A quantitative description of the active sites in the dehydrated acid catalyst HSAPO-34 for the conversion of methanol to olefins

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A neutron diffraction study of the deuterated form of a microcrystalline specimen of the H^+SAPO-34 catalyst for converting methanol to light olefins reveals two distinct bridging hydroxyl Brønsted sites. These sites are also identified by IR spectroscopy which distinguishes their acid strength from the shift in O–H frequencies following adsorption of CO at 77 K. Protons attached to the O(4) bridging oxygen (OH distance 0.95 Å) exhibit greater acidity than those attached to O(2) (OH distance 0.91 Å).

Keywords: active site; acid site; solid acid; microporous catalyst

1. Introduction

HSAPO-34 is acknowledged to be a powerful catalyst, with attractive performance in converting methanol to light alkenes, principally ethene, propene and butene [1,2]. The silicoaluminophosphate catalyst is structurally analogous to, but compositionally distinct from, the zeolitic mineral chabazite [3,4], but whereas in chabazite all the tetrahedral (T) sites are tenanted either by Si^{4+} or Al^{3+} ions, Al and P ions are thought to occupy the T sites alternately in HSAPO-34 and some Si ions reside in the sites normally occupied by P. In HSAPO-34 two distinct kinds of bridging hydroxyls have been identified through IR studies [3] and are characterised by stretching frequencies at 3630 cm^{-1} (high frequency (HF) mode) and at 3601 cm^{-1} (low frequency (LF) mode). Many earlier studies have sought to identify the location of the acid sites in the zeolite, and based on their results on the interactions of molecular hydrogen with the framework Zubkov et al. [5] theorised that one hydroxyl group existed on the six ring (six T sites) of the structure. By using powder neutron diffraction, we have now determined the precise locations of the acid sites in this important catalyst (fig. 1). Our results are corroborated by IR spectroscopic studies of the dehydrated solid before and after adsorption of the acid-site probe CO.

2. Experiments and results

The templated form of SAPO-34 was synthesised according to a previously outlined procedure [6], the acid form being obtained by calcination of the SAPO-34 at 550°C in oxygen. The powder sample was deuterated through prolonged exchange with D_2O at 60 to 80°C and eventually dehydrated. Powder neutron diffraction data were collected at 15 K at Brookhaven National Laboratory with a neutron wavelength of 1.8857 Å, and the structure was refined by the Rietveld method using the GSAS suite of programs [7]. A framework structure based on the single crystal structure of ZYT-6 was used as the starting model in space group R3 [8]. However, upon further refinement, the space group R3 was found to yield a more satisfactory solution. Silicon was substituted exclusively at phosphorus sites and held at fixed fractional occupancies early in the refinement to match known chemical trends [9], but these soft constraints were later removed. The positions of the deuterium atoms from the acid sites were initially restrained geome-

