Hexadeuteriobenzene Locations in the Cavities of ZSM-5 Zeolite by Powder Neutron Diffraction

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A powder neutron diffraction study at 77 K of a ZSM-5 zeolite containing adsorbed deuteriobenzene (C_6D_6) indicates three distinct deuteriobenzene regions within the zeolite cavities.

Synthetic zeolites are widely used as molecular sieves and industrial catalysts; ZSM-5 is one of the more important catalysts, being used in the Mobil process to convert natural gas into motor fuel, benzene being one of the products.[1] Benzene molecules must therefore fit into the ZSM-5 framework, even though the critical diameter of the benzene molecule, 7 Å, is somewhat larger than the 10-ring openings which are usually assumed to have a diameter of 5.1—5.5 Å. Sorption studies[2] show that eight molecules of benzene are adsorbed per unit cell by ZSM-5 at 30 °C. Little is known about the stereochemistry of sorbed molecules in ZSM-5.

High-resolution powder neutron diffraction is a powerful technique which can show the shape of zeolite frameworks and the whereabouts of adsorbed species; recent examples are the location of xenon in zeolite rho,[3] deuteriobenzene in Y,[4] deuteriopyridine in L,[5] and carbon monoxide in A.[6] Whereas the above zeolite structures have of the order of 5—10 atoms in the asymmetric unit of the framework, ZSM-5 presents a refinement problem of a much greater magnitude, as it has 38 atoms in the asymmetric unit. Some structural work has recently appeared on ZSM-5 with adsorbed organic species. Jobic *et al.*[7] have studied the adsorption of methanol on H^+-ZSM-5 by incoherent quasi-elastic neutron scattering, while Mentzen[8] has proposed a location for *p*-xylene in the framework of boralite, isostructural with ZSM-5. We continue the studies of ZSM-5 sorbates with the present neutron diffraction study of deuteriobenzene (C_6D_6) in ZSM-5.

The ZSM-5 sample was prepared from Bu^nNH_2 template with an Si : Al atomic ratio of 100 : 1. It was heated to 500 °C and the required amount of deuteriobenzene added dropwise to the cooled sample in a dry-box. Neutron powder diffraction data were collected at 77 K on a high resolution neutron diffractometer on HIFAR, the Lucas Heights research reactor (λ = 1.893 Å). An excess deuteriobenzene pattern was subtracted from the raw data with the help of a calculated C_6D_6 pattern. The large ZSM–C_6D_6 structure was refined with a specially written profile refinement program which links in the single crystal program SHELX.[9] Restraints were applied by SHELX to the geometry as follows. Framework: Si–O = 1.58(5) Å (48 restraints); O–O = 2.58(10) Å (72 restraints); Si–Si = 3.09(10) Å (26 restraints) (which effectively restrains the tetrahedral angle around 109.5° and the Si–O–Si angle around 155.8°). The C_6D_6 molecules were restrained to be planar with ideal geometry. The refinement gave Si and O co-ordinates precise to ±0.03 Å, and Si–O (1.48—1.68 Å, mean deviation 0.04 Å), O–O (2.39—2.78 Å, mean deviation 0.07 Å), and Si–Si (2.99—3.29 Å, mean deviation 0.05 Å) distances which were reasonable (the restraints were relaxed in the final cycles). The structure refined in the orthorhombic space group *Pnma* [a = 19.961(2), b = 19.824(2), c = 13.398(4) Å], and there was no evidence for the monoclinic symmetry found in some ZSM-5 derivatives. The final values for *R*(profile) and *R*(Bragg) were 0.22 and 0.08, for 944 (*hkl*) reflections to 2θ = 80°. The expected *R*(profile) is 0.12.

