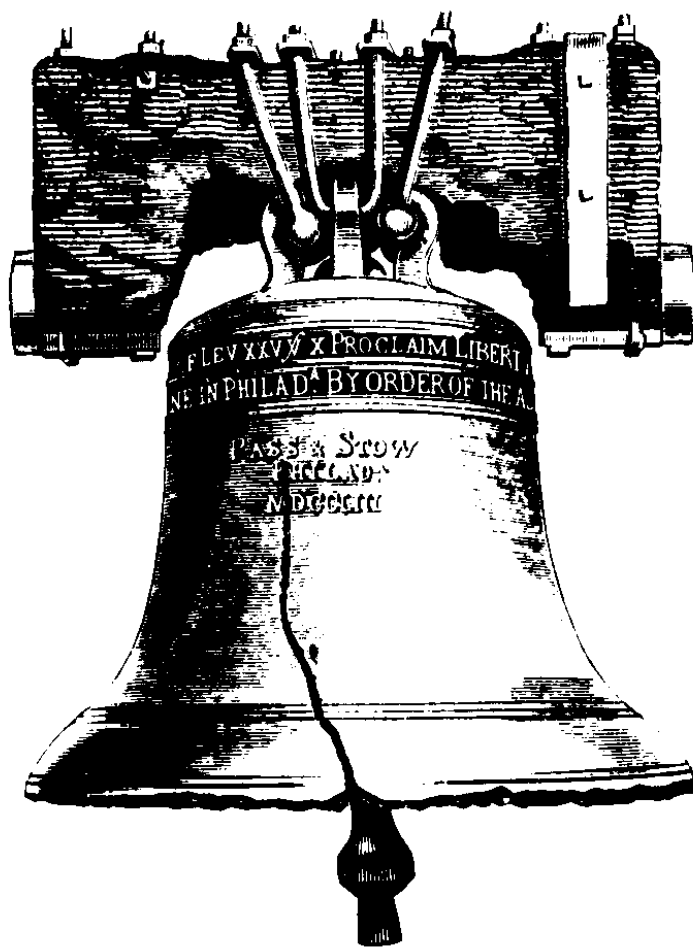


**The Catalysis Club of Philadelphia
2009 Spring Symposium**



Thursday, May 21, 2009

John M. Clayton Hall, University of Delaware

Route 896 North, Newark, DE 19176

The Catalysis Club of Philadelphia

2008-2009 Sponsors

Platinum Sponsors



Gold Sponsors



Silver Sponsors



degussa.



The Catalysis Club of Philadelphia

2009 Spring Symposium

Thursday, May 21, 2009

*John M. Clayton Hall, University of Delaware
Route 896 North, Newark, DE 19716*

8:00 AM	REGISTRATION AND CONTINENTAL BREAKFAST	
8:25	WELCOME	
8:30	Robert Schlögl - Fritz Haber Institute - Max Planck Society	Selectivity in Oxidation Catalysis
9:15	Stu Soled - Exxon-Mobil Research	Reversible and Irreversible Changes in Co Fischer-Tropsch Catalysts During Synthesis
10:00	Michael Smith - Symyx	<i>Platinum Sponsor presentation</i>
10:10	COFFEE BREAK	
10:30	Allen Burton - Chevron	Synthesis Strategies for New Zeolite Catalysts with Diquaternary Ammonium Molecules
11:15	Mike Ward - New York University	Hydrogen-Bonded "Zeolite-like" Frameworks and Functional Materials
12:00	ANNOUNCEMENT OF 2009 CATALYSIS CLUB OF PHILADELPHIA AWARD	
12:05 PM	LUNCH	
1:15	Suljo Linic - University of Michigan	Well-defined, highly uniform metallic nano-structures as selective heterogeneous catalysts, photo-electro-catalysts, and platforms for chemical characterization
2:00	Chris Kiely - Lehigh University	A More Realistic View of Gold Based Catalysts Using Aberration Corrected Analytical Electron Microscopy
2:45	Danielle Hansgen -University of Delaware <i>Winner 2009 Poster Competition</i>	Computational and experimental studies of a Ni/Pt bimetallic catalyst for H ₂ production from ammonia decomposition
3:15	AFTERNOON BREAK	
3:45	Gary Haller - Yale University	Synthesis and Characterization of V-MCM-41 and V-SBA-15 Catalysts for C-1 Hydrocarbon Oxidation
4:30	Jochen Lauterbach - University of Delaware	Chemically sensitive imaging in heterogeneous catalysis – from microscale to macroscale
5:15	CLOSING THANKS	

Selectivity in Oxidation Catalysis

Robert Schlögl

*Fritz-Haber-Institut der Max-Planck-Gesellschaft
Berlin, Germany*

The activation of dioxygen into a selective oxidising species and the requirement of activating C-H bonds lead to conflicting structures of active sites. Material solution of metals and oxide systems will be discussed for the increasingly demanding cases of oxidation of methanol, ethylene and propane.

