HIGH RESOLUTION SOLID-STATE $^1$H NMR STUDIES OF ZEOLITES

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INTRODUCTION

Surface sites capable of donating protons or accepting electrons from adsorbed molecules cause the phenomenon of heterogeneous catalysis. The strong acidity of zeolites is generated by bridging hydroxyl groups. Their acid strength depends on the electronic charge of the hydrogen atom which can be measured by means of nuclear magnetic resonance (NMR). An early attempt to obtain information about OH groups on surfaces from $^1$H NMR line shape and chemical shift was made 30 years ago by O'Reilly et al. (ref. 1). But it was only with the advent of superconducting magnets and the development of magic-angle-spinning (MAS) that it became possible to measure highly resolved solid-state spectra of zeolites. Whereas $^{29}$Si and $^{27}$Al MAS NMR measurements can be performed on hydrated samples, for $^1$H MAS NMR the re-adsorption of water from the atmosphere must be prevented. The need to use sealed glass ampoules fitting the spinner in the MAS experiment is the reason why $^1$H MAS NMR experiments on zeolites first reported (ref. 2) in 1981 are not more popular.

$^1$H MAS NMR yields quantitative information about Brønsted acidity, structural defects and also about dealumination and realumination of zeolites, since in the H-form of zeolites the number of framework aluminium atoms is equal to the number of acidic OH groups. This review is divided into the following parts: (1) NMR methods; (2) acidity of zeolites; (3) studies on sites with enhanced catalytic activity; (4) OH groups in alkaline earth exchanged zeolites; (5) OH groups in framework defects; and (6) dealumination and realumination of zeolites.

NMR METHODS

For hygroscopic adsorbents, the humidity of air has a significant influence on the proton NMR spectrum. It is therefore necessary to use samples activated at temperatures above 300°C and contained in sealed glass ampoules during the MAS measurements. Only with such equipment is it possible to investigate extremely hygroscopic samples, such as zeolite H-Y. Otherwise the spectrum contains a signal from adsorbed water (ref. 3), and changes in the other signals due to hydrogen bonding interactions and hydrogen exchange must also be taken into consideration. The equipment for the rotation of the sealed glass ampoules must be carefully cleaned to avoid spurious proton signals. Home-made proton probes were used for the experiments in Leipzig and in Cambridge.
Another difficulty in applying $^1$H MAS NMR to aluminosilicates arises from
the heteronuclear dipole-dipole-interaction with the non-resonant spins of $^{27}$Al
nuclei (ref. 4). The quadrupole frequency $V_Q$ of $^{27}$Al is in general lower than its
Larmor frequency $V_L$ in the middle- and high-field NMR. In this case the second
order quadrupole interaction limits the line narrowing factor by MAS to a value of
$0.9V_Q/V_L$. This was the reason why the first $^1$H MAS NMR spectra acquired at 90
MHz (i.e. $V_Q$=23 MHz for $^{27}$Al) were poorly resolved. An upper limit for the
quadrupole frequency of the aluminium nucleus in the neighbourhood of a
bridging hydroxyl group was recently estimated (ref. 5) as 3.85 MHz. This means that
proton resonance frequency of 300 MHz (78 MHz for $^{27}$Al) gives sufficient
resolution.

A further difficulty arises from the presence of the homonuclear $^1$H-$^1$H
interaction. Calculations on a model consisting of three spins, two of them in
resonance, show that the residual MAS linewidth is increased if the static linewidth
(or, more precisely, the reciprocal value of the root of the second moment)
corresponding to the homonuclear dipole-dipole interaction of the resonant spins is
equal to or higher than the rotational frequency (ref. 6). Yesinowski et al. (ref. 7)
demonstrated experimentally that MAS linewidth increases linearly as the average
hydrogen density in samples of minerals increases. In zeolites the highest
concentration of bridging hydroxyl groups is found in zeolites H-Y (fully exchanged
samples of zeolites A and X are not stable during deammoniation). The portion of
the second moment caused by $^1$H-$^1$H interaction could be determined (ref. 5) as
$0.055 \times 10^{-8} \text{T}^{-2}$. The root of this value corresponds to 1 kHz. This is not sufficiently
low in comparison with a rotational frequency of 3 kHz and therefore the resolution
of the $^1$H MAS spectrum is poor. Enhanced resolution can be achieved by means of
the WAHUHA pulse sequence (ref. 8), CRAMPS (ref. 3) and by the use of partially
deuterated samples (ref. 5). Fortunately, for all other zeolites containing less than
two structural hydrogen groups per 24 T atoms, MAS alone at a rotational frequency
of 3 kHz gives good resolution. This cannot be increased further using pulse
sequences.

The so-called "hydroxyl nests" represent a high concentration of protons on the
sites of aluminium vacancies. However, the investigation of dealuminated
mordenite (ref. 9) showed 4 OH groups per vacancy only in the sample evacuated at
room temperature. After vacuum treatment at 100°C, 2 OH groups and above 200°C
less than 0.5 OH per nest remain (ref. 9). Therefore, proton concentration in OH
nests in zeolitic samples activated at 400°C is low and consequently the lines due to
residual protons on framework defects and the outer surface of the crystallites can
also be resolved by MAS alone.

It is well known that the integral of the NMR line as well as the initial value of
the FID after a $\pi/2$ pulse are proportional to the number of the resonant nuclei in
the sample coil. Using a reference sample with a known number of resonant nuclei, we can determine the absolute number of resonant nuclei in the actual sample. In such experiments, for which MAS is not necessary, the following requirements must be satisfied:

1. The time interval between two rf pulses must be longer than $5T_1$, where $T_1$ is the longitudinal relaxation time. Note that $T_1$ of hydroxyl groups is ca. 10 seconds.
2. The volume of both samples should be much larger than the volume of the coil. If it is not, the shape of the reference sample and the actual sample must be identical. In the former case the number of nuclei per length of sample, in the latter the number of nuclei in both samples is compared.
3. The quality factor of the NMR coil containing the actual sample must be the same as that of the coil with the reference sample. That means that, if an aqueous solution is used for the reference, it must be placed in a capillary. The use of a high-power probe with low quality factor of the coil and a short ringdown time is recommended, whereas for the MAS experiments on samples with low concentrations of protons a low-power MAS probe with high quality factor should be used. To separate quantitatively the relative intensities of different lines in an $^1$H MAS NMR spectrum the signals of the spinning sidebands must be added to the main signal.

