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The Location of Deuterium Ions in Zeolite Y by Pulsed-Neutron Powder Diffraction

Many structural studies have been conducted to determine the cation positions in faujasite type zeolites (*1*), including some (*1–6*) to locate the hydrogens which play a central role in acid catalysis. Olson and Dempsey (*2*) deduced the hydrogen positions from the four independent Si(Al)–O distances; two positions were found: one on a highly accessible bridging double 6-ring oxygen, O(1), and the other in the sodalite cavity near O(3). Semiquantitative considerations by Mortier *et al.* (*3*) indicated that 17 protons per unit cell should bind to O(1), 10 to O(2), 28 to O(3), and 3 to O(4).

Using neutron diffraction, which facilitates the determination of the positions of hydrogen atoms in zeolites, Jirak *et al.* (*4*) studied H,Na–Y zeolites. Four different positions were found: those near O(1) and O(3) were highly occupied and those near O(2) and O(4) were nearly unoccupied. However, because protons are strong incoherent scatterers, there can be some question about these results. The same is true of the work of Cheetham and Thomas (*5*), who claimed (without reporting atomic coordinates nor bonding distances) to have located hydrogen positions in La,H–Y by neutron diffraction methods; the position they found, bound to O(4), is the site least favored by Mortier's calculation (*3*). Very recently, Czjzek *et al.* (*6*) located D in D,Na–Y and H in H,Na–Y by high-resolution neutron powder diffraction. A difference Fourier function unambiguously disclosed the deuterium position near O(1). Deuteriums near O(2) and O(3) were refined using Jirak's coordinates initially. None were found near O(4). They found that the site occupancies followed the order O(1) > O(3) > O(2); the O–H bond lengths ranged from 0.83 to 1.17 Å. Fischer *et al.* (*7*) studied zeolite D-Rho by neutron powder diffraction and found three deuterium equipoints with D–O distances ranging from 0.96 to 1.01 Å.

In this report, pulsed-neutron powder diffraction techniques were employed to determine the crystallographic positions of deuterium ions, and to learn the structure and placement of PbS species, in zeolite Y.

Zeolite Y powder of composition $Na_{55}Si_{137}Al_{55}O_{384}$ was refluxed with 0.1 *M* $Pb(NO_3)_2$ at 100°C for a week. After dehydration at 400°C and 1×10^{-6} Torr for 48 hr, the colorless zeolite sample was exposed to excess D_2S (g) at 25°C for 6 hr, which caused it to become orange-brown. It became light yellow after it was maintained under vacuum at 25°C for 24 hr to remove excess D_2S. The zeolite sample was sealed under vacuum in its Pyrex tube until it was loaded (in a helium glovebox) into a vanadium sample container (sealed with an indium ring) for the diffraction experiment.

Chemical composition analysis by atomic absorption (Huffman Laboratory) indicated the following formula: $Na_{10}Pb_{25}S_{23.5}Si_{137}Al_{55}O_{384}$. Deuterium analysis was not done. However, for charge balance in this sample, approximately 42 deuterium ions must be present.

Neutron diffraction data were collected at 10 K on the General Purpose Powder Diffractometer (GPPD) instrument at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. Beam flight times between 3.007 and 29.98 msec were measured. Pulses were accumulated for 14

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TABLE 1

Positional, Thermal, and Occupancy Parameters[a]

Atoms	Wyckoff position	x	y	z	U_{11} or U_{iso}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy
Si(Al)	192(i)	−0.0540(2)	0.0360(2)	0.1248(2)	479(35)	32(15)	13(20)	51(20)	4(21)	−97(17)	192
O(1)	96(h)	−0.1062(2)	0.1062(2)	0.0000	223(19)	223(19)	356(33)	−213(22)	−143(16)	−143(16)	96
O(2)	96(g)	−0.0038(1)	−0.0038(1)	0.1428(2)	234(18)	234(19)	242(28)	212(23)	−86(16)	−86(16)	96
O(3)	96(g)	0.1780(1)	0.1780(1)	−0.0331(2)	218(18)	218(18)	449(36)	155(16)	−115(16)	−115(16)	96
O(4)	96(g)	0.1757(1)	0.1757(1)	0.3212(2)	94(17)	94(17)	509(38)	302(18)	−12(19)	−12(19)	96
Pb(1)	32(e)	0.2581(5)	0.2581(5)	0.2581(5)	200[c]						5.5
Pb(2)	32(e)	0.0681(10)	0.0681(10)	0.0681(10)	200[c]						3.3
Pb(3)	32(e)	0.1882(11)	0.1882(11)	0.1882(11)	200[c]						3.4
D(1)	96(h)	−0.1423(8)	0.1423(8)	0.0000	200[c]						18.0
D(3)	96(g)	0.1886(7)	0.1886(7)	0.0156(11)	200[c]						16.1
Na	16(c)	0.0000	0.0000	0.0000	200[c]						2.7

