^{1}H solid-state NMR studies of the geometry of Brønsted acid sites in zeolites H-ZSM-5

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Broad-line ^{1}H NMR and ^{1}H MAS NMR were used to determine the geometry of the Brønsted acidic sites in zeolites H-ZSM-5. The signals obtained correspond to bridging hydroxyl groups in Si–OH–Al arrangements with an H–Al distance of 0.246–0.252 nm. The concentration of hypothetical SiOHSi groups must be less than 0.26 species per unit cell.

1. Introduction

Structural (bridging) hydroxyl groups are the source of Brønsted acidity in zeolite catalysts and much attention has been paid to a determination of their structure. Powder X-ray [1] and neutron [2] diffraction yield structural details of the aluminosilicate framework, but no information about the position of hydroxyl protons on the framework oxygens. Based on ab initio quantum-chemical calculations [3,4], values for the atom–atom distances and bond angles of the bridging OH cluster could be derived (see fig. 1). Also by ab initio calculations Derouane et al. [5] came to the conclusion that the bridging hydroxyl protons should be delocalized if the T sites of a zeolite framework are occupied in such a way by the silicon and aluminium atoms that two neighbouring silicon atoms are connected to aluminium atoms as shown in fig. 2. The

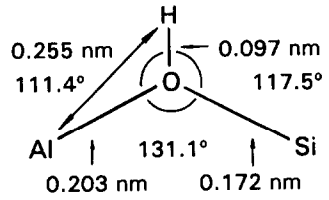

Fig. 1. Atom–atom distances (nm) and bond angles in the structure of a bridging OH group as determined by an ab initio quantum-chemical calculation [3].

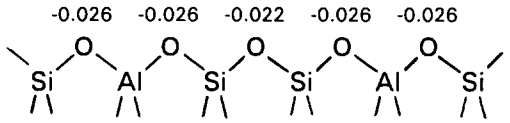

Fig. 2. Ab initio quantum-chemical model cluster of a aluminosilicate with an intermediate Su/Al ratio and the calculated distribution of negative excess charges on the oxygen atoms [5].

Si–O–Si bridge between the two aluminium sites bears an excess charge of $-0.022\ |e|$ which is about equal to that of the Si–O–Al bridges ($-0.026\ |e|$). Hence, Derouane et al. [5] proposed the existence of Si–OH–Si groups in zeolites with an intermediate Si/Al ratio. For this kind of bridging OH groups the proton–aluminium distance is much larger than for the Si–OH–Al groups.

Stevenson [6] has derived from the ^{1}H broad-line signal an H–Al distance of 0.238 nm for bridging OH groups in zeolite H–Y. He found that the second moment of the ^{1}H NMR signal is dominated by the magnetic dipole interaction between the hydroxyl proton and the neighbouring framework aluminium atom. Later on the contributions of additional interactions to the ^{1}H NMR signal of bridging OH groups in zeolites were discussed in detail [7]. For bridging OH groups in zeolite H-ZSM-5, Freude and Klinowski [8] have determined the H–Al distance from an analysis of the shoulders which appear in the ^{1}H NMR spectrum and which are caused by the

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$\pm 5/2$ Pake doublet of the ^1H–^{27}Al magnetic dipole interaction. In a more recent paper [9] a procedure to analyze the ^1H MAS NMR sideband pattern has been described and successfully applied to zeolites which allows a separate determination of (i) the ^1H–^{27}Al distance, (ii) the magnetic dipole interaction of the bridging hydroxyl protons with other nuclei, and (iii) the chemical-shift anisotropy of the hydroxyl protons.

The present work combines ^1H NMR and ^1H MAS NMR studies to determine the second moment of the ^1H–^{27}Al magnetic dipole interaction of bridging hydroxyl protons in zeolites H-ZSM-5 with suitable values of the Si/Al ratio in order to decide whether the Si–OH–Si groups proposed by Derouane et al. [5] do exist or not.

2. Experimental

^1H NMR measurements were carried out using a home-made NMR pulse spectrometer with a resonance frequency of 90 MHz. The spectra were obtained by a Fourier transformation of Hahn's spin echo with acquisition triggered at 2τ. As usual, τ denotes the pulse distance between the $\pi/2$ and the π pulse which has been chosen as 100 μs. No difference in the spectra was detected upon increasing τ from 50 to 300 μs. The $\pi/2$ pulse width was 1.5 μs. ^1H MAS NMR experiments were carried out on a Bruker MSL 300 spectrometer using a homemade MAS probe to spin sealed glass ampoules. The $\pi/2$ pulse width and the MAS frequency were chosen as 3 μs and 2000 ± 5 Hz, respectively. The samples were also characterized by ^{27}Al and ^{29}Si MAS NMR in order to determine values for the Si/Al ratio and the relative concentrations of the $SiO_4Si_{4-i}Al_i$ units [10].

