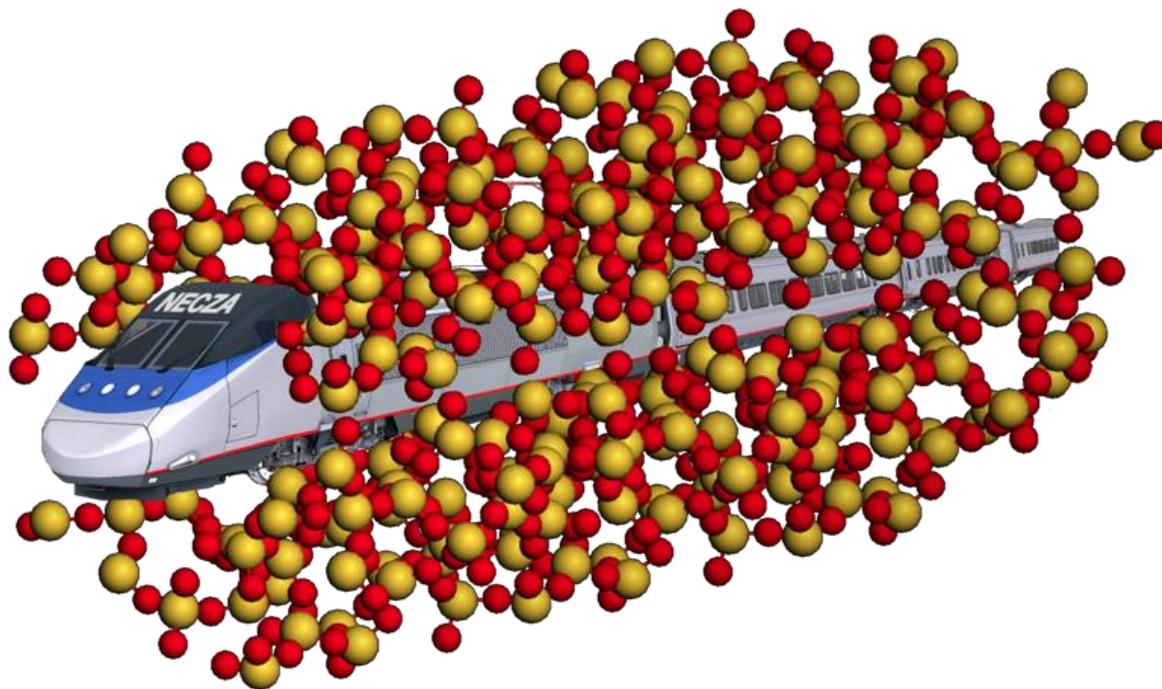


NECZA 2017

The 21st Meeting of the North-East Corridor Zeolite Association



Friday, December 15, 2017

The Bodek Lounge, Houston Hall

3417 Spruce St.

University of Pennsylvania

20th Annual NECZA Meeting – Organizing Committee

| | | |
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|----------------------|--|
| 8:15 – 8:55 | <i>Registration, Breakfast, Poster Setup</i> |
| 8:55 – 9:00 | <i>Welcome Remarks</i> |
| 9:00 – 9:40 | <u>Ray Gorte</u> (University of Pennsylvania) Zn- and Ga-Promoted H-ZSM-5 for Endothermic Reforming of Alkanes |
| 9:40 – 10:20 | <u>Francois Batllo</u> (Nalco Water: An Ecolab Company) “Modified Precursors for Zeolite Synthesis” |
| 10:20 – 11:00 | <i>Coffee Break – Poster Session I</i> |
| 11:00 – 11:40 | <u>Junhang Dong</u> (University of Cincinnati) Proton-Selective Ion Transport Phenomenon in Zeolite Membranes and Its Application as Ion Separator for Redox Flow Batteries |
| 11:40 – 12:20 | <i>Poster Session II</i> |
| 12:20 – 1:20 | <i>Lunch and Business Meeting</i> |
| 1:20 – 2:00 | <u>Peter Ravikovitch</u> (Exxon Mobil) “Adsorption in Flexible Structures: Experiments and Simulations” |
| 2:00 – 2:40 | <u>Selected Poster Presentations (2 x 15 min each)</u> |
| 2:40 – 3:00 | <i>Coffee break</i> |
| 3:00 – 3:40 | <u>Valentin Valtchev</u> (Université de Caen, France) “Enhancement of Zeolite Active Site Accessibility: In-situ versus Post-synthesis Methods” |
| 3:40 – 4:20 | <u>Bruce Gates</u> (UC Davis) “Molecular Metal Complex and Metal Cluster Catalysts on Zeolite Supports: Advances Emerging from Electron Microscopy and Spectroscopy” |
| 4:20 | Final remarks and meeting adjournment |

