

NECZA 2009

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The 13th Meeting of the NorthEast Corridor Zeolite Association

Wednesday, December 16, 2009

**Lynch Seminar Room, Department of Chemistry
University of Pennsylvania**

Program:

8:30 - 9:30 Registration, Refreshment, Poster set-up

9:25 Meeting opening and Introduction

9:30 – 10:00 Raul F. Lobo (University of Delaware)

Zeolite-Host Electron Transfer Processes: New Insights and Potential for New Chemistry

10:00 – 10:30 Charles G. Coe (Villanova University)

Some Examples of Cation and Framework Influences on Selective N₂ Adsorption

10:30 – 10:45 Break, Posters

10:45 – 11:15 Thomas F. Degnan (ExxonMobil)

Dodecylbenzene Transformations: Dealkylation and Disproportionation Over Immobilized Ionic Liquids

11:15 - 11:45 Michael D. Ward (New York University)

Hydrogen-bonded “Zeolite-like” Frameworks and Functional Materials

11:45 - 1:00 Lunch

1:00 - 1:30 Kai Landskron (Lehigh University)

Chemical Synthesis with Periodic Mesostructures at Extreme Pressure

1:30 - 2:00 Dick Hinchey

The Chemistry of LZ-210

2:00 – 2:45 Break, Posters

2:35 – 2:45 Business Meeting

2:45 – 3:00 Selected poster presentation 1

3:00 - 3:15 Selected poster presentation 2

3:15 – 3:30 Selected poster presentation 3

3:30 – 4:00 Matthias Thommes (Quantachrome Corporation)

Progress and Challenges in the Structural Characterization of Micro-Mesoporous Zeolites and Hierarchical Pore Structures by Physical Adsorption

4:00 – 4:30 Possible 8th speaker

4:30 Close of meeting

Zeolite-Host Electron Transfer Processes: New Insights and Potential for New Chemistry

Raul F. Lobo*

Center for Catalytic Science and Technology, Department of Chemical Engineering,
University of Delaware

Electron transfer processes at interfaces are central to many important chemical processes and are vital to the operation of energy conversion and storage technologies such as photovoltaic devices, batteries, fuel cells, water splitting, photocatalysis, and many others. Zeolites and other porous solids are often used as hosts for electron-transfer processes because they serve to stabilize radical cations for extended periods of time. In a sense, the zeolite acts as a solvent for the organic moieties not only stabilizing intermediates but also stopping unnecessary recombination and coupling reactions. Their pore intersections serve as microreactors where intermolecular reactions are blocked from proceeding to completion.

Electron transfer of adsorbed molecules to the zeolite framework can be produced through four different processes:

- Adsorption of molecules with low ionization potentials after heating the acid zeolites to high temperatures.
- Using ionizing radiation on zeolite-adsorbate complexes to form radical cations and trapped electrons.
- Photo generation of radical species pre-adsorbed into the zeolite pores
- Spontaneous ionization of molecules with low ionization potentials without preactivation.

In this talk I will provide a short summary of some of the work that has been carried out on this topic in the recent past and I will present some recent findings on Ga-containing zeolites from our group. We show that electrons can shuttle back and forth between adsorbed molecules and zeolite acid sites with relative ease. We also show that at high temperatures acid sites can decompose through a redox channel that leaves electron trapping sites (i.e. holes) in the zeolite framework. This may have important consequences to zeolite catalytic chemistry at high temperatures. The energetics underpinning these processes will be discussed.

Some Examples of Cation and Framework Influences on Selective N₂ Adsorption

Charles G. Coe^{1*}, Thomas. R. Gaffney, John. F. Kirner, Herbert. C. Klotz, James. E. MacDougall, Scott. J. Weigel ,and Brian. H. Toby

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Selective N₂ adsorption in cation-rich zeolites has been known for over 40 years and provides the basis for the equilibrium-based production of O₂ from air. At the heart of this important process is a highly tailored adsorbent that combines the proper composition and pore structure to allow the economical production of 100 ton/day quantities of oxygen.