The standard sample preparation for $^1$H MAS NMR measurements is as follows: samples are subjected to shallow-bed activation in a glass tube 5.5 mm inner diameter with a zeolite layer 10 mm thick. The temperature is increased at a rate of 10 K per hour. The samples are kept at the final activation temperature of 400°C under a pressure below $10^{-2}$ Pa for 24 hours, and then cooled and sealed.

ACIDITY OF ZEOLITES

Three aspects of zeolitic acidity must be considered:

1. The strength of acidity, defined as the ease of proton transfer from a zeolitic hydroxyl group (Brønsted site) to an adsorbed base or of an electron pair transfer from an adsorbed base to a Lewis site.
2. The amount of acid given by the concentration of acid sites.
3. The access of the base molecules to the acid sites.

Early $^1$H NMR studies concerning the Brønsted acidity of zeolites (discussed in ref. 10) used the rate of proton exchange between hydroxyl groups and base molecules as a measure of acidity. The number of proton transfers per second and per cavity with respect to a reference molecule such as pyridine took all these three aspects into consideration. New probe molecules were often used to study Lewis acidity, such as CO, (ref. 11), NO$_2$ (ref. 12) and P(CH$_3$)$_3$ (ref. 13). In the case of bulky probe molecules only the accessible acid sites can be studied.
In order to interpret $^1$H MAS NMR spectra of Brønsted catalysts we use the rule that the strength of acidity increases with the decreasing electronic charge of the hydrogen atom, which corresponds to a larger value of the chemical shift of the proton magnetic resonance. This agrees with the dependence of the chemical shift for the hydroxyl proton of various molecules on their gas-phase acidities (ref. 14). On the other hand, NMR intensity of a resolved line of a OH species is directly proportional to the amount of its Brønsted acidity. Hence, the NMR spectrum may be interpreted as a distribution function of acidity. However, it must still be shown that the species under study is accessible for adsorbed molecules and that the electronic charge of its hydrogen atom is not reduced by hydrogen bonding.

Experiments involving different materials and loading samples with bases, such as ammonia and pyridine, which react with acid sites have led to the assignment of the various proton resonances. In zeolite $^\text{Y}$ five proton resonances have been assigned (ref. 15):

Signal a at 1.3-2.3 ppm from tetramethylsilane (TMS), due to non-acidic (silanol) hydroxyls on the surface of zeolite crystallites and crystals defects sites.

Signal b at 3.8-4.4 ppm from bridging OH groups involving $O_1$ oxygen atoms and pointing towards the zeolitic supercages.

Signal c at ca. 5 ppm from protons on $O_3$ atoms and pointing towards the other oxygens in the sodalite cages.

Signal d at 6.5 - 7.0 ppm, due to residual $\text{NH}_4^+$ cations.

Signal e at 2.6-3.6 ppm, due to Al-OH groups attached to non-framework Al.

These lines could be found also in spectra of other zeolites: line a is present in all spectra, line b in the spectra of all hydrogen forms, line c in the spectra of SAPO-5 (ref. 16), line d shows the presence of residual ammonium ions in ammonium-exchanged mordenites and zeolite ZSM-5 activated at 400°C or below and line e is typical for dealuminated samples of zeolite H-ZSM-5 and mordenite (ref. 17).

Fenzke gave an empirical relation between the values of the chemical shift $\delta$ of hydroxyl groups and their infrared frequencies (cited in ref. 18):

$$v / \text{cm}^{-1} = 3906 - 74.5 \delta / \text{ppm}$$

A similar connection between the two spectroscopic parameters is demonstrated in Fig. 1, which shows values of the chemical shift of line b and of the corresponding frequencies of stretching vibration measured by diffuse reflection on the same specimen contained in sealed glass tubes as used for the $^1$H MAS NMR studies (refs. 15,19). Both values were given versus the relative amount $A$ of aluminium in the framework of hydrogen forms of zeolites some of these dealuminated. The value $A$ is related to the framework silicon-to-aluminium ratio Si/Al by the formula: $1/A =$
To enhance the accuracy of the chemical shift measurements, the samples were loaded with a small amount of methane as an inner standard.

Fig. 1. Chemical shift of line b in the $^1$H MAS NMR spectrum (squares) and infrared frequencies of stretching vibration (HF band) (diamonds) versus the amount of aluminium in the framework of various hydrogen zeolites. X, Y, E, M, Z denote zeolites of type X, Y, erionite, mordenite and zeolite ZSM-5, respectively.

In an attempt to rationalize stretching frequencies of OH groups in hydrogen zeolites, Jacobs and Mortier (ref. 20) found a linear dependence for the HF band of bridging OH groups on Sanderson's intermediate electronegativity of the zeolites which is a linear function of $A$. Fig. 1 shows that both the IR and the NMR values are linearly dependent on $A$. For $Si/Al>10$ no significant difference can be found. This confirms that the strength of acidity of the bridging OH groups should be constant above a $Si/Al$ ratio of 10. It should be noted that the zeolite $H_{0.25}Na_{0.75}$-A giving $\delta=4.05$ ppm and $v=3620$ cm$^{-1}$ cannot be included in this series.

