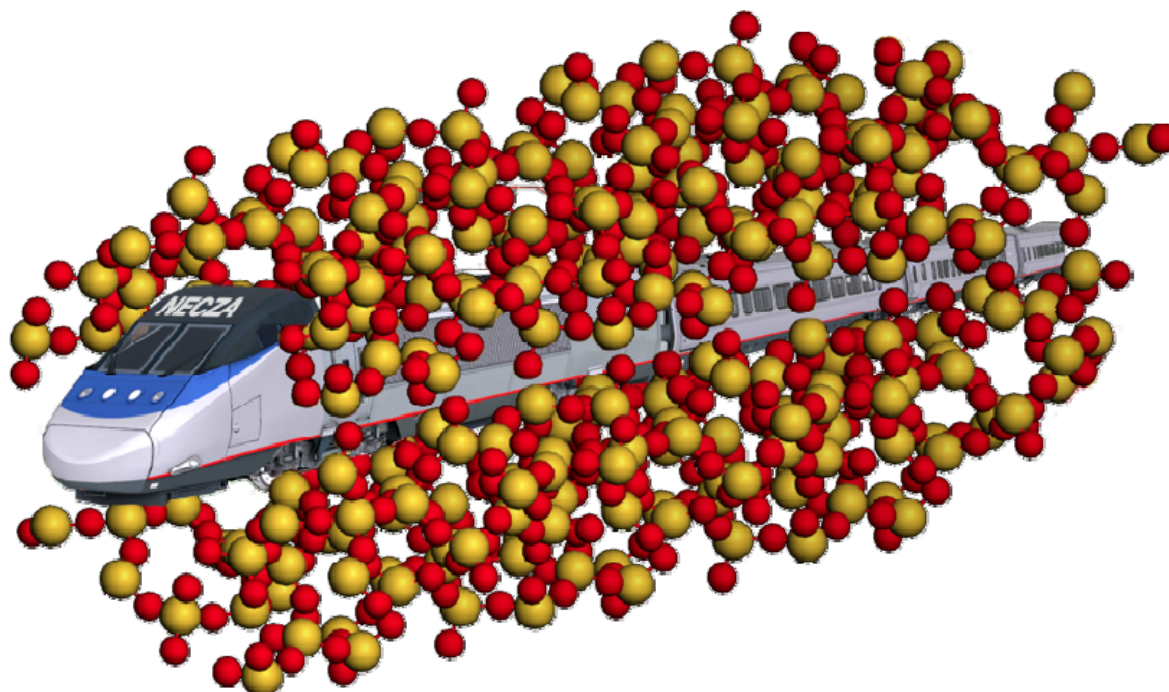


NECZA 2016

The 20th Meeting of the North-East Corridor Zeolite Association



Friday, December 09, 2016

The Bodek Lounge, Houston Hall

3417 Spruce St.

University of Pennsylvania

20th Annual NECZA Meeting – Organizing Committee

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Meeting Venue



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Scientific Program

8:15 – 8:55	<i>Registration, Breakfast, Poster Setup</i>
8:55 – 9:00	<i>Welcome Remarks</i>
9:00 – 9:50	<u>Michael Tsapatsis</u> (University of Minnesota) “2-dimensional Zeolites”
9:50 – 10:30	<u>Mirosław A. Derewinski</u> (Pacific Northwest National Laboratory) “Robust Zeolites and Related Nanoporous Materials for Catalytic Processes in Condensed Phases”
10:30 – 11:00	<i>Coffee Break – Poster Session I</i>
11:00 – 11:40	<u>Ahmad Moini</u> (BASF) “Synthesis and Chemistry of CHA Zeolite”
11:40 – 12:10	<i>Poster Session II</i>
12:10 – 1:30	<i>Lunch and Business Meeting</i>
1:30 – 2:30	<u>Jörg Kärger</u> (Leipzig University) “Diffusion in Porous Materials: Insights, Surprises and Challenges”
2:30 – 3:10	<u>Jing Li</u> (Rutgers, The State University of New Jersey) “Microporous Metal Organic Frameworks: Designer Materials for Selective Gas Capture and Separation”
3:10 – 3:25	<i>Coffee break</i>
3:25 – 3:55	<u>Selected Poster Presentations (2 x 15 min each)</u>
3:55 – 4:35	<u>Udayshankar Singh</u> (W. R. Grace & Co.) “Unit Cell Volume as a Tool to Monitor the Deactivation of ZSM-5 in FCC Catalyst”
4:35	Final remarks and meeting adjournment

