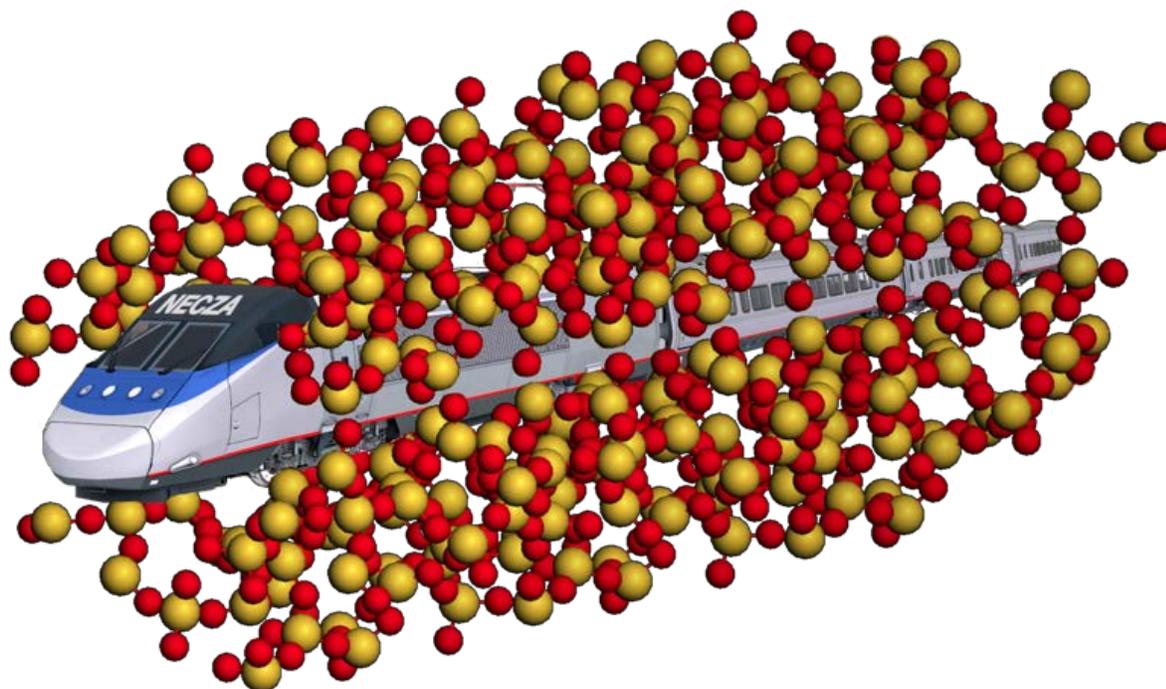


# **NECZA 2016**

## **The 20<sup>th</sup> Meeting of the North-East Corridor Zeolite Association**



**Friday, December 9, 2016**

**The Bodek Lounge, Houston Hall**

**3417 Spruce St.**

**University of Pennsylvania**

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## 20<sup>th</sup> Annual NECZA Meeting – Organizing Committee

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# Scientific Program

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

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## 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 department 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

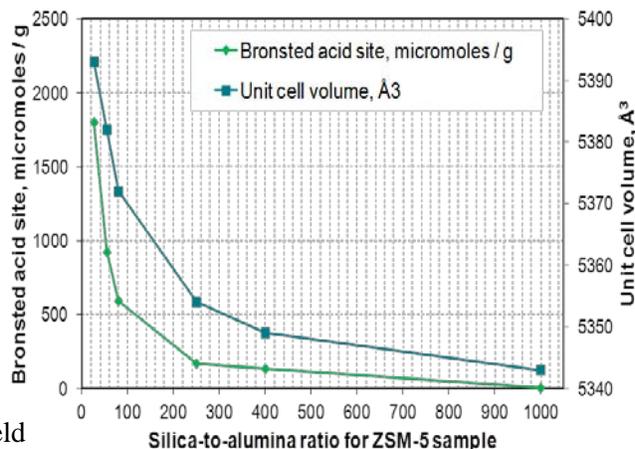
Udayshankar Singh<sup>a</sup>, Jürgen Knöll<sup>b</sup>, Mike Ziebarth<sup>a</sup>, Wu-Cheng Cheng<sup>a</sup>

<sup>a</sup> W.R. Grace & Co.-Conn, 7500 Grace Drive, Columbia, MD 21044, USA

<sup>b</sup> Grace 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.



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## 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.





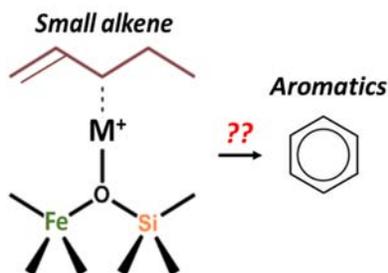
## **Poster Abstracts**

## A Study of Zn and Ga Exchange in H-[Fe]ZSM-5 and H-[B]ZSM-5 Zeolites

Yu-Hao Yeh and Raymond J. Gorte

*Department of Chemical & Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States*

