

**The NorthEast Corridor Zeolite Association
December 13, 2002 - Philadelphia, PA
Program**

8:30-9:30 Registration (and poster set-up)

9:00-10:15 Poster Session

10:15-11:15 Janos Nagy Notre-Dame de la Paix, Namur, Belgium: "Zeolite Synthesis in Fluoride Media"

11:15-11:45 Raul Lobo, University of Delaware: "Shared Patterns of Disorder in High-Silica Zeolite Structures"

11:45- 12:15 Scott Auerbach, University of Massachusetts, Amherst: "Nonequilibrium Molecular Dynamics of Microwave-driven Zeolite-Guest Systems: Loading Dependence of Athermal Effects"

12:15- 1:15 Lunch

1:15-1:45 Camille Jones, NIST: "Cold Neutron Prompt-Gamma Activation Analysis of Hydrogen in H-ZSM-5"

1:45-2:15 Istvan Halasz, PQ Corporation: "Fast and efficient catalytic oxidation of n-hexane by aqueous H₂O₂ over TS-PQ™, a new titanium based silicate"

2:30-3:00 Break/Executive Meeting

3:00-3:30 Selected Poster presentations

3:30-4:00 Eric Senderov, PQ Corporation: "Ti Incorporation into Pentasil-Type Silicate Molecular Sieve, TSPQ"

4:00-?? Closing remarks/Informal Poster Session

Organizers: Christopher Cahill- Program Chair; David Olson- Local Chair; Istvan Halasz- All around help/advice. Ned Corcoran- Finances/Registration.

Website: http://www.gwu.edu/~cahill/necza_02.html

Abstracts (Oral Sessions)

Shared Patterns of Disorder in High-Silica Zeolite Structures

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Disorder is a frequent phenomenon in zeolite structures, a phenomenon of potentially critical importance in terms of the zeolite properties. Disorder can make the solution of zeolite structures extremely difficult, although on the other hand, there is information about crystal growth on the types of disorder and defects that are observed. In this talk I will discuss a small group of families of zeolite materials renowned for their disordered character. I will emphasize common themes that can be discovered between these families. We will start with a detailed description of disorder in zeolite ZSM-48, a structure recently reevaluated. Similarities between ZSM-48, SSZ-31 and UTD-1 will be described as well as the nature of intergrowths and epitaxy between zeolites SSZ-31 and beta. We will take a detailed look at defects in these disordered materials and will consider what they tell us as far as the detailed mechanism of crystal growth. We will learn that there is order within disorder and that the underlying common themes can help both to elucidate how zeolites grow and enlighten our understanding of the zeolite world.

Nonequilibrium Molecular Dynamics of Microwave-driven Zeolite-Guest Systems: Loading Dependence of Athermal Effects

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We have performed molecular dynamics (MD) simulations of zeolite-guest systems driven by microwaves (MW), to study how energy is distributed in these systems as a function of guest loading. Expanding on a previously published communication [J. Am. Chem. Soc. 124, 6250 (2002)], we have found that MW-driven MD with the Andersen thermostat gives robust steady states, while MW-driven MD with the Nose-Hoover chain thermostat does not. We studied MW-driven zeolites NaY, DAY and silicalite, as well as benzene and/or methanol in DAY or silicalite. DAY and silicalite exhibit little MW heating, while NaY gives strong MW heating primarily through the Na cations, whose kinetic energy was found to equilibrate on picosecond time scales. Zeolite-benzene systems show minimal MW heating, while zeolite-methanol systems exhibit significant MW heating with steady-state temperatures increasing linearly with methanol loading. MW-driven equimolar mixtures of benzene and methanol at low to medium loadings in DAY or silicalite obey $T_{\text{methanol}} \gg T_{\text{benzene}} > T_{\text{zeolite}}$, suggesting that MW heating of binary mixtures in zeolites can produce novel effects. However, MW-driven MD at higher loadings shows that $T_{\text{methanol}} \sim T_{\text{benzene}} > T_{\text{zeolite}}$, suggesting that closely related MW sorption studies can produce markedly different results viz. athermal effects.

