2. Characterization

2.1 NMR Studies Concerning the Acidity and Catalysis in Zeolites

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Abstract
Two NMR techniques, namely $^2$H MAS NMR and echo Fourier $^{27}$Al NMR, have been applied for the first time to study Brönsted acidity of dehydrated zeolites. The $^{27}$Al signal of Si-OH-Al sites, which was NMR-invisible until now, yielded a quadrupole coupling constant $C_{QCC} = 16$ MHz for zeolite H-ZSM-5. The values of $C_{QCC}$ determined from the $^2$H MAS NMR spectra of Si-OH-Al sites increase with the framework aluminium content of the zeolites from 208 kHz (H-ZSM-5) to 236 kHz (H-X and H-Y) due to the decreased acid strength of the bridging OH groups. The state of art of the two techniques, $^2$H MAS NMR and $^1$H MAS NMR, applied to study Brönsted acidity of dehydrated zeolites is compared.

Concerning the methanol to hydrocarbons conversion (MTG process) in the zeolite H-ZSM-5 we observed the time dependence of the first step of the reaction at 200 °C using a MAS (magic-angle spinning) probe with laser heating system and found that the concentration of protons in the species with stronger polarized O-H bonds increases during the reaction up to 60% at equilibrium.

1. INTRODUCTION

Surface sites capable of donating protons or accepting electrons from adsorbed molecules are essential for the phenomenon of heterogeneous catalysis. The strong acidity of zeolites is generated by bridging hydroxyl groups. Their strength of acidity depends on the electronic charge of the hydrogen atom which can be measured by means of $^1$H or $^2$H MAS NMR spectroscopy of dehydrated samples. The nature of non-framework aluminium compounds plays an important role for the Lewis acidity of partly dealuminated zeolites and can be studied by $^{27}$Al NMR. The NMR investigations of the adsorption and reaction of probe molecules in zeolites can elucidate the acidic properties but also the nature of the catalytic activity of the zeolites. The field of solid-state NMR has developed very rapidly during the last years. The number of published NMR studies of zeolites amounts now to 200 per year and a significant portion of those papers is devoted to the acidity and basicity of zeolites, cf. [1].

The Brönsted sites in zeolites are bridging hydroxyl groups of type Si-OH-Al of the aluminosilicate framework. They can be characterized by various NMR parameters: chemical shift, intensity, dipole broadening, and quadrupole parameters (spin > 1/2). The bare sites can be studied by $^1$H, $^2$H (after H-D exchange), $^{17}$O (cf.[2]), $^{29}$Si (cf.[3]), or $^{27}$Al NMR measurements of the dehydrated (also denoted as activated or calcined) samples.

Numerous $^1$H NMR studies concerning the acidity of zeolites can be found in the literature and are reviewed by Pfeifer and Ernst [1] and Freude [4]. However, studies concerning the geometry of Brönsted sites are rare [3-7]. Vega et al. have measured the $^2$H NMR powder pattern of the zeolite RHO exchanged with ND$_4^+$ ions [8]. On heating the samples above 400 °C without evacuation
results in a spectrum with a spin = 1 quadrupole powder pattern which is due to rigidly bound hydroxyl groups and can be described by a quadrupole coupling constant $C_{qqc} = 251$ kHz and an asymmetry parameter of the electric field gradient (EFG) tensor $\eta = 0$. Gluszak et al. [9] have discussed the two components of the $^2$H NMR signal of a deuterium exchanged and partly dealuminated zeolite NH$_4$-Y which was evacuated under vacuum to 450 °C. They ascribe the quadrupole powder pattern to hydroxyl deuterons with $C_{qqc} = 234$ kHz and $\eta = 0.03$ and a Gaussian shaped signal with a FWHM (full width at half maximum) of 63.1 kHz to silanol groups.