Speaker Biography: Robert Schlögl studied chemistry and completed his PhD on graphite intercalation compounds at the Ludwig Maximilians University in Munich (1982). After postdoctoral stays at Cambridge and Basle he carried out his habilitation under the supervision of Professor Ertl at Fritz Haber Institute in Berlin (1989). Later he accepted the call for a Full Professorship of Inorganic Chemistry at Frankfurt University. In 1994 he was appointed his current position as Director at the Fritz Haber Institute of the Max Planck Society in Berlin. His research activities range from interfacial reactions of inorganic solids, heterogeneous catalysis, spectroscopy of surfaces during chemical reactions, solid state reactions, acid-base chemistry on surfaces, carbon chemistry, chemistry of oxide systems to cluster chemistry. Specific focus is on the investigation of heterogeneous catalysts based upon inorganic solids with the aim to bridge experimentally the gap between surface science and chemical engineering in the field of oxidation catalysis. He is author of about 500 publications and registered inventor of more than 20 patent families. He is a Fellow of the Royal Society of Chemistry and member of numerous international organizations. His research activities have been recognized with several international awards.

Reversible and Irreversible Changes in Co Fischer-Tropsch Catalysts During Synthesis

Stuart Soled

*Exxon Mobil Research and Engineering Co.,
Annandale, NJ 08801 (USA)*

With the resurgent interest in Fischer-Tropsch catalysis, it is important to understand any catalyst changes that can occur during the synthesis. In this presentation we report on three intrinsic modes of deactivation that have been observed in studies of experimental supported Co catalysts. These include reversible surface oxidation, irreversible mixed metal oxide formation, and cobalt particle growth. Techniques to monitor these changes are presented as well as some hypotheses regarding the mechanisms that are responsible for them.

Speaker Biography: Stu Soled received his Ph.D in chemistry focused primarily on x-ray crystallography from Brown University in 1973. He then did 4 year of post-doctoral work in solid state chemistry both at Brown University and in France, focusing on the synthesis and characterization of novel oxide and sulfide materials. He has been at Exxon's Corporate Research Labs for more than 28 years. His research interests lie in the synthesis, characterization and evaluation of novel catalytic materials. He has worked extensively on Fischer-Tropsch chemistry, solid acid and metal catalysis, and hydrotreating. He is the coauthor of more than 70 publications and 80 U.S. patents. He is credited with the discovery of the Nebula catalyst and has worked on a joint ExxonMobil-Albemarle team to bring it to commercial reality. Nebula has been producing low sulfur diesel fuels in over a dozen refinery units worldwide. He is the recipient of the New York Catalysis Society Excellence in Catalysis Award, the North American Catalysis Society Frank Ciapetta Lectureship Award, the American Chemical Society Northeast Division Industrial Innovation Award and the ACS Heroes in Chemistry Award.

Synthesis Strategies for New Zeolite Catalysts with Diquaternary Ammonium Molecules

Allen Burton

*Chevron Research
Richmond, California*

The zeolite community has recently prepared a number of new zeolite structures by employing diquaternary ammonium molecules as structure directing agents (SDAs). In particular, several novel multidimensional medium-pore zeolites have been discovered that provide interesting comparisons with ZSM-5 in their structural features and catalytic behaviours. I will first discuss how we have used diquaternary pyrrolidinium molecules in fluoride-mediated gels to synthesize new zeolites like SSZ-74, SSZ-75, and SSZ-83. I will emphasize the structural elucidation and properties of SSZ-74, an exceptional zeolite that possesses ordered tetrahedral site vacancies. In the second part of the discussion, I will describe how we have prepared diquaternary ammonium molecules from enamine precursors. One of these SDA is used to prepare the novel zeolite SSZ-82, and several of the molecules are selective for the aluminosilicate and borosilicate versions of the SSZ-26/33 family, which has very few known SDA molecules.