2-dimensional zeolites

Michael Tsapatsis
*Department of Chemical Engineering and Materials Science
University of Minnesota*

It is only recently that single-unit-cell thick zeolite nanosheets (2-dimensional zeolites; *AICHE Journal* 60(7), 2374-2381 (2014)) with intact crystal and micropore structure were shown to be possible. The structural integrity and uniformity of these microporous nanosheets open exciting possibilities for technological breakthroughs in molecular sieve membrane fabrication, synthesis of hierarchical catalysts and polymer-zeolite nanocomposites. Moreover, zeolite nanosheets enable for the first time zeolite pore mouth adsorption and catalysis to be studied by traditional uptake methods as well as surface science techniques. Synthesis of high aspect ratio zeolite and other crystalline nanoporous nanosheets, methods to characterize their structure and properties, along with their processing and assembly to create membranes and catalysts will be the focus of this talk.

Speaker Biography

Michael Tsapatsis joined the Department of Chemical Engineering and Materials Science at the University of Minnesota in September 2003 as a professor and he currently holds the Amundson Chair. He received an Engineering Diploma (1988) from The University of Patras, Greece, and MS (1991) and Ph.D. (1994) degrees from the California Institute of Technology (Caltech) working with G.R. Gavalas. He was a post-doctoral fellow with M.E. Davis at Caltech (1993/94). Before joining the University of Minnesota he was a faculty member (assistant and associate professor) in the Chemical Engineering Department at the University of Massachusetts Amherst (1994-2003). His research group's accomplishments include development of hierarchical mesoporous zeolite catalysts, oriented molecular sieve films, molecular sieve/polymer nanocomposites for membrane applications, crystal structure determination of adsorbents and synthesis of precisely sized oxide nanoparticles that have been recently commercialized.



Robust zeolites and related nanoporous materials for catalytic processes in condensed phases

Mirosław A. Derewinski

*Pacific Northwest National Laboratory, Institute for Integrated Catalysis,
902 Battelle Boulevard, Richland 99352 WA*

The introduction of microporous materials such as zeolites into the field of condensed phase reactions imparts many of their beneficial properties. In particular, in the field of catalytic transformation of biomass and its derived compounds, zeolites provide an opportunity for astonishing enhancements. However, the large percentages of water in biomass feedstocks have a detrimental effect on the zeolite stability. We have recently proposed a mechanism for the selective hydrolysis of the zeolite framework in hot liquid water. Zeolite defects were found to compromise the structural integrity of the zeolite in water. These defects were eliminated by a stabilization approach involving the healing of defect nests deep within the crystal lattice using a reactive silane. While the defect concentration plays a significant role in pure water environments, under catalytically relevant conditions, the intraporous water concentration determined by the material's intrinsic hydrophobicity, was found to be the most crucial factor in prolonging the zeolite's lifetime. Ways to increase the hydrophobicity and, in turn reduce the intraporous water concentration, involve the healing of defects and deposition of hydrophobic moieties into the crystal, thereby reducing the overall framework Al concentration through the design and synthesis in fluoride media.

A second theme will be the design, preparation and full characterization of a system composed of protozeolitic nanoparticles (below 10 nm in size) that have been assembled into a highly porous, layered material. The main advantage of this new material is the considerably higher accessibility of active sites making it an effective catalyst for reactions carried out in a liquid organic phase. The results of catalytic performance (terpene hydrocarbon isomerization, synthesis of methylenedianiline (MDA)) of these materials will be presented and compared to those of standard (micron size) zeolite.