After giving an introduction to adsorptive separations, examples from our past research at Air Products will be reviewed and used to illustrate the remarkable importance of cation siting and structure in controlling selective N₂ adsorption. A multidisciplinary approach involving experimental synthesis, modeling, and extensive analytical characterization elucidated some new insights leading to improved air separation processes as well as other new applications. We found that both the N₂ capacity and selectivity are strongly influenced by not only the framework structure, but the type, size, location, and number of accessible and effective cations present in the zeolite. Comparisons of adsorptive properties on a series of Na, Ca, and Li exchanged X and Y type zeolites were made. In combination with known cation sitings for some of the compositions along with some additional structural findings, these studies showed that the site specific effectiveness of Li and Ca for selective N₂ adsorption was very different. Whereas Ca is effective in site II, Li is only effective in site III. Structural studies on CaLSX (Si/Al = 1.0) and ab initio calculations on six-ring clusters explain the observations and show there is a substantial difference in partial charges of Li and Ca due to local coordination geometries.

The importance of cation siting is not limited to X-type adsorbents. We also found an unexpected maximum in the N₂ capacity at ambient conditions for chabazite at a specific Si/Al ratio of 2.0 and developed a model to describe the strong variation in N₂ capacity with composition and aluminum distribution. The model also allowed us to define chromatographic chabazite-based adsorbents that can analyze trace oxygen in argon at ambient conditions, greatly simplifying the analytics for this important analysis. This review will hopefully reinforce the critical importance of using fundamental approaches to optimize adsorbent properties for a given application.

Dodecylbenzene Transformations: Dealkylation and Disproportionation Over Immobilized Ionic Liquids

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AlCl₃-based ionic liquids (ILs) supported on silica and MCM-41 have been used for disproportionation and dealkylation of dodecylbenzene (DDB) at modest reaction temperatures (~120°C). AlCl₃-based ionic liquids supported on MCM-41 were highly active for the conversion of DDB. Up to 55 mol% conversion and selectivity to benzene of up to 60 mol% at 120 °C after 2 h reaction time were found for the transformation of DDB. The molar ratio of didodecylbenzenes to benzene in the reaction product is lower than 1 over such AlCl₃-based ionic liquids supported on MCM-41. That means a part of the 1-dodecylbenzene is catalytically dealkylated and not disproportionated. An induction period (reaction time less than 2 h) has been found for such a catalyst. The catalytic dealkylation of DDB requires a high density of very strong Lewis acid sites. A detrimental influence of n-decane (used as solvent) on DDB conversion was observed. The presence of an increased amount of naphthalene in the initial reaction mixture led to a strong decrease of selectivity towards didodecylbenzenes in favor of selectivity for benzene and formation of dodecyl-naphthalene.

Hydrogen-bonded “Zeolite-like” Frameworks and Functional Materials

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Lamellar inclusion compounds synthesized by directed assembly of guanidinium organomonosulfonates (GMS) and disulfonates (GDS) display a variety of framework architectures that are characterized by “zeolite-like” pores bounded by organic walls and a common two-dimensional (2D) network of complementary guanidinium ions (G) and sulfonate moieties (S) assembly through charge-assisted hydrogen bonds. The structural robustness of this network and the versatility of organic synthesis provides an avenue to frameworks with well-defined pores with sizes, shapes and physicochemical characteristics that can be tuned systematically without loss of generic architectural features, representing a rare example of true “crystal engineering.” These pores can be occupied by functional guest molecules with retention of framework architecture, illustrating a materials design strategy wherein function and solid-state structure are regulated independently. Furthermore, guest molecules serve as templates for the cooperative assembly of a number of compositionally identical framework isomers, not unlike templating strategies employed for zeolite synthesis. Notably, the framework architecture often can be predicted based on simple steric principles that account for the relative sizes of the guest and the organosulfonate substituent. This capability has permitted the development of protocols for inclusion-based separations, design of non-linear optical materials, new prospects for lasing materials, and unusual “*endo*-inclusion” compounds. GMS compounds also display an unusual form of structural isomerism that mimics the behavior of soft matter microstructures, which exhibit order at much larger length scales. Certain GMS host-guest combinations prompt formation of tubular inclusion compounds in which the typically planar GS sheet curls into cylinders with retention of the 2D GS network. The large number of GMS host-guest combinations permits grouping of the inclusion compound architectures according to simple molecular parameters, enabling more reliable structure prediction for this class of compounds than for molecular crystals in general. In more recent developments, these frameworks have been used for the inclusion of laser dyes, with control of aggregation state, construction of “*endo*-inclusion cavities” through the use of multivalent calixarenes, and a new generation of 3D zeolite-like compounds constructed entirely from hydrogen bonds using design principles based on Archimedean solids.