$^{27}$Al NMR (as well as $^{29}$Si NMR) experiments were mainly carried out on hydrated samples. From the strongly broadened signal of the $^{27}$Al nuclei in a dehydrated zeolite Na-Y the following quadrupole parameters could be determined [6]: $C_{qqc} = 6.8$ MHz and $\eta \approx 0.5$. The signal of the $^{27}$Al nuclei being constituents of the Si-OH-Al sites in the dehydrated of zeolites was "NMR-invisible" until now.

In the present paper it is shown that the $^{27}$Al NMR signal of the bridging Brönsted sites becomes visible at 11.744 T using an echo Fourier technique. The MAS technique cannot improve the resolution of the second-order powder pattern of the $^{27}$Al signal. But for the first-order quadrupole broadened $^2$H NMR signal of the deuterated zeolites by means of the MAS technique a two-dimensional spectrum can be obtained giving information about the chemical shift and the first-order quadrupole shift as well.

The gradual transition of heterogeneous systems contained in sealed samples from the initial to the final state, i.e. the catalytic reaction itself, can be studied either by a cyclic heating of the sample to increasing temperatures and measurement of the NMR spectra at a low temperature, mostly room temperature, where the reaction is frozen (method A) or by in situ variable temperature measurements (method B) [1]. The introduction of the magic-angle spinning (MAS) technique to $^{13}$C NMR spectroscopy of heterogeneous catalytic reactions has led to two important improvements: (i) The resolution of the spectra and hence the sensitivity to ascertain reaction products could be enhanced significantly, and (ii) it has become possible to observe also the carbon-13 signals of strongly bound reaction products including coke. Among the MAS NMR studies the catalytic conversion of methanol to hydrocarbons (MTG process) using zeolite ZSM-5 has attracted a great deal of attention because this process is used on an industrial scale. In situ NMR investigations of this process were performed by Anderson and Klinowski (cf. [10],[11]) and Haw et al. (cf. [12]). In our report we present $^1$H and $^{13}$C MAS NMR results of the time dependence of the conversion of methanol in the zeolite H-ZSM-5. Compared with the previous NMR in situ techniques (A) and (B), the temperature switching behaviour in the laser heated sample is closer to that in a gaseous flow reactor.

2. EXPERIMENTAL

The zeolite H-Y 92 containing 8% Na$^+$ of the original content of cations, was prepared by a repeated exchange of a sample of Na-Y (Si/Al = 2.6) in an aqueous solution of NH$_4$NO$_3$ followed by calcination. The samples H-Y 85 were prepared from a 85% NH$_4^+$ and 15% Na$^+$ containing zeolite Y (Si/Al = 2.4). The zeolite H-X 50 (Si/Al = 1.4) contains 50% of the original content of sodium ions. Zeolites Na-ZSM-5 and H-ZSM-5 with Si/Al = 22 were synthesized using mono-n-butyramine as template, and then exchanged with 0.5 N HCl. A template-free synthesized zeolite H-ZSM-5 (Si/Al = 15) was used for the methanol conversion.

Samples for $^1$H and $^2$H MAS NMR were prepared by heating 8 mm deep layers of zeolite in glass tubes 4 mm or 5 mm diameter. The temperature was increased at a rate of 10 K h$^{-1}$ under vacuum. After maintaining the samples at 400 °C and at a pressure less than 10$^{-2}$ Pa for 24 h, several samples were partially deuterated by contact with 2 kPa D$_2$O at 400 °C or 230 °C for 30 minutes, followed by evacuation. This procedure was repeated 8 times followed by a final evacuation at 300 °C for 12 h. The samples were then loaded under a pressure of 13 kPa of O$_2$ and sealed off.
The adsorption of \( \text{O}_2 \) shortens the spin-lattice relaxation time \( T_1 \) for the \(^1\text{H} \) and \(^2\text{H} \) nuclei, so that the MAS NMR spectra could be acquired with 1 s repetition time. Without oxygen, the proton longitudinal relaxation times \( T_1 \) of the OH groups have been found to be ca. 10 s, while an average value of 26 s has been determined for the corresponding deuteron \( T_1 \) [9].