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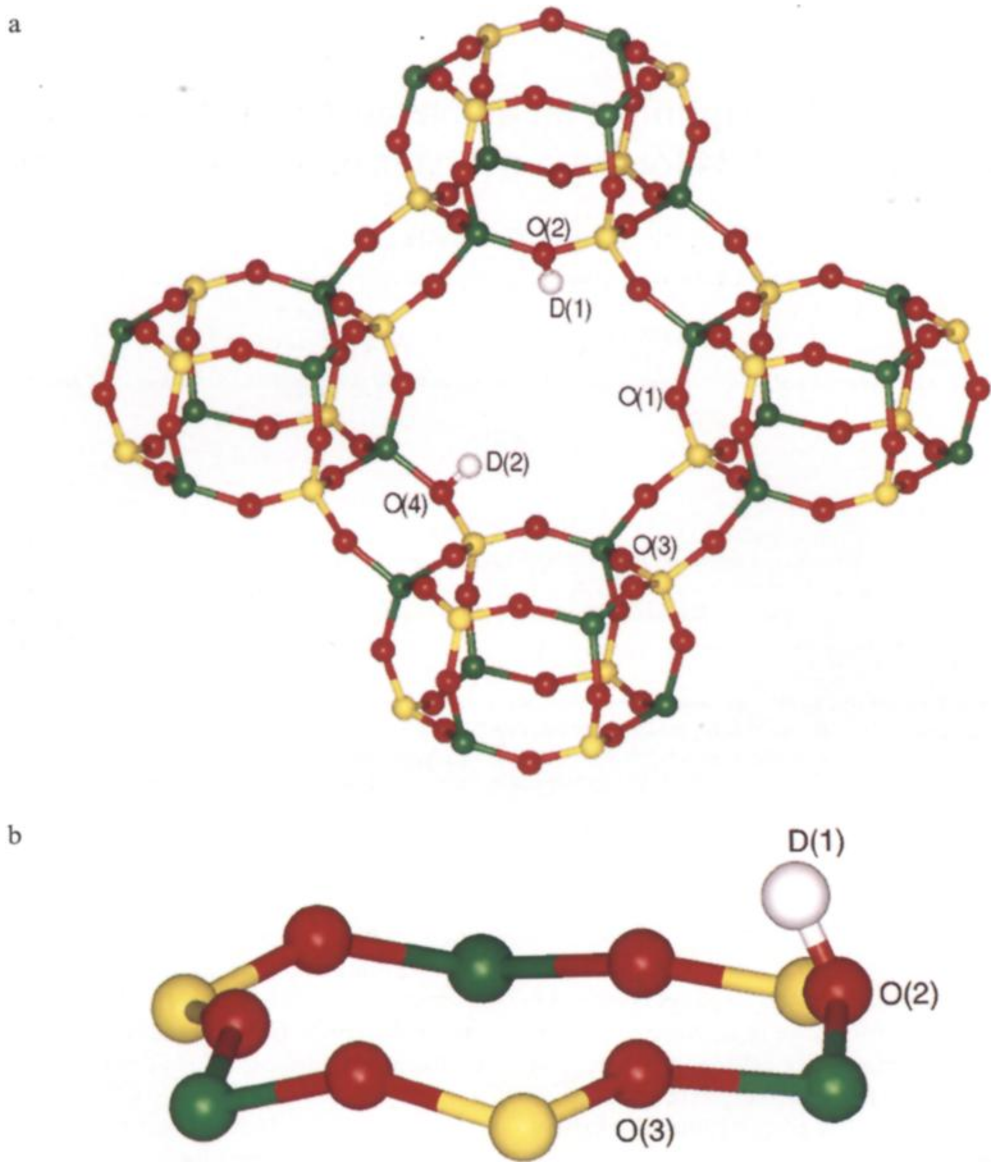

Fig. 1. (a) A ball and stick representation of the structure of dehydrated HSAPO-34. Atom types are designated by colour: aluminum by yellow, silicon and phosphorus by green, oxygen by red, and deuterium by white. (b) A close view of the six-atom ring which constitutes the hexagonal prism. Note the perturbed nature of the D–O bond.

trically using an O–D bond distance of 1.00 Å. The positions and fractional occupancies of the deuterons of the acid sites were later refined individually. Isotropic temperature factors were refined by two atom types, oxygen and T atoms, whereas those of the hydrogen atoms were fixed at the value reported by Czjzek et al. [10]. The bimodal distribution of bond lengths (table 1) determined from the final refinement (fig. 2) confirm the alternation of framework aluminium and phosphorus, as observed, for example, in ALPO$_4$-5 [11] and DAF-4 [12].

Table 1
Distribution of T–O bond lengths in dehydrated HSAPO-34

P(1)/Si(2)–O(4)	1.509 (12)	Al(3)–O(4)	1.702 (15)
P(1)/Si(2)–O(5)	1.547 (16)	Al(3)–O(5)	1.667 (20)
P(1)/Si(2)–O(6)	1.483 (13)	Al(3)–O(6)	1.818 (17)
P(1)/Si(2)–O(7)	1.598 (13)	Al(3)–O(7)	1.707 (16)

Two distinct acid sites were found in the refinement. The fractional occupancies of the different proton sites were: 4.0% for the deuteron attached to O(2) and 3.4% for the one attached to O(4). The deuteron from the acid site at O(2) is at a distance of 0.91 Å from the oxygen atom, whereas in the other acid site the deuteron sits 0.95 Å from O(4). Both of the deuterons are at large angles out of the plane formed by the Si–O–Al bonds. The deuteron at O(2) tilts towards the centre of the six ring of the hexagonal prisms of the framework at an angle of 46°, whereas that at O(4) sits at an angle of 63° below the four ring formed by the T–O(4) bonds. D(1) is situated also 2.36 Å from the other oxygen atom in the six ring. Weak hydrogen bonding occurs along the edge