Chemical Synthesis with Periodic Mesostructures at Extreme Pressure

Kai Landskron*

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The synthesis of periodic mesoporous materials has gained considerable interest since the discovery of the first periodic mesoporous material MCM-41 by surfactant directed self-assembly (soft self-assembly). While soft-assembly is widely applicable for the synthesis of periodic mesoporous oxides with amorphous channel walls it does not extend easily to periodic mesostructures of other compositions or mesostructures with crystalline channel walls. Nanocasting is a strategy that is able to circumvent these limitations and allows for the synthesis of a range of materials that are not or not easily accessible by soft-assembly. The talk will discuss nanocasting of periodic mesostructures at extreme pressure, and the synthesis of mesoporous high pressure phases. Furthermore, it will be shown that periodic mesoporous silicas with different symmetries yield different crystalline silica phases and phase morphologies when exposed to the same pressure-temperature conditions. A further topic will be diamond formation from periodic mesoporous carbons.

The Chemistry of LZ-210

Dick Hinchey*

The late Don Breck and the late Gary Skeels demonstrated that zeolite frameworks were labile and susceptible to transformations of chemical composition accomplished rapidly under mild conditions leaving essentially undamaged zeolite structures.

Many, but not all, zeolites can be treated with a solution of ammonium fluorosilicate, $(\text{NH}_4)_2\text{SiF}_6$, effecting significant, but not unlimited, framework Al extraction and Si substitution. LZ-210 is the zeolite Y (FAU) product that has been manufactured commercially in the range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 6-12. LZ-210 synthesis will be described in terms of plausible mechanisms that provide insight into the chemical nature of zeolites.

Progress and Challenges in the Structural Characterization of Micro-Mesoporous Zeolites and Hierarchical Pore Structures by Physical Adsorption

Matthias Thommes*

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A comprehensive structural characterization of novel nanoporous materials has become more important than ever for the optimization of systems used in many important existing and potentially new applications. The most popular method to obtain surface area, pore size, pore size distribution and porosity information from powders and porous solids is gas adsorption. During recent years major progress has been achieved in the understanding of the adsorption and phase behavior in ordered micro- and mesoporous materials with simple pore geometries (e.g., M41S materials). This has led to major advances in the structural characterization by physical adsorption, also because of the development and availability of advanced theoretical approaches based on statistical mechanics (e.g. density functional theory, molecular simulation). However, there are still open questions concerning the structural characterization of more complex porous systems. (e.g., micro-mesoporous zeolites, hierarchically structured, nanoporous materials).

For instance, fluids adsorbed in hierarchically structured micro-mesoporous materials can exhibit very complex, but interesting pore condensation and hysteresis behavior. A combination of phenomena such as delayed pore condensation, initiated pore condensation, pore blocking/percolation and cavitation induced evaporation can be observed, which is reflected in characteristic types of adsorption hysteresis. These complex hysteresis loops introduce of course a considerable complication and challenge for pore size/structure analysis, but if interpreted correctly (*we will also discuss pitfalls*), they can provide important information about the pore structure/network which is crucial for obtaining a comprehensive and accurate structural analysis of advanced micro-mesoporous materials.

