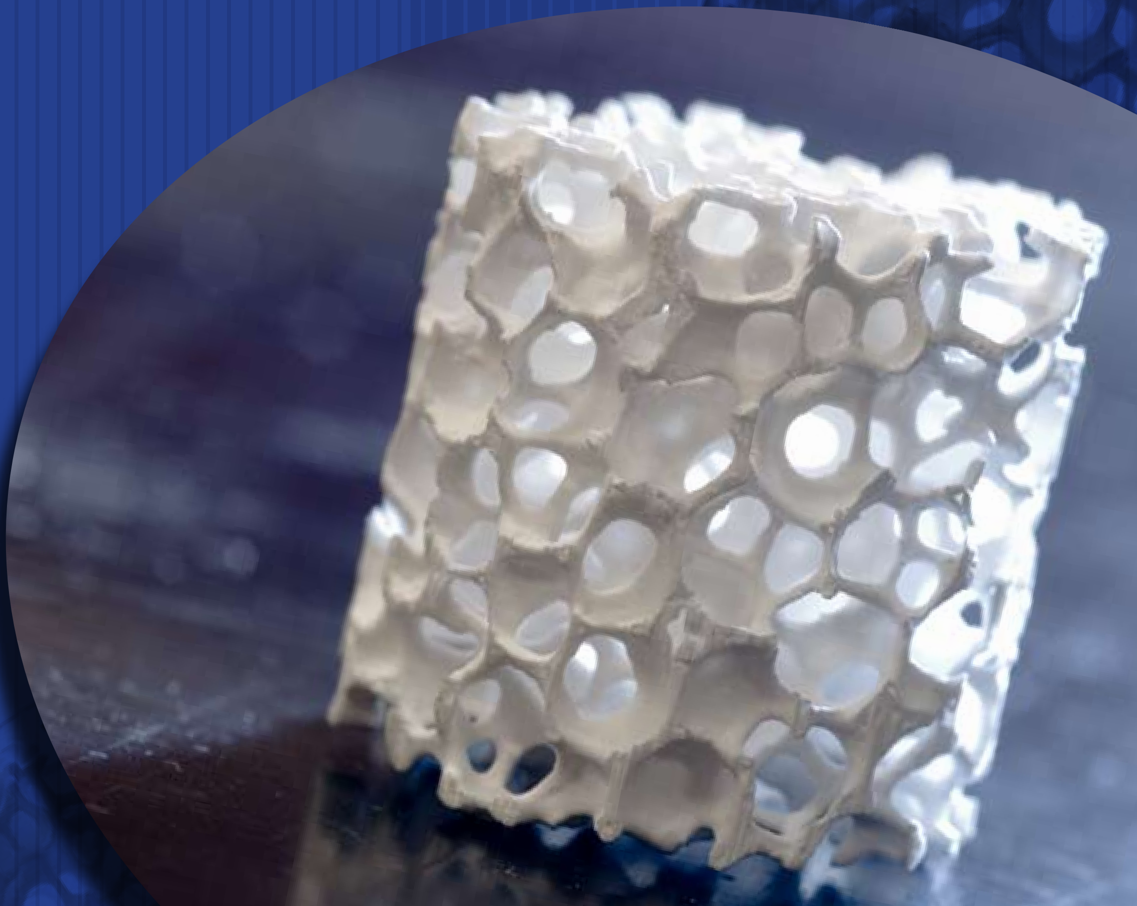
University of Delaware

2007

Center for Catalytic Science and Technology

Research Report



Meet the CCST Faculty

Mark A. Barteau

ASSOCIATE DIRECTOR

Professor of
Chemical Engineering

Douglas J. Buttrey

Professor of
Chemical Engineering

Jingguang G. Chen

DIRECTOR

Professor of
Chemical Engineering

Douglas J. Doren

ASSOCIATE DIRECTOR

Professor of
Chemistry and
Biochemistry

Jochen A. Lauterbach

ASSOCIATE DIRECTOR

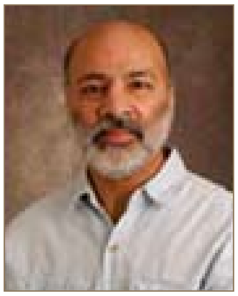
Professor of
Chemical Engineering

Raul F. Lobo

ASSOCIATE DIRECTOR

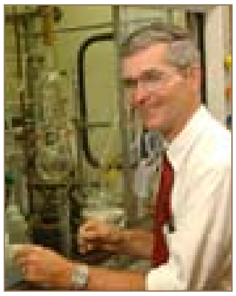
Professor of
Chemical Engineering

S. Ismat Shah



Professor of Physics
and Materials Science

Douglass F. Taber

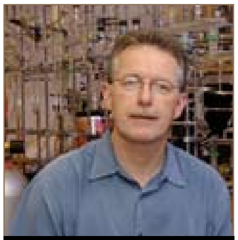


Professor of
Chemistry and
Biochemistry

Andrew V. Teplyakov

Associate Professor
of Chemistry and
Biochemistry

Klaus H. Theopold



ASSOCIATE DIRECTOR

Professor of
Chemistry and
Biochemistry

Dionisios G. Vlachos

ASSOCIATE DIRECTOR

Professor of
Chemical Engineering

Brian G. Willis

Assistant Professor
of Chemical
Engineering

Table of Contents

Sponsors

Faculty

Funding

Selected Recent Publications

Students, Visiting Researchers and Postdoc Fellows

Facilities

Research

Photography Credits:
Jon Cox
George Whitmyre
Photographic Services

Publication Design/Layout:
Sheila Boulden

UNIVERSITY OF DELAWARE

CENTER FOR CATALYTIC SCIENCE AND TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING

University of Delaware
Newark, Delaware 19716-3119
Ph: 302/831-8056
Fax: 302/831-2085

From the CCST Director:

2006-07 has been a time of rewarding growth for the Center for Catalytic Science and Technology. We are enjoying continued success in the Center's research funding from federal funding agencies, the State of Delaware, and industries. Currently, CCST consists of 12 faculty members from the Departments of Chemical Engineering, Chemistry and Biochemistry, and Materials Science and Engineering, with over sixty graduate students and over twenty visiting scientists and postdoctoral fellows. During 2006-2007, the CCST research groups have produced over one hundred journal publications and presented many invited talks at national and international conferences. The quality and productivity of our research efforts continue to make CCST recognized as one of the leading academic catalysis centers in the world.

In addition to our traditional strength in surface science, heterogeneous and homogeneous catalysis, and theoretical modeling, many CCST faculty members are expanding their efforts in the areas of energy-related research. We are also more actively involved in the utilization and organization of national synchrotron and neutron facilities. For example, CCST is the lead organization in the recently established Synchrotron Catalysis Consortium at the Brookhaven National Laboratory.

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

Jingguang G. Chen

Introducing Our Sponsors

ABB Lummus Global Inc.

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

Air Liquide - Medal

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

BASF

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

British Petroleum

Dr. Angelo Amorelli
BP Gas, Power & Renewables
Sunbury-on-Thames
United Kingdom

Eastman Chemical Company

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

ExxonMobil Research & Engineering Co.

Dr. Thomas Degnan Jr.
Clinton Township, Route 22 East
Annandale, NJ 08801

Headwaters

Dr. Bing Zhou
10653 S River Front Parkway, Suite 300
South Jordan, Utah 84095

Mitsubishi Chemical Corporation

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

Rohm & Haas Company

Dr. Scott Han
727 Norristown Road
Spring House, PA 19477

UOP LLC

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

W.L. Gore & Associates

Dr. Will Johnson
555 Papermill Road
Newark, DE 19711

The Center's Industrial Sponsors Program embodies the principal mechanisms for industry-university cooperation as they have evolved over the Center's nearly two 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.

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

1. Grant of $10,000 to CCST
2. Total grants to CCST faculty of $25,000
3. Gifts-in-kind of $25,000 or more
4. Full support of graduate student fellowship
5. Research contract with direct costs of $50,000
6. Joint industry-academic grant of $50,000

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.

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
- Interaction with CCST collaborators

Mark A. Barteau

Professor of Chemical Engineering

Associate Director

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

Education:

Ph.D. – Stanford University (1981)
M.S. – Stanford University (1977)
B.S. – Washington Univ. (1976)

Contact Information:

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

Honors & Awards:

2006: National Academy of Engineering
2001: Alpha Chi Sigma Award, American Institute of Chemical Engineers
2001: Catalysis Club of Philadelphia Award
1998: International Catalysis Award, International Association of Catalysis Societies
1995: Ipatieff Prize, American Chemical Society
1993: Canadian Catalysis Lecture Tour Award, Catalysis Division, Chemical Institute of Canada
1993: Paul H. Emmett Award in Fundamental Catalysis, The Catalysis Society
1991: Allan P. Colburn Award, American Institute of Chemical Engineers
1985: Presidential Young Investigator Award, National Science Foundation
1982: Victor K. LaMer Award, Division of Colloid and Surface Chemistry, American Chemical Society

Current Professional Activities:

Associate Editor: *Topics in Chemical Engineering,* Oxford University Press
Associate Editor: *Journal of Vacuum Science and Technology A,* American Vacuum Society
Member, Editorial Board: *Journal of Catalysis*
Member, Editorial Board: *Catalysis Letters* and *Topics in Catalysis*
Member, Consulting Committee: *Journal of Chemical Industry and Engineering* (China)
Member, Science Advisory Committee: Environmental Molecular Sciences Lab., Pacific Northwest National Lab

Professional Experience:

2005-Present: Robert L. Pigford Chair of Chemical Engineering, University of Delaware (UD)
2000-2007: Chairperson, Dept. of Chemical Engineering, UD
1996-2000: Director, Ctr. for Catalytic Science & Technology, UD
1994-2005: Robert L. Pigford Professor of Chemical Engineering, UD
1997: Visiting Professor of Chemistry, University of Auckland
1990-1994: Professor of Chemical Engineering, UD
1991-1992: Visiting Professor of Chemical Engineering, University of Pennsylvania
1990-Present: Professor of Chemistry, UD
1987-1990: Associate Professor of Chemical Engineering and Chemistry, UD
1982-1996: Associate Director, Center for Catalytic Science and Technology
1982-1987: Assistant Prof., Dept, of Chem. Engineering, UD
1981-1982: NSF Postdoctoral Fellow, Institut für Festkörperphysik, Physik Dept., Technische Universität München

Douglas J. Buttrey

Professor of Chemical Engineering

Research Interests:

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

Education:

Ph.D. – Purdue University (1984)
M.S. – Purdue University (1978)
B.S. – Wayne State Univ. (1976)

Contact Information:

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

Honors & Awards:

1988: DuPont Young Faculty Award
1984-1985: SOHIO Research Fellow, Cambridge University, England
1981-1983: David Ross Fellow, Purdue Research Foundation, West Lafayette, Indiana

Professional Activities:

Member, American Institute of Chemical Engineers
Member, American Chemical Society
Member, Microscopy Society of American
Member, American Association for the Advancement of Science

Professional Experience:

2007: Visiting Professor, NanoCenter, University of South Carolina, Columbia, SC
2005-Present: Professor of Chemical Engineering, University of Delaware
1993-2005: Associate Professor of Chemical Engineering, University of Delaware
1994-1996: Summer Visitor, Neutron Scattering Group, Physics Department, Brookhaven National Laboratory
1991-1993: Summer Visitor, Neutron Scattering Group, Physics Department, Brookhaven National Laboratory
1987-1993: Assistant Professor of Chemical Engineering, University of Delaware
1986-1987: Visiting Assistant Professor, Department of Chemistry and MRL Central Crystal Growth Facility, Purdue University
1984-1985: Postdoctoral Research Associate, Department of Physical Chemistry, University of Cambridge, England

Jingguang G. Chen

Professor of Chemical Engineering

DIRECTOR

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

Education:

Ph.D. – Univ. of Pittsburgh (1988)
B.S. – Nanjing Univ., China (1982)

Contact Information:

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

Honors & Awards:

2004: Catalysis Club of Philadelphia Award
1988-1989: Alexander von Humboldt Fellow, Germany
1987: Leybold-Heraeus Corporation Award
1986: Russell and Siguard Varian Fellow (American Vacuum Society)
1986: Graduate Student Award (American Vacuum Society)
1984-1986: Andrew W. Mellon Predoctoral Fellow (University of Pittsburgh)
1983-1984: USA-China Chemistry Graduate Program (CGP) Fellowship

Professional Activities:

2006-Present: Secretary-General of Catalysis, American Chemical Society
2005-Present: Director-at-Large, North American Catalysis Society
2005-Present: Principle Investigator, Synchrotron Catalysis Consortium
2004-Present: Editorial Board: *Surface Science Reports*
2004: Chair of Philadelphia Catalysis Club
2002: Chair for Gordon Research Conference on Catalysis
2001-2003: Editorial Board: *Surface Science*
1988-2000: Editorial Board: *Langmuir*

Professional Experience:

2000-Present: Director, Center for Catalytic Science and Technology (CCST), University of Delaware
2002-Present: Professor of Chemical Engineering, University of Delaware
2005-Present: Professor of Chemistry (courtesy appointment), University of Delaware
1998-2002: Associate Professor of Materials Science & Engineering and Associate Professor of Chemical Engineering, University of Delaware
1989-1998: Research Staff, Corporate Research Laboratories, Exxon Research and Engineering Company
1994-1998: Spokesperson for Exxon U1A Beamline, National Synchrotron Light Source, Brookhaven National Lab

Douglas J. Doren

Prof. of Chemistry & Biochemistry

ASSOCIATE DIRECTOR

Research Interests:

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

Education:

Ph.D. – Harvard University (1986)
A.M. – Harvard University (1981)
B.S. – Univ. of Berkeley (1979)

Contact Information:

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

Honors & Awards:

2000: Visiting Scientist, Fritz-Haber Institute, Berlin (Germany)
2002-2003: Visiting Scientist, DuPont

Professional Activities:

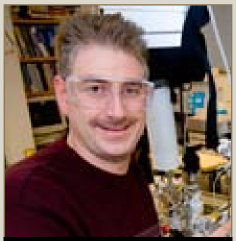
Member, Center for Molecular and Engineering Thermodynamics
1998, 2002, 2006: Chair, Telluride Workshop on Semiconductor Surface Chemistry
2002-2005: General Committee, Physical Electronics Conference
2000: Organizer, "Patterning, Functionalization and Reactivity of Complex Solid Surfaces" (American Chemical Society Symposium)

Professional Experience:

2007-2008: Interim Associate Dean, College of Arts and Sciences, University of Delaware
2006-Present: Professor (joint appointment), Physics and Astronomy, University of Delaware
1999-Present: Professor, Chemistry and Biochemistry, University of Delaware
2001-Present: Professor (joint appointment), Department of Chemical Engineering, University of Delaware
1994-1999: Associate Professor, Chemistry and Biochemistry, University of Delaware
1988-1994: Assistant Professor, Chemistry and Biochemistry, University of Delaware
1986-1988: Postdoctoral Member of Technical Staff, AT&T Bell Laboratories, Murray Hill, NJ, Postdoctoral Advisor: John C. Tully

Jochen A. Lauterbach

Professor of Chemical Engineering



ASSOCIATE DIRECTOR

Research Interests:

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

Education:

Ph.D. – Free University of Berlin, Germany (1994)
B.S. – University of Bayreuth, Germany (1992)

Contact Information:

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

Honors & Awards:

2000: Union Carbide Innovation Recognition Award
1998: Faculty Early Career Development Award (CAREER) from National Science Foundation
1994: Feodor-Lynen-Fellowship of the Alexander von Humboldt-Foundation Bonn, Germany

Professional Experience:

2006-Present: Professor of Chemical Engineering, University of Delaware
2002-2006: Associate Professor of Chemical Engineering, University of Delaware
2000-2002: Associate Professor, School of Chemical Engineering, Purdue University
1996-2000: Assistant Professor, School of Chemical Engineering, Purdue University
1994-1996: Postdoctoral Researcher, Department of Chemical Engineering, University of California

Raul F. Lobo

Professor of Chemical Engineering

ASSOCIATE DIRECTOR

Research Interests:

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

Education:

Ph.D. – California Institute of Technology (1995)
M.S. – California Institute of Technology (1993)
B.S. – Univ. of Costa Rica (1989)

Contact Information:

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

Honors & Awards:

2004: Ipatieff Prize, American Chemical Society
2001: Catalysis Innovation Award (Dow Chemical Company)
1999: Camille Dreyfus Teacher-Scholar Award (Henry & Camille Dreyfus Foundation)
1999: Young Scholars Award (Francis Alison Society, University of Delaware)
1999: Outstanding Young Faculty Award (College of Engineering, University of Delaware)
1997: CAREER Award for Young Investigators (National Science Foundation)

Professional Activities:

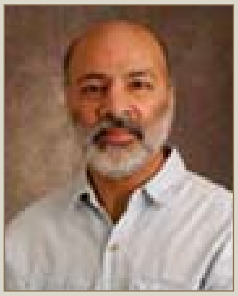
Member, American Institute of Chemical Engineers
Member, American Chemical Society
Member, American Association for the Advance of Science
Member, American Society for Engineering Education
Member, North American Catalysis Society
1998 Member, Executive Committee, International Zeolite Conference, Baltimore

Professional Experience:

2006-Present: Professor of Chemical Engineering, University of Delaware
2000-2006: Associate Professor of Chemical Engineering, University of Delaware
1996-Present: Associate Director of CCST, University of Delaware
2001-2002: Visiting Fellow, Centre for High-Resolution Electron Microscopy, Delft University of Technology, The Netherlands
2001: Visiting Professor, Dept. of Chemical Engineering, Universidad Rey Juan Carlos, Spain
1995-2000: Assistant Professor of Chemical Engineering, University of Delaware
1994-1995: Postdoctoral Fellow, Theoretical Chemistry and Molecular Physics Group, Los Alamos National Laboratory
1989-1990: Project Evaluation Engineer, V-J Centroamerica S. A., San Jose, Costa Rica

S. Ismat Shah

Prof. of Physics & Materials Science



Research Interests:

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

Education:

Ph.D. – University of Illinois at Urbana-Champaign (1986)
B.E. – University of Karachi, Pakistan, Bachelor of Engineering (1976)

Contact Information:

(302) 831-1618
ismat@udel.edu
www.udel.edu/mse/Faculty/Shah.htm

Honors & Awards:

2003-Present: Chair, Education Committee, Society of Vacuum Coaters
1986-1987: Postdoctoral Fellow, Department of Material Science, University of Illinois at Urbana-Champaign

Professional Experience:

2004-Present Professor, Materials Science & Engineering and Physics & Astronomy, University of Delaware
1999-2004: Associate Professor, Materials Science & Engineering and Physics & Astronomy, University of Delaware
1988-Present: Adjunct Associate Professor, Department of Physics and Astronomy, University of Delaware
1987-Present: Senior Research Scientist, Central Research and Development, E.I. du Pont de Nemours & Company
1980-1986: Research Assistant, Coordinated Science Labs, Department of Material Science, University of Illinois at Urbana-Champaign
1978-1979: Manager, Production, Metropolitan Steel Corp., Karachi, Pakistan
1976-1978: Manager, Quality Control, Lahore Alloys Ltd., Lahore, Pakistan

Douglass F. Taber

Prof. of Chemistry & Biochemistry

Research Interests:

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

Education:

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

Contact Information:

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

Honors & Awards:

1983-1987 Fellow of the Alfred P. Sloan Foundation
1970-1973 NSF Graduate Fellow

Professional Activities:

2004: Member (ad hoc), BNP Study Section, NIH
2003: Member, Fellowship Review Panel, NIH
2003: Member, Ernest Guenther Award Canvassing Committee, ACS
2001: Visiting Professor, South China Agricultural University, Guangzhou
2001-2003: Short Course, “Intermediate Organic,” DuPont Agricultural Chemistry
2000: Reviewer, National Research Council
2000: Expert Witness, Kenyon & Kenyon, New York
1998: Member, Fellowship Review Panel, NIH
1998: Symposium Organizer, “Practical Applications of Computational Organometallic Chemistry,” American Chemical Society National Meeting, Boston
1995: Consultant, Bausch & Lomb Pharmaceuticals, Tampa
1995-2002: Consultant, DuPont Company
1995-1996: Visiting Research Scientist, DuPont Merck Pharmaceuticals
1996: Symposium Organizer, “Guided Inquiry in the Organic Lecture and Laboratory,” 14th Biennial Conference on Chemical Education, Clemson University

Professional Experience:

1993-Present: Professor, Department of Chemistry, University of Delaware
1984-1993: Associate Professor, Department of Chemistry, University of Delaware
1982-1984: Assistant Professor, Department of Chemistry, University of Delaware
1978-1982: Research Assistant Professor, Department of Chemistry, Vanderbilt University
1977-1982: Assistant Professor, Department of Pharmacology, Vanderbilt University
1975-1977: Research Instructor, Department of Pharmacology, Vanderbilt University

Andrew V. Teplyakov

Assoc. Prof. of Chemistry & Biochemistry

Research Interests:

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

Education:

Ph.D. – Columbia University (1997)
M.S. – Columbia University (1993)
B.S. – Moscow State University (1992)

Contact Information:

(302) 831-1969
andrewt@udel.edu
www.udel.edu/chem/teplyakov/teplyakov.htm

Honors & Awards:

1996: Columbia University Pegram Award for the Meritorious Achievement by Graduate Students in their progress toward the Ph.D.

1992: Best Undergraduate Project in Physical Chemistry Section, Moscow State University

1992: Diploma with Excellence, Moscow State University

Professional Activities:

Member, Mendeleev Chemical Society (Russia)

Member, American Chemical Society (USA)

Member, American Vacuum Society (USA)

Member, Sigma Xi (Columbia University Chapter, New York)

2003, 2005: Organizer of “Chemistry of Carbonaceous Materials Symposium” at the National Meeting of the American Chemical Society (New Orleans, San Diego)

2000: Moderator, Surface Science Session, 47th National Meeting, American Vacuum Society, Boston

1999: Moderator, Physical Chemistry Session, 219th National Meeting of the American Chemical Society, San Francisco

Professional Experience:

2004-Present: Associate Professor, Department of Chemistry and Biochemistry, University of Delaware

1998-2004: Assistant Professor, Physical Chemistry, Department of Chemistry and Biochemistry, University of Delaware

1996-1998: Postdoctoral Research with Prof. Stacey Bent, New York University

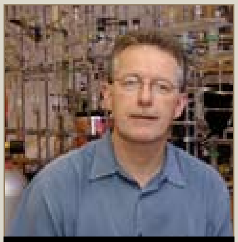
1992-1996: Doctoral Research with Prof. Brian Bent, Columbia University

1990-1992: Undergraduate Research with Prof. Igor Beckman, Moscow State University, Division of Chemical Engineering and A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

1988-1990: Undergraduate Research with Professor Eduard Filatov, Moscow State University, Division of Radiochemistry

Klaus H. Theopold

Prof. of Chemistry & Biochemistry



Associate Director

Research Interests:

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

Education:

Ph.D. – University of California, Berkeley (1982)
B.S. – Universität Hamburg, Germany (1977)

Contact Information:

(302) 831-1546
theopold@udel.edu
www.udel.edu/theopold/theopold.html

Honors & Awards:

2004: JSPS Invitation Fellowship, Japan Society for the Promotion of Science

1995: AAAS Fellow, American Association for the Advancement of Science

1992: Alfred P. Sloan Research Fellow, Alfred P. Sloan Foundation

1985: Presidential Young Investigator, National Science Foundation

1983: Award for Newly Appointed Young Faculty in Chemistry, Camille and Henry Dreyfus Foundation

Professional Experience:

2001: Visiting Scientist, Dept. of Chemistry, University of British Columbia

1996: Associate Director, Center for Catalytic Science and Technology

1996: Acting Chairman, Dept. of Chemistry and Biochemistry, University of Delaware (spring semester)

1995-Present: Professor of Chemistry, University of Delaware

1994: Visiting Scientist, Inorganic Chemistry Laboratory, Oxford University

1993: Joint appointment in Department of Chemical Engineering

1990-1995: Associate Professor, University of Delaware

1983-1990: Assistant Professor, Cornell University

1982-1983: Postdoctoral Associate with Prof. R.R. Schrock, Massachusetts Institute of Technology

Dionisios G. Vlachos

Professor of Chemical Engineering

ASSOCIATE DIRECTOR

Research Interests:

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

Education:

Ph.D. – Univ. of Minnesota (1992)
M.S. – Univ. of Minnesota (1990)
B.S. – National Technical Univ. of Athens, Greece (1987)

Contact Information:

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

Honors & Awards:

2002-2004: Provost's Merit Award, University of Delaware
2003: Who's Who in America, 57th Edition
2001: Who's Who in America, 55th Edition
1997: Outstanding Junior Faculty Award, College of Engineering, University of Massachusetts
1997: National Science Foundation Career Award
1996: Office of Naval Research Young Investigator Award
1996-1997: Outstanding Advisor Service Award in College of Engineering, University of Massachusetts

Professional Activities:

2002-2005: Director of the Catalysis and Reaction Engineering (CRE) Division of the AIChE
2005: Organizer of the Topical Conference on Multiscale Simulation, AIChE Meeting
1995-1997: Secretary, The Catalysis Society of New England
International Advisory Committee Member of 3rd International Conference on Computational Modeling and Simulation of Materials

Professional Experience:

2003-Present: Professor, Chemical Engineering Department, University of Delaware
2005-Present: Affiliated Member, Institute of Chemical Engineering and High Temperature Chemical Processes (ICE-HT) of FORTH (Foundation for Research and Technology, Hellas), Patras, Greece
2002-2005: Director, Catalysis and Reaction Engineering (CRE) Division of the AIChE
2000-2003: Associate Professor, Chemical Engineering Department, University of Delaware
2000-2003: Adjunct Professor, Chemical Engineering Department, University of Massachusetts
2000-Present: Associate Director, Center for Catalytic Science and Technology (CCST)
2000: Visiting Fellow, Princeton University
1998-2000: Associate Professor, Chemical Engineering Department, University of Massachusetts
1993-1998: Assistant Professor, Chemical Engineering Department, University of Massachusetts
1992-1993: Research Associate, Army High Performance Computing Research Center, Univ. of Minnesota, (parallel supercomputing on reacting flows using the connection machines CM-200 and CM-5)

Brian G. Willis

Assistant Prof. of Chemical Engineering

Research Interests:

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

Education:

Ph.D. – Massachusetts Institute of Technology (1999)
B.S. – Northwestern University, Illinois (1993)

Contact Information:

(302) 831-6856
bgwillis@udel.edu
www.che.udel.edu/willis

Honors & Awards:

2005: Emmert Faculty Fellow
2003: CAREER Award (National Science Foundation)

Professional Activities:

Member, Materials Research Society
Member, American Institute of Chemical Engineers
2006: AIChE Session Chair/co-Chair, National Meeting San Francisco, CA.
2004: AIChE Session Chair/co-Chair, National Meeting, Austin, TX.

