# 12th NECZA Meeting

Friday, December 12, 2008  
Lynch Seminar Room, Chemistry Department  
University of Pennsylvania

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Hierarchical Nanomanufacturing of Porous Metal Oxide Materials:  
From Ordered Nanoparticulate Films and Gels to Templated Zeolite Synthesis |
| 4:00 - 4:30 | **Joe Fedeyko (Johnson Matthey)**  
Development of Thermally Durable Cu/SCR Catalysts                         |
| 4:30     | Meeting conclusion                                                       |
Unique Studies Into the Structure-Property Relationship of Inorganic Materials

Tina M. Nenoff
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Selectivity for ion exchange in zeolites and molecular sieves is dependent on a number of factors including pore size and shape, framework composition, and surface adsorption properties. In an effort to establish a comprehensive knowledge base for tuned framework design, our research is directed toward developing a structure/property relationship between zeolites and their ion exchange capabilities. In particular, we are interested in the role of the occluded water molecules.

We have focused on two different sieving systems: Sandia Octahedral Molecular Sieves (SOMS; $Na_2Nb_{2-x}Ti_{x}O_{6-x}(OH)_x\cdot H_2O$) and traditional aluminosilicate zeolites, like Clinoptilolite ($[X]_{4-6}[Al_6(Al, Si)_4Si_{26}O_{72}]\cdot xH_2O$). Characterization methods used in this study include inelastic neutron scattering (INS), MAS NMR, crystallographic structure refinement, and modeling/simulation. The correlation between structure and property of the materials studied will be discussed.

- INS and NMR data of the SOMS indicate that the water in high exchange materials can be described as rotationally free, highly-mobile and bulk-like water species. In sharp contrast, the occluded water in a low exchange analog behaves Ice-like and is one of the most rigid water environments investigated in inorganic materials to date.

- By contrast, studies with the CLI/HEU systems show that the charge density of the extra-framework cations have the greatest influence on occluded water molecules, while the anionic charge of the framework (Si:Al) has a lesser impact. MD simulations support the INS and NMR data for all systems studied.

Sandia is a multiprogram laboratory operated by Sandia Corporation, Lockheed Martin Company, for US DOE’s NNSA, Contract DE-AC04-94-AL85000.
Selective oxidation catalysis is used in production of roughly 25% of all important organic chemicals and intermediates used for making consumer and industrial products [1]. Current processes used to produce high-demand C3 derivatives, namely acrylic acid and acrylonitrile, make use of multicomponent bismuth molybdate catalysts with propene feeds [1-2]. Significant cost savings exist if propene can be replaced by propane as the feedstock. The dominant candidate for this process is based on the multiphase MoVTeNbO complex oxide system [1-3]. The best MoVTeNbO catalysts with respect to selectivity and activity are two-phase mixtures comprised of a nanoporous orthorhombic network bronze majority phase (M1) and a hexagonal tungsten bronze (HTB)-type minority phase (M2) [2-3]. Structural models currently exist for both phases based on simultaneous Rietveld refinement of high-resolution synchrotron X-ray and neutron powder diffraction data [2]. The focus in this talk will be on the nanoporous M1 phase. As an extension of this work, we have characterized several compositional and structural variants. These include omission of Te and/or Nb, replacement of Nb with Ta [5,6], Te with Sb, and changing the basic framework structure. Understanding relationships between crystal chemistry, structure, and catalyst performance is central to the development of these catalysts.

References
A mineralogical approach to the discovery of new synthetic zeolites-PSU-2, PSU-3, PSU-4.

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Routine examination of zeolite synthesis reaction products usually is restricted to an X-ray diffraction analysis and occasionally a cursory SEM analysis. Powder XRD usually misses phases in concentrations less than about 5% and SEM pictures a small sample. Our main interest is in synthesizing large zeolite crystals for X-ray structure analysis and we routinely examine reaction products using a stereo optical microscope at a magnification between 20 and 100. This facilitates a large field of view and different morphology phases can be readily observed at concentrations much less than 1%. Such an approach has resulted in the recognition of several new structures. PSU-2 is an orthorhombic potassium aluminophosphate (a=12.74 Å; b=10.22 Å; c=6.22 Å). PSU-3 is a monoclinic ammonium aluminophosphate (a=9.60 Å; b=9.55 Å; c=9.60 Å; α=90°; β=103.7°; γ=90°). Both PSU-2 and -3 are built from 3-rings. PSU-4 is a cubic potassium gallosilicate with an equivalent structure found in the IZA/Treacy file of theoretical zeolite structures.

