

NECZA MEETING

DECEMBER 7, 2001
University of Pennsylvania

Program

8:30- 9:00	Registration, Poster Set Up
9:00-10:00	Coffee, Poster Session
10:00-11:00	<u>Studies of Adsorption, Diffusion and Molecular Simulations Of Cyclic Hydrocarbons in MFI Zeolites</u> , Lovat Rees
11:00-11:30	<u>Why call it SCR?</u> Julie d'Itri
11:00-11:30	<u>Mesoporous Molecular Sieves – The Past, Present and Future</u> , Jim Vartuli
12:00-13:00	Lunch
13:00-13:30	<u>X-Ray Data Bases and Their Use With Microporous materials</u> , Mike Bennett
13:30-14:00	<u>ETS-4 Pore Contraction: The Molecular Gate Effect</u> , Valerie Bell
14:00-14:30	<u>Combinatorial Heterogeneous Catalysis: High -Throughput Preparation and Screening of Catalytic Materials</u> , Craig Leidholm
14:30-14:45	Break
14:45-15:15	<u>Selected Student Poster Presentation</u>
15:15-15:45	<u>Applications of Thermal Analysis and Calorimetry in the Field of Catalysis</u> , Iggy Chan
15:45-16:15	<u>Antiferromagnetic Pairing in Polyaniline Salt-Zeolite Nanocomposites</u> , Nan-Loh Yang

ORAL PRESENTATIONS

STUDIES OF ADSORPTION, DIFFUSION AND MOLECULAR SIMULATIONS OF CYCLIC HYDROCARBONS IN MFI ZEOLITES

Lovat Rees

University of Edinburgh, U. K.

Adsorption isotherms of various aromatic and saturated cyclic hydrocarbons will be presented. An attempt will be made to use molecular simulation to explain the differences in packing efficiencies of these molecules and the hysteresis loops observed with p-xylene and p-dichlorobenzene. The diffusivities of these molecules have been measured using the Frequency -Response Method. Once again molecular simulation will be used to help to explain the important differences found in these diffusivities.

WHY CALL IT SCR?

In memoriam: Keith Hall

Julie d'Itri

University of Pittsburgh, PA

MESOPOROUS MOLECULAR SIEVES – THE PAST, PRESENT AND FUTURE

J. C. Vartuli and W. J. Roth

*Corporate Strategic Research; ExxonMobil Research and Engineering
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With the discovery of the M41S family, the past several years have seen explosive growth in research on ordered mesoporous molecular sieves. Major advances in understanding and exploiting the synthesis protocols and the mechanism of formation of these materials have allowed designed tailoring of composition, pore size, structure, texture and active site location and density through functionalization to produce many potential catalysts, supports, and separation media. The basic synthesis protocols of these mesoporous molecular sieves will be reviewed with an emphasis on the methods of functionalization within the pore walls to produce active materials.

X-RAY DATA BASES AND THEIR USE WITH MICROPOROUS MATERIALS

Mike Bennett

Consultant

At the present time, the number of materials of interest to the microporous materials community continues to expand at an ever increasing rate. X-ray diffraction is one of the first analytical techniques used to identify/characterize a microporous material. However, the ability to locate the available characterization data has not kept up with the increasing knowledge base. Questions will be asked as to how this knowledge can be made both readily available and in a format useful to the x-ray user. How can the information that is currently available via groups such as the IZA Structure Commission, ICDD, ICSD, NIST and others be brought rapidly to the attention of interested users? Do these 'suppliers' provide the information in a timely and cost effective manner? Are there better approaches and if so, how does the microporous materials community get this done?

