Behavior of Halocarbons in Zeolitic Materials

Final DOE Report for 1999-2002

Principal Investigator:

**Dr. Anthony K. Cheetham
Materials Research Laboratory
University of California
Santa Barbara, CA 93106**

E-mail: cheetham@mrl.ucsb.edu

Tel. (805) 893-8767

Fax (805) 893-8797

1. Introduction

This report describes results on the above grant over the 3 year period, 1999-2002. The emphasis of our work has continued to shift during 2001-2 from halocarbon adsorption in zeolites towards other separation processes in zeolites. These additional areas include (i) work on lithium-containing zeolites for non-cryogenic air separation, and (ii) the study of nickel phosphate molecular sieves for hydrogen storage. Nevertheless, we continued our experimental and computational work on halocarbons in zeolites.

2. Progress during 1999-2002

Our work over the last three years has spanned two areas: (i) the continuation of our previous research on halocarbon molecules in zeolites, and (ii) preliminary work on hydrogen storage and lithium ion-exchange on nanoporous nickel phosphates (VSB-1 and VSB-5).

2.1 Halocarbons in zeolites

The work on halocarbon adsorption and separation processes in zeolites, which was originally funded under an environmental RFP, has continued to progress very well. We completed our inelastic neutron scattering and IR/Raman study of chloroform in zeolites, which revealed not only the importance of hydrogen bonding interactions in both systems but also revealed that, unlike the situation with ethylene adsorption, there is no $\text{Na}^+-\pi$ interaction with unsaturated halocarbons.¹ Our computer simulations confirmed that the origins of this effect lie in the presence of strong Na^+-Cl interactions and the positive charges of the carbon atoms in unsaturated halocarbons. We also reviewed all of our DOE-funded work to date on halocarbon separation processes,² and published a state-of-the-art review of the simulation of adsorbed molecules in zeolites.³

Our work in this area has been extended on several other fronts. We have completed our neutron diffraction and computer modeling study of a mixed chlorofluorocarbon system: CFCl_3 in NaY ,⁴ a system that reflects a delicate balance between a wide variety of host-guest interactions. In addition, our ground-breaking work on the direct observation of host-guest hydrogen bonding by neutron scattering using a H/D pair distribution function has been published in JACS.⁵ In relation to our computer simulations, we have been exploring the merits of using a more sophisticated charge distribution to describe the electrostatic potential of the halocarbon sorbates. Not only does this lead to a dramatic improvement in our ability to reproduce the electrostatic potentials obtained from our first principles calculations, but it also seems probable that it will have more general utility (e.g. for the simulation of liquids). This work, which was carried out by Dr. Anne Boutin during her sabbatical leave here at UCSB, was recently published.⁶

Work that is currently being completed and has yet to be written up includes a systematic study of aromatic halocarbons in zeolites. NMR and Raman spectroscopy studies, coupled with

Monte Carlo simulations, show that the model system, C_6F_6 in zeolite Na-Y, illustrates many of the differences between halocarbons and hydrocarbons. With benzene in Na-Y, the sorbate is tightly bound to the Si cations in a π -complex that stems from the strong electrostatic interactions between the sodium ions and the negative carbon atoms; the interaction energy is ~ 75 kJ/mol. With C_6F_6 in NaY, however, the reverse polarity leads to entirely different behavior in which the cations interact primarily with the fluorine atoms; there is a weaker interaction energy of ~ 50 kJ/mol. The strength of this interaction is similar to that of benzene in the siliceous form of faujasite, suggesting that C_6F_6 should be highly mobile in this system. We are currently undertaking molecular dynamics simulations to confirm this expectation. We are also exploring systems in which there is only partial fluorination, e.g. C_6F_5H , in NaY.

2.2 Hydrogen adsorption in nanoporous nickel phosphates

The discovery of the nanoporous nickel phosphates, VSB-1 and VSB-5, was achieved when I was on leave in Paris in 1998.^{7,8} As part of our DOE-funded work on Separations, we have recently begun to explore the potential of these materials for hydrogen storage. Hydrogen sorption in the nanoporous nickel phosphates VSB-1 and VSB-5 has been studied with combination of BET, temperature programmed desorption (TPD), and inelastic neutron scattering (INS) measurements. H_2 BET isotherms (Fig. 1) for VSB-1 are similar to those seen in nanoporous zeolites, while VSB-5 adsorbs substantially more hydrogen due to a steep initial uptake at low partial pressures. TPD data (Fig. 2) show that hydrogen interacts strongly with VSB-5, with desorption peaks at 109 K and 149 K in a nitrogen flow, whereas the absence of similar peaks for

VSB-1 suggests a weaker interaction. INS spectra (Fig. 3) of the rotational tunnel transition of the adsorbed H_2 also reveal a strong interaction with the VSB-5 host. These data strongly suggest the existence of coordinatively unsaturated Ni^{2+} sites accessible to H_2 molecules in the pores of VSB-5. This work was recently published in JACS.⁹

Figure 1: Hydrogen uptake for several microporous sorbents.

