty: Dion Vlachos, Raul Lobo (Chemical Engineering), Michael Tsapatsis (University of Minnesota), Stavros Caratzoulas (Visiting Researcher)

Graduate Student: Khalid Al-Majnouni (Chemical Engineering)

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, makes 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 demand 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.

Chemical Modification of Si(100) Surface and Multilayer (Sandwich) Structures on Silicon

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)

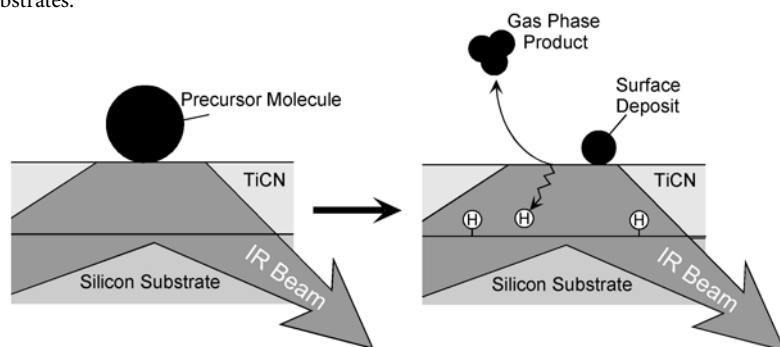
Collaborators: Doug Doren, Steven Brown (Chemistry & Biochemistry), Chaoying Ni (Materials Science & Engineering), George Flynn (Chemistry, Columbia University), Maynard Kong (PUCP, Peru)

Postdoc: Olga Dmytrenko (Chemistry & Biochemistry)

Graduate Students: Kathryn Perrine, Juan Carlos Rodriguez-Reyes, Keith Douglass (Chemistry & Biochemistry)

The goal of this project is the atomic-level control of deposition and nanostructuring of thin films on silicon substrates. It is also focused on the mechanisms of impurity introduction and distribution in solid films. In semiconductor technology, the direct deposition of metal onto silicon substrates is done very rarely because of relatively easy interdiffusion of these materials and poor adhesion properties. To overcome these problems, barrier materials are normally used. One of the most prominent materials with high thermal stability, good diffusion barrier, and low electrical resistivity is titanium nitride, TiN. Chemical vapor deposition schemes for TiN normally involve such precursor molecules as tetrakis-(dimethylamino)-titanium and the films deposited from this precursor often have a high carbon content. In fact, titanium carbonitride has a set of very attractive properties, making it a good diffusion barrier. The barrier layer in industrial applications is usually deposited on a thin layer of SiO₂.

We have successfully applied multiple-internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR) to study the formation and chemistry of such multilayer systems. For example, when 10 nm of TiCN is deposited onto a clean Si(100)-2x1 surface, surface hydrogen (either from partial decomposition of the precursor molecules or generated on a hot tungsten filament) easily diffuses through this film even at room temperature. The recombinative desorption of hydrogen turns out to coincide with the temperature at which most diffusion barriers break down. This is the first, to the best of our knowledge, spectroscopic confirmation of hydrogen diffusion in such systems. In addition to understanding the structure of the diffusion barrier films, chemical properties on the TiCN-covered Si(100) surface with respect to a common copper deposition precursor, (hfac)Cu(VTMS), have been analyzed. A set of papers describes the spectroscopic and thermodynamic benchmarks for (hfac)Cu(VTMS) chemistry both on a clean Si(100)-2x1 surface and on a TiCN-precovered substrate. A major novel approach developed in our laboratory combines microscopic, spectroscopic, and computational investigation of reactive binding sites on a poorly understood surface of TiCN film. A significant portion of this work is still in progress, as well as the studies of the effects of silicon surface modification, nitridation, carbidization, and oxidation in particular, on the deposition of the diffusion barriers onto silicon substrates.

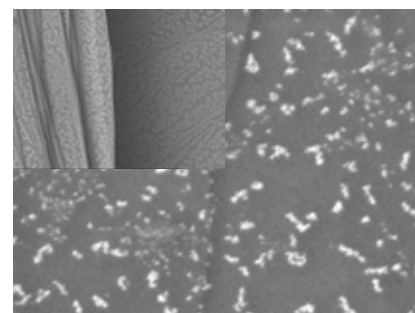


Nanoscale Investigations of Electrocatalysis

Faculty: Brian Willis (Chemical Engineering)

Graduate Student: Dimitri Skliar (Chemical Engineering)

Electrocatalyst durability is one of the main hurdles facing the development of fuel cell technology. A loss of catalytic activity from the degradation of the Pt/support interface is one of the main failure mechanisms of PEM fuel cells. Our research program is investigating the mechanisms of degradation at the nanoscale through a combination of scanning tunneling microscopy and electron microscopy with electrochemical measurements of model electrocatalysts. Degradation of the electrocatalytic activity is observed at the nanoscale where Pt particles detach from the surface and aggregate into larger particles. The figure on the right illustrates the change from dendritic aggregates of 2-3 nm Pt particles that cover the carbon surface to larger particles and less surface coverage after 10 hours of cycling 0-1.0V (NHE). Through this research program, we are investigating alternative catalyst and support materials to improve the durability of electrocatalyst formulations.



Pt/C before (inset) and after electrochemical measurements

(“Photoelectrochemical Splitting of Water Using N:TiO₂ Anode” continued from page 15)

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

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

1. Band gap of the semiconductor material, which governs the amount of the photon that can be utilized through photoexcitation process. The reduction of semiconductor band gap can be done by doping of impurities that creates impurity electronic states within its intrinsic forbidden band and reduces its effective band gap.
2. Relative energy positions between the redox species and Fermi energy or band edge energy of electrodes. This dictates the direction of electron flow and determines the performance of PEC system.

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Process Intensification in Multifunctional Microchemical Systems

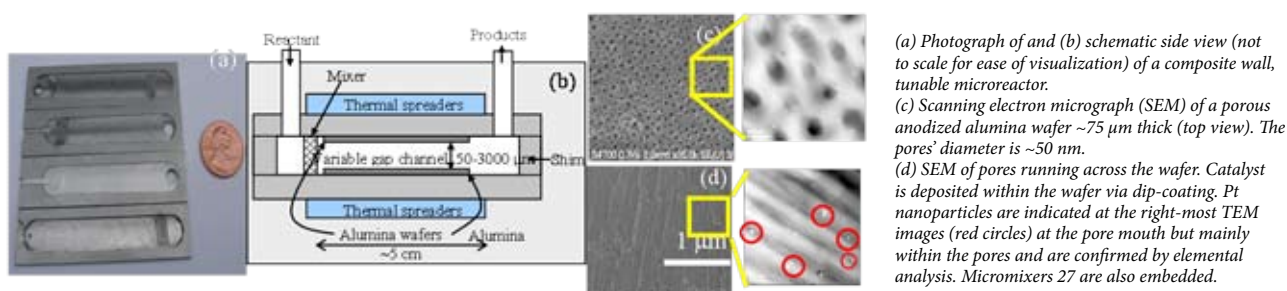
Faculty: Dion Vlachos (Chemical Engineering), Erich Wetzel (Army Research Lab)

Postdoc: George Stefanidis (Chemical Engineering)

Graduate Students: Justin Federici, Matthew Mettler (Chemical Engineering)

Undergrad Student: Megan Zagrobelny (Chemical Engineering)

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.