The same exchange treatment at 230 °C, except for the use of \( \text{H}_2\text{O} \) instead of \( \text{D}_2\text{O} \), has been carried out on zeolite H-Y 85. By comparing the \(^1\text{H}\) MAS NMR spectrum of this sample with the spectrum of the sample which had not treated at 230 °C, it could be shown that the deuteration did not change the concentration of hydroxyl groups in the zeolite.

In order to obtain a signal of residual water molecules and residual ammonium ions, the zeolite H-Y 92 was evacuated at a maximum temperature of only 230 °C and denoted as H-Y 92/230.

For \(^{27}\text{Al}\) and \(^{29}\text{Si}\) NMR measurements on dehydrated samples, the zeolites were treated as described above using a final evacuation at 400 °C, then loaded with ca. 300 mg n-octane per gram zeolite under vacuum and sealed off. After the homogenisation of the sample at 100 °C the zeolite was fully immersed in octane. Before the measurements the glass tubes (10 mm diameter) were opened and the samples were transferred into the MAS sample container under air.

The NMR measurements at room temperature were carried out using a Bruker MSL 500 spectrometer. The \(^{27}\text{Al}\) pulse length was 0.5 μs, which corresponded to a \( \pi/6 \) pulse for non-selective excitation (\( \pi/2 \) pulse for selective excitation of the central transition, cf.[13]). The rf power used corresponds to a (non-selective) nutation frequency of \( v_{\text{rf}} = 167 \text{ kHz} \), so that for all samples \( v_{\text{rf}} \) exceeds the spectral width of the central transition. If the latter value exceeded 50 kHz, a phase cycled selective echo sequence [14] (\( \pi/2.5_{\text{s,t}}, \text{delay}_{20 \mu\text{s}}, \pi_{1\mu\text{s}} \)) was used, starting the acquisition 20 μs after the second pulse. For \(^1\text{H}\) MAS NMR (\( v_{\text{rot}} = 12.5 \text{ kHz} \)) and \(^2\text{H}\) MAS NMR (\( v_{\text{rot}} = 5 \text{ kHz} \)), the acquisition was initiated one rotation period after the single pulse. The number of scans varied from 1000 for \(^1\text{H}\) to 100 000 for \(^2\text{H}\) MAS NMR.

For the \textit{in situ} methanol conversion the zeolite H-ZSM-5 was loaded with 8 methanol molecules (99% enriched in \(^{13}\text{C} \)) per unit cell corresponding to two molecules per channel intersection. Fused quartz ampoules were used for the temperature dependent experiments and the \(^1\text{H}\) and \(^{13}\text{C}\) MAS NMR measurements (partially with decoupling) were performed at spinning rates of about 1 kHz using a Bruker MAS NMR probe with a \( \text{CO}_2 \) laser heating system together with the MSL 300.

3. RESULTS

Some of the \(^1\text{H}\) MAS NMR spectra of the dehydrated zeolites are given in Fig. 1. The different proton signals are denoted by (a) - (e), cf. Refs [1,4]: Line (a) at 1.9 ppm is due to non-acidic hydroxyl groups at framework defects and in the amorphous part of the sample. Line (b) at 3.7 ppm for H-X 50, 3.9 ppm for H-Y 85, 4.0 ppm for H-Y 92, and 4.3 ppm for H-ZSM-5 is due to bridging OH groups pointing into the large zeolite cages or into the intersections, respectively. Line (c) at 4.8 - 4.9 ppm in the spectra of zeolites H-Y is caused by bridging OH groups pointing into the sodalite cage. Line (d) at 7 ppm is assigned to residual ammonium cations. Line (e) at ca. 2.7 ppm represents hydroxyl groups associated with non-framework aluminium species and bonded to framework oxygen atoms. The spinning sidebands not shown in Fig. 1, contain less than 10% of the total intensity of the spectra. By a comparison of the signal intensities of deuterated and non-deuterated samples an exchange degree of 75% - 95% of the hydrogen species has been found.