Zn and Ga-Promoted H-ZSM-5 for Endothermic Reforming of Alkanes

Yu-Hao Yeh and Raymond J. Gorte

*Department of Chemical & Biomolecular Engineering
University of Pennsylvania, Philadelphia, PA, USA*

Abstract

A major challenge associated with hypersonic aircraft is thermal protection of the engine, since air cooling is not possible at high velocities. An approach that has been used for controlling the temperatures of critical engine components in the US Air Force X-51A program involves using the fuel itself as a coolant before it enters the combustion chamber. While the amount of heat that can be taken up by the fuel is limited by the maximum temperature to which the fuel can be heated, it is possible to increase the cooling capacity of the fuel by performing endothermic reactions on it. Two possible reactions that have been investigated in this work are the acid-catalyzed cracking reactions that occur in acidic zeolites and the aromatization reactions that occur over Ga- and Zn-exchanged zeolites.

Initial work focused on supercritical, high-pressure reactions of n-hexane over H-ZSM-5, with and without the addition of Pt, Ga, or Zn, and determined reaction endothermicities from the product distributions. For unpromoted H-ZSM-5, the product distribution indicated that the endothermicity is low and decreases with increasing pressure. The addition of Ga or Zn to H-ZSM-5 significantly increased the endothermicity of the reactions by increasing the selectivity to form small aromatics. By contrast, the addition of Pt had a minor effect on both the rate and product distribution. Adsorption studies aimed at understanding the role of Zn in H(Zn)ZSM-5 showed that at low ion-exchange levels, less than 0.5 Zn/Al, each Zn cation displaced one Brønsted-acid site. FTIR of adsorbed acetonitrile-d₃ and calorimetric measurements of adsorbed CO at 195 K indicated that the exchanged Zn cations form Lewis-acid centers. A model in which the Zn cations, acting as Lewis-acid centers, polarize intermediates formed at Brønsted sites provided a way of understanding the observations.

The heat flows associated with conversion of n-hexane on H-ZSM-5 and H(Zn)-ZSM-5 were also measured directly for reaction at 60 bar and both 673 and 773 K. The acid-catalyzed reactions over H-ZSM-5 were found to be only mildly endothermic (<10 kJ/mol) at low conversions and exothermic at all conversions above 50%. The reactions on H(Zn)-ZSM-5 were significantly more endothermic (40 to 50 kJ/mol) for conversions below 70%; however, the reactions also became exothermic at very high conversions. Measurements of the product distributions showed that the reaction endothermicity for H(Zn)-ZSM-5 at lower conversions was likely due to formation of significant amounts of benzene, toluene, and xylene but that these were converted to higher molecular weight products at high conversions.

Bio sketch

Ray joined the faculty at the University of Pennsylvania in 1981 after receiving his PhD in Chemical Engineering from the University of Minnesota. He is currently the Russell Pearce and Elizabeth Crimian Heuer Professor of Chemical & Biomolecular Engineering, with a secondary appointment in Materials Science & Engineering. Since joining Penn, Ray served as Chairman of Chemical Engineering from 1995 to 2000. He received the 1997 Parravano Award of the Michigan Catalysis Society, the 1998 Philadelphia Catalysis Club Award, the 1999 Paul Emmett Award of the North American Catalysis Society, the 2001 Penn Engineering Distinguished Research Award, and the 2009 AIChE Wilhelm Award. He served as Chairman of the Gordon Conference on Catalysis (1998) and Program Chairman of the 12th International Zeolite Conference (1998). He is an Associate Editor of the Journal of the Electrochemical Society and became a Fellow of the society in 2015.