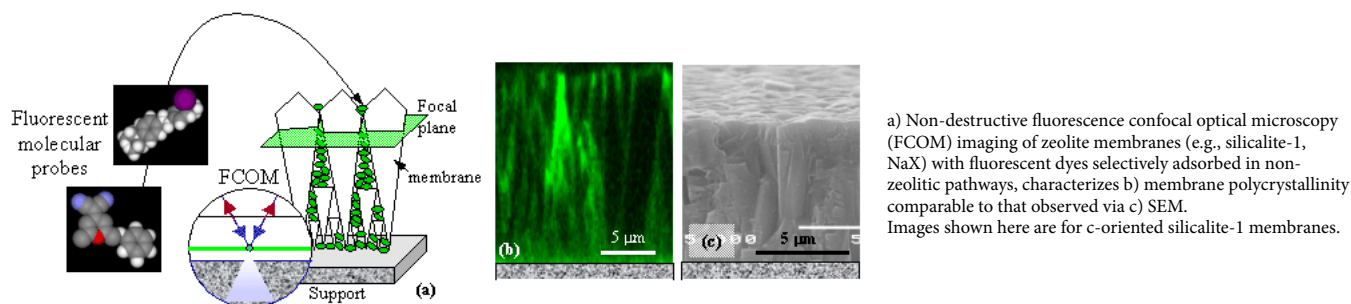


Non-Destructive Characterization of Polycrystalline Microporous Thin Films

Faculty: Dion Vlachos, Raul Lobo (Chemical Engineering), Michael Tsapatsis (University of Minnesota), Stavros Caratzoulas (Visiting Researcher)

Graduate Student: Khalid Al-Majnoui (Chemical Engineering)

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 below. 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.



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 Saliccioli (Chemical Engineering)

Undergrad Students: Zachary Ullissi, Anshu Arya (Chemical Engineering)

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 enable 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 Figure 1.

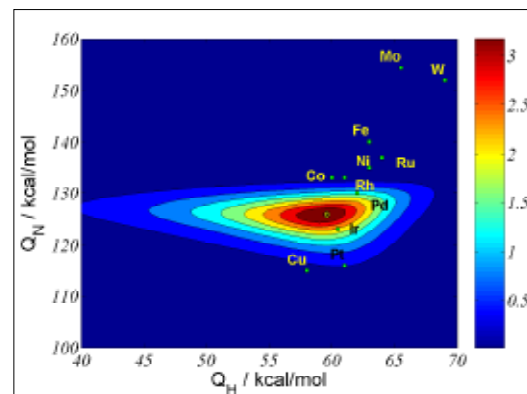


Figure 1: Example of predicted volcano mountain projected to two-dimensions for identification of optimal catalysts for ammonia decomposition to hydrogen: ammonia conversion (normalized scale) vs. element heats of adsorption (kcal/mol). The elements indicate the performance of known catalysts.

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 Saliccioli (Chemical Engineering)

Undergrad Students: Zachary Ullissi, Anshu Arya (Chemical Engineering)

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 Figure 2. The power of our hierarchical multiscale approach is that we develop predictive reaction mechanisms that can describe multiple experiments from UHV conditions to high pressures (pressure gap) and from single crystals to industrial catalysts (materials gap) over a wide range of operating conditions. Our close collaboration with industry is essential in developing reaction mechanisms of practical interest. Due to the hierarchical approach, we can develop mechanisms in short periods of time and improve important parameters with higher-level theory only when needed.

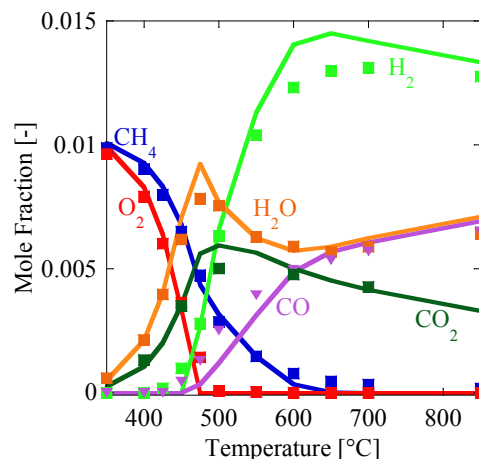
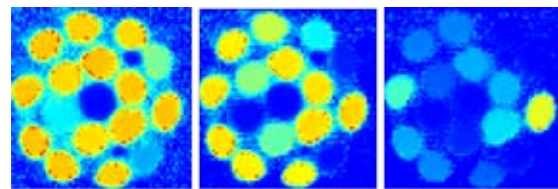
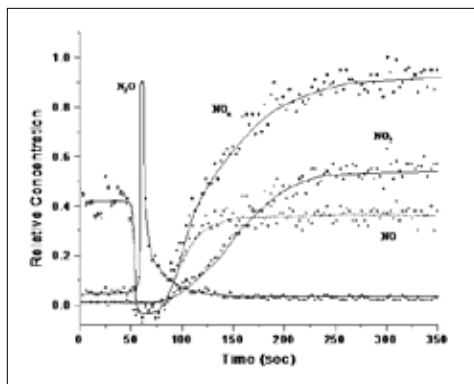


Figure 2: Comparison of experimental data (points) and simulations using our newly developed full microkinetic model (lines) for methane partial oxidation on Rh/Al₂O₃ catalysts.



Transient spectra from a 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 ($t \sim 60$ seconds), the CO is completely oxidized to CO_2 , the N_2O band grows and decays and later ($t=90$ seconds) the NO_x and NO bands appear.



Relative concentrations for three species, derived from IR spectra

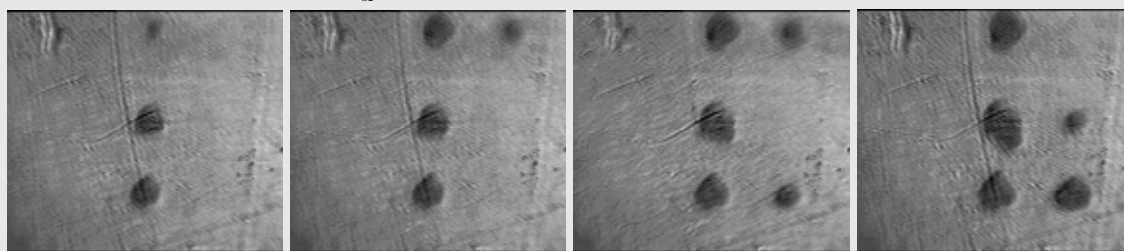
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fed into an integrated modeling effort, which makes use of all information created about the catalyst samples under investigation.

