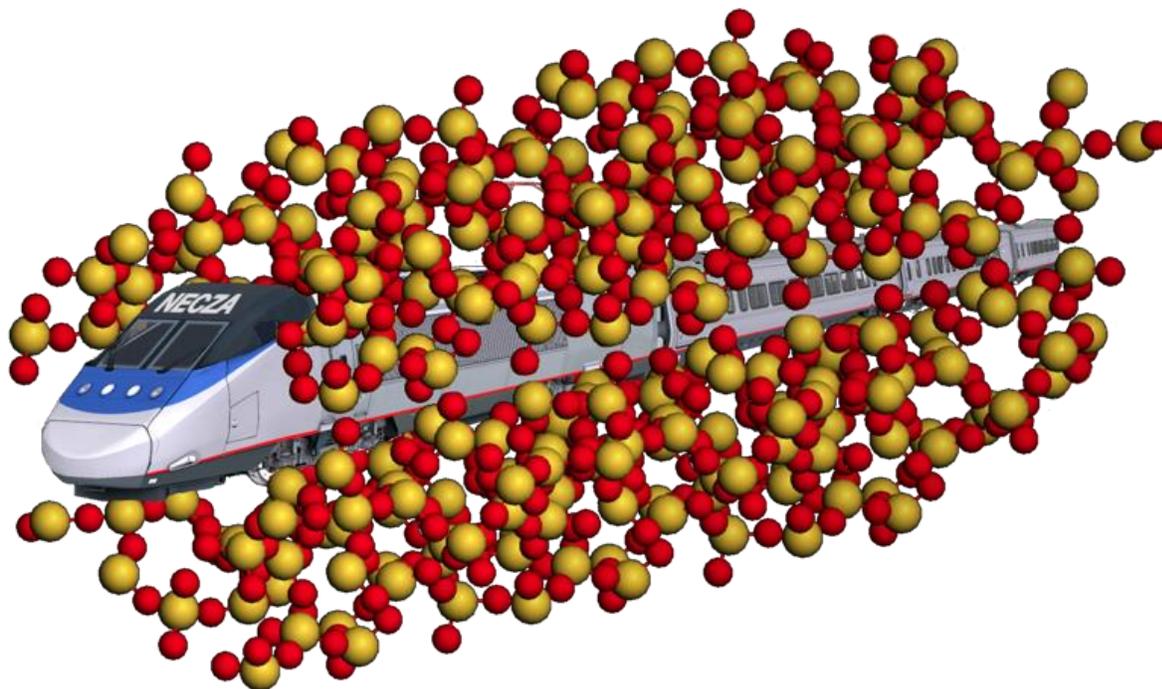


# **NECZA 2019**

## **The 23<sup>rd</sup> Meeting of the North-East Corridor Zeolite Association**



**Friday, December 6, 2019**

**The Bodek Lounge, Houston Hall**

**3417 Spruce St.**

**University of Pennsylvania**

---

---

## 23<sup>rd</sup> Annual NECZA Meeting – Organizing Committee

---

President:	Josh Pacheco	<i>Zeolyst International</i>
Secretary:	Ned Corcoran	<i>ExxonMobil Corporation</i>
Program Chair:	Nicholas McNamara	<i>Johnson Matthey</i>
Past Program Chair:	Bingjun Xu	<i>University of Delaware</i>
Poster Session Chair:	Marat Orazov	<i>University of Delaware</i>
Arrangements Chair:	Preeti Kamakoti	<i>ExxonMobil Corporation</i>
Treasurer:	Anton Petushkov	<i>Zeolyst International</i>
Webmaster:	Kirk Schmitt	<i>ExxonMobil Corporation</i>

---

*The organizing committee is grateful for the following contributions that help make this meeting possible*