The catalytic properties of H-[Fe]ZSM-5 and H-[B]ZSM-5 were explored after addition of Zn or Ga. TPD-TGA of 2-propanamine adsorbed on Zn- and Ga-exchanged H-[Fe]ZSM-5 showed a decrease in Brønsted-site densities and formation of new dehydrogenation sites, similar to what is observed following exchange in H-[Al]ZSM-5 and in an amorphous silica-alumina. Exchanged Zn cations in [Fe]ZSM-5 also exhibited Lewis-acid character, as demonstrated by a  $\nu(\text{CN})$  stretch at  $2310\text{ cm}^{-1}$  upon adsorption of  $\text{CD}_3\text{CN}$ . By contrast, the sites in H-[B]ZSM-5 are not capable of protonating 2-propanamine, do not form dehydrogenation sites when Zn or Ga were added, and show no evidence for sites with Lewis-acid character from FTIR of  $\text{CD}_3\text{CN}$ . Neither H(Zn)-[Fe]ZSM-5 nor H(Zn)-[B]ZSM-5 catalyzed reactions of n-hexane at 773 K but TPD-TGA of adsorbed propene on H(Zn)-[Fe]ZSM-5 showed strong interactions between the Zn and olefins that may be responsible for dehydrocyclization of light alkanes in Zn-exchanged, Al-containing zeolites.



# Prins condensation of formaldehyde with propylene over Lewis acidic zeolites

**Efterpi (Efi) Vasiliadou<sup>1</sup> and Raul Lobo<sup>1,2\*</sup>**

<sup>1</sup>Catalysis Center for Energy Innovation, University of Delaware, Newark, Delaware 19716, United States

<sup>2</sup>Center for Catalytic Science and Technology, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States

\* lobo@udel.edu

Carbon-carbon bond formation (C-C) reactions are of fundamental importance because they provide an efficient pathway to build more complex compounds. An important C-C bond formation pathway is the ‘ene’ reaction, a six electron pericyclic reaction occurring between an alkene with an allylic hydrogen (the ‘ene’), and an electron-deficient multiple bond (the enophile). Two new sigma bonds form and a pi-bond migrates as indicated in Figure 1.<sup>1</sup>

The condensation of formaldehyde with olefins is an example of the ‘ene’ reaction specifically referred to as the Prins reaction.<sup>2,3</sup> Although discovered about a century ago, it currently finds important applications because of the availability of inexpensive lower olefins, as well as the availability of formaldehyde as a one-carbon electrophile. The Prins reaction forms unsaturated alcohols, diols, alkyl dioxanes, pyrans and dienes. Homogeneous acid catalysis is prevalent in this reaction, but heterogeneous catalysts have not been investigated in detail before.<sup>4,5</sup>

We have investigated solid Lewis acid catalysts for the ene reaction and have found that Zn ion-exchanged zeolites Beta and ZSM-5 efficiently catalyze the Prins condensation of formaldehyde with propylene. Zn-Beta was very active for the formaldehyde condensation with propylene producing a mixture of products (Figure 2, left) that can be divided into compounds with four carbon atoms (3-buten-1-ol and 1,3-butadiene) and compounds having five carbon atoms (1,3-Dioxane, 4-methyl-, tetrahydro-4H-pyran-4-ol and 3,6-dihydro-2H-pyran). The primary product was 3,6-dihydro-2H-pyran, a five-carbon molecule formed primarily by Diels-Alder reaction between 1,3-butadiene and formaldehyde. To minimize reactions forming five carbon compounds, a series of Zn-exchanged zeolites were investigated. Zn-ZSM-5 showed high selectivity towards the formation of 3-buten-1-ol (~65% selectivity, see Figure 2, right), while the extent to five-carbon products decreased. 3-buten-1-ol is highly desirable because it forms 1,3-butadiene upon dehydration. Experiments with H-ZSM-5 reveal that Zn incorporation increases the overall reaction rate and 3-buten-1-ol product selectivity.