Cold Neutron Prompt-Gamma Activation Analysis of Hydrogen in H-ZSM-5

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The success of neutron diffraction experiments in the determination of hydrogen (H) sites in ZSM-5 and other zeolitic materials from deuterated samples depends in part on the amount of H remaining in the samples. We have investigated the application of cold neutron prompt-gamma activation analysis (PGAA) to the quantitative analysis of H in H-ZSM-5. Previous results from neutron powder diffraction experiments on samples of dehydrated H-ZSM-5 back-filled with D₂O(g) indicated that at least three half-filled H sites were present.[1] However, the exact state of hydration and the total H content of those samples was unknown. In order to obtain the most accurate structure determination from powder diffraction data, H should be removed completely from samples and replaced with deuterium. Experimentally, a low H content in samples for neutron diffraction will reduce incoherent scattering, and H/D exchange will provide good isotopic scattering contrast.

Samples of H-ZSM-5 (nominal chemical formula Si₁₁Al₁O₂₄H₁) were dehydrated at 100-400 °C under high vacuum with dehydration times of 2 h to 12 h. Standards for H, Al, and Si, were prepared from mixtures of urea, Al₂O₃, and SiO₂ powders. Data were collected on the neutron guide NG-7 at the NIST Center for Neutron Research. The neutron beam was collimated to a diameter of 1 cm with a ⁶Li glass aperture. The irradiation times were 1 h to 12 h inside an evacuated sample chamber.

The elemental ratios Al/H and Al/Si were calculated rather than absolute amounts of the elements, in order to eliminate analytical bias.[2] The Al/H ratios fell in the range 0.1(0.01) to 0.7(0.05), where the ratio increased with increasing dehydration temperature and time and indicates the presence of residual H. The Al/Si ratios fell in the range 11.2(0.5) to 12.2(0.5) and were independent of temperature and time. The results obtained so far on H-ZSM-5 and other zeolitic materials identify the degree to which various methods of dehydration and H/D exchange remove H from the material. Small changes in H content in H-ZSM-5 can have an enormous impact on the appearance and interpretation of diffraction and spectroscopic data; observations from the present study may provide explanations for some of the discrepancies among results and conclusions from H siting studies reported in the literature.

A structure model for H-ZSM-5 must contain H sites with occupancy factors and total concentration consistent with quantitative results from PGAA. The method developed here for H-ZSM-5 may also be applied to the study of H content and H siting, and their implications for acid-based catalysis, in other microporous and mesoporous systems. The method of PGAA will be explained, and examples of the application of PGAA to the analysis of H content in H-ZSM-5 and other zeolitic materials will be presented.

References

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2. Paul, R. L. *J. Radioanal. Nuc. Chem.* **1995**, *191*(2), 245-256.

FAST AND EFFICIENT CATALYTIC OXIDATION OF n-HEXANE BY AQUEOUS H₂O₂ OVER TS-PQ™, A NEW TITANIUM BASED SILICATE

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The pentasil titanium silicate, TS-PQ™ (a trademark of PQ Corporation for this titanium silicate material) contains both tetrahedral and higher coordinated Ti⁴⁺ ions attached to the silicate lattice. When dehydrated, this material generates only weak UV absorption at $\geq 47,000\text{ cm}^{-1}$ that characterizes the isolated, tetrahedral, isomorphously positioned Ti⁴⁺ ions in TS-1. Liquid H₂O has little effect on the tetrahedral Ti⁴⁺ ions of TS-PQ in contrast to TS-1 that has mostly octahedral Ti⁴⁺ in H₂O. H₂O₂ develops a stronger UV band near $34,000\text{ cm}^{-1}$ on TS-PQ than on TS-1 that might be related to the high rate in the title reaction over TS-PQ. The impact of various reaction variables on catalyst activity and selectivity are discussed.