Professional Experience:

2002-Present: Assistant Professor of Chemical Engineering, University of Delaware
2001-2002: Agere Systems, High Speed Devices and Interfaces Laboratory, New Jersey
1999-2001: Bell Laboratories (Lucent Technologies), Silicon Device Research Laboratory, New Jersey
1993-1999: Graduate Research Assistant, Massachusetts Institute of Technology

Research Grants

Mark A. Barteau

NIRT: Semiconductor Metal Oxide Nanoparticles for Visible Light Photocatalysis (with Shah, Chen, Doren, and Huang)

NSF – NIRT
8/02-7/06

Experimental and Theoretical Studies of Surface Oxametallacycles-Connections to Heterogeneous Olefin Epoxidation

Department of Energy
3/06-3/09

From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity (with Buttrey, Chen, Lauterbach, Lobo, and Vlachos)

Department of Energy
9/03-9/09

Douglas J. Buttrey

From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity (with Barteau, Chen, Lauterbach, Lobo, and Vlachos)

Department of Energy
9/03-9/09

An Integrated Approach Toward Rational Nanocatalyst Design for Hydrogen Production (with Lauterbach and Vlachos)

Department of Energy
9/05-8/08

Jingguang G. Chen

Structure/Property Relationship in Metal Carbides and Bimetallic Alloys

Department of Energy
8/00-11/09

Dedicated Synchrotron Facilities for Catalysis

Department of Energy
9/05-8/08

From First Principles Design to Realization of Bimetallic Catalysts for Ultrahigh Selectivity (with Barteau, Buttrey, Lauterbach, Lobo, and Vlachos)

Department of Energy
9/03-8/09

Removal of Perchlorate from Wastewater by Hydrogenation (with Huang)

Department of Defense
2/05-1/08

USA-China Collaborative Research on Bimetallic Catalysis

National Science Foundation
9/04-8/07

Evaluating and Improving Activity of Bimetallic Cathode Electrocatalysts

W.L. Gore Inc. & Delaware Clean Energy Partnership
8/05-7/08

Alternative Electrocatalysts

National Science Foundation
9/05-8/08

Catalyst Characterization Using Synchrotron Techniques

UOP
10/05-10/07

Catalyst Characterization

ABB Lummus
3/07-2/08

Alternative Electrocatalysts for Improving CO-Tolerance

British Petroleum
7/04-6/07

Tungsten Carbides as Cathode Materials

Department of Energy
1/07-12/09

Douglas J. Doren

Novel Photocatalysts With One- and Two-Dimensional Nanostructures (with Lobo)

Department of Energy
9/07-8/10

Black Carbon-Mediated Reduction of Environmental Contaminants (with P. Chiu)

National Science Foundation
(EPSCOR sub-grant)
9/06-8/07

Jochen A. Lauterbach

Combined High-Throughout Spectroscopic and Modeling Approach to the Study of Heterogeneous Catalysts

National Science Foundation
4/04-4/08

From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity (with Barteau, Buttrey, Chen, Lobo, and Vlachos)

Department of Energy
9/03-9/09

An Integrated Approach Toward Rational Nanocatalyst Design for Hydrogen Production (with Buttrey and Vlachos)

Department of Energy
9/05-8/08

Solar Hydrogen (with Honsberg, Beebe, Opila and Advani)

National Science Foundation
7/06-6/11

Raul F. Lobo

IMR: Acquisition of a Small-Angle X-Ray Scattering Camera for Research and Education (with Kaler and Pochan)

National Science Foundation
(Active) 7/04

From Nanoparticles to Porous Silicas: Understanding the Self-Assembly of Hybrid Organic-Inorganic Materials

National Science Foundation
(Awarded) 2/05

Catalytic Activation of Oxygen for Conversion of Hydrocarbon to Fuels and Chemicals (Continuation)**: Photocatalysis using ETS-10 Materials** (with Doren)

Department of Energy
(Active) 5/03

From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity (with Barteau, Buttrey, Chen, Lauterbach, and Vlachos)

Department of Energy
9/03-9/09

Structural Evolution of Organic-Silica Hybrid Nanoparticles: Understanding the Early Stages of Zeolite Crystallization

Petroleum Research Fund/ACS
(Awarded) 9/05

S. Ismat Shah

Investigation of the Fundamental Processes Involved in the Energetic Condensation for Low Temperature Thin Film Growth on Temperature Sensitive Substrates

ACS/PRF

Collaborative Research on Magnetic Nanoparticles Between University of Delaware and Quaid-i-Azam University, Pakistan

NSF/INT Pakistan

Synthesis, Characterization, and Catalytic Studies of Transition Metal Carbide Nanoparticles as Environmental Nanocatalysts (with J.G. Chen)

EPA/STAR

NIRT: Semiconductor Metal Oxide Nanoparticles for Visible Light Photocatalysis (with M.A. Barteau, J.G. Chen, D.J. Doren and Y. Huang)

NSF – NIRT
8/02-7/06

Heavy Metal Removal for Industrial Wastes

NSF/INT Egypt

Ge Quantum Dots for Photovoltaic Applications

NSF/ACT

Douglass F. Taber

Structural Investigation of Prostaglandin Conjugates

1) NIH MERIT Award

National Institutes of Health Research Grant
GM 42056
1993-2011

2) Physiologically Active Natural Products

National Institutes of Health Research Grant
GM 60287
2000-2008

Andrew V. Teplyakov

Atomic-Level Control of Interface Chemistry for Metal Deposition on Semiconductors

National Science Foundation
9/04-8/07

Surface Chemistry of Silicon Oxide Nanostructures in Molecule Corrals (with T.P. Beebe)

National Science Foundation
9/04-8/07

Klaus H. Theopold

Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer

Department of Energy
9/06 - 8/09

Computationally Guided Design of Catalysts for Fluoroolefin Polymerization

National Science Foundation (with DFG)
8/06 -7/09

Dionisios G. Vlachos

From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity (with M.A. Barteau, D.J. Buttrey, J.G. Chen, J.A. Lauterbach and R.F. Lobo)

Department of Energy
9/03-9/09

Bridging Length and Time Scales in Catalytic Reaction Systems

National Science Foundation
3/04-2/07

Microkinetic Models for Acrylic Acid Production

Rohm & Haas
7/04-8/09

Multiscale Modeling of Spatially Distributed Biological Systems

Department of Energy
8/05-8/08

An Integrated Approach Toward Rational Nanocatalyst Design for Hydrogen Production (with D.J. Buttrey and J.A. Lauterbach)

Department of Energy
7/06-6/09

Portable Power From Fuels Using High Temperature Thermoelectrics

US Army Research Laboratory
6/06 - 5/08

Hierarchical Multiscale Model-based Process Engineering

National Science Foundation
3/07 - 2/10

Brian G. Willis

Perovskite Buffer Layers for Compound Semiconductor Silicon Heteroepitaxy

National Science Foundation Career Award
2/03-2/08

Engineering the Molecule-Electrode Contact with Novel Molecular Tunnel Junctions

National Science Foundation
7/06-7/07

Tunneling Spectroscopy for Nanofabricated Biochemical Sensors

National Science Foundation
6/06-6/09

Heteroepitaxy of Perovskite Oxide Layers on Si(100) by CVD

Intel Corporation
06/07-06/08

Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells (with J.G. Chen)

Department of Energy
06/07-06/10

Selected Recent Publications

Mark A. Barteau

A.C. Lukaski, M.C.N. Enever and M.A. Barteau, **“Structure and Reaction of Oxametallacycles Derived from Styrene Oxide on Ag(110),”** *Surface Science* (in press).

G.J. Fleming, K. Adib, J.A. Rodriguez, M.A. Barteau and H. Idriss, **“Proline Adsorption on TiO_2 (110) Single Crystal Surface. A Study by High Resolution Photoelectron Spectroscopy,”** *Surface Science* (in press).

A.B. Mhadeshwar and M.A. Barteau, **“Computational Strategies for Identification of Bimetallic Ethylene Epoxidation Catalysts,”** *in Mechanism in Homogeneous and Heterogeneous Epoxidation Catalysis,* S.T. Oyama (ed.), Elsevier (in press).

O. Skoplyak, C.A. Menning, M.A. Barteau and J.G. Chen, **“An Experimental and Theoretical Study of Reactivity Trends for Methanol on Co/Pt(111) and Ni/Pt(111) Bimetallic Surfaces,”** *Journal of Chemical Physics* (in press).

S. Linic and M.A. Barteau, **“Heterogeneous Catalysis of Alkene Epoxidation,”** Chapter 14.11.6 in the *Handbook of Heterogeneous Catalysis, 2nd edition*, G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (eds.), Wiley-VCH, (in press).

I.K. Song, M.S. Kaba, K. Nomiya, R.G. Finke and M.A. Barteau, **“Scanning Tunneling Microscopy (STM) and Tunneling Spectroscopy (TS) Studies of Polyoxometalates (POMs) of the Wells-Dawson Structural Class,”** *Journal of Molecular Catalysis A: Chemical,* **262,** 216 (2007).

J.C. Dellamorte, R. Vijay, C.M. Snively, M.A. Barteau and J. Lauterbach, **“A High-throughput Reactor System With Individual Temperature Control for the Investigation of Monolith Catalysts,”** *Review of Scientific Instruments,* **78,** 072211 (2007).

M.H. Youn, D.R. Park, J.C. Jung, H. Kim, M.A. Barteau and I.K. Song, **“Reduction Potentials of Heteropolyacid (HPA) Catalysts Probed by Scanning Tunneling Microscopy and UV-visible Spectroscopy,”** *Korean Journal of Chemical Engineering,* **24,** 51 (2007).

J.C. Dellamorte, J. Lauterbach and M.A. Barteau, **“Rhenium Promotion of Ag and Cu-Ag Bimetallic Catalysts for Ethylene Epoxidation,”** *Catalysis Today,* **120,** 182 (2007).

K.P. Barteau, J.E. Lyons, I.K. Song and M.A. Barteau, **“UV-Visible Spectroscopy as a Probe of Heteropolyacid Redox Properties: Application to Liquid Phase Oxidations,”** *Topics in Catalysis,* **41,** 55 (2006).

M.H. Youn, H. Kim, I.K. Song, K.P. Barteau and M.A. Barteau, **“UV-Visible Spectroscopy Study of Solid State 12-Molybdophosphoric Acid Catalyst,”** *Reaction Kinetics Catalysis Letters,* **87,** 85 (2006).

O. Skoplyak, M.A. Barteau and J.G. Chen, **“Reforming of Oxygenates for H_2 Production: Correlating Reactivity of Ethylene Glycol and Ethanol on Pt(111) and Ni/Pt(111) with Surface d-band Center,”** *Journal of Physical Chemistry B,* **110,** 1686 (2006).

A.M. Goda, M.A. Barteau and J.G. Chen, **“Correlating Electronic Properties of Bimetallic Surfaces with Reaction Pathways of C_2 Hydrocarbons,”** *Journal of Physical Chemistry B,* **110,** 11823 (2006).

T. Qiu and M.A. Barteau, **“STM Study of Glycine on TiO_2 Single Crystal Surfaces,”** *Journal of Colloid and Interface Science,* **303,** 229 (2006).

M.A. Barteau, **“Surface Science and the Advancement of Direct Olefin Epoxidation,”** *Surface Science,* **600,** 5021 (2006).

J.R. Kitchin, J.K. Nørskov, M.A. Barteau and J.G. Chen, **“Trends in the Chemical Properties of Early Transition Metal Carbide Surfaces: A Density Functional Study,”** *Catalysis Today,* **105,** 66 (2005).

S.C. Chan and M.A. Barteau, **“Preparation of Highly Uniform Ag/TiO_2 and Au/TiO_2 Supported Nanoparticle Catalysts by Photodeposition,”** *Langmuir,* **21,** 5588 (2005).

M.B. Zellner, A.M. Goda, O. Skoplyak, M.A. Barteau and J.G. Chen, **“Trends in the Adsorption and Decomposition of Hydrogen and Ethylene on Monolayer Metal Films: A Combined DFT and Experimental Study,”** *Surface Science,* **583,** 281 (2005).

M.H. Youn, H. Kim, J.C. Jung, I.K. Song, K.P. Barteau and M.A. Barteau, **“UV-visible Spectroscopy Studies of $H_3PMo_{12-x}W_xO_{40}$ Heteropolyacid (HPA) Catalysts in the Solid State: Effects of Water Content and Polyatom Substitution,”** *Journal of Molecular Catalysis A: Chemical,* **241,** 227 (2005).

J.T. Jankowiak and M.A. Barteau, **“Ethylene Epoxidation Over Silver and Copper-Silver Bimetallic Catalysts: I. Kinetics and Selectivity,”** *Journal of Catalysis,* **236,** 366 (2005).

J.T. Jankowiak and M.A. Barteau, **“Ethylene Epoxidation over Silver and Copper-Silver Bimetallic Catalysts: II. Cs and Cl Promotion,”** *Journal of Catalysis,* **236,** 379 (2005).

A.L. Becerra, R. Martinez, M.C. Huff and M.A. Barteau, **“Catalytic Synthesis of Butylketene and Hexylketene From Hexanoic Acid and Octanoic Acid on Functionalized Silica Monoliths a Short Contact Times,”** *Catalysis Today,* **107-108,** 244 (2005).

M. Enever, S. Linic, K. Uffalussy, J.M. Vohs and M.A. Barteau, **“Synthesis, Structure and Reactions of Stable Oxametallacycles from Styrene Oxide on Ag(111),”** *Journal of Physical Chemistry B,* **109,** 2227 (2005).

Douglas J. Buttrey

D.J. Buttrey, **“A Survey of the Bi_2O_3 – MoO_3 Binary System,”** Book chapter contribution to *“Adventures in Solid-State and Surface Chemistry,”* **Ed.** P.P. Edwards and K.D.M. Harris, Royal Society of Chemistry (2007).

W.D. Pyrz, S. Park, T. Vogt, and D.J. Buttrey, **“Electron Beam Induced Fragmentation (EBIF) and Dispersion of Bi-Ni Nanoparticles,”** *J. Phys. Chem. C,* (2007).

C.C. Homes, J.M. Tranquada, and D.J. Buttrey, **“Stripe order and Vibrational Properties of $La_2NiO_{4.133}$,”** *Phys. Rev. B,* **75,** 045128 (2007).

M. Hücker, M. v. Zimmermann, R. Klingeler, S. Kiele, J. Geck, S. Bakee, J.P. Hill, A. Revcolevschi, D.J. Buttrey, B. Büchner, and J.M. Tranquada, **“Unidirectional Order and 3D Stacking of Charge Stripes in Orthorhombic $Pr_{1.67}Sr_{0.33}NiO_4$ and $Nd_{1.67}Sr_{0.33}NiO_4$,”** *Phys Rev. B,* **74,** 085112-1 to 085112-12 (2006).

P. DeSanto Jr., D.J. Buttrey, R.K. Grasselli, W.D. Pyrz, C.G. Lugmair, A.F. Volpe, B.H. Toby, and T. Vogt, **“Comparison of MoVTaTeO and MoVNbTeO *M1* Crystal Chemistry,”** *Topics in Catalysis,* **38(1-3)**, 31-40 (2006).

R.K.Grasselli, D.J. Buttrey, J.D. Burrington, A. Andersson, J. Holmberg, W. Ueda, J. Kubo, C.G. Lugmair and A.F. Volpe Jr., **“Active Centers, Symbiosis and Redox Properties of MoV(Nb,Ta)TeO Ammoxidation Catalysts,”** *Topics in Catalysis,* **38(1-3)**, 7-16 (2006).

Jingguang G. Chen

W. Huang, J.R. McCormick, R.F. Lobo, and J.G. Chen, **“Selective Hydrogenation of Acetylene in the Presence of Ethylene on Zeolite-Supported Bimetallic Catalysts,”** *Journal of Catalysis,* **246,** 40-51 (2007).

E.C. Weigert, M.B. Zellner, A.L. Stottlemyer and J.G. Chen, **“A Combined Surface Science and Electrochemical Study of Tungsten Carbides as Anode Electrocatalysts,”** *Current Topics in Catalysis* (2007, accepted).

S. Wang, W. Lin, Y. Zhu, Y. Xie, J.R. McCormick, W. Huang, and J.G. Chen, **“Pd-Based Bimetallic Catalysts Prepared by Replacement Reactions,”** *Catalysis Letters,* **114,** 169-173 (2007).

L.E. Murillo, A.M. Goda and J.G. Chen, **“Selective Hydrogenation of C=O Bond in Acrolein through Architecture of Bimetallic Surface Structures,”** *Journal of American Chemical Society* (2007, accepted).

E.C. Weigert, M.P. Humbert, Z.J. Mellinger, Q. Ren, T.P. Beebe, Jr., L. Bao, and J.G. Chen, **“PVD Synthesis of Phase-Rich Tungsten Carbide Thin Films on Different Carbon Substrates,”** *Journal of Vacuum Science and Technology B* (2007, submitted).

D.M. Wang, C.P. Huang, J.G. Chen, H.Y. Lin, and S.I. Shah, **"Reduction of Perchlorate in Dilute Aqueous Solution over Monometallic Nanocatalysts Exemplified by Tin,"** *Separation and Purification Technology* (2007, accepted).

K. Beadle, R. Gupta, A. Matthew, J.G. Chen, and B.G. Willis, **"CVD Synthesis of Phase-Rich WC Thin Films on Silicon and Carbon Substrates,"** *Thin Solid Films* (2007, accepted).

O. Skoplyak, M.A. Barteau and J.G. Chen, **"An Experimental and Theoretical Study of the Trend in the Reactivity of Methanol on Co/Pt(111) and Ni/Pt(111) Bimetallic Surfaces,"** *Journal of Chemical Physics* (2007, accepted).

D.M. Wang, S.I. Shah, J.G. Chen and C.P. Huang, H.Y. Lin, and S.I. Shah, **"Catalytic Reduction of Perchlorate by H_2 Gas in Dilute Aqueous Solutions,"** *Separation and Purification Technology* (2007, accepted).

W. Huang, R.F. Lobo and J.G. Chen, **"Characterization of Na^+-β-Zeolite Supported Pd and PdAg Bimetallic Catalysts Using EXAFS, TEM and Flow Reactor,"** *Journal of Molecular Catalysis A* (2007, submitted).

H. Shao, E.L. Kugler, D.B. Dadyburjor, A.A. Rykov and J.G. Chen, **"NEXAFS Measurements of Co-W and Ni-W Bimetallic Carbide Catalysts for Dry Reforming of Methane,"** *Catalysis Letters* (2007, submitted).

M.B. Zellner, C.A. Menning and J.G. Chen, **"General Trends in the Electronic and Chemical Properties of Monolayer Bimetallic Surfaces,"** *Surface Science Reports* (Invited Review), (2007, submitted).

S. Wang, W. Lin, Y. Zhu, Y. Xie, J.G. Chen, **"Preparation and Catalytic Activity of Monolayer Dispersed Pt/Ni Bimetallic Catalysts for C=C and C=O Hydrogenation,"** *Chinese Journal of Catalysis,* **27,** 301-303 (2006).

O. Skoplyak, M.A. Barteau and J.G. Chen, **"Reforming of Oxygenates for H_2 Production: Correlating Reactivity of Ethylene Glycol and Ethanol on Pt(111) and Ni/Pt(111) with Surface *d*-band Center,"** *Journal of Physical Chemistry B,* **110,** 1686-1694 (2006).

M.S. Angelo, B.E. McCandless, R.W. Birkmire, S.A. Rykov and J.G. Chen, **"Contact Wetting as a Diagnostic Tool for Surface Energy Analysis of Semiconductor Thin-Films,"** *Progress in Photovotaics: Research and Applications* (2006, accepted).

A. M. Goda, M. A. Barteau, and J. G. Chen, **"Correlating Electronic Properties of Bimetallic Surfaces with Reaction Pathways of C2 Hydrocarbons,"** *Journal of Physical Chemistry B,* **110,** 11823-11831 (2006).

S. Buzby, M. A. Barakat, H. Lin, C. Ni and S. Ismat Shah, S. A. Rykov, J.G. Chen, **"Visible Light Photocatalysis with Nitrogen Doped Titanium Dioxide,"** *Journal of Vacuum Science and Technology B,* **24,** 1210-1214 (2006).

C.A. Menning, H.H. Hwu, and J.G. Chen, **"An Experimental and Theoretical Investigation of the Stability of Pt-3d-Pt Bimetallic Surfaces under Oxygen Environment,"** *Journal of Physical Chemistry B,* **110,** 15471-15477 (2006).

A.M. Gaffney, S. Chaturvedi, M.B. Clark, S. Han, S.A. Rykov and J.G. Chen, **"Characterization and Catalytic Studies of PVD Synthesized Mo/V/Nb/Te Oxide Catalysts,"** *Journal of Catalysis,* **229,** 12-23 (2005).

H.H. Hwu, M.B. Zellner, and J.G. Chen, **"The Effect of Oxygen Modification on the Electronic and Chemical Properties of C/Mo(110),"** *Journal of Catalysis,* **229,** 35-49 (2005).

B. Zhao, K. Uchikawa, C. Ni, J.R. McCormick, J.G. Chen and H. Wang, **"Ultrafine Anatase TiO_2 Nanoparticles Produced in Premixed Ethylene Stagnation Flames,"** *Proceedings of the Combustion Institute,* **30,** 2569-2576 (2005).

H.H. Hwu and J.G. Chen, **"Surface Chemistry of Transition Metal Carbides,"** *Chemical Reviews,* **105,** 185-212 (2005).

E.C. Weigert, J. South and J.G. Chen, **"Multifunctional Composites Containing Molybdenum Carbides as Potential Electrocatalysts,"** *Catalysis Today,* **99,** 285-290 (2005).

