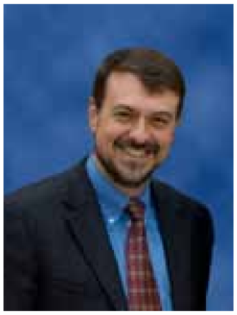
Center for Catalytic Science and Technology

ccst

2009 research report

University of Delaware



From the Director:

Reflection of the Past Year

This past year has been remarkable for CCST. In the spring of 2009, we were awarded an Energy Frontier Research Center (EFRC) grant by the Department of Energy (DOE) to establish a new center on heterogeneous catalysis for biomass conversion to chemicals, fuels, and electricity. This new center, the Center of Catalysis for Energy Innovation (CCEI), is being funded at $17.5M for 5 years and is one of 2 DOE centers to focus on heterogeneous catalysis of renewables. It will be founded based on CCST and will encompass 6 more universities as well as the Brookhaven National Laboratories. While we are very excited about this opportunity to grow and diversify our research portfolio, we plan to continue the breadth of CCST activities, which have been an attraction pole for industrial collaborations and the cornerstone for our students' education.

Our faculty and students have won numerous awards. Jingguang Chen won the Excellence in Catalysis Award from the New York Catalysis Society and became a Fellow of the American Vacuum Society; Mark Barteau won the Giuseppe Parravano Award of the Michigan Catalysis Society following his selection in the "One Hundred Engineers of the Modern Era" by the AIChE; Dion Vlachos was selected in the Top 100 Engineers (International Biographical Centre) and was named the Elizabeth Inez Kelley Professor of Chemical Engineering; Doug Buttrey was a Visiting Professor in the Catalysis Research Center of Hokkaido University in Japan. A large number of publications in high impact journals including a number of journal covers were published by many of the CCST faculty. CCST faculty, including Klaus Theopold, Doug Doren, Mark Barteau, and Jingguang Chen, continue to provide leadership in key administrative positions at UD. The quality and productivity of our research efforts continue to make CCST one of the leading academic catalysis centers worldwide.

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

Spotlight on the New Center of Catalysis for Energy Innovation (CCEI)

The Center of Catalysis for Energy Innovation (CCEI) aims at developing innovative, science-based heterogeneous catalytic technologies for transformation of biomass materials into fuels, chemicals, and electricity. Biomass offers a unique opportunity for a sustainable society with unprecedented impact on the U.S. economy, energy security and independence. For this vision to be realized, major scientific hurdles need to be overcome due to the inherent complexity of biomass materials and associated processes. Reactions typically take place in a complex multiscale environment that renders the rational design of these processes and catalysts very challenging.

The overall objectives of the CCEI-EFRC are to develop the enabling science that can eventually lead to viable, economic operation of biorefinery technologies from various biomass feedstocks and to educate the workforce needed for these new positions that can lead to further, sustainable economic growth of the U.S.

We plan to exploit 3 complementary catalytic technological platforms that are anticipated to play key roles in biorefineries and energy/chemical production: Non-aqueous phase processing to produce fuels; aqueous phase processing to selectively produce chemicals; and direct conversion of biomass derivatives to electricity using novel direct carbon fuel cells.

In order to overcome the scientific barriers arising from handling these feedstocks, the CCEI will develop 3 crosscutting research thrusts: (1) multiscale modeling, to handle the inherent complexity of the environment in which reactions take place; (2) hierarchical multiscale materials that are hydrothermally stable, possess tunable porosity with bio-inspired functionality grafted, and minimize molecular traffic resistance while allowing shape selectivity; (3) cutting-edge characterization methods to probe reactions often under in situ environment.

UD faculty members of the new center include D.G. Vlachos (director), J.G. Chen (co-director), R.F. Lobo (outreach co-director), M.A. Barteau, J.A. Lauterbach, D.J. Buttrey, D.J. Doren, S.I. Sandler, and K.H. Lee. The center will also include faculty from the University of Pennsylvania (R.J. Gorte and J.M. Vohs), Lehigh University (M.A. Snyder), University of Massachusetts, Amherst (S.M. Auerbach, G.W. Huber), University of Minnesota (M. Tsapatsis, A. Bhan), California Institute of Technology (M.E. Davis), University of Southern California (H. Wang), and Brookhaven National Laboratories (A. Frenkel).

D. Vlachos

Photography credits: Jon Cox and UD Office of Communications & Marketing
Publication design and layout: Sheila Boulden

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sponsors

Air Liquide

Dr. Pavol Pranda
Delaware Research & Technology Center
200 GBC Drive
Newark, DE 19702

Air Products and Chemicals Inc.

Dr. Pete DeSanto
7201 Hamilton Blvd.
Allentown, PA 18195-1501

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

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

Dr. Carmo J. Pereira
DuPont Engineering Research & Technology
P.O. Box 80304
Wilmington, DE 19880-0304

Eastman Chemical Company

Dr. Guy Steinmetz
P.O. Box 1972
Kingsport, TN 37662

ExxonMobil Research and Engineering Company

Dr. José Santiesteban
Clinton Township, Route 22 East
Annandale, NJ 08801

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 and 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.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. Sponsorship fee of $10,000
2. Total grants to CCST faculty of $30,000 or more
3. Gifts-in-kind of $30,000 or more
4. Graduate student fellowship
5. Research contract to support a graduate student or a postdoc
6. Joint research grant of $50,000 or more

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

meet the faculty

DIRECTOR

Dionisios G. Vlachos

Elisabeth Inez Kelley Professor of Chemical Engineering

PhD – Univ. of Minnesota (1992)
MS – Univ. 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/Accomplishments:

2009: Top 100 Engineers, International Biographical Centre
2009: Elizabeth Inez Kelley Professorship of Chemical Engineering, University of Delaware
2007: George Piercy Distinguished Visiting Professor, Chemical Engineering and Materials Science Department, University of Minnesota

ASSOCIATE DIRECTOR

Mark A. Barteau

Senior Vice Provost for Research and Strategic Initiatives and Robert L. Pigford Chair of Chemical Engineering

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

Contact Information:

(302) 831-4007
barteau@udel.edu
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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 microcopies

Recent Awards/Accomplishments:

2009: Giuseppe Parravano Award, Michigan Catalysis Society
2008: Named as one of the "One Hundred Engineers of the Modern Era" by the American Institute of Chemical Engineers
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
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Research Interests:

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

Recent Awards/Accomplishments:

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

ASSOCIATE DIRECTOR

Jingguang G. Chen

Claire D. LeClaire Professor of Chemical Engineering

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

Contact Information:

(302) 831-0642
jgchen@udel.edu
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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/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

meet the faculty

Associate Director

Douglas J. Doren

Associate Dean of Arts & Sciences and Professor of Chemistry and Biochemistry

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

Contact Information:
(302) 831-1070
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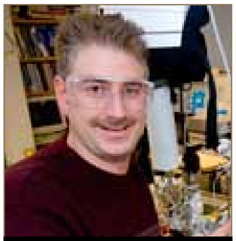
www.udel.edu/doren

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

Recent Awards/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)



Associate Director

Jochen A. Lauterbach

Professor of Chemical Engineering

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

Contact Information:
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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/Accomplishments:

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

Associate Director

Raul F. Lobo

Professor of Chemical Engineering

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

Contact Information:
(302) 831-1261
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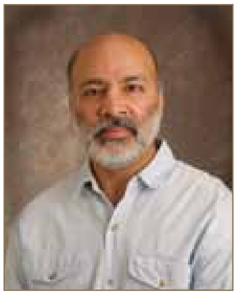
Research Interests:
Synthesis, characterization and discovery of novel microporous and mesoporous materials; structure-property relationships in catalysts and adsorbents; novel photocatalysts preparation and characterization; redox processes in porous materials for applications in catalysis

Recent Awards/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 decompositionof 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 fluidize catalytic cracking, could lead to the formation of these new sites in FCC catalysts
- Discovered a new photocatalyst containing zinc-gallium oxygen and nitrogen in the structure



S. Ismat Shah

Professor of Physics and Materials Science

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

Contact Information:
(302) 831-1618
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/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

Douglass F. Taber

Professor of Chemistry and Biochemistry

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

Contact Information:
(302) 831-2433
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Research Interests:
Stereoselective synthesis of natural products; organometallic catalysis; computational organometallic chemistry

Recent Awards/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

Associate Professor of Chemistry and Biochemistry

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

Contact Information:
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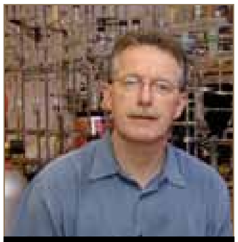
Research Interests:
Experimental and computational surface and thin film chemistry, diffusion barriers, nucleation, growth, self-assembly, surface modification

Recent Awards/Accomplishments:

- Research on dehydrative cyclocondensation reactions on hydrogen-terminated Si(100) and Si(111) highlighted in *Chemical and Engineering News* (2008)
- Invited presentation at the Iberoamerican Congress of Chemistry and XXIV Congress of the Peruvian Chemical Society, Cuzco, Peru (2008)
- Organizer of the Surface Science session at the EAS (2008)
- Research featured on the cover of *Langmuir* (2008)
- Invited Review, *Surface Science Report* (2008)
- 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* (2007)



ASSOCIATE DIRECTOR

Klaus H. Theopold

Professor and Chair of Chemistry and Biochemistry

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

Contact Information:
(302) 831-1546
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Research Interests:
Homogeneous catalysis, coordination polymerization of olefins, activation of dioxygen by novel oxidation catalysis

Recent Awards/Accomplishments:

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

PhD candidates

Name	Advisor	Degree	Research Topic
Ali, Bakhtyar	Shah	PHYS	Nanocomposite solar cells
Al-Majnouni, Khalid	Lobo/Vlachos	CHEG	High-temperature decomposition of Brønsted acid sites in zeolites
Bai, Sha	Taber	CHEM	Ru-catalyzed ring construction
Bao, Leijie	Shah	MSEG	High K dielectric thin films
Bedenbaugh, John	Lauterbach	CHEG	Model catalysts for high-pressure spectroscopic investigations
Berry, James	Taber	CHEM	Enantiomerically-pure natural products from prochiral cyclohexenones
Bilbao, Danny	Lauterbach	CHEG	Non-linear dynamics of No + NH_3 reaction
Boppana, Venkata Bharat Ram	Lobo	CHEG	Novel photocatalysts
Cheney, Beth	Chen/ Lauterbach	CHEG	Synthesis of catalytic materials
Choudhary, Vinit	Vlachos	CHEG	Design of reactive extraction and multiphase systems
D'Addio, Elizabeth	Lauterbach	CHEG	Discovery of NH_3 decomposition catalysts
Dai, Fang	Theopold	CHEM	Activation of O_2 with low-valent Cr complexes
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
Fickel, Dustin	Lobo	CHEG	Redox sites in zeolites
Foster, Andrew	Lobo	CHEG	Development of catalysts for fast catalytic pyrolysis of biomass
Gerstenhaber, David	Taber	CHEM	Enantiomerically-pure cyclohexanones from cyclohexenones
Guo, Pengfei	Taber	CHEM	Fe-catalyzed bicyclic ring construction
Guralnick, Brett	Lobo	CHEG	Development of new concepts in hybrid photovoltaic cell 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	Chen	CHEG	Synthesis of Tungsten carbides
Javadekar, Ashay	Barteau	CHEG	Mechanisms of promoters in olefin epoxidation
Kelly, Thomas	Chen	CHEG	Electrocatalysts for ethanol fuel cells
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
Lin, Jia-Ming	Teplyakov	CHEM	Thin films on semiconductors
Lonergan, William	Chen/Vlachos	CHEG	Synthesis and characterization of supported catalysts
Madachik, Mark R.	Teplyakov	CHEM	Surface self-assembly and Co-adsorption on semiconductors
McGill, Jacob	Vlachos/Ogunnaike	CHEG	Control of heteroepitaxial growth of nanomaterials
Mellinger, Zach	Chen	MSEG	Supercapacitors and electrochemistry
Mettler, Matthew	Vlachos	CHEG	Process intensification in catalytic reactors
Miao, Yinghong	Shah	MSEG	Quantum dot solar cells
Miller, Timothy	Teplyakov	CHEM	Photovoltaic materials
Nelson, Christopher	Taber	CHEM	Tandem catalytic Rh-Mn ring construction
Paquette, Craig	Taber	CHEM	Enantiomerically-pure cyclic quatenary centers by catalytic epoxidation of cyclohexenes
Perrine, Kathryn A.	Teplyakov	CHEM	Photochemistry in metal deposition on semiconductors
Ren, Hui	Chen	CHEM	Bimetallic catalysts
Rodriguez-Reyes, Juan Carlos	Teplyakov	CHEM	Diffusion barriers and interface chemistry
Salciccioli, 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
Shen, Jingmei	Theopold	CHEM	alpha-Diimine complexes of chromium in ethylene oligomerization catalysis
Sheth, Ritesh	Taber	CHEM	Fe-mediated cyclohexenone annulation
Sirianni, Eric	Theopold	CHEM	The effect of redox-active ligands on coordinated ligands and proton coupled electron transfer (PCET)
Smith, Natalee	Taber	CHEM	α-Methylene lactones by Pd-catalyzed hydroformylation
Stottlemyer, Alan	Chen	CHEG	Carbides as alternative electrocatalysts
Sutton, Jonathan	Vlachos	CHEG	First principle design of bimetallic catalysts
Tian, Fangyuan	Teplyakov	CHEM	Surface self-assembly
Tupy, Sarah	Vlachos	CHEG	Kinetics of hydrocarbon and alcohol reforming
Yessetepe, Emre	Shah	MSEG	Thermoelectric nanocomposites
Young, Owen	Chen	CHEG	Membranes for battery and fuel cells
Yu, Weiting	Chen/Barteau	CHEG	H_2 and chemicals from oxygenates
Zhang, Xiaochun	Teplyakov	CHEM	Interface chemistry of biochemical systems on semiconductors

alumni, visiting researchers and 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, Yiannis	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	Multiple bonds to iron - the reactivity of Tp iron imido complexes
Guo, Peiming	Taber	Cyclohexanones
Prasad, Vinay	Vlachos	Microkinetic model-based design of experiments and catalysts
Rykov, Sergey	Chen	Characterization of surfaces and catalysts
Snively, Chris	Lauterbach	Development of novel spectroscopic techniques
Stamatakis, Michael	Vlachos	Multiscale modeling of surface phenomena
Stefanidis, George	Vlachos	Short contact time multifunctional reactors
Xing, Xianjie	Chen	Batch and flow reactor systems
Yamada, Soichiro	Lauterbach	High-throughput catalysis

2008-2009 Alumni

Name	Advisor	Current Employer
Karim, Ayman	Vlachos	Pacific Northwest National Laboratories
Tian, Weiwei	Taber	Postdoc, Scripps Research Institute
Chan, Sze Chi (Joan)	Barteau	
Chung , Kimberly	Buttrey	
Collins, Stuart	Vlachos	
Dellamorte, Joseph	Barteau/Lauterbach	BASF
Federici, Justin	Vlachos	ExxonMobil
Goda, Amit	Chen/Barteau	
Humbert, Michael	Chen	UTC Power
Jove, Fernando	Theopold	Postdoc, Temple University
Kreisel, Kevin	Theopold	
Lukaski, Adrienne	Barteau	ExxonMobil
Menning, Carl	Chen	ExxonMobil
Nash, Michael	Lobo/Doren	Eastman Chemical Company
Pyrz, William D.	Buttrey/Lobo	
Shough, Anne Marie	Doren	ExxonMobil
Skliar, Dimitri	Willis	
Skoplyak, Orest	Chen/Barteau	DuPont
Vijay, Rohit	Lauterbach	ExxonMobil
Winski, David	Lauterbach	
Yang, Hua M.	Buttrey	
Young, John	Theopold	Exelus, Inc.

recent publications

Mark A. Barteau

J.C. Dellamorte, J. Lauterbach, M.A. Barteau, **"Effect of preparation conditions on Ag catalysts for ethylene epoxidation,"** *Topics in Catalysis* (2009, in press).

J.C. Dellamorte, M.A. Barteau, J. Lauterbach, **"Opportunities for catalyst discovery and development: Integrating surface science and theory with high throughput methods,"** *Surf. Sci.*, **603,** 1770 (2009).

A.C. Lukaski, M.A. Barteau, **"Investigation of ethylene oxide on clean and oxygen-covered Ag(110) surfaces,"** *Catalysis Letters,* **128,** 9 (2009).

J.C. Dellamorte, J. Lauterbach, M.A. Barteau, **"Promoter-induced morphological changes of Ag catalysts for ethylene epoxidation,"** *I&ECR,* **48,** 5943 (2009).

O. Skoplyak, M.A. Barteau, J.G. Chen, **"Enhancing H_2 and CO production from glycerol using bimetallic surfaces,"** *ChemSusChem,* **1,** 524 (2008).

G.J. Fleming, K. Adib, J.A. Rodriguez, M.A. Barteau, J.M. White, H. Idriss, **"The adsorption and reactions of the amino acid proline on rutile TiO_2(110) surfaces,"** *Surf. Sci.,* **602,** 2029 (2008).

A.M. Goda, M. Neurock, M.A. Barteau, J.G. Chen, **"Effect of hydrocarbon chain length and cyclization on the adsorption strength of hydrocarbons on Pt/3d bimetallic surfaces,"** *Surf. Sci.,* **602,** 2513 (2008).

H. Idriss, M. Scott, J. Llorca, S.C. Chan, W. Chiu, P.Y. Sheng, A. Yee, M.A. Blackford, S.J. Pas, A.J. Hill, F.M. Alamgir, R. Rettew, C. Petersburg, S. Senanake, M.A. Barteau, **"A phenomenological study of the metal/oxide interface: The role of catalysis in hydrogen production from renewable sources,"** *ChemSusChem,* **1,** 905 (2008).

O. Skoplyak, C.A. Menning, M.A. Barteau, J.G. Chen, **"Reforming of oxygenates for H_2 production on 3d/Pt(111) bimetallic surfaces,"** *Topics in Catalysis,* **51,** 49 (2008).

O. Skoplyak, M.A. Barteau, J.G. Chen, **"Ethanol and ethylene glycol on Ni/Pt(111) bimetallic surfaces: A DFT and HREELS study,"** *Surf. Sci.,* **602,** 3578 (2008).

Douglas J. Buttrey

W.D. Pyrz, D.A. Blom, M. Sadakane, K. Kodato, W. Ueda, T. Vogt, D.J. Buttrey, **"Atomic-scale investigation of two-component MoVO complex oxide catalysts using aberration-corrected high-angle annular dark-field imaging"** (2009, accepted).

M. Sadakane, K. Yamagata, K. Kodato, K. Endo, K. Toriumi, Y. Ozawa, T. Ozeki, T. Nagai, Y. Matsui, N. Sakaguchi, W.D. Pyrz, D.J. Buttrey, W.Ueda, **"Synthesis of orthorhombic Mo-V based oxides by assembly of pentagonal Mo6O21 polyoxometalate building blocks,"** *Angew. Chem. Int. Ed.,* **48,** 3782-3786 (2009).

D.A. Blom, W.D. Pyrz, T. Vogt, D.J. Buttrey, **"Aberration-corrected STEM investigation of the M2 phase of MoVNbTeO selective oxidation catalyst,"** *J. Electron Microscopy,* **58,** 193-198 (2009, special issue on advanced electron microscopy in materials physics).

