MAS NMR STUDIES OF SILANOL GROUPS IN ZEOLITES ZSM-5 SYNTHESIZED WITH AN IONIC TEMPLATE

M. HUNGER, D. FREUDE, H. PFEIFER
Sektion Physik der Karl-Marx-Universität Leipzig, Linnéstrasse 5, DDR-7010 Leipzig, German Democratic Republic

and

W. SCHWIEGER
Sektion Chemie der Martin-Luther-Universität Halle, Schlossberg 2, DDR-4020 Halle, German Democratic Republic

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^{1}H magic angle spinning nuclear magnetic resonance (MAS NMR) measurements on ZSM-5 synthesized with tetrapropylammonium ions as structure-directing template, calcined and hydrogen exchanged, indicate high concentrations of silanol groups (up to 4.6×10^{20} SiOH g^{-1}). ^{1}H NMR, ^{23}Na and ^{29}Si MAS NMR studies of zeolites ZSM-5 with different Si/Al ratios support a model which attributes the majority of these silanol groups to SiOH pairs located on the site of the removed TPA^+ cations with an intra-pair distance of 0.31 nm.

1. Introduction

Acidic ("bridging") OH groups in zeolites ZSM-5 are responsible for the catalytic activity [1,2]. Silanol groups were ascribed to framework defects [3,4]. A certain number of internal SiOH groups can be healed by strong thermal treatment [5] as shown by Datka and Tuznik [3] and Qin et al. [4]. The question arises as to the nature of these OH groups.

We have used ^{1}H MAS NMR for the quantitative determination of bridging OH groups giving rise to a signal at 4.3 ± 0.1 ppm in silicon-rich zeolites and different types of silanol groups giving rise to signals at 1.4–2.2 ppm [6,7]. The results are in agreement with a model of the structure of silanol groups proposed earlier [8], which explains a hydroxylation by removal of the template tetrapropylammonium during the calcination procedure followed by the hydrogen exchange [9,10].

2. Experimental

All ZSM-5 samples under study were synthesized according to ref. [11] using tetrapropylammonium iodide as structure-directing template (TPA^+) at a temperature of 450 K and with precursor Si/Al ratios between 12.5 and 200. After synthesis the material was heated to 850 K for 24 h to remove the organic components. These so-called as-synthesized (as-s) samples were hydrogen exchanged at room temperature using an aqueous solution of 0.1 N NH_4NO_3 or HCl.

Framework Si/Al ratios were determined by ^{27}Al MAS NMR measurements of hydrated samples at a resonance frequency of 70.5 MHz on a home made NMR pulse spectrometer (HFS 270) which was also used for the ^{1}H NMR measurements. ^{1}H, ^{23}Na and ^{29}Si MAS NMR studies were carried out on a Bruker MSL 300 spectrometer. Chemical shifts in ppm were referred to TMS as external standard for ^{1}H, an aqueous solution of 3 N $NaClO_4$ for ^{23}Na, $Al(H_2O)_6^{3+}$ for ^{27}Al and Q_8M_8 for ^{29}Si MAS NMR. Concentrations of hydroxyl protons and framework aluminium atoms were determined with an accuracy of $\pm10\%$ by comparison with a well characterized sample of zeolite ZSM-5.

For the ^{1}H NMR studies all samples were acti-

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vated similarly to shallow-bed conditions (SB): In a glass tube of 5.5 mm inner diameter and with zeolite layer of 10 mm thickness, the temperature was increased at a rate of 10 K h^{-1} and the samples were kept at the final temperature of 670 K under a pressure below 10^{-2} Pa for 24 h. After cooling and sealing, the samples were measured at a MAS frequency of ≈ 3 kHz.

3. Results and discussion

^{1}H MAS NMR spectra of ZSM-5 samples activated at 670 K are shown in fig. 1. The spectra consist of two lines: the line at 1.8 ± 0.1 ppm is due to non-acidic silanol groups at the outer surface of the zeolite crystals (SiOH), at lattice defects and on amorphous components and a line at 4.3 ± 0.1 ppm which is ascribed to acidic OH groups (SiOHAl), known to be of bridging-type. Table 1 gives the concentrations of the above-described OH groups in columns 3 and 4. Columns 5 and 6 give the concentration of framework aluminium atoms (Al_{IV}) and the corresponding Si/Al ratios as determined from the intensity of the 60 ppm line in ^{27}Al MAS NMR spectra.