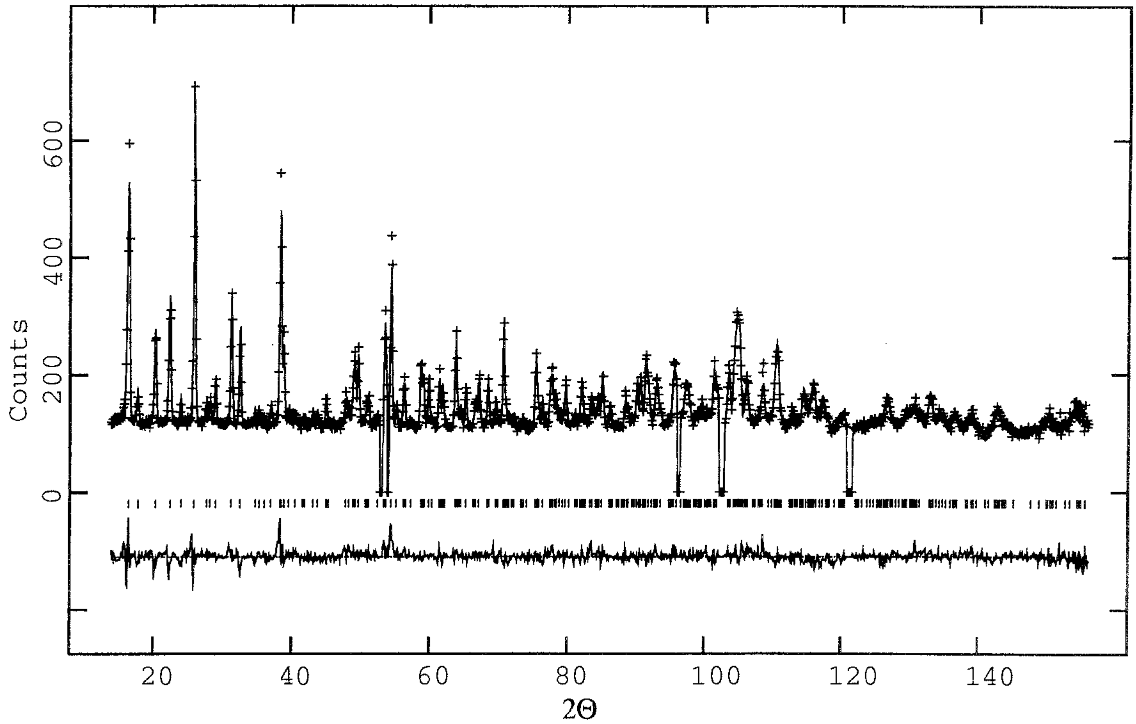

Fig. 2. Final observed, calculated and difference profile plots for the neutron refinement of dehydrated HSAPO-34 (R3; $a = 13.7739(4)$ Å; $c = 15.0160(6)$ Å; $R_p = 5.46\%$; $R_{wp} = 4.23\%$; $\chi^2 = 3.194$. There is strict alternation of Al and P in the framework with Si substituting for P). Five excluded regions are present in the profile in order to remove small peaks from an unidentified impurity.

