Zeitschrift für Physikalische Chemie Neue Folge, Bd. 152, S. 171 – 182 (1987)
© by R. Oldenbourg Verlag, München 1987 – 0044-3336/87 $3.00 + 0.00

# Investigation of Acidic Properties of Zeolites by MAS NMR*

By D. Freude, M. Hunger and H. Pfeifer

Sektion Physik der Karl-Marx-Universität Leipzig, DDR-7010 Leipzig, German Democratic Republic

(Received July 22, 1986)

$^1$H-MAS NMR / $^{27}$Al-MAS NMR / *Zeolites* / *Bronsted acidity*

Proton magic angle spinning nuclear magnetic resonance has been applied to study hydroxyl groups in hydrogen zeolites of ZSM-5, mordenite and faujasite type. Five different lines can be resolved in the $^1$H-MAS NMR spectra of these samples. The signals of the non-acidic hydroxyl groups contain information about structure defects in the zeolites. The Bronsted acidity of the samples can be described by the signals of bridging OH groups. The two signals observed in zeolites HY are correlated with the so-called high and low frequency bands in infrared spectroscopy. The value of the chemical shift of the isolated acidic hydroxyl groups is a measure of their strength of acidity and increases with the Si/Al ratio for faujasites but remains constant above Si/Al $\approx$ 10.

The accessibility of OH groups could be proved by their interaction with deuterated pyridine causing a line shift of the proton resonance. A reammoniation of the zeolites gives rise to an increase of the intensity of the ammonium line and a decrease of the line of the acidic hydroxyl groups proving that all bridging OH groups can be reammoniated.

Combining $^1$H and $^{27}$Al-MAS NMR the hydrothermal dealumination process in hydrogen zeolites was studied. No exception could be found for the rule: The number of bridging hydroxyl groups is equal to the number of fourfold coordinated framework aluminium atoms. An additional line in the $^1$H-MAS NMR spectrum due to OH groups associated with non-framework aluminium appears only in the case of strong hydrothermal dealumination. The Si/Al ratio in the zeolite framework is determined by means of $^{27}$Al-MAS NMR. Three types of non-framework aluminium atoms can be distinguished.

$^1$H-MAS NMR-Messungen an Hydroxylgruppen in den H-Formen der Zeolithe erlauben Aussagen sowohl über Zahl und Stärke azider Brönsted-Zentren als auch über Strukturdefekte, an denen Silanolgruppen entstehen. Es wird am Beispiel verschiedener Zeolithe gezeigt, daß die NMR durch Anwendung der schnellen Rotation um den magischen Winkel im hohen Magnetfeld eine mit der Infrarotspektroskopie vergleichbare Auflösung

* Presented as a Plenary Lecture at the IV. International Symposium on Magnetic Resonance in Colloid and Interface Science, Münster, FRG, July 21 – 25, 1986.

erzielt, gegenüber letzterer aber den Vorteil einer einfachen quantitativen Auswertbarkeit besitzt. Durch Einbeziehung der $^{27}$Al-MAS NMR kann die Zahl der Aluminiumatome in Gitterpositionen und in unterschiedlichen Koordinationen außerhalb des Zeolithgerüstes bestimmt werden.

## Introduction

Surface sites acting as proton donators or electron acceptors are able to adsorb molecules and to cause the phenomenon of acid catalysis. In hydrogen zeolites the bridging hydroxyl groups and non-framework aluminium complexes represent acid sites. Especially zeolites of H-ZSM-5 type have the important property of selectively producing high yields of gasoline-range hydrocarbons from methanol [1].

In the last few years $^{29}$Si and $^{27}$Al-MAS NMR has successfully been applied to the investigation of the lattice structure and of lattice defects in zeolites [2, 3]. $^{1}$H-MAS NMR spectra of zeolites contain quantitative information about the acidity and the extent of non-structural hydroxyl groups, loaded samples may be used to prove the accessibility of OH groups [4, 5]. Since in contrast to infrared spectroscopy the intensity (area) of a NMR line is directly proportional to the concentration of the corresponding nuclei, MAS NMR is a good tool for characterizing the products of the different procedures to prepare zeolites and to treat them under hydrothermal conditions.