[a] $a = 24.7027(3)$ Å, space group $Fd\bar{3}m$, origin at center.

[b] The anisotropic temperature factor $= \exp((-2\pi^2/a^2)(h^2U_{11} + k^2U_{22} + l^2U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23}))$. Values given are × 10^4.

[c] This thermal parameter was fixed in least-squares refinement.

hr at a beam current of approximately 14 μA. Data from the $2\theta = 148°$ banks with a channel width of 5 msec were used. The range of data with d-spacing below 0.616 Å was not used. A total of 684 reflections were used to generate the intensity profile. Structure solution and refinement were carried out using the Rietveld technique (*8*) and the GSAS crystallographic software system (*9*).

Profile refinement began in space group $Fd\bar{3}m$ using the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), O(3), and O(4)] of H,Na–Y (*4*). Anisotropic refinement of the framework atoms converged to

$$R_p = \sum_i |I(\text{obs})_i - (1/c)I(\text{calc})_i| / \sum_i I(\text{obs})_i = 0.0511,$$

and

$$R_{wp} = \left[\sum_i w_i (I(\text{obs})_i - (1/c)I(\text{calc})_i)^2 / \sum_i w_i I(\text{obs})_i^2 \right]^{1/2} = 0.0704,$$

where w is the weight at each 2θ step, $I(\text{obs})_i$ and $I(\text{calc})_i$ are the observed and calculated intensities, respectively, at that point, and c is the scale factor. A subsequent difference Fourier function revealed two peaks on the threefold axes at $x = y = z = 0.2581(2)$ and 0.0681(10), which refined as Pb^{2+} ions: Pb(1) in the supercage and Pb(2) in the sodalite cavity. This refinement lowered the residuals to $R_p = 0.0354$ and $R_{wp} = 0.0468$. Jirak's four deuterium positions were refined, but only his two principle positions refined nicely to significant occupancies. One position is in the supercage of zeolite Y, where it interacts with O(1), a bridging oxygen of a double 6-ring; the other, near O(3), lies in one 6-ring of a double 6-ring. Simultaneous refinement with all four cation positions led to $R_p = 0.0327$ and $R_{wp} = 0.0440$. A second difference Fourier function showed two new peaks: one refined as Na^+ at the center of the hexagonal prism and the other as Pb^{2+} on a threefold axis within the sodalite cavity (Pb(3) at site II′). Least-squares refinement converged to the final residuals $R_p = 0.0320$ and $R_{wp} = 0.0430$. Positions for many sulfur, lead, and sodium atoms have not been found. Final structural parameters are given in Table 1, and selected interatomic distances and angles for framework atoms and deuterium ions appear in Table 2. Figure 1 shows the agreement between observed and calculated peak profile intensities.

The two deuterium positions were very stable in refinement. They have the same D–O bond distances, 1.26 Å. They are in full agreement with Olson's model (*2*), with

TABLE 2

Selected Bond Distances (Å) and Angles (Degrees)

