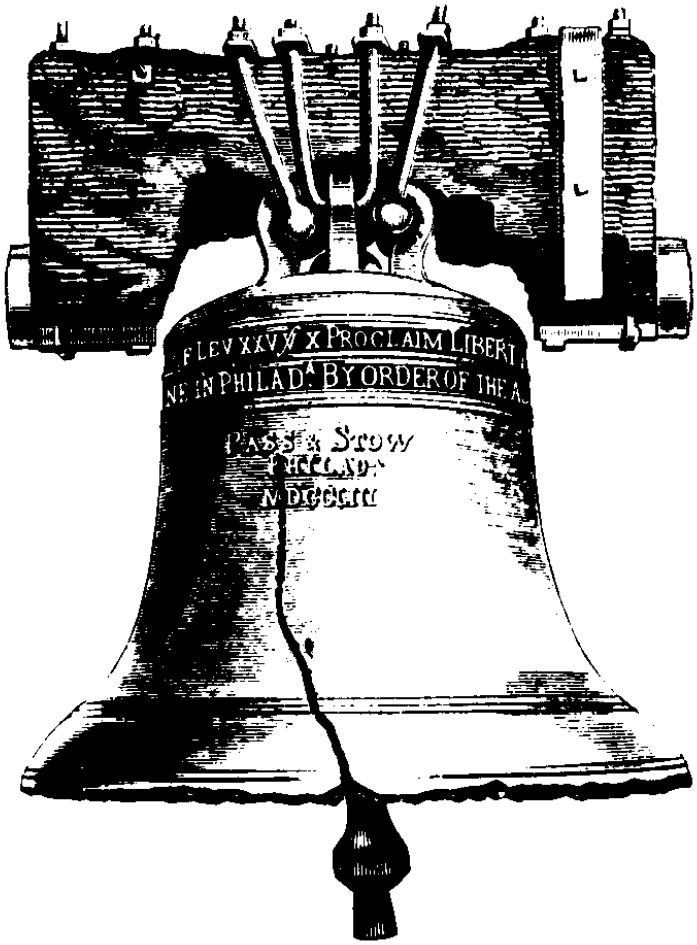
The Catalysis Club of Philadelphia

2013 Spring Symposium



Thursday, May 9, 2013

DoubleTree Hotel

4727 Concord Pike, Wilmington, DE 19803

The Catalysis Club of Philadelphia

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Program

8:00am	Registration and Continental Breakfast
8:55am	Opening Remarks
9:00am	**Charles H.F. Peden**, Pacific Northwest National Laboratory "New Insights into the Synthesis of Methanol on Copper"
9:50am	**Jeffrey Greeley**, Purdue University "A First Principles View of Reactivity Trends in Heterogeneous Catalysis and Electrocatalysis"
10:40am	Coffee Break
11:00am	**Michael A. Smith**, Villanova University "Supported Catalysts: Does Surface Roughness Matter? A Case Study With VO_x-SBA-15"
11:50pm	**Thomas R. Gordon**, University of Pennsylvania (CCP student poster winner) "Nonaqueous Strategies to Manipulate the Morphology, Phase, and Photocatalytic Activity of Monodisperse TiO_2 Nanocrystals"
12:10pm	Lunch Buffet
1:10pm	**Thomas F. Degnan, Jr.**, ExxonMobil (2012 Ciapetta Award Lecture) "Catalysis in a Pocket: The MCM-22 Story"
2:10pm	**Dongxia Liu**, University of Maryland – College Park "Catalytic Characterization of Hierarchical Meso-/microporous Lamellar Zeolite Catalysts"
3:00pm	Announcement of 2013 Catalysis Club of Philadelphia Award Winner
3:05pm	Coffee Break
3:20pm	**Michael T. Klein**, University of Delaware "Software Tools for the Construction of Detailed Kinetic Models"
4:10pm	**Andrew M. Rappe**, University of Pennsylvania "Polar substrates and nonstoichiometric surfaces: new routes to active and controllable heterogeneous catalysts"
5:00pm	Closing Remarks

New Insights into the Synthesis of Methanol on Copper

Charles H.F. Peden[1], Charles A. Mims[2], Yong Yang[1,3], Donghai Mei[1], Charles T. Campbell[3]

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[2] *Department of Chemical Engineering and Applied Chemistry University of Toronto, Toronto ON M5S3E5 Canada*