Our group has developed the first truly parallel, chemically sensitive high-throughput screening technique for supported catalyst samples. Most other high-throughput screening methods for heterogeneous catalysts are sequential analysis techniques, such as mass spectrometry or gas chromatography, which have severe drawbacks. Scale-up is the most obvious problem. Data for different catalysts should be compared under the same conditions and deactivation may occur to one catalyst while another is being tested in a sequential system. We now routinely measure the effluent of 16 supported catalyst samples in one second. 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.

The vast amount of quantitative data generated by our array-based high-throughput technique makes it necessary to approach catalysis research from a slightly different angle. It becomes almost impossible for the researcher to follow all results obtained and to keep the “big picture” in focus. It, therefore, becomes mandatory to make use of the 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 NSR problem. This organized approach has led to a considerable reduction in experiments, while preserving the quantity and quality of information. This level of understanding allows the derivation of mathematical models of catalyst performance as a function of catalyst composition and operating conditions. The ultimate goal of this vein of research is to gain a complete understanding of this system, such that the intelligent design of novel catalytic materials with improved performance will be possible.

Metastable CO islands grow while surrounded by chemisorbed oxygen on Pt(100) using microdosing. Each island is prepared by locally dosing hydrogen over the surface for ~2s. After the appearance of the CO island, the hydrogen doser is turned off and moved to a different location above the surface. $T = 193^\circ\text{C}$, $P_{\text{O}_2} = 1 \times 10^{-4}$



the effect of local chemical perturbation on a chemical reaction, thus enabling us to study on a mesoscopic scale the interactions between incident molecular beams and adsorbed species.

Non-Linear Phenomena in Heterogeneous Catalysis

Faculty: Jochen Lauterbach (Chemical Engineering)

Graduate Student: Danny Bilbao (Chemical Engineering)

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.

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, spatio-temporal 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 non-linear 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 perturbation of spatio-temporal pattern formation using microdosing of reactant onto the surface. The situation is more complicated than using laser light to locally heat the surface because of the following issues: 1) The gas beam has to be well focussed if we have to attain a good enough spot size. This can be achieved only using molecular beams; 2) The effectiveness of the gas beam in cleaning off the surface depends on the local dynamics of the adsorbed chemical species on the surface, as well as the interaction between the beam molecules and the catalyst surface. This leads to a highly complex situation where the beam may or may not be effective, depending on the local surface dynamics. The experiment affords us the advantage of studying

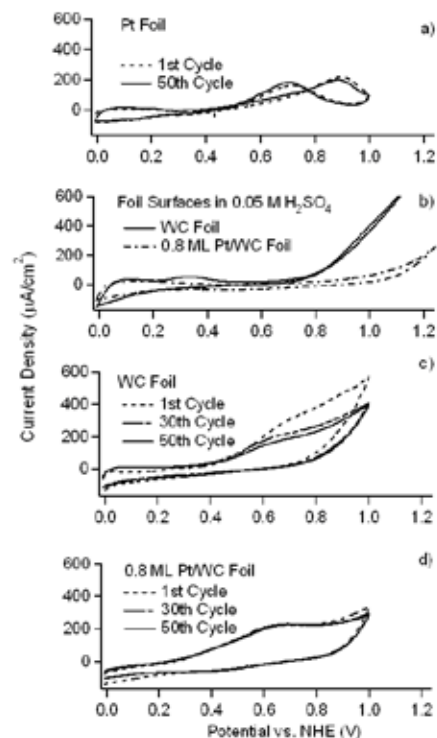
Metal Carbides as Anode Electrocatalysts for Fuel Cells

Faculty: Jingguang Chen (Chemical Engineering)

Graduate Students: Erich Weigert (Materials Science & Engineering), Chelsea Ren (Chemistry & Biochemistry)

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 submonolayer 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.

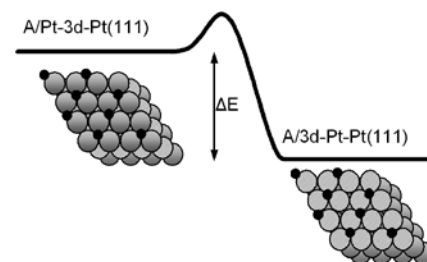


Photoelectrochemical (PEC) Devices for Water Splitting

Faculty: Jingguang Chen (Chemical Engineering), Robert Birkmire (Institute of Energy Conversion)

Graduate Student: Dan Esposito (Chemical Engineering)

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.



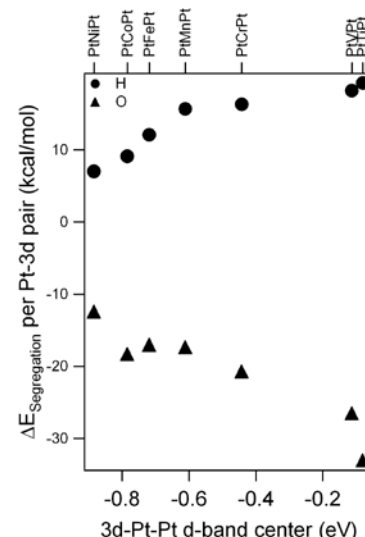
Stability of Pt and Pt-3d Bimetallic Electrocatalysts for Fuel Cells

Faculty: Jingguang Chen (Chemical Engineering)

Graduate Students: Carl Menning, Michael Humbert (Chemical Engineering)

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

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





NEXAFS and EXAFS Characterization of Catalytic Materials

Faculty: Jingguang Chen (Chemical Engineering), Sergey Rykov (Visiting Professor)

Graduate Student: Wei Huang (Chemical Engineering)

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.

Novel Properties of Bimetallic Surfaces and Supported Catalysts

Faculty: Jingguang Chen, Mark Barteau, Raul Lobo (Chemical Engineering)

Graduate Students: Amit Goda, Orest Skoplyak, Wei Huang, William Lonergan (Chemical Engineering)

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.

Structure-Property Relationship in Transition Metal Carbides

Faculty: Jingguang Chen (Chemical Engineering)

Graduate Students: Michael Humbert, Alan Stottlemeyer (Chemical Engineering)

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.

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.