Molecular Aspects of Silica Gel Formation

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Gelling is an important phase in the formation of zeolites, mesostructured silicates, catalyst supports, adsorbents, coatings, adhesives, fillers, insulators, and many other commercial products made from various silica sources most commonly from the relatively cheap aqueous alkaline silicate solutions. Despite a long history of related technologies, the gelling process relies mostly on empirical skills since little is known about the molecular constitution of either the dissolved or the gelled silicates and even less about the networking steps of the former molecules into the latter structure. The general view is that a random set of separate siloxane rings connects into a random 3D network of larger and smaller rings hence the molecular constitution of any amorphous silica gel is indistinguishably similar to any other one.

In this talk we will show examples for alkaline silicate solutions and silica gels having distinctly different $Q^0$, $Q^1$, ...$Q^4$ connectivities and siloxane rings which can be detected by the quick, relatively cheap, non invasive FTIR and Raman spectroscopic techniques. Examples for some difficulties pertaining to modeling realistic vibrational spectra of silica molecules and testing in situ the formation of D4R structured $[(\text{Me}_4\text{N})_8(\text{Si}_8\text{O}_{20})] \times 65 \text{ H}_2\text{O}$ crystals from TEOS containing solutions will also be presented.
Metal-Organic Frameworks (MOFs) for Gas Storage and Selective Gas Adsorption

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The talk consists of three parts: hydrogen storage, methane storage, and mesh-adjustable molecular sieves in MOFs.

Hydrogen Storage in MOFs

For any potential hydrogen-storage system, raw uptake capacity must be balanced with the kinetics and thermodynamics of uptake and release. MOFs provide unique systems with large overall pore volumes and surface areas, adjustable pore sizes, and tunable framework–adsorbate interaction by ligand functionalization and metal choice. These remarkable materials can potentially fill the niche between other physisorbents such as activated carbon, which have similar uptake at low temperatures but low affinity for hydrogen at ambient temperature, and chemical sorbents such as hydrides, which have high hydrogen uptakes but undesirable release kinetics and thermodynamics.

Representative articles:
Methane Storage in MOFs

The search for alternative fuels has led to the development of research in the field of methane storage. Metal-organic frameworks (MOFs) can be feasible candidates for methane storage due to their large surface areas, uniform and adjustable pore sizes, and modifiable pore walls. Research is being conducted in the field of MOFs to meet the Department of Energy’s methane storage target of 180 v/v (standard temperature and pressure equivalent volume of methane / volume of the sorbent). While several MOFs have been evaluated for methane storage previously, none met the DOE target. Recently, a MOF containing nanoscopic cages that provides an absolute methane uptake of 230 v/v has been made in our laboratory. Efforts will continue to produce methane storage materials with even greater adsorption capabilities at affordable costs.

Representative articles:

MOF-Based Mesh-Adjustable Molecular Sieves

Inorganic zeolite molecular sieves are currently the most commonly used adsorbents in industry for gas separation. The rigidity of the bonds in zeolites affords them with fixed mesh sizes, which is advantageous when the mesh size precisely fits the separation needs. However, when the size disparity of the two gases is very small, a zeolite molecular sieve with the precise mesh size is not always readily available. In such cases, mesh-adjustable molecular sieves (MAMSs) that can always meet the separation needs are highly desirable. Recently, we developed the MOF-based mesh-adjustable molecular sieves. These MAMSs typically have a graphitic structure consisting of hydrophilic channels and hydrophobic chambers, which are interconnected with each other through a size-adjustable mesh. The mesh size is linearly related to temperature. Therefore, by precisely controlling the temperature, one can achieve an accurate pore-size, which is essential for a clean separation of a gas mixture by size-exclusion methods. Our ongoing work focuses on designing and systematically tuning the ligands to tailor the adsorption properties of MAMSs to achieve gas separation at ambient temperatures and applicable pressures.
Representative article:
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. Using a combinatorial library of 24 GMS hosts and 26 guest molecules, a total of 304 inclusion compounds out of a possible 624 possible host-guest combinations were realized, revealing a remarkable capacity of the GMS hosts to form inclusion compounds despite the facile formation of the corresponding guest-free compounds and the absence of “predestined” inclusion cavities like those in related guanidinium organo-disulfonate host frameworks. 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 cylinders assemble into hexagonal arrays through interdigitation of the organosulfonate residues that project from their outer surfaces, crystallizing in high symmetry trigonal or hexagonal space groups. 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.
Hierarchical nanomanufacturing of porous metal oxide materials: From ordered nanoparticulate films and gels to templated zeolite synthesis

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Drawing motivation from ubiquitous biomineralized silica structures in nature, we recently identified the formation of stable, highly monodisperse silica nanoparticles resulting from the hydrolysis of a silica source in aqueous amino acid (e.g., L-Lysine) solutions.\(^1\)\(^-\)\(^3\) Despite its simplicity, this benign (i.e., more neutral pH) approach yields a range of handles capable of tuning highly monodispersed silica nanoparticles in the once elusive range from 5 nm to more than 25 nm. Particle stability has been found to persist even after further purification of the nanoparticle sols. Facile particle assembly into colloidal crystals and ordered nanoparticle films\(^2\) or porous gels\(^4\) has been realized by respective evaporation-induced convective assembly and di-lysine titration.