Fig. 2A shows the \(^2\text{H}\) MAS NMR sideband pattern of sample H-Y 92/230. In this presentation the structure of the spinning sidebands is lost. Fig. 2B presents the same spectrum in a two-dimensional stack-plot. The 2D plot was created using the Bruker WINNMR software by dividing the sideband spectrum (32768 points) into single sideband files. The shape of the sidebands is plotted in the second dimension, representing the chemical shift, whereas the first (horizontal) dimension represents the first-order quadrupole broadened (static) linewidth of species having the corresponding value of the chemical shift. This type of representation of a sideband spectrum by a
Figure 1. ¹H MAS NMR spectra of some samples. The two observable spinning sidebands in the distance of 12.5 kHz (ca. 30 ppm and -20 ppm) contain less than 10% of the total intensity of the spectra. Concentrations of species can be determined from the spectra after multiplication of their intensities with the factor C given for each of them in the Figure.

Figure 2. A shows the ²H MAS sideband pattern of sample H-Y 92/230. B presents the same spectrum in a two-dimensional stack-plot. The 2D plot was created using the Bruker WINNMR software by dividing the sideband spectrum (32768 points) into single sideband files. The shape of the sidebands is plotted in the second dimension, representing the chemical shift, whereas the first (horizontal) dimension represents the first-order quadrupole broadened linewidth of species having the corresponding value of the chemical shift. vQ represents the angular dependent first-order quadrupole shift for the both transitions -1,0 and 0,+1.
two dimensional spectrum was used for the first time by Blümich et al. [15]. $v_Q$ represents the angular dependent first-order quadrupole shift for the transitions $-1,0$ and $0,+1$:

$$v_Q = \pm \left( \frac{3}{8} \right) C_{qcc} \left( 3 \cos^2 \beta - 1 + \eta \sin^2 \beta \cos 2\alpha \right).$$

$C_{qcc} = e^2 q Q / h$ denotes the quadrupole coupling constant with $e Q$ as the electric quadrupole moment and $q = (V_{xx} - V_{yy})/V_{zz}$ with $|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|$ define the components of the traceless EFG tensor. $\alpha$ and $\beta$ are the Euler angles for the rotation of the principal axes system with respect to the laboratory system. The distance between the two singularities in a theoretical powder spectrum, which are due to both transitions in the case of $\beta = \pi / 2$ and $\eta = 0$, corresponds to the quadrupole frequency $v_Q$. For spin=1 nuclei $v_Q$ is equal to $(3/4) C_{qcc}$. Figure 3 shows contour plots of the $^2$H MAS NMR spectra. Although from these figures the values of $C_{qcc}$ can be estimated only roughly, a MAS sideband simulation of Fenzke et al. [7] allows the exact determination of the quadrupole parameters, which are presented in table 1 for the bridging hydroxyl groups. Four different species can be distinguished due to different quadrupole coupling parameters: bridging hydroxyl groups ($C_{qcc} = 208 - 236$ kHz, $\eta = 0.10 \pm 0.05$), AlOH groups ($C_{qcc} = 67$ kHz, $\eta = 0.2$), silanol groups (quadrupole broadened structureless signal with FWHM $= 65$ kHz), and residual ammonium ions (weak quadrupole broadening, FWHM $< 5$ kHz).