Homogeneous Models for Chromium Polymerization Catalysts

Faculty: Klaus Theopold (Chemistry & Biochemistry)

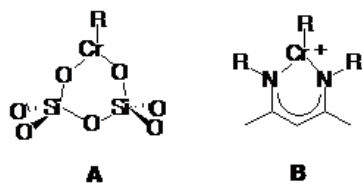
Graduate Students: Abdulmalik BinTaleb, Kevin Kreisel, Mahitha Reddy Peddy, Wesley Monillas (Chemistry & Biochemistry)

Chromium Alkyls: We are constructing a homogeneous model system for the Phillips catalysts for ethylene polymerization (i.e. inorganic Cr/SiO_2 , see “A” below). To mimic the coordinatively unsaturated chromium on a hard oxide support, we have chosen N, N'-disubstituted diketiminate ligands [$(\text{R})_2\text{nacnac}$], 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 $(\text{Ar})_2\text{nacnac}$ ligands ($\text{Ar}=\text{Ph}$, 2,6-Me₂Ph, 2,6-ⁱPr₂Ph). These paramagnetic complexes feature chromium in a range of formal oxidation states (II–V). Structurally characterized cationic Cr(III) alkyls of the general type $[(\text{Ar})_2\text{nacnacCr(R)(OEt}_2)]^+\text{BARF}^-$ ($\text{Ar}=2,6\text{-Me}_2\text{Ph}$, 2,6-ⁱPr₂Ph; $\text{R}=\text{Me}$, 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 ($M_w/M_n=1.1\text{--}1.4$) provide evidence for “living” polymerization catalysis, and the polymer microstructure of polyethylene produced with sterically encumbered $[(2,6\text{-}^i\text{Pr}_2\text{Ph})_2\text{nacnac Cr(OEt}_2)\text{Me}]\text{BARF}$ 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 $\text{Cp}^*\text{Cr(py)Me}_2$ on a zeolite (MCM-22) and characterized the resulting olefin polymerization catalysts by a variety of spectroscopic methods.



Mechanistic Investigation of Higher Olefin Epoxidation

Faculty: Mark Barteau (Chemical Engineering)

Graduate Student: Adrienne Lukaski (Chemical Engineering)

Our previous surface science and computational studies have identified the central intermediate in epoxidations of both ethylene and butadiene by examination of the reverse reactions. This intermediate is a surface oxametallacycle that can be formed in UHV experiments by opening the epoxide ring. The oxametallacycle controls the selectivity of epoxidation through competing steps: ring-closure to form the epoxide and isomerization to aldehyde species. The aldehyde is the gateway species to combustion products. Stable, spectroscopically verified oxametallacycles have been synthesized from 2-iodo-ethanol on Ag(110) and Ag(111), ethylene oxide on Ag(111), epoxybutene on Ag(110) and Ag(111), and styrene oxide on Ag(110) and Ag(111).

Demonstration of oxametallacycle formation via ring opening non-allylic epoxides on Ag surfaces is an important step in the understanding of olefin epoxidation; there has been no report to date of oxametallacycle synthesis from more complex, allylic epoxides. It is the presence of allylic hydrogen atoms and their facile abstraction by adsorbed oxygen that make direct oxidation of propylene difficult. The lower bond dissociation energy of the allylic C-H bond in propylene (77 kcal/mol) relative to that of the vinylic C-H bond in ethylene (112 kcal/mol) leads to an energetic preference for hydrogen abstraction and propylene decomposition over electrophilic oxygen addition to the olefin function and selective epoxidation.

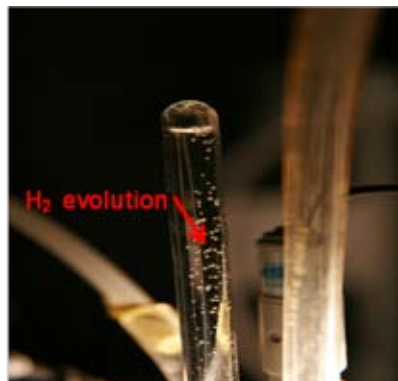
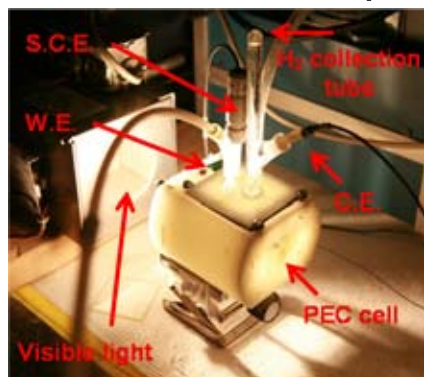
Temperature-programmed desorption (TPD) and Density Functional Theory (DFT) have been used in this work to probe the reactions of complex epoxides on Ag-surfaces. We have investigated the interaction of ethylene oxide with the Ag(110) surface and demonstrated the formation of an oxametallacycle intermediate by activated ring-opening of the epoxide on both clean and O-covered Ag(110) surfaces. On the clean Ag(110) surface, the oxametallacycle reacts to reform the parent epoxide at 280 K; the aldehyde isomer, acetaldehyde, is formed at higher oxametallacycle coverages. On the O-covered Ag(110) surface, the oxametallacycle exhibits lower selectivity to the epoxide than on the clean surface and undergoes combustion through formation of acetaldehyde and acetate species. The presence of pre-adsorbed oxygen on Ag(110) decreases the selectivity to ethylene oxide and also opens additional combustion pathways. While the structure of the reaction network is not surprising, the connection of oxametallacycles to combustion has not previously been established in surface science studies.

Propylene oxide also forms a strongly bound oxametallacycle intermediate on the Ag(110) surface. Following adsorption of propylene oxide on the clean Ag(110) surface at 120 K, propylene oxide desorbs molecularly from the respective multilayer and monolayer states at 140 and 180 K. When the crystal is heated to 230 K following adsorption of propylene oxide at 120 K, however, higher temperature features appear. Adsorption of low coverages of propylene oxide leads to desorption of the epoxide in a single peak at 280 K during TPD. The selectivity to propylene oxide decreases as the oxametallacycle coverage increases and small amounts of acetone and allyl alcohol are also formed during TPD of higher coverages of propylene oxide derived oxametallacycles. The oxametallacycle undergoes ring-closure to reform propylene oxide in two peaks at 280 and 330 K when synthesized from large doses of epoxide at 120 K with subsequent flash of the crystal surface to 230 K prior to TPD. Isomerization of the oxametallacycles formed from large doses of the epoxide leads to desorption of acetone and allyl alcohol. This work represents the first demonstration of a surface oxametallacycle species derived from propylene oxide.

("Photoelectrochemical Splitting of Water Using N:TiO₂ Anode" continued from page 17)

We have used a N doped TiO₂ thin film anode to allow broader photon spectrum harvesting. Using this electrode, a photoelectrochemical cell is fabricated, shown in the figure 2. 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.

Figure 2: A photoelectrochemical cell using N:TiO₂ as the anode



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 (Figure 3), 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 Figure 4 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 Figure 4c 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 Figures 4a and 4b, 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 Figure 4b 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.