Speaker Biography: Allen Burton received his BS in Chemistry at the University of Maryland at College Park, and his PhD in Chemical Engineering from the University of Delaware under the guidance of Prof. Raul Lobo. It was here Allen discovered his passion for zeolite synthesis, which he continued under the postdoctoral guidance of Prof Mark Davis at CalTech. In 2001, Allen accepted a position in the research group at Chevron's Research facility in Richmond, CA. Despite his admitted ineptitude in the game of golf, on weekends he can sometimes be found at the golf range (swearing at golf balls and throwing his irons).

Architectural Diversity and Elastic Networks in Hydrogen-bonded Host Frameworks: From Molecular Jaws to Cylinders to Capsules

Michael Ward

*New York University - Department of Chemistry
New York, NY*

Guest-free guanidinium organomonosulfonates (GMS) and their inclusion compounds display a variety of lamellar crystalline architectures distinguished by different “up-down” projections of the organomonosulfonate residues on either side of a two-dimensional (2D) hydrogen-bonding network of complementary guanidinium ions (G) and sulfonate moieties (S), the so-called GS sheet. The GS sheets in the inclusion compounds behave as “molecular jaws” in which organomonosulfonate groups projecting from opposing sheets clamp down on the guest molecules, forming ordered interdigitated arrays of the host organic groups and guests. Guest-free and inclusion compounds display a variety of architectures that reveal the structural integrity of two-dimensional GS sheet and the unique ability of these hosts to conform to the steric demands of the organic guests. Certain GMS host-guest combinations prompt formation of tubular inclusion compounds in which the GS sheet curls into cylinders with retention of the 2D GS network. The cylinders assemble into hexagonal arrays through interdigitation of the organosulfonate residues that project from their outer surfaces, crystallizing in high symmetry trigonal or hexagonal space groups. This unique example of network curvature and structural isomerism between lamellar and cylindrical structures, with retention of supramolecular connectivity, is reminiscent of the phase behavior observed in surfactant microstructures and block copolymers. The large number of host-guest combinations explored here permits grouping of the inclusion compound architectures according to the shape of the guests and the relative volumes of the organomonosulfonate groups, enabling more reliable structure prediction for this class of compounds than for molecular crystals in general. More recent results that demonstrate the inclusion of laser dyes with controlled states of aggregation, the introduction of molecular capsules, and unusual high symmetry structures will be described.

Speaker Biography: Michael Ward earned his B.A in Chemistry from William Paterson College of New Jersey in 1977, and PhD in Chemistry from Princeton University in 1981. He currently serves as the Silver Professor and Chair, Department of Chemistry, Director of Molecular Design Institute and Director of Materials Research Science and Engineering Center at New York University, New York City, NY. He is also Editor of *Chemistry of Materials*. His research interests include synthesis of molecular materials and crystal engineering, physical and electronic properties of molecular solids, nucleation and growth of organic and protein crystals, scanning probe microscopy and interfacial phenomena.

Well-defined, highly uniform metallic nano-structures as selective heterogeneous catalysts, photo-electro-catalysts, and platforms for chemical characterization

Suljo Linic

*Department of Chemical Engineering - University of Michigan
Ann Arbor, MI*

1. The central objective of our research effort is to employ combined experimental/theoretical approaches to develop predictive theories of heterogeneous catalysis and to apply these theories to formulate energy-efficient, selective, and stable catalysts. We are motivated by a realization that recent scientific advancements, mainly in the area of molecular science, have potential to bring a revolutionary transformation to the field of discovery in heterogeneous catalysts.

I will present our recent work where we explored potential utilization of highly uniform metallic nano-structured materials as selective heterogeneous catalysts. The advantage of these materials compared to conventional catalytic materials is that their structure can be controlled with almost atomic precision, and that it is possible to synthesize highly homogeneous structures. We demonstrated some of these advantages recently when we showed that well-defined, tailored Ag nano-structures are much more selective in heterogeneous epoxidation of ethylene to form ethylene oxide (EO) ($\text{ethylene} + \frac{1}{2} \text{O}_2 \rightarrow \text{EO}$) than conventional industrial catalysts.