ETS-4 PORE CONTRACTION: THE MOLECULAR GATE EFFECT

Steven M. Kuznicki*, Valerie A. Bell*, Richard M. Jacubinas*, Sankar Nair†, Carola M. Braunbarth†, Hugh W. Hillhouse†, Michael Tsapatsis†

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ETS-4 (Engelhard Titanosilicate-4) was the first reported synthetic mixed octahedral/tetrahedral molecular sieve. This material has been found to possess molecular sieving properties quite different from traditional tetrahedral-based molecular sieves which can be tuned to an unprecedented degree. We report that the effective pore size of ETS-4 can be systematically contracted to differentiate gas molecules through the size range of about 4.0 Å to 2.5 Å with a precision of 0.1 Å. This is achieved by heat treatment at elevated temperatures, typically 200°C to 350°C which dehydrates the framework structure. The range of stable materials generated by heat treatment (referred to as Contracted Titanium Silicate, CTS) may be employed to separate molecules of similar size such as N₂/CH₄, Ar/O₂ and N₂/O₂ opening new opportunities in industrial gas separations. The first field demonstration unit for removing nitrogen from natural gas has recently been successfully brought on stream.

COMBINATORIAL METHODS FOR ZEOLITE CATALYSIS

Craig Leidholm

Laboratory Catalyst Systems, CA

APPLICATIONS OF THERMAL ANALYSIS AND CALORIMETRY IN THE FIELD OF CATALYSIS

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Thermal analysis techniques are very useful tools for the characterization of catalysts, especially zeolites. Among the thermal techniques, thermogravimetry and calorimetry are the most used in the field.

Thermogravimetry measures the variation of the mass of the sample according to temperature, in a controlled atmosphere. This technique is well adapted to characterize the preparation of the catalyst by heating the sample under reducing atmosphere, before the adsorption. Used in an isothermal mode, thermogravimetry allows one to follow the adsorption and desorption processes at different temperatures under different reduced pressures. Thermogravimetry is also very useful for investigating the regeneration of used catalyst under reduced atmosphere.

Calorimetry, including DSC, is another important technique for the characterization of catalysts. With such a technique, the heat flux coming from an endothermic or exothermic reaction is measured. Calorimetry is ideal for measuring heats of adsorption and desorption in different atmospheres. From the adsorption curve and depending on the gas used, it is possible to measure the coverage of the catalyst, and also to detect the acid or basic sites.

Calorimetry or DSC can be connected with gas analyzers (GC, MS), in order to measure at the same time, the amount of gas that has not been adsorbed.

Adsorption can be run in gaseous phase or in liquid phase. For the investigation in the liquid phase, a titration calorimeter is used.

ANTIFERROMAGNETIC PAIRING IN POLYANILINE SALT-ZEOLITE NANOCOMPOSITES**Harry L. Frisch, Huihong Song, Junqing Ma, Miriam Rafailovich*, Shaoming Zhu*, Nan-Loh Yang#, Xingzhong Yan#***Dept. of Chemistry, State University of New York at Albany, Albany, NY 12222***Materials Science & Engineering State University of New York at Stony Brook, Stony Brook, NY 11794-2275**#Dept. of Chemistry, Staten Island College, City University of New York, Staten Island, NY 10314*

Polyaniline (PANI) zeolite composites have been prepared by oxidative polymerization of aniline in the presence of zeolite 13X, producing composite materials with PANI/zeolite weight ratios from about 0.5 to 55. The DC conductivity of the composite materials decreased exponentially with the zeolite weight fraction. Pure PANI was paramagnetic while the PANI/zeolite complexes with weight ratios larger than 20 showed an appreciable antiferromagnetic component as indicated by temperature dependence of their electron spin resonance spectra. This novel antiferromagnetism is speculated to arise from **p**-dimer pairing of PANI chains layers stacking on the zeolite particle surface.

POSTERS

Imprinting of the Surface of Mesoporous Silicates using Organic Structure Directing Agents

Kaveri R. Sawant and Raul F. Lobo

Center for Catalytic Science and Technology, The University of Delaware

Siliceous MCM-22 supported Chromium catalyst for olefin polymerization

Saji P. Varkey

Center for Catalytic Science and Technology, The University of Delaware

Local Structure of Zeolite Beta from Neutron Scattering Data

Peral Inmaculada, Accardi Robyn J., Martinez-Inesta Maria, Proffen Thomas and Lobo Raul F.