Bridging OH groups cannot be found in as-synthesized TPA$^+$/ZSM-5 samples (see table 1, column 4). After hydrogen exchange by aqueous NH_4NO_3 and heating, or HCl solution, a signal of bridging OH groups appears. Considering an accuracy $\pm 10\%$ for the values given in table 1, the concentration of these OH groups is in good agreement with the concen-

Table 1
Values for the concentrations of silanol groups (SiOH), bridging OH groups (SiOHAl), framework aluminium atoms (Al_{IV}) and the Si/Al ratio. The concentration of intersections in ZSM-5 is 4.18×10^{20} g^{-1}

Sample	Exchange form	Concentration (10^{20} g^{-1})			Si/Al ratio
		SiOH	SiOHAl	Al_{IV}	
1	as-s	3.2	0	6.3	15
	NH_4^+	3.7	5.0	5.9	16
	HCl	4.2	4.5	5.6	17
2	as-s	1.9	0	3.6	27
	NH_4^+	3.3	3.8	4.6	21
	HCl	4.2	3.8	4.6	21
3	as-s	1.6	0	2.0	50
	NH_4^+	3.9	2.3	1.7	57
	HCl	4.6	2.5	1.7	57
4	as-s	1.6	0	0.6	176
	NH_4^+	3.8	0	0.6	176
	HCl	4.6	0.4	0.6	176

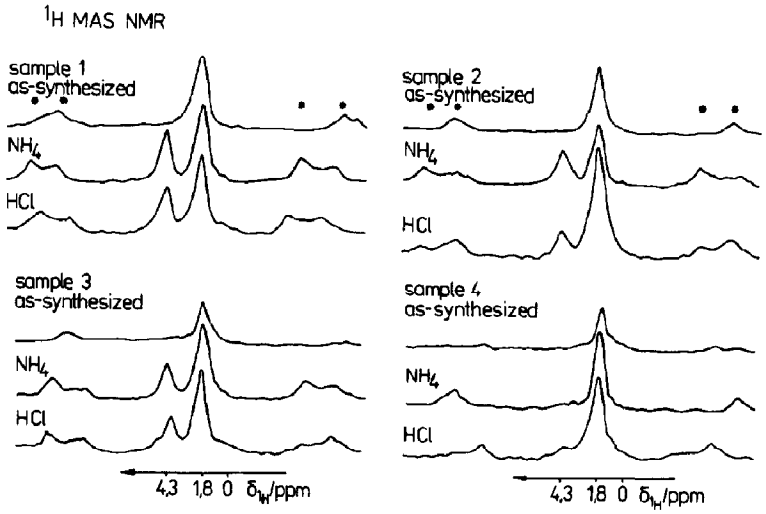


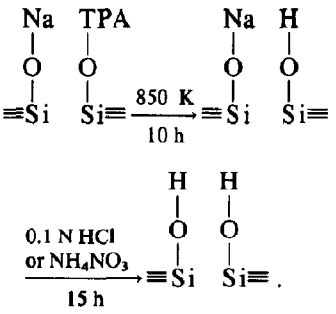
Fig. 1. ^{1}H MAS NMR spectra of TPA$^+$ synthesized zeolites ZSM-5 activated at 670 K. The numbers of samples correspond to the numbers in table 1. Asterisks denote spinning sidebands.

tration of framework aluminium atoms determined by ^{27}Al MAS NMR.

As shown in column 3 of table 1 a remarkable increase of SiOH concentration was observed after hydrogen exchange. For example, in sample 4 a concentration of 1.6×10^{20} SiOH g^{-1} was determined in the as-synthesized form and 3.8×10^{20} and 4.6×10^{20} SiOH g^{-1} in the NH_4^+ and HCl exchanged forms, respectively. The latter value corresponds with silanol groups at 4.6% of all silicon atoms. Neither the concentration of silanol groups of the as-synthesized form nor the concentration of the hydrogen-exchanged form can be explained by terminal bonds on the outer surface of the crystallites: the number n of OH groups per gram of a dehydrated zeolite terminating the outer surface of the crystallites can be estimated from the formula $n=0.12\times10^{20}\,d^{-1}$, where d denotes the mean diameter of the crystallites [6]. For diameters between 1 and 10 μm there are only $(0.01\text{–}0.12)\times10^{20}$ SiOH groups g^{-1}.