M.B. Zellner and J.G. Chen, **"Surface Science and Electrochemical Studies of W_2C and WC Electrocatalysts,"** *Catalysis Today,* **99,** 299-307 (2005).

J.K. Norskov, T. Bligaard, A. Logadottir, J.R. Kitchin, J.G. Chen, S. Pandelov and U. Stimming, **"Trends in the Exchange Current for Hydrogen Evolution,"** *Journal of Electrochemical Society,* **152,** J23-J26 (2005).

J.R. Kitchin, J.K. Norskov, M.A. Barteau and J.G. Chen, **"Trends in the Chemical Properties of Early Transition Metal Carbide Surfaces: A Density Functional Study,"** *Catalysis Today,* **105,** 66-73 (2005).

M.B. Zellner and J.G. Chen, **"Potential Application of Tungsten Carbides as Electrocatalysts: Synergistic Effect of Pt-Modification on the Reactions of Methanol, Water, and CO on C/W(110) Surfaces,"** *Journal of Electrochemical Society,* **152,** A1483-A1494 (2005).

E.C. Weigert, N.A. Smith, B.G. Willis and J.G. Chen, **"PVD Synthesis and Characterization of Pt-Modified Molybdenum Carbides as Potential Electrocatalysts,"** *Solid State and Electrochemical Letters,* **8,** A337-A340 (2005).

M.B. Zellner, A.M. Goda, O. Skoplyak, M.A. Barteau and J.G. Chen, **"Novel Chemistry of Hydrogen and Ethylene on Monolayer Metal Films: A Combined DFT and Experimental Study,"** *Surface Science,* **583,** 281-296 (2005).

L.E. Murillo, N.A. Khan and J.G. Chen, **"The Effect of Hydrocarbon Structure and Chain Length on the Low-Temperature Hydrogenation Activity on Ni/Pt(111) Bimetallic Surfaces,"** *Surface Science,* **594,** 27-42 (2005).

M.B. Zellner and J.G. Chen, **"Supporting Monolayer Pt on W(110) and C/W(110): Modification Effects on the Reaction Pathways of Cyclohexene,"** *Journal of Catalysis,* **235,** 393-402 (2005).

M.B. Zellner, H.H. Hwu and J.G. Chen, **"Comparative Studies of Methanol Decomposition on Carbide-Modified V(110) and Ti(0001),"** *Surface Science,* **598,** 185-199 (2005).

N.A. Khan, L.E. Murillo, Y. Shu, J.G. Chen, **"Correlating Low-Temperature Hydrogenation Activity of Co/Pt(111) Bimetallic Surfaces to Supported Co/Pt/γ-Al_2O_3 Catalysts,"** *Catalysis Letters,* **105,** 233-238 (2005).

Douglas J. Doren

A.M. Shough, D.J. Doren and R.F. Lobo, **"A Visible Light Photocatalyst: Effects of Vanadium Substitution on ETS-10,"** *Phys. Chem. Chem. Phys.* (submitted).

M.J. Nash, S. Rykov, R.F. Lobo, D.J. Doren, I. Wachs, **"Photocatalytic Activity of Vanadium-substituted ETS-10,"** *J. Phys. Chem. B* (in press).

A.M. Shough, D.J. Doren, M. Nash and R.F. Lobo, **"Effects of Vanadium Substitution on the Structure and Photocatalytic Behavior of ETS-10,"** *J. Phys. Chem. C,* **111,** 1776 (2007).

A.M. Zimmerman, D.J. Doren and R.F. Lobo, **"Electronic and Geometric Properties of ETS-10: QM/MM Studies of Cluster Models,"** *J. Phys. Chem.,* **110,** 8959 (2006).

J.Z. Liu, L. Yang and D.J. Doren, **"Free Energy Perturbation and Dynamical Nucleation Study of Water Dimer and Trimer Through TIP5P Water Model,"** *Chemical Physical Letters,* **417,** 63 (2006).

J.Z. Liu, L. Yang and D.J. Doren, **"Comparison of TIP5P Water Model and TIP4P Water Model in Cluster Nucleation Kinetics Study Through Umbrella Sampling and Free Energy Perturbation,"** *Chemical Physics,* **323,** 579 (2006).

H. Dong, W. Liu, D.J. Doren, and R. Wood, **"Structure of an Accurate ab initio Model of the Aqueous Cl^- ion at High Temperatures,"** *J. Phys. Chem. B,* **110,** 18504 (2006).

J.B. Witkoskie and D.J. Doren, **"Neural Network Models of Potential Energy Surfaces: Prototypical Examples,"** *J. Chem. Theory Comput.,* **1,** 14 (2005).

(continued on page 12)

Selected Recent Publications

(Douglas J. Doren, continued)

Y. Wang and D.J. Doren, **“Electronic Structure of V-doped Anatase TiO_2,”** *Sol. St. Comm.,* **136,** 142 (2005).

Y. Wang and D.J. Doren, **“First-principles Calculations of TiO_2 Doped by N, Nd, and Vacancy,”** *Sol. St. Comm.,* **136,** 186 (2005).

Jochen A. Lauterbach

B. Taylor, J. Lauterbach and W.N. Delgass, **“The Effect of Mesoporous Scale Defects on the Activity of Au/TS-1 for the Epoxidation of Propylene,”** *Catalysis Today* (2007, in press).

J.C. Dellamorte, R. Vijay, C.M. Snively, M.A. Barteau, and J. Lauterbach, **“Investigation of Ag Catalysts for Ethylene Epoxidation using High-Throughput Catalytic Reactor Experimentation,”** *Measurement Science and Technology* (2007, in press).

S. Washburn, J. Lauterbach, and C.M. Snively, **“Polymerizing the Unpolymerizable – The case of 1,2-disubstituted Ethylenes,”** *Macromolecules,* **39(24),** 8210-8212 (2007).

J.C. Dellamorte, J. Lauterbach and M.A. Barteau, **“Rhenium Promotion of Ag and Cu-Ag Bimetallic Catalysts for Ethylene Epoxidation,”** *Catalysis Today,* **120(2),** 182-185 (2007).

N. McMillan, C.M. Snively, and J. Lauterbach, **“Spatio-temporal Phenomena During NO Reduction with NH_3 on Polycrystalline Platinum,”** *Surface Science,* **601(3),** 772-780 (2007).

R. Hendershot, R. Vijay, C.M. Snively, and J. Lauterbach, **“Response Surface Study of the Performance of Lean NO_x Storage Catalysts as a Function of Reaction Conditions and Catalyst Composition,”** *Applied Catalysis B,* **70(1-4),** 160-171 (2007).

N. McMillan, D. Bilbao, C.M. Snively, and J. Lauterbach, **“Spatio-temporal Control of Reaction-diffusion Patterns Through Local Micro-dosing,”** *Physical Review Letters* (2007, submitted).

S. Washburn, J. Lauterbach, and C.M. Snively, **“Mixed Monomer Adsorbate Multi-layers of Pyrrole and Styrene,”** *Applied Surface Science,* **252(18),** 6228-6235 (2006).

R.J. Hendershot, R. Vijai, C.M. Snively, and J. Lauterbach, **“High-throughput Study of the Influence of H_2O and CO_2 on the Performance of Nitrogen Storage and Reductions (NSR) Catalysts,”** *Applied Surface Science,* **252(7),** 2588-2592 (2006).

R. Hendershot, R. Vijay, C.M. Snively, and J. Lauterbach, **“Performance of NOx Storage and Reduction Catalysts as a Function of Cycling Conditions and Catalyst Composition,”** *Chemical Engineering Science,* **61(12),** 3907-3916 (2006).

B. Taylor, J. Lauterbach, G. Blau, W.N. Delgass,” **“Reaction Kinetic Analysis of the Gas-Phase Epoxidation of Propylene Over Au/TS-1,”** *Journal of Catalysis,* **242(1),** 142-152 (2006).

R. Vijay, C.M. Snively, and J. Lauterbach, **“High-throughput Study of Co-containing Lean NO_x Storage Catalysts,”** *Journal of Catalysis,* **243(2),** 368–375 (2006).

R. J. Hendershot, B. Feist, R. Vijai, C.M. Snively, B. Ogunnaike, and J. Lauterbach, **“Multivariate and Univariate Analysis of Infrared Imaging Data for High-throughput Studies of NH_3 Decomposition and NO_x Storage and Reduction Catalysts,”** *Measurement Science and Technology,* **16(1),** 302-208 (2005).

R. Vijay, R.J. Hendershot, S.M. Rivera-Jiménez, W.B. Rogers, B.J. Feist, C.M. Snively, J. Lauterbach, **“Noble Metal Free NO_x Storage Catalysts Using Cobalt Discovered via High-throughput Experimentation,”** *Catalysis Communications,* **6(2),** 167-171 (2005).

R.J. Hendershot, C.M. Snively, and J. Lauterbach, **“High-throughput Catalytic Science,”** *Chemistry – A European Journal,* **11,** 806-814 (2005).

A. Deskins, J. Lauterbach, and K. Thomson, **“Lifting the Pt{100} Surface Reconstruction Through Oxygen Adsorption: A DFT Analysis,”** *Journal of Chemical Physics,* **122,** 184709 (2005).

B. Taylor, J. Lauterbach, and W.N. Delgass, **“Gas-phase Epoxidation of Propylene Over Small Gold Ensembles on TS-1,”** *Applied Catalysis A,* **291(1-2),** 188-198 (2005).

N. McMillan, T. Lele, C.M. Snively, and J. Lauterbach, **“Subsurface Oxygen Formation on Pt(100): Experiments and Modeling,”** *Catalysis Today,* **105(2),** 244-253 (2005).

C.M. Snively and J. Lauterbach, **“Experimental Aspects of Asynchronous Sampling in FTIR Imaging,”** *Applied Spectroscopy,* **59(9),** 1075-1081 (2005).

M. Fasolka, J. Lauterbach, and I. Takeuchi, **“Combinatorial Materials Science – From Electronic Materials Over Polymers to Catalysts,”** *Materials Today,* **8(10),** 18-26 (2005).

B. Taylor, L. Cumarananatunge, J. Lauterbach, and W.N. Delgass, **“Gas-phase Epoxidation of Propylene Over Small Gold Ensembles on TS-1,”** *Gold Bulletin,* **38(3),** 133-133 (2005).

Raul F. Lobo

J.D. Rimer, D. Roth, D.G. Vlachos and R.F. Lobo, **“Self-assembly and Phase Behavior of Germanium Oxide Nanoparticle in Basic Aqueous Solutions,”** *Langmuir,* **23,** 2784 (2007).

M. Nash, R.F. Lobo, S. Rikov, D.J. Doren, **“Photocatalytic Activity of Vanadium-substituted ETS-10,”** *J. Phys. Chem. C,* **111,** 7029 (2007).

J.M. Fedeyko, H. Fox, D.G.Vlachos and R.F. Lobo, **“Initial Stages of Self-Organization of Silica-Alumina Gels in Zeolite Synthesis,”** *Langmuir,* **23,** 4532 (2007).

R.F. Lobo, **“The Promise of Emptiness,”** *Nature,* **443,** 757 (2006, Commentary).

W. Huang, J.R. McCormick, R.F. Lobo, J. Chen, **“Selective Hydrogenation of Acetylene in the Presence of Ethylene on Zeolite-supported Bimetallic Catalysts,”** *J. Catal,* **246,** 40-51 (2007).

M.A.M. Martinez-Inesta, R.F. Lobo, , **“Investigation of the Structure of Pplatinum Clusters Supported in Zeolite Beta Using the Pair Distribution Function,”** *J. Phys. Chem. C,* **111,** 8573 (2007).

Y.C. Cheng, R.F. Lobo, S.I. Sandler and B. Lenhoff, **“Kinetics and Equilibria of lysozime Precipitation and Crystallization in Concentrated Ammonium Sulfate Solutions,”** *Biotech. Bioeng.,* **94,** 177-188 (2006).

A.M. Zimmerman, D.J. Doren and R.F. Lobo, **“Electronic and Geometric Properties of ETS-10: QM/MM Studies of Cluster Models,”** *Journal of Physical Chemistry B,* **110,** 8959-8964 (2006).

J.D. Rimer, J.M. Fedeyko, D.G. Vlachos and R.F. Lobo, **“Silica Self-Assembly and the Synthesis of Microporous and Mesoporous Silicates,”** *Chem. Eur. J.,* **12,** 2926-2934 (2006).

J.M. Fedeyko, D.G. Vlachos and R.F. Lobo, **“On the Connection between Zeolite Precursor Nanoparticles and M41S-type Ordered Mesoporous Silicas,”** *Micropor. Mesopor. Mater.,* **90,** 102-111 (2006).

M.A. Smith and R.F. Lobo, **“The Local and Surface Structure of Ordered Mesoporous Carbons from Nitrogen Sorption, NEXAFS and Synchrotron Radiation Studies,”** *Micropor. Mesopor. Mater.,* **92,** 81-93 (2006).

J.D. Rimer, D.G. Vlachos and R.F. Lobo, **“Physical Basis for the Formation and Stability of Silica Nanoparticles in Basic Solutions of Monovalent Cations,”** *Langmuir,* **21,** 8960-8971 (2005).

J.M. Fedeyko, D.G. Vlachos and R.F. Lobo, **“Formation and Structure of Self-assembled Silica Nanoparticles in Basic Solutions of Organic and Inorganic Cations,”** *Langmuir,* **21,** 5197 (2005).

A. Kumar, R.F. Lobo and N.J. Wagner, **“Porous Amorphous Carbon Models from Periodic Gaussian Chains of Amorphous Polymers,”** *Carbon,* **43,** 3099 (2005).

M.M. Martinez-Inesta and R.F. Lobo, **“Investigation of the Negative Thermal Expansion Mechanism of Zeolite Chabazite Using the Pair Distribution Function Method,”** *Journal of Physical Chemistry B,* **109,** 9389 (2005).

J.D. Rimer, D.G. Vlachos and R.F. Lobo, **“Evolution of Self-Assembled Silica-Tetrapropylammonium Nanoparticles at High Temperatures,”** *Journal of Physical Chemistry B,* **109,** 12762 (2005).

H. Koller, C. Fild and R.F. Lobo, **“Variable Anchoring of Boron in Zeolite Beta,”** *Micropor. Mesopor. Mater.,* **79,** 215 (2005).

R.F. Lobo and A.E.C. Palmqvist, **“Mechanistic Insights into Templated Materials Synthesis,”** *Curr. Op. Coll. Interf. Sc.,* **10,** 185-187 (2005, Editorial).

S. Ismat Shah

S. Buzby and S.I. Shah, **“Photocatalytic Properties of TiO_2 Nanoparticles,”** *Dekker Encyclopedia of Nanoscience and Nanotechnology (Taylor & Francis),* **1,** 1 (2007). http://www.informaworld.com/smpp/content~content=a773324789~jumptype=rss.

A. Goyal, S. Hazra and S.I. Shah, **“Titania-Germanium Nanocomposites for Quantum Dot Solar Cells,”** *Mater. Res. Soc. Symp. Proc.,* **974,** Materials Research Society (2007).

M.M. Waite, D. Glocker and S.I. Shah, **“Sputtering Sources,”** *50 Years History of Vacuum Coating Technology,* Edts. D. Mattox and V. Mattox, Society of Vacuum Coaters (2007).

A.K. Rumaiz, S. Franklin, S. Buzby, and S.I. Shah, **“Thin Film Formation Techniques,”** *Kirk-Othmer Encyclopedia of Thin Films,* **24,** 721 (2007).

M. Raffi, A.K. Rumaiz and S.I. Shah, **“Studies on Growth Parameters of Silver Nanoparticles Synthesis by Inert Gas Condensation Process,”** *J. Mater. Res.* (Feb. 2007, accepted).

M. Rafi, J. Thiel, A. Ahmad, S. Buzby and S.I. Shah, **“Structural Effects of Silver Doping on Titanium Dioxide Nanoparticles,”** *J. Mater. Res.* (Feb. 2007, submitted).

M.M. Waite and S.I. Shah, **“Reactive Sputtering of Silicon with Oxygen and Nitrogen,”** *Materials Science B,* accepted (2007).

A.K. Rumaiz, H.Y. Lin, I. Baldytchev and S.I. Shah, **“Reactive Sputtering of Nanostructured WCx,”** *J Mat. Res.,* accepted (2007). www.mrs.org/s_mrs/sec_subscribe.asp?CID=2574&DID=118952&action=detail

A. Ahmad, S. Buzby, C. Ni and S.I. Shah, **“Effect of Nb and Sc Doping on the Phase Transformation of sol-gel Processed TiO_2 Nanoparticles,”** *J. Nanostructure and Nanotech,* in press (2007).

A. Ceylan, A.K. Rumaiz, and S.I. Shah, **“Core-Shell Structured Ni-CoO Nanoparticles: Synthesis and Characterization,”** *J Appl. Phys.,* in press (2007).

A. Goyal, S. Chatterji, S.I Shah, **“Synthesis and Characterization of TiO_2-Ge Nanocomposites,”** *J. Vac. Sci. Tech.,* accepted (2007).

J. Thiel, L. Pakstis, S. Buzby, M. Raffi, D. Pochan and S.I. Shah, **“Antibacterial Properties of Silver Doped Titania,”** *Small 3,* **799** (2007).

A. Ceylan, S.K. Hasanain, and S.I. Shah, **“Field Dependent Activation of Core and Surface Spins in Ni-ferrite Nanoparticles,”** *Phys. Rev. B,* submitted (Dec. 2006).

M. Naeem, S.K. Hasanain, M. Kobayashi, Y. Ishida, A. Fujimori, S. Buzby, S.I. Shah, **“Effect of Reducing Atmosphere on the Magnetism of Zn1-xCoxO Nanoparticles,”** *Nanotechnology,* **17,** 2675 (2006).

S. Chatterji, A. Goyal, and S.I. Shah, **“Inorganic Nanocomposites for Next Generation Solar Cells,”** *Materials Letters,* **60,** 3541 (2006).

H. Lin, C.P. Huang, W. Li, C. Ni , S.I. Shah, and Y. Tseng, **“Size Dependency of Nanocrystalline TiO_2 on its Optical Property and Photocatalytic Reactivity Exemplified by 2-chlorophenol,”** *Appl. Catalysis B: Environmental,* **68,** 1–11 (2006).

A. Ceylan, C.C. Baker, S.K. Hasanain, S.I. Shah, **“Effect of Particle Size on the Magnetic Properties of Core-Shell Structured Nanoparticles,”** *J. Appl. Phys.,* **100,** 034301 (2006).

C.C. Baker, A. Ceylan, and S.I. Shah, **“Reactive Gas Condensation Synthesis of Aluminum Nitride Nanoparticles,”** *Journal of Nanoscience and Nanotechnology,* **6,** 1 (2006).

A. Ceylan, K. Jastrzembski, and S.I. Shah, **“Enhanced Solubility Ag-Cu Nanoparticles and Their Thermal Transport Properties,”** *Metallurgical and Materials Transactions,* **37A,** 2033 (2006).

S. Buzby, M.A. Barakat, H. Lin, C. Ni, S.A. Rykov, J.G. Chen and S.I. Shah, **“Visible Light Photocatalysis with Nitrogen Doped Titanium Dioxide Nanoparticles Prepared by Plasma Assisted Chemical Vapor Deposition,”** *J. Vac. Sci. Technol. B,* **24,** 3 (2006).

L.R. Shah, B. Ali, S.K. Hasanain, A. Mumtaz, C. Baker,S.I. Shah, **“Effective Magnetic Anisotropy and Coercivity in Fe Nanoparticles Prepared by Inert Gas Condensation,”** *International Journal of Modern Physics B,* **20,** 37 (2006).

W. Li, A.I. Frenkel, J.C. Woicik, C. Ni, S.I. Shah, **“Dopant Location Identification in Nd^{3+}-Doped TiO_2 Nanoparticles,”** *Phy. Rev. B,* **72,** 155315 (2005).

Douglass F. Taber

D.F. Taber, J. Liang, **“Single Enantiomer Epoxides by Bromomandelation of Prochiral Alkenes,”** *J. Org. Chem.,* **72,** 431-434 (2007).

D.F. Taber, P.W. DeMatteo, K.V. Taluskie, **“Synthesis of Symmetrical and Unsymmetrical Pyrazines,”** *J. Org. Chem.,* **72,** 1492-1494 (2007).

D.F. Taber, W. Tian, **“Rhodium-catalyzed Intramolecular C-H Insertion of α–aryl-α-diazo Ketones,”** *J. Org. Chem.,* **72,** 3207-3210 (2007).

D.F. Taber, J.M. Joerger, **“Preparation of the 5/5-spiroketal of the Ritterazines,”** *J. Org. Chem.,* **72,** 3454-3457 (2007).

D.F. Taber, M.I. Sikkander, P.H. Storck, **“Enantioselective Synthesis of (+)-Majusculone,”** *J. Org. Chem.,* **72,** 4098-4101 (2007).

D.F. Taber, S. Patel, T.M. Hambleton, E.E. Winkel, **“Vanillin Synthesis from 4-hydroxybenzaldehyde,”** *J. Chem. Educ.,* **84,** 1158 (2007).

D.F. Taber and K.J. Frankowski, **“Grubbs’s Cross Metathesis of Eugenol with cis-2-butene1,4-diol to Make a Natural Product: An Organometallic Experiment for the Undergraduate Lab,”** *J. Chem. Educ.,* **83,** 283 (2006).

D.F. Taber and Z. Zhang, **“Synthesis of the Enediol Isofurans, Endogenous Oxidationproducts of Arachidonic Acid,”** *J. Org. Chem.,* **71,** 926 (2006).

D.F. Taber and W. Tian, **“The Neber Route to Substituted Indoles,”** *J. Am. Chem. Soc.,* **128,** 1058-1059 (2006).

D.F. Taber, D.A. Gerstenhaber, X. Zhao, **“Convenient Preparation of tert-butyl Esters,”** *Tetrahedron Lett.,* **47,** 3065 (2006).

D.F. Taber, K. V. Taluskie, **“Computationally Guided Organometallic Chemistry: Preparation of the Heptacyclic Pyrazine Core of Ritterazine N,”** *J. Org. Chem.,* **71,** 2797(2006).

D.F. Taber, C.G. Nelson, **“Potassium Hydride in Paraffin: A Useful Base for Organic Synthesis,”** *J. Org. Chem.,* **71,** 8973-8974 (2006).

D.F. Taber and Y. He, **“Opening of aryl-substituted Epoxides to Form Quaternary Stereogenic Centers: Synthesis of (-)-Mesembrine,”** *J. Org. Chem.,* **70,** 7711-7714 (2005).

D.F. Taber, R. Sheth, P.V. Joshi, **“Simple Preparation of α-diazo Esters,”** *J. Org. Chem.,* **70,** 2851-2854 (2005).

(continued on page 14)

Selected Recent Publications

(Douglass F. Taber, continued)

D.F. Taber and L. Cai, **“Preparation of Ketones from Nitriles and Phosphoranes,”** *J. Org. Chem.,* **70,** 4887-4888 (2005).

D.F. Taber and K.J. Frankowski, **“Synthesis of (+)-Sulcatine G,”** *J. Org. Chem.,* **70,** 6417-6421 (2005).

D.F. Taber and R.A. Plepys, **“Effect of Solvent Polarity on N-H insertion vs. Rearrangement of Alkylidene Carbenes,”** *Tetrahedron Lett.,* **46,** 6045-6047 (2005).

D.F. Taber and Z. Zhang, **“A Linchpin Approach to Unsaturated Fatty Acids: 11,12 Epoxyeicosatrienoic Acid and 11*S*,12*S*-dihydroxyeicosatrienoic Acid Ethyl Esters,”** *J. Org. Chem.,* **70,** 8093-8095 (2005).

D.F. Taber, J. Liang, B. Chen, L. Cai, **“A Model Study Toward the Total Synthesis of N-deacetyllappaconitine,”** *J. Org. Chem.,* **70,** 8739-8742 (2005).

D.F. Taber, L.J. Roberts II, **“Nomenclature Systems for the Neuroprostanes and for the Neurofurans,”** *Prostaglandins & Other Lipid Mediators,* **78,** 14-18 (2005).

Andrew V. Teplyakov

J.C.F. Rodríguez-Reyes and A.V. Teplyakov, **“Chemistry of Diffusion Barrier Film Formation: Adsorption and Dissociation of tetrakis-(dimethylamino)-titanium on Si(100)-2x1,”** *J. Phys. Chem. C,* **111(12),** 4800-4808 (2007).