The aim of this talk will be to highlight various stages of hierarchical materials assembly, beginning with techniques for controlled synthesis of the primary nanoparticle building units, and encompassing descriptions of their assembly into porous structures and use even as templates for synthesizing higher-order materials. In a first example application motivated by the possibility of permeselectively encapsulated cells for novel therapeutics, we will show how the physiologically relevant conditions of the nanoparticle sols and the ability to trigger nanoparticle assembly can be employed for three-dimensional encapsulation of living mammalian cells within a porous silica gel.\(^4\) In a second example, we will highlight how colloidal crystals composed of the size-controlled silica nanoparticles serve as versatile templates for the formation of three-dimensionally ordered mesoporous (3DOM) carbon replicas. Subsequent use of these replicas for confined materials (e.g., zeolite) synthesis has led, for the first time, to size-tunable, uniformly shaped silicalite-1 nanocrystals and 3DOM-imprinted single crystal zeolite particles.\(^3\) The aim of the talk will, therefore, be to highlight novelties of the nanoparticle synthesis and the salient features of the resulting nanoparticle sols that make them attractive for a wide range of benign and controlled nanomaterials syntheses.

References
Development of Thermally Durable Cu/SCR Catalysts

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Selective catalytic reduction (SCR) of NOx by NH3 is under intensive development as a technology to enable diesel engines to meet stringent NOx emission regulations. Cu/zeolite SCR catalysts are leading candidates because of their ability to catalyze NOx reduction at the low temperatures encountered on many diesel vehicles. However, both engine evaluation and laboratory studies indicated that commonly available Cu/zeolite SCR catalysts did not have sufficient thermal stability to maintain performance during the full useful life of a vehicle. Characterization of aged Cu/zeolite catalysts revealed that the loss of zeolite acidity was the main deactivation mechanism. On the other hand, it was found that the zeolite support maintained its framework structure after aging. Improvement of the hydrothermal stability of the zeolite acid sites resulted in a new generation of SCR catalysts. The new catalysts exhibit higher NOx conversion over a wider temperature window and excellent hydrothermal stability. These improvements were confirmed under both laboratory and engine testing conditions.
Commensurate Adsorption in the Metal Organic Framework RPM-5

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RPM-5 is a 1-dimensional, medium pore size metal organic framework with a pore size and volume similar to that of ZSM-5. Both materials show commensurate adsorption of several different hydrocarbon materials.

Commensurate adsorption refers to cases where adsorption levels/capacities are controlled by specific channel features such as channel segment lengths, or cavity shape and size. It results in the number of molecules adsorbed per unit cell relating to crystal symmetry, e.g. multiplicity of general or special crystallographic positions. Commensurate adsorption of benzene, p-xylene, propanol and butanol in RPM-5 will be described where 8, 4, 8 and 8 molecules per unit cell, respectively, are adsorbed.

A novel faujasite occurrence in a Jordanian volcanic ash.

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Several years ago a new faujasite occurrence was reported from the Aritayn volcanic formation in Jordan (Ibrahim et al (1995)). Analysis of a “grab sample” of a mixed volcanic ash from the location showed the presence of several zeolites by X-ray diffraction and confirmed by optical microscopy. However, no crystals were observed having the expected typical faujasite morphology in the form of variants of octahedra, even though the X-ray pattern indicated that FAU was present. Close optical microscopy examination of the sample showed many glass globules of varying shapes and sizes and within these faujasite crystals were clearly in embryonic stages of growth. Such was subsequently confirmed by SEM. Similar crystal entrapment in glasses have been observed in glass reactivity experiments.
Structure and colloidal stability of nanosized zeolite beta precursors

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The crystal growth of zeolite beta in solutions of composition 1 SiO2 : 80 H2O : 0.5 TEAOH : 0.1 NaOH : 0.02 NaAlO2 : Z B(OH)3 where Z is 0 and 0.05 was shown to proceed through aggregation of nanosized zeolite precursor particles near zeolite nucleation (between 6 and 20 days heating at 120°C) and by solution mediated monomer dissolution an addition at later heating times (Hould, N. D.; Lobo, R. F. Chem. Mat. 2008). Direct observation of these precursor particles using cryogenic transmission electron microscopy (cryo-TEM) shows that in the absence of aluminum they are spherical with a mean diameter of (16±3 nm) and that when aluminum is added to the synthesis solution they have a smaller diameter and form string-like aggregates. This observation was incorporated into a small angle scattering model used to determine that the secondary particles’ stability is dependent upon the type (or number) of heteroatoms (Al or B) in the synthesis solution. Zeolite beta crystals nucleated from solutions containing boron have a higher coherence length (by x-ray diffraction) that increases linearly with heating time similar to that for crystals formed in the absence of boron.