In the present work we have studied various specimens synthesized without and with template, mostly tetrapropylammoniumiodide (tpa), in order to determine the concentration of Bronsted acid sites and the extend of structure defects in the final form of these H-ZSM-5 samples. The results of the hydrothermal treatment of some zeolites (HY, mordenite) are presented.

The next topic of this paper is the Bronsted acidity of OH groups. One has to distinguish between two independent quantities, both measurable by $^{1}$H-MAS NMR: $S_a$, the strength of acidity, which is defined as the ease of proton transfer from a surface site to an adsorbed base and $A_a$, the amount of acid, which is given by the concentration of the respective acid sites. According to ab-initio quantum chemical calculations [6, 7] $S_a$ increases with decreasing electronic charge of the hydrogen atoms, that means with a larger value for the chemical shift $\delta_H$ of the proton magnetic resonance [4, 5]. On the other hand the NMR intensity is directly proportional to $A_a$. In this paper it is shown that the appearance of two lines of bridging hydroxyl groups in the $^{1}$H-MAS NMR spectra of zeolite HY must be discussed similarly to the interpretation of high and low frequency stretching vibrations in infrared spectroscopy. The dependence of the chemical shift for unperturbed bridging OH groups in zeolites on the

Si/Al ratio can be interpreted on the basis of Sanderson's intermediate electronegativity and hence through a different strength of acidity.

The last topic of this paper is a $^1$H-MAS NMR study of the reammoniation of hydroxyl groups in zeolites HY and H-ZSM-5.

## Experimental

All NMR spectra were measured at room temperature in a magnetic field of 6.3 $T$ (270 MHz and 70 MHz for $^1$H and $^{27}$Al, respectively) using a homemade pulse spectrometer at the Karl-Marx-Universität Leipzig. The magic angle spinning equipment for $^1$H (speed of rotation of the ampoules is 3 kHz) was carefully cleaned to avoid spurious proton signals. The samples for $^1$H-NMR were pretreated similar to shallow bed (SB) or deep bed (DB) conditions: The zeolite batches were heated in a glass tube with 6 mm inner diameter and 10 mm height of the zeolite layer. For samples denoted by SB the activation takes place under vacuum with a rate of 10 K/h. If the zeolites were activated in the open tube under atmospheric pressure with a rate of 100 K/h the samples are denoted by DB. After keeping all samples for 2 h at 400°C they were evacuated to a pressure below 0.01 Pa for 20 h and sealed off. Before sealing off one portion of the samples was loaded at room temperature under vacuum with $6 \times 10^{20}$ molecules deuterated pyridine per gramme or with a pressure of 5 kPa methane or with different amounts of ammonia. The total concentration of protons for each zeolite was determined by measuring the free induction decay after a $\pi/2$-pulse and comparing its initial value with that of a standard. For $^{27}$Al-MAS NMR measurements hydrated samples were used. The silicon to aluminium ratio in the zeolite framework was determined comparing the intensity of the 60 ppm line in the spectrum of the sample under study with that of a reference sample.

## Results and discussion

In agreement with earlier publications [4, 8, 9] in the $^1$H-MAS NMR spectra of the unloaded zeolites shown in Figures 1, 3 and 5 five lines may be discussed:

Line (a) at 1.8...2.3 ppm is caused by non-acidic OH groups at the outer surface of zeolite crystals (terminal OH groups), at lattice defects and on amorphous components of the zeolites.

Line (b) at 3.8...4.4 ppm is ascribed to acidic OH groups, which are known to be of bridging type.

Line (c) at about 5.2 ppm appears additionally in zeolites of faujasite type and is ascribed also to acidic bridging OH groups.

Line (d) at 6.5...7.0 ppm is due to residual amounts of ammonium ions.

Line (e) at 2.6...3.6 ppm represents hydroxyl groups associated with non-framework aluminium.