Speaker Biography

Mirosław (Mirek) Derewinski is a senior scientist in Institute of Integrated Catalysis at the Pacific Northwest National Laboratory (PNNL) since 2013. He received Ph.D. in 1981 at Warsaw Technical University. In 2014 he became Professor of Chemistry at the Polish Academy of Sciences. He was a research-fellow with F. Fajula at CNRS, Montpellier (1988-1989) and with D. Barthomeuf at CNRS, Paris (1991-1992). He served as Deputy Director of the Institute of Catalysis and Surface Chemistry, Krakow (1993-2002), President of the Polish Zeolite Association (1997-2000) and President of the Federation of European Zeolite Associations (FEZA) (2003-2006). His current research activity is focused on fundamental studies of the formation and stability of ordered microporous materials and related solids and uses that knowledge to design complex catalysts.



Synthesis and chemistry of CHA zeolite

Ahmad Moini
BASF Corporation, Iselin, NJ, USA

Automotive exhaust conditions present unique challenges for the design of effective catalysts. In addition to the need for catalytic activity over a wide temperature range, the catalyst must show durability towards extreme hydrothermal aging conditions. The use of zeolitic materials under such conditions is especially challenging due to the vulnerability of zeolites to steam aging. The BASF discovery of the Cu-CHA catalyst for selective catalytic reduction (SCR) of NO_x demonstrated an effective balance between favorable active sites and zeolite framework durability. It also paved the way for the implementation of urea SCR as the key approach for NO_x reduction in diesel vehicles. In addition to highlighting the development of Cu-CHA SCR catalyst, this presentation will primarily focus on various synthesis approaches for the crystallization of CHA zeolites.

Speaker Biography

Dr. Ahmad Moini is a Research Fellow at BASF Corporation in Iselin, NJ. He obtained his Ph.D. in Chemistry from Texas A&M University, and held a postdoctoral appointment at Michigan State University. Dr. Moini started his career at Mobil Research & Development Corporation (now ExxonMobil), where he conducted research on microporous materials. With a focus on exploratory zeolite synthesis, he studied the mechanism of zeolite crystallization and the role of specific classes of organic directing agents in the formation of various zeolite frameworks. He joined Engelhard Corporation (now BASF) in 1996. Since then, his primary research interests have been in the area of materials synthesis, directed at a range of catalytic and functional applications. He applied high throughput methods for the synthesis and evaluation of catalytic materials, and used these tools for the development of new products. A significant part of his work has been directed towards catalysts for environmental applications. These efforts, in collaboration with the extended BASF team, led to the discovery and development of Cu-CHA catalyst for selective catalytic reduction (SCR) of NO_x from diesel vehicles. He holds 48 US patents relating to various aspects of materials and catalyst development.



Diffusion in Porous Materials: Insights, Surprises and Challenges

Jörg Kärger

Leipzig University, Institute of Experimental Physics

After, with the first measurement of guest diffusion in nanoporous materials over microscopic dimensions, pulsed field gradient NMR gave rise to a paradigm shift in our understanding of zeolitic diffusion, with the potentials of microimaging to observe the evolution of molecular ensembles, finally also microscopic diffusion measurement under non-equilibrium conditions became possible [1]. Examples of the novel insight thus accessible include

- (i) the measurement of transport resistances of the external surface of the adsorbent particles (“surface barriers”) as a crucial, but so far inaccessible parameter deciding about the technological feasibility of these materials where, depending on the host-guest system under study, the surface barriers are found to be caused by essentially impermeable layers with dispersed “holes” or by quasi-continuous layers of dramatically reduced permeability [2],
- (ii) the potentials for immediately deciding about the applicability of Fick’s diffusion laws for describing mass transfer in a given nanoporous host-guest system [3],
- (iii) simultaneous recording of adsorption and conversion within catalytically active nanoporous crystals/particles, with direct (“one-shot”) measurement of effectiveness factors as the key number describing the efficiency of the industrial application of such materials [4],
- (iv) measurement of two-component adsorption and diffusion, with the option of the direct recording of “uphill” fluxes and “overshooting”, i.e. of profiles with concentrations temporarily exceeding the equilibrium ones [5], and
- (v) recording of pore filling and emptying upon gas pressure variation as a function of space and time as a novel route towards exploring the fundamentals of sorption hysteresis [6].

