SOLID-STATE NMR STUDIES OF THE GEOMETRY OF BRØNSTED ACID SITES IN ZEOLITIC CATALYSTS

Dieter FREUDE a, Jacek KLINOWSKI b and Halimaton HAMDAN b

a Sektion Physik, Karl-Marx-Universität Leipzig, Linnéstrasse 5, DDR-7010 Leipzig, German Democratic Republic
b Department of Physical Chemistry, Lensfield Road, University of Cambridge, Cambridge CB2 1EP, UK

Received 2 May 1988; in final form 14 June 1988

1H, 27Al and 29Si solid-state NMR was used to determine the geometry of the Brønsted acid site in zeolites. The mean distance between acidic protons in bridging hydroxyl groups and the nearest framework Al atom is 2.38 ± 0.04 Å in zeolite H-Y and 2.48 ± 0.04 Å in H-ZSM-5. The quadrupole frequency of framework Al is 1.02 ± 0.05 and 3.1 ± 0.8 MHz in dehydrated Na-Y and H-Y, respectively.

1. Introduction

Structural (bridging) hydroxyl groups are the source of Brønsted acidity in zeolitic catalysts. Much attention has been devoted to the determination of their number and structure, as well as to the measurement of acid strengths of various zeolites. Powder X-ray [1] and neutron [2] diffraction yield structural details of the aluminosilicate framework, but diffraction methods have not provided exact details of the angles and distances in the Si–OH–Al grouping. 1H NMR is a particularly convenient tool for the determination of the Al–H distance and provides the only value which can be used to assess the results of ab initio calculations [3].

In his 1971 paper Stevenson [4] used 1H NMR to determine the Al–H distance in zeolite H-Y as 2.38 Å, which remains the most reliable value for this vital parameter. He found that the second moment of the proton spectra, which is inversely proportional to the sixth power of the distance between the dipole-coupled nuclei, is dominated by the 1H–27Al interaction. It is now clear that Stevenson’s early work poses a number of unresolved questions. The most important concerns sample preparation: his samples were calcined in air at 550°C and therefore contained more non-framework than framework aluminium in addition to a significant amount of non-bridging hydroxyl groups. Furthermore, solid-state NMR has made enormous advances since 1971 and it is now possible to monitor all the elemental constituents of the aluminosilicate framework with great sensitivity. Modern multinuclear NMR techniques, especially those involving magic-angle spinning (MAS) allow us to adopt a more quantitative approach to the vital question of the structure of the active site in zeolitic catalysts, and we reconsider the various problems involved.

2. Experimental

Broad-line 1H NMR spectra needed for the determination of the total concentration of the hydroxyl groups and the second moment of the lineshape were measured in Leipzig at 270 and 90 MHz on homemade spectrometers. The concentration of OH groups was determined in a probehead with a short ring-down time by comparing the maximum amplitude of the free induction decay (FID) from the zeolite samples with the FID of a capillary filled with water. The frequency-domain NMR signal resulted from the Fourier transformation of the FID following the π/2–π pulse sequence with 1.5 μs π/2 pulses and τ = 100 μs. Acquisition was triggered at 2τ. No difference in lineshape was detected upon increasing τ from 50 to 300 μs. The longitudinal relaxation time of the hydroxyl protons in the samples was ~8 s and
at least 100 scans were acquired to achieve a signal-to-noise ratio better than 100. $^1$H MAS NMR measurements were carried out using a Bruker MSL-300 spectrometer in Leipzig, while $^{29}$Si and $^{27}$Al spectra were measured in Cambridge using a Bruker MSL-400 instrument. For $^{27}$Al measurements of non-spinning dehydrated samples quartz ampoules, sealed off under vacuum, were used in an aluminium-free probehead. The $^{27}$Al pulse length was $1 \mu$s, which corresponded to a $\pi/12$ pulse for non-selective excitation.