In Fig. 1 $^1$H-MAS NMR spectra of unloaded zeolites H-ZSM-5 are shown. They consist of lines (a) and (b). These specimens were obtained as follows: Samples 1, 2 and 3 were synthesized without template, sample 1 according to patent DD-WP 207186. Sample 4 was prepared with n-butylamine (DE-OS 2442240), samples 5, 6 with tpa (US-P 3702886) and

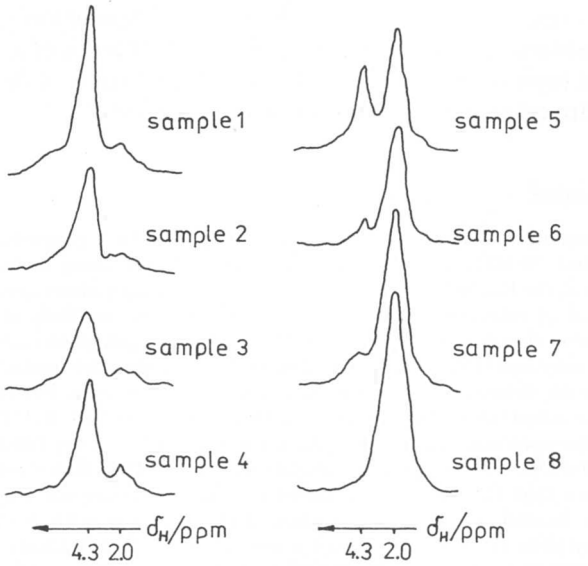


**Fig. 1.** $^1$H-MAS NMR spectra of the unloaded H-ZSM-5 samples. Denotation according to Table 1.

samples 7, 8 corresponding to 5, 6 but at the Institute of Industrial Chemistry, Warsaw. After synthesis the organic compounds were removed by heating the material for 5 h at 600° C. The $Na^+/H^+$ ion exchange was carried out at room temperature with an aqueous solution (0.5 *N*) of HCl.

Values for the concentration of protons giving rise to lines (a) and (b) and of framework aluminium atoms are collected in Table 1. The number of terminal OH groups per gramme of dried zeolite is calculated by the equation: $n_T = 1.2 \times 10^{19}/d$, where $d$ denotes the diameter of the crystallites in $\mu$m. The Si/Al ratio can be determined from the intensity of the $^{27}$Al line at 60 ppm since the fraction of amorphous components of these zeolites is negligible.

In Fig. 2 $^1$H-MAS NMR spectra of some specimens loaded with deuterated pyridine are shown. For silanol groups [line (a)] hydrogen bonding between OH and N of pyridine causes a resonance shift of 7...8 ppm [5]. Therefore the signal of protons giving rise to line (a) at 2.0 ppm must be shifted to 9.5 ppm if they are accessible for pyridine. Acidic OH groups which are involved in the protonation of pyridine to pyridinium ions give rise to an additional broad line at about 15 ppm due to $HNC_5D_5^+$ and a corresponding reduction of the intensity of line (b). The signal at 15 ppm is not narrowed by MAS since the motion of the pyridinium ions is faster than the speed of rotation of the sample. Due to the experimental result that line (b) vanishes on loading the zeolite with

**Table 1.** Denotation of the H-ZSM-5 specimens under study. The concentration of the terminal OH groups was calculated using the diameter of the crystallites. All other values were determined by $^{1}H$- or $^{27}Al$-MAS NMR with an experimental error not exceeding $\pm 10\%$.

| Sample | Template | Si/Al in framework | Diameter of the crystallites in $\mu m$ | Concentration in $10^{20}$ per gramme | | | |
|---|---|---|---|---|---|---|---|
| | | | | terminal OH groups | protons of line(a) | protons of line(b) | framework Al-atoms |
| 1 | none | 15 | 3.2 | 0.04 | 0.6 | 4.9 | 5.8 |
| 2 | none | 26 | 3 | 0.04 | 0.5 | 3.2 | 3.6 |
| 3 | none | 34 | 3 | 0.04 | 0.7 | 2.8 | 2.7 |
| 4 | n-butylamine | 30 | 1.1 | 0.12 | 0.8 | 3.4 | 3.1 |
| 5 | tpa | 40 | 1.7 | 0.08 | 3.6 | 2.5 | 2.3 |
| 6 | tpa | 100 | 1.5 | 0.08 | 3.3 | 0.4 | 0.9 |
| 7 | tpa | 60 | 10 | 0.01 | 5.5 | 1.2 | 1.6 |
| 8 | tpa | 500 | 10 | 0.01 | 6.3 | 0 | 0.2 |

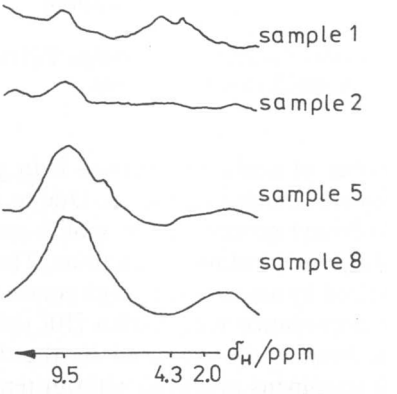


**Fig. 2.** $^{1}H$-MAS NMR spectra of H-ZSM-5 samples loaded with $6 \times 10^{20}$ molecules deuterated pyridine per gramme zeolite. Denotation according to Table 1.