Boxhoorn et al. [12] have shown by ^{13}C MAS NMR on ZSM-5 precursors that TPAH and TPABr are occluded in the same way at the intersections of the zeolite framework. But no Br^+ cations could be found by chemical elemental analysis of TPABr ZSM-5 and also identical ^{13}C MAS NMR spectra of TPA^+ occluded in aluminium-containing and aluminium-free ZSM-5 zeolites were observed [12]. The question arises whether the negatively charged fourfold coordinated framework aluminium anions compensate the TPA^+ cations. Samples 1 and 2 contain more than 4×10^{20} Al_{IV} g^{-1} or more than one negatively charged aluminium atom per channel intersection. As described above no bridging OH groups or organic compounds were observed in the ^1H MAS NMR spectra of the as-synthesized form of these samples after thermal decomposition of TPA^+. The possibility that TPA^+ cations are compensated by framework aluminium anions can therefore be excluded.

Using the values of table 1 obtained on samples with different Si/Al ratios we are able to confirm our model [8] of the hydroxylation of TPA^+ synthesized zeolites during calcination and hydrogen exchange:



(1)

Non-closed Si–O–Si linkages produce two neighbouring SiO^- anions. One of these anions compensates one TPA^+ cation and the other is compensated by a sodium cation. After thermal decomposition of TPA^+ at 850 K the template ion is replaced by one SiOH group. Exchange visa NH_4^+ or HCl replaces the sodium cation by a hydroxyl proton, so that paired hydroxyl groups are formed. The experimentally determined values for the SiOH concentration in the as-synthesized samples 2, 3 and 4 can be explained by $(1.6\text{–}1.9)\times10^{20}$ g^{-1}, cf. column 3 in table 1) correspond to about one TPA^+ ion per two crossing intersections. After hydrogen exchange two SiOH groups per TPA^+ cation should be formed and accordingly the concentration is enhanced by a factor of about 2 $(3.3\text{–}4.6)\times10^{20}$ g^{-1}, cf. column 3 in table 1).

The second moment M_2 of the ^1H NMR lineshape contains information about the arrangement of the SiOH groups [13]. To exclude a superposition of bridging and silanol OH groups in the ^1H NMR signal we have determined the second moment of the lineshape of sample 4, which has only a small portion (less than 10%) of bridging OH groups. For the as-synthesised form we find $M_2=1.3\times10^{-9}$, and 4.0×10^{-9} T^2 for the hydrogen-exchanged form. The contribution of the H–Si magnetic dipolar interaction to the second moment can be calculated as $M_2^{H\text{-}Si}=0.02\times10^{-9}$ T^2, taking into account the nearest silicon atom. The contribution of framework aluminium atoms can be neglected in view of their small concentration. For the as-synthesized sample the second moment is dominated by the H–Na magnetic dipolar interaction. Using eq. (2) (cf. ref. [13])

$$M_2^{H\text{-}Na}/10^{-14}\,T^2=55.7\times r_{H\text{-}Na}^{-6}/nm^{-6} \qquad (2)$$

a value of 2.75 nm results for the distance between

the hydrogen and sodium nuclei. Considering the hydrogen-exchanged sample, the second moment is dominated by the intra-pair H–H magnetic dipolar interaction. The experimental value of $M_2 = 4.0 \times 10^{-9}\,T^2$ introduced into eq. (3) (cf. ref. [13])

$$M_2^{H-H}/10^{-14}\,T^2 = 358.1 \times r_{H-H}^{-6}/nm^{-6} \quad (3)$$

gives an intra-pair H–H distance of 0.031 nm. The inter-pair distance can be calculated by (cf. ref. [14])

$$T_2^{Hahn}/ms = 0.347 \times (n/nm^{-3})^{-1}\,, \quad (4)$$

where T_2^{Hahn} denotes the time constant for the decay of Hahn's spin echo and n the pair density per nm^3. The experimentally obtained value $T_2^{Hahn} = 0.375$ s gives a concentration of spin pairs $n = 0.92\ nm^{-3}$. Since the volume of the unit cell which includes 4 intersections is 5.36 nm^3 [15] the value of n corresponds to ≈ 0.7 spin pairs per intersection. This result is in reasonable agreement with the value of 0.5 spin pairs determined by the number of SiOH groups.