Zeolite Na, NH$_4$-Y containing 88 ± 3% NH$_4^+$ was prepared by repeated exchange of a sample of Na-Y (Si/Al=2.60) in an aqueous solution of NH$_4$NO$_3$. One portion of the product was calcined at 550°C in air for 2 h, which reproduces Stevenson’s sample preparation [4]. Shallow-bed (SB) samples for $^1$H NMR were prepared by heating in glass tubes 5.5 mm inner diameter with zeolite layer 10 mm thick. The temperature was increased at a rate of 10 K h$^{-1}$. After maintaining the samples at 400°C and at less than $10^{-2}$ Pa pressure for 24 h, several samples were partially deuterated by contact with 16 Torr D$_2$O at 400°C for 2 h. They were then evacuated again at 400°C for 2 h and sealed off. The weak hydrothermal treatment during deuteration does not significantly affect the zeolitic framework, as has been shown by comparing $^1$H, $^{27}$Al and $^{29}$Si spectra of samples exposed to H$_2$O instead of D$_2$O and of the sample which was not subjected to vapour treatment. Zeolite H-ZSM-5 with Si/Al=15, prepared by template-free synthesis followed by exchange with aqueous HCl, was provided by Dr. W. Schwieger, Halle.

3. Results and discussion

$^1$H MAS NMR spectra of zeolite Y are given in fig. 1. The four different proton signals are best seen in partially deuterated H-Y (spectrum (D)). Line (a) at 1.9 ppm 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. Line (b) at 3.9 ppm comes from bridging OH groups involving O$_1$ atoms and pointing towards the zeolitic supercages, and the line (c) at 4.9 ppm from protons on O$_2$ atoms and pointing towards the other oxygens.

![Fig. 1. $^1$H MAS NMR spectra of zeolite Y (arbitrary intensities). Asterisks denote spinning sidebands. (A) 88 NH$_4$-Y calcined at 550°C, reactivated at 400°C and sealed. 3.6 ± 0.3 H atoms per supercage. (B) 88 NH$_4$-Y SB-activated at 400°C and sealed. 6.5 ± 0.4 H atoms per supercage. (C) 88 NH$_4$-Y calcined at 550°C, reactivated at 400°C, partially deuterated and sealed. (D) 88 NH$_4$-Y SB-activated at 400°C, partially deuterated and sealed. 1.2 ± 0.2 H atoms per supercage. (E) Na-Y SB-activated at 400°C and sealed. 0.25 ± 0.05 H atoms per supercage.](image-url)
in the sodalite cages. Line (d) at 7 ppm is assigned to residual ammonium cations [5]. Spectral resolution for non-deuterated samples is worse than that reported in refs. [6,7], which used the WAHUHA multiple-pulse sequence to reduce the dipole–dipole interaction between protons. At the spinning rate of \( \approx 3 \text{ kHz} \) the dipole interaction reduces the spectral resolution if the concentration of protons is larger than two per supercage. Despite relatively poor resolution, spectrum (A) in fig. 1 clearly shows a shoulder at 1.9 ppm due to the high concentration of terminal SiOH groups in the sample. This is even more in evidence in spectrum (C), where the signal at 1.8 ppm dominates and the line corresponding to acidic hydroxyls is merely a shoulder. The difference in the intensity of the two lines between the deuterated and non-deuterated samples is probably due to the higher affinity of the deuterons for the acidic hydroxyl groups than for the silanol groups (some of which may be inaccessible) in the H-Y/D\(_2\)O exchange system. The well-resolved (WAHUHA) spectrum of the SB-treated zeolite 88 NH\(_4\)-Y [7] corresponds to 0.5 SiOH groups, 5.75 bridging OH groups and 0.1 residual ammonium ions per supercage (the original NH\(_4\)-Y contains 5.87 NH\(_4\)+ per supercage). Spectrum (D) in fig. 1 shows that O\(_2\) and O\(_3\) hydroxyls appear in equal populations, which agrees with the results of neutron diffraction [2].

