

# NECZA 99

U. Pennsylvania, Philadelphia, PA

December 10, 1999

## PROGRAM

9:00 - 10:00	Coffee and Poster viewing
10:00 - 10:30	Poster presentations
	<b>Synthesis Discussion Leader - Terry Roberie</b>
10:30 - 11:00	Synthesis John Parise
11:00 - 11:30	Synthesis Raul Lobo
11:30 - 12:00	Synthesis Guenter Kuehl
12:00 - 1:00	Lunch
	<b>Applications Discussion Leader - Chuck Coe</b>
1:00 - 1:30	Applications Todd Ballinger
1:30 - 2:00	Applications Theo Maesen
2:00 - 2:30	Applications Jeff Hufton
2:30 - 3:00	Break
	<b>Characterization Discussion Leader - Brian Toby</b>
3:00 - 3:30	Characterization Clare Grey
3:30 - 4:00	Characterization Karl Mueller

# NECZA 99 Scientific Program Abstracts

## Synthesis

### Nucleation and Growth

John Parise, SUNY

It appears a detailed understanding of the processes occurring during the nucleation and growth of solid state materials is completely unnecessary for the discovery of new materials. Maddox's denunciation of the "scandal" in synthetic solid state chemistry notwithstanding, the community has produced and will continue to produce new materials aplenty. And this while only possessing an empirical knowledge of many of the processes underlying solid state synthesis. Should we then concentrate on combinatorial approaches, by recruiting ever-larger numbers of graduate students or purchasing robots? Much is lost using this approach, including education and the development of chemical intuition. More importantly, zeolite synthesis is often route-dependent (not a state function). That simple observation suggests more complete knowledge of the process might eventually lead to experimentally testable predictions. By grappling with the problem of nucleation and growth, using structural and intuitive approaches, new insights and ideas emerge. What approaches might be fruitful? Sub-micron single crystal diffraction suggests short-lived intermediates in zeolite synthesis will be accessible for study. Some experience with time resolved X-ray scattering will be combined with recent small angle scattering results and rumors of what might be possible with thermochemistry, to optimize zeolite synthesis. Small-angle neutron scattering (SANS) and light scattering are useful approaches for the study of zeolite crystallization, while traditional WAXS remains a powerful tool for optimization.

### Synthesis and Calcination of Zeolite Alpha.

Oferi Kresnawahjuesa, Ralf Heussner, Guenter H. Kuehl, and Raymond Gorte, U. Penn

A reproducible method of crystallizing zeolite alpha (high-silica LTA), while minimizing the quantity of TMAOH, is reported. Evidence of co-crystallization of sodalite in early preparations and transformation of high-silica LTA to high-silica sodalite upon extended digestion in the mother liquor is presented. Procedures for separating the very small crystals from the highly alkaline solution will be discussed.

Although the sodium ions can be removed by ion exchange with  $\text{NH}_4^+$  in the presence of TMA<sup>+</sup>, it is preferred to decompose the TMA<sup>+</sup> ion in the Na,TMA-form of the zeolite. Strict adherence to the proper calcination conditions is required to obtain a highly crystalline product. Preliminary results on the dehydroxylation of the Na,H-form indicate a framework  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the product in the range of 7-9. The acid site concentration, as determined by TPD of n-propylamine, will be correlated with the composition of the zeolite.

### Guest/Host Interactions in the Synthesis of High-Silica Zeolites

Raul Lobo, U. Delaware

Structure-Direction in the synthesis of zeolites in a process of molecular recognition between an organic molecule and inorganic silicate species in solution. Here I will present a review of recent results that bring new light into this problem and I will attempt to clarify the key issues that need to be addressed in the near future.

## Applications

### Zeolite Application in Automotive Catalysis

Todd Ballinger, Johnson Matthey

Zeolites have been studied in automotive three-way catalysts as hydrocarbon adsorbents in one approach to solve vehicle cold-start hydrocarbon emission requirements of future emission regulations. However, vehicle application of zeolites has been limited by the harsh conditions of automotive exhaust. Investigations studying the different types of zeolites used for hydrocarbon adsorption, the types of hydrocarbons adsorbed, and durability requirements for automotive catalysts will be discussed.