Ti Incorporation into Pentasil-Type Silicate Molecular Sieve, TSPQ

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A method has been developed for the preparation of nanosize Ti silicate molecular sieve materials of the pentasil family (MFI and MEL) based on the use of high-purity, colloidal silica sol or silica gel as a silica source [1]. Variation in size, morphology, contamination level in the product is described.

A large variety of composition and process parameters has been found to affect the degree and nature of Ti interaction with the crystalline silica matrix and the distribution of Ti between solid and liquid phases as a consequence of synthesis and post-synthesis treatment. Different types of Ti centers in a solid product have been identified and characterized by a variety of complementary analytical techniques including X-ray fluorescence (XRF) analysis, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and ultraviolet diffuse reflectance vacuum spectroscopy (FTUV DRVS), and laser Raman spectroscopy.

FTUV DRV spectra (Figure 1) distinguish additional absorption bands between the extremes typically assigned to isolated, tetrahedral, Ti atoms in the crystal framework and massive Ti-oxide. Acid extraction experiments with un-calcined products combined with analyses of mother liquor and solid phases, suggests that these intermediate bands are associated with non-framework species that are likely to be present with a range of coordination and degrees of oligomerization as surface deposits or incorporated in amorphous residues, probably as low molecular weight particles. Such non-framework,

highly dispersed, species with a low degree of polymerization may contribute significantly to catalytic activity [2].

Evidence is presented that the limit for isomorphic Ti substitution in the silicalite structure is about 1.3 to 1.5 atom percent independent of the method of Ti-silicalite synthesis. Reported higher levels of Ti substitution most likely include contributions from dispersed, amorphous as well as crystalline, admixtures of Ti-species. The stability and catalytic character of these various non-framework Ti centers depend not only on the synthesis reagents and conditions of starting mixture preparations, but also on the subsequent synthesis process and the post synthesis treatment. Contamination by massive Ti-oxide, anatase in particular, increases after crystallization as a function of time, temperature and alkalinity in the mother liquor suggesting mobilization and transport of Ti species that have not been fixed in the crystal structure.

Improved understanding of the influence of various process parameters on Ti incorporation should lead to better control and a more favorable distribution of Ti centers.

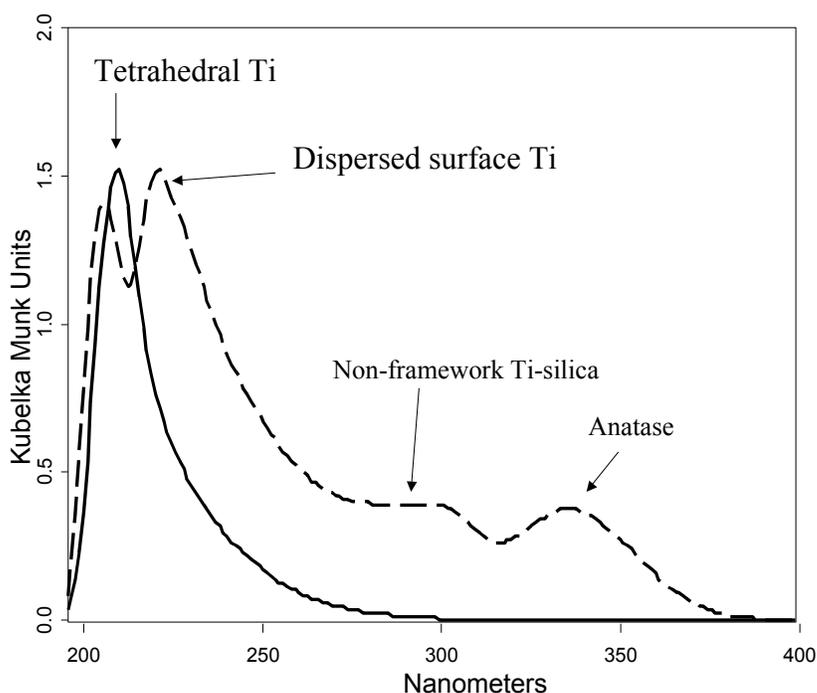


Figure 1.
Comparison of FTUV DRV spectra of a pentasil Ti silicate with a predominance of Ti atoms in framework tetrahedral position and a sample with a diversity of Ti centers.