C. Ni, Z. Zhang, M. Wells, T.P. Beebe Jr., L. Pirolli, L.P. Méndez De Leo and A.V. Teplyakov, **“Effect of Film Thickness and the Presence of Surface Fluorine on the Structure of a Thin Barrier Film Deposited from tetrakis-(dimethylamino)-titanium onto a Si(100)-2x1 Substrate,”** *Thin Solid Films,* **515,** 3030-3039 (2007).

L. Pirolli and A. V. Teplyakov, **“Adsorption and Thermal Chemistry of 1,1,1,5,5,5,-hexafluoro-2,4-pentanedione (*hfacH*) and (hexafluoro acetylacetonate)Cu (vinyltrimethylsilane) ((*hfac*)Cu(VTMS)) on TiCN-covered Si(100) Surface,”** *Surf. Sci.,* **601**, 155-164 (2006).

L.P. Méndez De Leo, L. Pirolli and A.V. Teplyakov, **“Chemistry of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione on Si(100)-2x1,”** *J. Phys. Chem. B,* **110,** 14337-14344 (2006).

L. Pirolli and A.V. Teplyakov, **“Molecular View of Copper Deposition Chemistry: (hexafluoro acetylacetonate)Cu(vinyltrimethylsilane) on a Si(100)-2x1 Surface,”** *Surf. Sci.,* **600**, 3313-3320 (2006).

S. Bocharov; O. Dmytrenko; L.P. Méndez De Leo and A.V. Teplyakov, **“Azide Reactions for Controlling Clean Silicon Surface Chemistry: Benzylazide on Si(100)-2x1,”** *J. Am. Chem. Soc.,* **128,** 9300-9301 (2006).

L.P. Méndez De Leo and A.V. Teplyakov, **“Nitro Group as a Means of Attaching Organic Molecules to Silicon: Nitrobenzene on Si(100)-2x1,”** *J. Phys. Chem. B,* **110,** 6899-6905 (2006).

L. Pirolli and A.V. Teplyakov, **“Vinyltrimethylsilane (VTMS) as a Probe of Chemical Reactivity of a TiCN Diffusion Barrier-Covered Silicon Surface,”** *J. Phys. Chem. B,* **110,** 4708-4716 (2006).

L. Pirolli and A.V. Teplyakov, **“Complex Thermal Chemistry of Vinyltrimethylsilane (VTMS) on Si(100)-2x1,”** *J. Phys. Chem. B,* **109(17),** 8462-8468 (2005).

M.J. Watras and A.V. Teplyakov, **“An Infrared and Computational Investigation of Vanadium-substituted Keggin $[PV_nW_{12-n}O_{40}]^{(n+3)-}$ Polyoxometallic Anions,”** *J. Phys. Chem. B,* **109(18),** 8928-8934 (2005).

S. Bocharov, Z. Zhang, T.P. Beebe Jr. and A.V. Teplyakov, **“Structure of a Thin Barrier Film Deposited From Tetrakis-(dimethylamido)-titanium onto a Si(100) Substrate,”** *Thin Solid Films,* **471,** 159-165 (2005).

Klaus H. Theopold

L.A. MacAdams, G.P. Buffone, C.D. Incarvito, A.L. Rheingold, K.H. Theopold, **“A Chromium Catalyst for the Polymerization of Ethylene as a Homogeneous Model System for the Phillips Catalyst,”** *J. Am. Chem. Soc.,* **127,** 1082 (2005).

D.T. Shay, G.P.A. Yap, L.N. Zakharov, A.L. Rheingold, and K.H. Theopold, **“Intramolecular C-H Activation by an Open-Shell Cobalt(III) Imido Complex,”** *Angew. Chem. Int. Ed.,* **44,** 1508 (2005); Corrigendum: *Angew. Chem. Int. Ed.,* **45**, 7870 (2006).

K.H. Theopold, **“The 2004 Benjamin Franklin Medal in Chemistry Presented to Harry B. Gray,”** *J. Franklin Inst.,* **342,** 583 (2005).

K.H. Theopold, **“Chromium: Inorganic and Coordination Chemistry,”** *Encyclopedia of Inorganic Chemistry 2nd ed.,* R.B. King ed., Wiley: New York (2005).

K.H. Theopold, and R.R. Kucharczyk, **“Chromium: Organometallic Chemistry,”** *Encyclopedia of Inorganic Chemistry,* 2nd ed., R.B. King ed., Wiley: New York (2005).

K.A. Kreisel, G.P.A. Yap, K.H. Theopold, **“A Chelating N-heterocyclic Carbene Ligand in Organochromium Chemistry,”** *Organometallics,* **25,** 4670 (2006).

K.A. Kreisel, G.P.A. Yap, K.H. Theopold, **“Tetra(μ-chloro)-dimethyl-tetrakis(tetrahydrofuran)-chromium(II)dizinc(II),”** *Acta Cryst. C,* **C62,** m569 (2006).

K.H. Theopold, **“Dioxygen Activation by Organometallics of Early Transition Metals,”** *Organometallic Oxidation Catalysis,* F. Meyer, C. Limberg (Eds.) Topics in Organometallic Chemistry Vol 22, Springer, Berlin, p.17 (2007).

K.A. Kreisel, G.P.A. Yap, K.H. Theopold, **“A Bimetallic N-heterocyclic Carbene Complex Featuring a Short Cr-Cr Distance,”** *Chem. Commun.,* 1510 (2007).

B.A. Salisbury, J.F. Young, G.P.A. Yap and K.H. Theopold, **“Synthesis and Reactivity of Pyrrolatodiimine Complexes of Chromium,”** *Collect. Czech. Chem. Commun.,* **72,** 637 (2007). Invited contribution to a special issue dedicated to Dr. Karel Mach.

W.H. Monillas, G.P.A. Yap, L.A. MacAdams, K.H. Theopold, **“Binding and Activation of Small Molecules by Three-coordinate Cr(I),”** *J. Am. Chem. Soc.,* **129,** 8090 (2007).

W.H. Monillas, G.P.A. Yap and K.H. Theopold, **“A Tale of Two Isomers - A Stable Phenyl Hydride and a High Spin (S=3) Benzene Complex of Chromium,”** *Angew. Chem. Int. Ed.* (in press).

Dionisios G. Vlachos

N.S. Kaisare and D.G. Vlachos, **“Optimal Reactor Dimensions for Homogeneous Combustion in Small Channels,”** *Catalysis Today,* **120,** 96 (2007).

A. Chatterjee and D.G. Vlachos, **“Temporal Acceleration of Spatially Distributed Kinetic Monte Carlo Simulations,”** *Journal of Computational Physics,* **211,** 596–615 (2006).

K. Mayawala, D.G. Vlachos and J.S. Edwards, **“Spatial Modeling of Dimerization Reaction Dynamics in the Plasma Membrane: Monte Carlo vs. Continuum Differential Equations,”** *Biophysical Chemistry,* **121,** 194–208 (2006).

A. Chatterjee and D.G. Vlachos, **“Multiscale Spatial Monte Carlo Simulations: Multigriding, Computational Singular Perturbation, and Hierarchical Stochastic Closures,”** *Journal of Chemical Physics,* **124,** 0641101-06411016 (2006).

D.G. Vlachos, A.B. Mhadeshwar and N. Kaisare, **“Hierarchical Multiscale Model-based Design of Experiments, Catalysts, and Reactors for Fuel Processing,”** *Proceedings of Chemical and Process Control,* **7,** Paper No. 45, (2006).

S. Caratzoulas, D.G. Vlachos and M. Tsapatsis, **“On the Role of Tetramethylammonium Cation and Effects of Solvent Dynamics on the Stability of the Cage-like Silicates $Si_6O_{15}^{-6}$ and $Si_8O_{20}^{-8}$ in Aqueous Solution, A molecular Dynamics Study,”** *Journal of the American Chemical Society,* **128,** 596-606 (2006).

J. Ludwig, D.G. Vlachos, A.C.T. v. Duin, and W.A. Goddard III, **“Dynamics of the Dissociation of Hydrogen on Stepped Platinum Surfaces Using ReaxFF,”** *Journal of Physical Chemistry B,* **110,** 4274-4282 (2006).

D.G. Norton, E.D. Wetzel and D.G. Vlachos, **“Thermal Management in Catalytic Microreactors,”** *Industrial Engineering Chemical Research,* **45,** 76-84 (2006).

J.M. Fedeyko, D.G. Vlachos and R.F. Lobo, **"Understanding the Differences Between Microporous and Mesoporous Synthesis Through the Phase Behavior of Silica,"** *Micro. Meso. Mat.,* **90** (1-3), 102-111 (2006).

J.D. Rimer, J.M. Fedeyko, D.G. Vlachos and R.F. Lobo, **"Silica Self-Assembly & the Synthesis of Microporous & Mesoporous Silicates,"** *Chemistry – A European Journal,* **12,** 2926-2934 (2006).

J. L. Provis and D.G. Vlachos, **"Silica Nanoparticle Formation in the TPAOH-TEOS-H_2O System: A Population Balance Model,"** *Journal of Physical Chemistry B,* **110(7),** 3098-3108 (2006).

A.B. Mhadeshwar and D.G. Vlachos, **"Hierarchical Multiscale Mechanism Development for Methane Partial Oxidation and Reforming and for Thermal Decomposition of Oxygenates on Rh,"** *Journal of Physical Chemistry B,* **109,** 16819-16835 (2005).

K. Mayawala, D.G. Vlachos and J.S. Edwards, **"Computational Modeling Reveals Molecular Details of Epidermal Growth Factor Binding,"** *BMC Cell Biology,* **6,** Art. No. 41, Nov. 30 (2005).

D.G. Vlachos, **"A Review of Multiscale Analysis: Examples from Systems Biology, Materials Engineering, and Other Fluid-surface Interacting Systems,"** *Advances in Chemical Engineering,* **30,** 1-61 (2005, invited).

S.R. Deshmukh and D.G. Vlachos, **"Novel Micromixers Driven by Flow Instabilities: Application to Post-reactors,"** *AIChE Journal,* **51(12),** 3193-3204 (2005).

M.A. Snyder and D.G. Vlachos, **"The Role of Molecular Interactions and Interfaces in Diffusion: Permeation Through Single-crystal and Polycrystalline Microporous Membranes,"** *Journal of Chemical Physics,* **123,** 184708-1-11 (2005). Also in Nov. 21, 2005 issue of *Virtual Journal of Nanoscale Science & Technology*.

M.A. Snyder and D.G. Vlachos, **"The Role of Molecular Interactions and Interfaces in Diffusion: Transport Diffusivity and Evaluation of the Darken Approximation,"** *Journal of Chemical Physics,* **123,** 184707-1-11 (2005).

A. Samant and D.G. Vlachos, **"Overcoming Stiffness in Stochastic Simulation Stemming from Partial Equilibrium: A Multiscale Monte Carlo Algorithm,"** *Journal of Chemical Physics,* **123,** 144114-1-8 (2005).

A.B. Mhadeshwar and D.G. Vlachos, **"Is the Water-gas Shift Reaction on Pt Simple? Computer-aided Microkinetic Model Reduction, Lumped Rate Expression, and Rate-determining Step,"** *Catalysis Today,* **105(1),** 162-172 (2005).

J.D. Rimer, R.F. Lobo and D.G. Vlachos, **"Physical Basis for the Formation and Stability of Silica Nanoparticles in Basic Solutions of Monovalent Cations,"** *Langmuir,* **21,** 8960-8971 (2005).

A.B. Mhadeshwar and D.G. Vlachos, **"A Thermodynamically Consistent Surface Reaction Mechanism for the CO Oxidation on Pt,"** *Combustion Flame,* **142,** 289–298 (2005).

A.B. Mhadeshwar and D.G. Vlachos, **"Hierarchical, Multiscale Surface Reaction Mechanism Development: CO and H_2 Oxidation, Water-gas Shift, and Preferential Oxidation of CO on Rh,"** *Journal of Catalysis,* **234(1),** 48-63 (2005).

S.R. Deshmukh and D.G. Vlachos, **"Effect of Flow Configuration on the Operation of Coupled Combustor/reformer Microdevices for Hydrogen Production,"** *Chemical Engineering Science,* **60(21),** 5718-5728 (2005).

A. Chatterjee, M.A. Katsoulakis and D.G. Vlachos, **"Spatially Adaptive Grand Canonical Ensemble Monte Carlo Simulations,"** *Physical Review E,* **71,** 026702-1-6 (2005).

A. Chatterjee, D.G. Vlachos M.A. Katsoulakis, **"Binomial Distribution Based τ-leap Accelerated Stochastic Simulation,"** *Journal of Chemical Physics,* **122,** 024112-1-6 (2005).

S.R. Deshmukh and D.G. Vlachos, **"CFD Simulations of Coupled, Counter-current Combustor/reformer Microdevices for Hydrogen Production,"** *Industrial Engineering Chemical Research,* **44(14),** 4982-4992 (2005).

J.D. Rimer, D.G. Vlachos and R.F. Lobo, **"Evolution of Self-Assembled Silica-Tetrapropylammonium Nanoparticles at Elevated Temperatures,"** *Journal of Physical Chemistry B,* **109(26),** 12762–12771 (2005).

S. Caratzoulas, D.G. Vlachos and M. Tsapatsis, **"Molecular Dynamics Studies on the Role of Tetramethylammonium Cations in the Stability of the Silica Octamers $Si_8O_{20}^{-8}$ in Solution,"** *Journal of Physical Chemistry B,* **109(20),** 10429-10434 (2005).

M.A. Snyder and D.G. Vlachos, **"Molecular Valves Actuated by Intermolecular Forces,"** *Phys. Rev. E,* Rapid Communications **71,** 060201-1-4 (2005). Selected also for the July 4, 2005, issue of *Virtual Journal of Nanoscale Science & Technology*, http://www.vjnano.org.

M.A. Snyder and D.G. Vlachos, **"Molecular Sieve Valves Driven by Adsorbate-adsorbate Interactions: Hysteresis in Permeation of Microporous Membranes,"** *Journal of Chemical Physics,* **122,** 204706-01-10 (2005).

K. Mayawala, D.G. Vlachos and B.J. Edwards, **"Heterogeneities in EGF Receptor Density at the Cell Surface Can Lead to Concave Up Scatchard Plot of EGF Binding,"** *FEBS (The Federation of European Biochemical Societies) Letters,* **579,** 3043-3047 (2005).

J.M. Fedeyko, D.G. Vlachos and R.F. Lobo, **"Formation and Structure of Self-Assembled Silica Nanoparticles in Basic Solutions of Organic and Inorganic Cations,"** *Langmuir,* **21,** 5197-5206 (2005).

A. Chatterjee, K. Mayawala, J.S. Edwards and D.G. Vlachos, **"Time Accelerated Monte Carlo Simulations of Biological Networks Using the Binomial τ-leap method,"** *Bioinformatics,* **21(9),** 2136-2137 (2005).

M.A. Snyder, A. Chatterjee, D.G. Vlachos, **"Net-event Kinetic Monte Carlo for Overcoming Stiffness in Spatially Homogeneous and Distributed Systems,"** *Computers and Chemical Engineering,* **29(4),** 701-712 (2005).

A. Chatterjee, D.G. Vlachos and M. Katsoulakis, **"Numerical Assessment of Theoretical Error Estimates in Coarse-grained Kinetic Monte Carlo Simulations: Application to Surface Diffusion,"** *Int'l Journal of Multiscale Computational Engineering,* **3,** 59 (2005).

D.G. Norton and D.G. Vlachos, **"Hydrogen Assisted Self-ignition of Propane/air Mixtures in Catalytic Microburners,"** *Procedures of the Combustion Institute,* **30,** 2473-2480 (2005).

Brian G. Willis

A. Mathews, R. Opila and B. Willis, **"Bonding States and Coverage Calculations for HfO_2 Deposited on H_2O terminated Si (100)-2x1 using Atomic Layer Deposition,"** E4 Symposium *"High Dielectric Constant Materials and Gate Stack 5"* of the 212th Meeting of the Electrochemical Society (2007, submitted).

R. Gupta and B.G. Willis, **"Nanometer Spaced Electrodes Using Selective Area Atomic Layer Deposition,"** *Virtual Journal of Nanoscale Science & Technology,* **16(1)** (2007).

R. Gupta and B.G. Willis, **"Nanometer Spaced Electrodes Using Selective Area Atomic Layer Deposition,"** *Applied Physics Letters,* **90,** 253102 (2007).

D. Skliar, C. Gelmi and B.G. Willis, **"STM Investigation of the Product Distribution From the Interaction of 2,2,6,6-tetramethyl-3,5-heptandionate with Si(100)-2x1,"** *Surface Science,* **601,** 2887 (2007).

K. Beadle, R. Gupta, A. Mathew, J.G. Chen, B.G. Willis, **"Chemical Vapor Deposition of Phase-rich WC Thin Films on Silicon & Carbon Substrates,"** *Thin Solid Films* (2006, accepted).

L.P. Shepherd, A. Mathew, B.E. McCandless and B.G. Willis, **"Oxygen Pressure Dependence of Copper Ion Transport in SiO_2 Dielectrics,"** *J. Vac. Sci. Technol. B,* **24(3),** 1297 (2005).

E.C. Weigert, N.A. Smith, B.G. Willis and J.G. Chen, **"PVD Synthesis and Characterization of Pt-Modified Molybdenum Carbides as Potential Electrocatalysts,"** *Electrochemical and Solid State Letters,* **8(7),** A 337 (2005).

Ph.D. Candidates

Name	Advisor	Degree	Research Topic
Ali, Bakhtyar	Shah	Ph.D. PHYS	Nanocomposite Solar Cells
Bai, Sha	Taber	Ph.D. CHEM	Phosphonate Reagents for Aldehyde Homologation
Bao, Leijie	Shah	Ph.D. MSEG	High K Dielectric Thin Films
Berry, James	Taber	Ph.D. CHEM	Rh-mediated Amination of Esters
Bilbao, Danny	Lauterbach	Ph.D. CHEG	Non-linear Dynamics of No + NH_3 Reaction
Buzby, Scott	Shah	Ph.D. MSEG	Anion Doping for TiO_2 Band Modification
Ceylan, Abdullah	Shah	Ph.D. PHYS	Core Shell Interactions in Magnetic Nanoparticles
Chan, Joan	Barteau	Ph.D. CHEG	Photochemistry and Photocatalysis of Oxide Nanoparticles
Chatterjee, Abhijit	Vlachos	Ph.D. CHEG	Multiscale Modeling of Self-assembly Processes
Chung , Kimberly	Buttrey	Ph.D. CHEG	Characterization of Complex Layered Nickelates
Collins, Stuart	Vlachos	Ph.D. CHEG	Multiscale modeling of diffusion-reaction processes
Dellamorte, Joseph	Barteau/ Lauterbach	Ph.D. CHEG	Investigation of Silver Catalyzed Olefin Epoxidation Through Traditional and High-Throughput Techniques
DeMatteo, Peter	Taber	Ph.D. CHEM	Polycarbocycles from Alkenes
Esposito, Daniel	Chen/ Birkmire	Ph.D. CHEG	Photoelectrochemical Device for Water Splitting
Fang, Dai	Theopold	Ph.D. CHEM	Dioxygen Activation with Chromium
Federici, Justin	Vlachos	Ph.D. CHEG	Microreaction Technology for Portable Power generation
Gerstenhaber, David	Taber	Ph.D. CHEM	Enantiomerically-pure Cyclohexenones from Epoxides
Goda, Amit	Chen/Barteau	Ph.D. CHEG	C-H Bond Activation by Bimetallic Surfaces
Guo, Pengfei	Taber	Ph.D. CHEM	One-electron and Two-electron Construction of Alkylated Quaternary Centers
Gupta, Rahul	Willis	Ph.D. CHEG	Electrode Strategies for Molecular Electronics Devices
Hansgen, Danielle	Vlachos/Chen	Ph.D. CHEG	Hydrogen Production from Alternative Fuels
Hassanain, Ghulam	Shah	Ph.D. PHYS	Nanomagnetism
Hsu, Irene	Willis	Ph.D. CHEG	Electrode Structure Effects in Molecular Devices
Huang, Wei	Chen/Lobo	Ph.D. CHEG	Selective Hydrogenation on Zeolite-Supported Bimetallic Catalysts
Humbert, Michael	Chen	Ph.D. CHEG	Synthesis and Evaluation of Electrocatalysts
Javadekar, Ashay	Barteau	Ph.D. CHEG	Mechanisms of Promoters in Olefin Epoxidation
Jove, Fernando	Theopold	Ph.D. CHEM	Small Molecule Activation with Iron Complexes
Leftwich, Timothy R.	Teplyakov	Ph.D. CHEM	Surface Chemistry on Silicon Surfaces and in Molecule Corrals
Li, Xin	Barteau/ Buttrey	Ph.D. CHEG	Synthesis and Reactivity of Complex Bismuth Molybdates
Lonergan, William	Chen/Vlachos	Ph.D. CHEG	Synthesis and Characterization of Supported Catalysts
Lukaski, Adrienne	Barteau	Ph.D. CHEG	Olefin Epoxidation on Bimetallics
Madachik, Mark R.	Teplyakov	Ph.D. CHEM	Surface Self-assembly and Co-adsorption on Semiconductors
Menning, Carl	Chen	Ph.D. CHEG	Bimetallic Cathode Electrocatalysts
Miao, Yinghong	Shah	Ph.D. MSEG	Quantum Dot Solar Cells
Monillas, Wesley	Theopold	Ph.D. CHEM	Small Molecule Activation with Chromium Complexes
Murillo, Luis	Chen	Ph.D. MSEG	Bimetallic Catalysis
Nelson, Christopher	Taber	Ph.D. CHEM	Applications of KH in Organic Synthesis
Niehaus, Anne-Marie	Vlachos	Ph.D. CHEG	Multiscale Simulation of Plasma Membrane Processes
Perrine, Kathryn A.	Teplyakov	Ph.D. CHEM	Photochemistry in Metal Deposition on Semiconductors
Pyrz, William D.	Buttrey/Lobo	Ph.D. CHEG	Characterization of Catalytic Materials using Analytical and High-Resolution Electron Microscopy
Qiu, Tingzhu	Barteau	Ph.D. CHEG	Reactions of Multifunctional Reagents on Oxide Surfaces
Rodriguez-Reyes, Juan Carlos	Teplyakov	Ph.D. CHEM	Diffusion Barriers and Interface Chemistry
Rumaiz, Abdul	Shah	Ph.D. PHYS	Dilute Magnetic Semiconductors Dilute Magnetic Semiconductors
Samant, Asawari	Vlachos	Ph.D. CHEG	Multiscale Simulation of Biological Diffusion-reaction Processes

Ph.D. Candidates

Name	Advisor	Degree	Research Topic
Schmidt, Heather	Doren	Ph.D. CHEM	Doped Metal Oxides for Solar Fuel Production
Schulz, Meghan	Shah	Ph.D. MSEG	Nanostructured Oxides for Photochemical Reactions
Sheth, Ritesh	Taber	Ph.D. CHEM	Fe-mediated Cyclohexenone Annulation
Shough, Anne Marie	Doren	Ph.D. CHEM	Photocatalytic Oxidation of Hydrocarbons in a Nanoporous Titanosilicate
Skliar, Dimitri	Willis	Ph.D. CHEG	Chemistry of Atomic Layer Deposition of $SrTiO_3$
Skoplyak, Orest	Chen/Barteau	Ph.D. CHEG	Oxygenate Reactions on Bimetallic Surfaces
Stottlemyer, Alan	Chen	Ph.D. CHEG	Carbides as Alternative Electrocatalysts
Tian, Weiwei	Taber	Ph.D. CHEM	Synthesis of Sordaricin
Vijay, Rohit	Lauterbach	Ph.D. CHEG	Develop. of Novel High-throughput Screening Techniques for Supported Catalyst Samples
Yang, Hua M.	Buttrey	Ph.D. CHEG	Advanced Characterization of Nanocatalysts for Ammonia Decomposition
Yessetepe, Emre	Shah	Ph.D. MSEG	Thermoelectric Nanocomposites
Young, John	Theopold	Ph.D. CHEM	Selective Ethylene Oligomerization Catalyzed by Chromium
Zhang, Xiaochun	Teplyakov	Ph.D. CHEM	Interface Chemistry of Biochemical Systems on Semiconductors

