The Complete Structure of a Hydrated Gallosilicate Zeolite with the ABW Framework determined by Powder Neutron Diffraction

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In the first complete structure determination of a hydrated polycrystalline zeolite, powder neutron diffraction and molecular modelling have been used to determine proton positions in a hydrated lithium gallosilicate with the ABW framework.

Although many hydrated zeolites have been studied by *X*-ray diffraction,[1] a combination of disorder and the low *X*-ray scattering power of hydrogen has, in all these studies, prevented determination of the positions of the protons associated with the sorbed water molecules. Neutron diffraction provides much better sensitivity to scattering by hydrogen or deuterium, as has been well demonstrated in recent single crystal diffraction experiments on natural[2] and synthetic zeolite crystals.[3] Most synthetic zeolites are, however, polycrystalline and the potential for using powder neutron diffraction to study zeolite structures has only recently been realized.[4] Jirak *et al.*,[5] Cheetham *et al.*,[6] and Haselden *et al.*[7] have used powder neutron diffraction to determine hydroxylic proton positions, and structural studies of zeolites containing sorbed xenon,[8] CO,[7] benzene,[9] and pyridine[10] have been described. However, although measurements on hydrated zeolite rho have also been reported,[11] proton positions were not determined. We have now successfully used powder neutron diffraction data to determine and refine the complete structure of a hydrated gallosilicate zeolite with the ABW framework.

Lithium gallosilicates with the ABW framework were produced by appropriate modifications to the procedures described by Barrer and White.[12] A selected sample of approximate composition $LiGaSiO_4 \cdot H_2O$ was then treated twice with a large excess of D_2O, effecting *ca.* 50% D-for-H exchange (full analytical details are given in ref. 13). Powder neutron diffraction data were collected at 19 K on the Special Environment Powder Diffractometer at IPNS-I, Argonne National Laboratory and, at 298 K, on the powder diffractometer of the Missouri University Research Reactor facility. The earlier powder *X*-ray diffraction study of Kerr[14] provided initial atomic co-ordinates for the structure refinements which

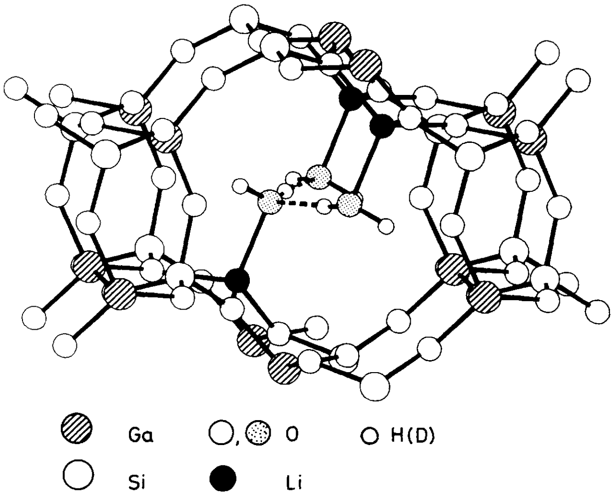

Figure 1. View along the channel of the ABW framework gallosilicate at 298 K showing the lithium cation position, the position of the sorbed water molecule, and the weak hydrogen bonding.

were achieved by full-profile analysis methods.[15] Proton (deuteron) positions were determined by an iterative combination of profile refinements and interactive three-dimensional modelling of local sections of the structure.

At both temperatures only two proton (deuteron) sites were found to be occupied and their co-ordinates and occupancies were allowed to vary without constraint in the final refinements. The occupancies converged to similar values of 0.11(1) and 0.18(2) (at 19 K) and 0.12(1) and 0.14(1) (298 K), the relatively low values reflecting the only partial extent of the deuterium exchange [the scattering length of hydrogen, -0.374 fermi (10^{-15} m) is opposite in sign to that of deuterium, 0.667 fermi]. The structure of the hydrated gallosilicate zeolite is well ordered at both 19 and 298 K. There is a single lithium cation site that is tetrahedrally co-ordinated by three framework oxygen atoms and by the sorbed water molecule (Figure 1). The position of the water molecule is clearly dictated by interaction with the lithium cation, not by interaction with the framework. Thus, although the proton locations are such that they are both involved in hydrogen-bonded linkages, the relevant distances [O(W1)–O(1) 2.95(1), D(1)–O(W1) 2.33(4), O(W1)–O(W1′) 2.92(4), D(2)–O(W1) 1.95(4) Å at 298 K] are long and the interactions must therefore be relatively weak.

The interaction of the sorbed species, particularly water, with zeolite frameworks is a key factor in determining their commercial utility. The interaction of water with zeolite precursor components and the nonframework cations must also play an important role in directing the products of zeolite crystallizations. It will now be interesting to use powder neutron diffraction to study the structures and structural consequences of sorbed water within other synthetic zeolites including those that have much higher sorption capacities.

Received, 11th April 1986; Com. 480

References

1 W. J. Mortier 'Compilation of Extra Framework Sites in Zeolites,' Structure Commission of the International Zeolite Association, Butterworths, London, 1982.
2 A. Kvick, K. Stahl, and J. V. Smith, *Z. Kristallogr.*, 1985, **171**, 141, and references cited.
3 V. I. Bukin and Y. S. Makarov, *Geokhimiya*, 1967, **1**, 31 (translated in *Geochem. Intern.*, 1967, **4**, 19).
4 J. M. Newsam, *Physica B*, 1986, 213.
5 Z. Jirak, S. Vratislav, J. Zajicek, and V. Bosacek, *J. Catal.*, 1977, **49**, 112; Z. Jirak, S. Vratislav, and V. Bosacek, *J. Phys. Chem.*, 1980, **41**, 1089; V. Bosacek, S. Beran, and Z. Jirak, *ibid.*, 1981, **85**, 3856.
6 A. K. Cheetham, M. M. Eddy, and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1984, 1336.
7 J. M. Adams and D. A. Haselden, *J. Solid State Chem.*, 1984, **55**, 209.
8 P. A. Wright, J. M. Thomas, S. Ramdas, and A. K. Cheetham, *J. Chem. Soc., Chem. Commun.*, 1984, 1338.
9 A. N. Fitch, H. Jobic, and A. Renouprez, *J. Chem. Soc., Chem. Commun.*, 1985, 286.
10 P. A. Wright, J. M. Thomas, A. K. Cheetham, and A. Nowak, *Nature (London)*, 1985, **318**, 611.
11 J. B. Parise, T. E. Gier, D. R. Corbin, and D. E. Cox, *J. Phys. Chem.*, 1984, **88**, 1635.
12 R. M. Barrer and E. A. D. White, *J. Chem. Soc.*, 1951, 1267.
13 J. M. Newsam, submitted for publication.
14 I. S. Kerr, *Z. Kristallogr.*, 1974, **139**, 186.
15 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.