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Poster Abstracts

Imprinting of the Surface of Mesoporous Silicates using Organic Structure Directing Agents: Catalysts for Large Organic Molecules

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Mesoporous materials and zeolites are porous silicates that differ in their pore sizes and structures. Mesoporous materials such as SBA-15 [1] have relatively large pore diameters in the range of 50-60Å compared to zeolites such as ZSM-5 with a pore diameter of 6Å. This difference in their pore sizes leads to advantages and disadvantages in their use as catalysts. In an attempt to combine some of the features of different porous materials, partial recrystallization of the surface of MCM-41 resulted in a mesoporous material with surface-tectosilicate structures [2]. Also, dual templating of macroporous silicates with zeolitic microporous frameworks has been reported [3].

This study reports a new protocol that has been developed for the synthesis of a novel porous silicate with accessible acid sites on the inner surface of large mesopores. This material aims to combine the meso-structure of SBA-15 and the microporous structure of the zeolite ZSM-5 *within* the pore walls of SBA-15. This new material would combine the positive features of both types of materials. Namely, hydrocarbon reactions involving large organic molecules that cannot enter the small pores of a zeolite catalyst may be catalyzed by the new material having a mesoporous framework structure with accessible strong acid sites on the surface of these large mesopores. The synthesis strategy involves the transformation of the thick amorphous pore walls of SBA-15 (~53Å) into domains of ZSM-5-like structures using tetrapropyl ammonium (TPA) ions as a template for the formation of the microporous structure.

The synthesis consists of calcined SBA-15, which serves as a mesoporous precursor, aqueous tetrapropylammonium hydroxide (TPAOH) (40% solution), which provides the TPA⁺ ions, and glycerol, which serves as a solvent in the recrystallization of the silica phase [2]. The important synthesis parameters are temperature, reaction time and the amount of TPAOH used.

Low angle powder X-ray diffraction (XRD) patterns indicate that the original hexagonal mesoporous structure of SBA-15 is retained in the treated samples. Nitrogen adsorption-desorption data for the calcined samples indicate that the pore diameter increases from 48Å to 68Å, the BET surface area decreases from 750m²/g to 370m²/g while the total pore volume remains the same. ²⁹Si MAS NMR spectra show that silica phase of SBA-15 becomes denser upon the treatment and subsequent calcination. Thermo gravimetric analyses of the synthesized samples reveal a 3-4% weight loss event at a temperature of 400°C, which can be attributed to the presence of TPA incorporated into the mesoporous framework. ¹³C-¹H Cross Polarization MAS NMR spectra of the

treated SBA-15 samples show the presence of peaks at 10ppm and 16ppm, which confirms the presence of TPA in the treated samples. We will present further results from the characterization of aluminum containing SBA-15 and catalytic tests to verify the difference between the materials.

References

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High-Pressure Powder Diffraction Experiments on Zeolites at NSLS

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Pressure is a basic thermodynamic variable transforming matter from one state to another. However, our knowledge of pressure-induced phase transformations in zeolites are still very limited compared to the vast number of temperature-dependent structural characterizations performed over the past decades. This is largely due to the experimental difficulties involved in both the need for specialized equipment and the development of expertise in the use of high-pressure cells. Over the last couple of years, we have developed necessary techniques performing high-pressure experiments using diamond-anvil cells (DAC) and monochromatic synchrotron X-ray diffraction and initiated a research program focusing on pressure-dependent chemistry in zeolitic nanopores. A number of successful experiments have been made using either a medium-resolution ($\Delta d/d \approx 10^{-3}$) position-sensitive detector (PSD) at beamline X7A or an imaging plate (IP) area detector at beamline X7B. Some characteristics of the two beamlines in high-pressure mode are discussed and selected experimental results on zeolites are presented here.