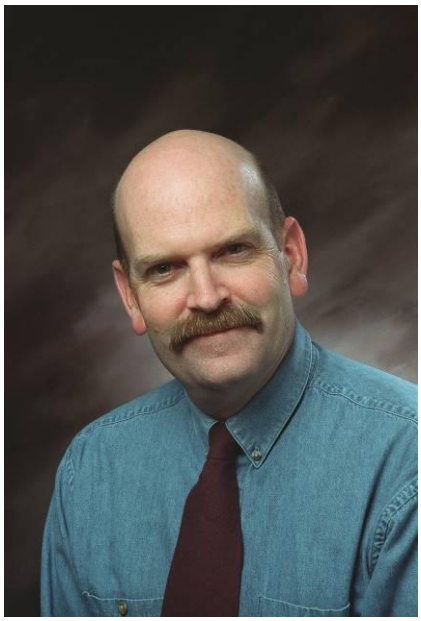
[3] *Department of Chemistry University of Washington, Seattle WA 98195 USA*

Abstract: The mechanism of methanol synthesis on copper-based catalysts has been extensively studied and remains a target of research because of the significance of this reaction in the chemical industry and methanol's potential as a liquid energy/hydrogen carrier. A recent DFT and microkinetic modeling study by Grabow and Mavrikakis [1] contains a thorough review of the current state of our understanding of this reaction. These recent models allow for conversion of both CO (by direct hydrogenation) and CO_2 (via formate intermediates) to methanol. Although tracer experiments have shown that CO_2 is the preferred reactant over CO in H_2:CO:CO_2 mixtures under commercial conditions, the relative importance of these channels under various conditions is still uncertain [1]. Furthermore, the role of water in the reaction mechanism has received little attention, despite long established effects of water and CO_2 in the conversions of syngas [2]. Our recent DFT study has pointed out that water can have significant effects in methanol synthesis and that a separate methanol formation mechanism via a carboxyl intermediate is energetically possible [3]. In this presentation, we describe particularly strong effects of water on the conversion of both CO and CO_2 at temperatures below those of commercial practice, and support for an intermediate common to both CO and CO_2 [4].

References

1. Grabow, LC; Mavrikakis, M *ACS Catal*. **1** (2011) 365.
2. Parameswaran, VR; Lee, S; Wender; I *Fuel Science Techn. Intl*. **7** (1989) 899.
3. Zhao, Y-F; Yang, Y; Mims, CA.; Peden, CHF; Li, J; Mei, D *J. Catal.* **281** (2011) 199.
4. Yang, Y; Mims, CA.; Mei, DH; Peden, CHF; Campbell, CT *J. Catal.* **298** (2012) 10.

Biography of Dr. Charles H.F. Peden



Chuck Peden is Associate Director of the Institute for Integrated Catalysis at Pacific Northwest National Laboratory (PNNL). He is also a Laboratory Fellow, and manages and participates in multiple technical projects within the Physical Sciences Division at PNNL. He joined PNNL in 1992 following a nine-year tenure at Sandia National Laboratories in Albuquerque, New Mexico, as a Senior Member of the technical Staff in the Inorganic Materials Chemistry Department. Peden's main research interests are in the surface and interfacial chemistry of inorganic solids; in particular, the heterogeneous catalytic chemistry of metals and oxides with an emphasis on reaction mechanisms and materials structure/function relationships. He is best known as a leader in the development of the mechanisms of automobile exhaust catalytic reactions. After graduating with distinction from California State University, Chico with a B.S. in chemistry, Peden completed his Ph.D. in physical chemistry at the University of California, Santa Barbara under the direction of Ralph G. Pearson. He then spent two years as a postdoctoral associate with D. Wayne Goodman at Sandia National Laboratories in Albuquerque, New Mexico before joining the scientific staff there. Peden has written or contributed to more than 235 peer-reviewed publications (H-factor > 40) and 3 issued U.S. patents on topics such as automobile exhaust catalysis, hydrocarbon reforming on bimetallic catalysts, the structure of hydroprocessing catalysts, the synthesis and characterization of novel supported solid acid catalysts, and the structure and chemistry of oxide surfaces. He is a member of the American Chemical Society, the American Institute of Chemical Engineers, the Society of Automotive Engineers, and the North American Catalysis Society. Peden was elected a Fellow of the American Vacuum Society in 2000, and the American Association for the Advancement of Science in 2009 and the American Chemical Society in 2012. He currently serves as Past-Chair of the ACS Catalysis Science and Technology (CATL) Division.