Calcination at 550°C reduces the number of bridging hydroxyls and increases the number of terminal hydroxyls. The total content of hydroxyl groups is 3.6 per supercage. The spectrum of zeolite 88 NH\(_4\)-Y, deep-bed treated at 500°C, i.e. prepared under conditions similar to those used here, gives 0.9 SiOH and 1.9 bridging OH per supercage [7].

Fig. 2 gives the \(^{27}\text{Al} \) NMR spectra of the samples. Spectrum (A), of a dehydrated sample of Na-Y, shows a typical second-order quadrupolar pattern, the first to be reported for a zeolite. The two peaks, centered at 34 and 93 ppm, cannot be interpreted in terms of chemical shift and do not therefore correspond to different sites for aluminium. The centre of gravity of the spectrum is at 33 ppm, and the second moment with respect to the centre of gravity is \( 1.48 \times 10^{-8} \text{T}^2 \). Eqs. (4) and (5) of ref. [8] give for the quadrupole frequency \( \nu_Q = 1.06(1 + \eta^2)^{-1/2} \text{ MHz} \). The lineshape of spectrum (A) is intermediate between those typical for \( \eta = 0 \) and \( \eta = 1 \). Assuming \( \eta = 0.5 \) we find \( \nu_Q = 1.02 \text{ MHz} \). Without reference to the magnitude of \( \eta \) we may calculate the quadrupole shift from [8]

\[

\nu_L - \nu_{cg} = \left( \frac{7M_2}{23} \right)^{1/2},

\]

where \( \nu_L \) and \( \nu_{cg} \) denote the Larmor frequency and the centre of gravity of the line. In the case under consideration the result is 27.4 ppm, which must be added to the resonance shift of the centre of gravity. The corrected value of the chemical shift is 60.4 ppm, very close to the experimental value of 60 ppm measured in the hydrated sample (see spectrum (D) in fig. 2). Note that on going from dehydrated Na-Y (spectrum (A)) to dehydrated H-Y samples (spectra (B) and (C)) the intensity of the NMR signal is drastically reduced, because Al atoms in the vicinity of bridging hydroxyl groups in dehydrated zeolites are “NMR invisible” [9]. This is because of heavy distortion of the tetrahedral symmetry around the Al atom in the Si–OH–Al grouping. For the probehead ringdown time of 10 \( \mu \)s, a 40 kHz wide spectrum is only 1/11 as intense as the 15 kHz broad line corresponding to the same number of \(^{27}\text{Al} \) nuclei. Spectrum B indicates therefore that \(^{27}\text{Al} \) NMR signals from nuclei close to bridging OH groups are broader than 40 kHz or the quadrupole frequency is larger than 2.3 MHz. Ref. [10] incorrectly claims that such Al atoms do contribute to NMR signal intensity from dehydrated samples. The error arose from Al impurity in the glass ampoules. In the present work we have ensured that no background Al was present.

The hydrated samples do not contain “NMR invisible” aluminium. During rehydration the protons of bridging hydroxyls coordinate to water and to non-framework Al to produce H\(_3\)O\(^+\) and Al(H\(_2\)O)\(_6\)\(^+\) complexes, respectively, thus restoring symmetry to the Al. Spectrum (E) in fig. 2 shows that upon rehydration of H-Y about 1/4 of the Al is present as aluminium hexaaquocomplexes with the chemical shift of \( \approx -3 \text{ ppm} \). Spectra (F) and (G) contain three signals: two narrow lines at 60 and \(-2 \text{ ppm} \), respectively, and a broad line, \( \approx 130 \text{ ppm} \) wide, at about 30 ppm, corresponding to the majority of the Al in the sample. This line was interpreted [11,12] as due to non-framework AlOOH in which Al is in tetrahedral coordination by its proximity to two framework oxygens. The fact that a broad line ap-
Fig. 2. $^{27}$Al NMR spectra of zeolite Y (relative intensities for (A), (B), (C) and for (D), (E), (F)). Asterisks denote spinning side-bands. (A) Na-Y SB-activated at 400°C and sealed, static sample. (B) 88 NH$_4$-Y SB-activated at 400°C and sealed, static sample. (C) 88 NH$_4$-Y calcined at 550°C, reactivated at 400°C and sealed, static sample. (D) Na-Y hydrated, MAS at 4.5 kHz. (E) 88 NH$_4$-Y SB-activated at 400°C and rehydrated, MAS at 4.5 kHz. (F) 88 NH$_4$-Y calcined at 550°C and rehydrated, MAS at 4.5 kHz. (G) Spectrum (F) with intensities $\times 6$. 
pears in the spectrum of the dehydrated calcined sample (spectrum (C)), but only at a low intensity, indicates that non-framework Al is in tetrahedral environment only in the hydrated zeolite.