### 2019 Sponsors



## Scientific Program

- 8:15 – 8:55**      ***Registration, Breakfast, Poster Setup***
- 8:55 – 9:00**      ***Welcome Remarks***
- 9:00 – 9:40**      **Allen Burton (ExxonMobil Research and Engineering Company)**  
“Design Strategies for the Synthesis of Zeolites with Large or Extra-Large Features”
- 9:40 – 10:20**      **Istvan Halasz (PQ Corporation R&D Center)**  
“Exploring Delicate Structural Features on Zeolites via Combined Experimental and Computer Simulation Methods”
- 10:20 – 11:00**      ***Coffee Break – Poster Session I***
- 11:00 – 11:40**      **Tracy M. Davis (Chevron Energy Technology Co.)**  
“Targeted Discovery: Small Pore Zeolites for Industrial Applications”
- 11:40 – 12:20**      ***Poster Session II***
- 12:20 – 1:20**      ***Lunch and Business Meeting***
- 1:20 – 2:00**      **Javier Garcia-Martinez (Universidad de Alicante)**  
“Recent Advances in the Textural Characterization of Hierarchically Structured Nanoporous Materials”
- 2:00 – 2:40**      **Selected Poster Presentations (2 x 15 min each)**
- 2:40 – 3:00**      ***Coffee break***
- 3:00 – 3:40**      **Eric Bloch (University of Delaware)**  
“Gas Storage in Porous Coordination Cages”
- 3:40 – 4:20**      **William F. Schneider (University of Notre Dame)**  
“Proximity matters: Catalytic consequences and control of active site proximity in zeolites”
- 4:20**              **Final remarks and meeting adjournment**
- 5:30**              ***Optional Chinese banquet at Sang Kee Noodle House (3549 Chestnut Street, Philadelphia, PA 19104)***

# Design Strategies for the Synthesis of Zeolites with Large or Extra-Large Features

Allen Burton

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

## Abstract

Organic structure directing agents (SDAs) are instrumental in guiding the formation of high-silica zeolites. A strategy in our efforts has been to avoid the promotion of common zeolites (e.g. ZSM-5, ZSM-12) by employing diquatery ammonium molecules (diquats) with bulky end groups that make them unlikely to fit within the channel systems of these “default” phases. Although these prior efforts produced a few novel zeolites phases, we still were unable to avoid known phases like ZSM-50 (EUO) or the SSZ-26/33 family of zeolites. We postulated that the placement of additional bulk within the center of the diquatery ammonium molecules would make the SDA molecules less likely to form common materials. To be effective SDAs, it is also important that the molecules be relatively stable under the conditions of synthesis. Zeolites are typically prepared under highly basic conditions at high temperatures, and the first appearance of a novel zeolite may require weeks or even months of heating. To this end, we have prepared diquat molecules with phenyl or cyclohexyl cores that have at least 3 methylene carbons between them and the bulky end groups. This family of molecules provides many avenues for design in terms of the o,m, or p-placement of the methylene chains to the phenyl core, the nature of the core, the nature of the ends groups, and the length of the methylene chains. Small changes in this family have dramatic effects on the zeolite phase selectivity. This strategy led to the discovery of zeolites with novel frameworks: EMM-28, EMM-31, EMM-41, and EMM-59.

We continued the theme of bulky SDA molecules by examining quats or diquats synthesized from benzimidazolium derivatives. These efforts led to the discovery of zeolites that either have very large cages or extra-large pores or windows. In one case, we discovered a highly siliceous composition of a zeolite that previously has been prepared as a low-silica zeolite. Our examination of this material led to the realization that the diquatery ammonium analogues have the ability to intramolecularly pi-stack to form large molecular assemblies. Here we introduce the concept of intramolecular assembly that is akin to folding of biologically-based

macromolecules. We subsequently designed other molecules that can intramolecularly pi-stack by using simple 1-step alkylation reactions with inexpensive chemical reagents. We will show how these easily prepared molecules are able to direct zeolites that previously required molecules that are expensive or difficult to prepare. Furthermore, we will show how some of these molecules are able to make “exotic” zeolite phases in compositions not previously attainable.

### **Bio sketch**

Allen Burton received his Ph.D. from the University of Delaware (1995-2000) where he worked with Professor Raul Lobo. He did a short post-doc at Cal Tech with Professor Mark Davis and then worked at Chevron in Richmond, CA for 8 years. Since December 2009 he worked at ExxonMobil in Clinton, NJ. He is an inventor/co-inventor on at least 50 patents or pending patent applications relating to zeolite synthesis, zeolite modification, or zeolite applications.



# Exploring Delicate Structural Features on Zeolites via Combined Experimental and Computer Simulation Methods

Istvan Halasz

*PQ Corporation R&D Center  
Conshohocken, Pennsylvania*

## Abstract

Researchers usually have assumptions and conjectures about the structural cause when see some unexpected phenomena pertaining to a just made zeolite. Yet, when it seems not to be critical, they often skip or postpone the tedious work needed to a thorough exploration of the cause especially in industrial R&D environment. Here I will show three examples when PQ R&D researchers along with some non-PQ colleagues indeed went after the deeper understanding of some peculiar phenomena pertaining to variously made and treated zeolites.