The zeolite denoted as H-ZSM-5/1 (Si/Al=23) was synthesized using *n*-butylamine as a template and the zeolite H-ZSM-5/2 (Si/Al=15) without a template [11]. The template was removed by heating the zeolite at 600°C for 5 h. The Na^+/H^+ ion-exchange was performed at room temperature with an aqueous solution of 0.5 N HCl. For all ^1H NMR and ^1H MAS NMR studies the samples were activated under vacuum with a temperature increase at a rate of 10 K/h to 670 K [12] and sealed in glass ampoules.

3. Results

The ^1H NMR spectrum of the zeolite H-ZSM-5/1 presented in fig. 3a was recorded at low field so that the influence of chemical shift anisotropy which amounts to 14–20 ppm [9] can be neglected. Nevertheless, the spectrum does not show clearly a superposition of three doublets as expected for an isolated ^1H–^{27}Al pair. The theoretical lineshape in fig. 3b consists of three doublets, where the distances between the singularities are $D_m = 2\Delta\nu$, $6\Delta\nu$ and $10\Delta\nu$ for $m = \pm 1/2$, $m = \pm 3/2$ and $m = \pm 5/2$, respectively. The value $\Delta\nu$ is given by the well-known equation

$$\Delta\nu = \frac{1}{2\pi}\frac{\mu_0}{4\pi}\frac{\gamma_H\gamma_{Al}\hbar}{2r_{HAl}}, \qquad (1)$$

with the proton aluminium distance r_{HAl}, the gyromagnetic ratios γ_H and γ_{Al}, Planck constant $\hbar = h/2\pi$ and the permeability of vacuum μ_0. Inserting the values for μ_0, γ_H, γ_{Al} and $\hbar$ into eq. (1), it follows

$$r_{HAl} = 2.501 \times 10^{-9}(\Delta\nu)^{-1/3}, \qquad (2)$$

with r_{HAl} in m and $\Delta\nu$ in Hz. r_{HAl} may be also calculated from the second moment M_2^{HAl} determined in T^2 for the whole ^1H NMR spectrum [7]:

$$r_{HAl} = (1.261 \times 10^{-66}/M_2^{HAl})^{1/6}. \qquad (3)$$

Magnetic dipole interactions of the hydroxyl proton with nuclei other than the neighbouring ^{27}Al lead to a smoothing of the Pake doublets, which can be simulated by a convolution with a Gaussian line-broadening function (figs. 3c and 3d). Therefore only two shoulders can be seen in the spectrum of sample H-ZSM-5/1 in fig. 3a. A fitting of the spectrum with the corresponding simulated spectra (cf. figs. 3c and 3d) yield $D_{5/2} = 10\Delta\nu = 10.3 \pm 0.2$ kHz with a line-broadening of 1 kHz. From eq. (2) follows an H–Al distance $r_{HAl} = 0.248 \pm 0.002$ nm. This is a reliable value for the ^1H–^{27}Al distance in an isolated bridging hydroxyl group, since the position of the singularities is not affected to first order either by the superimposed relatively narrow signal of silanol groups [12] or by other line-broadening effects. The ^1H