Fig. 3 gives the $^{29}$Si MAS NMR spectra of the hydrated samples. Si/Al ratios can be calculated from deconvoluted spectra using Gaussian lineshapes [13-15]. The results are $\text{Si/Al} = 2.5 \pm 0.2$, $2.7 \pm 0.4$ and $6.5 \pm 0.4$ for the hydrated samples Na-Y, H-Y and calcined H-Y, respectively.

Under certain conditions a simple expression based on van Vleck’s formula can be used [16] to calculate the aluminium-proton distance, $r_{\text{Al-H}}$, from the second moment, $M_2$:

$$r_{\text{Al-H}} = \left( \frac{126.09}{M_2} \right)^{1/6},$$

where $r_{\text{Al-H}}$ is in Å and $M_2$ in units of $10^{-8}$ T$^2$. The conditions which must be met are:

1. Dipole–dipole interactions additional to the interaction between a single proton and a single aluminium nucleus are either absent or taken into account.
2. The non-resonant spins (e.g. $^{27}$Al when observing $^1$H) are oriented in the Zeeman field and not in the quadrupole field.
3. Line broadening due to chemical shift anisotropy (CSA) is either negligible or taken into account.
4. The protons are immobile and the apparent second moment is not motionally reduced.

Consider (1) first. The dipole–dipole interaction with $^{23}$Na can be neglected because the concentration of sodium is low ($\approx 0.7$ per supercage) and Na$^+$ ions are far from the protons. The contribution of $^{29}$Si nuclei (0.64 per supercage) to the second moment of $^1$H is only about 1/500 that of the contribution of $^{27}$Al. The magnitude of the $^1$H–$^1$H dipolar interaction can be estimated by taking into consideration that the free induction decay can be extended by a factor of about 4 for zeolite 88 H-Y by means of Hahn’s echo. Since 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 proton–proton interaction to the second moment is $I_p \times 0.88 \times 10^{-8} T^2 = 0.055 \times 10^{-8} T^2$. Similar result is obtained from the difference between the second moments in the deuterated sample (D) and the non-deuterated sample (B) (see table 1). The concentration of protons in the former is 1/5 of that in the latter and therefore the contribution of the proton–proton interaction is also 1/5. If follows that the correction for $^1$H–$^1$H interactions is $\frac{3}{4} (0.88 - 0.84) \times 10^{-8} T^2 = 0.05 \times 10^{-8} T^2$.

The question arises whether one must consider
more than one aluminium neighbour to a given proton. The X-ray structure of zeolite H-Y [1] and the 
29Si MAS NMR work [14,15] show that the second-
nearest Al atom is at a distance of 3.21 Å from the
proton associated with O3. For the proton on the O1
the distance is 4.7 Å, which means that the contribu-
tion of the second-nearest Al to \( M_2 \) is negligible.
Interactions with still further Al atoms are always
negligible. The mean total contribution of second-
nearest Al atoms to \( M_2 \) of \( O_1 \) and \( O_3 \) hydroxyls is
\( 0.06 \times 10^{-8} \text{ T}^2 \).