$NC_5D_5$ all acidic OH groups are accessible for pyridine. With the exception of sample 1 in all other cases the whole intensity of line (a) is shifted to 9.5 ppm. For sample 1 about 30% of the intensity of line (a) remains unshifted. For the same sample with vanishing line (b) a broad line at a chemical shift of 3.3 ppm appears, which can be ascribed to AlOH on non-framework aluminium species.

From Table 1 and Figs. 1 and 2 the following conclusions can be drawn: For all specimens the concentration of non-acidic hydroxyl groups is much greater than the value which follows from the number of terminal

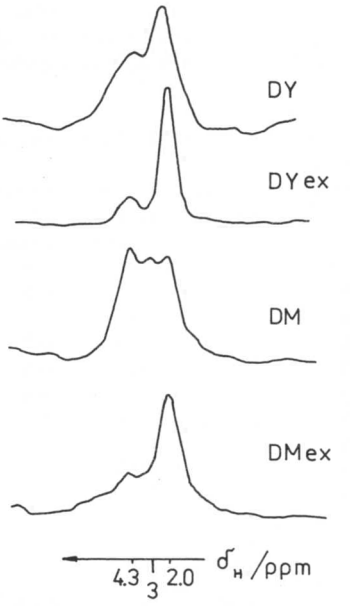


**Fig. 3.** $^1$H-MAS NMR spectra of dealuminated zeolites Y (DY) and mordenite (DM). ex denotes acid leaching. All samples are SB-activated.

OH groups. The number of acidic OH groups is in good agreement with the number of framework aluminium atoms. Due to their accessibility for pyridine all acidic hydroxyl groups of the zeolite specimens under study should be able to take part in catalytic reactions. The zeolites synthesized with tpa are characterized by an extremely high concentration of non-acidic hydroxyl groups. In accordance with Datka [10] this can be ascribed to defects of the zeolite framework produced by the decomposition of the template. For zeolite specimens prepared without template the concentration of non-acidic OH groups is relatively small. For sample 1 (Si/Al ratio 15) these hydroxyl groups are to a certain degree inaccessible for pyridine and also an additional line appears, which can be ascribed to OH groups on non-framework aluminium species. The investigations show, that is it possible to synthesize ZSM-5 zeolites without template (samples 2 and 3 with a Si/Al ratio of nearly 30), which possess neither structure defects, characterized by inaccessible silanol groups, nor AlOH groups at non-framework sites.

Proton and aluminium MAS NMR spectra of dealuminated zeolites are presented in Figs. 3 and 4, respectively. The mordenite denoted as DM is ammonium exchanged and heated for 3 h at 600° C in air. A subsequent aluminium extraction with $HNO_3$ (6 *N*) for 2 h at 108° C, washing at room temperature and drying at 130° C gives the specimen denoted as DMex.

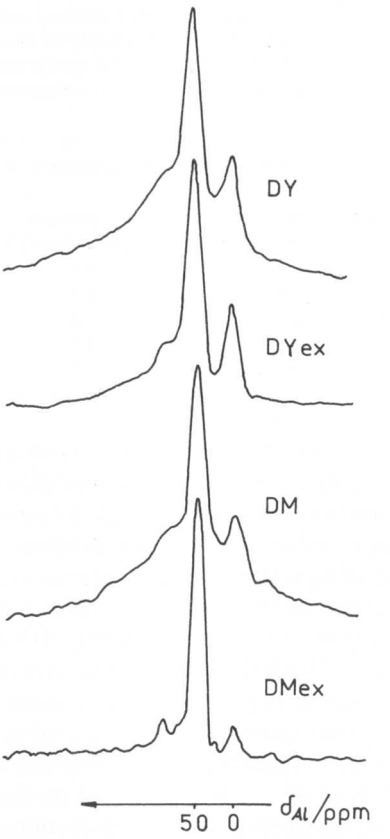


**Fig. 4.** $^{27}$Al-MAS NMR spectra of dealuminated zeolites Y (DY) and mordenite (DM). ex denotes acid leaching. All samples are partially hydrated.