Modified Precursors for Zeolite Synthesis

Francois Batllo, Wenyong Lin

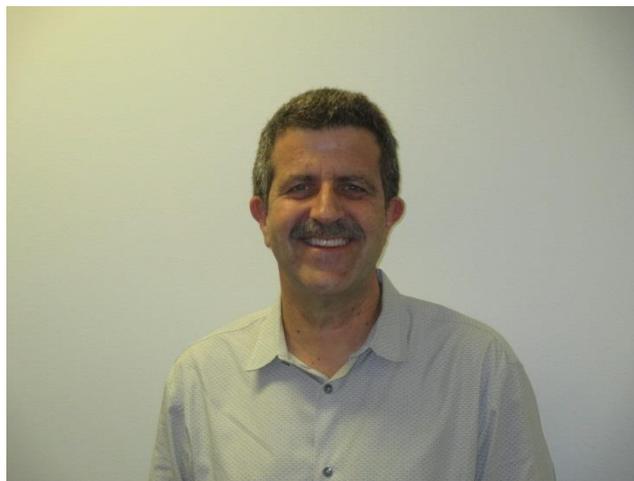
*Nalco Water: An Ecolab Company
Naperville, IL, USA*

Abstract

Silica and alumina are materials of considerable practical importance in the catalysis industry. They are used as binders to support active catalytic components (precious metals or zeolites) where they sometimes bring additional catalytic functions. They are also the base precursors for the production of zeolites. The influence of physicochemical characteristics of silica, alumina and their mixtures on the crystallization, physical and catalytic properties of the final zeolite has been the object of many studies. Results have shown that the chemistry, morphology, structure and homogeneity of the individual precursors and their mixtures have a significant impact on the crystallization kinetics and physicochemical characteristics of the resulting catalyst materials. The present work describes the development of silica and alumina precursor materials in various controlled physicochemical molecular configurations and state of homogeneity and their influence on the crystallization kinetics and physical properties of zeolites.

Bio sketch

Dr. Francois Batllo is currently a R&D Director for Nalco Water in Naperville, IL. He holds a Ph.D. in Physical Chemistry from Université de Bourgogne in Dijon, France. Professional interests focus on nanotechnology, system and material development for various industries. His current projects include: development of colloidal materials for catalysts, abrasive and investment casting applications. Authored over 15 patents and applications and over 30 publications in renowned international scientific journals.



Proton-Selective Ion Transport Phenomenon in Zeolite Membranes and Its Application as Ion Separator for Redox Flow Batteries

Zhi Xu, Ioannis Michos, Zishu Cao, and Junhang Dong

Department of Biomedical, Chemical, and Environmental Engineering

University of Cincinnati, Cincinnati, Ohio, USA

Abstract

Zeolite membranes have been recently demonstrated in our labs to have the capability of purifying water from brines through reverse osmosis process and selectively conducting protons in aqueous solutions when operating in “electrolyte mode”. Experimental and theoretical findings have indicated that ion separation by zeolite membranes relies primarily on the size exclusion (steric) effect enabled by the zeolite’s uniformly subnanometer-sized pore openings. It has also been revealed that the zeolite surface properties, such as hydrophilicity and surface charges, and operating conditions, including temperature, pressure and solution composition, could significantly influence the ion separation efficiency. This presentation discusses the proton transport behaviors through MFI-type zeolite membranes with different framework Si/Al ratios, including the non-ionic silicalite and the aluminum-containing ionic ZSM-5 zeolite membranes. These MFI-type zeolite membranes are also evaluated as a new type of ion separator for the all-vanadium and iron-chromium redox flow batteries (RFBs) in comparison to the state-of-the-art benchmark Nafion® membranes. Results of this research have shown that ionic microporous zeolite membranes may be able to overcome the challenge of tradeoff between ion selectivity and conductivity associated with conventional polymeric ion separators. These early stage studies of zeolite membranes for highly selective ion separation could open new opportunities for developing novel inorganic and inorganic-organic composite membranes for highly efficient water treatment and flow battery systems.