A First Principles View of Reactivity Trends in Heterogeneous Catalysis and Electrocatalysis

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Abstract: Heterogeneous catalysis and electrocatalysis have, in recent years, contributed significantly to the development of renewable and energy-efficient technologies, ranging from the production of biorenewable fuels to the efficient generation of electricity in fuel cells. Computational techniques, based primarily on Density Functional Theory (DFT) calculations, have, at the same time, played an increasingly important role in scientific and engineering studies of these catalytic processes. These techniques have permitted the elucidation of fundamental catalytic reaction mechanisms and, in some cases, have contributed to the computational design of new catalysts.

In this talk, I will describe some recent developments in the use of DFT-based analyses to describe trends in the science and engineering of interfacial catalysis. Drawing on examples in both heterogeneous catalysis and electrocatalysis, I will outline some simple strategies for computational analysis of complex catalytic reaction networks and will show how, by taking advantage of fundamental correlations between the thermodynamics and kinetics of the relevant reacting species, it is often possible to describe reactivity trends in terms of simple volcano plots. I will demonstrate the application of these trends-based analyses to traditional concepts of catalytic activity and will further illustrate how important questions of catalyst selectivity and electrochemical corrosion may further be addressed. Next, I will describe how it is now becoming possible, using novel extensions of bond order conservation theories, to understand and describe trends in complex biocatalytic reaction networks that have previously been beyond the reach of electronic structure calculations. I will close with a discussion of a novel heterogeneous catalytic and electrocatalytic materials, including bifunctional materials, to which these techniques may be applied in the future.

Biography of Professor Jeffrey Greeley

Dr. Jeffrey Greeley obtained his PhD from the University of Wisconsin-Madison in 2004. He then postdoc'd with Jens Nørskov at the Technical University of Denmark and developed methods to rapidly screen transition metal alloys for promising catalytic properties. From 2007 to 2013, he was a staff scientist at Argonne's Center for Nanoscale Materials where he developed a research program in computational nanocatalysis and electrochemistry. In 2013, he joined the Department of Chemical Engineering at Purdue University as an associate professor.

Supported Catalysts: Does Surface Roughness Matter?

A Case Study With VO_x-SBA-15

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Abstract: SBA-15 is a template-synthesized mesoporous silicate that has found extensive use as a model support for studies of supported catalysis.[1, 2] Thorough structural analyses clearly describe the dual micropore-mesopore structure with a broad distribution of micropore sizes.[3] Silicas such as SBA-15 have long been considered a relatively inert support, quite in contrast to other oxides such as titania or ceria. We find the effect of surface roughness of SBA-15 has an underappreciated effect on catalyst performance. Specifically, samples of VO_x-SBA-15 where the support surface roughness was systematically varied were charaterized using UV-vis and Raman spectroscopy, then tested in the catalytic partial oxidation of methanol to formaldehyde, and propane to propene. Results show that supports with smoother surfaces permit the development of more polymeric vanadia species at the same surface density loading. Such smoother-surface catalysts result in a lower selectivity of methanol to formadehyde, yet conversely show a higher selectivity of propane to propene. This result is significant with respect to our understanding the role of vanadium in in partial oxidation catalysts, and illustrates the importance of considering differences in support surface morphology in analyzing catalytic behavior.

References

[1] V. Dufaud, M. E. Davis, J. Am. Chem. Soc. 125 (2003) 9403-9413.
[2] R. K. Zeidan, S. J. Hwang, M. E. Davis, Angew. Chem.-Int. Edit. 45 (2006) 6332-6335.
[3] M. Kruk, M. Jaroniec, R. Ryoo, J. M. Kim, Chem. Mat. 11 (1999) 2568-2572.

Biography of Professor Michael A. Smith

Professor Michael A. Smith is currently an Assistant Professor in the Department of Chemical Engineering at Villanova University. He received his BS in Chemical Engineering from Lafayette College in 1980, then worked in a variety of assignments with the DuPont Company for 17 years. Dr. Smith returned to school to obtain a Masters at Villanova University, and obtained his PhD in Chemical Engineering from the University of Delaware in 2004 working with Prof Raul Lobo. Since he has work as a research scientist for an SBIR startup, and has been at Villanova since 2006, first as a Visiting Assistant Professor, then in a tenure track position since 2008. Dr Smith's research interests include the synthesis and characterization of nanostructured materials made using colloidal self-assembly and sol-gel techniques, and heterogeneous catalysis with an emphasis on catalysis by metal oxides.