Fig. 2 TPD profiles for H_2 in (a) VSB-1 (enlarged in inset) and (b) VSB-5

Figure 3: INS spectra obtained on the QENS spectrometer of IPNS at $T = 10$ K: dehydrated VSB-5 (bottom), and with one H_2 molecule (middle) and 3 H_2 (top) adsorbed per formula unit.

2.3 Lithium-containing zeolites for non-cryogenic air separation and batteries

In our related work on the use of lithium-containing zeolites for non-cryogenic air separation, we published a seminal paper in JACS¹⁰ in which we demonstrate the power of using a combined solid state NMR (7Li and ^{23}Na) and neutron diffraction approach to probe the cation distribution in the mixed Na,Li-chabazite system as a function of composition. Lithium is always difficult to locate by powder diffraction methods since it is a poor scatterer with both X-rays and neutrons, but the complementary use of the NMR and diffraction approaches enables the subtle interplay between the factors controlling the cation distribution to be probed with great sensitivity. This in turn has lead to a better understanding of the manner in which the efficacy of the air separation changes with chemical composition. We have also published a study of an even more complex system in which three cations are present: Li,Na,K-CHA.¹¹ The potassium is found to have an unexpected influence on the Li,Na distribution due to the lattice expansion that results from its presence.

One of the key objectives in the air separation area is the discovery of materials in which the density of accessible lithium ions exceeds that of the Li-LSX (low-silica zeolite X). This material shows the best performance, but is very expensive to manufacture and has not yet been commercialized. The density of available Li^+ (i.e. lithium in SIII sites) in Li-LSX is $\sim 2/1000\text{\AA}^3$. In our recent work on Li ion-exchange into VSB-1, $K_4[Ni_{18}(HPO_4)_{14}(OH)_5F_9] \cdot 12H_2O$, we made the intriguing discovery that exchange with LiOH, rather than LiCl, lead to the incorporation of almost

15 lithiums per formula unit.¹² This corresponds to $9/1000\text{\AA}^3$, which is dramatically better than LiLSX. Unfortunately, we have been unable to access the porosity because the structure over-exchanged LiVSB-1 collapses prior to full dehydration, which takes place at higher temperatures than normal, presumably due to the very high charge density that is associated with the high Li⁺ content. We believe that the origin of the over-exchange lies in the availability of exchangeable protons associated with the 14 (HPO₃) groups per formula unit. As far as we are aware, exchange of such protons has never previously been observed in a molecular sieve (most phosphate sieves dissolve in base). Nevertheless, the creation of a material with very high Li⁺ content in the channels may open up other possibilities.

In a separate facet of this work, we have also undertaken an electrochemical study of the VSB-1 material and evaluated its performance as a potential battery electrode. These results were published.¹³

We have also carried out H₂ adsorption as well as co-adsorption (H₂/O₂ or H₂/N₂) experiments using INS on Li containing zeolites to probe binding sites with H₂. For example, our results on the loading-dependence of H₂ in LiA demonstrates the existence of one site per supercage with a very high barrier to rotation. We take this to be evidence for simultaneous occupation of two type II sites in the 8-ring window, as Li is not found in type III sites in LiA. The existence of such a configuration was suggested by MD simulations (F. R. Trouw, personal communication), and provides an explanation for the fact that LiA is not useful for air separation. This example illustrates the power of this method, and ways in which we will use it to study cation-hydrogen interactions in the VSB materials in the future.

3. Publications

A. K. Cheetham Publications under DOE Funding, 1996-2002

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 13. Forster, P.M., J. Eckert, J-S. Chang, S-E. Park, G. Férey, and A.K. Cheetham, "Hydrogen adsorption in nanoporous nickel(II) phosphates," *J. Amer. Chem. Soc.* **2003**, *125*, 1309.