

A Neutron Diffraction Study of Acid Sites in H-SAPO-37

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A powder neutron diffraction study of H-SAPO-37 ($Fd\bar{3}$; $a = 24.804(2)$ Å; $R_p = 2.98\%$, $R_{wp} = 3.73\%$, $\chi^2 = 1.966$) reveals Al/P alternation in the framework, with Si substituting for P; protonation, in order of decreasing occupancy, is observed at O(1), O(2) and O(3).

Acid zeolites that adopt the faujasite (FAU) structure, including La-Y, H-Y and ultrastabilized-Y (US-Y), find widespread use as catalysts for petroleum cracking in gasoline manufacture.¹ The locations of the acid sites in La-Y² and H-Y³ have been established by neutron diffraction. In the case

of H-Y, protons have been found, in order of decreasing occupancy, at O(1) in the α -cage, at O(3) near to the SI' cation site in the β -cage, and at O(2) close to the SII cation site (Fig. 1). By contrast, results for La-Y² suggest that the acid sites are located at O(4), which protrudes into the supercage.

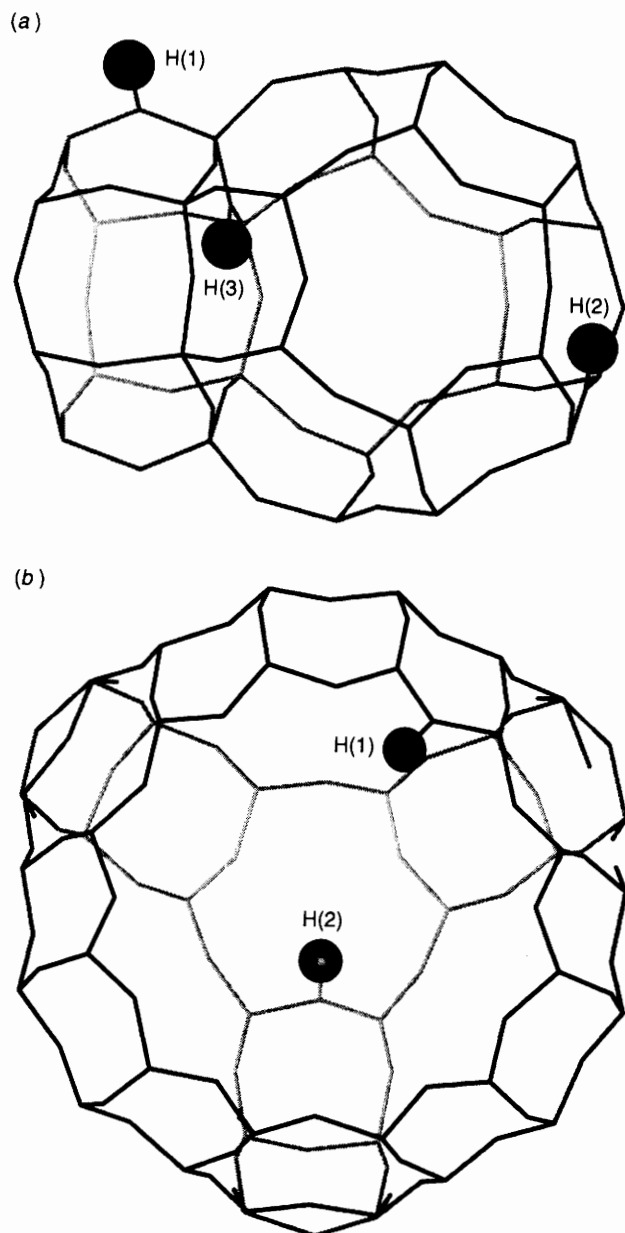


Fig. 1 FAU framework structure adopted by H-Y and H-SAPO-37: (a) a side view of the double-six ring and the β -cage, and (b) a view into the α -cage through the 12-ring window. The three occupied proton positions are indicated. H(1) is in the plane of the 12-ring window, H(2) is in the six-ring window (which normally accommodates the SII cation site) and protrudes slightly into the supercage, and H(3) is located in the plane of the six-ring window between the β -cage and the double-six-ring (normally known as the SI' site).