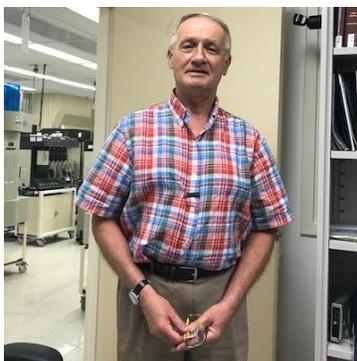
One example relates to an unexpectedly large difference between the FTIR spectra of the Brønsted acidic hydroxyls (BA-OH) on a commercial SAPO-34 material when measured with diffuse reflectance (DRIFT) and transmission (TR) sampling techniques. We proved that DRIFT emphasizes sites from a 15-20 Å deep surface layer of crystallites while TR emphasizes the average of bulk sites. Also ascertained that, contrary to suggestions in the literature, the surface specific BA-OH sites are not phosphorous related. They belong to an Al atom on the surface positioned into a geometrically specific lattice position.

In the second example we deal with the cause of the strong hydrophobicity of two commercial, proton exchanged, Si/Al ~ 40 ratio Y zeolites from Zeolyst International, CBV 901 and CBV 780. The former one adsorbs about one order of magnitude less water than a Si/Al ~ 4330 ratio MFI structured Silicalite while the latter one adsorbs about twice as much water than the Silicalite. Employing the above-described DRIFT versus TR FTIR comparisons, we show that the CBV 901 crystallites are surrounded with a thin hydrophobic layer, which has no BA-OH groups. Using computer modeling, we compared the role of the Al associated BA-OH groups and the Si-OH containing lattice defects to explain why two hydrophobic Y zeolites with identical Si/Al ratios adsorb substantially different amounts of H<sub>2</sub>O.

The third example is about the stability of hydroxyl nests  $[\text{Si-OH}]_4$  in acid leached zeolites. We could not detect with thermogravimetry and FTIR spectroscopy any sign of the presence of such nests when about 20% of Al was “rived” out from a Si/Al  $\sim 2.55$  ratio commercial Y zeolite (CBV 100), even when the material remained at room temperature during the whole process. Despite the wide spread belief that a thermally stable (up to  $400^\circ\text{C}$ !)  $[\text{Si-OH}]_4$  would remain on the place of the removed tetrahedral Al atoms, we could not find any solid proof for their existence in the literature. By creating such entities artificially in computer models, we demonstrate that FTIR would be able to show their presence. Molecular dynamics calculations indicate that even if they form their existence may be ephemeral on a picosecond scale at  $25^\circ\text{C}$ .

### **Bio sketch**

Istvan obtained Ph.D. degree from the Hungarian Academy of Sciences (HAS) while studying the fundamentals of acid-base catalysis and developing efficient processes for pharmaceutical, fine chemical and petrochemical industries in the Hungarian Hydrocarbon Institute. Later his research focused on zeolite catalysis, oxide superconductor synthesis, and catalytic fume abatement from mobile and stationary exhausts in the chemical research laboratories of HAS, Technical University of Vienna, Wayne State University in Detroit and University of Iowa. He joined PQ R&D about 21 years ago to characterize the structure and properties of silica based materials. He organized scientific meetings and served in various board positions in scientific organizations, including chairing the Philadelphia Catalysis Club and being president of the North-East Corridor Zeolite Association (NECZA). Edited one book on catalysis, (co)authored ca.120 papers, book chapters and patents, and held 100 conference presentations.



# Targeted Discovery: Small Pore Zeolites for Industrial Applications

Tracy M. Davis

*Chevron Energy Technology Co.  
Richmond, CA, USA*

## Abstract

Small-pore zeolites show unique functionality in industrial applications including small-molecule gas separations and selective catalytic reduction (SCR) of NO<sub>x</sub>. As an example, Chevron's SSZ-13 and SSZ-39 small-pore zeolites continue to serve as catalysts in mobile exhaust clean-up applications worldwide. Driven by tightening air quality regulations and demands for improved separation technology, researchers are challenged to discover new small-pore zeolites with novel structures and broader composition range. Accelerated by molecular modeling and structural analysis techniques, our research program at Chevron has recently discovered more than a dozen novel small-pore zeolites.

Chevron's synthetic methodology from conception to realization of novel zeolite structures will be presented during the first part of this presentation. Subsequently, two applications for these novel zeolites will be considered: 1) light gas separation and 2) methanol conversion. It will be shown that the exemplified separations are critical processes in chemical plants and provide a low-cost alternative for recovering high purity products. In consideration of methanol conversion chemistry, small-pore zeolites with extraordinarily high ethylene selectivity will be presented.

**Bio sketch**

Tracy Davis joined Chevron in 2007 and is currently the New Business Development Manager for Materials and Catalysts. Prior to this, Dr. Davis worked as a research engineer for 10-years where she designed new zeolites for various applications including hydroprocessing of refinery feeds, gas separation technologies and emission control catalysts.