References

- M. Thommes, Textural Characterization of Zeolite and Ordered Mesoporous Materials by Physical Adsorption, invited review article for: *Introduction to Zeolite Science and Practice* (3rd revised Edition), (Cejka, J., van Bekkum, H., Corma, A., Schüth, F., eds.), *Stud. Surf. Sci. Catal.*, **168**, Chapter 15, pp. 495-525, Elsevier, 2009.
- A. V. Neimark, K. S.W. Sing, M. Thommes, Surface Area and Porosity invited review for *Handbook of Heterogeneous Catalysis*, Second Edition (Ertl, Koezinger, Schueth & Weitkamp, eds), pp. 721 -737, Wiley, 2008.
- M. Thommes, B. Smarsly, M. Groenewolt, P.I. Ravikovitch, A.V. Neimark, Adsorption hysteresis of nitrogen and argon in pore networks and characterization of novel micro- and mesoporous silicas *Langmuir* **2006**, 22 756.
- D. P. Serrano, J. Aguado, G. Morales, J. M. Rodríguez, A. Peral, M. Thommes, J. D. Epping and B. F. Chmelka, Molecular and Meso- and Macroscopic Properties of Hierarchical Nanocrystalline ZSM-5 Zeolite Prepared by Seed Silanization, *Chem. Mater.* **2009**, 21, 641.

- Poster Abstracts -

Production of Fuel Aromatics by Catalytic Fast Pyrolysis of Biomass

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The widespread use of petroleum-based fuels has led to an unsustainable rate of crude oil consumption, and biomass pyrolysis is one possible route for producing liquid fuels from a renewable source. A zeolite catalyst present during biomass pyrolysis can direct the formation of hydrocarbon aromatics. Prior work¹ has shown that zeolites with 10-membered ring pore mouths are the more effective than other pore sizes for the formation of benzene, toluene, and xylenes (BTX) from glucose. Using this work as a foundation, the pyrolysis of glucose has been further studied over synthesized zeolite samples with five different framework types (MFI, MEL, MWW, IMF, and TUN). Silica-to-alumina ratio was also varied within each framework type to measure the effects of introducing additional Brønsted acid sites. The carbon yield of glucose pyrolysis to aromatic compounds was measured over zeolite samples using an experimental pyrolysis reactor and coupled gas chromatography. In addition to tests with glucose, samples of ZSM-5 and MCM-22 were also tested for pyrolytic formation of aromatics from lignin.

The initial results of this work have indicated that reaction of glucose occurring on exterior surface sites are undesirable, perhaps due to the lack of spatial confinement of reactants outside of the micropore network. Because of this, improving access to Brønsted sites contained within the micropores should improve catalytic yield. Samples of ZSM-5 were synthesized containing mesopores using two different methods: an alkaline desilication treatment, and an organic templating method. These samples were then tested for glucose pyrolysis activity. Future work will be focused on poisoning surface Brønsted sites using silylating agents and dealuminating agents too large to enter the zeolite micropores, and synthesizing ZSM-5 with a crystal habit allowing easier access to micropores.

ZSM-5 proved to be the most effective zeolite framework for conversion of glucose to BTX compounds with 16.7% carbon yield to BTX and 18% yield to naphthalene. Lignin pyrolysis over ZSM-5 had a BTX yield of up to 12.7%, with 8.8% to naphthalene. Higher SiO₂/Al₂O₃ was shown to have a positive impact on BTX yield for both glucose and lignin pyrolysis. Alkaline treatment also had a positive effect on BTX yield for most samples tested.

References:

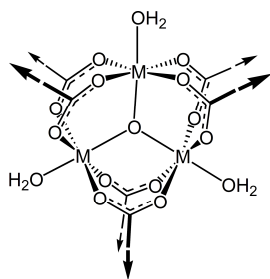
1. T R. Carlson et al. *Topics in Catalysis*. 2009, 52, 241-252.

Synthesis and Characterization of Metal-Organometallic Frameworks Derived from Cyclopentadienyliron Arenecarboxylates.