Using ^{23}Na NMR, two different kinds of sodium were detected by Debras et al. [16] in zeolite ZSM-5 synthesized with TPA^+: sodium cations which compensate the negative charge of zeolite framework aluminium atoms and sodium bonded as Si–O–Na. The ^{23}Na NMR chemical shifts were found to be -15 and 0 ppm, respectively, and a mean resonance shift was observed as a result of fast chemical exchange between the two species [16]. Fig. 2 shows the ^{23}Na MAS NMR spectra of the as-synthesized form of samples 2 and 4. The centres of gravity of the signals

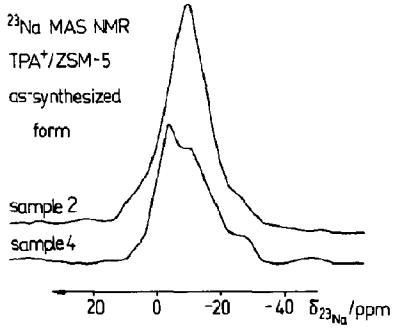


Fig. 2. ^{23}Na MAS NMR spectra of the as-synthesized forms of samples 2 and 4.

appear at -10 and -2 ppm, respectively. The intensity of the signal of sample 4 is about one half of that of sample 2. The appearance of shoulders at -20 and -10 ppm in sample 4 suggests a reduced exchange rate at at lower sodium concentrations.

The difference in the concentrations of the SiOH groups in the as-synthesized and the hydrogen-exchanged zeolites, which should be equal to the concentration of Si–O–Na sites, is of the same order of magnitude (about $2 \times 10^{20}\,g^{-1}$, see table 1) for samples 2 and 4. However, 4.6×10^{20} and only 0.6×10^{20} Na^+ should be present to compensate the charge of the zeolite framework aluminium atoms in sample 2 and sample 4, respectively. Therefore, the Na^+-to-SiONa ratio is significantly lower in sample 4 than in sample 2. This result follows from both ^{23}Na and ^1H MAS NMR.

Kraushaar and Haan [17] claimed that sililation with trimethylchlorosilane (TCS) gives rise to the appearance of dimethyldisiloxysilane and methyltrisiloxysilane signals in the ^{29}Si CP MAS NMR spectra of zeolites ZSM-5 synthesized in the presence of TPA^+. These molecules can be formed by an interaction with two or three SiOH groups, respectively, in agreement with our model. In contrast to our model however, it was proposed [18] that SiOH groups should be formed by hydrolysis of Si–O–Si linkages after a treatment with an aqueous solution of hydrochloric acid, and by impurities such as transition-metal ions.

We have measured the ^{29}Si MAS NMR spectra of sample 4 in the as-synthesized and NH_4 exchanged form without cross-polarization (fig. 3) to get quantitative information. The spectrum of the hydrogen-exchanged sample contains a line at about -102 ppm due to SiOH groups [5,19]. The corresponding concentration of 0.8 ± 0.2 SiOH per intersection agrees with the value of 0.92 ± 0.1 SiOH per intersection determined by ^1H MAS NMR. Since we have used the hydrogen form of sample 4 prepared by NH_4 exchange, it follows that hydrolysis of Si–O–Si linkages caused by an acid cannot be the main origin of the observed silanol groups as suggested by Kraushaar-Czarnetzki [18].

It is well known that paramagnetic impurities may strongly enhance nuclear magnetic spin–lattice relaxation. The value of ^1H spin–lattice relaxation time of the hydroxyl protons on the surface of pure silica

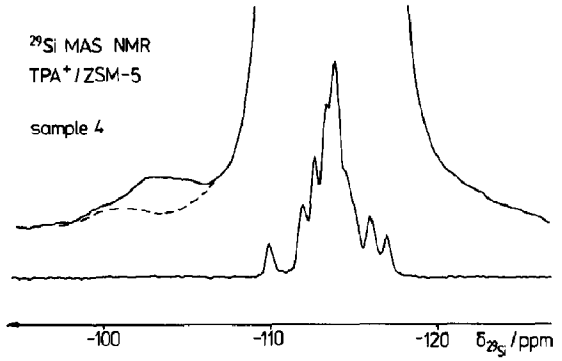


Fig. 3. ^{29}Si MAS NMR spectra of the as-synthesized (---) and NH_4^+ (——) exchanged form of sample 4.