We showed using quantum chemical Density Functional Theory (DFT) calculations, where we studied critical elementary chemical steps that govern the selectivity to EO in the process, that the Ag(100) surface should be inherently more selective than the Ag(111) surface. We note that catalytic particles, synthesized using conventional synthesis procedure and currently used in commercial ethylene epoxidation process, are dominated by the (111) surface. To synthesize Ag nano-structures which are dominated with the Ag(100) faces, we employed a synthesis procedure which uses organic stabilizer molecules to direct the growth of the nano-structure in a particular direction and to control the surface facets that terminate the nano-structure. This synthetic strategy allowed us to synthesize well-defined and highly uniform Ag nano-wires and nano-cubes which are dominated by the (100) facet. Subsequent experiments showed that Ag nano-wires and nano-cube catalysts can achieve selectivity to EO, which is, at differential conversion, by ~ 40 % higher than for conventional Ag catalysts.

We have also recently started exploring these metallic nano-structures as possible platforms for chemical characterization. The features of these nano-structures that are particularly appealing are: (i) the nanostructures are well defined on atomic level, and their surface to volume ratio is fairly high, which makes these structures inherently better suited for the studies of surface chemical processes compared to traditional single crystal model systems, which are while very well defined, characterized by low surface to volume ratio. (ii) we can synthesize the nanostructures with high degree of uniformity in size and shape, which rules out possible effects due to diversity in size and shape, i.e. these, (iii) the nanostructures are effective scatterers of electromagnetic radiation which make them suitable as platforms for a number of chemical characterization techniques including surface enhanced Raman (SERS) or IR spectroscopies. We will demonstrate the utility of the nano-structures for chemical characterization by a way of an example, where we monitored in-situ ethylene epoxidation.

We will also show that the well-defined metallic nano-structures exhibit interesting properties when exposed to UV and visible light. We will show how these characteristics can be used to design novel photo-electro-catalytic materials and processes.

Speaker Biography: Suljo Linc came to the United States from Bosnia under the auspices of a Soros Foundation Fellowship, here he received a BS degree in Physics from West Chester University (1998) , and a PhD in Chemical Engineering under Professor Mark Barteau (2003) where he investigated the theoretical and experimental aspects of alkene partial oxidation on silver. He accepted a postdoctoral position in Matthias Scheffler's Theory Group at the Fritz Haber Institute of the Max Planck Society in Berlin, and in 2004 took a position in the Department of Chemical Engineering at the University of Michigan. Suljo has received a number of awards, including NSF Career Award in 2006, and Young Scientist Prize from the Council of the International Association of Catalysis Societies, Paris, France, July 2004. Suljo's research interests include fuel cells, chiral synthesis, carbon catalysis, catalysis at nano-scales, and the fundamentals of surface activity and selectivity.

A More Realistic View of Gold Based Catalysts Using Aberration Corrected Analytical Electron Microscopy

Dr Christopher J. Kiely

*Center for Advanced Materials and Nanotechnology, Lehigh University
Bethlehem, PA*

Supported gold clusters and gold-palladium nanoparticles are intensely studied materials primarily because of their exciting potential applications in catalysis. The recent availability of aberration corrected analytical electron microscopes is revolutionizing our ability to characterize the morphology, crystallography and chemical composition of such nanoscopic volumes of materials and for the first time are giving us more realistic views of these catalyst systems. To illustrate the superior imaging performance of this new generation of electron microscopes, we will present a high angle annular dark field (HAADF) imaging study of a systematic set of gold on iron oxide CO oxidation catalysts, ranging from those with little or no activity, to others with very high activities. Using this approach, combined with XPS analysis, we will unambiguously demonstrate that the high catalytic activity for CO oxidation derives from the presence of bi-layer clusters which are ~0.5 nm in diameter. We will also demonstrate that core-shell structures in sub-5nm Au+Pd, Pd@Au and Au@Pd bimetallic nanoparticles can be directly visualized using the z-contrast sensitivity of the HAADF imaging technique. To illustrate the chemical analysis capabilities of aberration corrected analytical microscopes, we will describe the potential advantages of combining X-ray Energy Dispersive Spectroscopy (XEDS) spectrum imaging with multivariate statistical analysis (MSA) techniques. Through several case studies of the Au-Pd bimetallic catalyst systems, we will demonstrate that STEM-XEDS can provide invaluable high spatial resolution compositional information on (i) alloy homogeneity and phase segregation effects within individual nanoparticles, (ii) particle size - alloy composition correlations, and (iii) alloy composition changes that can occur as these catalysts are used.