Nonaqueous Strategies to Manipulate the Morphology, Phase, and Photocatalytic Activity of Monodisperse TiO_2 Nanocrystals

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Abstract: Control over faceting in nanocrystals (NCs) is pivotal for many applications, but most notably when investigating catalytic reactions which occur on the surfaces of nanostructures. Titanium dioxide (TiO_2) is one of the most studied photocatalysts, but the dependence of its activity on morphology and phase has not yet been satisfactorily investigated, due to a lack of appropriate models. We report the nonaqueous surfactant-assisted synthesis of highly uniform TiO_2 NCs with tailorable morphology in the 1-100 nm size regime. Methods are described to engineer the percentage of {001} and {101} facets in anatase and to control the morphology and phase of TiO_2 nanorods. The surfactants on the surface of the NCs, which direct growth of uniform particles, may be removed through a simple ligand exchange procedure, allowing for the shape dependence of photocatalytic hydrogen evolution to be studied using monodisperse TiO_2 NCs prepared without any high temperature annealing. Such highly uniform nanocrystals may act as model systems to investigate the influence of faceting on a variety of processes under operating conditions.

Biography of Dr. Thomas R. Gordon

Dr. Thomas R. Gordon recently earned his Ph.D in Physical Chemistry from the University of Pennsylvania, under the direction of Prof. Christopher B. Murray, after defending his thesis in February 2013, entitled “Directed Synthesis and Doping of Wide Bandgap Semiconducting Oxides.” He received a B.S. in Chemistry with a minor in Mathematics (summa cum laude) from Lebanon Valley College. Dr. Gordon is the 2006 recipient of the Dr. Judith Bond Endowed scholarship winner awarded to outstanding chemistry major attending a college or university in southeastern Pennsylvania. His research interests include the precise synthesis of nanocrystalline materials and their applications in catalysis, photocatalysis, and plasmonics. In June 2013, he will begin work as a postdoctoral fellow in the laboratory of Prof. Raymond Schaak at Pennsylvania State University as a member of the Materials Research Science and Engineering Center (MRSEC). He is the author or co-author of 9 scientific publications.

Catalysis in a Pocket: The MCM-22 Story

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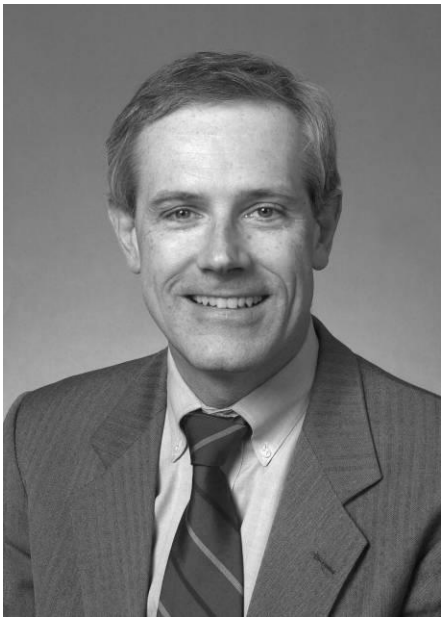
Abstract: MCM-22 (MTW) is among a unique class of multidimensional pore shape selective zeolites wherein the principal locus for catalysis is in 12 member ring (12-MR) surface pockets. The zeolite contains two independent pore systems, both of which are accessed through rings comprised of ten tetrahedral (T) atoms (such as Si, Al, and B). One of these pore systems is defined by two-dimensional, sinusoidal channels and the other is defined by large 12-MR supercages with an inner free diameter of 0.71 nm and a height of 1.82 nm. Virtually all acid catalyzed reactions take place in pockets formed from the surface termination of the 1.82 nm high and 0.71 nm diameter supercages. The zeolite has been evaluated and found promising for a number of acid-catalyzed reactions. Most importantly, it has been found to be unusually selective for aromatic alkylation in the presence of a wide range of olefins under liquid phase conditions. This presentation will describe the discovery, development and commercial deployment of this zeolite that is used widely in several aromatic alkylation processes.

Biography of Dr. Thomas F. Degnan, Jr.



Tom received his B.S. in chemical engineering from the University of Notre Dame, a Ph.D. in the same discipline from the University of Delaware, and an M.B.A. in Finance from the University of Minnesota. He spent four years in 3M's Central Research organization in St. Paul, MN before moving to Mobil Research and Development in 1980.