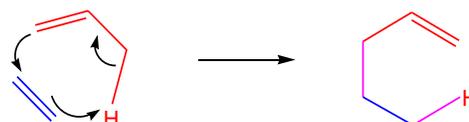


Figure 1. ‘Ene’ Reaction

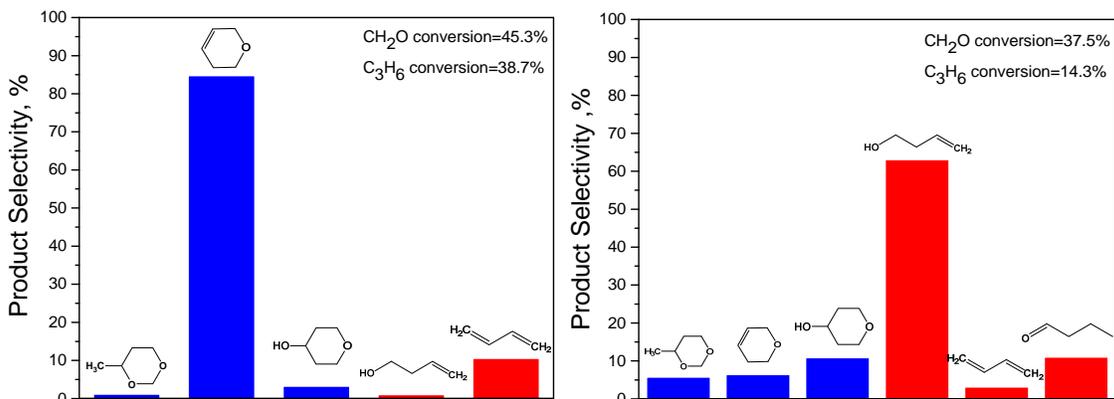


Figure 2. Product selectivity: left, Zn-H-Beta, right, Zn-H-ZSM-5

## References

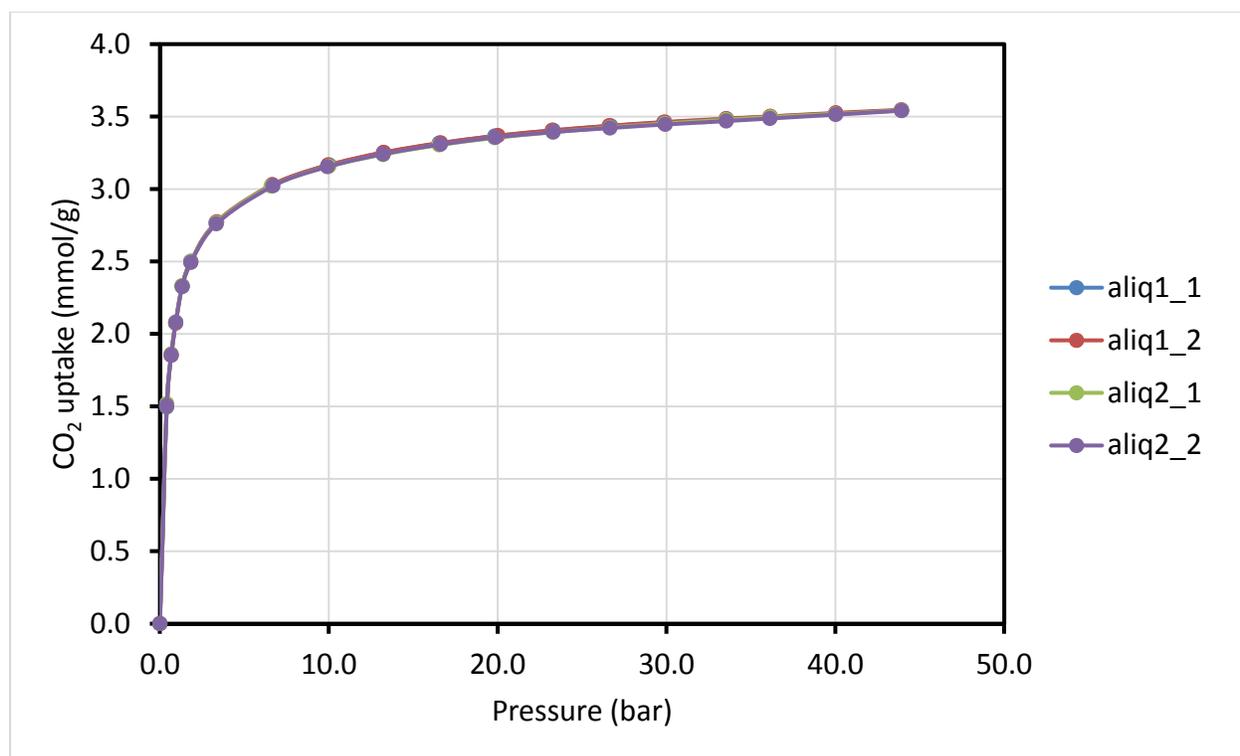
- [1] M. Yamanaka, K. Mikami, *Helv. Chim. Acta* **85** (2002) 4264
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- [5] A.R. Workman, US Patent 2,412,762 (1946)

## Round Robin Test on High-Pressure CO<sub>2</sub> Adsorption Isotherms

**Giang Nguyen, Laura Espinal, Matthias Thommes, Roger van Zee**

*Facility for Adsorbent Characterization and Testing, Material Measurement Laboratory  
National Institute of Standards & Technology, Gaithersburg MD*

Adsorbent materials have many applications. Despite major progress in adsorption technology and physical adsorption characterization during the past two decades, measurement challenges still exist. For example, protocols for measuring high-pressure gas adsorption isotherms on well-characterized porous materials have not been standardized.<sup>1</sup> In response to this situation, the National Institute of Standards and Technology (NIST) in partnership with the US Department of Energy's Advanced Research Projects Agency-Energy (ARPA-E) launched the Facility for Adsorbent Characterization and Testing ("FACT Lab").<sup>2</sup> NIST inaugurated the FACT Lab at a workshop on "Measurement Needs in the Adsorption Sciences."<sup>3</sup> At the workshop, a recommendation was made that the FACT Lab lead a round-robin test to measure high-pressure CO<sub>2</sub> isotherms on the NIST reference material RM<sup>TM</sup>-8852, an ammonium ZSM-5 zeolite,<sup>4</sup> as a means of establishing reference adsorption data. Twelve labs from around the world were invited to participate in the round-robin. A detailed protocol for sample handling and activation was provided to the participants. Isotherms were measured up to 4.5 MPa (45 bar) on a variety of custom and commercial instruments, both manometric and gravimetric. This poster provide a progress report on the status of this round-robin.



Typical data set for duplicate measurements on two aliquots, showing good agreement.