The first $^1$H NMR study of the geometry of Brønsted acid sites in zeolite Y was carried out by Stevenson (ref. 21). The Al-H distance in zeolite H-Y, given as 2.38Å, remains the most reliable value for this vital parameter. It is now clear that Stevenson's 1971 work (ref. 21) 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 and more non-acidic than bridging hydroxyl groups. It seems fortuitous that a recent study involving multinuclear MAS experiments on shallow-bed activated zeolite H-Y with negligible amounts of non-framework aluminium and non-acidic hydroxyl groups arrived at the same Al-H distance (ref. 5). The $^{27}$Al quadrupole frequency of aluminium in a SiOHAl grouping (bridging hydroxyl group) in zeolites

$1 + Si/Al$. To enhance the accuracy of the chemical shift measurements, the samples were loaded with a small amount of methane as an inner standard.
HYDROLYTICALLY DEALUMINATED ZEOLITE H-ZSM-5 (ref. 24)

Hydrothermal treatment often leads to dealumination of the zeolitic framework, which is accompanied by dehydroxylation of the bridging hydroxyl groups (ref. 17). In certain circumstances this treatment enhances catalytic activity. Lago et al. (ref. 25) observed an increased activity of H-ZSM-5 after mild steaming at 540°C and attributed it to paired and partially hydrolyzed framework Al atoms. The question arises as to the nature of these sites of enhanced activity in mildly dealuminated zeolites.

The catalytic activity of various catalysts has been quantitatively related to the concentration and the strength of acidity of their Bronsted sites as determined by \(^1\)H MAS NMR (refs. 14,26,27). We shall now consider the status of hydroxyl groups and aluminium atoms on both framework and non-framework positions in zeolite H-ZSM-5 after mild hydrothermal dealumination. The zeolite with Si/Al=15 synthesized without template (ref. 28) was provided by Dr. Schwieger. The Na\(^+\)/H\(^+\) ion exchange was carried out at room temperature with a 0.5 M aqueous solution of HCl. Samples were steamed at 540°C for 150 min with water vapour pressures from 0 to 100 kPa and investigated by MAS NMR. The framework Si/Al ratio varied from 15 to 60 depending on the pressure of water vapour. Experimental details including the n-hexane cracking catalytic test are described in ref. 24.

The dependence of NF, the number of framework aluminium atoms per unit cell, on the water vapour pressure of steaming is given in Table 1. The framework Si/Al ratio is Si/Al=(96/NF)-1. NF was determined from the intensity of the narrow line at 60 ppm in the \(^{27}\)Al MAS NMR spectra. In general, the spectra show two narrow lines at 60 and -3 ppm due to 4-coordinated framework and 6-coordinated non-framework aluminium, respectively. For hydrothermally treated samples an additional broad line, ca. 130 ppm wide, appears at about 30 ppm due to non-framework AlOOH in which Al is in tetrahedral coordination through its proximity to two framework oxygens. In column (5) of Table 1 the concentration of aluminium atoms involved in the formation of the complex giving rise to the line
at 3 ppm is given versus steaming pressure. Upon mild dealumination the complex cannot be observed. Columns (6) and (7) in Table 1 give the concentrations of tetrahedral non-framework (acid-soluble) aluminium which can be converted and which cannot be converted to (acid-insoluble) 6-coordinated non-framework aluminium by treatment with 0.5 M aqueous solution of HCl.

**TABLE 1**

(1) Water vapour pressure; (2) concentration of framework aluminium atoms as determined by $^{27}$Al MAS NMR (60 ppm line); (3) and (4) concentration of non-framework aluminium species in an octahedral (-2 ppm line) and a tetrahedral (30 ppm line) coordination, respectively; (5) concentration of aluminium forming complex; (6) concentration of acid-soluble aluminium; (7) concentration of tetrahedral Al NF, which is acid-insoluble; (8) total concentration of OH groups obtained from the maximum amplitude of the free induction decay; (9), (10) and (11) concentration of SiOH, bridging OH and AlOH groups, respectively, determined by $^1$H MAS NMR; (12) reaction rate constant in mole MPa$^{-1}$ g$^{-1}$ hr$^{-1}$. Experimental error does not exceed 0.4 species per unit cell.

<table>
<thead>
<tr>
<th>Pressure in kPa</th>
<th>Concentration in &quot;species per unit cell&quot;</th>
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<tr>
<td>(1)</td>
<td>Al$^F$ Al$^{NF}$ Al$^{NF}$ Al$^{NF}$ Al$^{NF}$ $^1$H SiOH bOH AlOH</td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>oct. tetr. form. sol. insol.</td>
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<td>0</td>
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</tr>
<tr>
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<td>1.6 0.6 3.8 4.0 4.0 - 3.6 1.2 1.6 0.8</td>
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</table>

$^1$H MAS NMR spectra are shown in Fig. 2. Three different signals can be seen: line a at 2.0 ppm is due to non-acidic hydroxyl groups at the outer surface of zeolite crystallites, at framework defects and in the amorphous part of the sample; line b at 4.3 ppm is caused by bridging (acidic) OH groups; line e at ca. 3.0 ppm represents non-acidic AlOH groups on non-framework aluminium species pointing towards framework oxygen atoms. This line is resolved in the spectrum of Fig. 2(C) only, but the line fitting procedure shows the existence of line e also in the spectra of Figs. 2(B) and 2(D). The corresponding concentrations are given in Table 1.
Fig. 2. $^1$H MAS NMR spectra of zeolite H-ZSM-5 after hydrothermal treatment at $T=540^\circ$C for 150min and the following water vapour pressures: (A) 0 kPa; (B) 7 kPa; (C) 40 kPa; (D) 93 kPa. The samples were shallow-bed activated at 400$^\circ$C.