### Table 1. NMR parameters describing the hydrogen forms of the zeolites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>H-X 50</th>
<th>H-Y 85</th>
<th>H-Y 92</th>
<th>H-ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Al</td>
<td>1.4±0.1</td>
<td>2.4±0.1</td>
<td>3.1±0.1</td>
<td>22±1</td>
</tr>
<tr>
<td>NFAI</td>
<td>&lt; 2%</td>
<td>&lt; 2%</td>
<td>20±4%</td>
<td>5±2%</td>
</tr>
<tr>
<td>$^1$H c.s. [int.]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>line (a)</td>
<td>3.7 ppm [40±4]</td>
<td>3.9 ppm [23±2]</td>
<td>4.1 ppm [21±2]</td>
<td>4.3 ppm [4±0.4]</td>
</tr>
<tr>
<td>line (b)</td>
<td>3.0 ppm [10±3]</td>
<td>4.8 ppm [25±2]</td>
<td>4.9 ppm [22±2]</td>
<td>2.8 ppm [12±1]</td>
</tr>
<tr>
<td>C$_{qcc}$(H)</td>
<td>236±10 kHz</td>
<td>236±10 kHz</td>
<td>224±10 kHz</td>
<td>208±10 kHz</td>
</tr>
<tr>
<td>$\eta$</td>
<td>0.10±0.05</td>
<td>0.06±0.05</td>
<td>0.13±0.05</td>
<td>0.15±0.05</td>
</tr>
<tr>
<td>C$_{qcc}$(27Al)</td>
<td>10.8±1.0 MHz</td>
<td>12.7±1.0 MHz</td>
<td>12.7±1.0 MHz</td>
<td>16.0±1.0 MHz</td>
</tr>
<tr>
<td>$\eta$</td>
<td>0.9±0.1</td>
<td>0.7±0.1</td>
<td>0.7±0.1</td>
<td>0.1±0.1</td>
</tr>
</tbody>
</table>

The $^{27}$Al MAS NMR spectra of the hydrated samples, which are not shown here, consist of three signals: Framework aluminium gives rise to a narrow line at ca. 60 ppm, whereas the narrow line at ca. 0 ppm and the broad line at ca. 30 ppm must be attributed to non-framework aluminium. The relative amounts of non-framework aluminium atoms, obtained from the relative intensities of the lines at ca. 0 ppm and ca. 30 ppm in the spectra of the hydrated samples, are presented in table 1.
Figure 3. Contour plots of the $^2$H MAS spectra. An sideband simulation allows the exact determination of the quadrupole parameters. Four different species can be distinguished due to different quadrupole coupling parameters: bridging hydroxyl groups ($C_{qcc} = 208-236$ kHz, $\eta = 0.10 \pm 0.05$, see table 1), defect AlOH groups ($C_{qcc} = 67$ kHz, $\eta = 0.2$), defect silanol groups (quadrupole broadened structureless signal with FWHM = 65 kHz), and residual ammonium ions (weak quadrupole broadening, FWHM < 5 kHz).

Figure 4. $^{27}$Al NMR spectra of the dehydrated zeolites. Aluminium atoms in negatively charged oxygen tetrahedra, compensated by sodium cations, give rise to the spectra of the sodium zeolites and to the narrow component in the spectra of the hydrogen zeolites. Therefore, the spectra of the hydrogen forms must be split into two components. The lineshape simulation for the broad components gives the values:

$C_{qcc} = 12.7$ MHz, $\eta = 0.7$ for H-Y 92,
$C_{qcc} = 16$ MHz, $\eta = 0.1$ for H-ZSM-5,
$C_{qcc} = 5.5$ MHz, $\eta = 0.3$ for Na-Y,
$C_{qcc} = 4.7$ MHz, $\eta = 0.5$ for Na-ZSM-5.
$^{27}$Al NMR spectra of the dehydrated zeolites are shown in Fig. 4. The full width of the spectra varies from 24 kHz (Na-ZSM-5) to 100 kHz (H-ZSM-5). This means that the available maximum value of the MAS frequency $\nu_{\text{rot}} = 15$ kHz does not exceed the second-order broadening of the central transition and thus the application of MAS is pointless. Aluminium atoms in negatively charged oxygen tetrahedra, compensated by sodium cations, give rise to the spectra of the sodium zeolites and to the "narrow" component in the spectra of the hydrogen zeolites. Therefore, the spectra of the hydrogen forms must be split into at least two components. Moreover, different crystallographic positions of the aluminium atoms in the sodium form, and, in addition, different distances to the hydroxyl protons in zeolites H-Y, should give rise to a distribution of the quadrupole parameters. The values of $C_{\text{qee}}$, see Fig. 4, were determined by means of a lineshape simulation with the programme WINFIT (Bruker) assuming only one or two sets of parameters for the sodium and hydrogen form of the zeolites, respectively. A comparison of the FWHM of the dehydrated zeolite H-ZSM-5 with the rehydrated one (not shown here) yields a factor of about 100. Therefore, the absence of a component narrowed by water in the spectrum of a sample measured one month after the filling of the MAS rotor proves that the octane loading prevented the sample from rehydration while exposed to air.

The resonance position of the $^{27}$Al NMR (central transition) signal of the dehydrated samples is given by the centre of gravity of the line. The second moment of the line with respect to this centre of gravity gives a value for the (high field) second-order quadrupole shift of the centre of gravity, cf. Freude and Haase [13] p. 30. Finally, the chemical shift $\delta$ with respect to the reference Al$(\text{H}_2\text{O})_2^{3+}$ in aqueous solution is obtained by the addition of the resonance position of the centre of gravity and the magnitude of the quadrupole shift, giving $\delta = 105 \pm 20$ ppm for the dehydrated zeolites H-Y and $\delta = 82 \pm 20$ ppm for the zeolite H-ZSM-5.

Figure 5 shows the $^{27}$Al NMR spectra of dehydrated samples H-ZSM-5 before (Fig. 5A) and after a mild hydrothermal treatment at a water vapour pressure of 7 kPa, 13 kPa, and 93 kPa. The steaming procedure is described in Ref. [16]. All spectra must be split into at least two components. One component of the signals must be due to the framework aluminium atoms ($\eta = 0.1$, see Fig. 4), the other component, which seems to be caused by an asymmetric EFG tensor, must be explained by extra-framework aluminium atoms. The total intensities of all signals are about equal.

Some proton decoupled $^{13}$C MAS NMR spectra of the methanol conversion at 200 °C are given in Fig. 6. Relevant resonance positions are: methanol 50.5 ppm, dimethylether 60.5 ppm, CO $^{183.3}$ ppm, CO, $^{124.2}$ ppm, and methane -10.7 ppm. The time dependent molar concentrations of the species collected from a series of samples are presented in Fig. 7. The water content (dashed line) was calculated from the concentration of other reactants. Fig. 8 shows some corresponding proton spectra, which are well-resolved at the reaction temperature compared with the results of the room temperature measurements. Relevant resonance positions are: CH$_2$OH adsorbed in H-ZSM-5 ca. 9.1 - 10.5 ppm [10], water 4.78 ppm, hydroxonium ion ca. 10 ppm (cf.[17]), and bridging OH groups 4.3 ppm. The methane doublet at 0.23 ppm arises from the $^1$H-$^{13}$C coupling.

4. DISCUSSION

4.1. Acid Sites

The characterization of solid acids by $^1$H MAS NMR is now well-established. In order to interpret the spectra of Brønsted acid catalysts it is normally accepted that the strength of acidity increases with decreasing electronic charge of the hydrogen atom, which corresponds to a larger value of the chemical shift of the proton magnetic resonance. Since the NMR intensity of a resolved line in the high speed MAS spectrum is directly proportional to the concentration of its Brønsted acid sites, the spectrum may be interpreted as a distribution function of acidity. This approach allows an interpretation of lines (a) and (b) in the spectra. For example, when one considers the acidic hydroxyl groups, the values of the chemical shift of line (b) increases from 3.7 ppm for zeolite H-X...
Figure 5. $^{27}$Al NMR spectra of dehydrates samples H-ZSM-5 before A, and after mild hydrothermal steaming at a water vapour pressure of 7 kPa B, 13 kPa C, and 93 kPa D.