### References

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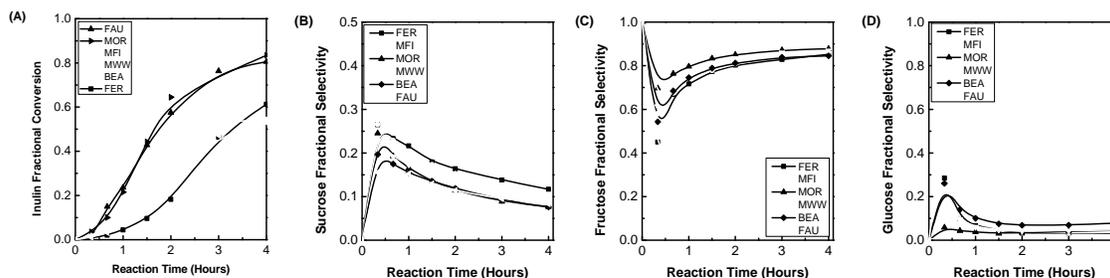
# External Surface Catalysis in Hydrolysis of Inulin over Zeolites with Different Micropore Topology and Mesoporosity

Su Cheun Oh,<sup>1</sup> Thien Nguyendo<sup>1</sup>, Yao He<sup>2</sup>, Amanda Filie<sup>1</sup>, Yiqing Wu<sup>1</sup> and D. Liu<sup>1\*</sup>

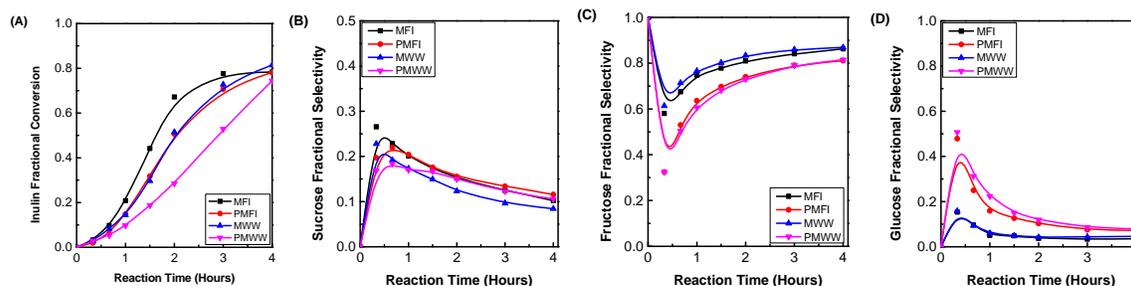
<sup>1</sup> Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742

<sup>2</sup> Institute of Clean Energy Utilization, School of Electric Power, South China University of Technology, Guangzhou, 510640, China

Inulin, consisting of usually 2 to 100 fructose units, is terminated with glucose and fructose units at each end. Studies have shown that hydrolysis of inulin occurs under mild temperature conditions (< 373 K) leads to partial decomposition of inulin to shortened inulin chains and production of free sugars (fructose, glucose and sucrose).[1]. However, the reaction could not be characterized by a single rate constant even though the reaction followed first order reaction kinetics. In this work, we assessed the catalytic consequences of micropore topology (FER, MFI, MOR, BEA, MWW and FAU) and mesoporosity (pillared MFI (PMFI) and pillared MWW (PMWW)) of zeolite catalysts on the hydrolysis of inulin and conducted a systematic understanding on the observed rate and product selectivity in the reaction kinetics. Inulin conversion possessed an initially depressed rate followed by a pseudo first-order kinetics. The fructose production occurred at a much faster rate than that of sucrose followed by glucose. The reaction was inclined to proceed on external surface acid sites of zeolites with cleavage of terminal sucrosyl to fructosyl and terminal fructosyl to fructosyl bonds. The increase in micropore size in zeolites promoted the pore mouth catalysis for cleavage of the terminal fructosyl to fructosyl bond and terminal glucosyl to fructosyl bond, while a further increase in micropore size (such as in BEA and FAU zeolites) enabled the pore mouth catalysis for cleavage of terminal glucosyl to fructosyl bond more significantly. The mesoporosity in PMFI and PMWW zeolites enhanced external surface and pore mouth catalysis of their microporous analogues, but did not enable new type of catalytic events. The inulin hydrolysis probed, for the first time, the transition from external surface to pore mouth catalysis depending on zeolite topology and mesoporosity in bulky biomass processing.



**Figure 1.** Conversion of inulin on the basis of same acidity (A) and product selectivity ((B) sucrose, (C) fructose and (D) glucose, respectively) in inulin hydrolysis over zeolite catalyst with different micropore topology.



**Figure 2.** Conversion of inulin on the basis of same acidity (A) and product selectivity ((B) sucrose, (C) fructose and (D) glucose, respectively) in inulin hydrolysis over zeolite catalyst with different micropore topology and mesoporosity.

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□

## Mesoporous alumina with a high D4 siloxane adsorption capacity

Wei Zhong,<sup>a</sup> Ting Jiang,<sup>b</sup> Tahereh Jafari,<sup>a</sup> Altug S. Poyraz,<sup>c</sup> Wei Wu,<sup>a,d</sup> David A. Kriz,<sup>e</sup> Shoucheng Du,<sup>a</sup> Sourav Biswas,<sup>e</sup> Michael Thompson Pettes<sup>a,d</sup> and Steven L. Suib<sup>\* a,b,e</sup>