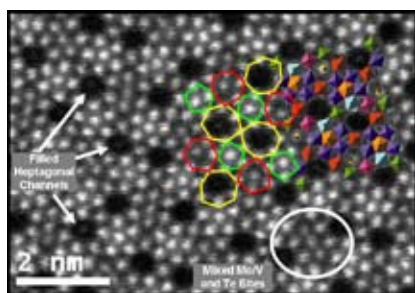


Figure 3: HR-STEM image of the MoVTeNbO 'M1' catalyst. Included in the image are two renderings of our diffraction-based atomic model that are superimposed on top of the image showing good agreement. In the image, the heptagonal channels are occupied and the contrast varies from one atomic column to another, providing clues to the overall composition.

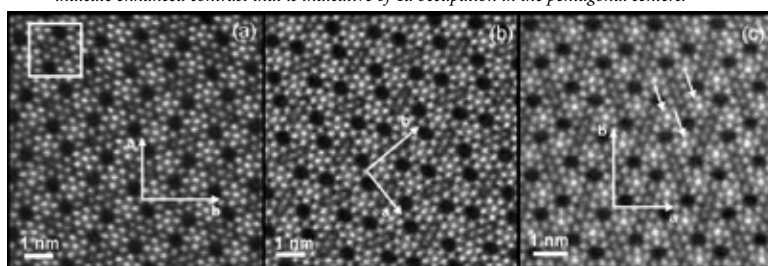


Figure 4: HR-STEM images of (a) MoVTeO (b) MoVNbTeO, and (c) MoVTaTeO 'M1' catalysts. The indicated a - b axes in each image show the orientation of a single unit cell within the image. The box shows a region within the MoVTeO catalyst that exhibits local contrast that differs from the other two catalysts suggesting compositional variation. The arrows in the MoVTaTeO catalyst indicate enhanced contrast that is indicative of Ta occupation in the pentagonal centers.

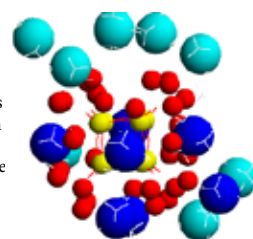
Thermodynamic and Kinetics of Nanozeolitic Precursor Formation

Faculty: Dion Vlachos, Stavros Caratzoulas, Raul Lobo (Chemical Engineering), Michael Tsapatsis (University of Minnesota)

Graduate Student: Khalid Al-Majnoui (Chemical Engineering)

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 Figure 1.

Figure 1: 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.



Growth Mechanisms of Siliceous Zeolite Crystals

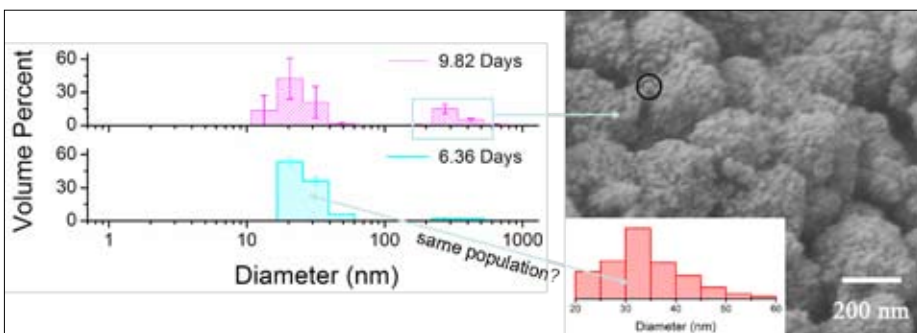
Faculty: Raul Lobo, Norm Wagner (Chemical Engineering)

Graduate Student: Nathan Hould (Chemical Engineering)

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 previous to 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 presence of the nanoparticles, before and during crystal growth, has been established by several groups, but their specific role remains unclear.

We have recently turned our attention to the synthesis of zeolite beta, another important industrial zeolite catalyst that can be prepared through nanoparticle precursors as zeolite ZSM-5. Two important differences are that zeolite beta is prepared using tetraethylammonium as the structure director and that the synthesis gel must contain some aluminum in addition to silicon for successful zeolite beta formation. As with ZSM-5, we find that the initial silica nanoparticles (~5 nm) form rapidly at room temperature. Upon heating, we find that these primary nanoparticles aggregate into secondary nanoparticles (20-30 nm in diameter) that are stable for 5-6 days. These secondary nanoparticles eventually form tertiary nanoparticles (300 nm) that have the structure of zeolite beta. If these tertiary particles are separated from solution early during their formation, we can see that they are clearly formed from sub-units that are identical in size to the secondary particles. It seems that zeolite beta initially forms by aggregation of the secondary particles that have changed over time into zeolite beta. TEM and x-ray diffraction investigations of these larger particles reveal that at this point of the synthesis, all the sub-units that have aggregated to form the particles have the structure of the zeolite beta. Independently, we have also shown that, on average, the secondary particle population (coexisting with the early tertiary particles) has a highly disordered structure. These studies show that the population of secondary particles consists of units that change structurally over time at different rates. As they change structurally, interparticle forces also change and a small fraction of secondary particles eventually form the structure of zeolite beta and aggregate selectively forming the observed tertiary particle population.

These detailed studies of zeolite synthesis should show allow us to design synthesis strategies that minimize (or maximize if desirable) the number of structural defects in the materials. They may provide insights as novel approaches to the formation of polycrystalline films of zeolite beta, a desirable candidate where success in effective film formation has remained elusive in the last decade.



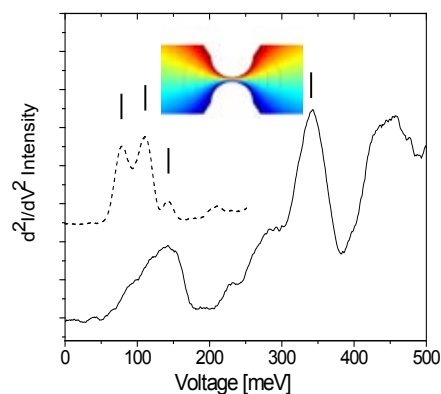
Comparison of the particle populations (by DLS) in the synthesis gel before and after centrifugation and separation of the tertiary particles. On the right, a SEM image of the tertiary particles show that they are indeed formed of subunits that have similar size distribution as the secondary particles left in solution (left).

Molecular Electronics and Nano-Sensors

Faculty: Brian Willis (Chemical Engineering)

Graduate Students: Rahul Gupta, Irene Hsu (Chemical Engineering)

Molecular electronics is a rapidly growing area of research that seeks to understand charge transport at the single molecule level. Such knowledge may create active nanostructures that extend computing, electronic memory, bio-chemical sensing, or energy harvesting beyond the limits of modern technologies. The research holds great promise due to the richness of molecular properties and the complexity of inorganic, organic, and biological molecules that can be synthesized. One of the most intriguing applications of molecular electronics is to fabricate nanosensors based on molecular recognition for sensing applications ranging from homeland security to medical diagnosis or forensics. Our work presents a novel experimental approach and a methodology to investigate tunneling spectroscopy in nanoscale junctions for the nanofabrication of billions of parallel tunnel junctions that can sense molecules from the environment. We use atomic layer deposition and nanoengineering principles to control the nanoelectrode microstructure and electrical properties for molecular tunnel junctions that contain electrodes spaced less than 2 nm apart. Molecular adsorption is detected as a change in the tunneling signal, and molecules are characterized using vibrational spectroscopy at the single molecule scale. The figure on the right demonstrates a vibrational spectrum of a few acetic acid molecules recorded with tunneling electrons. Molecules can be adsorbed and desorbed reversibly from the tunnel junction at room temperature to act like an “electronic nose.”