Visiting Researchers and Postdoc Fellows

Name	Advisor	Research Topic
Abbas, Manzar	Shah	Composite Nanostructures for Photovoltaics
Ahmed, Akhlaq	Shah	Co-Doped TiO_2: Optical and Electronic Properties
Andersson, Bengt	Vlachos	Microkinetic Modeling
Bourbakis, Yannis	Vlachos	First Principles Modeling of Catalyst Nanoparticle Synthesis and of Support Effects in Catalysis
Caratzoulas, Stavros	Vlachos	First Principles Simulations of Silicate Chemistry
Hazra, Sukti	Shah	Quantum Dot Solar Cells
Hinkle, Paul V.	Theopold	Silica/Polypropylene Nanocomposites
Jiang, Colin	Taber	Alkylidene C-H insertion: Synthesis of the Chamigrenes
Jiang, Qin	Taber	Isoprostane Synthesis by Rh-Mediated Intramolecular Cyclopropanation
Joerger, Jean-Michel	Taber	Synthesis of the Ritterazines
Kaisare, Niket	Vlachos	Microreactor and Microkinetic Modeling
Karim, Ayman	Vlachos	Fabrication of and Experimentation in Microchemical Systems
Lebedeva, Marina	Vlachos	Multiscale Modeling of Microreactors
Liang, Jianglin	Taber	Synthesis of the Bromochamigrenes
Liu, Jianzhong	Doren	Ab Initio Thermodynamics of Aerosols and Proteins
Maestri, Matteo	Vlachos	Microkinetic Modeling of Catalytic Partial Oxidation and Steam Reforming Processes
Mhadheswar, Ashish	Barteau	Surface Kinetics for Partial Oxidation
Nakajima, Katsumatsu	Taber	Fe-Catalyzed Carbonylations of Alkenyl Cyclopropanes
Palomeque, Liliam	Lobo	Transport and Reactivity of Vanadium Species in FCC Catalysts
Park, Gyo Ik	Barteau	STM Studies of Polyoxometalates
Prasad, Vinay	Vlachos	Microkinetic Model-based Design of Experiments and Catalysts
Reddy, Ganapati	Taber	Synthesis of the Neuroprostanes
Riemann, Stephan	Lobo	Low Si/Al Mesoporous Materials
Rykov, Sergey	Chen	NEXAFS and Surface Spectroscopies
Snively, Chris	Lauterbach	Development of Novel Spectroscopic Techniques
Stefanidis, George	Vlachos	Short Contact Time Multifunctional Reactors
Waddell, Michelle	Taber	Synthesis of Sordaricin Antifungals
Yamada, Soichiro	Lauterbach	High-throughput Catalysis
Zhang, Leon	Taber	5-5 Spiroethers From Lactones: Synthesis of Ritterazine N

Recent Alumni (2005-2007)

Name	Advisor	Current Employer
Addo, Ernest	Shah	GE Solar
Baker, Colin	Shah	Air Force Research Laboratory
Beadle, Kendra	Chen/Willis	
BinTaleb, Abdulmalik	Theopold	SABIC (Saudi Arabia)
Bocharov, Semyon	Teplyakov	
Buffone, Gerald	Theopold	Chipola College
Cuadra, Amalia	Willis	Philadelphia School District
Deshmukh, Soumitra	Vlachos	Velocys
Enever, Michael	Barteau	Air Products
Fedeyko, Joseph	Lobo/Vlachos	Johnson Matthey
Feist, Ben	Lauterbach/ Vlachos	Air Liquide
Frankowski, Kevin	Doren	University of Kansas
Frey, Jeffrey	Doren	University of Delaware
Goyal, Amita	Shah	University of Delaware
Guerin, Daniel	Shah	Naval Research Laboratories
Hinkle, Paul V.	Theopold	Norquay Technology Inc.
Jankowiak, Jerome	Barteau	Praxair
Juttu, Gopalakrishnan	Lobo	SABIC
Kreisel, Kevin	Theopold	Postdoc, University of Wisconsin at Madison
Li, Weidong	Shah	Nanophosphors
Lopez, Liza	Barteau	DuPont
Ludwig, Jeffrey	Vlachos	ExxonMobil
Martinez-Inesta, Maria	Lobo	Faculty, Chemical Engineering, University of Puerto Rico of Mayagüez
Mayawala, Kapil	Vlachos/ Edwards	Novartis
McCormick, John	Chen	Rohm & Haas
McMillan, Noah	Lauterbach	Eastman Chemicals
Méndez De Leo, Lucila P.	Teplyakov	Adsorption on Semiconductor Surfaces

Name	Advisor	Current Employer
Mhadheswar, Ashish	Vlachos	General Electric
Mukherjee, Soumen	Theopold	Reliance Industries Ltd. (India)
Nakajima, Katsu*	Taber	Novartis Pharmaceuticals
Neubert, Timothy	Taber	Vertex Pharmaceuticals
Norton, Daniel	Vlachos	General Electric
Pan, Yongchun*	Taber	J-Star
Peddy, Mahitha Reddy	Theopold	
Pirolli, Laurent*	Teplyakov	Schlumberger, Inc.
Pradhan, Anshu	Shah	Novellus
Rimer, Jeff*	Lobo/Vlachos	New York University
Sawant, Kaveri	Lobo	Rohm and Haas Electronic Materials
Shay, D.Travis	Theopold	Lyondell Chemical Corp.
Shepherd, Laura Parrish	Willis	W.L. Gore
Shu, Yuying	Chen	W.R. Grace Company
Sikkander, Inthi	Taber	Albany Molecular
Snyder, Mark	Vlachos	University of Minnesota
Storck, Pierre*	Taber	Johnson & Johnson (France)
Strano, Michael	Foley	Faculty, Chemical Eng., University of Illinois
Taluskie, Karen	Taber	Cambridge Isotopes
Teng, Dawei*	Taber	NAEJA Pharmaceutical Inc.
Waite, Matthew	Shah	Faculty, Physics, West Chester University
Wang, Yushan	Doren	Penn State
Washburn, Seth	Lauterbach	ExxonMobil
Weigert, Erich	Chen	Johnson Matthey
Xu, Ming*	Taber	DuPont Crop Protection
Zellner, Michael	Chen	Los Alamos National Laboratory

**Postdoc*

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

15 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 three Beowulf clusters, all running CentOS Linux version 4.2 deployed with Warewulf. These clusters have a total of ~140 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), a Silicon Graphics Indigo XZ R4400 (150 MHz and 32 bit microprocessor), and 1 Dual Alpha 833 MHz processor running Tru64 Unix.

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.

Research – Mark A. Barteau

TiO_2 Nanoparticle Catalysis and Photocatalysis

Heterogeneous photocatalysis based on TiO_2 has been the focal point of numerous investigations in recent years, because of the chemical stability of this material and its nontoxicity, and because of the potential for the total destruction of organic compounds in polluted air and wastewater. The band gap (E_g) of TiO_2 anatase is ~3.2 eV, which corresponds to only a limited portion (3-4%) of the solar spectrum. This relatively large band gap has significantly limited more widespread application, particularly to indoor situations. Various methods have been suggested to enhance the efficiency of the photocatalytic process involving TiO_2 under visible light irradiation, including doping, functionalization of the surface with metallic particles, and reduction of particle size to nanoscale.

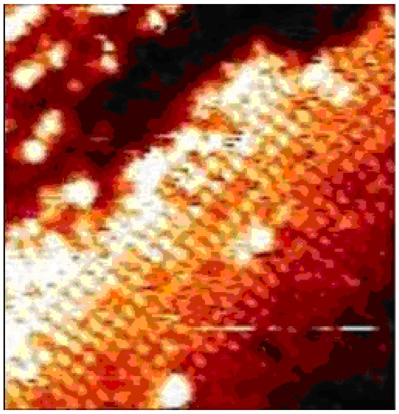
The present work demonstrates the advantages of combining high resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field (HAADF) techniques for direct visualization of the reactivity of submicron and nanoscale photocatalysts. The photocatalytic reduction of Ag salts to metallic Ag on the surfaces of TiO_2 particles was used to probe the spatial distribution of photoreactive sites on the sub-micrometer-scale and nanoscale TiO_2 particle surfaces. The size, spatial distribution and the wavelength dependence of the Ag nanoparticles photodeposition on the TiO_2 surfaces were quantified by analysis of the HRTEM and HAADF images. To further extend our study, we also investigated the photodeposition of Au nanoparticles on TiO_2 surfaces. Currently, we are focusing on scaling up the Ag photodeposition on TiO_2 nanoparticles. Ag/TiO_2 nanoparticles obtained from the scaled-up process were characterized by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), and HAADF. This study provides new insights into the particle size distribution, surface structures, and other physical properties of potential relevance to the catalytic performance of Ag and Au nanoclusters supported on TiO_2. The use of gold in catalyst application is attracting increasing attention. It has been shown that gold nanoparticles with sizes below 5nm exhibit unique catalytic properties for CO oxidation, the water gas shift reaction, and epoxidation of propylene, despite the inert character of gold. Information obtained from this study, therefore, will be of benefit in developing devices and techniques based on TiO_2 nanoparticles and TiO_2-supported metal nanoparticles, as from the HRTEM and HAADF results, we have been able to produce high loadings of uniform Au nanoparticles by photodeposition on TiO_2 nanoparticles.

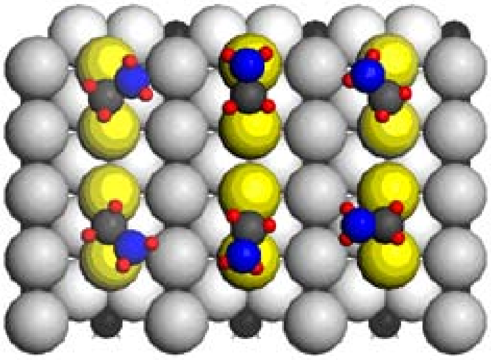
Mark A. Barteau (Chemical Engineering)
Sze Chi (Joan) Chan (Grad. Student, Chemical Engineering)

Adsorption of Amino Acids on Oxide Surfaces

It has been suggested that common minerals may have played an important role in the origin of life on earth. Many simple oxides and clay minerals exhibit activity for acid-base and redox catalysis, and it has been speculated that such processes may have been responsible for the assembly of small biomolecules such as peptides. In spite of the importance of such proposals (and of the interactions of proteins with surfaces in more contemporary settings) there is relatively little information available about the adsorption and reaction of amino acids and other multifunctional molecules with well-defined inorganic surfaces.

We have examined the adsorption of amino acids on single crystal surfaces of titanium dioxide using Scanning Tunneling Microscopy (STM). We wish to determine how these molecules bind to oxide surfaces, what reactions (including formation of peptide linkages) occur, and what local sites or extended crystallographic structures are needed by different chemistries. Our STM results show that the simplest amino acid, glycine, forms a (2x1) array of adsorbed carboxylate ligands on the TiO_2(110)-(1x1) surface, as shown below. This structure is directly analogous to those formed by formic and acetic acids on this surface, and suggests that the amino group of glycine should be accessible for reaction with species adsorbed in the second layer.

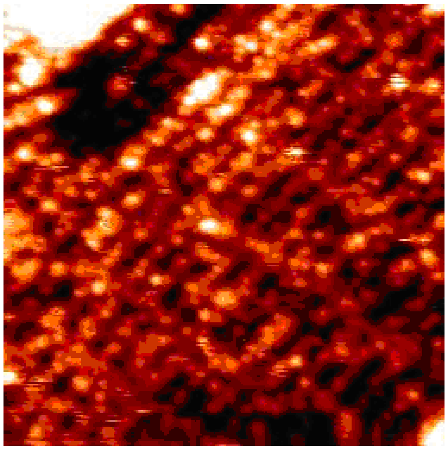

STM image (15nm x 15nm) of the TiO_2(110)-(1x1) surface after glycine adsorption


Schematic of (2x1) glycinate array on the TiO_2(110)-(1x1) surface

We have been unable to produce similarly ordered structures of the larger amino acid, proline on the TiO_2(110)-(1x1) surface, presumably because of greater steric interaction between the bulkier side groups on this molecule. However, on the (1x2) reconstructed surface, on which the rows of exposed Ti cations are twice as far apart, we do observe one-dimensional ordering of adsorbate molecules along the rows, consistent with decreased steric effects.

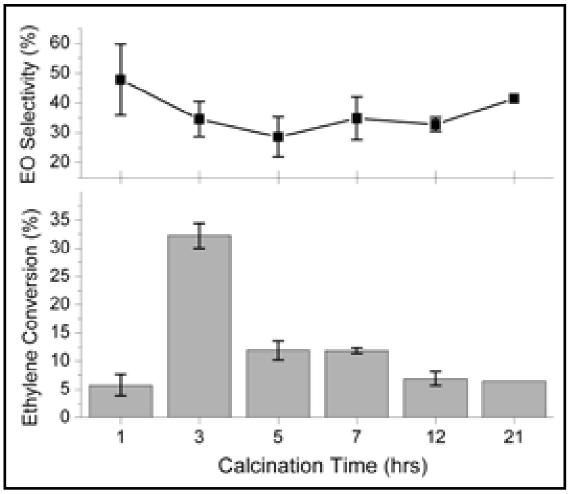
The goal of this project is to produce an understanding of interactions between complex molecules and inorganic surfaces needed to move hypotheses about molecular assembly processes from the realm of speculation. We hope to understand, not only how nature may have catalyzed such processes in the past, but also how we might apply them to problems in catalysis, surface modification, and a variety of other technologies in the future.

Mark A. Barteau (Chemical Engineering)
Tingzhu Qiu (Grad. Student, Chemical Engineering)


STM image (20nm x 20nm) of the TiO_2(110)-(1x2) surface after proline adsorption

High-Throughput Studies of Ag Catalysts for Ethylene Epoxidation

We have previously demonstrated the successful prediction of the superior performance of Cu-Ag bimetallic catalysts for ethylene epoxidation through the combination of DFT calculations and surface science experiments. These bimetallic catalysts maintain their selectivity advantage when modified with conventional promoters such as chlorine and cesium. However, systematic evaluation of multicomponent catalysts rapidly becomes a daunting task as the number of promoters is increased. Thus an important objective of our research is to create more efficient ways to test predictions and catalyst designs emerging from both fundamental studies and from the existing state of the art.



Ethylene conversion and EO selectivity for Ag catalysts calcined at 400°C for 1-21 hours

In order to establish a fundamental understanding of the performance of Ag and of bimetallic catalysts promoted with other known promoters, such as rhenium, we have carried out both single reactor and high-throughput reactor studies. As Figure 1 shows, Ag catalyst activity is dramatically affected by the calcination conditions, without change to the selectivity. Based on this result, it appears that catalyst sintering decreases activity with longer calcination times. Results from studies with Re-Ag indicate that Re increases the EO selectivity at the expense of catalyst activity. The optimum performance of 45% EO selectivity for the Re-Ag, compared to 30% for Ag, was found for catalysts with 25 ppm Re. Characterization, using SEM, shows that the addition of Re also causes an increase in the Ag particle size from 15-35 µm. An analysis of the oxygen reaction orders showed that the Re-Ag catalyst presents a more uniform distribution of sites for oxygen adsorption than do unpromoted catalysts. Thus, it is hypothesized that Re decreases the population of Ag step sites, increasing the EO selectivity.

Mark A. Barteau (Chemical Engineering)
Jochen Lauterbach (Chemical Engineering)
Joe Dellamorte (Grad. Student, Chemical Engineering)

In Situ Studies of the Mars Van Krevelen Mechanism in Hydrocarbon Oxidation

Conventional wisdom has held that metal oxide-catalyzed selective oxidations follow the Mars-van Krevelen mechanism. The organic reactant is oxidized by lattice oxide ions at the surface; these are replenished by dioxygen dissociation with surface and solid state diffusion to reoxidize surface sites. Our studies using a flow microbalance reactor to examine butane oxidation by vanadyl pyrophosphate catalysts have quantitatively determined the kinetics of catalyst reduction and reoxidation in the Mars-van Krevelen scheme. Comparisons with the steady-state rate demonstrate that oxygen removal from the lattice is too slow to account for the overall reaction rate. The Mars-van Krevelen mechanism using catalyst lattice oxygen can account for only about 5% of the total oxidation activity. Previous isotope exchange studies suggest that VPO catalysts for butane oxidation and Bi-Mo oxide catalysts for propene oxidation utilize lattice oxygen to much different extents, providing useful tests of microbalance-based mechanistic studies.

We have synthesized both pure phase bismuth molybdates and novel bismuth vanadomolybdate materials derived from the structure of the highly selective β-$Bi_2Mo_2O_9$. The vanadomolybdates showed an increase in the specific rate of propylene conversion, while retaining the high selectivity to acrolein of the parent oxide. This led to a reduction of ca. 40°C to operate at the same level of conversion as compared with β-$Bi_2Mo_2O_9$. This work sets the basic ground for the development of multicomponent oxides with potential application in alkane selective oxidations which retain the structure of the parent bismuth molybdates. We have quantified the relative contribution of the redox mechanism to the overall oxidation reaction in the bismuth molybdates and vanadomolybdates. It was found that all the propylene oxidation takes place by redox reactions involving the lattice, in accordance with the hypothesis of the Mars van Krevelen mechanism. Addition of a limited amount of vanadium to the structure of β-$Bi_2Mo_2O_9$ appears to increase the catalytic activity by enhancing the interaction of gas-phase oxygen with the surface.

Mark A. Barteau (Chemical Engineering)
Douglas J. Buttrey (Chemical Engineering)
Liza Lopez (Grad. Student, Chemical Engineering)

Research – Mark A. Barteau *(continued)*

Mechanistic Investigation of Higher Olefin Epoxidation

Silver-catalyzed direct oxidation processes, such as ethylene epoxidation, have been extensively researched due both to the uniqueness of the process among epoxidation methods and to the commercial significance of epoxide products. Ethylene oxide is the largest volume product generated via selective oxidation by the chemical process industry with annual production in excess of 8x10^9 lbs. With the exception of the small-scale commercial generation (now discontinued) of epoxybutene from Ag-catalyzed selective epoxidation of 1,3-butadiene by Eastman Chemical, production of ethylene oxide directly from ethylene and molecular oxygen remains unique among industrial epoxidation processes. Implementation of direct oxidation chemistry in the production of more complex epoxides, such as propylene oxide, has yet to be realized because there are no catalysts currently capable of epoxidizing propylene, the simplest homolog of ethylene, directly with acceptably high selectivities.

Our previous surface science and computational studies identified an oxametallacycle species as the central intermediate in Ag-catalyzed epoxidation of both ethylene and 1,3-butadiene. This species controls selectivity through competitive ring-closure to form the epoxide and isomerization to aldehydes. Oxametallacycles have also been synthesized from 2-iodo-ethanol on Ag(110) and Ag(111), epoxybutene on Ag(110) and Ag(111) , and styrene oxide on Ag(111).

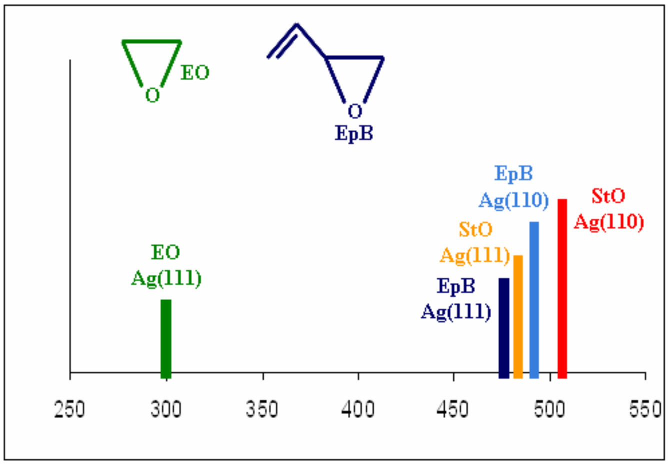
Surface science techniques and Density Functional Theory (DFT) are used in this study to probe the reactions of complex epoxides on Ag-surfaces. The initial part of this work explores the role of unsaturated substituents in intermediates derived from epoxides and includes the recent study of styrene oxide on Ag(110), while subsequent discussion explores reactions of the intermediate derived from ring-opening isoprene oxide, on Ag(110); the presence of allylic hydrogen and its facile abstraction by adsorbed oxygen species makes direct oxidation of propylene difficult.

Styrene oxide undergoes activated ring-opening upon adsorption above 200 K to form stable oxametallacycle on both Ag(111) and (110); the unsaturated phenyl group interacts with the Ag-surface and stabilizes the oxametallacycle relative to that derived from ethylene oxide. Ring-closure and isomerization of the oxametallacycle reforms the respective epoxide and aldehyde species near 505 K on Ag(110). Similar to the styrene oxide-derived oxametallacycle on Ag(111), DFT calculations predict that epoxide ring-opens at the carbon bound to the substituent group and adsorbs with the phenyl rings nearly parallel to the Ag(110) surface.

Isoprene oxide also forms a strongly bound oxametallacycle intermediate on the Ag(110) surface. The oxametallacycle undergoes ring-closure to reform isoprene oxide in two peaks at 320 and 460 K when synthesized by epoxide adsorption at low temperatures; the product distribution in these two states is identical and corresponds to the gas-phase cracking pattern of isoprene oxide. Epoxide doses at higher surface temperatures ca 300 K lead to isomerization of the oxametallacycle and desorption of the aldehyde isomer, 2-methyl-2-butenal, in a single peak at 460 K. This work represents the first demonstration of a surface oxametallacycle species derived from an allylic epoxide. The structure of the isoprene oxide-derived oxametallacycle resembles that formed from ring-opening the non-allylic counterpart, 1-epoxy-3-butene, on Ag(110), according to DFT calculations.

Identification of oxametallacycle intermediates from complex epoxides with similar surface chemistry and structure to the active species in Ag-catalyzed epoxidation of ethylene suggests a common mechanism for olefin epoxidation. Through investigation of a variety of epoxides, we hope to obtain a better understanding of the epoxidation pathways and facilitate the development of catalysts capable of oxidizing higher olefins directly.

Mark A. Barteau (Chemical Engineering)
Adrienne Lukaski (Grad. Student, Chemical Engineering)



Reaction temperatures for ring closure reactions of oxametallacycles on silver surfaces

Research – Douglas J. Buttrey

Complex Transition Metal Oxides for Selective Oxidation

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.

Similar arguments would apply for the case of controlling the extent of oxidation on the pathway from butane to maleic anhydride. It would be very desirable to be able to directly generate butenes ($2e^-$), butadiene ($4e^-$), tetrahydrofuran (THF) ($4e^-$), or furan ($6e^-$) rather than permitting the reaction to proceed all the way to maleic anhydride (14e-) or worse yet, to CO_2 ($26e^-$). As an illustrative example, the direct preparation of THF would obviate the two-step pathway involving oxidation of butane to maleic anhydride and then reduction to THF. Again, our approach would provide for a new, more energy efficient pathway.

We are building upon this site isolation principle in an attempt to design and synthesize new catalytic solids which will have precisely controlled surface morphology, i.e. sites isolated from each other by distances which can be tuned through choice of structure and elements arranged within it. We have recently identified an Sb-V-P-O phase iso-structural with $SbOPO_4$ that is a promising candidate for this purpose and forms a solid solution, thereby allowing us to control the amount of vanadium substitution. Structural refinement of neutron diffraction data has indicated that the type of site substitution is dependent on the vanadium stoichiometry. The vanadium-rich phase end of the solid solution has shown catalytic activity towards the combustion of both propane and butane. We hope to achieve selectivity toward lower oxidation products by moving toward the vanadium-deficient end of the solid solution. Further research includes the substitution of other Group 4 and 5 metals into the $SbOPO_4$ and NASICON-related structures (Figure 1). By introducing other metals into the V-P-O system, we expect to identify phases for which the V=O sites are more dilute and further separated from each other than in the binary phases. Judicious incorporation of Ti, Nb, or Ta may chemically modify the oxidation potential of the V=O sites as well. Our primary objective will be to synthesize structures with solitary V=O sites, although clustered motifs will make for interesting comparisons.