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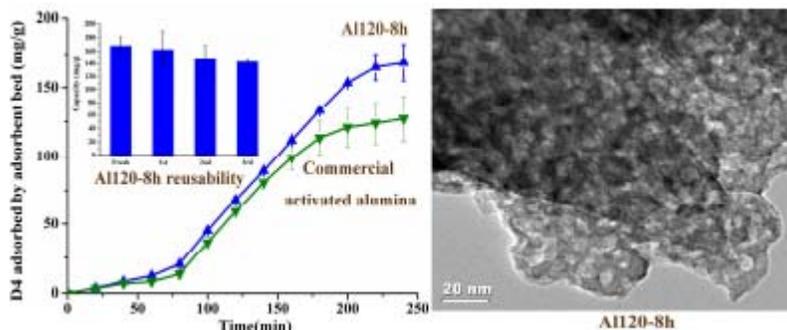
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Mesoporous aluminas (MAs) with uniform and monomodal pores were fabricated via a modified inverse micelle synthesis method, using a non-polar solvent and short reaction time. The effects of reaction times (4-8 h), surfactant chain lengths (non-ionic surfactants), and calcination temperatures and hold times (450-600 °C; 1-4 h) on the textural properties of MA were studied. The targeted pore sizes of MA were obtained in the range of 3.1-5.4 nm by adjusting the surfactant and reaction time. The surface area and pore volume were controlled by the calcination temperature and hold time while maintaining the thermal stability of the materials. The tuned MA of the large mesopore volume achieved 168 mg/g octamethylcyclotetrasiloxane (D4 siloxane) adsorption capacity, a 32% improvement compared to commercially activated alumina. After three adsorption recycles, the synthesized MA still maintained approximate 85% of its original adsorption capacity, demonstrating a sustainable adsorption performance and high potential for related industrial applications.



## **Anionic Porous Organic Frameworks for Rapid Removal of Organic Micropollutants**

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Porous organic frameworks (POFs) are an important class of porous materials for broad applications due to their excellent properties such as light weight, thermal and chemical stabilities, and high porosity. POFs can be used in gas adsorption and storage, separation, catalysis, purification, optics, energy storage and conversion. Here, we introduce new anionic porous organic frameworks (A-POFs) with phosphate functional groups. These materials are stable in strong acidic and basic conditions and have BET surface areas up to 2,019 m<sup>2</sup> g<sup>-1</sup>. The carbon dioxide uptake capacities of the polymers reach up to 103 cc g<sup>-1</sup> (1.0 bar and 273 K), making them promising candidates for CO<sub>2</sub> capture. In addition, the polymers show superior adsorption capacities and rates when adsorbing organic pollutants from water. For aqueous bisphenol A (BPA) adsorption, 1mg PAPOF-4 removes more than 90% of BPA from 80 mL 0.1 mM BPA solution within 1 hour. The maximum adsorption capacity of the material estimated by Langmiur model reaches incredibly as high as 3,366 mg g<sup>-1</sup>. It also rapidly removes various organic micropollutants of different sizes and functional groups. The material can be regenerated at least five times with no significant decrease in adsorption capacity.

# Acylation of Methylfuran with Acetic Anhydride on Brønsted and Lewis Acid Zeolites

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The first examples of Friedel-Crafts acylation were accomplished with homogenous Lewis acid catalysts such as aluminum chloride. Later, Brønsted acid zeolites were also found to be active for this chemistry and had advantages in separation, isomer selectivity and non-stoichiometric catalyst use [1]. Recently, solid Lewis acid zeolites have been developed and applied to chemistries involving the transformation of biomass [2]. The acylation of furans with zeolites is an efficient and selective means of C-C bond formation and previous work in our group has demonstrated its utility in making specialty chemicals from furans. It is thus of interest to determine how Brønsted and Lewis acid zeolites compare in Friedel-Crafts acylation of bio-derived furans. In this work, the rate of methylfuran acylation with acetic anhydride was studied for a number of Brønsted and Lewis acid zeolites. The highest initial rates were found on Lewis acid zeolites Sn-Beta and Zn-[Al]-Beta. Further study in a flow system revealed that the reaction has a much higher apparent activation energy on H-Beta compared to Sn-Beta so that at higher temperatures the rate of reaction on H-Beta surpasses that on Sn-Beta.

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## Acylation of Furans in Acidic Zeolites – A DFT Study

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The acylation of furans is a potentially valuable process for sustainable conversion of biomass-derived furans to aromatics such as para-methyl styrene, which is widely used in making plastics. The conventional Friedel-Crafts acylation is not environmentally friendly, as it uses Lewis acid catalysts like  $\text{AlCl}_3$ , which is corrosive, toxic and produces a large volume of acidic liquid quench during removal. Acidic zeolites have been found to be alternative heterogeneous catalysts for acylation because they offer good shape selectivity and are easy to regenerate.<sup>1,2</sup> In this paper, we use density-functional theory to investigate the acylation of methylfuran (MF) by acetic anhydride on two solid acids, the Brønsted-acidic Al-BEA and the Lewis-acidic Sn-BEA.

In Al-BEA, we find classic Brønsted-acidic catalytic pathways for aromatic electrophilic substitution whereby the acetic anhydride accepts the acidic proton and dissociates to form the acylium cation that subsequently electrophilically substitutes a hydrogen in the MF ring.