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research grants

Research Grant	Funding Agency	Investigators
From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity	Department of Energy (9/03-9/12)	Mark Barteau, Raul Lobo, Doug Buttrey, Jingguang Chen, Jochen Lauterbach, Dion Vlachos
An Integrated Approach Toward Rational Nanocatalyst Design for Hydrogen Production	Department of Energy (7/06-6/09)	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
Catalyst Characterization Using Synchrotron Techniques	UOP (10/05-12/09)	Jingguang Chen
Synthesis and Characterization of Electrocatalysts	UTC Power (12/07-12/09)	Jingguang Chen
Design of Bimetallic Catalysts	W.R. Grace & Co. (7/08-12/09)	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
Design of stable reforming catalysts	Air Liquide (1/09 - 12/09)	Jingguang Chen
Novel Photocatalysts With One- and Two-Dimensional Nanostructures	Department of Energy (9/07-8/10)	Doug Doren, Raul Lobo
MRI: Acquisition of a Facility for Computational Approaches to Molecular-Scale Problems	National Science Foundation (8/09 - 7/12)	Doug Doren, Dion Vlachos, et. al.
Sustainable Energy from Solar Hydrogen	National Science Foundation (7/06-6/11)	Jochen Lauterbach, Bob Opila, Thomas Beebe, Robert Opila, Suresh Advani, Andrew Teplyakov
Small Angle Neutron Scattering on Polymers and Complex Fluids	National Institute of Standards and Technology (9/07-8/12)	Raul Lobo, Norm Wagner, et. al.
ACS-Petroleum Research Fund: Redox Centers from Brønsted Acid Sites and Defects in H-Zeolites: Formation, Structure & Reactivity in Hydrocarbon Catalysis	Department of Energy, Basic Energy Sciences (2007-2009)	Raul Lobo
Unique Photoelectronic Processes	CIA ATP (7/07-7/10)	Ismat Shah
PAH removal with TiO_2 photocatalysis	National Science Foundation (6/08-5/11)	Ismat Shah
Thin Film and Nanoparticles Workshops	National Science Foundation (9/07-7/10)	Ismat Shah
Nanoscale Undergraduate Education for Renewable Energy	National Science Foundation (9/09-8/11)	Ismat Shah
Structural Investigation of Prostaglandin Conjugates (NIH MERIT Award)	GM 42056 (1993-2011)	Doug Taber
Chemical Control over Interface Formation and Impurity Distribution in Thin Solid Films	National Science Foundation (8/07-8/10)	Andrew Teplyakov
Role of Specific Reactive Sites on Silicon Nitride Surface in Catalysis of Isomerization and Addition Reactions	ACS-PRF (2/08-8/10)	Andrew Teplyakov
Cryoprobe Upgrade of a Cyberenabled NMR Spectrometer	National Science Foundation (2/09-1/12)	Klaus Theopold
Low-valent Chromium - Molecules, Reactivity and Catalysis	National Science Foundation (9/09-8/12)	Klaus Theopold
Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer	Department of Energy (9/09 – 8/12)	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
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
Multiscale mathematics for biomass conversion to renewable hydrogen	Department of Energy (8/09-7/12)	Dion Vlachos
Rational design of innovative catalytic technologies for biomass derivative utilization	Department of Energy (8/09-7/14)	Dion Vlachos, Jingguang Chen, Raul Lobo, Mark Barteau, Jochen Lauterbach, Doug Buttrey, Doug Doren, Stan Sandler, Kelvin Lee, et. al.
Center for Spatiotemporal Modeling of Cell Signaling (STMC)	National Institute of Health (8/09-7/14)	Dion Vlachos

High-throughput Reaction and Characterization Studies of Ag Catalysts for Ethylene Epoxidation

Faculty: Mark Barteau, Jochen Lauterbach (Chemical Engineering)
Graduate Student: Joe Dellamorte (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences

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. Figure 1 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.

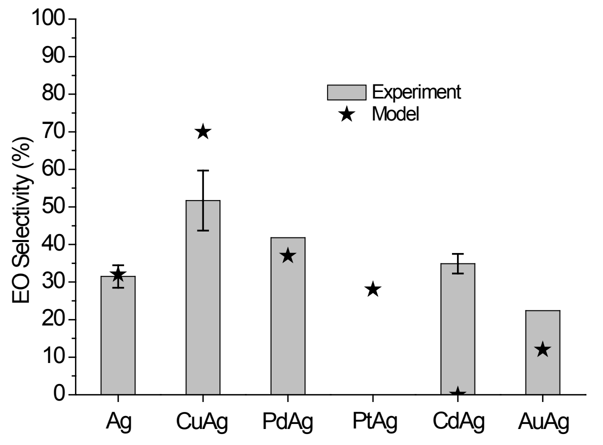


Figure 1

The combination of high-throughput reactor experiments and scanning electron microscopy analysis of promoted Ag catalysts provides critical insights into mechanistic and morphological changes. In particular, catalysts promoted with Cu, Cd, Au, Pt, and Re were analyzed to understand the morphological effects of these promoters on the Ag particles. Cu increases the sintering of Ag particles, while Cd and Re were found to alter the Ag particle sizes into a trimodal distribution. However, contrasting effects of Re and Cd were found on the catalyst activity. Cd-Ag catalysts exhibited a 5-fold increase in the ethylene conversion for a variety of Cd loadings, compared to unpromoted Ag. Moderate increases in conversion and selectivity were seen with the addition of 25 ppm Re, while further Re impregnation led to decreases in ethylene conversion and ethylene oxide selectivity. Au and Pt block surface Ag sites by nucleating as separate particles on the silver surface, as illustrated in Figure 2. In doing so, they reduce the activity of the catalyst, but also reduce the sintering of the Ag particles. ✧

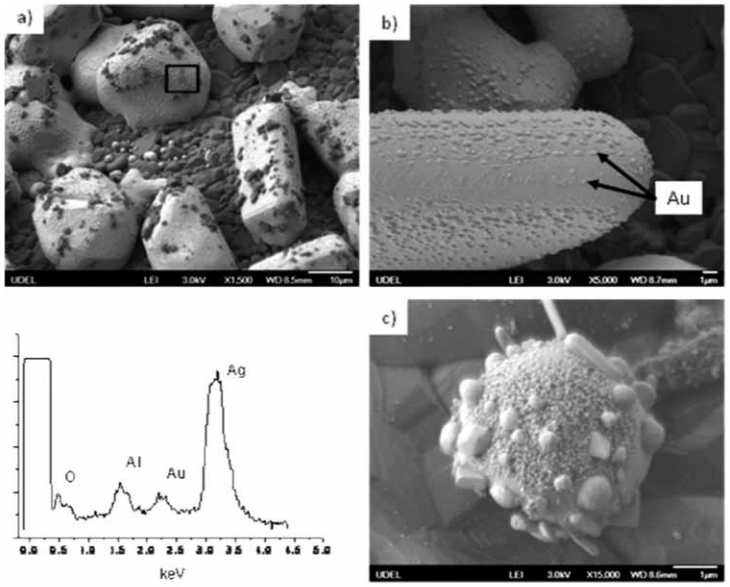


Figure 2:

SEM images of:

(a) 100 ppm Au-Ag-12 h catalyst with EDS analysis

(b) higher magnification image of region of 100 ppm Au-Ag-12 h catalyst

(c) 300 ppm Au-Ag-12 h catalyst. All catalysts were imaged after reaction. Black rectangle indicates region of EDS collection. White particles are Ag. Dark gray particles are α-Al_2O_3

Novel Photocatalytic Materials

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

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

Our contribution has centered on the use of novel precursor materials that increase the range of compositions (Zn/Ga ratios) that can be prepared as oxy-nitrides. Using sol-gel techniques we have prepared Zn/Ga mixed oxide precursor materials that have lead to two important discoveries. At low temperatures (less than 550°C) we have prepared a new phase of zinc-gallium oxy-nitrides with a spinel structure (See Figure 1). In these materials of base composition $ZnGa_2O_4$ the reaction with ammonia leads to $ZnGa_2O_{4-1.5x}N_x$ with a dramatic change is the bandgap (Figure 2). Using sol-gel precursors and higher reaction temperatures we have been able to prepare zinc-gallium oxy-nitrides with zinc contents near 30% approaching the optimum composition that has been predicted by theory to minimize the bandgap (Figure 2).

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

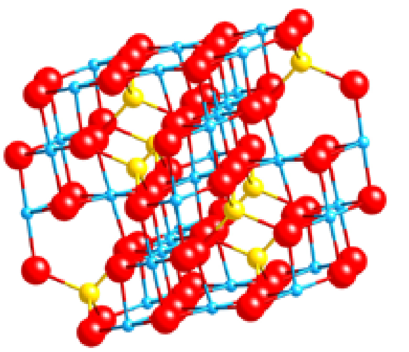


Figure 1: Spinel structure with metals in tetrahedral and octahedral coordination environments

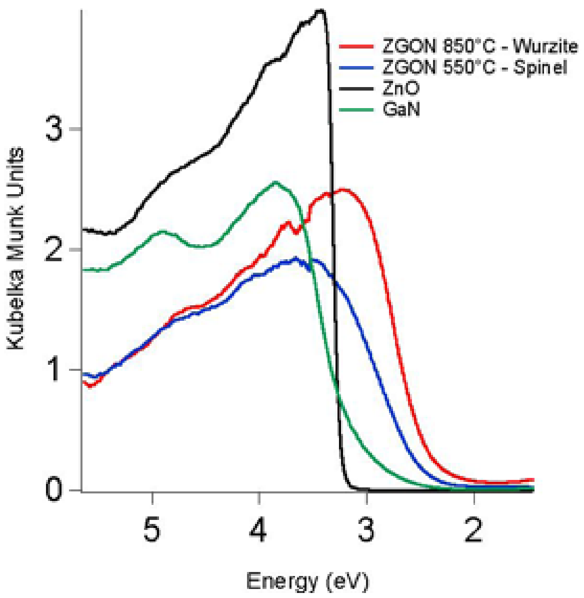


Figure 2: UV/vis diffuse reflectance spectra of ZnO and Zn/Ga oxinitrides (Zn/Ga = 1/2) treated in ammonia atmosphere at various temperatures

Complex Transition Metal Oxides for Selective Oxidation

Faculty: Doug Buttrey (Chemical Engineering)
Graduate Student: William Pyrz (Chemical Engineering)

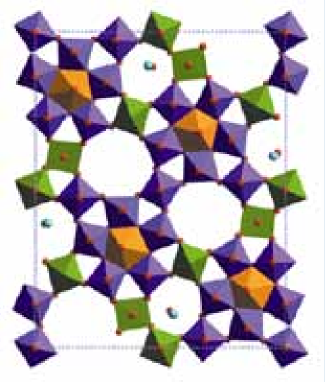
Highly selective, atom-efficient catalytic reactions are not only desired, but also mandatory in the petroleum and petrochemical industry. Since raw materials are increasingly becoming a proportion of the total end product cost, it is cost effective to preserve as much of the carbon from the feed material 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.