DY is an ammonium exchanged zeolite Y treated in water vapor (0.1 MPa) for 3 h at 600° C, followed by a second ammonium exchange and a second hydrothermal treatment at 770° C. The aluminium extraction with an equivalent amount of dilute HCl (0.001 *N*) gives the specimen denoted as DYex. These four samples were measured with $^{27}$Al-MAS NMR and activated due to the SB procedure described above for $^{1}$H-MAS NMR measurements. Table 2 contains values for the Si/Al ratio determined by chemical analysis and using the intensity of the whole $^{27}$Al-NMR signal and that of the 60 ppm-line only. Hence the latter value represents the Si/Al ratio in the zeolite framework.

A comparison of the values for the total Si/Al ratio determined by chemical analysis and those derived from the $^{27}$Al-MAS NMR spectra shows, that all $^{27}$Al-nuclei can be observed in the $^{27}$Al-MAS NMR spectra

**Table 2.** Results for hydrothermally treated and acid leached zeolites. Si/Al ratios were determined by chemical analysis, using the total intensity of the $^{27}$Al-NMR signal and the intensity of the 60 ppm line in the $^{27}$Al-MAS NMR spectrum. The concentration of OH groups is given due to lines (a), (b), and (e). The experimental error of all values is $\pm 10\%$.

| Sample | Si/Al ratios determined by | | | OH concentration in $10^{20}$ per gramme | | | |
|---|---|---|---|---|---|---|---|
| | chem. analysis | whole $^{27}$Al | 60 ppm in $^{27}$Al | protons of line(a) | protons of line(b) | protons of line(e) | framework Al-atoms |
| DM | 5.8 | 5.4 | 22 | 1.4 | 4.7 | 4.8 | 4.5 |
| DM ex | 39 | 43 | 43 | 2.0 | 2.4 | 0 | 2.3 |
| DY | 2.6 | 5.7 | 26 | 0.9 | 4.2 | 0 | 3.7 |
| DY ex | – | 10.6 | 30 | 2.3 | 2.8 | 0 | 3.2 |

of mordenites. However, for the DY samples a certain amount of non-framework aluminium cannot be seen spectroscopically. As already discussed in ref. [11] this portion is formed in an environment of low symmetry corresponding to large values of the quadrupole coupling constant ($\nu_Q \geq 1$ MHz). A new finding is that after hydrothermal treatment the whole non-framework aluminium in the case of mordenites (and one portion in the case of zeolites Y) exists in an environment of higher symmetry and can be detected in the $^{27}$Al-NMR spectra. The centres of gravity of the corresponding broad lines in Fig. 4 appear at a resonance shift of about 50 ppm. To derive the true chemical shift, this value must be corrected according to the influence of quadrupole coupling (see ref. [5], [12], or [13]) yielding a chemical shift of 60 . . . 80 ppm. $^{27}$Al-nuclei with this chemical shift are known to be in tetrahedral oxygen environment [2, 3].

A completely protonated non-framework aluminium complex in the activated samples must be excluded: Line (e) in the proton spectrum of DM represents $4.8 \times 10^{20}$ OH groups per gramme, whereas the broad aluminium line corresponds to $16 \times 10^{20}$ aluminium nuclei per gramme. In the spectra of zeolites DY line (e) cannot be observed. The intensity of line (a) increases after an acid treatment of the sample which decreases the amount of framework aluminium corresponding to a decrease of the intensity of the line at 60 ppm. Simultaneously the concentration of acid OH groups decreased [see line (b) in Fig. 3]. The concentration of non-framework aluminium giving rise to the broad line is reduced partially for DYex and completely for DMex which were treated by weak and strong acid leaching, respectively (see Table 2). One portion of the non-framework aluminium exists in the hydrated mobile complex $Al(H_2O)_6^{3+}$ causing a narrow line at about 0 ppm. The concentration of these sixfold coordinated $Al^{3+}$-ions increases or decreases after a weak or strong acid treatment, respectively. An investigation of various dealuminated and acid leached zeolites of Y, mordenite, and ZSM-5 type supports the above results [14].