In Sn-BEA, the nature and structure of the active site changes, depending on whether the Sn metal center is hydroxylated or not. The unhydrolyzed (“closed”) site behaves in a purely Lewis-acidic fashion whereby the acylium cation attacks the aromatic ring of MF while the acetoxo anion is stabilized by coordination to the metal center. Remarkably, we find that the hydrolyzed (“open”) active site has a mixed Lewis acid-Brønsted acid character, the latter by virtue of the silanol group (SiOH) in the vicinity of the hydroxylated metal center. Contrary to expectations, we find that the catalytic pathways that actively involve the SiOH of the “open” site are Brønsted-acidic in character and favored over those in which the SiOH is a mere spectator.

We present full energy profiles of all the calculated reaction pathways and make direct contact with available experimental data by computing turnover frequencies using the energy span model of Kozuch and Shaik.<sup>3</sup>

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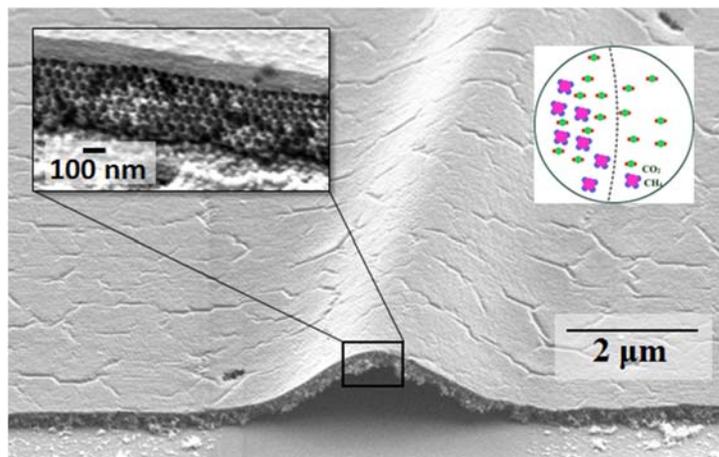
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## Fabrication of asymmetric, hierarchically porous polyimide-derived carbon thin films by hard templating

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The promise of inorganic membranes such as carbon molecular sieves (CMS) to revolutionize continuous high-selectivity gas and liquid separations has been quelled, in part, by persistent struggles to break through commercial performance barriers associated with the well-known trade-off between permeability and selectivity. Synthetic challenges common to CMS and other inorganic membrane materials include the need to minimize defect-free membrane thickness while simultaneously tailoring membrane texture and function as well as improving areal scaling in order to meet stringent demands for industrial separations. In this poster, we will present a facile hard-templating approach, which we have recently extended to produce ultra-thin microporous polyimide-derived CMS films that are self-supported on three-dimensionally ordered mesoporous (3DOM) carbon layers (Figure). This approach exploits convectively deposited, size-tunable silica nanoparticle colloidal crystal films as a sacrificial template and poly (pyromellitic dianhydride-co-4,4'-oxydianiline) (PAA) as the carbon source used for replicating the template voids. Replication is carried out by tuning viscosity of the PAA molecular replica precursor solution to facilitate infiltration into the template voids by simple immersion, followed by controlled spin-off of excess precursor. Precursor spin-off rates and the multi-layer thickness of the sacrificial template itself provide handles for independently controlling the thickness of the CMS over-layer and supporting 3DOM underlayer, respectively. A key feature of the hard-templating approach discussed in this poster is the multi-scale role of the silica colloidal crystal template. Namely, in addition to establishing mesoscale structure of the 3DOM underlayer, we find that the template-replica interface can be exploited to tune microscale structure as well. Specifically, we find that the  $sp^2$  carbon allotrope content, the origin of microporosity in CMS materials, is sensitive to and tunable by template and processing conditions as assessed by Raman spectroscopy. This poster will also highlight the process of polymer-mediated transfer of the asymmetric films among substrates (e.g., porous supports), and 'one-pot' template-replica co-assembly strategies that hold promise for transitioning from flat to three-dimensionally corrugated films, and, thereby, dramatically improving membrane area per volume.



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# Revealing Pathway of Zeolitic Imidazolate Frameworks Formation in Solution

**Debasis Banerjee,<sup>1</sup> Maxwell W. Terban,<sup>2</sup> Jinhui Tao,<sup>1</sup> Sanjit Ghose,<sup>3</sup> Benjamin A. Legg,<sup>1</sup> Simon L. Billinge,<sup>2</sup> James J. De Yoreo,<sup>1,4</sup> Jun Liu<sup>4,5</sup> & Praveen K. Thallapally<sup>1</sup>**