Important factors that influence acid site locations include the positions of other cations, if any, and the T-O-T angles, with protonation usually being favoured at oxygen atoms with smaller angles.⁴

The silicoaluminophosphate analogue of zeolite-Y, SAPO-37,⁵ can be prepared in the presence of templates such as TMA+OH⁻ and TPA+OH⁻, and the catalytic properties of its acid form, H-SAPO-37, have been reported.⁶ IR studies⁷ suggest that there are acid sites in the α - and β -cages, with O-H stretching frequencies of 3640 and 3575 cm⁻¹, respectively, similar to those found in H-Y.⁸ We now report the findings of a neutron diffraction study on the acid form of this important material.

Table 1 Selected bond lengths (\AA) and angles ($^\circ$) in H-SAPO-37 compared with those in H-Y³

H-SAPO-37		H-Y	
Si/P-O(1)	1.594 (13)	T-O(1)	1.677(6)
Si/P-O(2)	1.536 (14)	T-O(2)	1.632(7)
Si/P-O(3)	1.543 (11)	T-O(3)	1.654(6)
Si/P-O(4)	1.540 (14)	T-O(4)	1.636(7)
Mean	1.553	Mean	1.648
Al-O(1)	1.725 (15)	—	—
Al-O(2)	1.717 (18)	—	—
Al-O(3)	1.772 (14)	—	—
Al-O(4)	1.708 (17)	—	—
Mean	1.731	—	—
Si-O(1)-Al	137.86 (30)	T-O(1)-T	135.7(3)
Si-O(2)-Al	149.79 (27)	T-O(2)-T	144.6(5)
Si-O(3)-Al	144.47 (29)	T-O(3)-T	139.8(4)
Si-O(4)-Al	144.6 (4)	T-O(4)-T	143.9(5)
Mean	144.18	Mean	141.0

The templated form of SAPO-37 was synthesized according to example 43 of Lok *et al.*,⁵ except that the reaction was carried out at 150 °C for 27 days. The product was analysed by X-ray fluorescence spectroscopy (7.6 wt.% Si, 23.5% Al, 17.9% P). ²⁹Si and ³¹P MAS NMR measurements revealed no evidence for the presence of the silicon islands reported by Saldarriaga *et al.*⁹ The acid form of SAPO-37 was prepared by careful calcination of the SAPO-37 at 525 °C under dry oxygen (since the excellent crystallinity of the parent material is rapidly lost in the presence of moisture¹⁰). NMR measurements indicated that some Si clustering had taken place during calcination. Powder neutron diffraction data were collected in two frames, at 5 K, on the DUALSPEC diffractometer at Chalk River, Canada, with a neutron wavelength of 1.5043 \AA . The structure was refined by the Rietveld method¹¹ using the GSAS suite of programs.¹² An AlPO₄ starting model in space group *Fd3*, based on the aluminosilicate framework structure of sodium zeolite-X,¹³ was used. Silicon was introduced at the P site with the P/Si ratio fixed at the value determined analytically. Protons were placed geometrically on each oxygen in turn, assuming a coplanar configuration with the T-O-T atoms and an O-H bond length of 0.96 \AA ; only their occupancies were varied. Isotropic temperature factors were refined for two atom types, oxygen and T atoms, respectively, while those of the hydrogens were fixed at the value reported by Czjzek *et al.*³ No other restraints or constraints were used. We note that this is a more demanding refinement than that of H-Y³ because the structure is non-centrosymmetric.

The bond lengths (Table 1) determined from the final refinement (Fig. 2) confirm the alternation of framework aluminium and phosphorus, as observed, for example, in AlPO₄-5,¹⁴ and the mean P-O bond length is consistent with our assumption that silicon is substituting exclusively for phosphorus¹⁵ (typical P-O and Si-O bond lengths are, respectively, 1.53 and 1.60 \AA). The T-O-T angles in H-SAPO-37 are slightly larger than those found in H-Y (Table 1),³ a finding that might lead us to expect slightly higher acidity in the SAPO material. Experimental evidence on this point is conflicting.^{6,7,16}

Proton sites at O(1) (19.7% occupancy), O(2) (6.4%) and O(3) (4.4%) were found to be occupied, the sum of their occupancies accounting for 95% of the expected proton concentration. This finding is qualitatively consistent with that in H-Y. The preferential protonation of O(1) is expected on bond angle grounds, but is more pronounced in H-SAPO-37 than in H-Y. Protonation of O(3) is also found in both cases, although the T-O(3)-T angles in H-SAPO-37 are similar to