Speaker Biography: Chris Kiely obtained his BSc in Chemical Physics (1983) and PhD in Microstructural Physics (1986) from Bristol University. From 1986-89 he was a visiting postdoctoral research associate in the Materials Research Laboratory at the University of Illinois at Urbana-Champaign. He joined the Materials Science and Engineering Department at Liverpool University as a Lecturer in 1989, where he worked his way through the ranks until eventually being awarded a Personal Chair in Materials Chemistry in 1999. Kiely joined Lehigh University (Pennsylvania, USA) as Professor of Materials Science and Engineering in 2002. He is currently the Director of the Center of the Nanocharacterization Laboratory at Lehigh University, which houses an array of twelve electron microscopes, including two aberration corrected instruments. He also serves as the Director of the Lehigh Microscopy Schools. His research expertise lies in the application and development of transmission electron microscopy techniques for the study of nanoscale features in materials. His areas of interest include catalyst materials, nanoparticle self-assembly, carbonaceous materials, and heteroepitaxial interface structures. He is also involved in microscopy technique development, and his current interests include X-Ray Ultramicroscopy (XuM) and aberration corrected Analytical Electron Microscopy (AEM).

Computational and experimental studies of a Ni/Pt bimetallic catalyst for H₂ production from ammonia decomposition

Danielle A. Hansgen

*Department of Chemical Engineering - University of Delaware
Newark, DE*

The ammonia decomposition reaction has recently received increased attention due to the possibility of ammonia being used as a hydrogen storage medium in a possible hydrogen economy. We have explored this decomposition reaction through multiscale microkinetic modeling for a number of transition metal catalysts, including Cu, Pt, Ir, Ru, Pd, Rh, Co, Ni, Fe, W, and Mo, to better understand the reaction mechanism. An understanding of the reaction mechanism and electronic properties of these metals has given insight into how to tailor catalysts to improve catalytic activity for this reaction.

The mechanism consists of 12 elementary reaction steps and 5 surface species, namely N, H, NH, NH₂, and NH₃. For many of the metals, a large portion of the surface is covered by adsorbates. For these metals, repulsive adsorbate-adsorbate interactions were expected to change the binding energies of the surface species, thereby changing the elementary reaction activation barriers and modifying the catalytic activity [1]. Coverage dependant atomic heats of chemisorption were calculated through DFT using the Vienna Ab-initio Simulation Package (VASP) for the various transition metal catalysts. Coverage dependant molecular binding energies were calculated using a method based on scaling relationships published by Abild-Pederson et al. [2] and activation barriers were calculated through the bond-order conservation (BOC) method [3].

Inclusion of the interaction parameters to the models resulted in reduced nitrogen coverages and a peak shift in the volcano curve. The conversions were plotted against the characteristic nitrogen heat of chemisorption for each metal, which was found to be an adequate descriptor for this reaction. The volcano curve of the conversions calculated through the microkinetic models are in good agreement with experimental data of single metal catalysts by Ganley and coworkers [4]. The maximum activity was found at a nitrogen heat of chemisorption of approximately 130 kcal/mol.

A DFT study of nitrogen binding energies on Pt-3d bimetallic surfaces showed a binding energy of 131 kcal/mol on the Ni-Pt-Pt surface, indicating that it could be a potentially active catalyst; therefore surface science experiments were performed to assess the microkinetic model and DFT results. The Ni-Pt-Pt surface was found to be more active at decomposing ammonia at low temperatures and desorbed nitrogen at lower temperatures than a Ru(0001) surface [5], currently the most active single metal catalyst.

Speaker Biography: Danielle Hansgen received her Bachelor's degree in chemical engineering in 2005 from the University of Washington. She is currently a third year, PhD candidate in chemical engineering at the University of Delaware. She is advised by Dr. Dion G. Vlachos and Dr. Jingguang G. Chen and is working on the rational design of catalysts for the ammonia decomposition reaction.

Synthesis and Characterization of V-MCM-41 and V-SBA-15 Catalysts for C-1 Hydrocarbon Oxidation

Gary Haller

*Yale University - Department of Chemistry
New Haven, CT*

Mobil composition of material No. 41 (MCM-41) was disclosed in 1992 and shortly after a research project was initiated at Yale to use these materials to demonstrate a radius of curvature effect on catalytic activity. The “radius of curvature” effect implies a change in the solid surface tension of the pore wall as the pore diameter (curvature) is changed that is expected to change the activity/selectivity of an isolated catalytic site on the pore wall of the support. An isolated site can be formed by isomorphous substitution (during synthesis) of some Si cations by V cations in the MCM-41 silica matrix. Several labs have reported that isolated V sites on a silica support are preferable to dimers, oligomers or polymers of vanadia on a silica support for the oxidation of methanol to formaldehyde. MCM-41 might have an advantage relative to other silicas because of its very high surface area, >1000 m²/g. Both the air oxidation of methanol and methane to formaldehyde have been used as probe reactions for catalytic characterization of V-MCM-41. SBA-15 has a similar structure to MCM-41, but larger pores and thicker walls. Isomorphous substitution of V during synthesis is not practical, but well dispersed V can be prepared post-synthesis by grafting (reaction with surface hydroxyls). The activity for methanol oxidation on V-MCM-41 and V-SBA-15 will be compared and discussed.