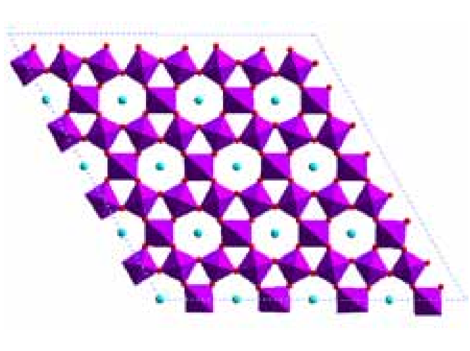
Controlled site isolation should give us the opportunity to stop oxidation reactions at desired products instead of resulting in complete combustion. This is accomplished by controlling the accessible extent of oxidation at the local site. For example, we should be able to convert propane to propylene, 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 Bi_2O_3-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 below). 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. ✧

Orthorhombic $Mo_{7.5}V_{1.5}NbTeO_{29}$





Hexagonal $Mo_6Te_2VO_x$ *found in active propane ammoxidation catalyst*

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 1), 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 2 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 2c 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 2a and 2b, 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 2b 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. ✧

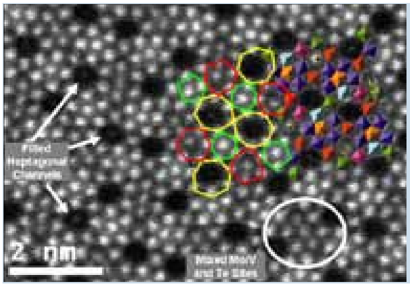


Figure 1:

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.

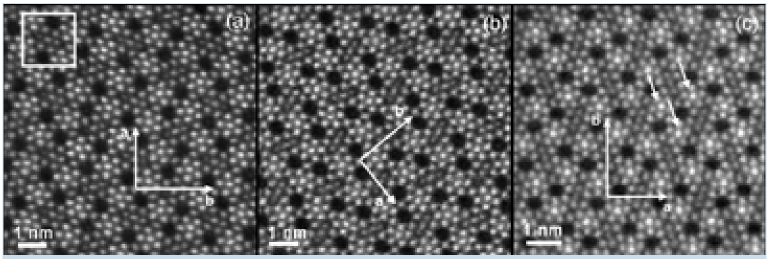


Figure 2: HR-STEM images of (a) MoVTeO (b) MoVNbTeO, and (c) MoVTaTeO 'M1' catalysts. The indicated a-b axes in each image show the orientation of a single unit cell within the image. The box shows a region within the MoVTeO catalyst that exhibits local contrast that differs from the other two catalysts suggesting compositional variation. The arrows in the MoVTaTeO catalyst indicate enhanced contrast that is indicative of Ta occupation in the pentagonal centers.

Synthesis and Characterization of Metallic and Bimetallic Nanoparticles Through Electron Microscopy

Faculty: Doug Buttrey, Dion Vlachos, Jochen Lauterbach (Chemical Engineering)
Collaborators: Jim Dumesic, Dante Simonetti, Edward Kunkes (Chemical & Biological Engineering, 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).

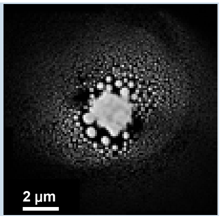


Figure 1: HAADF micrograph of a nano-particle field following an EBIF event

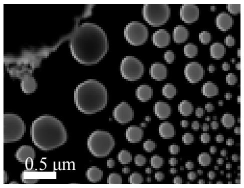


Figure 2a: Typical HAADF image of nanoparticles following EBIF

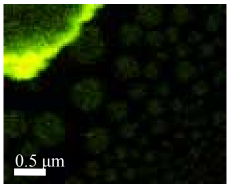


Figure 2b: Ni K edge x-ray map showing areas with Ni

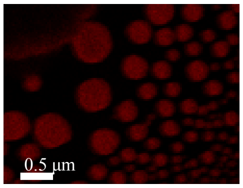


Figure 2c: Bi M edge x-ray map showing areas containing Bi

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 1 shows a HAADF image and Figure 2 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 3 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. ✧

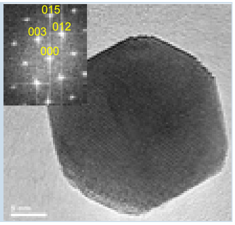


Figure 3 HREM image of a single Ni-Bi nanoparticle with the corresponding FFT image looking down the [100] zone axis

NEXAFS and EXAFS Characterization of Catalytic Materials

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

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

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

Metal Carbides as Anode Electrocatalysts and Capacitors

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

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

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

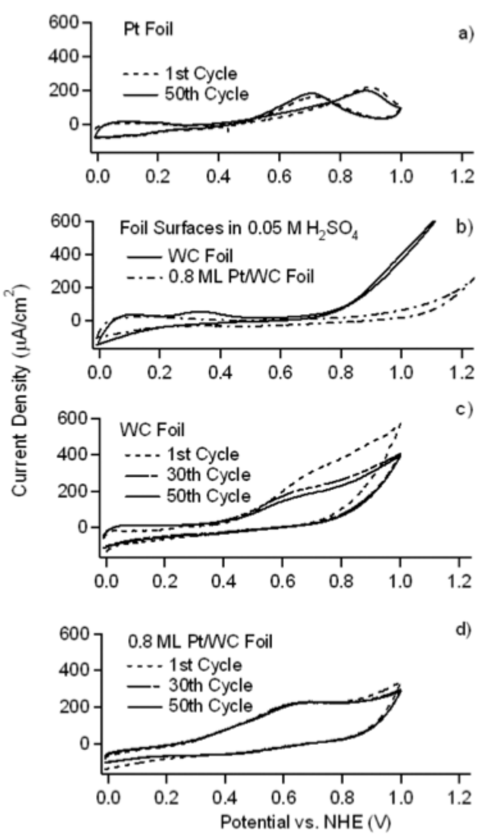


Figure 1

Novel Properties of Bimetallic Surfaces and Supported Catalysts

Faculty: Jingguang Chen, Dion Vlachos, Mark Barteau, Jochen Lauterbach (Chemical Engineering)
Graduate Students: Danielle Hansgen, William Lonergan, Weiting Yu, Beth Cheney (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences and NSF IGERT

Bimetallic surfaces and catalysts, in particular with the metal overlayer at a monolayer-thickness, often show chemical activities that are different from the bulk materials.Our studies in bimetallic catalysis include experimental and theoretical efforts on well-characterized single crystal surfaces. Using a combination of Temperature Programmed Desorption, High-Resolution Electron Energy Loss Spectroscopy, and Density Functional Theory (DFT) modeling, we have established a correlation between the unique chemical properties of Ni/Pt bimetallic surfaces to changes in the d-band center of surface Pt atoms.We have extended similar experimental and DFT modeling methods to investigate a wide range of bimetallic surfaces to determine a general correlation between the center and d-band and chemical properties.In addition to surface science studies, we also attempt to bridge the “materials gap” and “pressure gap” between model single crystal surfaces and realistic powder materials.We are currently synthesizing bimetallic catalysts on high surface area alumina supports and on zeolites.These bimetallic catalysts are evaluated using a combination of microreactor, transmission IR, and EXAFS under in-situ reaction conditions.

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

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

Faculty: Jingguang Chen (Chemical Engineering)
Graduate Students: Carl Menning (Chemical Engineering)
Funding: U.S. Department of Energy, EERE

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

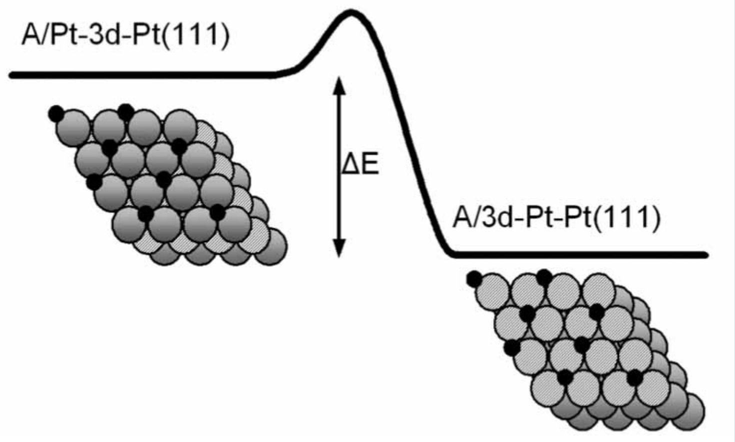


Figure 2

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. ✧

Photoelectrochemical (PEC) Devices for Water Splitting

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

The cathode reaction at PEC involves the reduction of H+ to produce H2.Currently the most common cathode catalyst is Platinum (Pt). Due to the high cost and limited supply of Pt, the utilization of large quantities of Pt will most likely hinder the commercialization of PEC. We will attempt to solve this problem using two parallel approaches: (1) to reduce the loading of Pt by using Pt-based bimetallic alloys and (2) to replace Pt with alternative catalytic materials.Currently we are exploring the possibility of utilizing these carbide materials for the cathode reduction of H+ to produce H2.The cathode activity and stability of W and Mo carbides are being compared to those of Pt.We plan to employ a combination of in-situ electrochemical measurements and theoretical modeling to identify and synthesize carbide structures and compositions as alternative cathode catalysts in PEC.

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

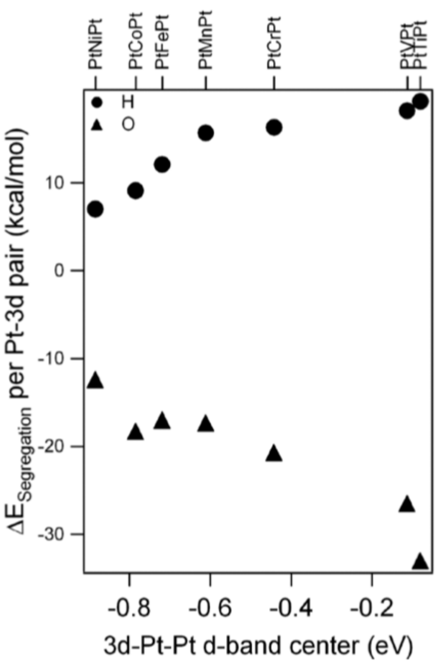


Figure 3

Structure-Property Relationship in Transition Metal Carbides

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

The carbides of early transition metals (Groups IVB-VIB) are characterized by many unique and intriguing catalytic properties.It is now well established that, compared to their parent metals, TMCs often demonstrate catalytic advantages in activity, selectivity, and resistance to poisoning. It has also been demonstrated that the catalytic performances of TMC are approaching or surpassing those of the more expensive Pt-Group metals (Pt, Pd, Ir, Rh and Ru), particularly in catalytic reactions involving the transformation of C-H bonds of hydrocarbons, such as in dehydrogenation, hydrogenation, hydrogenolysis, and isomerization reactions.