In contrast to SB-treated zeolite, the calcined sample
contains much non-framework aluminium. Some of
it is relatively close to the hydroxyl groups and therefore contributes to the second moment of \(^1\text{H}\) (see table 1). The terminal (non-bridging) OH groups are involved in much weaker H-Al interac-
tions, and thus their second moment in zeolite Na-
Y is only \( 0.40 \times 10^{-8} \text{ T}^2 \). The second moment of
\( 0.68 \times 10^{-8} \text{ T}^2 \) for the deuterated sample (C) is
therefore largely due to non-bridging hydroxyls, in
agreement with the \(^1\text{H}\) MAS NMR spectrum (see fig.
1).

To consider condition (2) we compare the Larmor frequency \( \nu_L \) of the non-resonant Al nuclei (70 MHz for \(^1\text{H}\) frequency of 270 MHz) with the quadrupole frequency \( \nu_Q \). The latter is unknown and we have estimated it at more than 2.3 MHz. The contribution of quadrupolar effects to \( M_2 \) of \(^1\text{H}\) is negligible only when \( \nu_L / \nu_Q > 5 \) [16]. We estimate an upper limit for \( \nu_Q \) as follows. The static \(^1\text{H}\) NMR linewidth of deuterated sample 88 H-Y is 8 kHz, while the MAS linewidth of bridging OH groups is 400 Hz, a factor of 20. On the other hand quadrupolar effects limit the narrowing factor [16] to
\( 1.11 \nu_L / \nu_Q \), which means that in our experiments
\( \nu_L / \nu_Q > 20/1.11 \) or \( \nu_Q < 3.85 \). We have therefore
\( 2.3 < \nu_Q < 3.85 \text{ MHz} \) and the contribution of quad-

rupolar effects to the second moment is negligible.

To consider condition (3) we need the value of the anisotropy of the chemical shift, \( \Delta \delta_{\text{OH}} \). For hydroxy
protons in silica gel Ernst [17] gave 5.5 ppm, a value which is reduced by the rotation of OH around the Si–O–H angle of 140°. Bridging hydroxyl groups cannot easily rotate and therefore their anisotropy is larger: the measured [18] and calculated [19] value is 15±3 ppm, which in the field of 6.3 T is 4.0±0.8 kHz. The contribution of this anisotropy to the second moment is \( 4 \Delta \delta_{\text{OH}}^2 / 45 = 0.08 \times 10^{-8} \text{ T}^2 \). Measurements on sample 88 H-Y in a 2.1 T field gave \( M_2 = (0.78 \pm 0.02) \times 10^{-8} \text{ T}^2 \), which, when compared with the value of sample B in table 1, leads to the conclusion that the CSA contributes \( 0.08 \times 10^{-8} \text{ T}^2 \) to the measured value of \( M_2 \).

As far as condition (4) is concerned, we have found that the second moment of H-Y samples did not change significantly in the temperature range 93 to 400 K. The question is therefore whether a very fast exchange of protons between \( O_1 \) and \( O_3 \), or be-
tween all oxygens around one aluminium, may not
narrow the line and therefore lower the apparent sec-
don moment already at liquid nitrogen tempera-
tures. The answer is no, because \(^1\text{H}\) MAS NMR
 detects two different lines corresponding to protons
on \( O_1 \) and \( O_3 \) oxygens, respectively. The chemical
shift difference between the two lines in 1 ppm (270 Hz) and therefore the mean residence time of a proton on a framework oxygen atom at room temper-
tature must be longer than 3 ms. It follows that for the purpose of the second moment the zeolitic frame-
work is rigid.

The final value of the second moment for an iso-
lated bridging hydroxyl group in zeolite H-Y is therefore
$M^2 = (0.88 - 0.05 - 0.06 - 0.08) \times 10^{-8} \text{T}^2$
$= 0.69 \times 10^{-8} \text{T}^2$,

where the terms in parentheses correspond, from left to right, to the experimentally measured second moment and to interactions with other protons, the second-nearest Al and to the correction for the CSA, as detailed above. This result is remarkably close to the value of $0.68 \times 10^{-8} \text{T}^2$ given by Stevenson [4], especially if one considers that his measurements were carried out on calcined zeolites equivalent to our samples A and C, while our own result is derived from samples B and D, which give very different respective values of $M^2$ (see table 1). The agreement between the two sets of results must therefore be described as fortuitous [20]. Our value of $M^2$ gives

$$r_{H-Al} = \left(\frac{126.09}{0.69}\right)^{1/6} = 2.38 \text{Å}.$$  

Even when we allow for the uncertainty in the asymmetry correction, the proton–proton correction, the correction for non-framework Al and for protons in other OH groups the accuracy of this final result is $\pm 0.04 \text{Å}$.