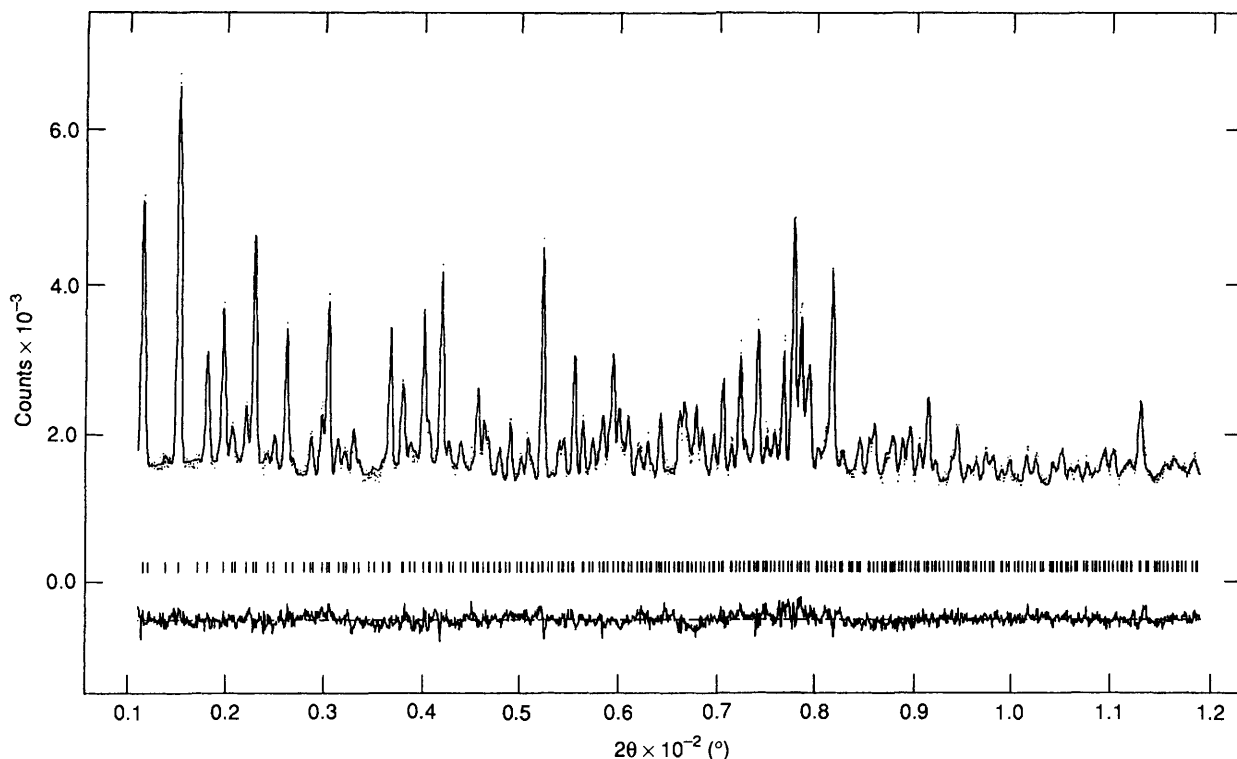


Fig. 2 Experimental, calculated and difference profiles of H-SAPO-37. The high and low angle data have only been merged for the purpose of the Figure.

those at O(4). Hydrogen bonding to other oxygens in the six-ring window may confer extra stability on this site. Protonation of O(2), which is again observed in both systems, was unexpected as it exhibits the largest T–O–T bond angle, but this site, too, may be stabilized by hydrogen bonding to the other oxygens in the six-ring window. Our observation of protons at O(1), O(2) and O(3) is broadly consistent with the previous interpretation⁷ of the IR spectra; we would assign the band at 3640 cm^{-1} to O(1)–H(1), and that at 3575 cm^{-1} to O(3)–H(3) [and possibly O(2)–H(2)]. The observation of protons at O(1) and O(2) would account for the acidity of this material for catalytic reactions that proceed in the α -cage, though paradoxically, since H(1) has the highest occupancy, it would appear that this site is actually the most stable, and hence the least acidic, of those available. It is interesting to speculate, therefore, that protons located at O(2) are the catalytically active species in this material, a possibility that is all the more attractive in the light of the fact that sorbate molecules show a marked tendency to bind in the vicinity of this position.

The authors are very grateful to R. L. Donabarger for his assistance in collecting the neutron data. L. M. B. acknowledges SERC and the University of California for financial support. This work made use of MRL Central Facilities supported by the National Science Foundation under Award No. DMR-9123048.

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Received, 28th April 1993; Com. 3/02442C