Chemical Engineering Department, The University of Delaware

Long-range order in crystalline materials can be obtained by examining Bragg diffraction peaks. However, the disorder in materials results in diffuse scattering which is of great importance in the characterization of the local structure.

The Pair Distribution Method (PDF) method is able to use data from the diffuse scattering as well as the Bragg diffraction and can be used as a way to study the local structure of the materials.

The translational periodicity of zeolite Beta is lost along one direction, thus zeolite Beta structure can be described as stacking layers along that direction. Neighboring layers (related by a mirror operation) can be connected in two different ways. Since Beta average structure has been proposed, we can compare the local structure obtained from the experimental PDF to the published average structure. We expect that the local and average structure comparison will aid in the understanding of Beta zeolite structure and properties.

A Simple and Reliable Method of Determining Acid-site Concentration of Solid Acids

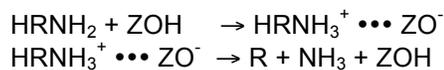
O. Kresnawahjuesa, J. Elsabe, R. J. Gorte

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Brønsted-acid site concentration is one of the most important parameters required to understand fundamental concepts of acidity in solid acids (i.e. zeolites). Knowledge of Brønsted-acid site concentration is of importance in many industrially important classes of reactions, such as acid-catalyzed and hydrocarbon cracking.

Ammonia TPD is the conventional method of determining Brønsted-acid concentration in solid acids. However, in addition to the difficulties in calculating adsorption energies from TPD results, there are problems in obtaining site densities from ammonia TPD. Ammonia is also known to react strongly on both Brønsted and Lewis sites and therefore it is not always possible to clearly distinguish between the two sites [1].

Our group proposed a new technique for measuring Brønsted-acid sites with TPD (mass spectrometer)-TGA (microbalance) measurements using alkyl amines with on different types of solid acids with different acid site concentrations [2-6]. The method is based on the observation that alkyl-ammonium ions, formed by protonation of amines at Brønsted sites, undergo decomposition reaction to form olefin and ammonia in a narrow and well-defined temperature range. The decomposition reaction is similar to the Hoffman elimination reaction (decomposition of quaternary ammonium salts to a tertiary amine and olefin), as shown below:



In fact, this technique is already adopted as the standard to measure acid site concentrations for many different solid acids. However, this measurement required the use of a microbalance (TGA) and mass-spectrometer (TPD) under vacuum, where the gas partial pressures and the sample weight were measured simultaneously.

The lack of availability of mass spectrometry (TPD) and the use of a vacuum environment causes difficulties in performing this measurement widely in an industrial environment. In order to make this techniques more appealing, we need to demonstrate that this measurement could be carried out in a flowing system environment, where the analysis could be performed simply with the use of a gas chromatograph (GC).

In this project, we will demonstrate that Brønsted-acid sites measurement with alkyl amines molecule can be performed in a flowing system where the desorption products (olefin and ammonia) are collected with liquid N₂ trap and analyzed via gas-chromatography. This measurement is shown to be a very reliable method for determining acid sites concentration in different types of solid acids over a wide range of acid site concentrations.

References

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Zeolites under High-Pressure

Yongjae Lee

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Study of ion-exchanged microporous lithosilicate Na-RUB-29 using synchrotron X-ray single crystal diffraction and ⁶Li MAS NMR spectroscopy

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A series of ion-exchange studies of recently discovered microporous lithosilicate RUB-29 (Cs₁₄Li₂₄[Si₇₂Li₁₈O₁₇₂]•14H₂O) using crystals in the 20~30 μm size range and varying exchange times were carried out in the presence of 5M NaCl aqueous solutions. The combined results of synchrotron X-ray single crystal diffraction and ⁶Li MAS HPDEC NMR spectroscopy allowed for a better understanding of the complex behavior of RUB-29 structure upon Na exchange. This exchange process involved seven Cs⁺- and four Li⁺ sites of RUB-29. The results from the investigation showed that Na cations can exchange with more than 90% of the Cs cations and 16% of the Li cations without resulting in any changes in the lattice symmetry. Most Li cations within the channels either remain or relocate. The successful removal of Cs and its replacement by the smaller sodium suggests the interior of RUB-29 may be made available for possible separations.