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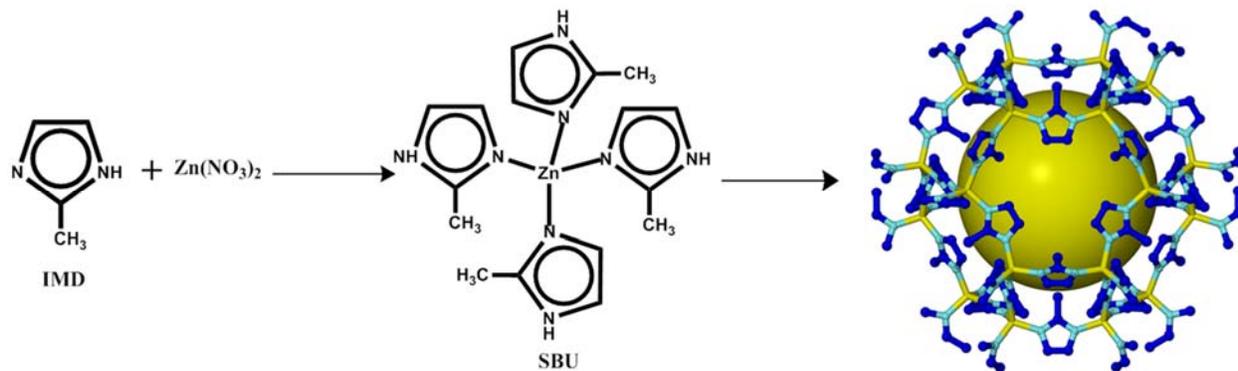
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Understanding the formation mechanism of matters at their native environment is a significant challenge that includes geological material and a significant number of *man-made* synthetic materials. For pure-organics, the mechanism of formation is well understood, partly because of the restricted coordination chemistry of carbon atom. The challenge is more daunting for pure inorganic or organic-inorganic hybrid materials because of the ensemble of mechanisms that can lead to their formation. *Ex-situ* time dependent technique is attempted but they are not necessarily representative of their *actual* synthetic condition, while *in-situ* techniques depicting the actual synthesis condition is often difficult to monitor accurately, particularly for soft inorganic-organic hybrid materials such as Metal Organic Frameworks (MOFs) because of the electron beam induced damage. Given the potential application of MOF materials in gas-adsorption-separation, catalysis and photonics, it is imperative to understand the formation mechanism of MOFs and related materials with atomic scale precision. Herein, we report the formation pathway of a benchmark MOF material, ZIF-8 using *in-situ* Pair distribution function (PDF) technique, complimented by ESI-MS and molecular simulation and transmission electron microscopy (TEM) study.



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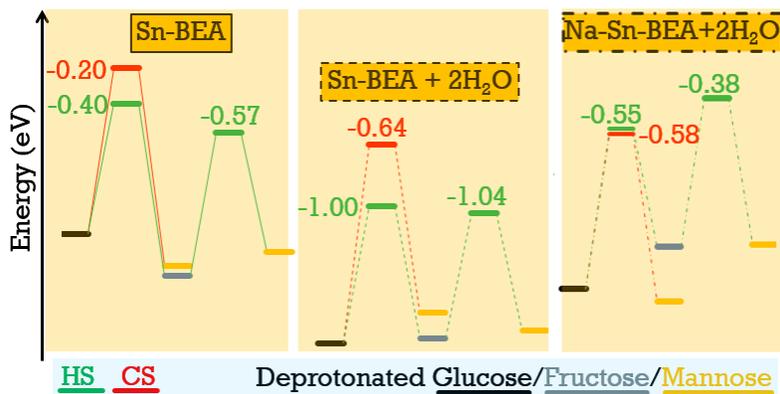
# On the Role of Na Cations and Solvent in Glucose Isomerization and Epimerization in Sn-BEA

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The efficient conversion of glucose to platform chemicals such as 5-hydroxymethylfurfural (HMF) is crucial in establishing new green chemistry routes to useful products ranging from transportation fuels to chemical intermediates. Since the direct conversion of glucose to HMF is challenging, isomerization of glucose to fructose provides an alternative path for the transformation by taking advantage of the favorable dehydration process of fructose to HMF. Davis and coworkers<sup>1,2</sup> have recently demonstrated that the hydrolyzed metal site of the Lewis-acidic zeolite Sn-BEA is particularly selective to glucose-fructose isomerization. However, the selectivity tilts in favor of the epimerization reaction to mannose in Na-exchanged Sn-BEA (Na-Sn-BEA). So far, no one has been able to explain the selectivity switch in the presence of Na cations. In this work, we explore the isomerization and epimerization reactions using periodic density functional theory (DFT) simulations, aim to understand the role of Na<sup>+</sup> and of the water solvent in determining the selectivity of the hydrolyzed (“open”) active site of Sn-BEA.

Isotope labelling experiments have shown that glucose-fructose isomerization proceeds via a hydride shift (HS) from the C2 to the C1 carbon atom, while there are two pathways for mannose production: a second HS from C1 to C2 through fructose or an intramolecular carbon shift (CS) from C2 to C1. We investigated all three pathways on Sn-BEA and Na-Sn-BEA to understand the Na effect and the water solvent effect was explored by including explicit water molecules in our simulations. Our calculations show that in Sn-BEA, the HS to fructose is preferred to the CS pathway to mannose by 0.20 eV (**Figure 1**), while the HS pathway to mannose via fructose, is preferred to the direct CS pathway by 0.37 eV, in complete agreement with experiments. With water solvent present in the vicinity of the Sn-BEA active site, we find even greater selectivity towards the HS pathway to fructose. The higher HS selectivity can be attributed to the extended hydrogen bonding network between water and the sugar, which has little effect on the HS but hampers the C3-C6 moiety shift from the C2 to the C1 carbon. In Na-Sn-BEA, the direct CS pathway to mannose is preferred to both HS pathways to fructose and to mannose. In water solvent, the combined inhibition effect of Na<sup>+</sup> on HS together with the promotion effect on CS result in a shift in reaction selectivity from fructose to mannose, in complete agreement with experiments. Our calculations resolve for the first time the role of water and Na cations in the chemistry while rationalizing the experimental data.