Si(Al)–O(1)	1.632(5)	O(1)–Si(Al)–O(2)	110.2(3)
Si(Al)–O(2)	1.644(5)	O(1)–Si(Al)–O(3)	108.4(4)
Si(Al)–O(3)	1.660(5)	O(1)–Si(Al)–O(4)	109.2(4)
Si(Al)–O(4)	1.630(4)	O(2)–Si(Al)–O(3)	107.4(4)
D(1)–O(1)	1.261(25)	O(2)–Si(Al)–O(4)	109.6(4)
D(1)–O(4)	2.671(8)	O(3)–Si(Al)–O(4)	112.1(4)
D(3)–O(3)	1.259(28)	Si(Al)–O(1)–Si(Al)	137.9(5)
D(3)–O(2)	2.620(7)	Si(Al)–O(2)–Si(Al)	146.1(4)
		Si(Al)–O(3)–Si(Al)	138.1(5)
		Si(Al)–O(4)–Si(Al)	145.9(6)
		Si(Al)–O(1)–D(1)	111.06(24)
		Si(Al)–O(3)–D(3)	110.43(26)

Jirak's principle positions (*4*) based on neutron diffraction from H,Na–Y, and with Czjzek's principle positions (*6*) by high-resolution neutron diffraction. Also, this result is supported by IR measurements: two stretching bands, at 3650 and 3550 cm^{-1} are seen, corresponding to bridging OH groups located in supercages (D(1)–O(1)) and sodalite cages (D(3)–O(3)), respectively (*10*). Both D(1) and D(3) lie in the Si(Al)–O–Si(Al) planes of the oxygen to which they are bound, D(1) exactly so by symmetry and D(3) almost exactly so (the sum of the angles about O(3) is 359°).

Eighteen D(1) ions per unit cell associate with O(1) framework oxygens, those which link 6-rings together to give double 6-rings. Each D(1) extends into the supercage, where it is highly accessible to large guest molecules. Sixteen D(3) ions associate with O(3) framework oxygens and lie in one 6-ring of a double 6-ring. D(3) ions are inaccessible to large guest molecules. The approximately eight additional deuterium ions which remain unlocated may exist as DS^- anions which interact with Pb^{2+} cations in supercages.

In this sample, deuterons are found at D(1) and D(3), in general agreement with all previous determinations (*2–4, 6*) except one (*5*). This result and those of Czjzek *et al.* indicate that the maximum occupancy at D(3) is 16 rather than 32 as predicted by Olson (*2*), possibly a result of the distribution of aluminum in the zeolite framework. The D–O bond lengths, both 1.26 Å, are longer than the 0.96–0.99 Å D–O distances Fischer found in D-rho (*7*) and the 0.83–1.17 Å distances Czjzek reported in H–Y and D–Y (*6*). This longer D–O distance may be

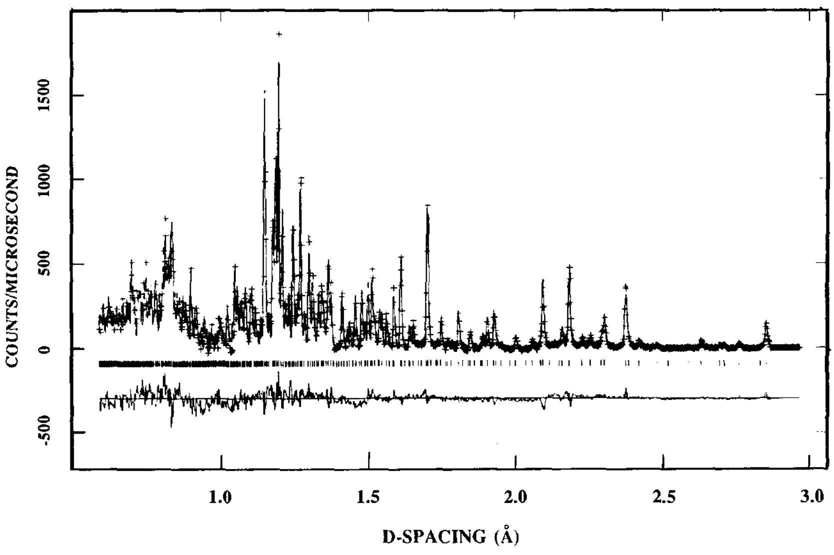

FIG. 1. Observed, calculated, and difference profiles.

attributed to D^+ interactions with unlocated S^{2-} ions. Perhaps the greater acidity of D–Y causes its D–O distances to be longer than those in Rho.

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