Tunneling spectroscopy data for acetic acid adsorption in a nanojunction. Electrical potential distribution between nanoelectrodes (inset).

Novel Photocatalytic Materials

Faculty: Raul Lobo (Chemical Engineering), Doug Doren (Chemistry and Biochemistry)

Graduate Students: Bharat Boppana (Chemical Engineering), Anne Marie Zimmerman, Heather Schmidt, Tim Lucas (Chemistry and Biochemistry)

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 semi-conductors (such as TiO_2 or ZnO) and tries to tune 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. This approach has been shown to be successful for various metal oxide semiconductors. The overall effect is to decrease the effective bandgap facilitating the formation of electron-hole pairs using visible light. These structural and chemical changes can be made by a solid-state reaction between zinc oxide powders and gallium oxyhydroxide powders in an ammonia atmosphere at high temperatures.

Figure 1 shows the UV/vis Diffuse Reflectance spectra of samples treated this way with a Zn/Ga ratio of 2 in the initial synthesis mixture. In this case, it is clear that the bandgap of the starting ZnO has been substantially reduced (from about 3.2 eV to about 2.6 eV) and that this change is very sensitive to the reaction temperature. Many questions remain about the new materials. We do not know in detail the coordination environment of Zn and Ga in the new oxynitrides nor, at this time, do we understand the formation and healing of structural defects, an important issue since defects can act as recombination centers reducing the quantum yield of the overall process. Currently the materials prepared at high temperatures have relatively low surface areas (4-6 m^2/g) compared to typical photocatalysts having more than ten times these values. The overall low surface area reduces the potential effectiveness of these new materials, and we are working towards improving our synthesis protocols.

To proceed with a systematic improvement of materials properties and understanding the mechanistic differences between the oxynitride solid solutions and the parent oxides, we are collaborating with Doug Doren's research group (see Doug Doren's research description). We strive to combine theory and experiment to understand how different chemical/structural changes can be "engineered" to make more reactive, yet photostable materials for photocatalysis.

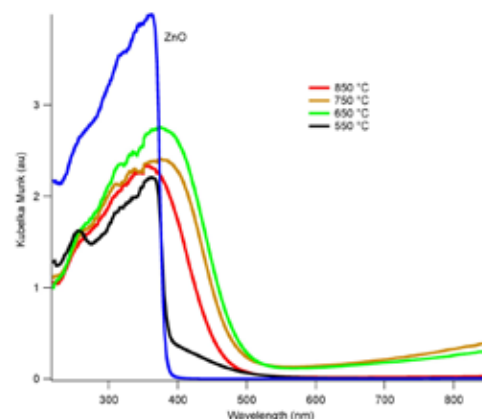


Figure 1: UV/vis DR spectra of ZnO and Zn/Ga oxynitrides ($\text{Zn/Ga} = 2$) treated in ammonia atmosphere at various temperatures.

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, University 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). Figure 2 shows a HAADF image and Figure 3 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 Figure 4 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.

(continued on page 28)

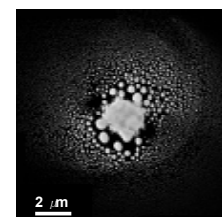


Figure 2: HAADF micrograph of a nano-particle field following an EBIF event

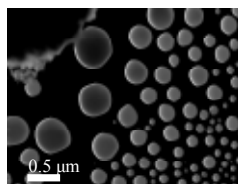


Figure 3a: Typical HAADF image of nanoparticles following EBIF

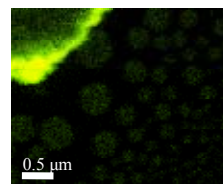


Figure 3b: Ni K edge x-ray map showing areas with Ni

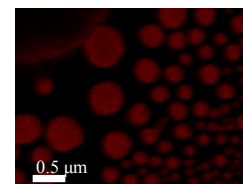


Figure 3c: Bi M edge x-ray map showing areas containing Bi

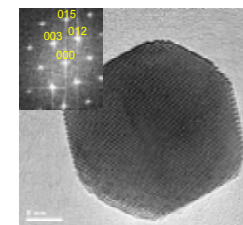


Figure 4: HREM image of a single Ni-Bi nanoparticle with the corresponding FFT image looking down the [100] zone axis

("Synthesis and Characterization of Metallic and Bimetallic Nanoparticles Through Electron Microscopy"
continued from page 27)

Our most recent work has been focused on understanding the role of promoters in Ru-based catalysts used in ammonia decomposition. The motivation is to use ammonia as a one-way carrier of H_2 for use in fuel cells that can power a wide array of devices. Traditionally, hydrogen generation involves the use of carbonaceous substances such as methanol and methane, but the combustion of these fuels gives off undesired CO_x ($x = 1, 2$) emissions. One alternative is ammonia because of its high hydrogen storage capacity (17.7 %), energy density (3000 Wh/kg), and the only by-product of the decomposition is environmentally benign N_2 . The decomposition reaction is endothermic, and the most effective catalysts are those that maximize the decomposition efficiency at the lowest possible temperatures.

Using high-throughput experimentation, we found that the potassium-promoted Ru catalysts supported on Al_2O_3 exhibited the best performance. These promoted catalysts demonstrated NH_3 decomposition activities that were approximately 50-80°C lower than those observed on the base Ru catalysts. Using HAADF, Figure 5 shows an image of the base unpromoted Ru catalyst that contains 5-100 nm nanoparticles and some larger agglomerates. However, on the better performing K-promoted catalyst shown in Figure 6, we discover nanowhiskers that have rectangular dimensions between 20-50 nm and lengths ranging from a few nm to several microns. Selected-area electron diffraction in the TEM shows that these whiskers have a KRu_4O_8 hollandite structure. We believe that this structure is a necessary component of our catalyst and may be responsible for the enhanced ammonia decomposition efficiencies. Although the exact nature of the KRu_4O_8 hollandite is not yet known, these results appear to be the first identification of the hollandite structure in an ammonia decomposition catalyst and a first step towards understanding the role of K in Ru catalysts supported on Al_2O_3 . Our continued efforts are focused on determining the exact role of the hollandite structure and its stability in the ammonia decomposition environment.