### The Shape Selectivity of Paraffin Hydroconversion on TON-, MTT- and AEL-type Sieves

Th.L.M. Maesen,

Zeolyst International, Shell International Chemicals, Amsterdam

M. Schenk, T.J.H. Vlugt, B. Smit

University of Amsterdam

J.P. de Jonge,

Shell International Chemicals, Amsterdam

Based on a comparison between simulated and measured adsorption properties, we demonstrate that both normal and mono-methylparaffins are able to fully enter the pores of TON-, MTT- and AEL-type molecular sieves. This disproves the theory that mono-methylparaffins only partially enter these pores and that normal-paraffins are predominantly hydroisomerized at the pore mouths of these sieves. Instead, we attribute the high selectivity for paraffins with terminal methyl groups to product shape selectivity, and the low selectivity for paraffins with neighboring methyl groups to transition state selectivity. These traditional shape selectivity concepts explain not only the detailed product distribution of n-heptane hydroconversion, but also that of longer-chain n-paraffins

### Sorption Enhanced Reaction Process

Jeffrey R. Hufton, Shivaji Sircar, Shankar Nataraj, Air Products and Chemicals, Inc.

A new process entitled the Sorption Enhanced Reaction Process (SERP) is described for carrying out simultaneous reaction (gas-phase) and separation of desired products in a single unit operation. It uses a fixed packed column of an admixture of a catalyst and a sorbent (e.g., zeolite) which selectively removes a reaction by-product of an equilibrium-controlled reaction from the reaction zone. The sorbent is periodically regenerated by using the principles of pressure swing adsorption. The process steps allow direct production of the desired product at high purity and at the reaction pressure. High conversion of the reactants to products for an endothermic, equilibrium-controlled reaction can be achieved while operating the reactor at a substantially lower temperature than would be necessary by a plug flow reactor packed with the catalyst alone. The application of this process scheme for the production of carbon monoxide via the reverse water gas shift reaction will be described.

## Characterization

### **New Solid State NMR Methods for Studying Gas Sorption in Zeolites**

Clare Grey, SUNY Stony Brook

Methods for probing the mode of gas binding rely on the measurement of a dipolar coupling (and therefore a distance), or a J coupling (which indicates a bond is formed) between the sorbent and sorbate. The talk will describe the application of different NMR methodologies to study hydrofluorocarbon (HFC) binding to basic zeolites and basic probe molecules to acidic zeolites. In the first example,  $^{19}\text{F}$ - $^{23}\text{Na}$  and  $^1\text{H}$ - $^{17}\text{O}$  cross-polarization experiments indicate that both electrostatic interactions (involving the sodium cations and the fluorine atoms) and hydrogen bonding control the mode of HFC binding. A combination of  $^{23}\text{Na}$  MQMAS and 1 pulse MAS NMR are used to quantify changes in cation positions and occupancies.

### **Probing Acid Sites in Catalytic Materials with Double- and Triple-Resonance NMR**

Karl T. Mueller, Murthy D. Karra, Penn State

The ability to determine the types and concentrations of acid sites in zeolites and fluid-catalytic cracking systems provides an increased understanding of structure/performance relationships in these materials. Experimental MAS NMR methods and calculation procedures are described for detection and quantification of the Brønsted- and Lewis-acid site concentrations in a variety of solid acid catalysts using trimethylphosphine oxide (TMPO) as a weakly basic probe molecule. We report TMPO studies of acid sites in several zeolite systems including HY, USY, dealuminated-Y, and ZSM-5. Comprehensive and consistent assignments to particular types of sites are made for all resonance lines in the phosphorus-31 MAS NMR signals from TMPO, and new chemical shift assignments are made for the TMPO/Lewis acid complex. The assignments of phosphorus-31 resonances from molecules not directly associated with nearby aluminum-27 nuclei (such as crystalline or physisorbed TMPO species) are supported using triple-resonance NMR methods. The concentrations of Brønsted acid sites from the NMR results are compared with concentrations obtained from isopropylamine/temperature-programmed-desorption measurements, and substantial agreement between the methods is found. In a sample of USY zeolite, simultaneous quantification of both Lewis- and Brønsted-acid site concentrations is accomplished with these methods.