**Figure 1.** Potential energy profiles for glucose isomerization and epimerization on Sn-BEA and Na-Sn-BEA w/o water presence. Green and red lines represent the hydride shift and carbon shift pathway, respectively. Numbers on the plot give transition state energies relative to the infinitely separated gas-phase glucose.

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## Synthesis of Nanoporous Materials for Energy Applications

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Nanoporous metal-based materials are particularly interesting for catalytic applications because they have large surface area, nano-sized walls, and three-dimensionally interconnected networks, thus exhibiting unique physical and chemical properties compared to other nanostructure and bulkier counter parts. Here, we present two techniques, dealloying and hard templating, to synthesize unique nanoporous materials. In dealloying, a metallic alloy containing binary or ternary elements is selectively leached which removes the less noble species, resulting in a highly porous metallic structure. Similarly, hard templating involves filling pores of a nanostructured template, followed by thermal treatment and then selective etching of the template which results in free standing nanoporous metal oxide/carbide/sulfide materials. Lastly, we also present their unique catalytic applications in carbon dioxide electroreduction, hydrogen evolution reaction, hydrodeoxygenation reaction, and photocatalytic decomposition.

# High-pressure Conversion of C<sub>5</sub>-C<sub>7</sub> Alkanes for Aircraft Endothermic Cooling

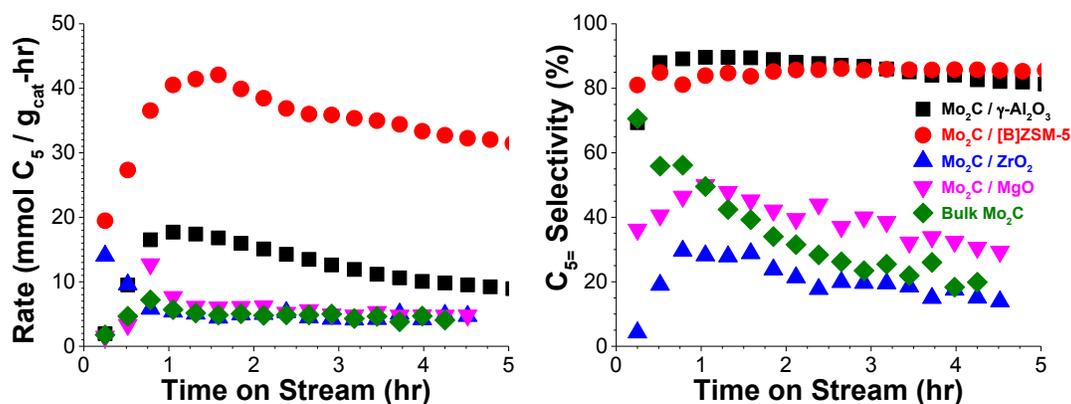
Edward P. Schreiner,<sup>1</sup> Shewangizaw Teketel<sup>1</sup>, Raul F. Lobo<sup>1</sup>

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Practical use of hypersonic planes (> Mach 5) has been hindered by overheating of aircraft engine and electronic components, caused by high fuel combustion rates and air friction<sup>1</sup>. Current military aircraft can use jet fuel as a heat sink, but future hypersonic aircraft will exceed the cooling capacity of the fuel<sup>2,3</sup>. Cooling capacity can be increased through use of so-called endothermic fuels, which remove thermal energy produced by the aircraft through endothermic chemical reactions<sup>4,5</sup>. Cracking reactions are endothermic and the solid acid zeolite, H-[Al]ZSM-5, was chosen to catalyze these reactions as it is known to yield light olefins with high selectivity in fluidized catalytic cracking units<sup>6</sup>. It was found, however, that secondary bimolecular reactions on H-[Al]ZSM-5 controlled product distribution and reduced process endothermicity<sup>7</sup>. Subsequently, supported molybdenum carbide catalysts were investigated as they can react with numerous hydrocarbons producing olefins<sup>8</sup>.

A number of pure and supported molybdenum carbides were investigated for the dehydrogenation of *n*-pentane. Two samples provided the highest reactivity and selectivity toward pentenes: Mo/H-[B]ZSM-5 (zeolite support) and Mo/Al<sub>2</sub>O<sub>3</sub>. These two catalysts exhibited an induction period, with the highest reaction rates observed 1 h after the start of the reaction. This increase in reactivity indicates that the most active form of the catalyst was formed in the reactor by interaction with the reactant. Slow deactivation was observed over the 5 h on stream investigated, but unlike the other catalysts tested, the selectivity of the dehydrogenation product from the zeolite support did not change with time on stream. Dehydrogenation of *n*-hexane and *n*-heptane were also tested on the most active catalysts.

The Mo/H-[B]ZSM-5 catalyst showed the highest conversion of all the catalysts investigated, while maintaining the same high selectivity towards the dehydrogenation product as Mo/Al<sub>2</sub>O<sub>3</sub>. Furthermore, by using H-[B]ZSM-5, the undesirable secondary bimolecular reactions observed in acidic H-[Al]ZSM-5, which include oligomerization and dehydrocyclization reactions, were suppressed, preserving the desired olefinic product.



**Figure 1.** Rates and pentene carbon selectivity of pentane conversion on various molybdenum carbide catalysts. Conditions: P = 40 bar, T = 723 K,  $m_{\text{cat}} = 100$  mg, WHSV = 188 g<sub>C<sub>5</sub></sub>/g<sub>cat</sub>-hr, residence time ~ 0.6 s.

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