Lastly, we are involved in collaborative efforts studying two additional nanoparticle systems. The first is characterizing Pt-Re bimetallic catalysts, and the second is characterizing Pt & Au nanoparticles synthesized using dendrimer templates. Figure 7 shows HAADF images of a 1:1 Pt:Re bimetallic catalyst supported on C. The images show a very finely dispersed nanoparticle catalyst with particle sizes between 1-3 nm. EDS analysis has confirmed the formation of bimetallic particles and current efforts are under way to quantify the extent of alloying. In the dendrimer encapsulated nanoparticles, Figure 8 shows HREM images of Au and Pt nanoparticles prepared using dendrimer templates. The templates allow particle size control based on the generation (size) of the dendrimer used in solution. FFT analysis of the HREM images show that both the Pt and Au nanoparticles exhibit their respective FCC structures, and the particle sizes range between 1-5 nm. The use of dendrimer templates and the development of controlled nanoparticle sizes and compositions are of great importance in chemical reactions that are structure sensitive. Our future efforts in this area are directed towards the production of bimetallic nanoparticles with controlled compositions, sizes, and microstructures (alloy, solid solution, or core-shell).

Atomic Layer Deposition of Oxides

Faculty: Brian Willis (Chemical Engineering)

Postdoc: Changbin Zhang (Chemical Engineering)

Graduate Students: Dimitri Skliar (Chemical Engineering), Anoop Mathew (Materials Science & Engineering)

Nanometer thin metal-oxide layers are being intensely studied for application as alternative gate dielectric materials for nanotransistor devices, with hafnium dioxide being the most extensively investigated. In these metal oxide layers, there is a strong link between chemical bonding and the electrical characteristics required for high performance device applications. Defects in the oxide layer and at the metal-oxide/semiconductor interface, as well as thermal stability and compositional uniformity, have made this an extremely challenging materials problem. The best results have been obtained using a pre-grown SiO_2 oxide layer, which gives a good electrical interface with the semiconductor substrate. However, the need to scale the overall electrical thickness to an equivalent oxide thickness (relative to SiO_2) of less than 1 nm presents difficulties for using the pre-grown oxides. On the other hand, attempts at oxide growth directly on the semiconductor lead to rough three dimensional island growth morphologies with poor electrical properties. We have investigated the growth chemistry of oxides at the single molecule scale to understand the competing reaction pathways involved in growth and to engineer the growth one layer at a time. The figure on the right illustrates an example of this approach with STM data on water terminated $Si(100)-2 \times 1$. By understanding the competing pathways of water adsorption, it is possible to create a near perfect surface for the initiation of oxide layer growth directly on the semiconductor, without a pre-grown SiO_2 layer.

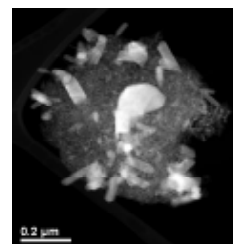


Figure 5: HAADF image showing the base unpromoted Ru catalyst supported on Al_2O_3

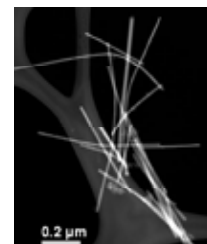


Figure 6: HAADF image showing the K-promoted Ru catalyst supported on Al_2O_3

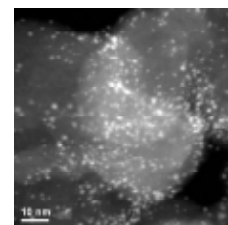


Figure 7: HAADF image showing dispersed 1-3 nm Pt-Re bimetallic nanoparticles supported on C

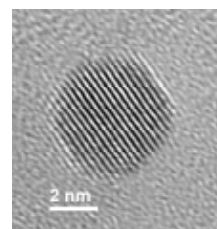


Figure 8a: HREM image of Au nanoparticles synthesized using the dendrimer template

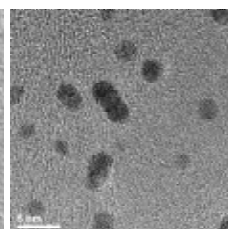
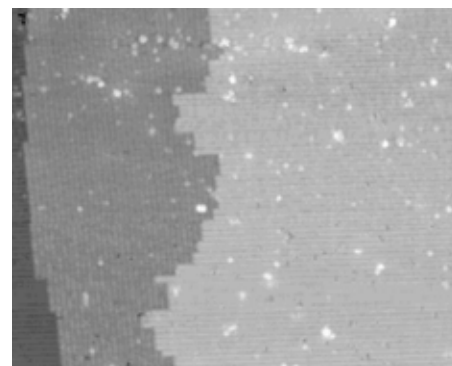


Figure 8b: HREM images of Pt nanoparticles synthesized using the dendrimer template



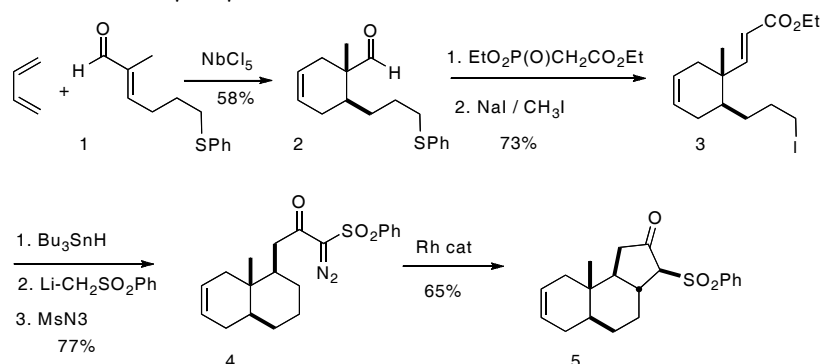
60x60 nm² occupied states image of the $Si(100)-2 \times 1$ surface H_2O terminated at 130 K

Rh-Catalyzed Cyclization of α -Diazo α -Sulfonyl Ketones

Faculty: Doug Taber (Chemistry & Biochemistry)

Graduate Student: Christopher Nelson (Chemistry & Biochemistry)

En route to the Veratrum alkaloids, we have found that Rh-catalyzed cyclization of an α -diazo α -sulfonyl ketone 4 proceeded to give the desired trans-6-5 ring fusion. The structure of the crystalline 5 was confirmed by x-ray.

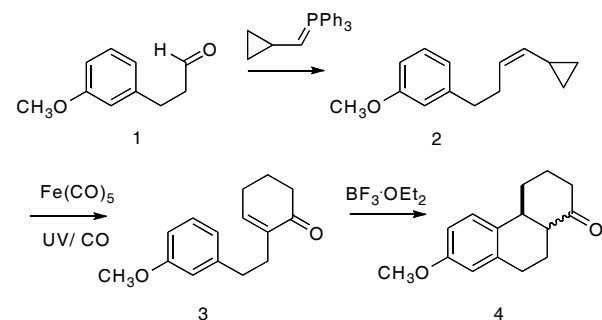


Cyclohexenones from Aldehydes

Faculty: Doug Taber (Chemistry & Biochemistry)

Graduate Student: Ritesh Sheth (Chemistry & Biochemistry)

Condensation of the aldehyde 1 with the commercially-available phosphonium salt gave the cyclopropane 2. Fe-catalyzed cyclocarbonylation smoothly converted 2 into the cyclohexenone 3, which was cyclized with acid to the steroid precursor 4.