- [1] J. Kärger, T. Binder, C. Chmelik, F. Hibbe, H. Krautscheid, R. Krishna, and J. Weitkamp, *Nat. Mater.* **13** (2014) 333–343.
- [2] J.C.S. Remi, A. Lauerer, C. Chmelik, I. Vandendael, H. Terryn, G.V. Baron, Denayer, Joeri F. M., and J. Kärger, *Nat Mater* **15** (2015) 401–406.
- [3] T. Titze, A. Lauerer, L. Heinke, C. Chmelik, N.E.R. Zimmermann, F.J. Keil, D.M. Ruthven, and J. Kärger, *Angew. Chem. Int. Ed.* **54** (2015) 14580–14583.
- [4] T. Titze, C. Chmelik, J. Kullmann, L. Prager, E. Miersemann, R. Gläser, D. Enke, J. Weitkamp, and J. Kärger, *Angew. Chem. Int. Ed.* **54** (2015) 5060–5064.
- [5] A. Lauerer, T. Binder, C. Chmelik, E. Miersemann, J. Haase, D.M. Ruthven, and J. Kärger, *Nat. Comms.* **6** (2015) 7697.
- [6] A. Lauerer, P. Zeigermann, J. Lenzner, C. Chmelik, M. Thommes, R. Valiullin, and J. Kärger, *Microporous and Mesoporous Materials* **214** (2015) 143–148.

Speaker Biography

Jörg Kärger got his PhD in Physics in 1970 at Leipzig University, followed by habilitation in 1978. In 1994 he became Professor of Experimental Physics and head of the Department of Interface Physics in Leipzig. He served as Dean of the Faculty of Physics and Earth Sciences at Leipzig University (1996 – 1999), President of the German Zeolite Association (1996 – 1999) and Ombudsman of Leipzig University (2002 – 2006). His research activities, unabatedly continued after retirement in 2009, are dedicated to diffusion phenomena and novel techniques of their measurement. They gave rise to the establishment of the Diffusion Fundamentals online journal and conference series. His book on Diffusion in Nanoporous Materials (Wiley-VCH, 2012), co-authored by Douglas Ruthven and Doros Theodorou, became standard in the field. His activities were recognized, among others, by the Donald W. Breck Award for zeolite research, the Max Planck Research Prize and election to the Saxon Academy of Sciences.



Microporous Metal Organic Frameworks: Designer Materials for Selective Gas Capture and Separation

Jing Li

*Department of Chemistry and Chemical Biology
Rutgers, The State University of New Jersey*

Piscataway, NJ 08854, USA epartment of Chemistry, University of Iowa

Metal-organic frameworks (MOFs) are a unique class of crystalline solids composed of metal cations or cluster and organic ligands that have shown enormous promise for a wide range of applications. Over the past 20 years MOFs have become one of the most intensively and extensively explored material families. As a relatively new type of solid adsorbents, MOFs have demonstrated numerous advantages over some conventional/traditional sorbent systems because of their nearly unlimited tunability in crystal/pore structures and adsorption properties. Among many interesting topics, MOF based gas adsorption and separation have attracted the most attention. This presentation will focus on our recent effort and progress in developing microporous MOFs for selective gas capture and separation for several important separation processes. Our studies show that both the capacity and selectivity of the MOF sorbents can be greatly enhanced by engineering their crystal structure, porosity, chemical composition and surface functionality.

Speaker Biography

Jing Li is a Distinguished Professor in the Department of Chemistry and Chemical Biology at Rutgers University. She received her Ph.D. from Cornell University in January 1990 under the guidance of Professor Roald Hoffmann. After two years of postdoctoral work with Professor Francis J. DiSalvo (Cornell University), she joined the chemistry faculty at Rutgers University in 1991 as Assistant Professor. She was promoted to Associate Professor in 1996, to Full Professor in 1999, and to Distinguished Professor in 2006. Her research primarily focuses on the development of functional materials that are both fundamentally important and potentially useful for clean and renewable energy applications, including metal-organic frameworks and inorganic-organic hybrid semiconductors. She has published more than 280 research articles, book chapters, and invited reviews. She currently serves as Associate Editor for *Crystal Growth & Design*, an ACS journal. Her recent awards and honors include the first-ever Clean Energy Education and Empowerment (C3E) Award for women (U.S. Department of Energy) in 2012 and a Humboldt Research Award (Alexander von Humboldt Foundation) in the same year. She was elected as a Fellow of the American Association for the Advancement of Science (AAAS) in 2012 and became a Fellow of the Royal Society of Chemistry (RSC) in 2015. She was recognized as a “Highly Cited Researcher” by Thomson Reuters in both 2015 and 2016.



