

The Localization of Benzene in a Y-Zeolite

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Powder neutron diffraction studies at 4 K on a Y-zeolite containing adsorbed benzene show the presence of two distinct sites for the benzene molecules in the cavities of the zeolite.

Synthetic zeolites have found widespread application owing to their capacity for selective adsorption and catalysis. Among them, X- or Y-zeolites, which have similar structures to the naturally occurring zeolite faujasite, play an important role. A number of studies^{1,2} demonstrate that powder neutron diffraction is a powerful technique for the detailed investigation of the framework structures and cation distribution found in zeolites. Recently, this method has been used to locate adsorbed xenon atoms in zeolite-rho.³ We present here a preliminary report involving the use of powder neutron diffraction to investigate the localization of adsorbed benzene molecules in the cavities of a Y-zeolite at 4 K.

An initial powder neutron diffraction pattern of the bare Y-zeolite, Na₅₆Si₁₃₆O₃₈₄Al₅₆, obtained at room temperature on the high resolution powder diffractometer DIA and the ILL (Grenoble) was analysed by the Rietveld method⁴ and showed that the framework and cation distribution of our sample were in reasonable agreement with previous studies.⁵⁻⁹ For the sodium ions, the SI sites in the hexagonal prism and the SI'

sites in the sodalite cage are both partially occupied with occupation factors of *ca.* 0.41 and 0.54 respectively, whereas the SII site in the supercage is full. An agreement factor on integrated intensities $R_I = 7.3\%$ was obtained. The space-group is *Fd3m* with a lattice parameter $a = 24.85(3)$ Å.

Diffraction patterns were obtained at 4 K on DIA at a wavelength of 1.909 Å from two zeolite samples containing different coverages of adsorbed deuteriated benzene, determined experimentally to be 1.1 and 2.6 benzene molecules per supercage. These patterns were both rather poorly fitted by an initial model involving just the framework and sodium ions. Fourier difference maps computed perpendicular to the unit-cell diagonal, which contains a three-fold symmetry axis and three intersecting mirror planes, reveal two distinct features which can easily be recognized as possible benzene molecules, Figure 1. Each benzene may be described crystallographically by a single carbon and deuterium atom, the rest of the molecule being generated by symmetry.

The first benzene molecule is in the supercage. It has its

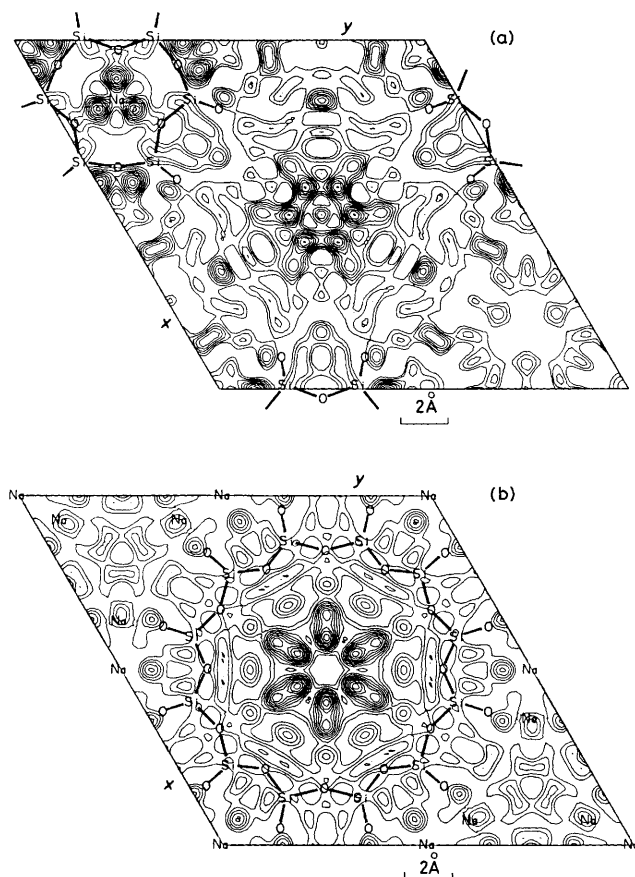


Figure 1. Fourier difference maps perpendicular to $\langle 1,1,1 \rangle$; x is parallel to $\langle -1,1,0 \rangle$ and y is parallel to $\langle -1,0,1 \rangle$. The sections are (a) about $(0.295, 0.295, 0.295)$ showing the first benzene site (for the sample with lower benzene coverage), and (b) about $(1/2, 1/2, 1/2)$ showing the second benzene site (for the sample with higher benzene coverage). The positions of some nearby framework atoms are also shown.

centre at the position $32e (x, x, x)$, which has $3m$ symmetry, with $x \approx 0.295$ corresponding to an average distance of ca. 2.62 \AA from the sodium ion in the SII site. To produce a regular hexagonal molecule, the carbon and deuterium atoms must be situated mid-way between the intersecting mirror planes. There are four such sites per supercage disposed tetrahedrally about the centre of the supercage at $8b (3/8, 3/8, 3/8)$, Figure 2.