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¹⁷O Solid State NMR Studies of Faujasite Type Zeolites

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Faujasite type zeolites, which play an important role in the catalytic reactions used in today's petroleum industry, serve as a class of important model systems for ¹⁷O NMR studies. ¹⁷O MAS and MQMAS NMR studies at field strengths of 8.45 and 14.0 T were used to investigate oxygen local environments in ¹⁷O-enriched NaLSX, Na-Y and NH₄Y. The resonances from Si-O-Al and Si-O-Si linkages can be readily resolved in zeolite Y through MQMAS. The effects of the silicon/aluminum ratio, extraframework cations and hydration level on the ¹⁷O chemical shifts, quadrupolar coupling constants and asymmetry parameters have been investigated. We are currently performing ¹⁷O NMR studies of Brønsted acidity in zeolite HY and are using phosphine probe molecules to probe the effects of gas binding to the Brønsted acid sites.

Novel Lanthanide/Actinide-Organic Frameworks

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Four novel lanthanide and actinide compounds have been produced via tailored linking of metal centers through bifunctional organic backbones. This was accomplished by combining either uranium oxynitrate or neodymium nitrate with adipic acid under hydrothermal conditions. UO₂(C₆H₈O₄)₂(H₂O)₂ [**1**, FW=630.18, tetragonal, *P*4₃2₁2, *a*=9.3606(6)Å, *c*=11.8125(10)Å, *V*=1095.59(13)Å³, *Z*=4] consists of a chain of UO₂(H₂O)₂(CO₂)₂ centers connected by the adipic acid backbone. UO₂(C₆H₈O₄)₂ [**2**, FW=414.15, triclinic, *P*-1, *a*=5.5835(12)Å, *b*=8.791(2)Å, *c*=9.2976(17)Å, *α*=87.769(9)^o, *β*=78.957(8)^o, *γ*=81.365(11)^o, *V*=442.83(16)Å³, *Z*=2] is a framework structure with edge shared UO₂(O)₆ polyhedra linked by the adipic acid backbone. Nd₂(C₆H₈O₄)₃(H₂O)₂ [**3**, FW=756.88, triclinic, *P*-1, *a*=8.0752(10)Å, *b*=11.637(2)Å, *c*=13.209(3)Å, *α*=106.759(9)^o, *β*=93.419(18)^o, *γ*=107.225(12)^o, *V*=1120.9(3)Å³, *Z*=2] and Nd(C₆H₈O₄)₄ [**4**, FW=728.80, monoclinic, *C*2, *a*=17.860(2)Å, *b*=7.7735(9)Å, *c*=10.2842(12)Å, *β*=121.923(3)^o, *V*=1211.9(2)Å³, *Z*=2] both consist of chains of edge shared NdO₉ polyhedra cross-linked by the adipic acid into a framework topology. The difference between the two frameworks is seen by the manner in which the chains are connected. Control of the dimensionality (i.e. one-dimensional chains to three-dimensional frameworks) is being explored as a function of reaction conditions.

X-ray diffraction studies of K⁺, Na⁺, and Li⁺ exchanged (Al, Ge)-GIS

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GIS related frameworks with high ion exchange capacity, MAP for example, have been studied as possible replacements for type-A as detergent builders. In the course of a general survey ways to improve ion exchange capacity and selectivity we are investigating the origins of structural changes in variety of ion exchangers.