## POSTERS

### **Solid State NMR Studies of Zeolite NaX Reacted With Hydrofluorocarbon-143(CH<sub>2</sub>F-CHF<sub>2</sub>) (poster only)**

Yi Xiao, Kwang-Hun, Lim, Clare P. Grey  
SUNY at Stony Brook

<sup>19</sup>F, <sup>27</sup>Al, <sup>23</sup>Na and <sup>29</sup>Si MAS NMR techniques are used to investigate zeolite NaX before and after reaction with hydrofluorocarbon-143 (CH<sub>2</sub>F-CHF<sub>2</sub>). Besides the gas product CHF=CHF, the Al-F, Si-F, and Na-F species are formed during the attack of the zeolite framework when the reactions are performed. TRAPDOR, CP/MAS and 2D NMR experiments (HETCOR, MQMAS) show the following facts: There are two types of Al-F species, and they have different Al-F distance, one of them is a tetrahedral Al-F species. If the reaction happens in an environment of excess HFC-143, more distorted Al-F species formed. Si-F bonds are formed between fluorine and the silicon sites that are connected to aluminum by oxygen bridge. Na<sup>+</sup>F<sup>-</sup> ion pair is most likely formed during the reaction, while other Na-F species has a longer Na-F distance.

### **Binary Mixture Adsorption in Zeolites:**

#### **A comparison between experiment and molecular simulation**

Flor R. Siperstein and Alan L. Myers University of Pennsylvania  
Orhan Talu Cleveland State University

The prediction of multicomponent adsorption equilibria from single-component data is one of the most challenging and important problems in adsorption. Experimental measurement of mixture adsorption is time consuming and difficult to obtain, therefore molecular simulation is an attractive alternative to predict mixture adsorption. Considering that gas-solid interactions are more important than gas-gas interactions, then the prediction of mixture adsorption should be possible if we have a realistic model for single gas-solid interactions. We present molecular simulation results for a binary mixture (CH<sub>4</sub>-SF<sub>6</sub> on silicalite). Simulation results agree well with experimental data.

### **In situ XRD and NMR study on Phase Transition from b- to a-CuAlCl<sub>4</sub> Molecular Sieves.**

H.Liu, C.Grey (Chemistry, SUNY @ Stony Brook)  
J.Hanson (Chemistry, BNL)  
J.Martin, R.Sullivan (Chemistry, N.C.State Univ.)

Phase transition from b- to a-CuAlCl<sub>4</sub> molecular sieves has been confirmed in situ by time-resolved synchrotron XRD and solid-state <sup>27</sup>Al, <sup>63</sup>Cu MAS NMR, which demonstrates the flexibility of the CuAlCl<sub>4</sub> framework structure. Simulations of NMR spectra by GAMMA enable estimation of quadrupolar interactions in consistence with corresponding site symmetry.

**The Structure of MCM-47: a Highly Crystalline Silicate Composed of Ferrierite Layers**  
Allen Burton, Robyn Accardi, and Raul F. Lobo  
U. Delaware

MCM-47 is a high silica material first reported by workers at Mobil in 1991. Its structure directing agent is a diquatery amine formed by reacting two molecules of 1-methylpyrrolidine with one molecule of 1,4-dibromobutane. Although its powder x-ray diffraction (XRD) pattern suggests that it is highly crystalline (unlike most layered materials), MCM-47 is not thermally stable to conventional calcination procedures used for removing organic templates from high silica zeolites. Here we present evidence that the structure is indeed a highly crystalline layered silicate.

The XRD pattern of the as made MCM-47 could be indexed in an orthorhombic setting ( $a = 7.386$ ,  $b = 22.453$ ,  $c = 14.018$  Å). The  $a$  and  $c$  parameters are similar to those found in ferrierite (FER). The systematic absences narrowed the space groups to  $Cmc2_1$  (36),  $C2cm$  (40), and  $Cmcm$  (63). Topology searches were performed with the FOCUS algorithm developed by Grosse-Kunstleve and coworkers. Space group  $Cmcm$  (63) yielded a structure composed of ferrierite layers similar to the PREFER structure reported by Gies and coworkers. Simulations of XRD patterns of MCM-47 with organic molecules placed in likely positions within the framework showed good qualitative agreement with the experimental pattern. A subsequent Rietveld refinement in space group  $Cmcm$  confirmed the proposed structure to be correct. The proposed structure of MCM-47 is also supported by  $^{29}\text{Si}$  MAS NMR which shows the Q3/Q4 ratio to be nearly the same as expected from the crystallographic assignment of the T sites. Also, the proportions of two of the Q4 signals are the same expected from the crystallographic assignments of the T sites.