Fig. 3 gives the $^{29}$Si MAS NMR spectrum of the parent H-ZSM-5 measured with 24,000 scans. Line fitting demonstrates that the spectrum consists of three lines at -111.5 ppm due to Si(0 Al) grouping, at -106.4 ppm due to Si(1 Al) grouping and at -100.8 ppm due to SiOH and Si(2 Al) groupings superimposed. $^{29}$Si CP MAS NMR gives a strong and a weak line at 100.8 ppm and 111.5 ppm, respectively. The line at -111.5 ppm corresponds to 79.5% of the total intensity, the line at -106.4 ppm to 18.8% and the line at -100.8 ppm to 1.5±0.5%. $^1$H MAS NMR (see Table 1) shows that there are 1.2 SiOH groups per 90 Si atoms in the unit cell, in other words 1.3% of the total $^{29}$Si signal must be assigned to the SiOH grouping and the portion of the signal due to the Si(2Al) grouping is 0.2±0.5%. The concentration of framework aluminium atoms can be calculated from deconvoluted spectra using Gaussian lineshapes. The result Si/Al=15 agrees well with the value determined by $^{27}$Al MAS NMR. After steaming the percentage of silicon with Si(1Al) environment decreases.
The samples in this study, including samples with enhanced catalytic activity, give spectra with a shift of 4.3 ppm for the bridging OH groups (see Fig. 2). This is in agreement with the infrared spectra of Lago et al. (ref. 25), which show that the IR line at 3610 cm\(^{-1}\), due to acidic bridging OH groups, does not shift upon steaming. The infrared spectra of the samples (in fused glass ampoules prepared for \(^1\)H MAS NMR) in the region of combination and overtone vibrations were measured. No shift of the OH vibrations in these regions could be observed. We conclude therefore that the enhanced catalytic activity cannot be explained by a decrease of the electron density on the hydrogen atom and the enhanced-activity site cannot be called a "stronger" Brønsted site.

Lago et al. (ref. 25) suggest that during the steaming one member of a paired Al site (Al-O-Si-O-Al) is modified (and possibly partially hydrolyzed) and acts as a strong electron acceptor for the remaining tetrahedral Al thus creating a stronger Brønsted site. This model disagrees with our \(^{29}\)Si MAS NMR measurements. The assumption (ref. 25) that aluminium atoms preferentially occupy positions in 4-rings yields for Si/Al=15 a concentration of 3.4 paired Al per unit cell and 4.2% of the silicon atoms in Si(2Al) grouping. A statistical distribution of aluminium on T-positions (note that Al-O-Al linkages are forbidden) gives, for Si/Al=15, 3.4 paired Al per unit cell and 2.3% of silicon as Si(2Al). However, the result of 1% of the silicon atoms in Si(2Al) groupings as determined from the spectrum in Fig. 3 is smaller than the values calculated above.

It seems that the aluminium atoms tend to occupy such positions where their mutual distance is maximum since the concentration of paired Al is smaller than predicted by the statistical distribution. Hence an increased concentration of paired Al groupings (0.5 Al-O-Si-O-Al groupings per unit cell for Si/Al=15), which is
required by the model of Lago et al. (ref. 25) must be rejected on the basis of $^{29}\text{Si MAS NMR}$.

$^{27}\text{Al MAS NMR}$ detects all the $^{27}\text{Al}$ nuclei in the hydrated samples under study with an accuracy of ±10%. This means that the samples do not contain "NMR-invisible" aluminium. The three lines at ca. 60ppm, 30ppm and -2ppm are due to 4-coordinated framework aluminium, 4-coordinated non-framework aluminium and 6-coordinated non-framework aluminium, respectively. $^{27}\text{Al MAS NMR}$ spectra of hydrated samples do not support the existence of partially hydrolyzed framework aluminium as proposed by Lago et al. (ref. 25). In conclusion, MAS NMR does not confirm the proposed structure of the enhanced-activity sites.

Table 1 shows that the concentration of 4-coordinated and 6-coordinated non-framework aluminium in the rehydrated samples increases with increasing water vapour pressure during steaming. Note that no $^{27}\text{Al MAS NMR}$ signals can be observed in the dehydrated samples. All aluminium in the such samples is "NMR-invisible", since a tetrahedral or octahedral symmetry of aluminium atoms in H-zeolites exists only in hydrated samples (ref. 5). The $^{27}\text{Al MAS NMR}$ spectra of hydrated samples show the presence of a 4-coordinated non-framework aluminium species formed in the rehydration process from a precursor, which must be assumed to be the catalytically important part of the enhanced-activity site. The concentration of octahedral aluminium atoms is constant in the samples under study (cf. Table 1).

It is well known that acid leaching removes only a part of the non-framework aluminium from the crystallite (ref. 29). We have used formic acid to investigate which portion of non-framework Al can be removed. The conclusion from our $^{27}\text{Al MAS NMR}$ and $^{13}\text{C NMR}$ measurements is that the H+ of the acidic bridging OH groups reacts with HCOOH forming H$_3$O$^+$ and CO. At temperatures up to 100°C one OH group splits one HCOOH molecule. However, at 200°C a catalytic reaction splits all molecules. If the number of loaded molecules is much larger than the number of acidic OH groups and the temperature is below 100°C, HCOOH can react with non-framework aluminium to give aluminium formate. This reaction did not occur in mildly dealuminated zeolites, which show the effect of the enhanced activity (see Table 1). Also the loading of an aqueous solution of 0.5 M HCl shows that the non-framework aluminium species produced by mild dealumination are acid-insoluble. It follows that the aluminium species which is the important part of enhanced-activity sites, is not easily removable although it could be easily removed from the framework position and must be accessible for the hexane cracking reaction.