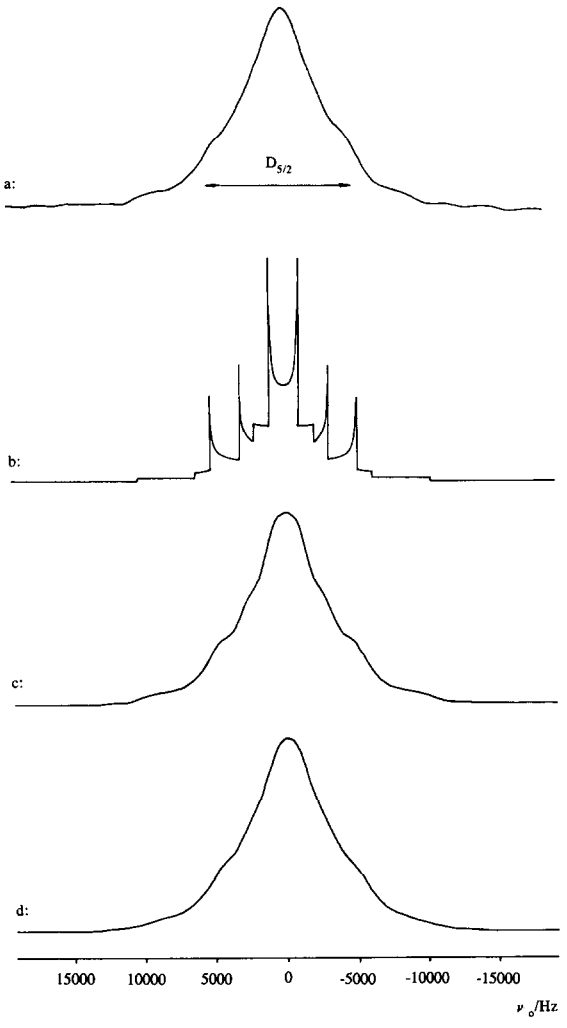

Fig. 3. ^{1}H NMR spectrum of zeolite H-ZSM-5/1 (Si/Al=23) with the shoulder–shoulder splitting $D_{5/2}$ measured at 90 MHz (a), superimposed Pake doublets caused by the dipolar interaction of hydroxyl protons (spin 1/2) with aluminium atoms in the spin state $\pm 1/2$, $\pm 3/2$ and $\pm 5/2$, simulated for an H–Al distance of 0.248 nm and assuming isolated spin pairs (b), spin pairs with an additional line-broadening of the hydroxyl protons (c) with 0.006×10^{-8} T^2 and (d) with 0.01×10^{-8} T^2.

NMR spectrum of sample H-ZSM-5/2 was presented in ref. [8] yielding a value $r_{HAl}=0.248\pm0.004$ nm.

To simulate the ^{1}H MAS NMR signal of bridging OH groups the envelope of the free induction decay has been described by the following equation [9]:

$$G(t)=G^{ext}(t)\left\langle\left\langle\exp\left(-i\int_0^t\omega(t)\,dt\right)\right\rangle\right\rangle_{powder}\Big\rangle_m. \quad (4)$$

The frequency function

$$\omega(t)=\boldsymbol{b}(t)[\mathbf{T}(\Delta\sigma_{OH})+m\mathbf{T}(M_2)]\boldsymbol{b}^T(t) \quad (5)$$

is defined as the difference of the angular resonance frequency between the bridging OH group fixed in space and under the conditions of a fast isotropic reorientation so that the chemical shift becomes isotropic and the magnetic dipole interaction is averaged to zero. $\boldsymbol{b}(t)$ denotes the unit vector along the direction of the static magnetic field in the bridging OH group system, which becomes a periodic function of time under MAS conditions. $\mathbf{T}(\Delta\sigma_{OH})$ is the traceless tensor of the chemical shift anisotropy $\Delta\sigma_{OH}$ and $\mathbf{T}(M_2)$ is the traceless tensor of the magnetic dipole interaction between I and S. The factor

$$G^{ext}(t)=\exp(-(\gamma_H^2M_2^{ext}/\omega_{rot}^2)\{\tfrac{2}{3}[1-\cos(\omega_{rot}t)] + \tfrac{1}{12}[1-\cos(2\omega_{rot}t)]\}) \quad (6)$$

accounts for homo- and hetero-nuclear magnetic dipole interactions between a bridging hydroxyl proton and ^{1}H and ^{27}Al nuclei outside of the bridging OH group with a minimum distance to the proton of the bridging OH group much larger than r_{HAl}. M_2^{ext} denotes the corresponding second moment and ω_{rot} the MAS angular frequency. The MAS NMR sideband analysis of bridging OH groups in crystalline molecular sieves is described in detail in ref. [9].

The ^{1}H MAS NMR spectrum of the zeolite H-ZSM-5/2 (fig. 4) shows two signals of hydroxyl protons which must be attributed to the lines (a) and (b) of silanol and bridging OH groups at chemical shifts of 1.8 ± 0.2 ppm and 4.3 ± 0.2 ppm, respectively. The intensities correspond to 1.2 OH per unit cell for line (a) and 5.2 OH per unit cell for line (b). The corresponding concentrations of sample H-ZSM-5/1 are 0.5 OH for line (a) and 4.0 OH for line (b). A numerical determination of M_2, M_2^{ext} and $\Delta\sigma_{OH}$, carried out by minimizing the normalized quadratic deviation ϵ of the first five sideband intensities of the simulated and experimentally recorded ^{1}H MAS NMR spectra, yields the following values: $\epsilon=$

