

## Solid-state $^1\text{H}$ N.M.R. Studies of the Structure of the Active Site in Zeolite H-ZSM-5

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Solid-state  $^1\text{H}$  n.m.r. shows that the mean distance between acidic protons in bridging hydroxyl groups and the nearest framework Al atom in zeolite H-ZSM-5 is  $2.48 \pm 0.04 \text{ \AA}$ .

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Much attention has been devoted to the determination of the number and structure of the bridging hydroxyl groups, the source of Brønsted acidity in zeolitic catalysts. Powder diffraction methods have yielded the framework structures of a number of zeolites,<sup>1-3</sup> but not the precise details of the Si-OH-Al grouping.  $^1\text{H}$  N.m.r. is a particularly powerful tool for the determination of the Al-H distance in view of the fact

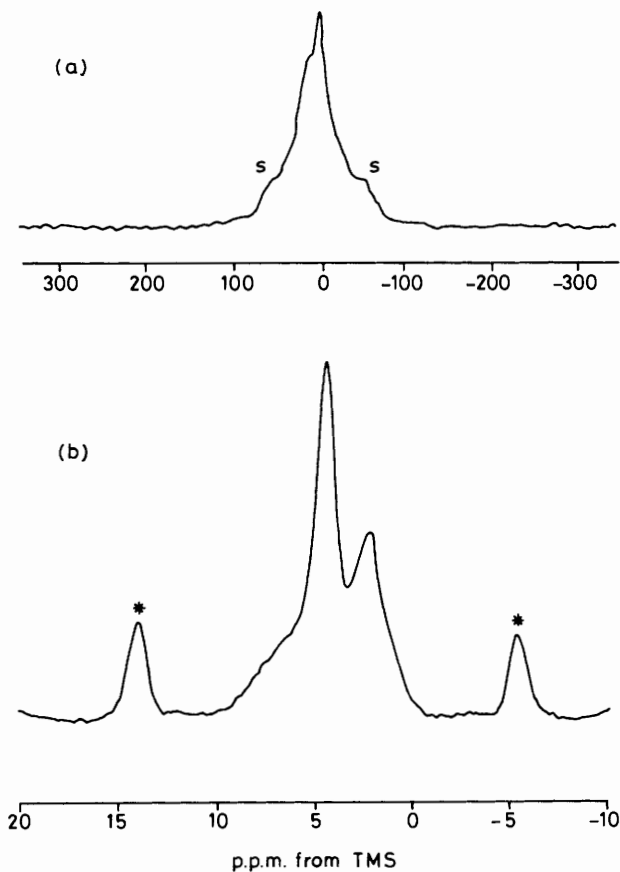
that, for rigid polycrystalline solids, the second moment (the root-mean-square width) of the n.m.r. resonance signal is inversely proportional to the sixth power of the internuclear distance between nuclei coupled *via* the dipolar interaction.

Stevenson<sup>4</sup> used  $^1\text{H}$  n.m.r. to determine the Al-H distance in zeolite H-Y as  $2.38 \text{ \AA}$ , which remains the most reliable value for this important parameter. The second moment,  $M_2$ ,

of the proton spectra was found to be dominated by the  $^1\text{H}$ - $^{27}\text{Al}$  interaction. Since 1971 solid-state n.m.r. has made enormous advances and it is now possible to monitor all the elemental constituents of the aluminosilicate framework with great sensitivity.<sup>5</sup> Furthermore, it is now possible to establish the structure of the Brønsted active site in zeolite H-ZSM-5, in which the concentration of protons and of aluminium is much lower than in zeolite H-Y.

Zeolite H-ZSM-5 (Si/Al = 15) was prepared by template-free synthesis followed by exchange with aqueous HCl.<sup>†</sup> Samples were heated in glass tubes with a 5.5 mm inner diameter and a zeolite layer 10 mm thick. The temperature was increased at a rate of 10 K h<sup>-1</sup> to 400 °C, whereupon the samples were sealed off.