The nature of the new site is not entirely clear. Some information was added to the knowledge about the enhanced-activity sites: the concentration of charged non-framework aluminium species in the dehydrated samples under study must be very small, because the concentration of framework aluminium does not significantly exceed the concentration of bridging hydroxyl groups (see Table 1). Therefore, the
concentration of negatively charged AlO₄-tetrahedra in the framework, which can compensate positively charged non-framework aluminium species, must be very low. Table 1 also shows that the concentration of non-acidic hydroxyl groups (the sum of intensities of lines a and e) does not increase with increasing concentration of non-framework aluminium. The intensity of line e due to AlOH groups on non-framework Al species pointing towards framework oxygen atoms is low, which means that the degree of hydroxylation of the non-framework aluminium species must be small (Table 1). The degree of polymerization of the species should be low, because the rehydration transforms them into AlOOH or Al(H₂O)₆³⁺ complexes.

Our conclusion concerning the "NMR-invisible" non-framework aluminium in the mildly dealuminated dehydrated samples is that it exists in small uncharged and unstable complexes, which are mostly non-hydroxylated. Since they cannot be easily removed from their position by acid treatment they must be immobilized by the zeolitic framework.

Using the crystal structure determined by Olson et al. (ref. 30) for a computer representation of ZSM-5, narrow channels can be shown parallel to the straight channels. In such a narrow channel small cavities exist, for instance a cavity with a diameter of 0.26 nm and a window of 0.19 nm to the straight channel (ref. 31). If an oxygen atom of a non-framework aluminium species were to be included in this small cavity it could not be easily removed.

The existence of non-framework aluminium obviously enhances the catalytic reaction but the presence of bridging OH groups is also necessary for the activity enhancement. A suitable spatial arrangement of a bridging OH group and non-framework aluminium species may be considered as the enhanced-activity site for the n-hexane cracking. The maximum number of such sites should be given by the smaller of the following two values: the number of non-framework aluminium complexes or the number of bridging OH groups. This model is in agreement with the results of the catalytic measurements and the concentrations determined by MAS NMR. In general, the conclusion with regard to the effect of the steaming process on the catalytic activity agrees well with the data of Lago et al. (ref. 25).

HYDROXYL GROUPS IN ALKALINE EARTH CATION-EXCHANGED ZEOLITE Y (ref. 32)

Plank (ref. 33) was the first to suggest that the polarizing action of alkaline earth cations in zeolite Y upon water molecules might be responsible for the formation of Brønsted acidity. This "Plank mechanism" is as follows (refs. 34-37):
Numerous infrared studies of zeolite Y containing Ca$^{2+}$ and Mg$^{2+}$ and a small amount of adsorbed water reported (refs. 34-41) five hydroxyl stretching vibrations at ca. 3740, 3690, 3650, 3600 and 3540 cm$^{-1}$. The band at 3740 cm$^{-1}$ represents silica-type hydroxyl groups on framework defects and on the external surface of the crystallites. The 3650 cm$^{-1}$ and the 3540 cm$^{-1}$ bands were attributed to bridging OH groups in the neighbourhood of framework aluminium atoms on O$_1$ and O$_3$ positions, respectively. Uytterhoeven et al. (ref. 40) and Ward (ref. 41) observed in zeolite Ca-Y a band at ca. 3600 cm$^{-1}$, which drastically increases after readesorption of water. This band does not react with pyridine and was attributed to CaOH groups (ref. 40). In samples exchanged with various cations except Ca$^{2+}$, Ward (ref. 36), Hall (ref. 37) and Angell and Schaffer (ref. 42) observed a band at ca. 3690 cm$^{-1}$. This is generally attributed to metal OH groups similar to AlOH in alumina. The adsorption of ammonia resulted in a decrease of 3650 and 3540 cm$^{-1}$ bands, but not the 3690 cm$^{-1}$ band (ref. 40).

The catalytic significance of hydroxyl species formed by the dissociation of water at divalent cations was shown by cracking (ref. 33) and alkylation (ref. 43). The increase in activity on re-addition of small amounts of water and the decrease in activity with increased calcination temperature observed for both reactions can be understood as a result of the formation and recombination of Brønsted sites in zeolites exchanged with alkaline earth cations.

For this study the zeolite Na-Y (Si/Al=2.6) from VEB Chemiekombinat Bitterfeld was exchanged at 343 K using an aqueous solution of 0.1 M Ca(NO$_3$)$_2$ or Mg(NO$_3$)$_2$ to give an exchange degree of 83 %, i.e. 2.77 divalent cations per cavity. After the exchange the zeolite was washed and calcined at 380 K. After activation at 400°C one portion of the sample was partially rehydrated at room temperature with doubly distilled water and, whenever stated, reactivated (RA) for 24 hrs under vacuum at 200°C, 300°C or 400°C. Some samples were activated after partial rehydration, loaded with fully deuterated pyridine and then sealed.

The spectrum of the activated zeolite MgNa-Y [Fig. 4(A)] contains a line due to silanol groups at ca. 1.6 ppm and a weak shoulder at 4.0 ppm. After loading with 0.5 H$_2$O molecules per cavity (H$_2$O/c) an additional line at ca. 0 ppm appears, and a separate signal due to bridging OH groups at 4.0 ppm (Fig. 4(B) and (C) for 0.5 and 1.0 H$_2$O/c, respectively). The line at ca. 0 ppm has weak spinning sidebands in comparison to those of bridging OH groups. As shown in Table 2, the intensity of the latter signal increases simultaneously with that of the bridging OH groups at
4.0 ppm. The poor spectral resolution in Fig. 4(D) indicates that 2.5 H₂O/c were not completely dissociated. Like water adsorbed on zeolite Na-Y, the non-dissociated molecules give rise to a broad line at 3.3 ppm with associated broad spinning sidebands. Reactivation of the sample at 200°C removes the broad line giving a spectrum [Fig. 4(E)] similar to that in Fig. 4(C) (1.0 H₂O/c). Fig. 4(F) shows the spectrum of the same sample (RA 200°C) but additionally loaded with two pyridine molecules per cavity, which causes a disappearance of the signal due to bridging OH groups.