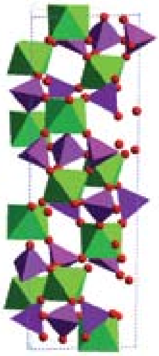
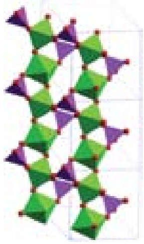


Figure 1:
The empty NASICON structure, $M_2(PO_4)_3$. This differs from the general NASICON form $A_xM_2\ (PO_4)_3$ by the absence of intercalated A-site cations.



The iso-structural $SbOPO_4$ phase of the Sb-V-P-O

Another topic of interest involves the relationships between composition, structure, properties, and catalytic performance in the bismuth molybdate family. 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.

Current research on propane ammoxidation and selective oxidation catalysts, particularly complex mixed-metal molybdenum oxide systems, has yielded insight on the structure and chemical composition of crystalline phases that are the major components in active catalyst materials (Figure 2). 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.

Douglas Buttrey (Chemical Engineering)
Peter DeSanto Jr. (Assistant Professor, Bloomsburg Univ.)
Robert Grasselli (Adjunct Professor, Chem. Engineering)

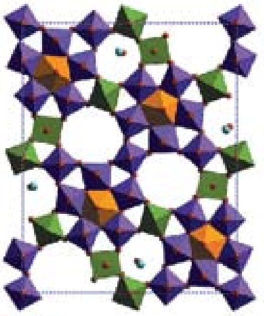
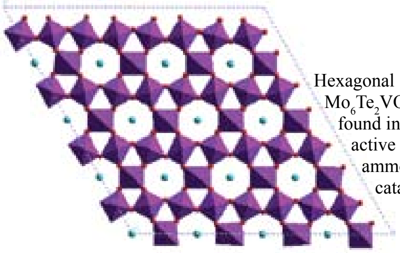


Figure 2:
Orthorhombic $Mo_{7.5}V_{1.5}NbTeO_{29}$



Hexagonal $Mo_6Te_2VO_x$ found in active propane ammoxidation catalyst

Synthesis and Characterization of Metallic and Bimetallic Nanoparticles Through Electron Microscopy

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

(continued on page 24)

Research – Douglas J. Buttrey *(continued)*

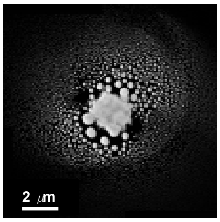


Figure 1: HAADF micrograph of a nano-particle field following an EBIF event

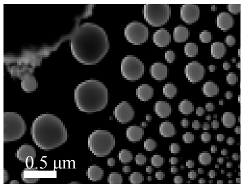


Figure 2a: Typical HAADF image of nanoparticles following EBIF

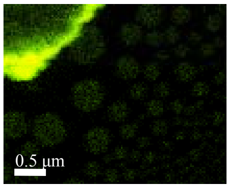


Figure 2b: Ni K edge x-ray map showing areas with Ni

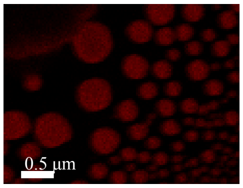


Figure 2c: Bi M edge x-ray map showing areas containing Bi

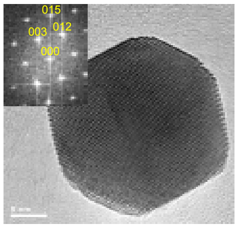


Figure 3: HREM image of a single Ni-Bi nanoparticle with the corresponding FFT image looking down the [100] zone axis

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).

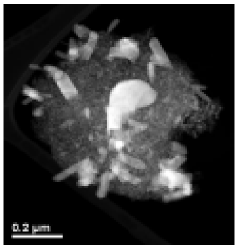


Figure 4: HAADF image showing the base un-promoted Ru catalyst supported on Al_2O_3

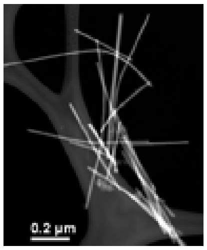


Figure5: HAADF image showing the K-promoted Ru catalyst supported on Al_2O_3

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.

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

Using high throughput experimentation, we found that the potassium promoted Ru catalysts supported on Al_2O_3 exhibited the best performance. These promoted catalysts demonstrated NH_3 decomposition activities that were approximately 50-80°C lower than those observed on the base Ru catalysts. Using HAADF, Figure 4 shows an image of the base unpromoted Ru catalyst that contains 5-100 nm nanoparticles and some larger agglomerates. However, on the better performing K-promoted catalyst shown in Figure 5, we discover nanowhiskers that have rectangular dimensions between 20-50 nm and lengths ranging from a few nm to several microns. Selected-area electron diffraction in the TEM shows that these whiskers have a KRu_4O_8 hollandite structure. We believe that this structure is a necessary component of our catalyst and may be responsible for the enhanced ammonia decomposition efficiencies. Although the exact nature of the KRu_4O_8 hollandite is not yet known, these results appear to be the first identification of the hollandite structure in an ammonia decomposition catalyst and a first step towards understanding the role of K in Ru catalysts supported on Al_2O_3. Our continued efforts are focused on determining the exact role of the hollandite structure and its stability in the ammonia decomposition environment.

Lastly, we are involved in collaborative efforts studying two additional nanoparticle systems. The first is characterization of Pt-Re bimetallic catalysts, and the second is characterizing Pt & Au nanoparticles synthesized using dendrimer templates. Figure 6 shows HAADF images of a 1:1 Pt:Re bimetallic catalysts supported on C. The images show a very finely dispersed nanoparticle catalyst with particle sizes between 1-3 nm. EDS analysis has confirmed the formation of bimetallic particles and current efforts are underway to quantify the extent of alloying. In the dendrimer encapsulated nanoparticles, Figure 7 shows HREM images of Au and Pt nanoparticles prepared using dendrimer templates. The templates allow particle size control based on the generation (size) of the dendrimer used in solution. FFT analysis of the HREM images show that both the Pt and Au nanoparticles exhibit their respective FCC structures and the particle sizes range between 1-5 nm. The use of dendrimer templates and the development of controlled nanoparticle sizes and compositions are of great importance in chemical reactions that are structure sensitive. Our future efforts in this area are directed towards the production of bimetallic nanoparticles with controlled compositions, sizes, and microstructures (alloy, solid solution, or core-shell).

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

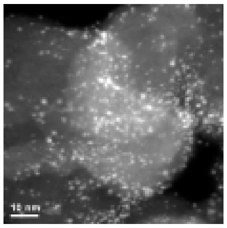


Figure 6: HAADF image showing dispersed 1-3 nm Pt-Re bimetallic nanoparticles supported on C

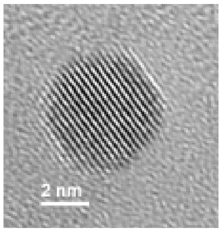


Figure 7a: HREM image of Au nanoparticles synthesized using the dendrimer template

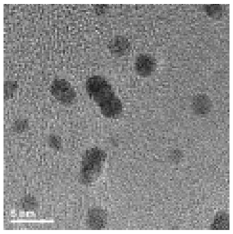


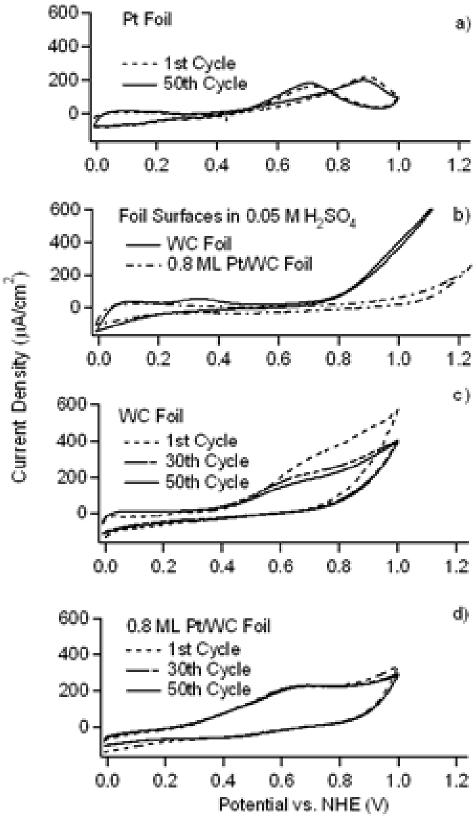
Figure 7b: HREM images of Pt nanoparticles synthesized using the dendrimer template

Metal Carbides as Anode Electrocatalysts for Fuel Cells

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.

Jingguang Chen (Chemical Engineering)
Erich Weigert (Graduate Student, MSEG)
Chelsea Ren (Graduate Student, Chemistry)



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

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

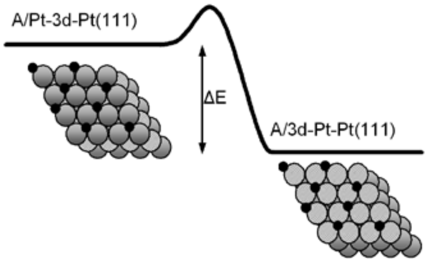
Another stability issue in PEM fuel cells is the particle size of Pt. We are utilizing the e-beam deposition technique to prepare Pt particles with well-controlled particle size, which are subsequently tested for hydrogen and methanol electrooxidation. TEM, XRD and XPS are utilized to compare the particle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

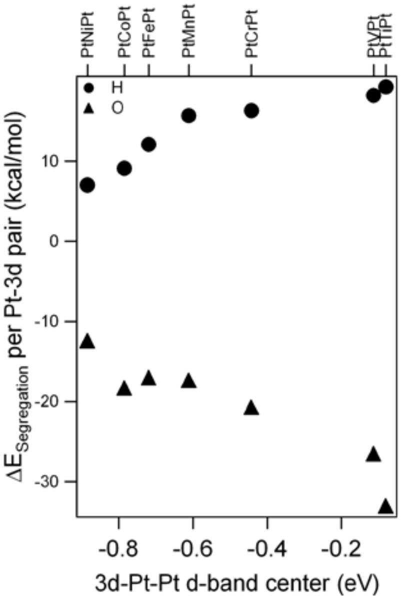
Jingguang Chen (Chemical Engineering)
Carl Menning (Grad. Student, Chemical Eng.)
Michael Humbert (Grad. Student, Chemical Eng.)

Photoelectrochemical (PEC) Devices for Water Splitting

The cathode reaction at PEC involves the reduction of H^+ to produce H_2. Currently the most common cathode catalyst is Platinum (Pt). Due to the high cost and limited supply of Pt, the utilization of large quantities of Pt will most likely hinder the commercialization of PEC. We will attempt to solve this problem using two parallel approaches: (1) to reduce the loading of Pt by using Pt-based bimetallic alloys and (2) to replace Pt with alternative catalytic materials. Currently we are exploring the possibility of utilizing these carbide materials for the cathode reduction of H^+ to produce H_2. The cathode activity and stability of W and Mo carbides are being compared to those of Pt. We plan to employ a combination of in-situ electrochemical measurements and theoretical modeling to identify and synthesize carbide structures and compositions as alternative cathode catalysts in PEC.

Jingguang Chen (Chemical Engineering)
Robert Birkmire (Institute of Energy Conversion)
Dan Esposito (Grad. Student, Chemical Eng.)





Research – Jingguang G. Chen *(continued)*

Novel Properties of Bimetallic Surfaces and Supported Catalysts

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.

Jingguang Chen (Chemical Engineering)
Mark Barteau (Chemical Engineering)
Raul Lobo (Chemical Engineering)
Luis Murillo (Grad. Student, Chemical Eng.)
Amit Goda (Grad. Student, Chemical Eng.)
Orest Skoplyak (Grad. Student, Chemical Eng.)
Wei Huang (Grad. Student, Chemical Eng.)
William Lonergan (Grad. Student, Chemical Eng.)

Structure-Property Relationship in Transition Metal Carbides

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

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

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

Jingguang Chen (Chemical Engineering)
Michael Humbert (Grad. Student, Chemical Eng.)
Alan Stottlemyer (Grad. Student, Chemical Eng.)

NEXAFS and EXAFS Characterization of Catalytic Materials

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.

Jingguang Chen (Chemical Engineering)
Wei Huang (Grad. Student, Chemical Eng.)
Luis Murillo (Grad. Student, Chemical Eng.)
Sergey Rykov (Visiting Professor)
Ned Marinkovic (Research Associate)

Photocatalysis in Doped TiO_2 Nanoparticles

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

Douglas J. Doren (Chemistry and Biochemistry)
Yushan Wang (Graduate Student, Physics)

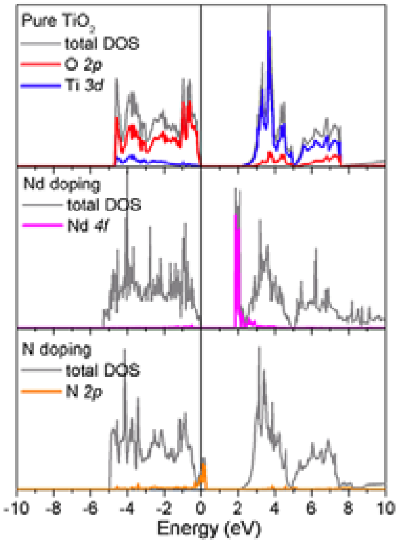


Figure 1: Density of electronic states in pure TiO_2 (anatase), and in anatase doped with Nd and N. Dopant levels in these calculations are at the 4 atom percent level, while experimental dopant levels are about 1 atom percent.

Photocatalysis in ETS-10, a Nanostructured Titanosilicate

ETS-10 contains one-dimensional chains of TiO_6 octahedra within a nanoporous silicate framework (see Figure 3). It is known to photocatalyze a variety of transformations of organic molecules. The structure and electronic properties can be controlled through synthesis, and this project is an effort to understand how this flexibility can be used to improve photcatalytic 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 accounts 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 are not as effective as V in reducing the band gap (see Figure 4). We are currently using the results of these first-principles calculations to develop a simple model that can predict the effect that transition metal substitutions (including combinations of different metals) are likely to have on the electronic energies in this system. This model will be used to guide choices of other materials to study with valence and conduction band positions chosen to permit specific redox reactions.

Douglas J. Doren (Chemistry and Biochemistry)
Anne Marie Shough (Grad. Student, Chemistry)

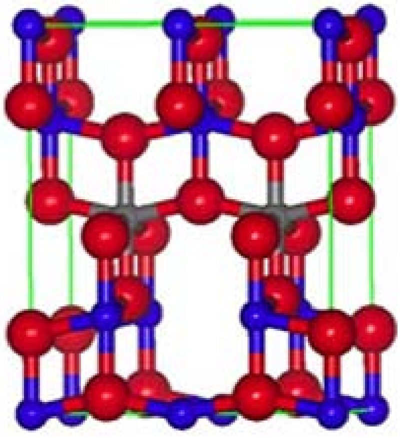


Figure 2: Model of Cr-doped anatase with an oxygen vacancy. The vacancy is required for charge neutrality, but the magnetic coupling between the Cr d electrons depends on the relative positions of the Cr atoms and the vacancy

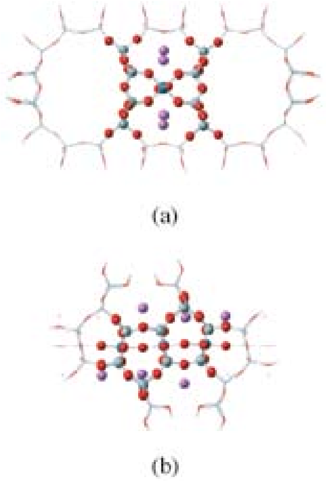

(a)
(b)

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

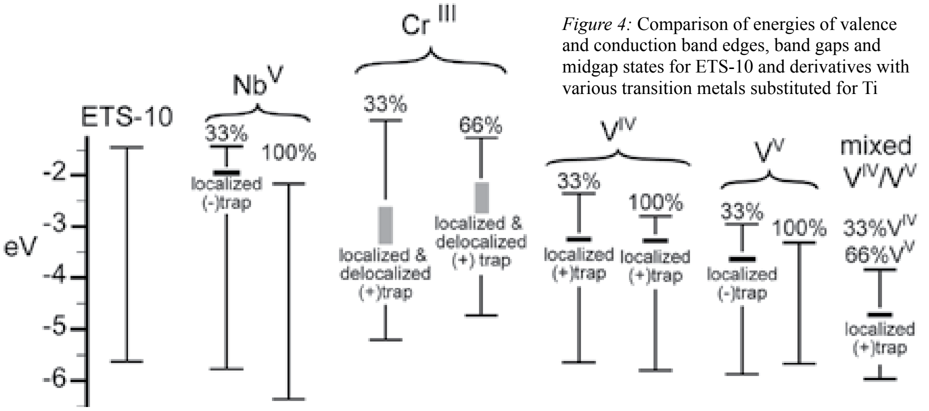


Figure 4: Comparison of energies of valence and conduction band edges, band gaps and midgap states for ETS-10 and derivatives with various transition metals substituted for Ti

Research – Jochen A. Lauterbach

High-throughput Analysis of Supported Catalysts

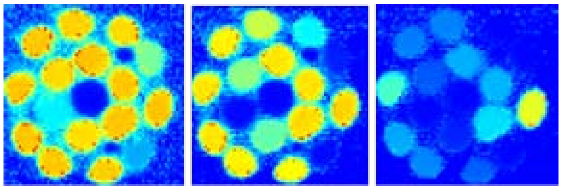
Historically, catalytic studies have been performed by testing a single catalyst formulation at a time. However, catalysts are very complex systems with compositional heterogeneity on both the nano- and mesoscales. Using a single reactor to systematically study hundreds or even thousands of catalyst formulations in order to understand reaction behavior as a function of composition, would entail 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. The true power of the combinatorial approach, however, will be realized with the ability to perform quantitative studies in parallel. This methodology, in combination with modeling, can take our understanding of heterogeneously catalyzed reactions to a higher level, accelerate discovery of novel catalyst formulations, and ultimately lead to 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.

Our research approach is two-fold: (1) We screen supported catalysts samples in a home-build reactor system for activity and selectivity, accepting the fact that we can screen "only" hundreds and not thousands of samples per month. However, important factors, such as non-isothermal effects and transport limitations, are taken into account; (2) We study adsorbates on multiple samples simultaneously, gathering information about the reaction mechanism as a function of the catalyst composition. All this information is fed into an integrated modeling effort, which makes use of all information created about the catalyst samples under investigation.

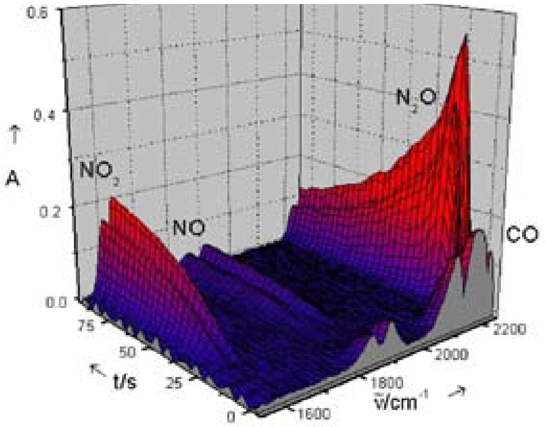
Our group has developed the first truly parallel, chemically sensitive high-throughput screening technique for supported catalyst samples. Most other high-throughput screening methods for heterogeneous catalysts are sequential analysis techniques, such as mass spectrometry or gas chromatography, which have severe drawbacks. Scale-up is the most obvious problem. Data for different catalyst should be compared under the same conditions and deactivation may occur to one catalyst while another is being tested in a sequential system. We now routinely measure the effluent of 16 supported catalyst samples in 1 second. In order to perform these experiments, we employ FTIR imaging of the gas-phase exit streams of a 16 channel reactor. This technique combines the chemically rich information available from mid-infrared spectroscopy with the ability to acquire this information in a spatially resolved manner. A single data set consists of both spatial and spectral information, with each pixel containing a full IR spectrum. The end result is the ability to visualize the distribution of chemical species within complex systems.

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

Jochen Lauterbach (Chemical Engineering)
Mark Barteau (Chemical Engineering)
Dionisios Vlachos (Chemical Engineering)
Doug Buttrey (Chemical Engineering)
Rohit Vijay (Graduate Student, Chemical Eng.)
Joseph Dellamorte (Grad. Student, Chemical Eng.)
Elizabeth d'Addio (Grad. Student, Chemical Eng.)



Visualization of catalyst activity via spectral images of NH_3 (N-H bend Q branch 1566cm^{-1}) measured by FTIR imaging for a 16 catalyst array for ammonia decomposition at 350, 450, and 550K. The disappearance of ammonia at various temperatures is a measure of catalyst performance.



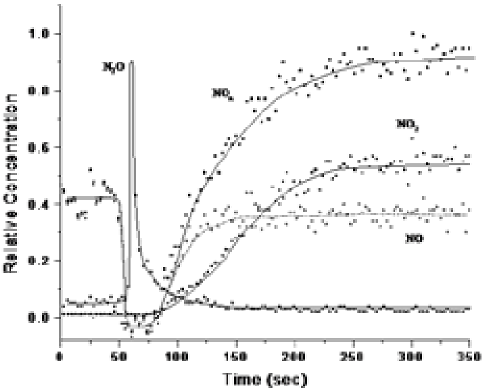
Transient spectra from fuel rich to fuel lean at 623 K for a nitrogen storage and reduction catalyst. The catalyst is 1.3 wt% Pt/ 9.0 wt% Fe/ 30 wt% Ba supported on γ-alumina. It can be seen that when O_2 is introduced to the reactor (t ~ 60 seconds), the CO is completely oxidized to CO_2, the N_2O band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

Non-linear Phenomena in Heterogeneous Catalysis

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

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

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



Relative concentrations for three species, derived from IR spectra

Jochen Lauterbach (Chemical Engineering)
Danny Bilbao (Grad. Student, Chemical Eng.)

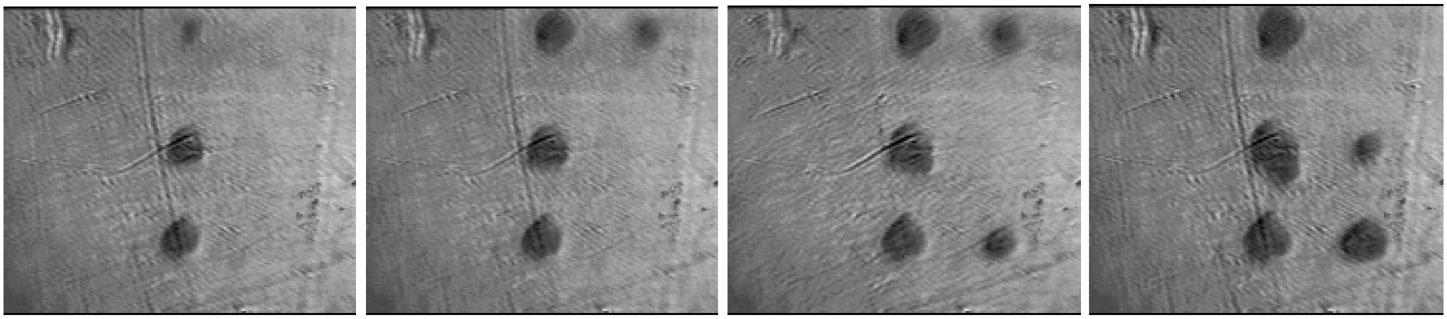
Surface Chemistry of Polymer Nanofilms

A third area of research in our group is the development of defect-free polymer nanofilms with thickness control in the nm range.