Can we visualize framework Li cations using IR and solid-state NMR spectroscopy?

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Lithium cations play important multifunctional roles as an framework and non-framework constituent in microporous lithosilicate structures such as RUB-23 ($\text{Cs}_{10}(\text{Li},\text{H})_{14}[\text{Li}_8\text{Si}_{40}\text{O}_{96}] \cdot 12\text{H}_2\text{O}$), RUB-29 ($\text{Cs}_{14}\text{Li}_{24}[\text{Si}_{72}\text{Li}_{18}\text{O}_{172}] \cdot 14\text{H}_2\text{O}$), and RUB-31 ($\text{Cs}_{10}\text{Li}_9[\text{Li}_3\text{Zn}_5\text{Si}_{40}\text{O}_{96}] \cdot 6\text{H}_2\text{O}$). To prove the presence of Li cations in the framework structure and to characterize the feature more accurately is the first essential step to investigation the novel lithosilicate materials. The low scattering power of Li made accurate characterization difficult and common static and dynamic disorder of Lithium cations further complicates crystallographic study. We present the recent results from IR spectroscopy to show the characteristic IR bands of lithosilicate at about 850 cm^{-1} . We suggest this due to Si-O-Li stretching lattice vibration, indicating directly the incorporation of lithium cations into the $[\text{SiO}_2]$ -frameworks. While NMR is a sensitive tool for the determination of Li mobility and site population, to date all attempts to distinguish non-framework and framework Li cation sites in the microporous lithosilicates by ^6Li - and ^7Li NMR spectroscopy were unsuccessful. Using high field (14.1 T) NMR spectroscopy, at least five separate ^6Li resonances could be resolved and assigned to Li in the framework and non-framework sites of the microporous lithosilicate materials for the first time by solid-state ^6Li MAS NMR spectroscopy.

Experimental Determination of Multi-Component Vapour Sorption on Active Carbon by combined Microgravimetry and Dynamic Sampling Mass Spectrometry

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Experimental methods for direct measurement of multi-component vapour sorption are evaluated in a prototype instrument, which combines the gravimetric method for determination of the kinetics and equilibria of the total adsorption and uses mass spectrometry for the analysis of each component. Results are presented for adsorption of water-octane and water-butane on carbon BAX950.

Investigation of the Negative Thermal Expansion in All-silica Chabazite

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Long-range order in crystalline materials can be determined by examining Bragg diffraction peaks. However, changes in the local environment within a material will result in broad diffuse scattering peaks, which, unfortunately, are lost when performing a background correction of the diffraction pattern. Recently, researchers have been using the pair-distribution function (PDF) method as a way to examine the local structure of crystalline materials¹. The PDF method is able to use data from both the diffuse scattering as well as the Bragg diffraction. We have studied the mechanism of the negative thermal expansion in siliceous chabazite using the PDF method to investigate the changes of the local structure with temperature. Previous work has indicated that the mechanism for contraction is due to dynamic rocking of rigid SiO_4 polyhedra². However recent research has implied that the negative thermal expansion is due to distortions in the tetrahedra themselves³. Normal refinements have not been able to determine which mechanism is correct. We have investigated both the long-range order using Rietveld refinement, and the local structure using the PDF method to better understand the framework contraction mechanism.

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INVESTIGATION OF THE CATION LOCATION CORRELATION IN NaX

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