Fig. 4. ¹H MAS NMR spectra of the samples of zeolite MgNa-Y. (A) activated at 400°C; (B) loaded with 0.5 H₂O/c; (C) 1.0 H₂O/c; (D) 2.5 H₂O/c; (E) 2.5 H₂O/c, reactivated at 200°C; (F) 2.5 H₂O/c, reactivated at 200°C and loaded with two molecules pyridine per cavity; (G) 2.5 H₂O/c, reactivated at 300°C; (H) 2.5 H₂O/c, reactivated at 400°C.
As is known from studies on zeolites H-Y (refs. 43,44) the high acid strength of bridging OH groups protonates adsorbed pyridine molecules and gives rise to a line at 15 ppm. The line at ca. 0 ppm decreases in intensity. It follows that the species giving rise to this line is partially accessible to pyridine. The weak signals at 8-10 ppm result from the hydrogen bonds between these OH groups and the pyridine molecules.

Fig. 5. $^1$H MAS NMR spectra of the samples of zeolite CaNa-Y. (A) activated at 400°C; (B) loaded with 0.4 H$_2$O/c; (C) 1.0 H$_2$O/c; (D) 2.0 H$_2$O/c; (E) 2.0 H$_2$O/c, reactivated at 200°C; (F) 2.0 H$_2$O/c, reactivated at 200°C and loaded with two molecules pyridine per cavity; (G) 2.0 H$_2$O/c, reactivated at 300°C; (H) 2.0 H$_2$O/c, reactivated at 400°C.
Zeolite CaNa-Y shows a similar behaviour of the bridging OH groups as zeolite MgNa-Y, but a different behaviour for OH groups associated with the metal. The spectrum of the activated zeolite CaNa-Y [Fig. 5(A)] consists of only one line due to silanol groups at 1.6 ppm and a weak shoulder at 4.0 ppm. After loading with 0.4 H$_2$O/c a line at 0.5 ppm appears, and a separate signal due to bridging OH groups at 4.0 ppm can be observed [Fig. 5(B)]. Increased water adsorption (1.0 and 2.0 H$_2$O/c) causes the formation of a line at 2.8 ppm with associated spinning sidebands, comparable to that of bridging OH groups [Fig. 5(C) and (D)].

As shown in Table 1, the intensity of the latter signal increases simultaneously with that of the bridging OH groups at 4.0 ppm. Reactivation of the sample with 2.0 H$_2$O/c at 200°C causes both a reduction of the line for bridging OH groups and a decrease of the line at 2.8 ppm [Fig. 5(E)]. Fig 5(F) shows the spectrum of the same sample (RA 200°C) additionally loaded with two pyridine molecules per cavity. This causes a disappearance of the signal due to bridging OH groups. The line at 2.8 ppm is not affected by the adsorption of pyridine, whereas the line at 0.5 ppm decreases in intensity. Hence the species giving rise to the line at 2.8 ppm is located in positions inaccessible to pyridine.

The question arises as to the assignment of the different metal OH groups giving rise to two signals in the $^1$H MAS NMR spectra which parallel the stretching vibrations at 3600 and 3690 cm$^{-1}$ in the infrared spectra. Costenoble et al. (refs. 45,46) determined the distribution of Ca$^{2+}$ cations in a zeolite CaNa-Y (Si/Al=2.37) by X-ray diffraction. In samples containing 1.3-3.5 H$_2$O molecules per cavity, 0.51-0.71 cations per cavity were at site SII, 2.28-2.68 cations at site SI' and 0.2 cations at site SI (the latter only for the sample with 1.3 H$_2$O/c).

The majority of Ca$^{2+}$ cations were located in the sodalite cages, where also non-framework oxygen species could be found at SII' positions. The number of these oxygen species equals the number of divalent cations at SI' positions (ref. 45). The observed SI' - SII' distances of 0.238-0.245 nm are in good agreement with the Ca-O bond length of 2.39 nm (ref. 45), which suggests the existence of CaOH groups in the sodalite cages.

Yesinowski et al. (ref. 7) gave an empirical relation for the dependence of the isotropic chemical shift of hydroxyl protons upon the oxygen-oxygen (OH...O) distances of hydrogen bonds in hydroxyapatites. According to this, the shift of the line from 0.5 ppm to 2.8 ppm can be explained by the presence of an additional hydrogen bond with an OH...O distance of 0.295 nm. This enables us to interpret the differences in the chemical shifts of hydroxyl groups in the zeolite CaNa-Y by CaOH groups pointing into the supercage (0.5 ppm) and CaOH groups in the sodalite cages hydrogen bonded to framework oxygen atoms (2.8 ppm).
### TABLE 2
Concentration of hydroxyl groups as determined by $^1$H MAS NMR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of OH groups per cavity giving rise to lines at about 0ppm</th>
<th>1.6ppm</th>
<th>2.8ppm</th>
<th>4.0ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgNa-Y</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgNa-Y, 0.5 H₂O/c</td>
<td>0.5</td>
<td>0.2</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>MgNa-Y, 1.0 H₂O/c</td>
<td>0.8</td>
<td>0.2</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>MgNa-Y, 2.5 H₂O/c</td>
<td>1.3</td>
<td>0.2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>MgNa-Y, 2.5 H₂O/c,RA 200°C</td>
<td>0.8</td>
<td>0.2</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>MgNa-Y, 2.5 H₂O/c,RA 300°C</td>
<td>0.3</td>
<td>0.2</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>MgNa-Y, 2.5 H₂O/c,RA 400°C</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaNa-Y</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaNa-Y, 0.4 H₂O/c</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>CaNa-Y, 1.0 H₂O/c</td>
<td>0.1</td>
<td>0.2</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>CaNa-Y, 2.0 H₂O/c</td>
<td>0.1</td>
<td>0.2</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>CaNa-Y, 2.0 H₂O/c,RA 200°C</td>
<td>0.4</td>
<td>0.2</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>CaNa-Y, 2.0 H₂O/c,RA 300°C</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>CaNa-Y, 2.0 H₂O/c,RA 400°C</td>
<td>0.2</td>
<td></td>
<td>&lt;0.1</td>
<td></td>
</tr>
</tbody>
</table>