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

Photocatalysis in ETS-10, A Nanostructured Titanosilicate

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

ETS-10 contains one-dimensional chains of TiO_6 octahedra within a nanoporous silicate framework (see Figure 2). 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 3). 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. ✧

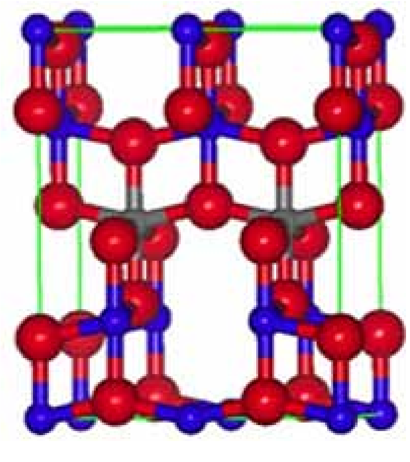


Figure 1:

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

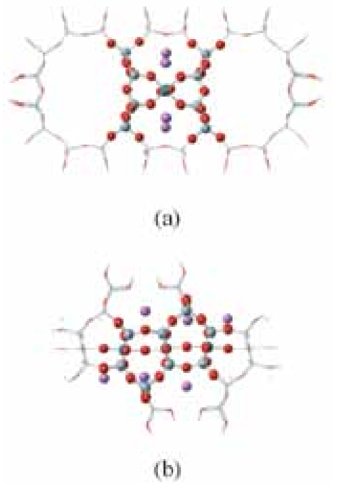


Figure 2:

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.*

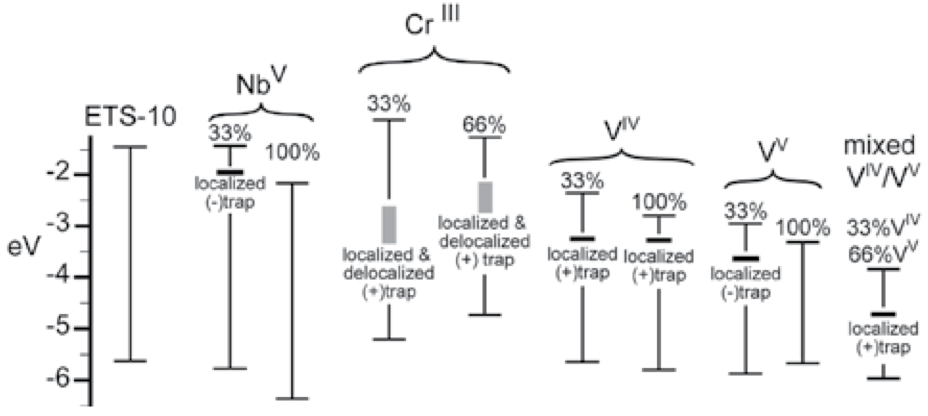


Figure 3:

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

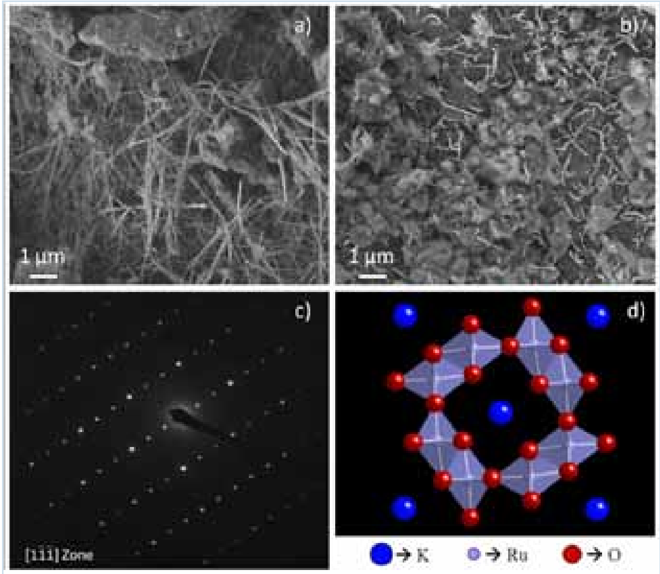
High-throughput Analysis and Preparation of Supported Catalysts

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

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

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

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

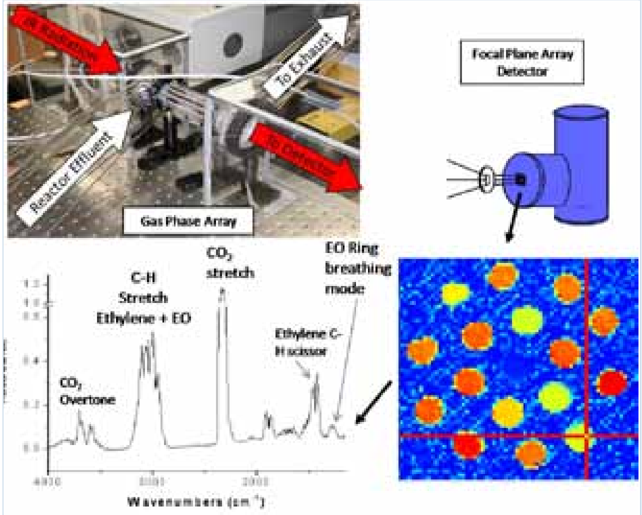


a) K-promoted Ru catalyst after calcination containing KRu_4O_8 Hollandite crystals, b) Hollandite degrades in reducing conditions to form highly dispersed Ru^0 phase, c) SAED image used to identify Hollandite on catalyst, d) [001] projection of KRu_4O_8.

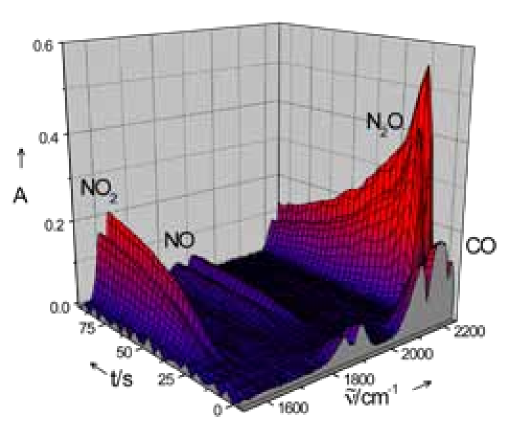
Currently, we explore the parameter space associated with ammonia decomposition catalysts. This chemistry is of interest because ammonia has been proposed as a chemical carrier of hydrogen for mobile alternative energy applications. However, high temperatures are currently required to attain a satisfactory ammonia conversion. This challenge necessitates rapid exploration of highly active novel catalytic materials for low temperature ammonia decomposition. The most active catalysts, potassium or rubidium promoted Ru, contained a unique "nanowhisker" morphology that we have identified using SEM and TEM techniques. The K-promoted catalysts formed single crystal hollandite (KRu4O8) after calcination. By varying preparation conditions, we have observed a consistent link between formation of hollandite and increased catalytic activity. Pure Hollandite crystals synthesized in our lab were active, but degraded after exposure to NH3. Chemisorption experiments paired with microscopy of these catalysts at each stage of their lifetime suggest that the hollandite acts as a structural precursor to a highly dispersed Ru phase.

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

We have explored several catalytic systems using this synthetic approach, including NOx storage and reduction catalysts (NSR) for automotive



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



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

exhaust applications, ammonia decomposition for hydrogen storage applications, and ethylene epoxidation. For example, Co/Pt/Ba NSR catalysts were synthesized in this manner and compared to their incipient wetness counterparts in a high-throughput reactor system. The nanoparticles were also analyzed using electron microscopy and elemental analysis techniques.

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

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

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

Model Catalysts for High-Pressure Spectroscopic Investigations

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

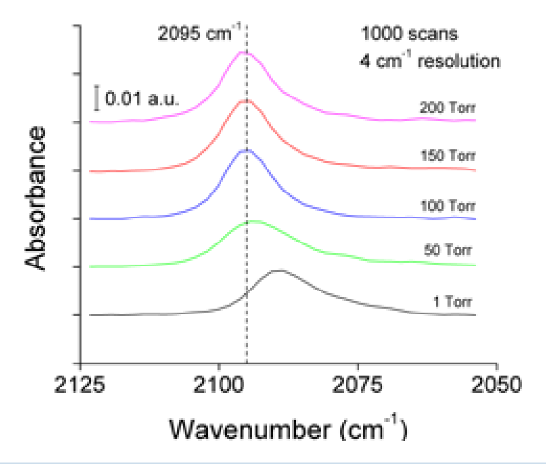
Molecular-level catalytic investigations have traditionally been performed using model catalysts consisting of single crystal surfaces under ultra-high vacuum (UHV) conditions. However, discrepancies can exist between surface science observations in UHV conditions and industrial catalytic performance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

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

(continued on page 22)

(continued from page 21)

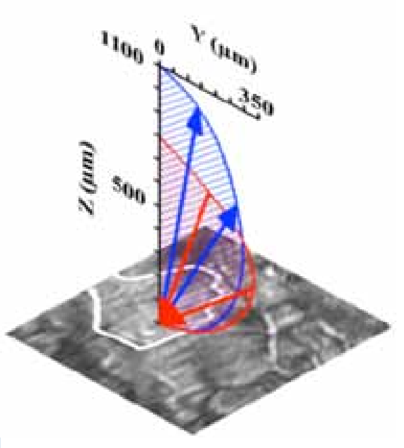
In work currently being performed in our laboratory, we seek to explore surface adsorption behavior in higher pressure environments during simple reactions, such as CO oxidation and NH_3 decomposition. Studying adsorption behavior on a catalyst surface using vibrational spectroscopy yields information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



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

Non-linear Phenomena in Heterogeneous Catalysis

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



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

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, spatiotemporal pattern formation can be observed in the 10^{-5} mbar pressure range. In an attempt to bridge the “pressure-gap,” EMSI is used to follow pattern formation up to atmospheric pressure. The features of the nonlinear phenomena, observed in different pressure regimes, are markedly different. This is shown by comparison of various qualitative and quantitative features of spatio-temporal pattern formation as well as the dynamics of the macroscopic reaction rate.

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

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)
Funding: Robert L. Pigford Professorship

Selective oxidation catalysis produces about 25% of the most important organic chemicals and intermediates. One example is selective oxidation of 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-$Bi_2Mo_2O_9$ 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-$Bi_2Mo_2O_9$ 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 the b parameter halved (β variant phase). Current efforts are focused on synthesis of M1 and M2 phase catalysts that have also shown promise for selective oxidation and ammoxidation of propane. ✧

Mechanistic Investigations of Olefin Epoxidation and Combustion Pathways

Faculty: Mark Barteau, Doug Buttrey (Chemical Engineering)
PhD 2009: Adrienne Lukaski (Chemical Engineering)
Graduate Student: Ashay Javadekar (Chemical Engineering)
Funding: U.S. Department of Energy, Basic Energy Sciences

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).