Bio sketch

Junhang Dong is a Professor of Chemical Engineering in the Department of Chemical and Environmental Engineering at University of Cincinnati. He received his Ph.D. in Chemical Engineering from the Nanjing University of Technology (China) in 1995. He was a visiting scholar at University of Cincinnati from 1997 to 1998 and then worked as a Research Associated at the Oak Ridge National Laboratory for over two years. In 2001, he became an Assistant Professor in the Department of Chemical and Petroleum Engineering at the New Mexico Institute of Mining and Technology, where he was promoted to Associate Professor with tenure in 2005. He joined the Chemical Engineering program at University of Cincinnati in 2006 and was promoted to Full Professor in 2012.

Dr. Dong's primary research interest is developing inorganic membranes and thin films for applications in molecular separations and chemical sensing that are relevant to clean energy productions and associated environmental management processes. Research activities in his group mainly include synthesis and characterization of inorganic membrane materials and understanding the relationships between the material structure and separation properties. For the past decades, zeolites and zeolite membranes have been continually a research focus of his team.



Adsorption in Flexible Structures: Experiments and Simulations

Peter Ravikovitch

*Corporate Strategic Research, ExxonMobil Research and Engineering Company
Clinton, NJ, USA*

Abstract

It is customary in adsorption science to consider solid adsorbents as rigid inert materials. Novel metal-organic frameworks and related materials demonstrate that this convenient simplification often fails. This talk will present experimental and molecular simulations studies of Zeolitic Imidazolate Framework (ZIF) materials. ZIFs are flexible crystalline frameworks, some of which undergo structural transitions upon adsorption of guest molecules and external stimuli. Combination of modeling and experiments allowed us to elucidate the thermodynamics of the phase transitions. We show that accounting for the framework flexibility is often critical for understanding and predicting adsorption and diffusion properties of microporous materials.

Bio sketch

Dr. Peter Ravikovitch is a member of technical staff and program leader at ExxonMobil Corporate Strategic Research laboratory in Annandale, New Jersey. He received his Ph.D. degree in Chemical Engineering from Yale University. His experience includes a year as a DAAD Fellow at the Johannes Gutenberg University in Mainz, Germany. Prior to joining ExxonMobil he had worked for eight years at TRI/Princeton on advancing and commercializing classical density functional theory methods for adsorption characterization of nanoporous materials. After joining ExxonMobil in 2007 he has been involved in a number of projects related to gas separations. His primary research interests include fundamentals of adsorption and transport in zeolites, MOFs, carbons, spanning modeling and experiments. He has authored and co-authored more than sixty publications, totaling eight thousand citations, and over fifteen patents. He currently serves on the board of directors of the International Adsorption Society and the editorial board of Adsorption journal.



Enhancement of zeolite active site accessibility: in-situ versus post-synthesis methods

Valentin Valtchev

*Laboratoire Catalyse & Spectrochimie, ENSICAEN - Université de Caen – CNRS,
Caen, France*

Abstract

The first part of the talk is devoted to the control of zeolite properties by in situ methods. The mechanism of zeolite formation from conventional hydrogel systems typically employed in industrial production of zeolites will be addressed and new insight in the very early stages of zeolite formation will be provided. The discussion is based on a recent study conducted with complementary methods (electron tomography, high resolution and analytical TEM, and hyper polarized ^{129}Xe NMR) in attempt to identify the spatial and temporal details of zeolite nucleation. It was revealed that the zeolite nucleation is limited to the shell structure of gel particles and thus the later controls the reaction kinetics. This new finding can be used to control the number of nuclei and thus the ultimate size of crystallites. Besides the impact of synthesis conditions on the physicochemical properties of zeolite crystals, important issues as crystalline yield, level of aggregation and colloidal stability of zeolite particles will be discussed.