The spectra of zeolites MgNa-Y and CaNa-Y partially rehydrated and then reactivated at 200, 300 and 400°C are shown in Figs. 4 and 5(E), (G) and (H). Table 2 demonstrates that the number of metal OH groups agrees well with the number of bridging OH groups. Fig. 6 gives the concentration of bridging OH groups as a function of the temperature of reactivation. Note that there are 2.77 divalent cations per cavity. Fig. 3 is also representative of samples activated after the ion exchange at temperatures of 300°C and above. After activation at 400°C fewer than 0.1 bridging OH group per cavity remain.

$^{27}$Al MAS NMR indicates no decrease in the concentration of framework aluminium after treatment. This means that hydroxyl groups produced by the dissociation of water molecules were completely removed by sample activation at 400°C and recombined to give water molecules.

### OH GROUPS IN FRAMEWORK DEFECTS ARISING FROM SYNTHESIS

The concentration, per gram of dried zeolite, of terminal OH groups located at the outer surface of the zeolitic crystallites, can be estimated as $N_T=0.12\times10^{20}/d$, where $d$ is the diameter of the crystallites in μm. This value is generally more than one order of magnitude smaller than the concentration of SiOH groups determined by $^1$H MAS NMR (line a). Quantitative results concerning the presence of internal silanol in zeolite ZSM-5 were also provided by $^{29}$Si MAS NMR with cross-polarization (refs. 47,48) and by silylation (refs. 48,49).
Concentrations of non-acidic hydroxyl groups on framework defects arising from the synthesis are determined in most of the \(^1\)H MAS NMR studies. Special attention to the influence of the synthesis upon concentration of SiOH groups on framework defects, including those which arise from the calcination of template containing zeolites, is given in refs. 28 and 50.

The values in Table 3 are taken from a study concerning synthesis of pentasil zeolites with and without organic templates (ref. 28). The concentrations of SiOH

**TABLE 3**

Concentrations of non-acidic hydroxyl species in the hydrogen (H) or sodium (Na) form of zeolites ZSM-5 synthesized with different organic templates and without organic templates.

<table>
<thead>
<tr>
<th>Form/Template</th>
<th>Si/Al ratio</th>
<th>Diameter (μm)</th>
<th>Concentration ((10^{20} \text{ species per gram}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/none</td>
<td>15</td>
<td>3.2</td>
<td>0.6</td>
</tr>
<tr>
<td>H/none</td>
<td>26</td>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>H/mono-n-propylamine</td>
<td>35</td>
<td>1.2</td>
<td>0.4</td>
</tr>
<tr>
<td>H/mono-n-butylamine</td>
<td>30</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Na/TPA(^+)</td>
<td>30</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>H/TPA(^+)</td>
<td>30</td>
<td>1.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Na/TPA(^+)</td>
<td>110</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>H/TPA(^+)</td>
<td>110</td>
<td>1.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Na/TPA(^+)</td>
<td>180</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>H/TPA(^+)</td>
<td>180</td>
<td>2.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>
groups (line a) for all specimens are much greater than the values obtained from the calculation of the number of terminal OH groups. The extremely high concentration of silanol groups observed for zeolites ZSM-5 synthesized with TPA+ shows, that this template leads to highly disturbed lattice with a high concentration of non-intact Si-O-Si bonds after calcination.

From the absence of amorphous material as seen by X-ray diffraction, it follows that up to 8% of the framework Si are present as SiOH groups. Woolery et al. (ref. 47) found a value of 7% by $^{29}$Si MAS NMR investigation on ZSM-5 synthesized with TPA+.

The enhanced concentration of SiOH groups in the hydrogen form of the zeolites indicates that about half the defect sites are present as Si-O-Na after sample calcination, the other half being present as internal silanol groups. Treatment with 0.5 M HCl leads to the exchange of Na$^+$ cations on the defect sites with H$, thus forming a maximum number of silanol groups. This behaviour can be explained (ref. 51) by the following reaction scheme of a defect site:

$$\text{Na}\quad\text{TPA}\quad\text{O}\quad\text{O}\quad850\text{ K, 10 h}\quad\text{Na}\quad\text{H}\quad\text{O}\quad\text{O}\quad0.5\text{ M HCl, 15 h}\quad\text{H}\quad\text{H}\quad\text{O}\quad\text{O}\quad\text{Si}\quad\text{Si}\quad\text{Si}\quad\text{Si}$$

Since hydrothermal treatment at 1100 K for 5 days leads to the healing of the zeolitic framework, most of the internal SiOH groups must be vicinal: neighbouring framework defects are transferred via dehydration into intact Si-O-Si bonds (ref. 51). On the other hand, ZSM-5 specimens from organic-free batches and those synthesized using n-butyl and n-propylamine as template have relatively intact frameworks with only a small concentration of internal silanol groups (ref. 28).

**DEALUMINATION AND REALUMINATION OF ZEOLITES**

Various $^1$H MAS NMR studies combined with $^{27}$Al MAS NMR measurements address the hydrothermal dealumination of the hydrogen form of zeolites (refs. 15,17,52-54). It could be shown that the dehydroxylation of bridging OH groups in hydrogen forms of zeolites is accompanied by the removal of aluminium from the zeolitic framework. All samples under study confirms the rule: the number of bridging hydroxyl groups is equal to the number of framework aluminium atoms.

