s5.m19.o3　　**Structural Study of Dye Modified Synthetic Mordenites.** Petra Simoncic and Thomas Armbruster, *Laboratory for chem. and mineral. Crystallography, University of Bern, Switzerland. E-mail: petra.simoncic@krist.unibe.ch*

Keywords: Zeolites; Single Crystal X-Ray Diffraction; Artificial Antenna Systems

Structural analysis of dye modified, synthetic mordenite single crystals characterising the arrangement and disorder of the organic cationic dyes are presented. Microporous materials like zeolites are more and more applied for design and development of new materials. With channel and cavity apertures of several angstroms, they allow stabilisation and incorporation of individual atoms, clusters or molecules. One aspect of modern technology and new materials are one-dimensional zeolite host-guest systems and miniaturized electronic devices, e.g. semiconductors organised as quantum dots or chains or luminescent dyes which mimic the natural function of chlorophyll in plants. Different kinds of microcrystalline ($< 1\mu m$) synthetic zeolites (zeolite L, zeolite Y, and ZSM-5) have hitherto been used as hosts for this kind of artificial antenna systems [1]. The incorporation of the organic dye molecules is dependent on the aperture of the zeolite channels. The orientation of the molecule in the channel is determined by the shape and size of the dyes and the zeolite channels. Furthermore, the charge distribution on the internal walls of the zeolite channels may influence the orientation of the trapped molecules. Very little is known about geometrical arrangement of the dyes in the zeolite channels. The exact position of the chromophores in the zeolite structure may provide better understanding how the antenna systems work and how the energy transfer can be improved. A suitable method to analyse the modified zeolite structure is single-crystal diffraction applying synchrotron radiation. Single crystals of self-synthesised mordenite-Na were used for incorporation of different cationic dye molecules as thionine blue ($C_{12}H_9N_3S^+$), methylene blue ($C_{16}H_{18}N_3S^+$) and DAMS ($C_{16}H_{19}N_2^+$). Mordenite is particularly suitable for the structural analysis of dye-zeolite systems, because the anisotropic shape of the channel cross-section limits disorder of the enclosed molecules. The organic, cationic molecules were incorporated by ion exchange in saturated dye solution during 8-12 weeks at 100 °C. Electron microprobe analysis showed that Na+ was partially exchanged by the cationic dyes. X-ray data collection of dye-loaded mordenite was performed at 120 K with synchrotron radiation ($\lambda = 0.7995$ Å) using the single-crystal diffraction beam line at SNBL (ESRF, Grenoble) where diffracted intensities were registered with a MAR image plate. Possible positions and arrangement of incorporated dye molecules were limited by the ellipsoidal shape of the large 12-membered ring channels (7.0×6.5 Å) of mordenite. Different low-populated molecule sites were defined which were highly disordered along the channel axis. Arrangement and preferred positions of S-containing dye molecules (thionine blue, methylene blue) were compared with the structural data of a Se-modified mordenite [2].

[1]　Calzaferri G., Pauchard M., Maas H., Huber S., Khatyr A., Schaafsma T. (2001) *J. Mater. Chem.*, **12**(1)
[2]　Simoncic P., and Armbruster T. (2004) *Microp. Mesop. Mater.* (submitted)

s5.m19.o4　　**Estimating Adsorption Energy in AlPO4-15 Molecular Sieve – Some Approaches Based on Experimental Charge Density Modelling.** Florence Porcher,[a] Emmanuel Aubert,[b] Mohamed Souhassou[a] and Claude Lecomte[a], *[a]LCM3B, UMR 7036 CNRS-UHP Nancy I, Faculte des Sciences, Vandoeuvre-les-Nancy, France, and [b]Frederick Seitz Materials Research Laboratory, 104 S. Goodwin, Urbana, IL 61801, USA. E-mail: florence.porcher@lcm3b.uhp-nancy.fr*

Keywords: Molecular Sieves; Charge Density; Interaction Energies

Charge density analysis is a unique tool for characterising inter/intramolecular interactions in solid state. In the case of guest-host systems like molecules trapped in molecular sieves, this method is of particular interest because of the numerous industrial utilisations of these compounds. However, in this case, accurate charge density is difficult to obtain either from high-resolution diffraction experiments (because of the poor quality and small size of the crystals) or from ab initio calculations (because of the size of the system). We will summarise some results[1] about experimental charge density determination in the model molecular sieve AlPO$_4$-15 ($(NH_4Al_2(OH)(H_2O)(PO_4)_2 \cdot H_2O$, $P2_1/n$, a=9,556(1) Å, b=9,563(1) Å, c=9,615(1) Å, β=103,58(1) °) derived from an accurate single crystal X-ray diffraction experiment. The experimental charge density was refined [2,3,4] against diffraction intensities using a multipolar expansion centred on atomic positions able to describe the redistribution of electron density due to chemical bonding. Intermolecular interactions between the framework and the (H_2O, NH_4^+) guest molecules/ions were studied through a Bader[5,6] analysis, enlightening the H-bonds network stabilising one of the water molecules. This analysis also provided an estimation of atomic charges and dipoles. The interaction energy U between the framework B and adsorbed species A was calculated according to the decomposition of U into electrostatic E_{elec}, repulsion E_{rep} and dispersion E_{disp} terms : $U=E_{elec}+E_{rep}+E_{disp}$, assuming that E_{rep} and E_{disp} terms were negligible in inorganic crystals such as zeolites as long as the interaction distances are large enough. The electrostatic energy E_{elec}, A/B. between interacting entities A and B was obtained by combining the charge density ρ_A of A with the electrostatic potential $V_{B,A}$ created by B at the position of A : E_{elec}, $_{A/B.} = \rho_A * V_{B,A}$. We will describe different approaches used for calculating E_{elec}, $_{A/B.}$ in AlPO$_4$-15 molecular sieve, using discrete (point charges) or continuous (charge density) descriptions of the material and various definitions (multipolar decomposition/topological analysis) of interacting entities.

[1]　Aubert E., Porcher F., Souhassou M., Lecomte C., *Acta Cryst.* **B59**, (2003). 687–700.
[2]　Lecomte, C. (1999). *Implications of Molecular and Materials Structure* ..., pp. 23-44. Kluwer Academic Publishers.
[3]　Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909-921.
[4]　Guillot, B.; Viry, L.; Guillot, R.; Lecomte, C.; Jelsch, C. (2001). *J. Appl. Cryst.*, **34**, 214-223.
[5]　Bader R. "Atoms in molecules : a quantum theory.", international series of monographs in chemistry. Oxford, Clarendon Press.
[6]　Souhassou M. & Blessing R. H., *J. Appl. Cryst.*, (1999), **32** : 210-217.