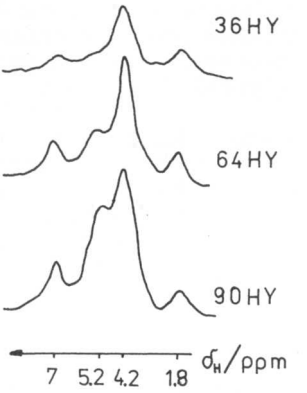


**Fig. 5.** $^1$H-MAS NMR spectra of unloaded zeolites HNaY. The degree of ammonium exchange is 36%, 64% and 90%. All samples are DB-activated.

No exception could be found for the rule: The number of fourfold oxygen coordinated framework aluminium atoms is equal to the number of bridging hydroxyl groups.

The $^1$H-MAS NMR spectra of DB activated zeolites Y for an ammonium exchange of 36%, 64% and 90% are shown in Fig. 5. In all spectra the lines (a), (b) and (d) can be seen. For values of the exchange degree greater than about 50% line (c) at 5.2 ppm appears additionally with increasing intensity, so that for 90% where the total concentration of hydroxyl groups is 3.7 per 1/8 unit cell, 2.2 OH groups give rise to line (b) and 1.1 OH groups to line (c). Line (d) represents 0.2 ammonium ions so that the sum of the concentration of acid sites, corresponding to lines (b), (c) and (d), yields 3.5 per 1/8 unit cell or $14.6 \times 10^{20}$ per gramme. This is nearly equal to the concentration of 3.7 framework aluminium atoms per 1/8 unit cell determined by $^{27}$Al-NMR. In analogy to the interpretation of the HF and LF stretching vibrations in infrared spectroscopy [15] we suggest that the larger chemical shift of the line (c) corresponding to the smaller vibrational frequency of the LF band in IR spectroscopy is not due to a higher strength of acidity, but related to the smallness of the cages (sodalite units) where these bridging OH groups are located. By a loading of the samples with pyridine the similar behaviour of line (c) and of the LF band can be shown directly [17].

In an attempt to rationalize stretching frequencies of OH groups in hydrogen zeolites, Jacobs and Mortier [16] found a linear dependence for the frequency of unperturbed bridging OH groups (HF band) on Sanderson's intermediate electronegativity of the zeolites. The experimental values are shifted from $\nu_{OH} = 3660\ cm^{-1}$ for Si/Al = 1.2 to $\nu_{OH} = 3610\ cm^{-1}$ for Si/Al $\geq$ 7 [15, 16].

**Table 3.** The Si/Al ratio in the framework, the value of the chemical shift of line (b) in the $^1$H-MAS NMR spectrum, which is due to the unperturbed bridging OH groups, and the corresponding frequencies of stretching vibration for various hydrogen zeolites. The zeolites Y and mordenites are partially dealuminated.

| Sample | Si/Al ratio | $\delta_{OH}$/ppm | $\nu_{OH}^{0\rightarrow 1}$/cm$^{-1}$ | $\nu_{OH}^{0\rightarrow 2}$/cm$^{-1}$ |
|---|---|---|---|---|
| 25 H NaA SB | 1 | 4.05±0.05 | 3620±3 | 7080±7 |
| 50 H NaX SB | 1.2 | 3.78±0.05 | 3658±3 | 7147±7 |
| 36 H NaY DB | 1.6 | 4.14±0.05 | 3645±3 | 7123±7 |
| 64 H NaY DB | 3 | 4.2 ±0.1 | 3642±3 | 7117±7 |
| 80 H NaY DB | 5 | 4.2 ±0.1 | 3642±3 | 7121±7 |
| HY SB | 10 | 4.36±0.05 | – | – |
| H-mordenite SB | 10 | 4.24±0.05 | 3610±3 | 7070±7 |
| H-mordenite SB | 30 | 4.27±0.05 | 3610±3 | 7062±7 |
| H-mordenite SB | 100 | 4.36±0.05 | – | – |
| H-ZSM-5 SB | 15 | 4.27±0.05 | 3610±3 | 7062±7 |
| H-ZSM-5 SB | 26 | 4.36±0.05 | – | – |