On the other hand, the concentration of SiOH groups does not change upon hydrothermal dealumination (ref. 17). $^1$H NMR studies of dealumination by acid treatment at room temperature showed that OH nests on sites of aluminium vacancies heal out by hydrothermal treatment and cannot be observed above 300°C.
Acid leaching increases the number of SiOH groups (ref. 17). One explanation of this effect is that non-framework aluminium is bonded to oxygen at framework defects; new SiOH groups are created by removal of non-framework aluminium species. Because in the hydrogen form of the zeolites the concentration of bridging OH groups is equal to the concentration of framework aluminium, $^1$H MAS NMR can be used to prove the realumination of zeolites.

Breck and Skeels were the first to suggest (ref. 56), that some non-framework aluminium present in dealuminated (ultrastable) zeolite Y can be reintroduced into the framework. It has been recently demonstrated by means of $^{29}$Si and $^{27}$Al MAS NMR that the reintroduction can be performed by treatment with strongly basic solutions at elevated temperatures (ref. 57). This could be confirmed by $^1$H MAS NMR (ref. 58) as shown in Fig. 7.

The $^1$H MAS NMR spectra of the samples, given in Fig. 7, are relatively poorly resolved because of the strong proton-proton dipolar interaction. Spectral deconvolution into Gaussian components was used to obtain relative intensities of the various signals, and Fig. 8 shows the deconvolution of the central signal of the spectrum of the realuminated sample 4. All five types of hydroxyls described above are clearly in evidence. The spectrum of the parent zeolite H-Y (Fig. 7) consists of three signals corresponding to different kinds of protons: signal b at 4.0 ppm due to bridging OH groups involving O$_1$ atoms and pointing towards the zeolitic supercages, signal c at ca. 4.9 ppm to protons on O$_3$ atoms pointing towards the other oxygens in the sodalite cages; signal a, corresponding to Si-OH groups, is weak, which indicates that the sample contains few defects. Dealumination results in a marked decrease of the intensity of signal b and the appearance of signal e, due to Al-OH groups attached to non-framework Al. In the spectrum of realuminated material, besides the shoulder attributable to line a and the signal e, there are signals in the chemical shift region corresponding to lines b and c. Their intensity is increased in comparison with the spectrum of dealuminated material (sample 2). There is also a weak signal due to the residual ammonium cations (line d).

Measurement of the intensity of NMR signals indicates that there are $4.2\pm0.4$ bridging OH groups per supercage in sample 1, $2.1\pm0.3$ OH groups in sample 2 and $4.4\pm0.4$ OH groups in the realuminated sample 4. The total number of bridging hydroxyl groups in the realuminated sample is therefore approximately the same as in the parent sample 1. On the other hand, the intensity of signal c is significantly higher in sample 4 than in sample 1, indicating that in the latter sample aluminium is preferentially substituted into sites associated with OH groups involving O$_3$ oxygen atoms.
Fig. 7. $^1$H MAS NMR spectra in the absolute intensity mode. Parent zeolite NH$_4$-Y (sample 1) after activation; ammonium-exchanged hydrothermally dealuminated material (sample 2), and ammonium-exchanged realuminated material (sample 4). Asterisks denote spinning sidebands.
Fig. 8. Spectral deconvolution (dotted lines) into Gaussian components of the $^1$H MAS NMR spectrum of the realuminated sample 4 (solid line, see Fig. 7). The labelling of the various signals is as described in the text.

It was shown by a combination of $^1$H MAS NMR, $^{27}$Al MAS NMR and adsorption methods that non-framework aluminium species created by hydrothermal dealumination (2.5 h, 540°C, 80 kPa water vapour pressure) of H-ZSM-5 (template free synthesized (ref. 28) Si/Al=15) are partly reintroduced into the framework upon treatment with 0.1 M aqueous solution of NaOH (2 h, 80°C) (ref. 59).

The $^1$H MAS NMR spectrum of the parent zeolite in Fig. 9(A) consist of two lines corresponding to different kinds of protons: signal b at 4.3 ppm due to bridging OH groups and signal a at ca. 1.7ppm due to framework defects. Dealumination of the zeolite [Fig. 1(B)] results in a marked decrease of the intensity of signal b and the appearance of signal e, due to Al-OH groups attached to non-framework Al at ca. 3 ppm. After treatment with NaOH the concentration of SiOH groups increases to 1.8 per unit cell [line a in Fig. 9(A)] in comparison to the value of 0.7 SiOH per unit cell [line a in Fig. 9(C)] for the parent sample. This is caused by the removal of framework silicon atoms during the treatment with NaOH. After converting the zeolite into the hydrogen form by treatment with 0.1 M HCl, the intensity of signal b is increased in comparison with the spectrum of dealuminated material. Measurement of the intensity of NMR signals indicates that there are 4.8, 1.3, 0.9 and 2.3 bridging OH groups per unit cell in the parent sample, the sample dealuminated at 80 kPa, the NaOH-treated sample and the hydrogen form of this, respectively. This means that only 30% of the bridging hydroxyl groups removed during
hydrothermal dealumination can be reintroduced by the realumination process followed by hydrogen exchange.

Fig. 9. $^1$H MAS NMR spectra in the absolute intensity mode. (A) Parent zeolite H-ZSM-5 (Si/Al=15) after activation; (B) hydrothermally dealuminated material (Si/Al=59); (C) material realuminated with NaOH (Si/Al=25); (D) hydrogen exchanged form of the realuminated material. The framework Si/Al ratios were determined by $^{27}$Al MAS NMR. Asterisks denote spinning sidebands.
ACKNOWLEDGMENTS

I am grateful to Professor H. Pfeifer and Dr. M. Hunger for valuable discussions, Dr. E. Brunner, Dr. H. Ernst, Dr. D. Fenzke, Dr. T. Fröhlich, Dr. J. Klinowski, Dr. W. Reschetilowski and Dr. W. Schwieger for stimulating advice, and to Dr. J. Klinowski and Mr. P.J. Barrie for their editorial help.

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