Speaker Biography: Gary L. Haller is the Henry Prentiss Becton Professor of Engineering and Applied Science at Yale University with joint appointments in the Departments of Chemical Engineering and Chemistry. Professor Haller received a B.S. in mathematics and chemistry from the University of Nebraska at Kearney in 1962 and a Ph.D. in physical chemistry from Northwestern University in 1966. Following a NATO Post-doctoral Fellowship at Oxford University, he joined the faculty of Yale where he has held a variety of administrative posts that include Chair of the Department of Chemical Engineering, Chair of the Council of Engineering, and Deputy Provost for Physical Sciences and Engineering. He was Master of Jonathan Edwards College, one of twelve residential colleges that comprise Yale College 1997-2008.

Professor Haller’s research involved the molecular understanding of heterogeneous catalysts. His research combines the inorganic chemistry of catalyst synthesis, physical chemistry of spectroscopic characterization of heterogeneous catalysts, and the kinetics and mechanism of simple organic reactions. Current research is focused on catalysts for the synthesis of single walled carbon nanotubes and the application of these carbon nanotubes as supports for novel catalytic reactions such as aqueous phase reforming (a route to renewable energy sources).

Chemically sensitive imaging in heterogeneous catalysis – from microscale to macroscale

Jochen Lauterbach

*Department of Chemical Engineering - University of Delaware
Newark, DE*

We have been using high-throughput (HT) approaches based on rapid-scan FTIR hyperspectral imaging in the mid-infrared to screen catalyst formulations for the discovery and optimization of new and improved materials. In combination with HT methods, we also employ a variety of more traditional spectroscopic methods to understand the underlying fundamental science. Two examples will be used to illustrate this research approach: de-NO_x for automotive exhaust after-treatment and ammonia decomposition catalysts for CO free hydrogen generation. While HT screening is a macroscopic analysis technique, we are also interested in observing non-linear phenomena on working catalysts in situ on the microscale using spectroscopic imaging based on ellipsometry. The collective, global behaviour of a catalytic system depends on the effective communication of local reactivity variations to distant points in the system. One mode of communication occurs via partial pressure fluctuations in the gas-phase above the catalytically active surface. This gas-phase coupling mode is considered to be most effective under vacuum conditions, where the mean free path between molecular collisions is large. We take advantage of a spatially distributed system of isolated chemical oscillators to investigate the details of gas-phase communication in the 10⁻³ Torr range. Characterization of local gas-phase variations, in conjunction with local kinetic activity on the surface, shows that surface/gas-phase interaction might differ from the conventional assumption of a gradient free, molecular flow environment near the surface. This analysis provides a quantitative estimate of the effective gas-phase coupling length in a heterogeneous system. This coupling length was found to be in agreement with surface imaging results which qualitatively showed coupling between oscillators.

Speaker Biography: Jochen Lauterbach received his Diploma in Physics at the University of Bayreuth, Germany under Prof. J. Küppers and his Doctorate in Physical Chemistry at the Fritz-Haber Institute of the Max-Planck-Society, Berlin, Germany under Professor G. Ertl. He came to the US in 1994 with a Feodor-Lynen-Fellowship of the Alexander von Humboldt-Foundation and performed his post-doctoral work at the University of California at Santa Barbara under Prof. W.H. Weinberg. He joined the faculty at Purdue in 1996 and, in 2002, moved to the University of Delaware, where he currently is a Professor in the Chemical Engineering Department. His research interests include the design of catalytic materials using high-throughput screening methodologies and in situ spectroscopic techniques, development of catalyst synthesis methodologies based on microemulsions, nano-engineered polymer films from renewable feedstock, and non-linear dynamics of chemical reactions, in particular external spatiotemporal forcing. Professor Lauterbach has published close to 100 papers/book chapters and has given over 150 invited presentations.