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

Jochen Lauterbach (Chemical Engineering)
David Winski (Grad. Student, Chemical Eng.)
Chris Snively (Materials Science & Engineering)

Metastable CO islands grow while surrounded by chemisorbed oxygen on Pt(100) using microdosing. Each island is prepared by locally dosing hydrogen over the surface for ~2s. After the appearance of the CO island, the hydrogen doser is turned off and moved to a different location above the surface. T = 193°C, $P_{O2} = 1x10^{-4}$



Research – Raul F. Lobo

Photocatalysis Using Microporous Silicates
(with Prof. Douglas Doren)

We are investigating photoinduced processes inside the pores of ETS–10, a crystalline microporous semiconductor containing one-dimensional units of TiO_2 octahedra. These semiconducting wires act as photocatalysts and promote intermolecular reactions between adsorbed species. We have approached our investigations by combining experimental measurements and electronic structure computations. This combination has been very fruitful and has allowed us to understand experimental observations in molecular terms at a level of detail that would have been impossible otherwise. Our aims are to develop a methodology for systematically changing electronic structure of a photocatalyst to facilitate electron-hole separation and at the same time, facilitate electron-transfer between reactants and the photocatalyst. Secondly, we aim to discover materials that can use photons in the visible range to promote photodecomposition reactions of volatile organic compounds (VOCs), similar to those that have previously been accomplished with TiO_2 photocatalysts. We have prepared new forms of ETS-10 containing other transition metals (V, Fe, Cr,) with the objectives of reducing the bandgap, increasing the quantum yield, changing the nature of the excited species formed upon irradiation. The interpretation of the experimental results and the selection of specific dopants are tied to concurrent electronic structure calculations by the Doren's group. The models used for our ETS-10 computations are single TiO_2 chains of varying lengths (containing 3-7 Ti atoms) encapsulated in the supporting SiO_2 framework. The 2-layer ONIOM (MM:MO) method has also been utilized to increase the accuracy of our geometry optimizations without greatly increasing the computational cost. The 2-layer ONIOM method allows for a region of interest to be treated with a high level of theory while the remainder of the structure is treated with a much lower level of theory. We have therefore been able to extend our model to include the SiO_2 pores on either side of the TiO_2 chains (Figure 1). Modeling is a proactive part of the research driving, in many instances, the experiments that will be conducted on different samples of ETS-10, and guiding the synthesis efforts of the research.

Raul Lobo (Chemical Engineering)
Michael Nash (Graduate Student, Chemical Engineering)
Anne-Marie Zimmerman (Grad. Student, Chem. & Biochem.)

Growth Mechanisms of Siliceous Zeolite Crystals (with Prof. Dionisios Vlachos)

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

We are investigating the properties and structure of these suspensions of TPA-silica nanoparticles and their relation to the growth of silicalite-1 crystals. We have found there are many similarities between the properties of the TPA-silica nanoparticles and the properties of surfactant self-assembled systems. We are studying the underlying chemical forces that drive the aggregation of the silica and the TPA and the physical basis for the high stability of concentrated suspensions of these nanoparticles. The solution properties can be understood by using the pseudo-phase separation approach coupled to the acid-base chemistry of silanol groups and the Poisson-Boltzmann equation. The silica nanoparticles have a core-shell structure with silica in the core and the organic cations at the shell. Individual particles are observed when the forces between particles are repulsive, as is the case for small cations such as tetramethylammonium or tetrapropylammonium. Extended structures such as M41S materials are formed when the forces are attractive, as is the case for surfactants such as cetyltrimethylammonium. These ideas are useful to understand the evolution of zeolite synthesis gels from nucleation to crystal growth. Although at room temperature the silica and the organic cations are segregated, upon heating the organic cations are embedded within the particles. These silica particles evolve upon heating to resemble some intermediate between an amorphous particle and a zeolite nanoparticle. After heating, these particles may be thought of as proto-nuclei, some of which will evolve into macroscopic crystals of MFI. The TPA-silica system is just a specific case of a broad class of entities formed in aqueous systems containing tetraalkylammonium cations and silica.

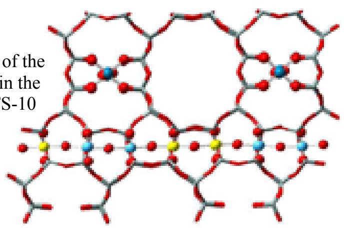


Figure 1: An atomistic view of the TiO_6 wire within the structure of ETS-10

Raul Lobo (Chemical Engineering)
Jeffrey Rimer (Graduate Student, Chemical Engineering)
Dustin Fickel (Graduate Student, Chemical Engineering)

Periodic Models of Amorphous Carbon
(with Prof. Norman Wagner)

We have developed an algorithm to create structural models for amorphous carbons using Monte Carlo simulations in the canonical ensemble. The simulation method used follows the experimental preparation of nanoporous carbons (NPC) by pyrolysis from polyfurfuryl alcohol as a guideline. The resulting structure exhibits properties that compare favorably to those observed experimentally for real NPCs. These atomistic NPC models are approaching a realistic representation of NPCs used for gas separations and, as such, are being used to study the diffusion of small gas molecules in these materials. At this time we are investigating the transport of small molecules through these carbon models.

In Figure 2, we show the evolution of the structure during the simulation from an amorphous, Gaussian polymer backbone folded into a periodic simulation box to a folded linear carbon polymer to a disordered carbon structure with sp^2 coordination. (a) Polymer backbone on a 7•7•7 cubic lattice, (b) starting polymer structure folded into a cubic simulation box and (c) final structure obtained after 4000 MC cycles at T=800°C and $q=1.72g/cm^3$. For clarity, bonds crossing the periodic boundary have not been shown in any of the cases.

Raul Lobo (Chemical Engineering)
Amit Kumar (Graduate Student, Chemical Engineering)

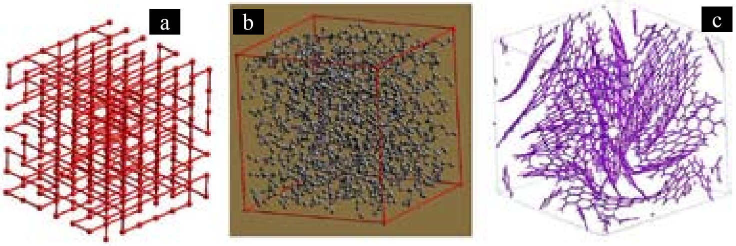


Figure 2: Structural evolution from a Gaussian chain (a) to a linear chain of carbon atoms (b) to a periodic model of amorphous carbon (c)

Iron Nanoparticles Synthesis by Inert Gas Condensation Technique

In addition to the traditional applications of Fe particles as a magnetic material, iron (Fe) particles, particularly the nanosize particles, draw attention as a promising catalyst for various applications as well. The ability of making and breaking carbon-carbon bonds makes Fe very critical for industrially important chemical transformations, production of clean fuels and synthesis of carbon nanotubes (CNT). CNT synthesis may be the most striking example for the use of Fe nanoparticles as a catalyst. Not only the property of decomposing carbon containing gaseous molecules but also the melting temperature, equilibrium vapor pressure, solubility of carbon and carbon diffusion rate in the catalyst make Fe nanoparticles perfect candidate for CNT synthesis. Cheung et al. have reported that Fe nanoparticles with average mean diameters of 3, 9 and 13 nm yielded CNTs with wall diameters of 3, 7 and 12 nm respectively. Other studies have shown the direct correlation between the size of the catalyst: small size catalysts produce single walled CNTs while double wall or multi wall CNTs are obtained with larger size catalysts.

Fe nanoparticles for catalysis applications can be efficiently synthesized by using inert gas condensation (IGC) technique. In this technique, a high purity Fe wire is melted on an Al_2O_3 coated tungsten boat via joule heating and the vaporized Fe is rapidly condensed in nanoparticle form by using a condenser gas that is usually Helium. Fe particles are collected on a cold surface. A schematic of the synthesis system is shown in Figure 1. Particle size and distribution are controlled by evaporation temperature, inert gas (condenser) pressure and particle residence time, which is controlled by the flow rate of the condenser gas. Controlled exposure of the nanopowder to atmospheric conditions results in the formation of thin oxide layer on the particles. Oxide shell size is dependent on the core size as the oxide shell formation stops at a point where the chemical stability is achieved. X-ray diffraction technique is used to determine the structure of the samples. In Figure 2, XRD patterns of two different size Fe/FeO particles synthesized by IGC technique are shown. Fe particles with thick oxide layer manifest oxide peaks in the XRD pattern however FeO formation for small particles is not readily realized. In that case, transmission electron microscopy (TEM) analysis as a complimentary technique to XRD is utilized. High resolution TEM images of the same samples are seen in Figure 3. Core/shell structure formation in both particles is evident.

S. Ismat Shah (Physics and Materials Science)
Abdullah Ceylan (Graduate Student, Physics and Materials Science)

Figure 1: IGC system

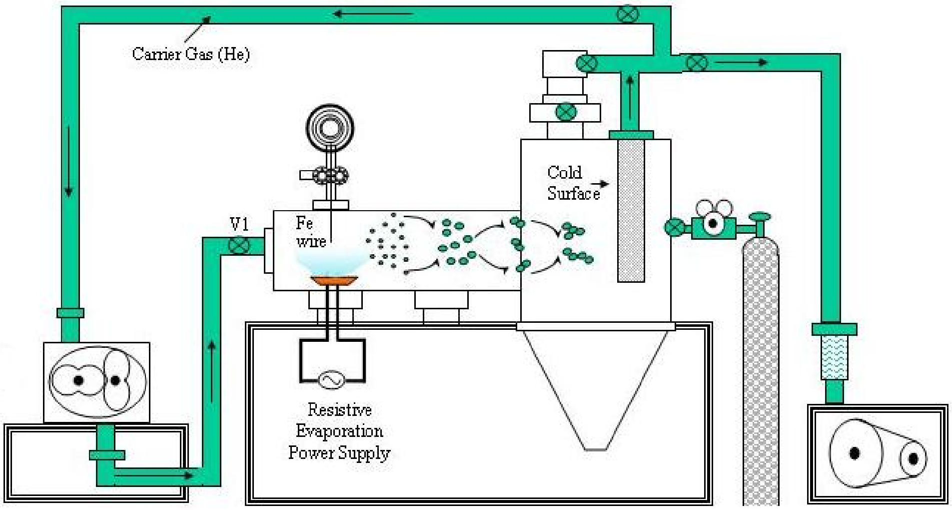


Figure 2: XRD patterns of small and large Fe/FeO particles.

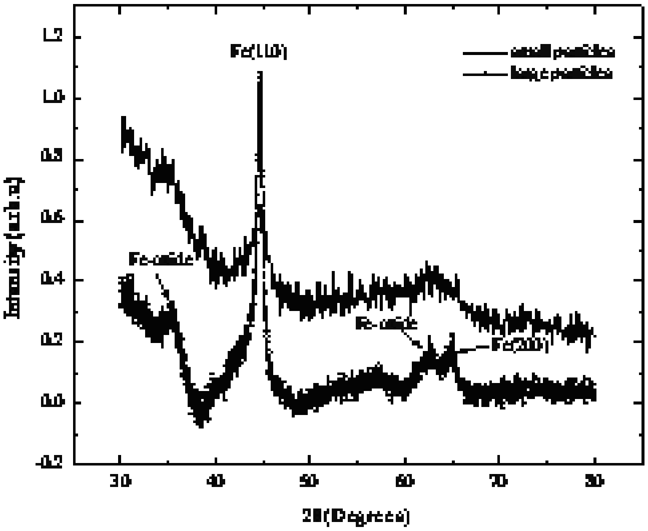
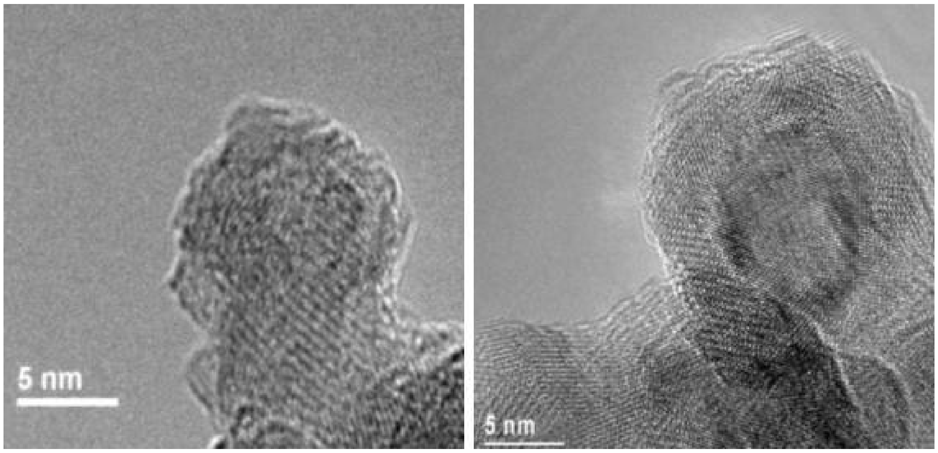


Figure 3: TEM bright field images of different size Fe/FeO core/shell particles

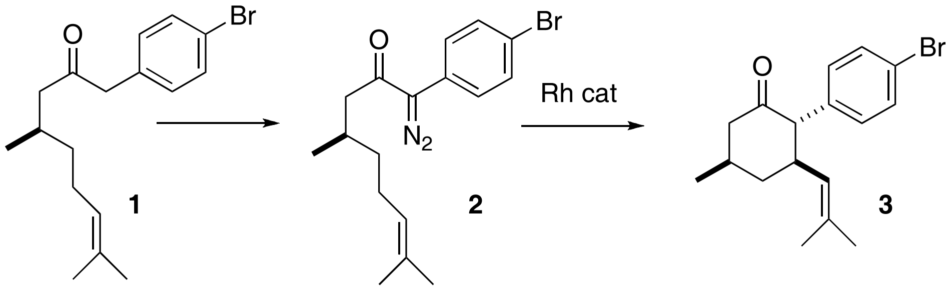


Research – Douglass F. Taber

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

We have found that diazo transfer to an α-aryl ketone **1** proceeds smoothly. The product α-diazo α-aryl ketone **2** cyclizes efficiently under Rh catalysis to the corresponding cyclohexanone **3**. This is the first general route to cyclohexanes using direct intramolecular C-H functionalization.

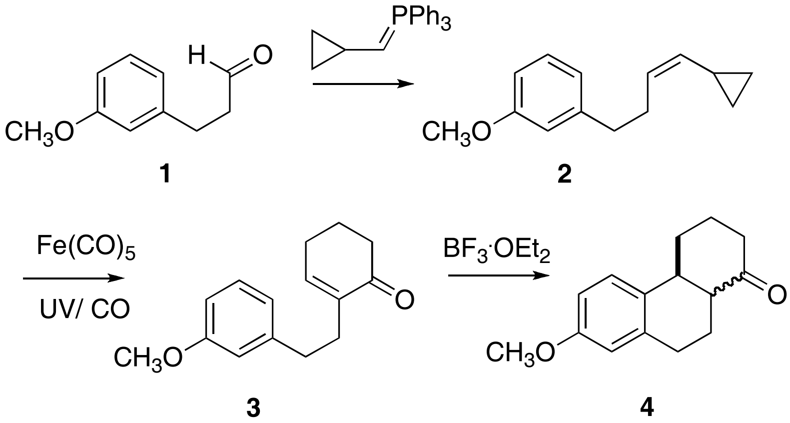
Douglass F. Taber (Chemistry and Biochemistry)
Weiwei Tian (Graduate Student, Chemistry and Biochemistry)



Cyclohexenones from Aldehydes

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

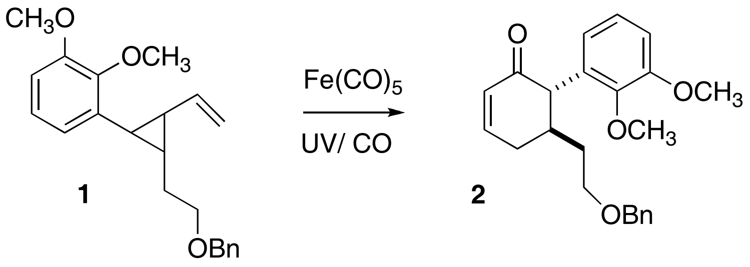
Douglass F. Taber (Chemistry and Biochemistry)
Ritesh Sheth (Graduate Student, Chemistry and Biochemistry)



An Fe Route to 6-Aryl Cyclohexenones

Our previous work with Fe-catalyzed alkenyl cyclopropane cyclocarbonylation was focused on mono- and disubstituted cyclopropanes. We have now found that a pendant arene is activating, so 1 is converted selectively into the 6-aryl-5-alkyl cyclohexenone 2.

Douglass F. Taber (Chemistry and Biochemistry)
David Gerstenhaber (Graduate Student, Chemistry and Biochemistry)



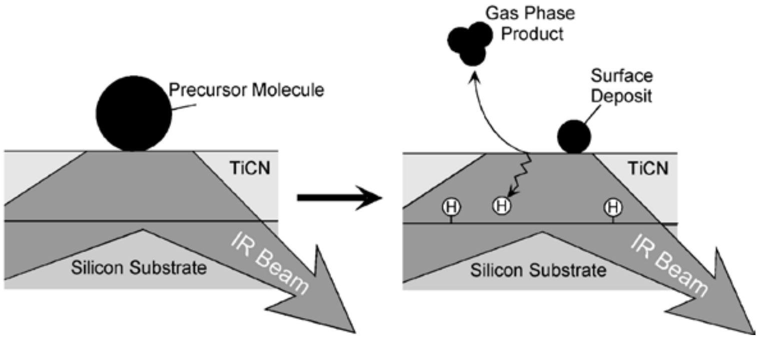
Research – Andrew V. Teplyakov

Our research program focuses on the interdisciplinary area of experimental surface chemistry. The beauty of this discipline is in its links with analytical, organic, and inorganic chemistry. Using the techniques and methods of physical chemistry, my group solves various problems related to surface and interface modification. Our group is using modern experimental analytical techniques together with computational methods to understand these complex processes on a molecular level. Vibrational spectroscopies, high-energy electron spectroscopies, mass spectrometry, and X-ray spectroscopies are used at my laboratory on campus as well as at the National Synchrotron Light Source at Brookhaven National Laboratory, Upton, NY. We plan to continue collaborative projects with theoretical groups in the Department of Chemistry and Biochemistry, and experimental groups in the Departments of Chemical Engineering and Materials Science and Engineering, as well as with industrial companies.

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

The goal of this project is the atomic-level control of deposition and nanostructuring of thin films on silicon substrates. It is also focused on the mechanisms of impurity introduction and distribution in solid films. In semiconductor technology, the direct deposition of metal onto silicon substrates is done very rarely because of relatively easy interdiffusion of these materials and poor adhesion properties. To overcome these problems, barrier materials are normally used. One of the most prominent materials with high thermal stability, good diffusion barrier, and low electrical resistivity is titanium nitride, TiN. Chemical vapor deposition schemes for TiN normally involve such precursor molecules as tetrakis-(dimethylamino)-titanium and the films deposited from this precursor often have a high carbon content. In fact, titanium carbonitride has a set of very attractive properties, making it a good diffusion barrier. The barrier layer in industrial applications is usually deposited on a thin layer of SiO_2.

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

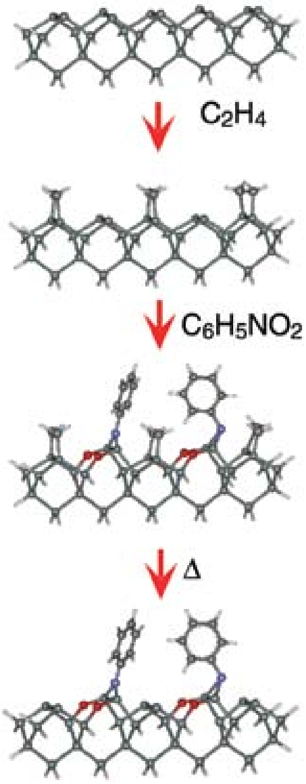


Self-assembly on Si(100) Surface and Molecular Electronics

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

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

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



Research – Klaus H. Theopold

Homogeneous Models for Chromium Polymerization Catalysts

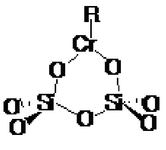
Chromium Alkyls: We are constructing a homogeneous model system for the Phillips catalysts for ethylene polymerization (i.e. inorganic Cr/SiO_2, see A below). To mimic the coordinatively unsaturated chromium on a hard oxide support, we have chosen N, N'-disubstituted diketiminate ligands ["$(R)_2$nacnac", 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-$^iPr_2Ph$). These paramagnetic complexes feature chromium in a range of formal oxidation states (II–V). Structurally characterized cationic Cr(III) alkyls of the general type $[(Ar)_2\text{nacnacCr}(R)(OEt_2)]^+BARF^-$ ($Ar=2,6\text{-}Me_2Ph$, 2,6-$^iPr_2Ph$; R=Me, CH_2SiMe_3) catalyze the polymerization of ethylene and the copolymerization of ethylene with α-olefins in the absence of any cocatalysts.

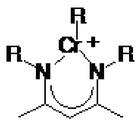
Extraordinarily low polydispersities (M_w/M_n=1.1-1.4) provide evidence for "living" polymerization catalysis, and the polymer microstructure of polyethylene produced with sterically encumbered $[(2,6\text{-}^iPr_2Ph)_2\text{nacanac Cr}(OEt_2)Me]BARF$ shows evidence for "chain walking."

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

Klaus Theopold (Chemistry & Biochemistry)
Abdulmalik BinTaleb (Grad. Student, Chemistry & Biochemistry)
Kevin Kreisel (Grad. Student, Chemistry & Biochemistry)
Mahitha Reddy Peddy (Grad. Student, Chemistry & Biochemistry)
Wesley Monillas (Grad. Student, Chemistry & Biochemistry)



A



B

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

Chromium Dioxygen Complexes: We have prepared a series of chromium(III) superoxide complexes via binding of O_2 to coordinatively unsaturated chromium(II) precursors. These complexes are the first structurally characterized representatives of their kind (i.e. chromium(III) superoxide complexes), and they all adopt the rare 'side-on' binding mode of superoxide that we first discovered in $T^{ptBu.Me}Co(O_2)$.

Dioxygen Activation: Reaction of the dioxygen complexes with their precursors results in splitting of the O-O bond and the formation of reactive chromium(IV) oxo intermediates. Avoiding all hydrogen atom donors in the reaction of $[T^{ptBu.Me}Cr(pz'H)]BARF$ 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.

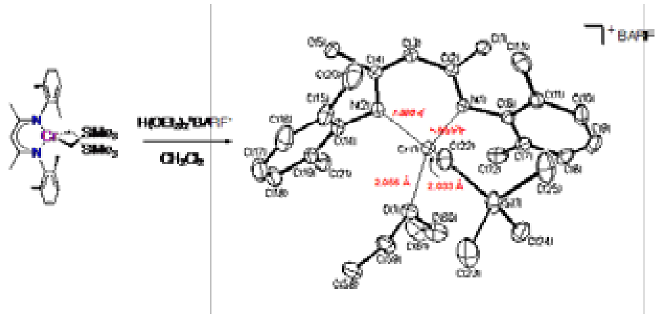
Hydrocarbon Activation: $[Tp^{tBu.Me}Cr(O)(pz'H)]BARF$ reacts with organic molecules containing weak C-H bonds ($D_{C\text{-}H}$ <90 kcal/mol) by hydrogen atom abstraction to yield the chromium(III) hydroxide $[Tp^{tBu.Me}Cr(OH)(pz'H)]BARF$. Activation parameters and isotope effects for several reactions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

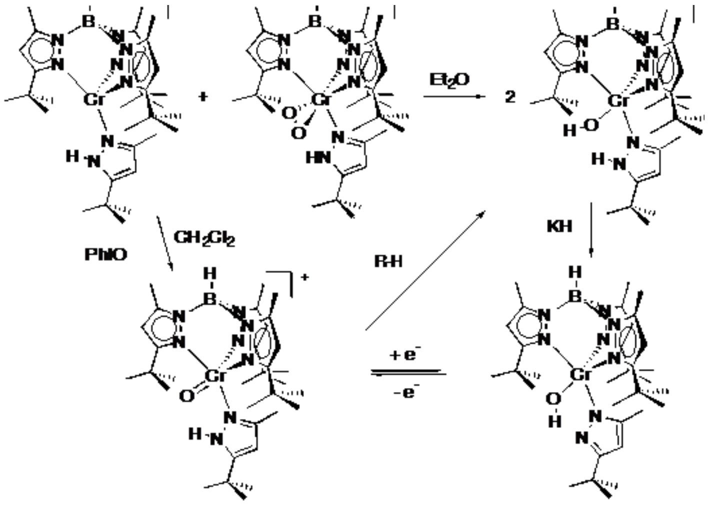
Determination of the temperature dependencies of the H- and D-abstraction reactions revealed large differences (ΔE_0 = 6.7(8) kcal/mol and $A_H/A_D = 2.7 \times 10^{-4}$). These values indicate a significant contribution of quantum mechanical tunneling to the hydrogen atom transfer. H-atom tunneling 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.