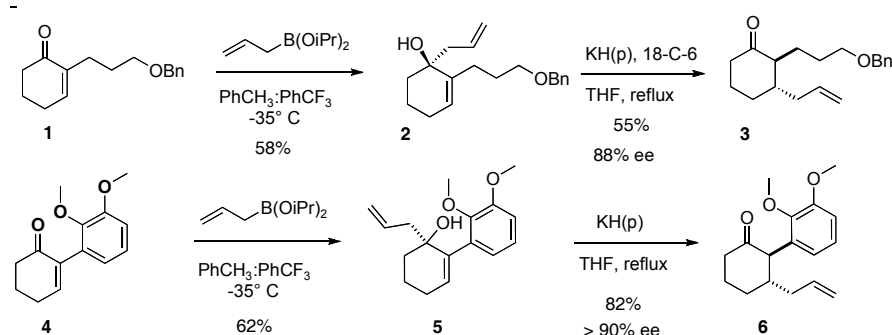


Asymmetric Organocatalytic Conjugate Allylation of Cyclic Enones

Faculty: Doug Taber (Chemistry & Biochemistry)

Graduate Student: David Gerstenhaber (Chemistry & 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.



Surface Chemistry of Polymer Nanofilms

Faculty: Jochen Lauterbach (Chemical Engineering), Chris Snively (Materials Science & Engineering)

Graduate Student: David Winski (Chemical Engineering)

One area of research in our group is the development of defect-free polymer nanofilms with thickness control in the nm range. One recent discovery is the ability to polymerize 1,2-disubstituted ethylenes using vacuum deposition/polymerization. Traditionally these molecules have been considered non-homopolymerizable because of steric hindrance surrounding the vinyl group, which decreases the rate of propagation versus termination, resulting in little or no polymer formation after relatively long reaction times. We have shown that vacuum deposition/polymerization is able to react 1,2-disubstituted ethylenes with high conversions after fairly short reaction times due to the fact that the polymerization is carried out in the solid phase. The tighter packing of the solid phase leads to faster reactions in spite of the steric hindrance. Also, since the molecular diffusion is extremely limited in the solid, radicals are unable to meet and terminate except through the polymer growth mechanism. This results in a much higher rate of propagation versus termination than seen in traditional wet chemistry approaches. To date, we have been able to polymerize for the first time crotononitrile, fumaronitrile, anethole, and betabromostyrene. This discovery is important in our research of conducting polymers since we now have the capabilities to create conducting polymers with the vacuum deposition/polymerization method that is impossible with traditional wet chemistry.

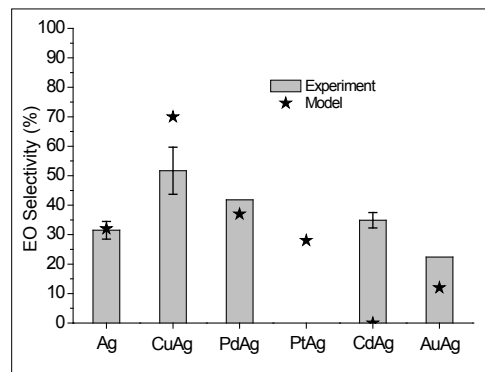
High-Throughput Studies of Ag Catalysts for Ethylene Epoxidation

Faculty: Mark Barteau, Jochen Lauterbach (Chemical Engineering)

Graduate Student: Joe Dellamorte (Chemical Engineering)

In the past, we have demonstrated the efficacy of rational catalyst design with the prediction and subsequent validation of the improved performance of a Cu-Ag bimetallic catalyst over the unpromoted Ag for ethylene epoxidation. In order to expand this analysis for the ethylene epoxidation system, several other catalyst combinations have been studied, including Au-Ag, Pt-Ag, Pd-Ag, and Cd-Ag. The figure on the right shows the comparison of EO selectivities between recent high-throughput experiments and microkinetic modeling results based on the oxametallacycle mechanism. Two metals, Pt and Cd, significantly deviate from the modeling results. Therefore, refinement of the model will be needed, particularly in the case of Cd, which shows a significantly higher selectivity than the prediction. Cd-Ag catalysts have shown large increases in the conversion as well. Characterization using SEM shows a redistribution of the Ag exhibiting a smaller average particle size and therefore a larger surface area.

Further improvements in the EO selectivity have also been seen for co-impregnated Re-Ag catalysts. Specifically, the addition of 1 ppm vinyl chloride to the feed stream of Re-Ag catalysts increases selectivities to >70%. The addition of vinyl chloride also causes an increase in the conversion of ethylene by the co-impregnated Re-Ag catalysts, contrary to previous results for Ag and Cu-Ag catalysts where activity decreases were seen. The change in conversion can be attributed to a change in Ag morphology, with an increase in surface area similar to the Cd-Ag system.



Facilities

Located in Colburn, Spencer, Brown, Drake and DuPont Laboratories, the Center has a wide array of equipment for preparation and advanced characterization of catalysts through spectroscopy and reaction. Included in these items are computational facilities for chemical and reaction engineering modeling. The following highlights facilities dedicated to catalysis studies:

Reactors

A variety of flow and batch reactor systems operate at pressures ranging from a few torr to 5000 psi. These reactors are interfaced with GC, MS, or GC/MS instruments for on-line product analysis.

Fourier Transform Infrared Spectrometers

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

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.

Microbalance Reactor Laboratory

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.

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.

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.

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).

Solid State NMR Spectrometers

Two NMR spectrometers with capabilities for analysis of solid samples are housed in the Chemistry Department, and are used to study the properties of catalyst surfaces. One instrument operates at low field and can probe carbon-containing reactants, surface intermediates, and products. The second instrument operates at 300 MHz and can probe heavier nuclei such as silicon and aluminum in the catalysts under investigation.

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.

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.

Computer Facilities and Modeling Software

The CCST computational facilities include six 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.

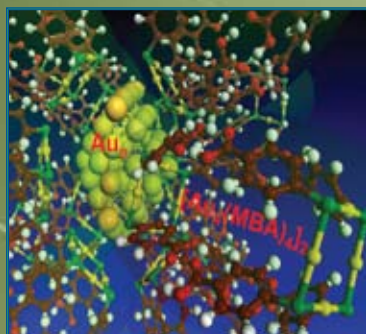
High-Throughput Screening Laboratory

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).

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.

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