We have carried out investigations of the combustion pathway for ethylene oxide (EO) on Ag(110) and (111) surfaces, utilizing both EO and acetaldehyde as entry points into the reaction sequence. EO ring-opens following adsorption at 250 K on both clean and O-covered Ag(110) to form a stable oxametallacycle. On the clean Ag(110) surface, the oxametallacycle reacts to reform the parent epoxide at 280 K during TPD, while the aldehyde isomer, acetaldehyde, is observed at higher oxametallacycle coverages. In the presence of coadsorbed oxygen atoms, a portion of the oxametallacycles dissociate to release ethylene. However, of those that react to form oxygen-containing products, the fraction forming ethylene oxide is similar to that on the clean surface. The acetaldehyde product of oxametallacycle reactions combusts via formation of acetate species; the acetates react to form CO_2 at temperatures as low as 360 K on the O-covered surface. This pathway was also demonstrated for combustion of acetaldehyde in excess oxygen on Ag(111). No evidence was observed for other combustion channels on either surface. This work provides experimental evidence for the connection of oxametallacycles to combustion via acetaldehyde formation as well as to ring-closure to form ethylene oxide. ✧

Growth Mechanisms of Zeolite Catalysts

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

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

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

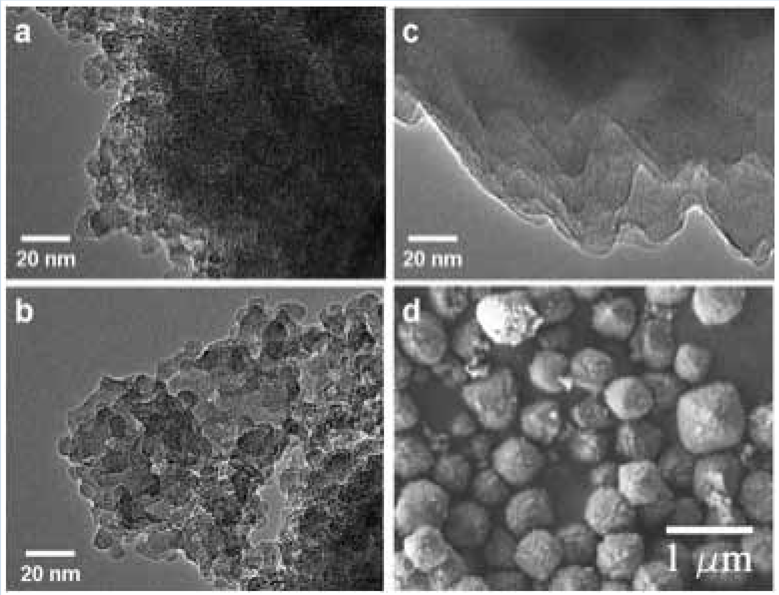
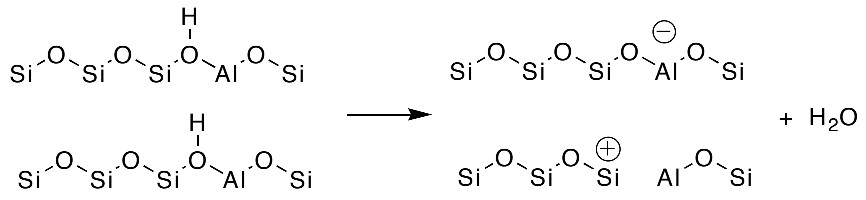


Figure 1:

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

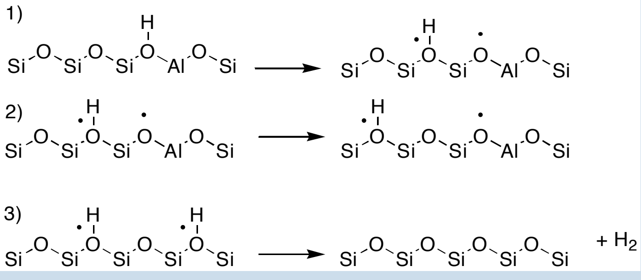
Redox Sites in Acid Zeolites

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



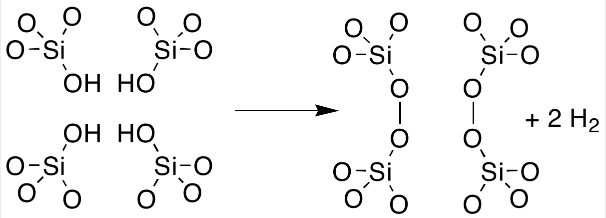
Scheme 1: Dehydroxylation via heterolytic decomposition of Brønsted acid sites

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



Scheme 2: Proposed homolytic decomposition of Brønsted acid sites

A plausible path for the formation of hydrogen from BAS (Scheme 2) suggests that the product should lead to the formation of $[\mathrm{AlO}_4]^0$ sites in the zeolite. Formally $[\mathrm{AlO}_4]^0$ sites can more clearly be described as $[\mathrm{AlO}_4/h]^0$ where *h* is a hole located (at low temperatures) on one of the oxygen atoms surrounding the aluminum —that is, one oxygen atom is oxidized to a formal oxidation state of 1–. This oxidized oxygen atom could be the source of the radical cations formed when organic molecules with low ionization potentials are adsorbed on acid zeolites.



Scheme 3: Proposed homolytic decomposition of Brønsted acid sites

In related research and in collaboration with Prof. Doren, we have found that zeolite 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 peroxo sites that we have also identified by UV/vis diffuse reflectance spectroscopy. The potential catalytic role of these sites remains unclear and we are currently studying the reactivity, formation and decomposition of the peroxo sites to determine under what conditions they can affect the expected catalytic chemistry of other sites such as Brønsted acid sites. ✧

Photoelectrochemical Splitting of Water Using N:TiO$_2$ Anode

Faculty: Ismat Shah (Physics and Materials Science)

The principle of photocatalytic reaction in colloidal systems is to oxidize the electron rich solutes (i.e. soluble organic compounds), through either a direct hole oxidation or an indirect oxidation by hydroxyl radical generated at the valence band. In such a reaction scheme, photoexcited electrons are scavenged mainly by dissolved oxygen molecules to complete the electron transfer cycle. Clearly, this leads to a waste of 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 TiO$_2$ semiconductor electrodes in 1972. Their attempt showed the feasibility of conversion of photon energy into chemical energy (H_2) without wasting of photo-induced electron excitation in photocatalytic systems. The photoelectrochemical 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 O_2 via an oxidation reaction:

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

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

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

To improve the quantum conversion efficiency in a TiO$_2$-based PEC system, the most efficient approach is to reduce the bandgap of the semiconductor. Theoretical studies based on first-principles orthogonalized linear-combinations of atomic-orbitals (OLCAO) and full-potential linearized augmented plane-wave (FLAPW) have revealed that upper valence band is predominately consists of O2*p* states and minimum of the conduction band is mainly constructed with Ti3*d* 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 TiO$_2$ lattice. The reported substitutional doping of cation and anion of TiO$_2$ catalysts have often been proven to improve the photocatalytic performance of TiO$_2$. Among all dopants reported, nitrogen doped TiO$_2$ is consistently recognized as one of the most visible light sensitive 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 N2*p* 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 TiO$_2$ could introduce deep N2*p* states within the forbidden band. Although this significantly reduces the bandgap of TiO$_2$, it also encourages the rate of recombination and reduces the charge carrier mobility, which could be a hindering effect for photocatalysis. For the soluble organic removal in a colloidal suspension system, the oxidative power not only depends on how low the valence band edge is in absolute energy scale, but it also requires the energy of the conduction band edge to be higher than the bottom of water stability limit (O_2/H_2O) to promote the conduction band electron scavenging and prolonging the electron transfer kinetic. Thus, deep N2*p* localized states created by interstitial doping may give a detrimental effect to photocatalysis.

To optimize the water splitting performance in a PEC system, the semiconductor photoanode is required to have its valance band edge positioned below the lower water stability limit. Several semiconductors that meet this requirement have been reported. Among these materials, Fe_2O_3 has the lowest band gap (Eg = 2.3 eV). However, it is unstable in aqueous environments due to corrosion problem.

The most commonly used semiconductor oxide for the PEC application have been reported to be TiO$_2$ and SrTiO$_3$. Although TiO$_2$ has lower band gap energy than that of SrTiO$_3$, it has been reported that SrTiO$_3$ yields one order higher quantum efficiency in photoelectrolysis comparing to TiO$_2$ electrode without additional voltage bias condition due to the lower electron mobility in TiO$_2$ 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 TiO$_2$/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 ($E_F^o{}_{redox}$) 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.

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

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

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

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

We have used a N doped TiO_2 thin film anode to allow broader photon spectrum harvesting. Using this electrode, a photoelectrochemical cell is fabricated, shown in the figure 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. ✧

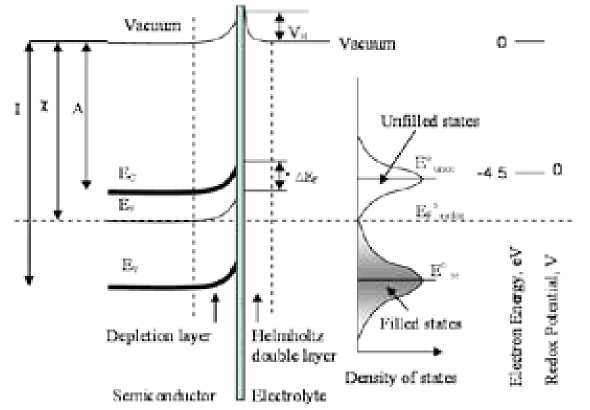


Figure 1: Energy band diagram of the interface between an n-type semi-conductor surface and an electrolyte