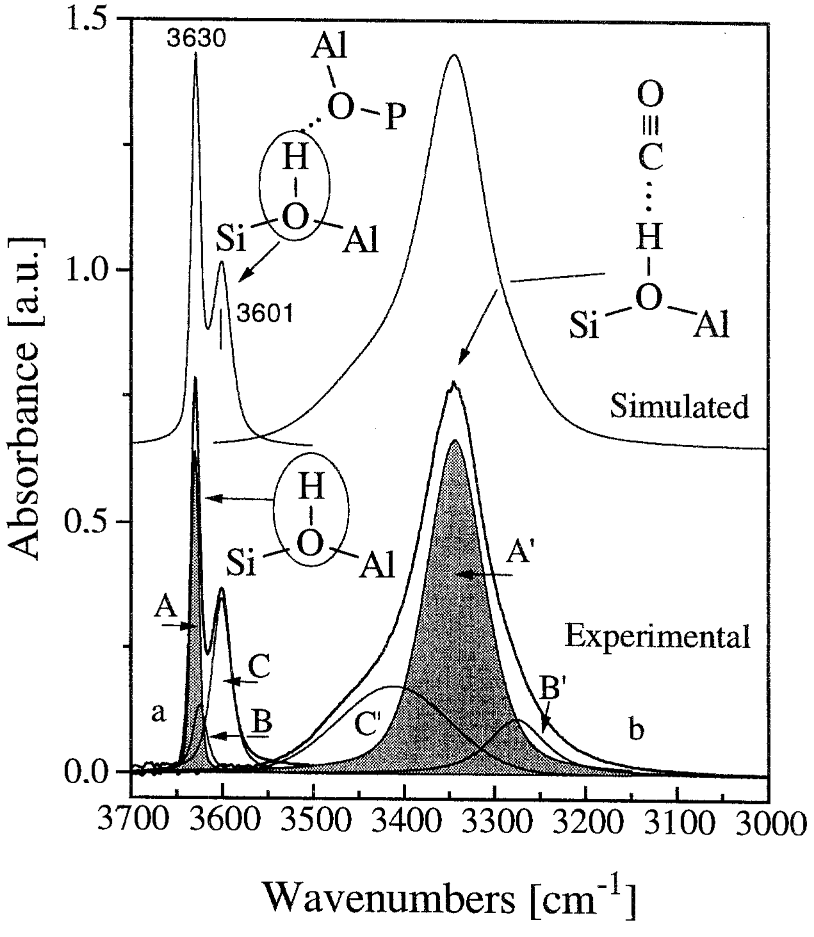

Fig. 3. IR spectra of Brønsted OH in HSAPO-34 at 77 K before (curve a) and after (curve b) the adsorption of CO. It is revealed, using a fitting procedure, that both bands are constituted of three components (A, B, and C). The overall fitted spectrum is reported on top of the figure.

Table 2
Spectroscopic features of the Brønsted OH in HSAPO-34 before and after CO adsorption

OH	ν_{OH}	Area	OH ··· CO	$\nu_{OH\text{-}CO}$	Area
A	3630	7.8	A′	3343	57.6
B	3625	3.1	B′	3276	10.2
C	3601	10.6	C′	3411	26.7
fit A + B + C	–	21.5	fit A + B + C	–	94.5
exp. (a)	–	20.8	exp. (b)	–	97.1

of the six ring and probably stabilises the tipping of the deuteron toward the centre of the ring. Such bonding would appear to constrain this proton in the six ring, confirming the earlier conclusions of Zubkov et al. [5]. Weak hydrogen bonding between D(2) and the oxygen atom of the six ring also appears to stabilise the large out-of-plane angle. The distance of D(2) from O(2) is 2.23 Å which is short enough to imply weak hydrogen bonding. The protons seem to be centred in a convergence of weak hydrogen bonds with neighbouring oxygen atoms.

Following Makarova et al. [13], Zecchina et al. [14] and Paukshtis et al. [15], CO has been used as a probe molecule in IR studies to explore the nature of the Brønsted sites in solid acid catalysts. When CO is adsorbed on HSAPO-34 at 77 K (fig. 3), the stretching frequencies of the two distinct bridging hydroxyls are significantly perturbed: they are shifted to lower frequencies and the intensity of the absorptions increases. Moreover, it has been established [13,16] that, from the magnitudes of the shifts in frequency ($\Delta\nu_{OH}$) and the integrated intensity of the absorption bands (table 2), it is possible to compute the percentages of the two distinct bridging hydroxyls present in the parent catalyst. From our data, we find that 55 ± 3 percent of the acid hydroxyls are of the high-frequency (HF) variety and 45 ± 3 percent of the LF variety. (We note in passing that CO perturbs the HF absorption more ($\Delta\nu = 287$ cm^{-1}) than the LF one ($\Delta\nu = 190$ cm^{-1}) signifying that these two kinds of hydroxyls have different acidities.)

3. Conclusions

Both our powder refinement results and of DSAPO-34 and the IR study of CO absorption of HSAPO-34 point to a nearly equal occupancy of acidic protons at both oxygen sites. The finer details of the different acidities of these acid sites have been revealed through a neutron diffraction and FTIR study of hydrated (deuterated) HSAPO-34 [17]. Upon partial hydration, the proton at O(4) was completely removed while the proton at O(2) was still bound signifying a greater acidity for the O(4) acid site. This would imply that the HF absorption observed in the IR study corresponds to the acid site located at O(4).

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