

## A Neutron Diffraction Study of the Acid Form of Zeolite Y and its Complex with Benzene

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A powder neutron diffraction study of the structures of D-Y [ $Fd\bar{3}m$ ,  $a = 24.722(1)$  Å,  $R_p = 2.52\%$ ,  $R_{wp} = 3.32\%$ ] and its complex with benzene [ $Fd\bar{3}m$ ,  $a = 24.712(2)$  Å,  $R_p = 3.24\%$ ,  $R_{wp} = 4.27\%$ ] shows that benzene molecules are located above the six-ring window in the supercage and in the plane of the twelve-ring window, and that no redistribution of deuterium atoms occurs upon adsorption of benzene.

Acid zeolites that adopt the faujasite (FAU) structure, including La-Y, H-Y and ultrastabilized-Y, find widespread use as catalysts for hydrocarbon cracking in gasoline manufacture.<sup>1,2</sup> The locations of acid sites in H-SAPO-37<sup>3</sup> and H-Y<sup>4-6</sup> have been established previously by neutron diffraction [Fig. 1(a)]. In the case of H-Y, protons have been found, in order of decreasing occupancy, at O(1) in the  $\alpha$ -cage, at O(3) near to the SII' cation site in the  $\beta$ -cage, and at O(2) close to the SII cation site. Similar proton site occupancies are observed in H-SAPO-37. This preference for protonation of O(1) and O(3), oxygen sites that have the smallest T–O–T bond angles, is in accordance with *ab initio* quantum chemical calculations<sup>7</sup> that predict that as the T–O–T angle increases the bond strength of the OH group decreases.

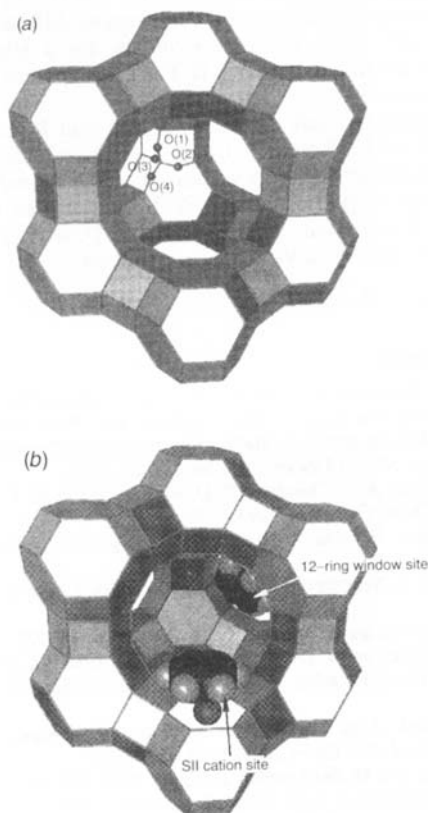
The structures of benzene adsorbed in Na-Y<sup>8</sup> and H-SAPO-37<sup>9</sup> have been reported previously. In Na-Y, two adsorption sites are observed; the first is above the six-ring window in the supercage where the benzene may interact facially with an SII site cation, and the second is in the plane of the twelve-ring window [Fig. 1(b)]. The same adsorption sites are observed for

benzene in H-SAPO-37. However, in H-SAPO-37, where no Na cations are present, protons are observed to redistribute themselves,<sup>9,10</sup> favouring the protonation of O(2) over O(1) and O(3) so that they may participate in a facial interaction with the benzene molecule similar to that observed for the SII cations in Na-Y. By contrast, infrared spectroscopy<sup>10</sup> showed no evidence for a redistribution of protons in H-Y. This paper reports the findings of a neutron diffraction study of H-Y and its complex with benzene.