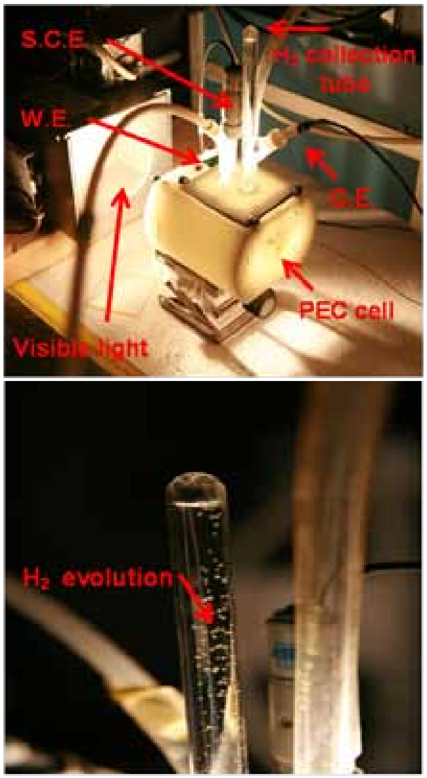


Figure 2:

A photoelectrochemical cell using $N:TiO_2$ as the anode

Cyclohexanones by Rh-Catalyzed Intramolcular C-H Insertion

Faculty: Doug Taber (Chemistry and Biochemistry)
Postdoc: Peiming Gu (Chemistry and Biochemistry)
Funding: NIH, GM42056

We have found that the Rh carbenes derived from α-diazo benzyl ketones are significantly more discriminating than are the Rh carbenes derived from β-ketoesters. When an electron rich C-H site is available six atoms away, cyclohexanone formation can dominate. This is in marked contrast to the cyclizations of α-diazo β-ketoesters, that consistently deliver cyclopentanone products. (Figure 1) ✧

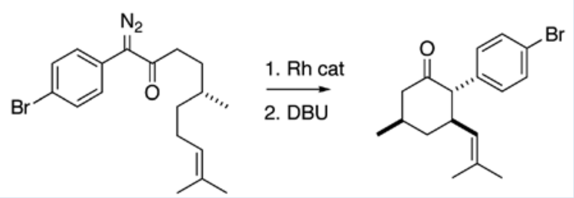


Figure 1

Bicyclic Construction by Net Fe-Mediated [1 + 4 + 1] Cycloaddition

Faculty: Doug Taber (Chemistry and Biochemistry)
Graduate Student: Pengfei Guo (Chemistry and Biochemistry)
Funding: NIH, GM42056

Carbocycles, as exemplified by calcitriol and taxol, can be potent drugs. Although computationally-driven lead generation often suggests potential new drug candidates that are polycarbocyclic, such candidates are usually not pursued, because of the assumption that a polycarbocyclic drug would be impractical to manufacture. We report a simple two-step route to the enantiomerically-pure carbobicyclic scaffold 3a from the acyclic ketone 1a. (Figure 2) ✧

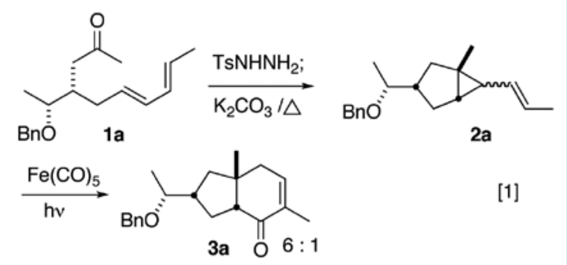


Figure 2

Asymmetric Organocatalytic Conjugate Allylation of Cyclic Enones

Faculty: Doug Taber (Chemistry and Biochemistry)
Graduate Student: David Gerstenhaber (Chemistry and Biochemistry)
Funding: NIH, GM42056

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. ✧

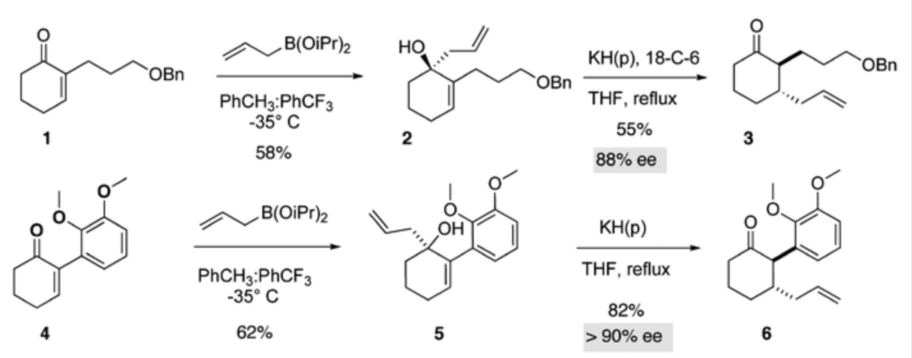


Figure 3

Chemical Modification of Semiconductor Materials

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)
Collaborators: Robert Opila (Materials Science & Engineering), George Flynn (Chemistry, Columbia University)
Graduate Students: Timothy Leftwich, Keith Douglass, Mark Madachik (Chemistry & Biochemistry)
Funding: NSF, ACS-PRF

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

Thin Solid Films for Microelectronics

Faculty: Andrew Teplyakov (Chemistry & Biochemistry)
Collaborators: Robert Opila (Materials Science & Engineering), Chaoying Ni (Chemical Engineering), Thomas P. Beebe Jr. (Chemisty & Biochemistry), Steven Brown (Chemistry & Biochemistry), Brian Willis (Chemical Engineering, Univ. of Connecticut)
Graduate Students: Kathryn Perrine, Juan Carlos Rodrígues-Reyes, Keith Douglas, Jia-Ming Lin (Chemistry & Biochemistry)
Funding: NSF

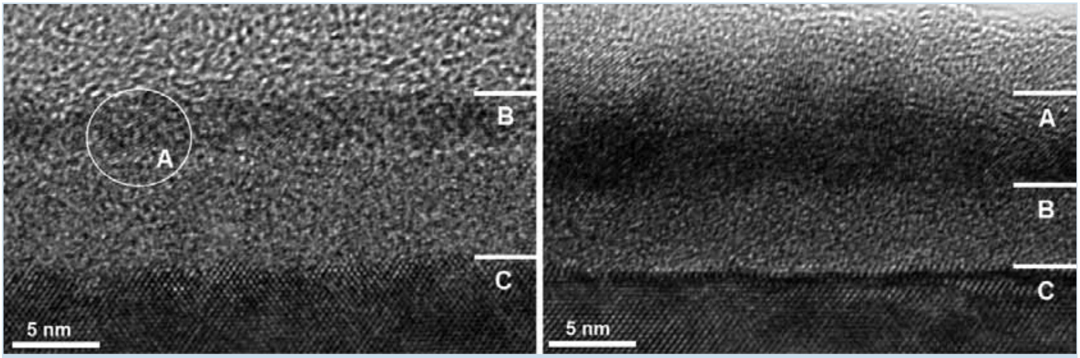


Figure 1: Cross-sectional TEM micrograph of a TiNC film before (left) and after (right) NH_3 post-annealing. The TiNC film is composed of crystalline nanostructures (A) embedded in an amorphous matrix (B) deposited onto a single crystalline silicon substrate (C). Upon post-annealing, the top layers of the film are mostly polycrystalline (A) and the inner portion of the film (B) remains amorphous. Crystallization in the top layers is attributed to the nitridation of the TiNC film to form TiN.

The main goal of this project is to develop molecular-level understanding, control, and predict chemical reactions relevant for the formation and properties of complex ultra-thin diffusion barrier films on semiconductor substrates. The current technologies dictate that the thickness of diffusion barriers will approach just a few nanometers within the next 15 years, as estimated by the International Technology Roadmap for Semiconductors. Therefore the questions of scaling the physical properties of the films enter a qualitatively new era: these properties now have to be analyzed and understood at the atomic level. The key objective of this project is to promote desired surface chemical reactions for clean Ta- and Ti-based film deposition, while preventing impurity incorporation (C, O, F) at the interfaces formed during this process. Our group employs thermal and photochemical methods to achieve this control. The structure of these amorphous or polycrystalline films presents many challenges. Our group has developed a novel approach to understand their properties. It combines a newly established experimental strategy with novel computational models designed recently in our laboratory to investigate local interactions in these complex systems. As summarized in Figure 1, we can deposit a predominantly amorphous Ti-based film and alter its surface properties by nitridation with ammonia. The surface chemisty of the film can be reversinly tuned by chemical methods. Modern deposition and characterization techniques designed for and tested on Ti-based films will be further applied to investigate the poorly characterized Ta-, Hf-, and W-based materials. With the new deposition precursor molecules becoming available, this project will both rely on the materials that are currently predicted to be suitable as diffusion barriers and branch into novel materials. ✧

Covalently Attached Macromolecules on Semiconductor Substrates

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

We have used C_{60} Buckminster fullerenes as spectroscopic and microscopic probes to establish the covalent nature of their binding to appropriately terminated self-assembled monolayers on silicon. We have investigated this chemistry using multiple spectroscopic and microscopic techniques and have verified the formation of a covalent link using computational investigation of core level energy shifts in N *1s* spectral region and vibrational signatures of covalently bonded fullerenes. Current studies, as illustrated in Figure 2, focus on shape-restricted DNA molecules covalently bonded to SAM-covered Si(111) single crystal surface. These DNA structures are designed in the research group of our collaborator, Professor Junghuei Chen (Department of Chemistry and Biochemistry, University of Delaware). We have successfully bonded triangular and rectangular DNA molecules to the self-assembled monolayers on silicon, confirmed that they are bonded covalently, and analyzed their apparent height. The plan for further development of this research direction in the future includes design of the 3D structures using DNA molecules for preferential binding to the semiconductor surface on one side of the structure, design of the covalently linked scaffolds with specific biochemical binding sites located within the Debye length from the interface, and testing the sensing capabilities of a device based on this approach, as well as ultimately designing a biosensor based on these studies. ✧

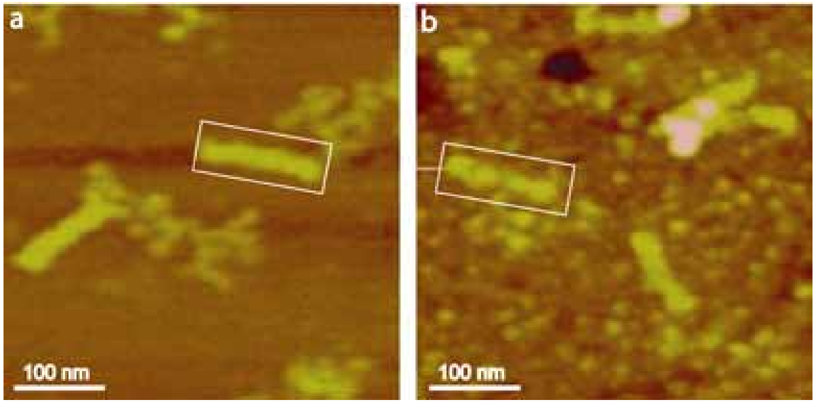


Figure 2: *AFM images of (a) the rectangular DNA molecules with thiol linkers on mica (b) the rectangular DNA molecules with thiol linkers on SSMCC modified amine-terminated Si(111)*

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

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

Chromium Dioxygen Complexes: We have prepared a series of chromium(III) superoxide complexes via binding of O2 to coordinatively unsaturated chromium(II) precursors. These complexes are the first structurally characterized representatives of their kind [i.e. chromium(III) superoxide complexes], and they all adopt the rare "side-on" binding mode of superoxide that we first discovered in TptBu.MeCo(O2).