Tom has spent most of his career in exploratory process development, catalysis, catalyst development, and research management working for Mobil and now ExxonMobil Research and Engineering Company. He is presently Manager, New Leads Generation and Breakthrough Technologies and is located at ExxonMobil's Clinton, NJ facility.

He is a member of the North American Catalysis Society, the American Institute of Chemical Engineers, the American Chemical Society and the Research and Development Council of New Jersey.

Catalytic Characterization of Hierarchical Meso-/microporous Lamellar Zeolite Catalysts

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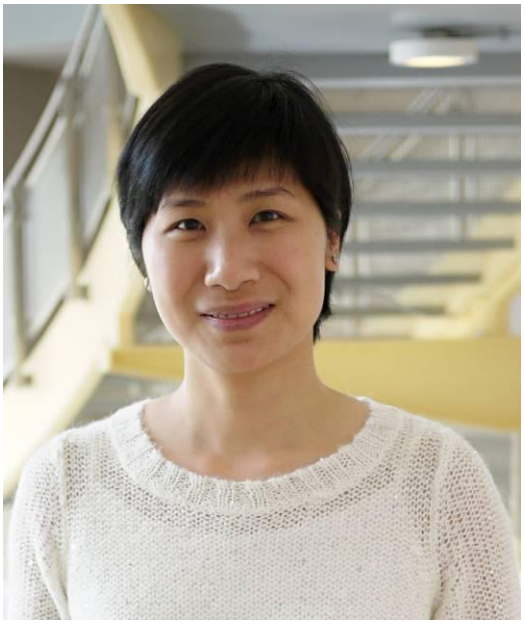
Abstract: The meso/micro-zeolites couple the catalytic features of micropores and the improved access and transport consequence of mesopores in a single material, possessing the capacity of processing large molecules. The synthesis and catalytic behavior investigation of meso/micro-zeolites has become the subject of intense research. This talk highlights the synthesis and catalytic characterizations of three emerging acidic meso-/micro-porous lamellar zeolite materials (self-pillared MFI, pillared MFI, multilamellar MFI), with a focus on their catalytic behavior investigations using ethanol dehydration, monomolecular conversion of propane and isobutane, and alkylation of mesitylene with benzyl alcohol as probe reactions. The rate and apparent activation energy of the catalytic ethanol and small alkane probe reactions in zeolites possessing dual micro- and meso-porosity was comparable to conventional microporous MFI materials, implying that the catalytic behavior of Brønsted acid sites in materials with dual meso-/micro-porosity is preferentially dominated by the microporous environment possibly because it provides a better fit for adsorption of small alkane or alcohol reactant molecules. The apparent rate constant of the catalytic alkylation of mesitylene with benzyl alcohol in meso/micro-porous zeolites was higher than that of their microporous analogues, revealing the role of the mesoporosity in space-demanding catalytic reactions. A mathematical model accounts for the external reaction, internal reaction, and diffusion developed to understand the catalytic behaviors of these catalysts.

Biography of Professor Dongxia Liu



Dongxia Liu received her Ph.D. in chemical engineering from University of Rochester in 2009. Her PhD work focused on Development of Novel Electrolyte Membranes for Intermediate Temperature Fuel Cells. After graduation, she did 2 year of post-doctorate in University of Minnesota with Prof. Michael Tsapatsis and Prof. Aditya Bhan, focusing on the synthesis and characterization of novel meso-/microporous zeolite catalysts. In 2012, Dongxia Liu joined the department of chemical and biomolecular engineering at the University of Maryland as an assistant professor. Her research interests lie in the synthesis, characterization and evaluation of novel hierarchical meso-/microporous materials, which are used as efficient catalysts in diffusion constrained reactions and as selective membranes for water purification applications.

Software Tools for the Construction of Detailed Kinetic Models

Michael T. Klein

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Abstract: The world-wide energy transportation sector is almost entirely dependent on petroleum, a remarkable resource on which a highly sophisticated refining and vehicle infrastructure has grown. Given the capital value of the existing world-wide refining and transportation infrastructures, and the decadal characteristic time for their change, it is likely that carbon-based resources, including unconventional feedstocks that will be upgraded for use with petroleum in the existing infrastructure, will be utilized for decades to come. Mathematical models of the chemistry of their upgrading and conversion will assist the commercial realization of these possibilities.