Crystallization of mordenite from clear solution

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Zeolite mordenite is one of the solid acid materials used in hydrocracking and isomerization processes. It has been widely prepared from hydrogel solutions in which a silica precursor and an alumina precursor are mixed and then taken to high temperature for hydrothermal synthesis. For fundamental studies, clear solutions in which all particles are in the nanometer scale have become the accepted norm. Synthesis of mordenite from clear a solution was first reported by Ueda (American Mineralogist, 65 (1980)). However, the synthesis protocol requires heating the sample to 100 °C to dissolve the gel phase by increasing the silica solubility. This step is not desirable for studying the early stages of the crystallization. We developed a new protocol to prepare mordenite starting from a clear solution at room temperature. Crystallization was studied using small angle x-ray scattering (SAXS), pH and conductivity, X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and nitrogen adsorption. SAXS showed that the starting particles grow rapidly during the first half hour from 7 nm to 25 nm and a precipitated solid is formed within the first hour. The condensation of these particles increases the pH of the system, a fact which can be attributed to the condensation reaction between charged particles and silanol groups. XRD showed that the initial particles are amorphous materials. It also showed that the crystallization process of mordenite is composed of a long induction time (20 hrs) and a rapid crystal growth (1 hr) period. Heterogeneous nucleation is proposed to be the main mechanism of mordenite crystallization in this system as indicated by electron microscopy. The absence of nanoparticles and the continuous change of pH during the crystallization course show that this is possibly a solution mediated mechanism for gel evolution and nuclei formation.
Metal-Organometallic Frameworks Derived from Facial ly Metalated Arylcarboxylates.

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In recent years, remarkable progress has been made in the use of coordination chemistry to design materials, commonly known as metal organic frameworks or coordination polymers, via the use of various transition metals and organic bridging ligands. 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 [CpFe-(η⁶-arencarboxylate)] bridging ligands. Depending on the reaction conditions, solid state structures ranging from simple 1D polymer chains to three dimensional square grid structures have been obtained. For example, the reaction of Ni(NO₃)₂·6H₂O with [CpFe]⁺-metalated 1,4-benzenedicarboxylic acid results in [Ni₃(I-H)(H₂O)₃(µ-H₂O)₂][NO₃]₂·solvent (2), a 3D framework material constructed of square grid nickel-carboxylate networks that are interconnected in the third dimension through additional nickel ions. The synthesis, structure and characterization of these materials will be presented.

Assemblies Derived From Resorcin[4]arenes and Their Derivatives

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Molecules and molecular assemblies capable of encapsulating smaller molecular species remain a subject of interest in relation to their ability to selectively bind, sequester, organize and transport their guests much like zeolites. The unifying feature of these molecular entities is that the ingress and egress of their guests is sterically restricted due to the closed surface nature of the host system. In addition, the kinetic stabilities of these host-guest complexes are greatly enhanced such that the complexes and some complexation behaviors can be studied in detail. A variety of molecular capsules have been made and may be classified broadly based on the means by which they are assembled, namely via covalent and non-covalent interactions. As the synthesis of these covalently assembled capsules are generally under kinetic control, their yields are often low. Thus there has been a continuous shift towards the use of self-assembly for their synthesis. We have sought to construct and study many component systems through the use of hydrogen bonds and metal ligand interactions. The subunits of interest are the well studied calix resorcin[4]arenes and derivatives thereof, our progress will be reported.
Acidic zeolites have long been backbone of petroleum industry as catalysts because of their high surface area, large adsorption capacities and shape selective properties. All these properties make them ideal candidates for bio-fuel industry except a basic catalyst would be a more ideal one. Amine Substituted zeolites can act as strong shape selective solid base catalyst. Nitridated zeolites have been synthesized using experiments and have shown high catalytic activity still the nature of basic sites and the mechanism of synthesis is unclear. We have performed DFT calculations to calculate the reaction pathway. The reaction proceeds via 4-ring intermediate comprising of Si-N-Si-O species. We have found that it is hard to make these catalysts and hard to break them. The high activation energy suggests the process is feasible only at high temperatures confirming with experiments. Also half life studies of these catalysts have shown that they are extremely stable at room temperature even with high water loadings. Temperature is an important factor governing stability of these catalysts.