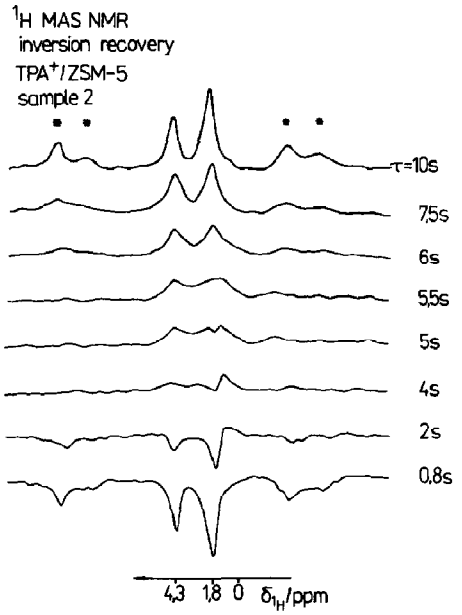


Fig. 4. ^{1}H MAS NMR inversion recovery spectra of the HCl-exchanged form of sample 2. The time constant τ corresponds to the delay of the second pulse. Asterisks denote spinning sidebands.

gel is of the order of some seconds [20]. Paramagnetic impurities decrease this value of T_1 to some hundred milliseconds [21,22]. ^{1}H MAS NMR inversion recovery measurements [20] performed on the HCl-exchanged form of sample 2 (fig. 4) show a two-component behaviour of the T_1 relaxation of protons for the signal at 1.8 ± 0.1 ppm which is due to SiOH groups. The total concentration of these silanol groups is 4.2×10^{20} SiOH g^{-1} and about 80% of them exhibit a relatively long relaxation time T_1 of 7.9 ± 0.2 s while the corresponding value for the other 20% is only 0.5–1.0 s. In agreement with the proposal of Kraushaar-Czarnetzki [18] we ascribe these latter silanol groups to T atom vacancies affected by paramagnetic impurities.

In conclusion, in zeolites ZSM-5 synthesized in the presence of tetrapropylammonium ions as structure-directing template, SiOH pairs with an intra-pair distance of 0.31 nm are formed at non-closed Si–O–Si linkages. The origin of these silanol groups which cause a maximum hydroxylation of 4.6% of the silicon atoms is the charge compensation of TPA^+ cations by $Si–O^-$ anions. As shown by Dessau et al. [5] most of the SiOH pairs can be healed out by a strong thermal treatment.

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References

[1] J. Datka, Z. Piwowarska, J. Rakoczy and B. Sulikowski, Zeolites 8 (1988) 199.
[2] M.W. Anderson and J. Klinowski, Nature 339 (1989) 200.
[3] J. Datka and E. Tuznik, Zeolites 5 (1985) 230.
[4] G. Qin, L. Zheng, Y. Xie and C. Wu, J. Catal. 95 (1985) 609.
[5] R.M. Dessau, K.D. Schmitt, G.T. Kerr, G.L. Woolery and L.B. Alemany, J. Catal. 104 (1987) 484.
[6] M. Hunger, D. Freude, T. Fröhlich, H. Pfeifer and W. Schwieger, Zeolites 7 (1987) 108.
[7] D. Freude, M. Hunger and H. Pfeifer, Z. Physik. Chem. NF 152 (1987) 429.
[8] M. Hunger, J. Kärger, H. Pfeifer, J. Caro, B. Zibrowius, M. Bülow and R. Mostowicz, J. Chem. Soc. Faraday Trans. I 83 (1987) 3459.
[9] E.J.J. Groenen, A.G.T.G. Kortbeck, M. Mackay and O. Sudmeijer, Zeolites 6 (1986) 403.
[10] W. Schwieger, K.-H. Bergk, D. Freude, M. Hunger and H. Pfeifer, ACS Symp. Ser. 398 (1989) 274.
[11] US-patent 4061 724.
[12] G. Boxhoorn, R.A. van Santen, W.A. van Erp, G.R. Hays, R. Huis and D. Clague, Chem. Commun. (1982) 264.
[13] D. Freude, Advan. Colloid Interface Sci. 23 (1985) 21.
[14] D. Freude and H. Schmiedel, Phys. Stat. Sol. (b) 54 (1972) 631.

[15] W.M. Meier and D.H. Olson, Atlas of zeolite structure types (Butterworths, London, 1987).
[16] G. Debras, A. Gourgue, J.B. Nagy and G. De Clippeleir, Zeolites 6 (1986) 161.
[17] B. Kraushaar and D. Haan, Z. Anorg. Allg. Chem. 564 (1988) 72.
[18] B. Kraushaar-Czarnetzki, Thesis, Technical University Eindhoven (1989).
[19] E. Lippmaa, M. Mägi, A. Samoson, M. Tarmak and G. Engelhardt, J. Am. Chem. Soc. 103 (1981) 992.
[20] C.E. Bronnimann, R.C. Zeigler and G.E. Maciel, J. Am. Chem. Soc. 110 (1988) 2023.
[21] H. Winkler, Catal. Today 3 (1988) 501.
[22] D. Michel, Z. Naturforsch. 22 (1967) 22.