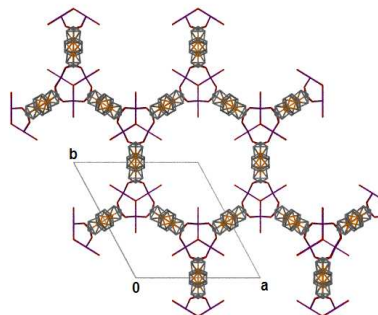
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Interest in the design and synthesis of metal-organometallic frameworks has grown drastically over the past few years. The use of multifunctional ligands, such as organometallic complexes, permits the introduction of other functionalities within the frameworks. We have synthesized and characterized a series of metal-organometallic framework (MOMF) materials derived from simple $[\text{CpFe}(\eta^6\text{-arenecarboxylate})]$ bridging ligands. Depending on the reaction conditions, solid state structures ranging from simple 1D polymer chains to flexible 3D frameworks have been obtained. For example, the reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with $[\text{CpFe}]^+$ -metalated 1,4-benzenedicarboxylic acid $[\text{H}_2\mathbf{1} \cdot \text{H}\mathbf{1}][\text{PF}_6]$ results in $[\text{Mn}_3(\mathbf{1})_3(\text{H}_2\text{O})_3(\mu\text{-O})][\text{Cl}] \cdot x\text{solv}$ (**2**), a 3D framework material consisting of manganese-oxo trimers building units. The synthesis, structure and characterization of these materials will be presented.



a) Manganese-oxo trimers (M=Mn)



b) Looking down the *c*-axis

Thermal Stability and VT Rietveld Refinement Study of Cu-SSZ-13 and Cu-SSZ-16 Zeolites

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Nitrogen oxides (NO_x) are a major atmospheric pollutant produced through the combustion of fossil fuels in internal combustion engines. Copper-exchanged zeolites are promising selective catalytic reduction (SCR) catalysts for the direct conversion of NO into N₂ and O₂ [1-10], and recently, the reports by Bull et al. at BASF have shown the enhanced performance of Cu-CHA catalysts over other zeolite frameworks in the NO decomposition of exhaust gas streams [11]. In the present study Rietveld refinement of variable temperature XRD synchrotron data obtained for Cu-SSZ-13 and Cu-SSZ-16 are used to investigate the location of copper cations in the zeolite pores and the effect of temperature on these sites and on framework stability. The XRD patterns show that the thermal stability of SSZ-13 is increased significantly when copper is exchanged into the framework compared to the acid form of the zeolite, H-SSZ-13. Cu-SSZ-13 is also more thermally stable than Cu-SSZ-16. From the refined diffraction patterns atomic positions of atoms, copper locations and occupancies, and thermal displacement parameters were determined as a function of temperature for both zeolites. Copper is found on the cages coordinated to 3 oxygen atoms of the 6-membered rings within the zeolite framework.

References:

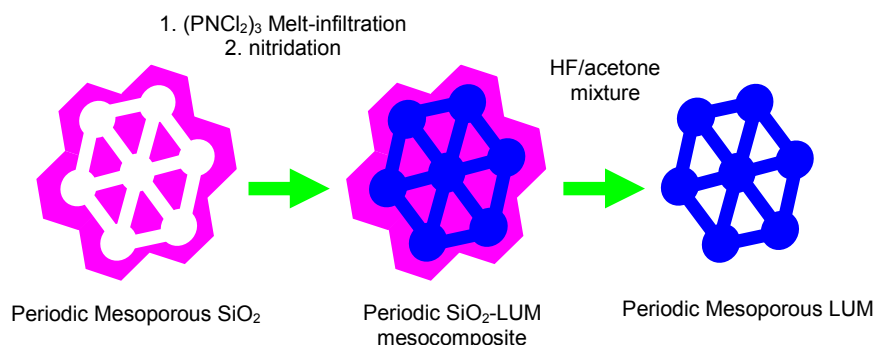
- [1] Iwamoto, M.; Yokoo, S.; Sakai, K.; Kagawa, S., *Journal of the Chemical Society-Faraday Transactions I* **1981**, 77, 1629-1638.
- [2] Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S. I.; Kagawa, S., *Journal of the Chemical Society-Chemical Communications* **1986**, (16), 1272-1273.
- [3] Iwamoto, M.; Yahiro, H.; Mine, Y.; Kagawa, S., *Chemistry Letters* **1989**, (2), 213-216.
- [4] Iwamoto, M.; Yahiro, H.; Kutsuno, T.; Bunyu, S.; Kagawa, S., *Bulletin of the Chemical Society of Japan* **1989**, 62, (2), 583-584.
- [5] Iwamoto, M.; Yahiro, H.; Shundo, S.; Yoshihiro, Y.; Mizuno, N., *Applied Catalysis* **1991**, 69, (2), L15-L19.
- [6] Iwamoto, M.; Yahiro, H.; Tanda, K.; Mizuno, N.; Mine, Y.; Kagawa, S., *Journal of Physical Chemistry* **1991**, 95, (9), 3727-3730.
- [7] Li, Y. J.; Hall, W. K., *Journal of Catalysis* **1991**, 129, (1), 202-215.
- [8] Centi, G.; Perathoner, S., *Applied Catalysis a-General* **1995**, 132, (2), 179-259.
- [9] Moretti, G., *Catalysis Letters* **1994**, 28, (2-4), 143-152.
- [10] Moretti, G.; Dossi, C.; Fusi, A.; Recchia, S.; Psaro, R., *Applied Catalysis B-Environmental* **1999**, 20, (1), 67-73.
- [11] Bull, I. B., R.S.; Jaglowski, W.M.; Koermer, G.S.; Moini, A.; Patchett, J.A.; Xue, W.M.; Burk, P.; Dettling, J.C.; Caudle, M.T. U.S. Patent. 20080226545, 2008.

Melt-infiltration Assisted Nanocasting Synthesis of Periodic Mesoporous Phosphorus-Nitrogen Frameworks Using Mesoporous Silicas as Templates

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Periodic mesoporous Phosphorus-Nitrogen (P-N) Frameworks with $p6mm$ hexagonal and $Im\bar{3}m$ body centered cubic symmetries were synthesized by a solvent-free nanocasting route using periodic mesoporous silicas (SBA-15 and SBA-16) as hard templates and $(\text{PNCl}_2)_3$ as precursor. The $(\text{PNCl}_2)_3$ was molten at 120 °C in nitrogen atmosphere and infiltrated into the pores of mesoporous silicas. The nitridization of $(\text{PNCl}_2)_3$ in an ammonia atmosphere at 700 °C followed by the SiO_2 template removal by etching with HF/acetone mixture resulted in the formation of the desired periodic mesoporous P-N frameworks with high surface area of 240 to 380 $\text{m}^2\cdot\text{g}^{-1}$ and pore volumes in the range of 0.29 to 0.53 $\text{cm}^3\cdot\text{g}^{-1}$. The excellent mesopore uniformity and periodicity of the obtained specimens were studied by electron microscopy, small angle X-ray diffraction, N_2 sorption, FT-IR, EDS, and element analysis. The materials are thermally stable up to 550 and 700 °C in an inert atmosphere depending on the pore systems and exhibit photoluminescence between 280 and 450 nm.



Schematic representation of the synthesis of LUMs

Structure and Colloidal Stability of Nanosized Zeolite Beta Precursors

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Crystal growth of zeolite beta in solutions of molar composition 1 Si(OCH₂CH₃)₄ / 80 H₂O / 0.5 TEAOH / 0.1 NaOH / 0.02 NaAlO₂ proceeds by aggregation of nanosized zeolite precursor particles near zeolite nucleation (between 6 and 20 days heating at 120°C). Amorphous silica nanoparticles (<3 nm) form spontaneously in solution at room temperature. When these solutions are heated some of these primary particles transform into larger secondary particles (6-50 nm). After 4 days of heating some of the secondary particles are stable as spheroidal monomers and others are unstable and aggregate. The secondary particles evolve structurally over the induction time of the synthesis from amorphous silica to zeolite beta. Simultaneously, the surface charge of the particles is changing and those particles that are highly organized aggregate into zeolite beta crystals. Zeolite beta nucleation is different from classical nucleation theory where the crystalline order changes simultaneously with the density.