In PREFER the ferrierite layers are separated by mirror planes so that all silanol groups in one layer are opposed by silanol groups in the neighboring layer. As a result, the PREFER material can be calcined to yield a stable material with the FER topology since the silanols, or "defects," can heal and the layers can fuse. However, in MCM-47 the ferrierite layers are shifted so that only half of the defects are near defects in the opposing layers. As a result, the structure falls apart when it is not calcined extremely carefully. When a slow, staged calcination is used, we believe that half of these defects heal to yield a structure in which the layers are connected. This is confirmed by the change in the  $d$ -spacing of the 0 2 0 peak from 22.4 to 18.4 Å after calcination, which is similar to what is observed in the calcination of PREFER. Although PREFER is stable to calcination temperatures well above 540 °C, the structure of the carefully calcined MCM-47 falls apart when heated beyond 540 °C. This supports the hypothesis that not all defects heal upon calcination.  $^1\text{H}$ - $^{29}\text{Si}$  CP MAS NMR spectra also confirm the presence of remaining silanols in the carefully calcined MCM-47. The XRD pattern of our proposed structure shows good qualitative agreement with the experimental pattern of the calcined material although there still remain some differences which require further investigation.

## **Double and Triple Quantum $^1\text{H}$ MAS NMR Studies of Defect Sites in All-Silica Zeolites**

Daniel F. Shantz, Joern Schmedt auf der Guenne, Hellmut Eckert, Hubert Koller, Raul F. Lobo, U. Delaware

### **A new modification of zeolite GIS structure type: Synthesis and Structural Characterization of Germanium containing zeolites.**

Akhilesh Tripathi, Sun Jin Kim and John B. Parise  
SUNY, Stony Brook

We have recently embarked on a systematic study on the isomorphous replacement of silicon by germanium in zeolitic materials, and its influence on structure and properties. Detailed synthetic and structural investigations have been reported for aluminogermanates with various zeolite topologies such as RHO, FAU (zeolite X), ABW, NAT, and CAN, The purposes of such a study are multifold. To provide insight into structure directing influence of alkali and alkaline earth metals in conjunction with/without organic amine, their role in growing crystals from powders and the fact that even a heteroatom can influence structure directing affects since different/new topologies are formed with different/no counterpart in identical conditions for other compositions. Here we report aluminogermanates with GIS and MON zeolite topology.

### **The Crystal Structure of Dehydrated CsZSM-5(5.8Al): Evidence for Non-Random Aluminum Distribution"**

David Olson, U. Penn  
Nazy Khosrovani, Molecular Simulations  
Alan Peters, WR Grace  
Brian Toby, NIST

The crystal structure of dehydrated CsZSM-5 (5.8 Al) has been determined by Rietveld refinement of synchrotron powder diffraction data. The Cs ions were found with partial occupancy in three different positions. One is in the channel intersection adjacent to a four membered ring, one is in the straight channel, and the other in the sinusoidal channel. Modeling of the effect of aluminum siting on the position of Cs ions in the zeolite channel indicates that the Cs<sup>+</sup> ion has its closest interaction with an oxygen atom attached to the aluminum atom for Al substitution at each of the 12 T sites in the unit cell. From this we conclude that Cs<sup>+</sup> ion positioning provides information on the aluminum atom distribution. The T sites 4, 7, 10, 11, 12 have Cs-O distances less than 3.55 angstroms indicating they are possible sites for Al atoms. The oxygen atoms attached to T sites 2, 8 and 9 have no Cs-O distances shorter than 3.9 angstroms suggesting that there is a low probability that these sites contain Al atoms.