To avoid line broadening by chemical shift anisotropy the second moment of OH groups was calculated from low field (90 MHz) static  $^1\text{H}$  n.m.r. spectra (see Figure 1). The concentration of hydroxyl groups was determined in a probehead with a short ringdown time by comparing the maximum amplitude of the free induction decay (f.i.d.) from the zeolite samples with the f.i.d. of a capillary filled with water. The frequency-domain n.m.r. signal resulted from the Fourier transformation of the f.i.d. following the  $\pi/2 - \tau - \pi$  pulse sequence with 1.5  $\mu\text{s}$   $\pi/2$  pulses and  $\tau = 100 \mu\text{s}$ . Acquisition was triggered at  $2\tau$ . No difference in lineshape was detected upon increasing  $\tau$  from 50 to 300  $\mu\text{s}$ . The longitudinal relaxation time of the hydroxyl protons in the samples was *ca.*



**Figure 1.**  $^1\text{H}$  N.m.r. spectra of zeolite H-ZSM-5 SB-activated at 400 °C and sealed: (a), broad-line spectrum measured at 90 MHz, 's' denotes a shoulder; (b), m.a.s. n.m.r. spectrum measured at 300 MHz, \* denote spinning sidebands.

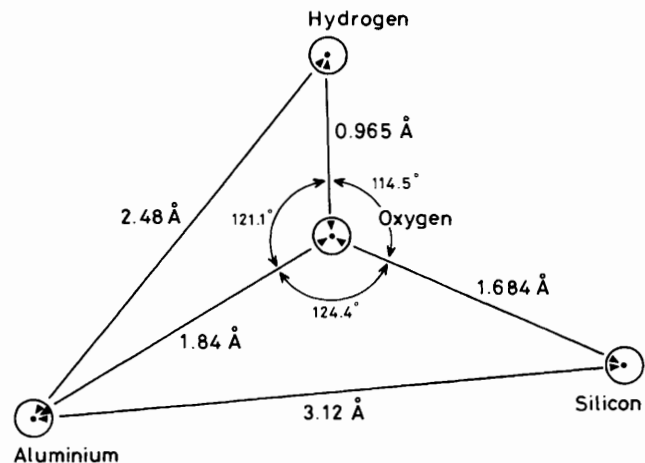
8 s and 500 scans were acquired. High-resolution  $^1\text{H}$  magic-angle spinning (m.a.s.) n.m.r. measurements were performed on a Bruker MSL-300 spectrometer.

$^1\text{H}$  m.a.s. n.m.r. spectra are given in Figure 1(b). The signal at *ca.* 2 p.p.m. is due to non-acidic hydroxyl groups at the outer surface of the crystallites, at framework defects and in the amorphous part of the sample, and the signal at 4.3 p.p.m. comes from bridging (acidic) OH groups. Under certain conditions a simple expression [equation (1);  $r$  in Å,  $M_2$  in  $10^{-8} \text{T}^2$ ] based on van Vleck's formula<sup>6</sup> can be used to calculate the aluminium-proton distance,  $r_{\text{Al-H}}$ , from the second moment,  $M_2$ , of the broad-line spectrum [Figure 1(a)].

$$r_{\text{Al-H}} = \sqrt[6]{(126.09)/M_2} \quad (1)$$

The main condition which must be met is that dipole-dipole interactions additional to the interaction between a single proton and a single aluminium nucleus are either absent or negligibly small. The concentration of aluminium is equal to that of bridging hydroxyl groups. Since there is no evidence of the presence of extra-framework Al in the activated sample, the strongest interaction to be considered is the  $^1\text{H}$ - $^1\text{H}$  interaction. The contribution of this interaction to the second moment of the  $^1\text{H}$  n.m.r. spectrum can be calculated using Hahn's echo decay. Different transverse relaxation times can be measured:  $T_2^{\text{f.i.d.}}$  from the free induction decay and  $T_2^{\text{HE}}$  from Hahn's echo decay. We have found  $T_2^{\text{f.i.d.}} = 65 \mu\text{s}$  and  $T_2^{\text{HE}} = 1 \text{ms}$ , the difference of a factor of 15.4. Because Hahn's echo decay depends solely on the proton-proton dipole interaction and  $M_2$  is proportional to  $1/T_2^2$ , the contribution of the  $^1\text{H}$ - $^1\text{H}$  interaction to the second moment is  $0.004225 M_2$  and can be neglected. Contributions to  $M_2$  from  $^1\text{H}$ - $^{29}\text{Si}$  and  $^1\text{H}$ - $^{27}\text{Al}$  interactions with second-nearest and further aluminiums are even smaller.