# Realizing the Commercial Potential of Hierarchical Zeolites

Javier Garcia-Martinez

*Laboratorio de Nanotecnología Molecular, Dpto. Química Inorgánica, Universidad de Alicante,  
Ap. 99, E-03690 Alicante, Spain  
Rive Technology, Inc., 1 Deer Park Drive, Monmouth Junction, NJ 08852, USA.*

## Abstract

The development of intracrystalline mesoporosity within zeolites has been a long-standing goal in catalysis as it greatly contributes to alleviate the diffusion limitations of these widely used microporous materials. During my presentation, I will discuss the main techniques that have been developed during the last years to produce zeolites with controlled mesoarchitectures comparing the different methods, their advantages and limitations. Among the different techniques used to characterize the composition, porosity and structure of these materials, I will present unprecedented insights on the formation of intracrystalline mesoporosity in zeolites obtained by *in situ* synchrotron X-ray diffraction, Atomic Force Microscopy (AFM), and Liquid Cell Transmission Electron Microscopy (Liq-TEM). By combining experimental results and theoretical calculations, the presence of intracrystalline mesoporosity was recently confirmed. Moreover, through the direct observation of individual zeolite crystals by *in situ* AFM and Liq-TEM, we have been able to provide the first time resolved visualization of the formation of mesoporosity in zeolites.

The presence of this mesoporosity was further evidenced through *ex situ* gas adsorption, which also confirmed the preservation of most of the microporosity of the zeolites. All these new insights, obtained by combining a number of time-resolved techniques, are an example of the enormous potential of current *in situ* characterization methods for the rational design of hierarchical zeolites with superior properties and optimal catalytic performance as it has been proved at lab, pilot plant, and industrial scale.

In a commercial operation in a refinery, a steady increase in LPG olifinicity was observed through replacing the incumbent FCC catalyst by another containing the mesostructured Y zeolite. Commercial data confirmed the observed trend using an equilibrium catalyst from the refinery and analyzed in an ACE unit. A gradual increase in the LPG olefinicity was also observed at the

refinery as the concentration of the FCC catalyst containing mesostructured Y zeolite in the circulating inventory steadily increased. In this commercial trial, the most important yield shift was the increase in butylene selectivity. Furthermore, a very valuable increase in gasoline octane was also observed due to a higher concentration of olefins in the lighter gasoline fraction.

The commercialization of hierarchical zeolites through the MIT spin-off Rive Technology as superior refining catalysts is an example of academic entrepreneurship, which is expected to foster the development of new hierarchical zeolites and their use in both existing processes and new opportunities. Finally, I cover other applications of hierarchical zeolites in catalysis, including biomass valorization and fine chemistry, ending with a personal view of the new directions, and opportunities in this field.

## **Bio sketch**

Professor of Inorganic Chemistry and Director of the Molecular Nanotechnology Laboratory of the University of Alicante (UA) where he teaches and leads a world's leading research center on nanomaterials for energy applications. Published extensively in the areas of nanomaterials and energy and is the author of more than twenty five patents. His latest books are “Mesoporous Zeolites” (Wiley-VCH 2015) and “Chemistry Entrepreneurship” (Wiley-VCH 2019)

Founder of the technology-based company Rive Technology, which markets the technology he developed during his Fulbright postdoctoral stay at the Massachusetts Institute of Technology (MIT). Since 2012, the catalysts commercialized by Rive Technology are already used in several refineries, significantly increasing the production of fuels and the energy efficiency of the process.

His scientific and business leadership has been recognized with some of the most important awards. In 2015 he received the Emerging Researcher and in 2018 the Kathryn C. Hach Award for Entrepreneurial Success both from the American Chemical Society. In 2014, Javier was presented with the King James I Award by the Queen of Spain. Javier is a member of the Emerging Technologies Council of the World Economic Forum, of the Young Global Academy, of the Executive Committee of the IUPAC, and Fellow of the Royal Society of Chemistry.