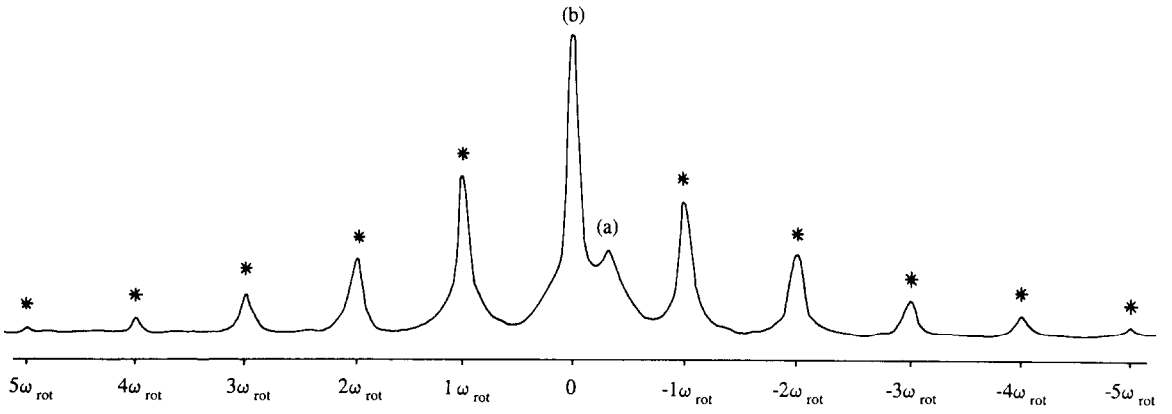

Fig. 4. ^{1}H MAS NMR spectrum of H-ZSM-5/2 (Si/Al=15). Asterisks denote MAS sidebands of line (b) of bridging OH groups.

0.25×10^{-2}, $M_2=(0.52\pm0.02)\times10^{-8}$ T^2 (corresponding to an H–Al distance of $r_{HAl}=0.250\pm0.002$ nm), $M_2^{ext}=(0.040\pm0.005)\times10^{-8}$ T^2, and $\Delta\sigma_{OH}=15.5\pm2.0$ ppm.

4. Discussion

As a result of an ab initio quantum-chemical investigation of Al siting in H-ZSM-5, Derouane and Fripiat [13] have concluded that framework aluminium atoms are incorporated at sites T12 and T2 in decreasing order of probability. These T sites are interconnected together via oxygen bridges in the sequence T12–O24–T12–O20–T3–O2–T2–O1. Assuming that Loewenstein's rule holds, only four aluminium atoms per unit cell can occupy a T12 position, corresponding to a Si/Al ratio of 23. Therefore, in the zeolite H-ZSM-5/1 (Si/Al=23) all aluminium atoms should be incorporated at T12 sites. This is consistent with isolated ^{1}H–^{27}Al spin pairs assumed for the broad-line ^{1}H NMR experiment mentioned above. In the zeolite H-ZSM-5/2 with a Si/Al ratio of 15 (6 Al per unit cell), two aluminium atoms must occupy position T2 due to the ab initio calculations of Derouane and Fripiat [13]. In ref. [10] ^{29}Si MAS NMR has been used to study Al siting in a zeolite ZSM-5 (Si/Al=15) equivalent to H-ZSM-5/2. At chemical shifts between −111 and −115 ppm and at −106.4 ppm lines appeared, which are due to Si(0Al) and Si(1Al) sites, respectively. An additional line of only small intensity (1.5 ± 0.5%) observed at −100.8 ppm has been attributed to a superimposed signal from Si(2Al) and SiOH groupings. Taking into account the intensity of this line and the number of 1.2 SiOH per unit cell, an upper limit of 0.2 ± 0.5 Si(2Al) per unit cell can be estimated [10]. The majority of framework aluminium atoms in the H-ZSM-5/2 under study occupy T sites not connected via single silicon atoms. Hence, in the zeolite H-ZSM-5/2 the incorporation of aluminium atoms at T2 sites causes Al(T12)–O24–Si(T12)–O20–Si(T3)–O2–Al(T2) sequences, as necessary for the existence of Si–OH–Si groups proposed by Derouane et al. [5].