In Table 3 values of the chemical shift of line (b) together with the fundamental and first overtone stretching vibrations of O–H bonds for hydrogen zeolites with different Si/Al ratios of the framework are presented. To enhance the accuracy of the chemical shift measurements the samples were loaded with a small amount of methane as an inner standard ($\delta_H = 0.175$ ppm [18]). The results for $\delta_{(b)}$ show the same dependence as published elsewhere [17], however the absolute values have to be shifted by 0.3 ppm. Using the same specimens contained in sealed glass tubes as for our $^1$H-MAS NMR studies, diffuse reflection IR spectra were measured at the Zelinsky Institute of Organic Chemistry in Moscow. From the values in Table 3 it follows that the zeolite HNaA cannot be included in this series. This result is not surprising if we remember the role of the zeolite NaA in the $^{29}$Si-MAS NMR [3, 4]. For values of the silicon-to-aluminium ratio greater than 10 no significant difference can be found. Samples with Si/Al ratios of 10...15 yield $\delta_{(b)} = 4.24$, 4.27 and 4.36 ppm for zeolites of mordenite, ZSM-5 and Y type, respectively. A higher resolution than ±0.05 ppm is necessary to distinguish between these zeolites. The maximum shift of 0.58 ppm can be observed for faujasites going from Si/Al = 1.2 to Si/Al = 10. The non-framework aluminium existing in the dealuminated mordenites and zeolites Y, but not existing in the zeolites H-ZSM-5 does not influence the values of $\delta_{(b)}$ and $\nu_{OH}$.

In conclusion, the present study confirms that the strength of acidity of the bridging OH groups should be constant above a silicon-to-aluminium ratio of 10.

Because the Bronsted acidity is connected with the ability of proton transfer, the existence of both an acid site and an adsorbed molecule is necessary. As an example for an $^1$H-MAS NMR study of the acid-base

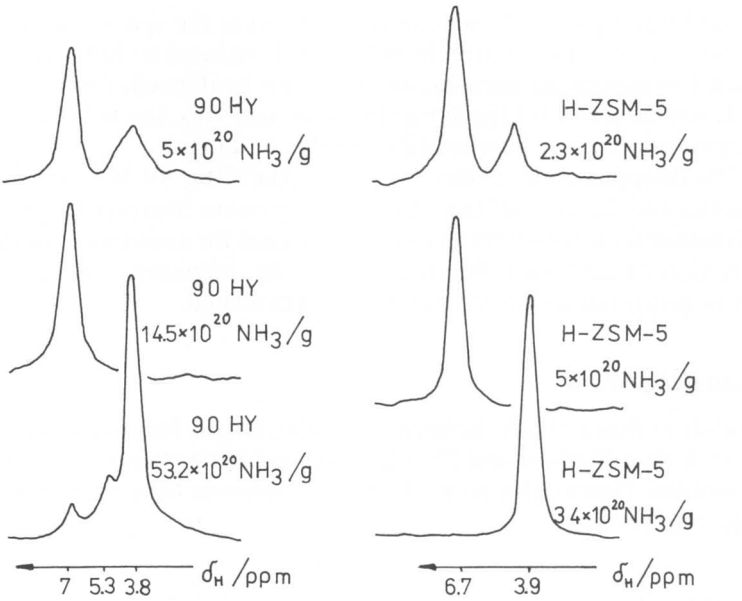


**Fig. 6.** $^1$H-MAS NMR spectra of DB-activated zeolites 90 HY and H-ZSM-5 loaded with an increasing amount of ammonia (for the lower spectra the intensity has been reduced by the factor of 2, 4, or 8).