# Gas Storage in Porous Coordination Cages

Eric Bloch

*Department of Chemistry and Biochemistry  
University of Delaware  
Newark, DE, USA*

## Abstract

Methane and hydrogen are becoming increasingly important fuels for a variety of factors. The depletion of worldwide petroleum supplies, coupled with the constantly increasing levels of accessible natural gas reserves, make them attractive alternative fuels. Although more than 64 million American homes utilize natural gas for heating, its poor volumetric energy density of just 0.04 MJ/L, compared to 32.4 MJ/L for gasoline, has prevented the widespread use of natural gas in the transportation sector. This problem is exacerbated for hydrogen which has negligible volumetric energy density at STP. Adsorbed gas systems offer promise in this regard, contingent on the advent of porous storage materials with sufficient capacity. Porosity in network solids, including zeolites, activated carbons, and metal-organic frameworks, has been widely interrogated for decades. In molecular systems, however, it is a relatively novel phenomenon. This is somewhat surprising given the fact that porous molecules can display surface areas that rival those of metal-organic frameworks. This talk will focus on the design, synthesis, and characterization of highly porous coordination cages for small molecule storage. Further, it will detail the intriguing interplay between surface area and solubility in a class of paddlewheel-based cages. We have recently shown that these materials, which conceptually serve as soluble metal-organic framework analogs, display impressive porosity under specific synthesis and activation conditions. Although these cages are typically amorphous upon activation, a strategy in which pillaring ligands are utilized endow the materials with high crystallinity and thus compatibility with diffraction methods for the identification and optimization of gas binding sites.

**Bio sketch**

Eric Bloch is an assistant professor in the Department of Chemistry and Biochemistry at the University of Delaware. Research in his group focuses on the design, synthesis, and characterization of novel porous materials for applications related to energy, the environment, and human health. The Bloch Group is particularly focused on the realization of new hybrid inorganic/organic molecular adsorbents for the storage of small molecules. Dr. Bloch Received his PhD in Inorganic Chemistry from the University of California-Berkeley in 2014 working for Prof. Jeffrey R. Long in the area of metal-organic frameworks for gas separations and catalysis. Prior to arriving at the University of Delaware, Bloch completed a postdoctoral fellowship in the labs of Prof. Daniel Nocera at Harvard University focusing on small molecule activation with bimetallic transition metal complexes.



# Proximity matters: Catalytic consequences and control of active site proximity in zeolites

William F. Schneider

*Department of Chemical and Biomolecular Engineering  
Department of Chemistry and Biochemistry  
University of Notre Dame  
Notre Dame, IN, USA*

## Abstract

Catalytic activity in zeolites is often associated with extralattice ions that charge compensate a minority of  $\text{Al}^{3+}$  ions on a lattice primarily populated by  $\text{Si}^{4+}$ . The density of those  $\text{Al}^{3+}$  ions (generally expressed as a silicon-to-aluminum ratio, or SAR) determines the total concentration of exchangeable sites, but the proximity of the  $\text{Al}^{3+}$  ions can exert influence over the reactivity and even the chemical identity of the extralattice ions at those exchange sites. While it can be difficult to interrogate these proximity effects in the laboratory, computational (density functional theory) models provide perfect control over atom locations and an ability to ask and answer questions about how this proximity influences ion exchange and reactivity. In this presentation I will describe our work to understand the relationship between Al proximity, ion exchange, and reactivity in the context of Cu-SSZ-13 zeolites (*Science* **2017**, 357, 898) used commercially for the selective catalytic reduction of  $\text{NO}_x$  and Fe-SSZ-13 zeolites (*ACS Catal.* **2018**, 8, 10119) of interest for partial methane oxidation. I will also discuss the use of computational models to discover approaches to develop reporters of Al proximity and even to control that proximity under synthetic conditions. The work highlights the role of proximity as a key design parameter in zeolite catalysis.

## Bio sketch

Bill Schneider's expertise is in chemical applications of density functional theory (DFT) simulations. After receiving his Ph.D. in Inorganic Chemistry in 1991 from the Ohio State University, he began his professional career in the Ford Motor Company Research Laboratory working on a variety of problems related to the environmental impacts of automobile emissions. At Ford he developed an interest in the catalytic chemistry of NO<sub>x</sub> for diesel emissions control, and he has published extensively on the chemistry and mechanisms of NO<sub>x</sub> decomposition, selective catalytic reduction, trapping, and oxidation catalysis. In 2004 he joined the Chemical and Biomolecular Engineering faculty at the University of Notre Dame as an Associate Professor. At Notre Dame he has continued his research into the theory and molecular simulation of heterogeneous catalysis, with particular emphasis on reaction environment effects on catalytic materials and their implications for mechanism and reactivity. He was promoted to Professor in 2010 and awarded the H. Clifford and Evelyn A. Brosey Chair in the College of Engineering in 2016. He has co-authored more than 190 papers and book chapters, is a Fellow of the American Association for the Advancement of Science, is a Senior Editor for *The Journal of Physical Chemistry*, and was the 2018 recipient of the Giuseppe Parravano Award of the Michigan Catalysis Society.