The question arises whether a rapid exchange of hydroxyl protons at O24, O20 and O2 atoms exists which apparently would influence the ^{1}H MAS NMR spectrum. Assuming equal tensors of anisotropic chemical shift for hydroxyl groups at O24, O20 and O2, the rapid proton exchange should lead to a mean tensor of chemical shift anisotropy. From a computer simulation of the H-ZSM-5 structure this mean tensor could be determined, its anisotropy is reduced by a factor −0.45 in comparison with the value without exchange. In agreement with ref. [9] in the ^{1}H MAS NMR spectrum of H-ZSM-5/2 neither a reduced nor a negative value of the chemical shift anisotropy was observed. Therefore a rapid proton exchange between different framework oxygen atoms can be excluded. This is in agreement with the result for zeolites of faujasite type and for silicoaluminophosphates of SAPO-5 type [9], where the appearance of separate signals in the ^{1}H MAS NMR spectra

with various chemical shift anisotropies stemming from OH groups in the 6-membered (line b) and 12-membered (line c) oxygen rings excludes a fast proton exchange as well.

In a cluster like that shown in fig. 2 the existence of rigid Si–OH–Si groups would give rise to a second sort of acidic hydroxyl protons with a magnetic dipole ^{1}H–^{27}Al interaction which must be much smaller than that of Si–OH–Al groups. The Si–OH–Al group is characterized by an H–Al distance of 0.248 ± 0.002 nm as determined by the broad-line ^{1}H NMR spectrum of zeolite H-ZSM-5/1. From computer simulation of the zeolite structure and the X-ray parameters of H-ZSM-5 obtained by Olson et al. [1], the distance of hydroxyl protons at O20 atoms to the nearest framework aluminium atoms at T2 and T12 positions could be determined to be 0.385 nm and 0.413 nm, respectively. Accordingly, for the second moment of the magnetic dipole ^{1}H–^{27}Al interaction of Si–OH–Si groups it follows $M_2^{SiOHSi} = 0.064 \times 10^{-8}$ T^2 corresponding to a line width of only 2.55 kHz. Hence the Si–OH–Si groups should contribute only to the central line in the ^{1}H MAS NMR spectrum. As mentioned above however the H–Al distances of Si–OH–Al groups, determined by broad-line ^{1}H NMR and ^{1}H MAS NMR, are equal within the limits of accuracy of these measurements. Therefore, the following statement can be made:

Using the values for the normalized quadratic deviation ($\epsilon = 0.25 \times 10^{-2}$) of the MAS sideband analysis of Si–OH–Al groups and for their concentration (5.2 per units cell), the concentration of the hypothetical Si–OH–Si groups must be less than 0.26 species per unit cell.

The value of $M_2^{ext} = (0.040 \pm 0.005) \times 10^{-8}$ T^2, obtained for the zeolite H-ZSM-5/2, corresponds to a proton–proton distance of 0.48 ± 0.02 nm. By a computer simulation of the structure of zeolite H-ZSM-5 with Al siting in Al(T12)–O24–Si(T12)–O20–Si(T3)–O2–Al(T2) sequences, a distance of 0.45 nm between bridging hydroxyl protons at O24 and O2 atoms was determined which is in fairly well agreement with the experimental value and the exclusion of a significant concentration of Si–OH–Si groups.

Acknowledgement

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References

[1] D.H. Olson, G.T. Kokotailo, S.L. Lawton and W.M. Meier, J. Phys. Chem. 85 (1981) 2238.
[2] Z. Jirak, S. Vratislav and V. Bosacek, J. Phys. Chem. Solids 41 (1980) 1089.
[3] L.A. Curtiss, H. Brand, J.B. Nicholas and L.E. Iton, Chem. Phys. Letters 184 (1991) 215.
[4] J. Sauer, J. Mol. Catal. 54 (1989) 312.
[5] E.G. Derouane, J.G. Fripiat and J.-M. Andre, Zeolites 10 (1990) 221.
[6] R.L. Stevenson, J. Catal. 21 (1971) 113.
[7] D. Freude, J. Klinowski and H. Hamdan, Chem. Phys. Letters 149 (1988) 355.
[8] D. Freude and J. Klinowski, J. Chem. Soc. Chem. Commun. (1988) 1413.
[9] D. Fenzke, M. Hunger and H. Pfeifer, J. Magn. Reson. 95 (1991), in press.
[10] E. Brunner, H. Ernst, D. Freude, T. Fröhlich, M. Hunger and H. Pfeifer, J. Catal. 127 (1991) 34.
[11] W. Schwieger, K.-H. Bergk, D. Freude, M. Hunger and H. Pfeifer, ACS Symp. Ser. 398 (1989) 274.
[12] M. Hunger, D. Freude, H. Pfeifer and W. Schwieger, Chem. Phys. Letters 167 (1990) 21.
[13] E.G. Derouane and J.G. Fripiat, Zeolites 5 ()1985) 165.