The static  $^1\text{H}$  n.m.r. spectrum is given in Figure 1(a). The sample contained  $1.5 \pm 0.1$  bridging hydroxyl groups, 1.5 framework Al atoms, and  $0.3 \pm 0.1$  silanol groups per channel intersection, *i.e.* per 1/4 unit cell. The second moment attributable to silanol groups on framework defects [line at *ca.* 2 p.p.m. in Figure 1(b)] measured in the parent zeolite Na-ZSM-5 (which contains very few bridging hydroxyls) was  $0.40 \pm 0.2 \cdot 10^{-8} \text{T}^2$ . Considering that in H-ZSM-5 the silanol groups amount to 20% of the total hydroxyl concentration, we find  $M_2 = 0.54 \pm 0.04 \cdot 10^{-8} \text{T}^2$  for the second moment due to bridging hydroxyl groups from the experimental value  $0.51 \pm 0.03 \cdot 10^{-8} \text{T}^2$  for the signal in Figure 1(a).



**Figure 2.** The geometry of the Brønsted acid site in zeolite H-ZSM-5. The various atomic radii are not to scale.

<sup>†</sup> Provided by Dr. W. Schwieger, Halle.

The signal is asymmetric because of the different chemical shifts of the bridging hydroxyl groups and the silanol groups. There are also two shoulders (denoted by 's') which are  $\Delta = 10.2 \pm 0.3$  kHz ( $2.40 \pm 0.08 \cdot 10^{-4}$  T) apart. The theoretical lineshape of the  $^1\text{H}$ - $^{27}\text{Al}$  pair is a superimposition of three Pake doublets: one due to the interaction of  $^1\text{H}$  with  $^{27}\text{Al}$  in the states with  $S = \pm 1/2$  and two doublets due to  $S = \pm 3/2$  and  $S = \pm 5/2$ . Spectral singularities of the 1/2 and 3/2 doublets are smoothed by dipolar interactions, but the broader 5/2 doublet gives rise to the shoulders as observed. Calculation of the moment using the distance between the  $\pm 5/2$  singularities gives  $M_2 = 7\Delta^2/75 = 0.54 \pm 0.05 \cdot 10^{-8}$  T<sup>2</sup>. Since the position of the singularities is unaffected either by the narrower superimposed SiOH signal or by other line-broadening effects, the value of the second moment is very reliable. This gives  $r_{\text{H-Al}} = 2.48 \pm 0.04$  Å. The Al-H distance of 2.48 Å in zeolite H-ZSM-5 is thus larger than that of 2.38 Å in zeolite H-Y.<sup>5</sup> This is because of the smaller T-O-T angles in a framework composed mostly of 5-membered rings. Figure 2 represents the planar SiOHAl arrangement. Since n.m.r. can provide only the Al-H distance, the remaining parameters had to be taken from other techniques. Sauer<sup>7</sup> performed *ab initio* quantum-mechanical calculations and obtained  $r_{\text{Si-O}} = 1.684$  Å,  $r_{\text{O-H}} = 0.965$  Å and the Si-O-H angle of 114.5°;  $r_{\text{Si-O}}$  is about 0.1 Å greater than the average T-O distance in ZSM-5,<sup>2</sup> which reflects the influence of the proton on the length of the Si-O bond. The Al-O distance is more difficult to determine. Stevenson<sup>4</sup> used  $r_{\text{Al-O}} = 1.72$  Å for zeolite H-Y,<sup>1</sup> while *ab initio* calculations give the values of 1.84 Å<sup>8</sup> and 1.94 Å.<sup>7</sup>

Using our value for  $r_{\text{Al-H}}$  in combination with the Si-O-H angle and  $r_{\text{Si-O}}$  and  $r_{\text{O-H}}$  distances from ref. 7 and  $r_{\text{Al-O}}$  distances equal, in turn, to 1.72, 1.84, and 1.94 Å, we arrive at Al-O-H angles of 132.9, 121.1, and 112.9 Å and Al-Si distances of 2.83, 3.12, and 3.32 Å, respectively. The structure reported in ref. 2 leads to the average T-T distance of 3.12 Å.<sup>9</sup> If one considers that framework relaxation favours a constant T-T distance, the Al-O distance of 1.84 Å seems to be the most appropriate. A combination of solid-state n.m.r. results and *ab initio* calculations leads to the geometry of the active site shown in Figure 2.

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