Dioxygen Activation: Reaction of the dioxygen complexes with their precursors results in splitting of the O-O bond and the formation of reactive chromium(IV) oxo intermediates. Avoiding all hydrogen atom donors in the reaction of $[T^{ptBu.Me}Cr(pz'H)]BARF$ with PhIO has allowed the isolation and full characterization of $[Tp^{tBu.Me}Cr(O)(pz'H)]BARF$. The redox chemistry of the latter was investigated in collaboration with Prof. D.H. Evans, in order to estimate the affinity of the oxo complex for a hydrogen atom.

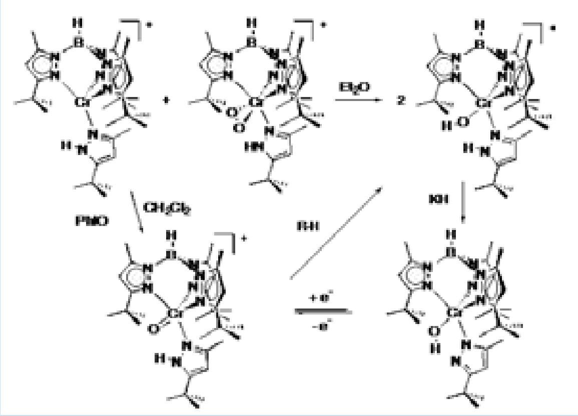


Figure 1

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

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

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

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

Homogeneous Models for Chromium Polymerization Catalysts

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

Chromium Alkyls: We are constructing a homogeneous model system for the Phillips catalysts for ethylene polymerization (i.e. inorganic Cr/SiO_2, see "A" below). To mimic the coordinatively unsaturated chromium on a hard oxide support, we have chosen N, N'-disubstituted diketiminate ligands ["$(R)_2$nacnac", as in B], i.e. bidentate nitrogen ligands that confer variable steric protection upon the chromium.

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

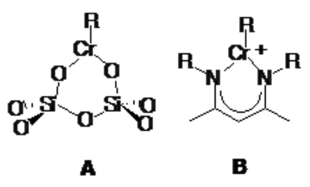


Figure 2

Extraordinarily low polydispersities (M_w/M_n=1.1-1.4) provide evidence for "living" polymerization catalysis, and the polymer microstructure of polyethylene produced with sterically encumbered $[(2,6\text{-}^iPr_2Ph)_2nacanac\ Cr(OEt_2)Me]BARF$ shows evidence for "chain walking."

Supported Polymerization Catalysts: Taking our earlier work on cyclopentadienyl chromium alkyls, which serve as models for the Union Carbide catalyst, one step closer to the actual heterogeneous catalyst, we have fixed $Cp^*Cr(py)Me_2$ on a zeolite (MCM-22) and characterized the resulting olefin polymerization catalysts by a variety of spectroscopic methods. ✧

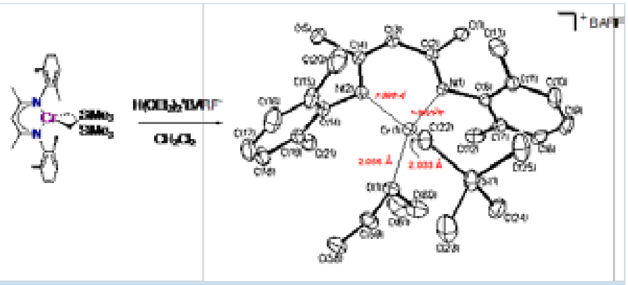


Figure 3

Model-based Design of Experiments and Catalysts

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

Experiments are typically carried out at certain conditions, and it is often found that only a small number of kinetic parameters are important (active) under those conditions. A natural question is whether one could design experiments based on a model, rather than statistical design, in order to increase the number of active model parameters and the accuracy of parameter estimation from data. We have developed a theoretical framework that 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.

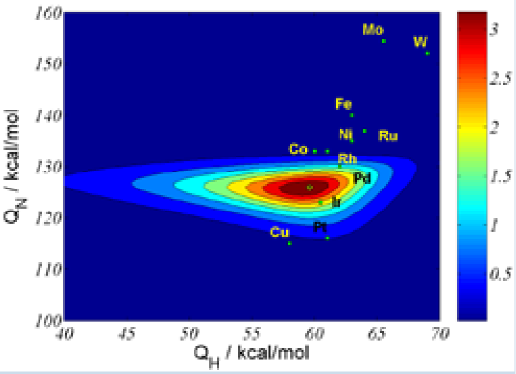


Figure 1: Example of predicted volcano mountain projected to two-dimensions for identification of optimal catalysts for ammonia decomposition to hydrogen: ammonia conversion (normalized scale) vs. element heats of adsorption (kcal/mol). The elements indicate the performance of known catalysts.

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. ✧

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)
Funding: NSF-NIRT

The demand for subnanometer control for nanomaterial fabrication and applications has refocused attention on microporous materials (e.g., zeolites). Their ordered crystalline microstructure and finely tuned nanometer-sized pores, coupled with well-established techniques for fabricating thin, oriented films, 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. ✧

Hierarchical Multiscale Microkinetic Model Development

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

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

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

We develop detailed reaction mechanisms for a variety of processes on noble metals and oxides. Examples include:

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

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

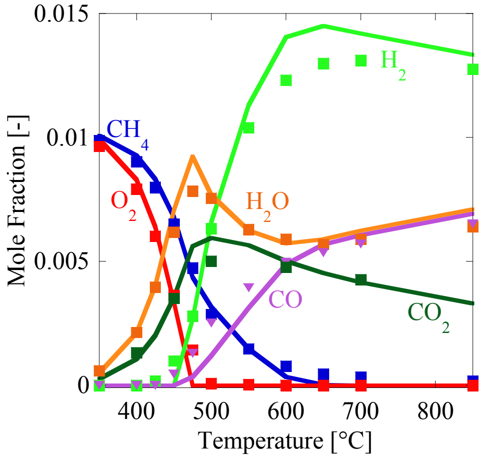


Figure 2: Comparison of experimental data (points) and simulations using our newly developed full microkinetic model (lines) for methane partial oxidation on Rh/Al_2O_3 catalysts.

Thermodynamic and Kinetics of Nanozeolitic Precursor Formation

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

We employ a variety of tools, such as classical chemical equilibria, population balances, surface complexation models, the Poisson-Boltzmann equation, and molecular dynamics to unravel the thermodynamic driving force for nanoparticle formation and the kinetics of nanoparticle formation. Furthermore, we study nucleation of zeolites and the role of templates (organic and inorganic cations) on nanoparticle stabilization. A snapshot from a molecular dynamics simulation investigating templating effects is shown in Figure 3. ✧

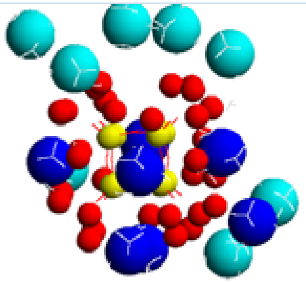
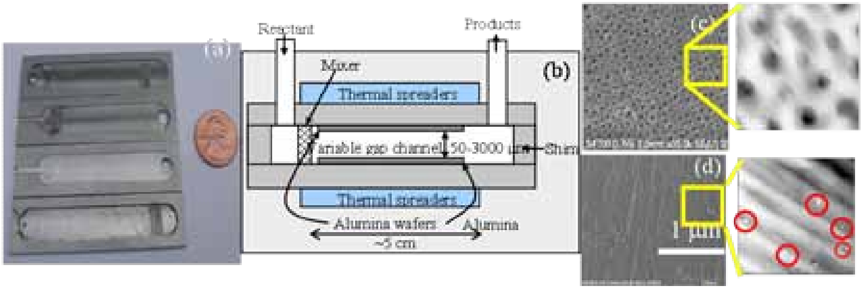


Figure 3: Snapshot from molecular dynamics simulation. The silica octamer in the center gets decorated by cations (tetramethyl ammonium cation), which expel water molecules from the bridged Si-O-Si oxygens protecting nanoparticles from hydrolysis.

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)
Funding: NSF-CBET

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

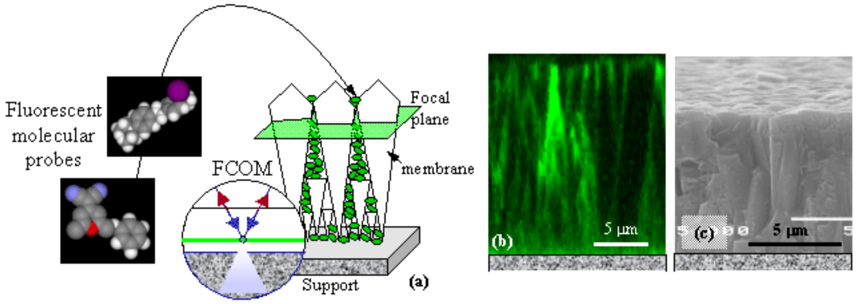


(a) Photograph of and (b) schematic side view (not to scale for ease of visualization) of a composite wall, tunable microreactor.
(c) Scanning electron micrograph (SEM) of a porous anodized alumina wafer ~75 μm thick (top view). The pores' diameter is ~50 nm.
(d) SEM of pores running across the wafer.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

Non-destructive Characterization of Polycrystalline Microporous Thin Films

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

A challenge in the development of theory and detailed simulation of diffusion through microporous thin films has been the prediction of permeation performance for real membranes that exhibit permeation anomalies (e.g., unexpectedly low selectivities and deviations from single-crystal theory). This underscores the need for quantitative characterization of microporous membrane polycrystallinity. Fluorescence confocal optical microscopy (FCOM) studies involving selective adsorption of dye molecules in polycrystalline features have highlighted the extent of this polycrystallinity in zeolite membranes. An example is shown in the figure 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. ✧



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

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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