The considerable interest in molecule-based models of these chemistries is motivated by the need to predict both upstream and downstream properties. This is because the molecular composition is an optimal starting point for the prediction of mixture properties. The challenge of building these models is due to the staggering complexity of the complex reaction mixtures. There will often be thousands of potential molecular and intermediate (e.g., ions or radicals) species. Clearly, the use of the computer to not only solve but also formulate the model would be helpful in that it would allow the modeler to focus on the basic chemistry, physics and approximations of the model.

Our recent work has led to the development of an automated capability to model development. Statistical simulation of feedstock structure casts the modeling problem in molecular terms. Reactivity information is then organized in terms of quantitative linear free energy relationships. The model equations are then built and coded on the computer. Solution of this chemical reaction network, in the context of the chemical reactor, provides a prediction of the molecular composition, which is then organized into any desired commercially relevant outputs. Of particular note is the Attribute Reaction Model approach that is useful when the number of desired components in the molecular mixture is constrained by the practical limits of hardware and software.

Biography of Professor Michael T. Klein

Michael T. Klein started his career at the University of Delaware, where he served as the Elizabeth Inez Kelley Professor of Chemical Engineering as well as Department Chair, Director of the Center for Catalytic Science and Technology, and Associate Dean. He then moved to Rutgers, The State University of New Jersey, to become the Dean of Engineering and the Board of Governors Professor of Chemical Engineering. On July 1, 2010, he returned to the University of Delaware to assume his present position as the Director of the University of Delaware Energy Institute and the Dan Rich Chair of Energy.

Professor Klein received a BChE from the University of Delaware in 1977 and a Sc. D. from MIT in 1981, both in Chemical Engineering. The author of over 200 technical papers and the lead author of the text *Molecular Modeling in Heavy Hydrocarbon Conversions*, he is active in research in the area of chemical reaction engineering, with special emphasis on the kinetics of complex systems. He is the Editor-in-Chief of the ACS journal *Energy and Fuels* and has received the R. H. Wilhelm Award in Chemical Reaction Engineering from the AIChE, the NSF PYI Award and the ACS Delaware Valley Section Award. In 2011 Professor Klein was elevated to the level of Fellow of the ACS.

Polar Substrates and Nonstoichiometric Surfaces: New Routes to Active and Controllable Heterogeneous Catalysts

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Abstract: The quest to design surfaces with useful catalytic activity has received a dramatic boost from modern techniques of oxide epitaxial growth and characterization. This unprecedented experimental control of oxide surfaces opens great opportunities to design new catalysts using theory and modeling. In this talk, I will describe a variety of new approaches for tailoring surface properties by controlling oxide composition and structure, before focusing on two specific examples. 1. Polar oxides show structural deformations that change the structure and composition of surfaces. 2. Annealing complex oxides can lead to surface reconstructions with compositions different from any bulk material. These techniques lead to surfaces with undercoordinated transition metal cations that should offer novel reactivity.

Biography of Professor Andrew M. Rappe

Andrew M. Rappe is a Professor of Chemistry and Professor of Materials Science and Engineering at the University of Pennsylvania. He received his A. B. in "Chemistry and Physics" summa cum laude from Harvard University in 1986, and his Ph. D. in "Physics and Chemistry" from MIT in 1992. He was an IBM Postdoctoral Fellow at UC Berkeley before starting at Penn in 1994.

Andrew received an NSF CAREER award in 1997, an Alfred P. Sloan Research Fellowship in 1998, and a Camille Dreyfus Teacher-Scholar Award in 1999. He was named a Fellow of the American Physical Society in 2006.

Andrew is one of the two founding co-directors of Pennergy: the Penn Center for Energy Innovation. He is also one of the founding co-directors of the VIPER honors program at Penn, the Vagelos Integrated Program in Energy Research.

His current research interests revolve around ferroelectric phase transitions in oxides, surface chemistry and catalysis of complex oxides, and the interplay between the two: a) He helped establish relationships between composition and ferroelectric phase transition temperature in bismuth-containing perovskites oxides, b) He predicted that changing chemical vapor composition above a ferroelectric oxide could reorient its polarization, c) He revealed the mechanism of domain wall motion in ferroelectric oxides, d) He showed that changing ferroelectric polarization dramatically changes catalytic activity of supported metal films and nanoparticles, and e) He uses computational materials design to invent new ferroelectric photovoltaics for solar applications.

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