The second part of the talk is devoted to a new demetallation process that allows non-selective dissolution of Si and Al in zeolite frameworks. The application of this approach results in a product with composition similar to the parent zeolite. The dissolution profiles obtained by this type of dissolution shed new light on the sub-structure of commercially relevant zeolite crystals (MFI, MOR, FER): particles that appear as single crystals on macroscopic level are segmented along defect zones exposing numerous nanometer sized crystalline domains, separated by low-angle boundaries. The concentration, morphology and distribution of such domains analyzed by electron tomography indicate that this is a common phenomenon in zeolites, independent of their structure and chemical composition. This is a milestone to better understand their growth mechanism and rationally design superior catalysts and adsorbents.

Non-selective chemical etching is also used to increase the micropore volume of cage-type zeolites. A 10 % increase in micropore volume of FAU-type zeolite resulting from the opening of some of the small (sodalite) cages is achieved. More active sites become accessible and the catalytic performances for these modified zeolites are substantially improved. The catalytic consequences of the new demetallation process leaving an additional macroporosity and/or mesoporous cages will be discussed.

Finally, the advantages and disadvantages of in-situ and post-synthesis methods for control of zeolite properties will be compared.

Bio sketch

Dr. Valentin Valtchev is Research Director at the Laboratory of Catalysis and Spectroscopy (LCS) in Caen, France and “Thousand Talents” Professor at the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry in Jilin University, China.

His research involves synthesis and modification of zeolites and other porous solids that can be used for catalysis, separation and molecular recognition. He has published about 200 papers, a number of review articles and book chapters, 6 books and 23 patents.

Dr. Valtchev is recipient of the highest recognitions of the Federation of European Zeolite Associations “Baron Axel Cronstedt” award (2014) and of the International Zeolite Association “Donald Breck” award (2016).

He is laureate of the award “La Recherche 2016: Chimie” in France. In 2016 Valentin Valtchev was elected President of the International Zeolite Association.



Molecular Metal Complex and Metal Cluster Catalysts on Zeolite Supports: Advances Emerging from Electron Microscopy and Spectroscopy

Bruce Gates

Department of Chemical Engineering, University of California, Davis

David, CA, USA

Abstract

Industrial catalysts range from the simple—molecules in solution—to the complex—the heterogeneous surfaces of robust solids. Advances in surface catalysis are emerging as researchers increasingly succeed in synthesizing and characterizing well-defined molecular species on supports. The best understood supported catalysts are highly uniform, being isolated on regular materials such as zeolites. Syntheses of supported molecular catalysts involve reactions of precursor compounds such as $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acetylacetonate})$ with support surface OH groups—to give structures such as anchored $\text{Ir}(\text{C}_2\text{H}_4)_2$, with the Ir atom bonded to two support oxygen atoms. X-ray absorption and infrared spectroscopies bolstered by atomic-resolution electron microscopy images and calculations at the level of density functional theory characterizing the supported species and their bonding to the supports are responsible for many of the recent advances. The subject is illustrated with examples of molecular catalysts supported on zeolites and, by contrast, MOFs, with a summary of new opportunities offered by scanning transmission electron microscopy and high-energy-resolution fluorescence detection X-ray absorption near edge spectroscopy and questions that might help to guide future research.

Bio Sketch

Professor Gates received his BS degree from UC Berkley in 1961 and the Ph.D. degree from the University of Washington in 1966.

After spending two years at Chevron Research Co. in Richmond, CA, as a Research Engineer, he joined the Department of Chemical Engineering at the University of Delaware as an Assistant Professor in 1969. He served as the director of the Center for Catalytic Science and Technology from 1981 to 1988. During those two decades, Prof. Gates made key contributions to hydroprocessing, a technique to remove contaminants from fuel, and used in oil refineries.

In 1992, Bruce returned to California to join the Department of Chemical Engineering at UC Davis. He is currently a Distinguished Professor at the department.

Prof. Gates was elected to the National Academy of Engineering in 2007 for his scholarship on catalysis, innovative research on hydroprocessing and supported molecular catalysts, and for his exemplary leadership in collaborative university/industry research. He has contributed more than 530 scientific publications and is the recipient of the 2016 UC Davis College of Engineering Outstanding Senior Faculty Research Award.