The NH<sub>4</sub>-Y starting material was kindly supplied by P. D. Hopkins, formerly of Amoco Oil Company. It was synthesized from Na-Y by ion exchange with NH<sub>4</sub>NO<sub>3</sub> six times at 358 K. The final chemical composition (anhydrous) was found to be Na(NH<sub>4</sub>)<sub>55</sub>Si<sub>136</sub>Al<sub>56</sub>O<sub>384</sub>. The deuterated ammonium ion form was prepared by stirring the NH<sub>4</sub>-Y in a 1 mol dm<sup>-3</sup> D<sub>2</sub>O solution of ND<sub>4</sub>Cl at room temperature. After stirring under a N<sub>2</sub> atmosphere for 24 h, the ND<sub>4</sub>Cl solution was changed and the procedure was repeated. The acidic form, D-Y, was prepared by careful calcination of the ammonium ion exchanged material at 673 K under dry oxygen. The crystallinity of the samples after calcination was confirmed by X-ray diffraction. The samples for neutron diffraction were packed in a glovebox into thin-walled vanadium cans. A known amount of deuterated benzene ( $\approx 1$  molecule per supercage) was added gravimetrically to one of the cans before both were screw-sealed using indium wire. The D-Y/benzene sample was heated at 333 K for 2 days in order to obtain a homogeneous distribution of the sorbate throughout the host material. The NMR sample of H-Y/C<sub>6</sub>D<sub>6</sub> was prepared in a similar fashion, packed into a 5 mm o.d. Pyrex tube, and then flame sealed at liquid-N<sub>2</sub> temperature, under vacuum.

Neutron diffraction data were collected at 5 K using the power diffractometer, DUALSPEC, at Chalk River Laboratories, Canada. The data were collected at  $\lambda = 1.5043$  Å, between 5 and 120° in  $2\theta$ . Diffraction data were analysed by the Rietveld method<sup>11</sup> using the GSAS package.<sup>12</sup> Trial structures were visualized using the Biosym Catalysis and Sorption package.<sup>13</sup> <sup>2</sup>H NMR spectra were collected on a Chemagnetics CMX500 spectrometer operating at 76.8 MHz, as described previously.<sup>9</sup>

The starting model used for the refinement of the D-Y structure was based upon the framework structure of D-Y reported by Czjzek *et al.*<sup>4</sup> The space group used was  $Fd\bar{3}m$ . Deuterons were placed at each oxygen in turn, assuming a coplanar configuration with the T–O–T atoms and an O–H bond length of 0.96 Å. The positions of the protons, their occupancies and isotropic temperature factors were then refined. No sodium ions were located. Using this as a starting model for the D-Y/benzene structure refinement, benzene was inserted at the two positions found for benzene adsorbed in Na-Y;<sup>8</sup> above the six-ring window and in the plane of the twelve-ring window. The deuterons were again placed at each of the four oxygen sites and their occupancies were refined together with a single isotropic temperature factor. Separate isotropic temperature factors were refined for the framework atoms as well as for the benzene molecules. Selected bond lengths and bond angles are reported for both refinements in Table 1.



**Fig. 1** (a) The faujasite structure showing the positions of the four oxygen sites that may be protonated. (b) The adsorption sites for benzene in Na-Y as observed from neutron diffraction<sup>8</sup> above the SII cation and in the plane of the twelve-ring window.

For D-Y, deuterons were found to be located at all four oxygen sites with occupancies of: O(1) 11(2)%, O(2) 5(2)%, O(3) 16(2)% and O(4) 7(2)%. These results are in broad agreement with other diffraction studies of H-Y and D-Y,<sup>4-6</sup> all of which confirm that O(1) and O(3) are the most favoured sites for protonation. Upon adsorption of benzene into the D-Y structure, the deuteron distribution is found to be O(1) 13(3)%, O(2) 3(3)%, O(3) 22(4)% and O(4) 4(3)%, and both adsorption sites previously observed for benzene in H-SAPO-37 are occupied [six-ring window site occupancy 13(1)%, twelve-ring site occupancy 16(2)%].

The temperature dependence of the <sup>2</sup>H NMR spectra of C<sub>6</sub>D<sub>6</sub> adsorbed in H-Y (the protonated sample was analogous to that used in the neutron diffraction study), H-SAPO-37 and Na-Y

are compared in Fig. 2. The low-temperature spectra for all the samples show axially symmetric, anisotropic lineshapes that are characteristic of benzene rotating rapidly (> 10<sup>6</sup> Hz) about its six-fold axis. At higher temperatures, a sharp feature emerges at the centres of the spectra taken from all the samples. This feature is ascribed to benzene molecules jumping between sites where the orientations of the benzene six-fold axes are related by tetrahedral or higher symmetry.