interaction we present some results for ammonia adsorbed in zeolites HY and H-ZSM-5. Fig. 6 shows spectra of the samples in dependence on the amount of adsorbed ammonia. The spectra of the unloaded samples are contained in Fig. 1 (H-ZSM-5, sample 1) and Fig. 5 (90 HY). The concentrations of the acid sites are $14.6 \times 10^{20}$ per gramme and $4.9 \times 10^{20}$ per gramme for zeolites 90 HY and H-ZSM-5, respectively. If $\eta$ denotes the number of adsorbed molecules divided by the number of acid sites the spectra shown in Fig. 6 are characterized by $\eta < 1$, $\eta = 1$ and $\eta > 1$. For zeolites HY the intensities of lines (b) and (c) decrease to zero if $\eta$ increases from 0 to 1, accompanied by a corresponding increase of the intensity of the line (d). In the spectrum corresponding to $\eta = 4$ an intensive line at $(3.8 \pm 0.1)$ ppm and additional lines at $(6.8 \pm 0.1)$ ppm and $(5.3 \pm 0.1)$ ppm can be observed. Taking into consideration the intensities of these lines the following explanation can be given: The line at 6.8 ppm is due to a single $NH_4^+$-ion in a sodalite cage. The proton exchange between the sodalite cage and the large cavity is hindered by ammonium ions occupying S II-positions [19]. The line at 5.3 ppm is due to a $NH_3$-$NH_4^+$-complex in a sodalite cage, that means a proton is jumping between two included molecules. The line at 3.8 ppm finally is due to 1.5 $NH_4^+$-ions and 9.5 $NH_3$-molecules per cavity having a fast chemical exchange of the protons.

No blocking of acid sites can be observed in the spectra of zeolite H-ZSM-5: For $\eta = 1$ the intensity of line (b) is reduced to zero, line (d) has reached its maximum intensity, and line (a) is unaffected. For $\eta = 7$ only a single line at $(3.9 \pm 0.1)$ ppm can be observed. This line is the result of a fast proton exchange between all molecules and ions.

The disappearance of lines (b) and (c) (the latter for HY only) and the simultaneous increase of line (d) to its maximum intensity for a loading with ammonia corresponding to $\eta = 1$, confirm the correctness of the concentration of acid sites determined from the unloaded samples. Silanol groups giving rise to line (a) cannot be ammoniated.

**Acknowledgements**

We wish to thank Dr. W. Schwieger (Halle), Dr. R. Mostowicz (Warsaw), Dr. U. Lohse (Berlin), and Dr. H.-G. Jerschkewitz (Berlin) for providing the zeolites. Thanks also go to Dr. L. M. Kustov in Moscow for doing the IR-investigations.

**Literature**

1. P. A. Jacobs, *Carboniogenic Activity of Zeolites*, Elsevier, Amsterdam, 1977.
2. J. Klinowski, Prog. Nucl. Magn. Reson. Spectrosc. **16** (1984) 237.
3. C. A. Fyfe, *Solid State NMR for Chemists*. Guelph 1983
4. H. Pfeifer, D. Freude and M. Hunger, Zeolites **5** (1985) 274.
5. D. Freude, Adv. Colloid Interface Sci. **23** (1985) 21.
6. J. Datka, P. Geerlings, W. Mortier and P. Jacobs, J. Phys. Chem. **89** (1985) 3488.
7. W. Mortier, J. Sauer, J. A. Lercher and H. Noller, J. Phys. Chem. **88** (1984) 905.
8. D. Freude, M. Hunger, H. Pfeifer, G. Scheler, J. Hoffmann and W. Schmitz, Chem. Phys. Lett. **105** (1984) 427.
9. U. Lohse, E. Löffler, M. Hunger, J. Stöcker and V. Patzelova, Zeolites, in press.
10. J. Datka and E. Tuznik, Zeolites **5** (1985) 230.
11. D. Freude, T. Fröhlich, H. Pfeifer and G. Scheler, Zeolites **3** (1983) 171.
12. D. Freude, J. Haase, J. Klinowski, T. A. Carpenter and G. Ronikier, Chem Phys. Lett. **119** (1985) 365.
13. E. Lippmaa, A. Samoson and M. Mägi, J. Am. Chem. Soc. **108** (1986) 1730.
14. J. Stöckner, Diplomarbeit, Leipzig 1986.
15. D. Barthomeuf, in: B. Imelik *et al.* (Editors), *Catalysis by Zeolites*, Elsevier, Amsterdam, 1980.
16. P. A. Jacobs and W. J. Mortier, Zeolites **2** (1982) 226.
17. D. Freude, M. Hunger and H. Pfeifer, Chem. Phys. Lett. **128** (1986) 62.
18. J. L. Bonardet and J. P. Fraissard, J. Magn. Reson. **22** (1976) 543.
19. D. W. Breck, *Zeolite Molecular Sieves*, J. Wiley and Sons. N. Y., 1974.