Unit Cell Volume as a Tool to Monitor the Deactivation of ZSM-5 in FCC Catalyst

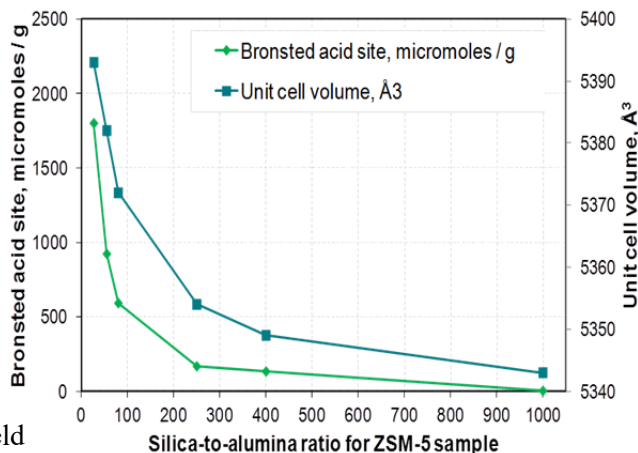
Udayshankar Singh^a, Jürgen Knöll^b, Mike Ziebarth^a, Wu-Cheng Cheng^a

^aW.R. Grace & Co.-Conn, 7500 Grace Drive, Columbia, MD 21044, USA

^bGrace GmbH & Co KG, In der Hollerhecke 1, 67547 Worms, Germany

In a fluid catalytic cracking (FCC) application, ZSM-5 containing catalysts are extensively used to boost gasoline octane, and maximize propylene yields to meet the demands for petrochemical feedstock. The severe hydrothermal conditions of a FCC unit gradually deactivate the ZSM-5 in the catalyst, by framework dealumination. The stability of the ZSM-5 with respect to surface area and framework dealumination, under FCC operating conditions, is important to maximize its effectiveness for propylene activity. The characterization of ZSM-5 in the commercial FCC catalyst has always been a challenge. The ability to determine its acidity is important to the successful development of new products and processes.

A simple and robust method based on unit cell volume (UCV) has been developed to characterize the ZSM-5 in the catalyst. The results show UCV is a powerful tool to monitor deactivation of ZSM-5 in a commercial unit. It can be measured by combining powder X-ray diffraction technique with Rietveld analysis. The measurement of UCV shows a good correlation with the acidity, and the catalytic properties of ZSM-5 catalyst. The data demonstrate that the technology can be applied to both laboratory and field deactivated ZSM-5 based catalysts.



[1] U. Singh; M. Ziebarth; W. Cheng; J. Nicolich; J. Knoll; C. Fougret; S. Brandt, *AFPM Annual Meeting AM-14-25*, 2014.

[2] J. Knoll; U. Singh; J. Nicolich; R. Gonzalez; M. Ziebarth; C. Fougret; S. Brandt, *Ind. Eng. Chem. Res.*, **53**, 2014, 16270.

Speaker Biography

Udayshankar Singh is Principal Research and Development Engineer in the Catalysts Technologies Business at the W.R. Grace & Co.-Conn. His job responsibilities include development and scale-up of new catalysts for application in refining industry. He joined Grace in 2007 and has made numerous valuable contributions to the Refining Technologies product line, especially in the area of environmental additives, propylene maximization, and in the field of fluid catalytic cracking (FCC) catalyst.

Dr. Udayshankar Singh holds a doctorate degree in Inorganic Chemistry from the University of Exeter, England. He did his postdoctoral research at the University of California-Santa Barbara, USA. He has nine years of experience in developing catalyst for refining technologies. He has published patents, and is author and co-author of numerous research articles published in renowned scientific journals.