Based upon the similarity of the Na-Y, H-Y and H-SAPO-37 NMR and diffraction data, it is concluded that benzene is facially coordinated to the proton/deuteron at O(2) in H/D-Y and H-SAPO-37. The location of this proton closely resembles that of the SII cation in Na-Y. However, even though the two acid systems are very similar, there is one subtle but interesting difference. The protons in H-SAPO-37 were observed to redistribute upon adsorption of benzene so that protons relocate to O(2) where they can participate in a facial interaction with the benzene. No such redistribution is observed to occur in D-Y. The precision of the deuterium occupancies in the D-Y/benzene system is rather poor, but an occupancy of 3(3)% at O(2) is sufficient to account for binding to ≈ 12% occupancy of benzene at the six-ring location [since there are three O(2) sites in the six-ring]. IR data confirm the observation that protons redistribute in H-SAPO-37, but not in H-Y.<sup>10</sup> The reason for the redistribution in H-SAPO-37 is unclear, since there would appear to be a sufficient number of protons at the O(2) sites in the parent structure<sup>3</sup> to bind the benzene molecules that are found at the six-ring position.

The proportion of benzene molecules in the twelve-ring windows is much higher in D-Y and H-SAPO-37 than it is in Na-Y, an observation that is consistent with the stronger binding of benzene to the SII sodium cations in the latter system. This finding is corroborated by the <sup>2</sup>H NMR results (Fig. 2), which show the onset of benzene hopping at lower temperatures in the acid materials. A qualitative estimate of the relative strengths of the benzene/proton interactions in H-Y and H-SAPO-37 may be gleaned from the observation that benzene diffuses at a slightly lower temperature in H-Y. Evidence for a slightly weaker benzene proton interaction in H-Y is also apparent in desorption experiments.<sup>10</sup>

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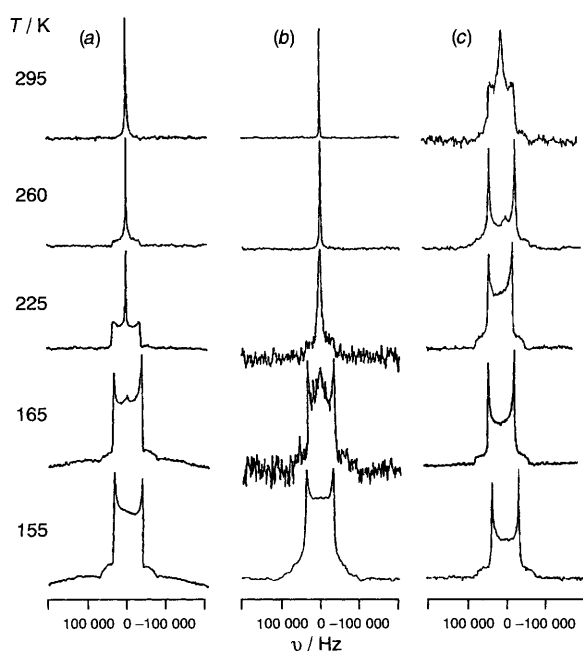
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**Table 1** Selected bond lengths (Å) and angles (°) in D-Y and D-Y + benzene

	D-Y	D-Y + Benzene
T-O(1)	1.635(12)	1.689(17)
T-O(2)	1.657(12)	1.626(13)
T-O(3)	1.624(11)	1.638(16)
T-O(4)	1.642(12)	1.614(17)
Average T-O	1.640	1.642
T-O(1)-T	138.2(12)	135.0(18)
T-O(2)-T	143.8(11)	148.8(14)
T-O(3)-T	139.2(13)	141.0(15)
T-O(4)-T	145.1(14)	144.0(19)
Average T-O-T	141.6	142.2
O(1)-D(1)	0.980(8)	0.972(13)
O(2)-D(2)	0.9792(8)	0.99(9)
O(3)-D(3)	0.980(8)	0.985(13)
O(4)-D(4)	0.9790(8)	0.981(13)
Average O-D	0.980	0.982
Si-O(1)-D(1)	110.9(6)	112.5(9)
Si-O(2)-D(2)	106.4(9)	105.6(9)
Si-O(3)-D(3)	110.0(6)	109.4(7)
Si-O(4)-D(4)	107.4(7)	107.9(9)
Average Si-O-D	108.68	108.85
D(2)-C <sub>6</sub> D <sub>6</sub> <sup>a</sup>		3.40
D(B)-O(4)		2.70

<sup>a</sup> Centre of benzene.



**Fig. 2** Temperature dependence of the <sup>2</sup>H NMR spectra of C<sub>6</sub>D<sub>6</sub> adsorbed in: (a) H-Y, (b) H-SAPO-37 and (c) Na-Y (Si:Al = 1.6:1)