Single crystal ex situ ion exchange and time resolved in situ X-ray diffraction (XRD) was used to determine the ion exchange mechanisms and pathways for Na⁺ and Li⁺ exchanged K-GIS (K₈Al₈Si₈O₂₄·8H₂O), and K⁺ exchanged Na-GIS (Na₂₄Al₂₄Ge₂₄O₉₆·8H₂O). Preliminary in-house in situ XRD for K⁺ exchange into Na-GIS showed the unit-cell transformed from an ordered super-group Na-GIS (C 2/c) to a disordered sub-group K-GIS (I 2/a). When K⁺ was substituted into Na-GIS, the transformation was seen as a phase change with a discontinuous volume decrease as the appearance of the sub-cell grew in the presence of the super-cell. Prior to sub-cell formation, occupancy parameters of K⁺ in the Na-GIS structure could be refined using the Rietveld method. The K⁺ ion had a preferred replacement for Na⁺ into the [101] channels of Na-GIS. Occupancy parameters could be refined only while one phase was present. Once the sub-cell formed, parameters of refinement exceeded the resolution of the data. Upon the reverse exchange, Na⁺ into K-GIS, slow growth of super-cell reflections were observed. Ion exchange of Li⁺ into K-GIS showed a sub-cell to super-cell transformation (I 2/a to C 2/c). The positions of Li⁺ could not be refined due to its low X-ray scattering power.

Rietveld refinement was used to determine that K⁺ exchange into Na-GIS proceeded to 90% completion. Using bond valence calculations, it is shown that the GIS structure has a higher affinity for K⁺ than for Na⁺ based on the bond valence contrast for K⁺ vs. Na⁺. The mechanics of the transformation was an unraveling of the crankshaft chains viewed perpendicular to [010]. For the reverse exchange, Rietveld refinement showed the Na⁺ for K-GIS exchange system achieved 10%. The structure solution of 50% Li⁺ exchange for K-GIS showed Li⁺ positions at the intersection of the perpendicular channels on a 2-fold axis. The ion exchanged form of Li₄K₄Al₈Ge₈O₃₂·8H₂O showed the coordination environment of Li⁺ is 2-fold to H₂O molecules. Bond valence calculations show H₂O acting as a bond valence transformer that contributes a higher degree of bond valence to framework O²⁻.

These experiments show that quantitative refinement of time-resolved in situ ion exchange can be used to determine cation mobility for zeolites using synchrotron radiation sources.

Nanoscale zeolite crystal growth

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To fabricate complex nanostructure materials, hierarchical assembly of supra-molecular precursors to form complex organic-inorganic structures is a promising strategy. Unfortunately, fundamental knowledge to pursue this goal rationally is lacking for many systems of interest. The synthesis of zeolites in the presence of organic cations is a prime example of such a synthesis, yielding a framework of periodically arranged silicate tetrahedra with 1-, 2-, or 3-dimensional network of pores in the 0.4 to 10 nm range. With over 100 framework topologies synthetically available, each with their own range of compositions, zeolites have found widespread application in shape selective catalysis, adsorption, and ion-exchange. In addition to their use as powders of micrometer size crystals, recent successes synthesizing zeolite single crystals [1] and zeolite films with controlled microstructure [2] present promise for optical-electronics, sensing, membrane technology, micro-reactors, and analytical applications.

In our studies, we focus on the growth mechanism of the silica polymorph silicalite (MFI). Typically, zeolite synthesis involves hydrothermal growth of crystals in the presence of organic cations that act as structure-directing agents. During the growth of large zeolite crystals, subcolloidal ‘nanoblocks’ of a few nanometers in diameter have been observed by several groups [3]; these nanoblocks can be isolated [4]. Our objective is to study their assembly mechanism towards larger silicalite crystals. By controlling the conditions of the crystal growth, the crystal morphology can be affected [5], giving control of the long-range assembly of nanostructure materials.