Klaus Theopold (Chemistry & Biochemistry)
Soumen Mukherjee (Postdoctoral Fellow, Chemistry & Biochemistry)
Travis Shay (Graduate Student, Chemistry & Biochemistry)
Fernando Jove (Graduate Student, Chemistry & Biochemistry)





Hierarchical Multiscale Microkinetic Model Development

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

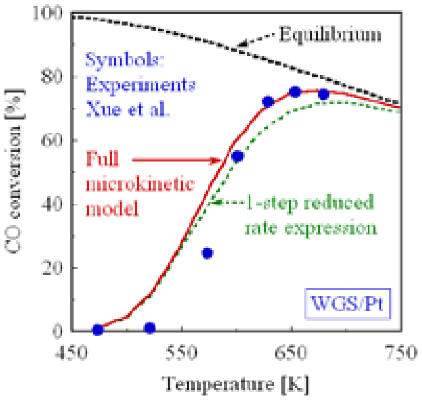


Figure 1: Comparison of a full microkinetic model comprising of 46 reactions, a reduced 1-step rate expression, and the experimental data (Xue et al.) for the water-gas shift (WGS) reaction on Pt. The experimental data is well captured by both models. For additional details, see Mhadeshwar and Vlachos, J. Phys. Chem. B. 108, 15246-15258 (2004) and Mhadeshwar and Vlachos, Cat. Today 105 ,162-172 (2005).

Model-based Design of Experiments and Catalysts

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

DFT-based rational catalyst design, while promising, is far from becoming a reality for complex reaction systems. Furthermore, what initially appears as a very active catalyst may be unsuitable due to reactor scale (e.g., heat/mass transfer, hot spots) effects. Our thesis is that development of a hierarchical multiscale theoretical framework can be invaluable in the course of catalyst design by gathering and extracting kinetic and catalyst information from quantitative experiments and characterization data and integrating it 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.

Reactor Optimization

The design of any chemical system involves tradeoffs, and hence optimizing a process flow sheet is a frequently studied problem. One of the more conceptually straightforward goals is to use the hierarchical multiscale reactor models to determine the optimal reactor network and operating conditions that optimize the objective function. Our works develops such optimization tools. Specifically, we use the superstructure optimization method with reliable microkinetic models to carry out reactor design and optimization. This method can give us optimal temperature, feed, and withdrawal profiles. An example for the water-gas shift (WGS) reaction is shown in Figure 2. An order of magnitude reduction of CO, in comparison to a single reactor, is feasible by reactor optimization (temperature profiling).

Dionisios Vlachos (Chemical Engineering)
Jeffrey Ludwig (Chemical Eng., Graduate Student)
Danielle Hansgen (Chem. Eng., Graduate Student)
Matteo Maestri (Visiting Scholar)
Ayman Karim (Postdoctoral Fellow)
Niket Kaisare (Postdoctoral Fellow)
Vinay Prasad (Visiting Faculty)
E. Tronconi (Polytechnic of Milan)

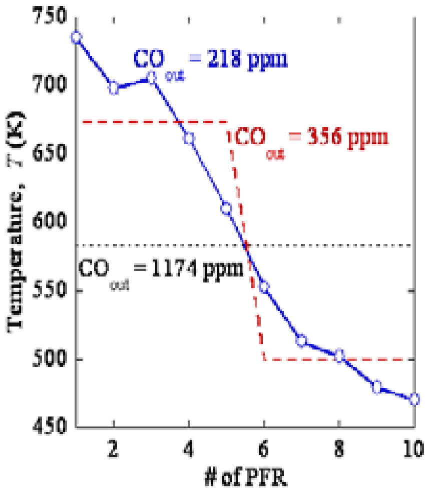


Figure 2: The solid line shows the optimum temperature profile for a reactor network consisting of 10-PFRs in series. The dotted line represents the optimal temperature for one isothermal reactor and the dashed line represents the optimal temperatures of two-stage WGS reactors. In all cases, the total reactor length was 2.0 cm. The fraction of CO at the exit for the three cases is indicated.

High Temperature Microchemical Systems: Microburners and Catalytic Microreactors for Hydrogen Production for Fuel Cells and Portable Power Generation

The rapid advances in microfabrication techniques have made possible the development of microreactors and Power Micro Electro-Mechanical Systems (Power MEMS), such as microburners. High temperature (≥ 1000°C) microchemical systems can exhibit major advantages compared to large scale reactors including higher rates and selectivities for chemical production, higher equilibrium

Research – Dionisios G. Vlachos *(continued)*

constants for endothermic reactions, abatement of pollutants for energy production, and elimination of large-scale plant accidents. However, design of high temperature microchemical systems, including microburners and hydrogen production for fuel cell applications, demands an understanding of fundamentals in these devices.

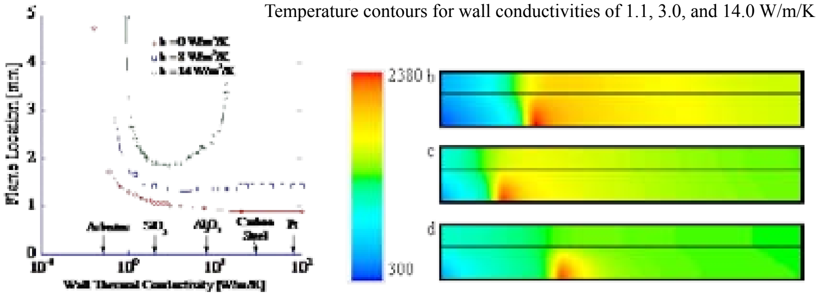
In an attempt to address the inadequacy of continuum scale models, we study oxidation of fuels in microchannels using two-dimensional simulations with detailed gas and surface chemistries, multicomponent transport, and variable properties giving emphasis on interfacial phenomena. Both natural gas microburners and catalytic microreactors are considered for syngas production needed for hydrogen generation for fuel cells. The effects of microchemical system dimensions and operating conditions, such as, preheating of the reactants and flow velocity, are investigated, and the microscale physics are illustrated. For example, we have found that the choice of materials in terms of thermal management is important at these scales, and the classic continuum models should be appropriately modified to explain the aforementioned experimental results. An example is depicted in Figure 3. Quantitative comparison to experiments and guidelines for high temperature microchemical systems design are being developed.

In a parallel effort, we study experimentally and theoretically reactions that lead to hydrogen production for fuel cells from alternative fuels. One of the reactions studied is ammonia decomposition (a good hydrogen storage medium). We develop detailed and reduced reaction mechanisms for this chemistry over various catalysts. An example of the reaction mechanisms developed and the CFD simulations in post-shaped microreactors is depicted in Figure 4. Furthermore, we develop guidelines for fast ignition, optimal structure, thermal management, and optimum operation of microreactors. In addition, we develop design guidelines for multifunctional microreactors to carry out traditionally slow chemistry (e.g., steam reforming) at short contact times for portable and distributed power generation.

We fabricate tunable microreactors with variable surface area, wall conductivity, surface to volume ratio, and no moveable parts for various portable and distributed energy generation applications. These microreactors are coupled with thermoelectric elements to produce electricity in the Watt range.

Dionisios Vlachos (Chemical Engineering)
Niket Kaisare (Postdoctoral Fellow)
George Stefanidis (Postdoctoral Fellow)
Ayman Karim (Postdoctoral Fellow)
Justin Federici (Graduate Student)
Eric Wetzel (Army Research Lab)

Figure 3: Example of CFD simulations in a microburner. a) Flame location versus wall thermal conductivity for three different exterior convective heat loss coefficients. (c)-(d) Temperature contours for wall conductivities of 1.1, 3.0, and 14.0 W/m/K, respectively. Very low or high wall thermal conductivities can lead to blowout or extinction. The parameters are inlet velocity of 0.5 m/s, burner opening of 300 µm, and wall thickness of 200 µm.



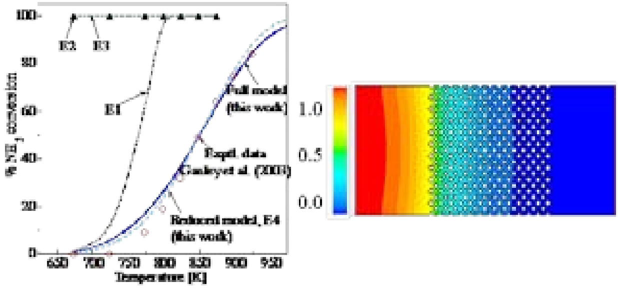


Figure 4:
Conversion of ammonia on Ru post-shaped microreactor vs. temperature (left). The circles are experimental points. The literature mechanisms E1-E3 fail to capture the experiments. Detailed (solid line) and reduced (dashed line) reaction mechanisms we develop do an excellent job in describing the data. (Right) Mass fraction contours of ammonia from CFD simulation in the post microreactor.

Thermodynamic and kinetics of nanozeolitic precursor formation

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 5.

Rational Strategies for Nanomaterials Design

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.

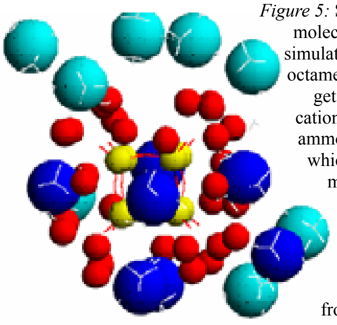


Figure 5: Snapshot from molecular dynamics simulation. The silica octamer in the center gets decorated by cations (tetramethyl ammonium cation), which expel water molecules from the bridged Si-O-Si oxygens protecting nanoparticles from hydrolysis.

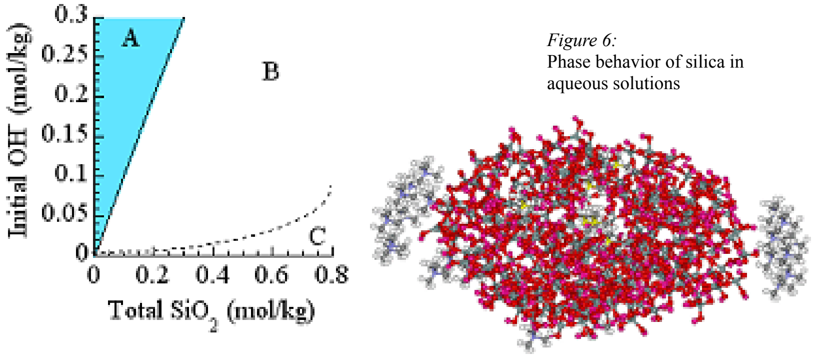


Figure 6:
Phase behavior of silica in aqueous solutions

Silica Phase Behavior

One area of study has been the phase behavior of silica in aqueous solutions. Conductivity and pH measurements display a critical point at a 1:1 molar ratio of SiO_2:[OH-]initial for systems containing both organic structure directing agents (quaternary ammonium cations) and inorganic cations (Na+ and Cs+). Three phases (left of Figure 6) have been discovered with small-angle scattering techniques: a monomer-oligomer phase, a stable suspension of silica nanoparticles, and a gel phase. For the nanoparticle phase, small-angle x-ray and neutron scattering pair distance distribution functions have been modeled using a simulated annealing Monte Carlo algorithm to determine the silica structure as well as the cation amount and location (right of Figure 6). We have found that the particles are ellipsoidal in shape, with cations located primarily on the ends. Simulations also exhibit the presence of internal cations (yellow).

Multiscale Modeling of Diffusion Through Zeolite Particles and Membranes

Molecular modeling has emerged as a powerful tool, providing deep fundamental insight into equilibrium and non-equilibrium dynamics of molecules within complex microporous materials. The current modeling paradigm focuses on host-guest systems characterized by relatively weak adsorbate-adsorbate forces, and on the inter-crystalline diffusion through perfect single-crystal membranes.

Our multiscale approach toward modeling diffusion through zeolite membranes involves:

- Rational, hierarchical parameterization of complex host-guest (e.g., benzene in NaX zeolite) molecular models via a coupled series of mean field models, sensitivity analysis, surface response techniques, and simulated annealing (figure 7).
- Enforcement of thermodynamic consistency in parameterizing molecular models simultaneously with multiple sets and types (e.g., adsorption isotherms and self-diffusivity) of equilibrium experimental data.
- Gradient KMC simulation of molecular diffusion through thin, single crystal and polycrystalline zeolite films with appropriate crystal termination, and dynamic exchange of adsorbate molecules between the membrane surface and adjacent bulk fluid phase (figure 8).
- Development of topology-specific continuum mesoscopic theories via rigorous coarse-graining of the molecular-level description (i.e., master equation). The resulting continuum framework is capable of accessing large length and time scales characteristic of realistic membranes while retaining molecular level detail of adsorbate interactions and diffusion dynamics.

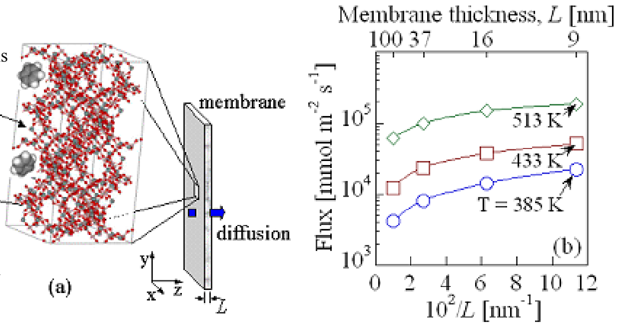


Figure 8: We carry out gradient KMC simulations of a) benzene diffusion through NaX with dynamic boundary conditions at the membrane/fluid interface to predict b) the thickness (L) and temperature-dependent benzene flux through thin microporous membranes.

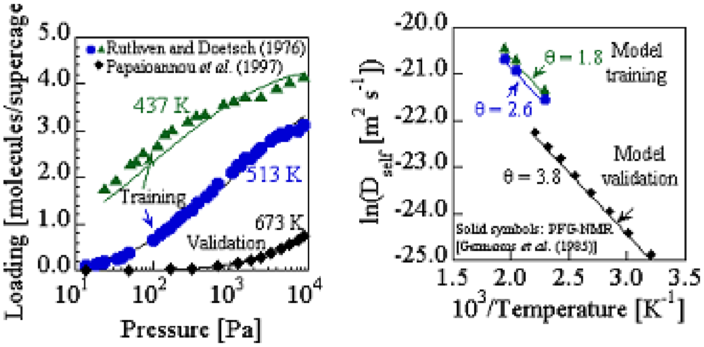


Figure 7: Comparison of equilibrium experiments with predictions of a hierarchically parameterized, complex molecular model of adsorption and diffusion in microporous materials (shown here for benzene in NaX zeolite).

Non-destructive Characterization of Polycrystalline Microporous Thin Films

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 Figure 9. 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.

D. G. Vlachos (Chemical Engineering)
J. Rimer (Graduate Student)
J. Fedeyko (Graduate Student)
S. Caratzoulas (Chemical Engineering)
Y. Bourbakis (Postdoc)
R. Lobo (Chemical Engineering)
M. Tsapatsis (U. Minnesota)

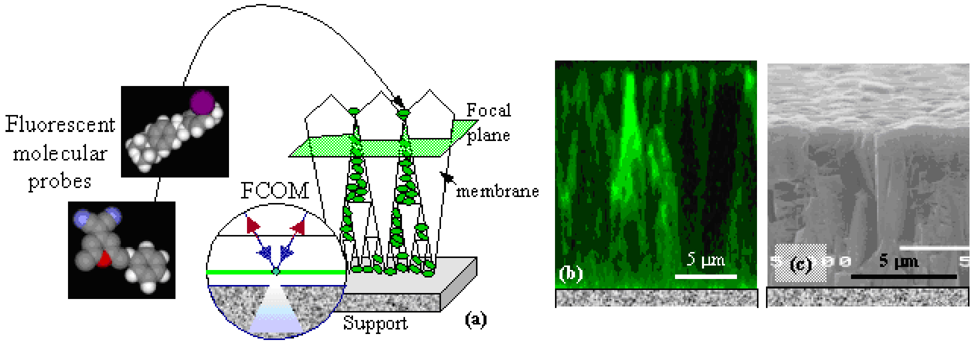


Figure 9: a) Non-destructive fluorescence confocal optical microscopy (FCOM) imaging of zeolite membranes (e.g., silicalite-1, NaX) with fluorescent dyes selectively adsorbed in non-zeolitic pathways, characterizes b) membrane polycrystallinity comparable to that observed via c) SEM. Images shown here are for c-oriented silicalite-1 membranes.

Research – Brian G. Willis

Atomic Layer Deposition for Epitaxial Oxides on Silicon

Nanometer thin metal-oxide layers are being intensely studied for application as alternative gate dielectric materials for nanotransistor devices, with Hafnium oxide being the most promising. In these metal oxide layers, there is a strong link between chemical bonding and the electrical characteristics required for high performance device applications. Defects in the oxide layer and at the metal-oxide/semiconductor interface, as well as thermal stability and compositional uniformity have made this an extremely challenging materials problem. The best results have been obtained using a pre-grown SiO_2 oxide layer, which gives a good electrical interface with the semiconductor substrate. However, the need to scale the overall electrical thickness to an equivalent oxide thickness (relative to SiO_2) of less than 1 nm presents difficulties for using the pre-grown oxides. On the other hand, attempts at oxide growth directly on the semiconductor lead to a rough three dimensional island growth morphology, with poor electrical properties. We have investigated an alternative process chemistry using H_2O terminated Si(100)-2x1 as a model system to understand the surface reactions that govern the chemical bonding and oxide layer properties at the interface. Figure 1 illustrates the ideal chemical bonding where $HfCl_4(g) + OH^* \rightarrow Cl_3Hf\text{-}O^* + HCl(g)$. These experiments have been successful, and a combination of experiments and computational chemistry data show that an abrupt two dimensional metal-oxide/semiconductor layer has been achieved. The results also show that surface coverage is not limited by steric interactions or a lack of reactive sites, but rather, by surface reaction processes that consume multiple sites.

Brian Willis (Chemical Engineering)
Dimitri Skliar (Graduate Student)
Amalia Cuadra (Graduate Student)
Anoop Mathews (Graduate Student, MSEG)

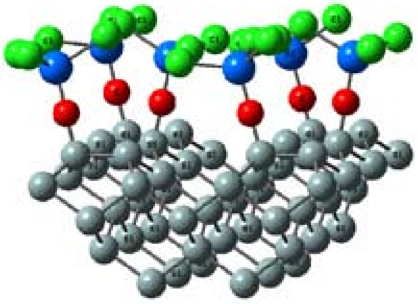


Figure 1: Molecular model showing the idealized surface from a 1:1 reaction of $HfCl_4$ and Si-OH. Hydrogen atoms have been removed for clarity.

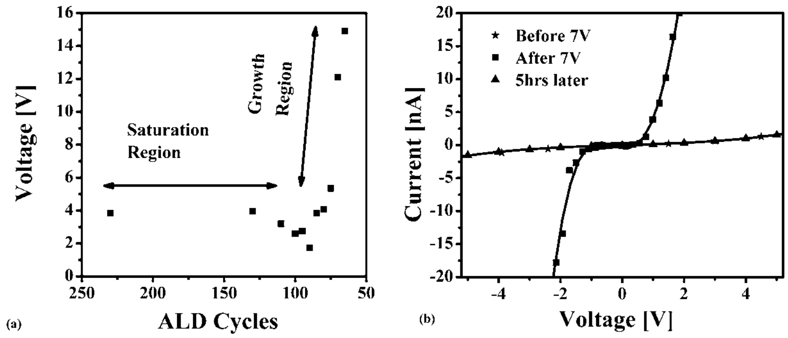


Figure 2. (a) Field emission voltage (at 3 nA) is plotted vs. the number of ALD growth cycles, showing two distinct growth regions, linear growth and saturation. (b) Resistance switching is observed for the application of a large voltage (7 V) to the tunnel junction, which relaxes back to the original configuration after several hours.

Nanofabrication of Molecular Electronic Devices

Molecular electronics is a rapidly growing area of research that seeks to understand charge transport at the single molecule level. Such knowledge may create active nanostructures that extend computing, electronic memory, bio-chemical sensing, or energy harvesting beyond the limits of modern technologies. Although there are many challenges to the realization of practical molecular devices, the area holds great promise due to the richness of molecular properties and the complexity of inorganic, organic, and biological molecules that can be synthesized.

The immense promise of molecular electronics has stimulated much interest in the measurement of electrical charge transport through single molecules. The growing body of data has demonstrated the importance of chemical structure, electrode bonding chemistry, and electrode material on the observed electrical transport characteristics. However, the understanding of electrode atomic structure and molecule-electrode chemical bonding in *metal-molecule-metal* tunnel junctions is lacking, and existing experimental techniques are not readily extended to address this problem. For example, scanning tunneling spectroscopy can probe single molecules, but the tip does not chemically bond to the adsorbed molecule, and experiments are restricted by the vacuum gap. There is a need for new approaches to the study of single molecule junctions that can address the effects of electrode structure on chemical bonding and charge transport at the molecule-electrode interface. Our work presents a novel experimental approach and a methodology to investigate the influence of nanoelectrode atomic structure on the stability and electronic transport properties of single molecule tunnel junctions. We use atomic layer deposition and nanofabrication engineering principles to control the nanoelectrode microstructure and electrical properties for molecular tunnel junction measurements. The devices contain electrodes spaced less than 1 nm apart, which is necessary for probing the electrical transport properties of single molecules. Figure 2 demonstrates two important characteristics of these devices and the fabrication process. On the left, the field emission voltage is plotted vs. the number of atomic layer deposition cycles. Two distinct growth regions are observed: (1) linear growth of ~0.05nm/cycle, and (2) saturation. The linear growth is characteristic of the atomic layer deposition of copper where a sub-monolayer of copper is deposited each cycle. The saturation region shows a plateau of the emission voltage, which indicates the electrode separation is no longer being reduced. This characteristic is important because it demonstrates a natural control mechanism for mass parallel fabrication. The right side demonstrates resistance switching in a tunnel junction from atomic rearrangements at the electrode tips. These rearrangements can be controlled with the application of a voltage pulse to the junction. The devices are targeted for nano-chemical-biological sensors with sensitivity down to the single molecule level.

Brian G. Willis (Chemical Engineering)
Rahul Gupta (Graduate Student)
Irene Hsu (Graduate Student)

Novel Fabrication Methods for Alternative Electrocatalysts

One of the failure mechanisms of PEM fuel cells is loss of catalytic activity from the degradation of the Pt/C interface. Tungsten carbide is an alternative electrocatalyst and/or catalyst support for fuel cell applications with the potential to improve the stability of electrocatalyst formulations. The properties of tungsten carbides, however, are sensitive to the bulk and surface composition, which requires careful control of the preparation procedures. Our research program is investigating chemical vapor deposition (CVD) methods to prepare tungsten carbide materials with controlled properties. CVD is a promising method to control and tune the bulk and surface properties for electrochemical activity, but requires understanding of complex deposition chemistry. We have successfully grown high quality, phase pure hexagonal WC by CVD and investigated the deposition chemistry. These materials are being evaluated for applications in hydrogen and direct methanol fuel cells.

Brian Willis (Chemical Engineering)
Kendra Beadle (Graduate Student)

Colburn Laboratory

The Center for Catalytic Science and Technology was founded at the University of Delaware in 1978. The Center has pioneered multidisciplinary research in the scientific and engineering principles of catalysis. Over the last two decades, the Center has provided research opportunities in all aspects of catalysis to more than 300 students and postdoctoral fellows in the academic departments that it spans (Chemical Engineering, Chemistry & Biochemistry, and Materials Science & Engineering).

The hallmark of the Center's research continues to be its strong connection to industrial practice. These ties have been forged through a number of mechanisms, including the Center's Industrial Sponsors Program, industrially supported grant and contract research, collaborative projects with industrial scientists and engineers, and industrial sabbaticals and exchanges of research personnel. The Center's laboratories, virtually all newly constructed or renovated since 1993, and wide range of research instrumentation represent one of the foremost facilities for catalysis research in academia.

The mission of the Center for Catalytic Science and Technology is the education of students via relevant research in the multidisciplinary field of catalysis science. The "products" of this venture include not only the participating researchers – more than 70% of whom have historically gone on to positions with Center Industrial Sponsors – but also a substantial body of publications in scientific literature, as well as a significant patent portfolio.

www.che.udel.edu/ccst

Center for Catalytic Science & Technology
University of Delaware
150 Academy Street
Newark, DE 19716-3117
Phone: (302) 831-8056
Fax: (302) 831-2085