The plane of the second benzene molecule is rotated by 30° with respect to the first, with the carbon and deuterium atoms residing on the mirror planes. The centre of the molecule is at $16d (1/2, 1/2, 1/2)$, which is a site of $\bar{3}m$ symmetry. This benzene is in the middle of the window formed between adjoining supercages by 12 Si/Al atoms and 12 bridging O atoms. The window has a free diameter of about 7.5 \AA and provides a rather well-tailored surround for the benzene molecule, Figure 3. Stabilization of this benzene position is presumably by van-der-Waals interactions. There is an average of two window sites per supercage.

The introduction into the structural refinement of these two types of benzene molecule, each constrained to be a regular hexagon and planar with C-C and C-D distances of 1.40 and

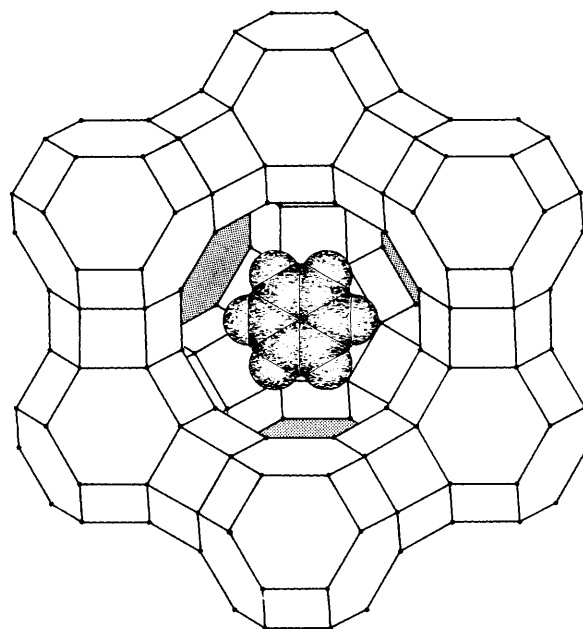


Figure 2. View of one of the four equivalent positions of the benzene(1) molecule in the supercage.

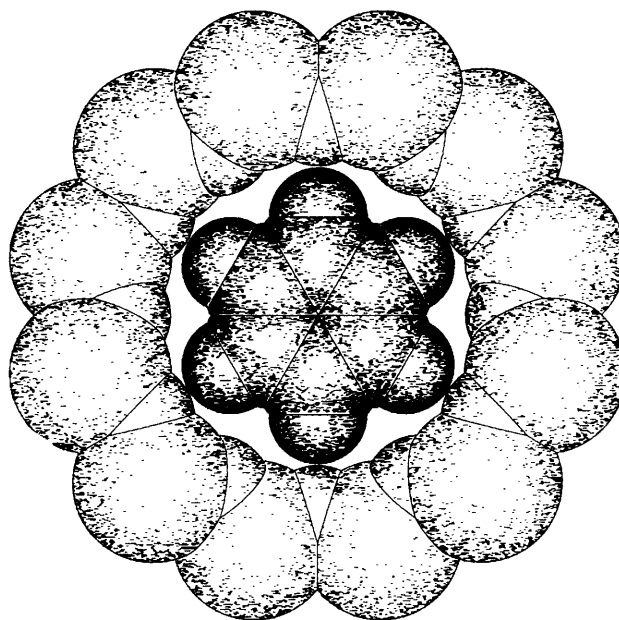


Figure 3. Molecular packing diagram using van-der-Waals radii of the benzene(2) molecule in the window between adjoining supercages.

1.09 \AA respectively,^{10,11} led to a marked improvement in the fit. For the sample with lower benzene coverage R_1 fell from 14.5 to 7.6% with refined occupancies of ca. 0.8 and 0.1 molecules per supercage for benzene(1) and benzene(2), respectively, whilst for the sample with higher coverage R_1 fell from 29.6 to 8.7% with refined occupancies of ca. 2.6 and 0.7 .

It appears therefore that the window site is the less favourable of the two with proportionately less occupancy at lower coverage.

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