Combining experimental and theoretical techniques we intend to elucidate mechanism(s) of the self-organization process during silicalite crystal growth at the nanometer scale. Silicalite crystals and isolated nanoblocks are analyzed by solid-state NMR, FTIR, TGA, and TEM to obtain information on their composition, connectivity and morphology. X-ray diffraction techniques are employed to study the long-range ordering. Modeling the x-ray diffraction from first principles facilitates the interpretation of experimental data. In addition, the stability of colloidal silicalite and of nanoblocks is studied by light scattering techniques. The stabilizing surface charge is assessed by measuring the zeta potential. Moreover, growth can be followed in situ by DLS [6]. Theoretical modeling is done by applying a simple growth model with various interaction potentials. Part of the interactions can be described by DLVO theory, but more sophisticated potentials are needed to obtain a more accurate model. Insight obtained from experimental studies is invaluable in refining the model. Iterative refinement of the interpretation of experiments

and of the theoretical modeling is expected to contribute to a more rational design of zeolite nanostructure materials.

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RPM-2: A Recyclable Porous Material with Unusual Adsorption Capability: Self Assembly via Structural Transformations

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As a continuation of our efforts to design and synthesize RPM type materials (RPM: Rutgers Recyclable Porous Materials), we have recently prepared and characterized RPM-2, [Co(bpdc)(bpy)]·0.5DMF (bpy = 4,4'-bipyridine, bpdc = biphenyldicarboxylate, DMF = dimethylformamide), a new member of the family. RPM-2 was assembled by mixing [Co(bpdc)(py)₂]·H₂O, a two-dimensional structure (obtained using [Co(bpdc)(H₂O)₂]·H₂O as a precursor immersed into pyridine) and bpy in the molar ratio of 1:4 in 5mL of DMF at 120°C in a Teflon-lined autoclave. Upon a mild chemical process, RPM-2 can be converted back to the precursor [Co(bpdc)(H₂O)₂]·H₂O. The single crystal structure of RPM-2 reveals a non-interpenetrating 3D framework with 1D rectangular channels (~ 5.6 × 3 Å opening based on van der Waals radius of carbon). The 3D framework consists of wave-like [Co(bpdc)] layers interconnected by 4,4'-bpy as pillars. The adsorption capacities for several hydrocarbons range from 9 to 15 wt% for the sorbed gases. The uptake of large molecules such as cyclohexane, xylenes and mesitylene is unexpected for RPM-2 with a small channel opening of 5.6 × 3Å. In particular, the uptake of large mesitylene molecules, which are too large for ZSM-5, a zeolite with 5.6 × 5.3Å channels, is surprising. This suggests a very high flexibility of RPM-2's channel windows and internal surface (composed of aromatic hydrocarbons). The heat of n-hexane sorption for RPM-2 is close to that of RPM-1 (66 kJ/mol), indicating that both RPM-1 and RPM-2 are highly hydrophilic and interact strongly with n-hexane.

Quantifying the n-Hexane Cracking Activity of Fe- and Al- Based Acid Sites in H-ZSM-5

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The relative n-hexane cracking activity of Brønsted acid sites in H-[Al]-ZSM-5, H-[Fe]-ZSM-5 and H-[Al, Fe]-ZSM-5 zeolites has been investigated as a function of temperature, Cs-exchange level and aging. Similar to H-[Al]-ZSM-5, acid sites in H-[Fe]-ZSM-5 are homogeneous. Per Brønsted acid site the reaction rate constant over H-[Fe]-ZSM-5 was found to be 15% of that over H-[Al]-ZSM-5. The acid sites in H-[Fe,Al]-ZSM-5 show inhomogeneity as expected for the co-existence of strong Al-based acid sites and weaker Fe-based acid sites. In Cs-exchanged materials, an equilibrium relationship has been found for the distribution of Cs between the two different Brønsted acid sites. Using equilibrium constants equal to the ratios of cracking activities, the activity decreasing effect of replacing protons with Cs⁺ ions can be described both for H-[Fe,Al]-ZSM-5 and mildly steamed H-[Al]-ZSM-5, respectively. FTIR results also indicated preferred Cs-poisoning on the more active acidic sites. The strong and weak sites are not distinguishable in H-[Fe,Al]-ZSM-5 by either FTIR or temperature programmed ammonia desorption. The aging of H-Fe sites appears to influence that of H-Al sites in [Fe,Al] ZSM-5.