To avoid line broadening by CSA the second moment of OH groups in zeolite H-ZSM-5 was determined from the low-field (90 MHz) spectrum (A) given in fig. 4. 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 (see spectrum (B)). Since the concentration of $^1\text{H}$ and $^{27}\text{Al}$ nuclei was very low, the second moment arising from the interaction with other protons and second-nearest aluminium atoms is always negligible. The second moment attributable to SiOH groups on framework defects (line at $\approx 2 \text{ ppm}$ in spectrum (B)) measured in the parent zeolite Na-ZSM-5 (which contains very few bridging hydroxyls) was $(0.40 \pm 0.2) \times 10^{-8} \text{T}^2$. Considering that in H-ZSM-5 the SiOH groups amount to 20% of the total hydroxyl concentration, we find $M^2 = 0.54 \pm 0.04 \times 10^{-8} \text{T}^2$ for the second moment due to bridging hydroxyl groups from the value $(0.51 \pm 0.03) \times 10^{-8} \text{T}^2$ measured from spectrum (A). 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") at $10.2 \pm 0.3 \text{ kHz} ((2.40 \pm 0.08) \times 10^{-4} \text{T})$ apart. Such shoulders are absent from the spectra of zeolite H-Y, because of the larger dipolar interactions. The theoretical lineshape of a $^1\text{H}^{-27}\text{Al}$ 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. Calculation of the second moment using the distance between the $\pm 5/2$ singularities gives $M^2 = 7d^2/75 = (0.54 \pm 0.05) \times 10^{-8} \text{T}^2$. 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 and corresponds to $r_{H-Al} = 2.48 \pm 0.04 \text{Å}$ for the bridging hydroxyl groups in zeolite H-ZSM-5. At 2.48 Å, the Al–H distance in pentasil zeolites is slightly larger than in H-Y because of the smaller T–O–T angles in a framework composed mostly of five-membered rings.
Stevenson [4] used 1.72 Å for the Al–O distance in a bridging hydroxyl group [1]. Recent ab initio calculations [3] gave a higher value $r_{\text{Al-O}} = 1.94$ Å and also $r_{\text{O-H}} = 0.965$ Å, $r_{\text{Si-O}} = 1.684$ Å and the Si–O–H angle of 114.5°. Using these together with our $r_{\text{H-Al}} = 2.38$ Å, we arrive at an Al–O–H angle of 105.0° and an Si–O–Al angle of 140.5° for zeolite H-Y. For zeolite H-ZSM-5 from $r_{\text{H-Al}} = 2.48$ Å we arrive at an Al–O–H angle of 112.9° and an Si–O–Al angle of 132.6°. The value of 140.5° for the Si–O–Al angle in zeolite H-Y falls in the usual range (cf. ref. [1]). However, when considered together with the Al–O distance of 1.94 Å (which exceeds the mean Al–O distance in the framework with cations and without bridging OH by $\approx 0.2$ Å), it would lead to the conclusion that the conversion of Na-Y into H-Y should increase the unit cell parameter, which is not observed [1]. It follows that the quantum chemical computations of ref. [3] do not agree with the Al–H distance directly measured by NMR.

Acknowledgement

We thank Professor H. Pfeifer and Professor J.M. Thomas, F.R.S., for their interest in this work; Frau D. Prager and Dr. M. Hunger for experimental assistance, and the British Council and Universiti Teknologi Malaysia for financial support.

References