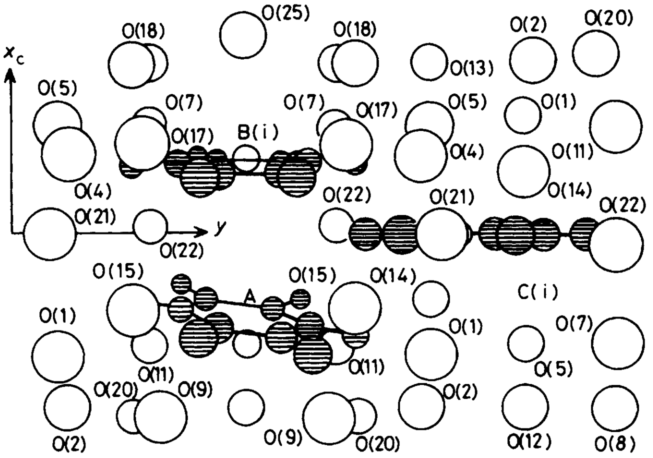

Figure 1. Diagram showing the locations of deuteriobenzene molecules A, B(i), and C(i) relative to the nearby framework oxygen atoms. The straight channel parallel to b runs to the right through x = 0 and the sinusoidal channel runs along the x direction along the mirror plane. Molecule A is slightly off an angle of 90° to the mirror plane because the SHELX benzene restraints are not fixed to the local symmetry. As the calculated profiled is insensitive to small sideways shifts of A (see text), the co-ordinates of C_6D_6 molecule A were left at the SHELX positions.

Difference syntheses showed the C_6D_6 molecules in the cavities of the ZSM-5 framework. The deuteriobenzene locations are illustrated with reference to the framework oxygen atoms in Figure 1.

There are three distinct deuteriobenzene types: A, B, and C. A and B are side-by-side at the intersection of the straight and sinusoidal channels, while C lies at a centre of symmetry $(0,\frac{1}{2},\frac{1}{2})$ in the straight channel. Molecule A lies approximately in the plane $x = -0.08$ (upright in the diagram), and molecule B at $x = 0.08$ (upright). The profile fit is insensitive to small sideways movements of molecule A, indicating translational disorder of A. The preferred position of C is upright, but the Fourier maps indicate a small amount of rotational disorder. B also has translational disorder in the z direction. The refined

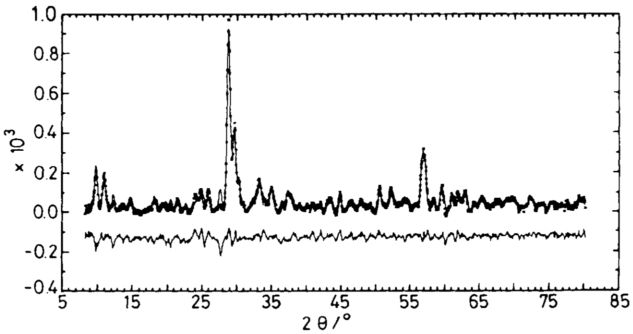

Figure 2. Observed (dots), calculated (line), and difference (line) profiles for ZSM-5–C_6D_6. The observed profile is the sum of two patterns each averaging 6 counters.

occupancies are A: 30.4(4), B(i): 14.3(4), B(ii): 15.2(4), C(i): 27.5(3), C(ii): 7.7(4), and C(iii): 5.5(4)%, giving a total deuteriobenzene occupancy in the unit cell of 8.05(8) molecules, in good agreement with the sorption data. Note that B(i) and B(ii) are the two translationally disordered positions of B and C(i)—(iii) are the three rotationally disordered positions of C in the model. The Fourier maps show evidence of a small cation and frozen-in water content in the channels; these 14 additional partial atomic sites refined and are included in the calculated profile. In all 124 atomic sites were included in the asymmetric unit, *i.e.* some 350 co-ordinate parameters, although these were not all independent owing to the restraints.

Figure 2 shows the observed and calculated neutron powder profiles for the full model. It has not yet been possible to reduce the profile R factor further, probably because of errors in subtracting the calculated excess benzene patterns and inability to model the benzene disorder completely.

The C_6D_6 molecules fit neatly in the ZSM-5 cavities. That they indeed lie in the three locations given as A, B, and C is shown by the fact that the agreement between observed and calculated profiles is much worse when A, B, and C are omitted from the calculated profile; when A, B, and C are omitted in turn, the profile R factor becomes 0.32, 0.38, and 0.39 respectively.

The tight C_6D_6 packing suggests the zeolite framework and/or benzene molecules would be distorted at the temperature of the Mobil process (370 °C) to allow reactants and products to counter diffuse. As C_6D_6 is a robust molecule, it is unlikely to break down in the framework to other products, which can happen with methanol.

This study demonstrates that a considerable amount of information can be derived from a diffraction profile even with a large structure. It is, however, important to use restraints to extract the information most effectively and prevent refinements from entering false minima in the early stages.

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