Figure 6. Proton decoupled $^{13}$C MAS NMR spectra of the methanol conversion. The zeolite H-ZSM-5 was loaded with 8 methanol molecules per unit cell. Spectrum A is measured at room temperature. In situ measurements started immediately after heating the sample up to 200°C (spectrum B), after 10 minutes (spectrum C), and after 40 minutes (spectrum D). The measuring time was 3 minutes for each of the spectra. Therefore, e.g. the spectrum B starting at 0 minutes represents the mean value between 0 and 3 minutes.
Figure 7. Time dependent molar concentrations of the $^{13}$C species for the conversion at 200 °C. The zeolite H-ZSM-5 was loaded with 8 methanol molecules per unit cell at room temperature. The water content (dashed line) was calculated from the concentration of the other reactants.

Figure 8. $^1$H MAS NMR spectra of the methanol conversion. The zeolite H-ZSM-5 was loaded with 8 methanol molecules per unit cell. Spectrum A is measured at room temperature. In situ measurements were performed 25 minutes (spectrum B) and 40 minutes (spectrum C) after heating the sample up to 200 °C. Spectrum D was measured at room temperature after cooling down the sample after the conversion.
through 3.9 - 4.0 ppm for zeolite H-Y to 4.3 ppm for zeolite H-ZSM-5 corresponding to the increasing acid strength, whereas the concentration of hydroxyl groups giving rise to line (b), decreases on going from faujasites to H-ZSM-5 (see table 1). With respect to the non-acidic hydroxyl groups, the intensity of line (a) at ca. 2 ppm is a measure of the concentration of defect silanol groups. However, the spectra in Fig. 1 show two more hydroxyl group signals, i.e. (c) and (e), for which the value of the chemical shift cannot be explained by the simple model above: The corresponding hydroxyl groups experience an additional electrostatic interaction with other oxygen atoms in the neighbourhood. This increases the value of the chemical shift but not the acid strength. These hydroxyl protons point to other framework oxygen atoms which reduces the accessibility of the hydroxyl protons to adsorbed molecules and therefore, their ability to act as acid sites.

In the present paper the \(^{1}H\) MAS NMR investigations were carried out in order to demonstrate the deuteration of the hydroxyl groups and to compare the \(^{2}H\) spectra with those of the \(^{1}H\) MAS NMR. The spectrum of zeolite H-92/230, Fig. 1A, consists of five signals including the line (d) due to the incomplete deammonisation (8.5 residual ammonium ions per unit cell) at the maximum treatment temperature of 230 °C. The quantitative comparison of spectra A, C, E, with B, D, F in Fig. 1 verifies the decrease (75% - 95%) of the lines (a) - (d) upon deuteration. In Fig. 1C the line (e) due to AlOH groups is best resolved. The concentration of 12 AlOH groups and 4.3 silanol groups per unit cell in sample H-Y 92 is caused by the calcination of the ammonium form under air during the modification from Na-Y to H-Y. In contrast, the spectrum of the zeolite H-Y 85 shows neither line (e) nor line (a). This characterizes the zeolite H-Y 85 as defect-free.

From the \(^{2}H\) MAS NMR spectra of the deuterated zeolites values for the chemical shift can be determined, which should be the same as from the \(^{1}H\) MAS NMR spectra. However, the separation of the two types of bridging OH groups giving rise to lines (b) and (c) with a separation of ca. 1 ppm in the \(^{1}H\) MAS NMR spectrum is not yet possible. The residual MAS linewidth (FWHM) due to second-order quadrupole broadening, cf. [13], is \(\delta_{\text{2nd-order}} = C_{\text{qcc}}/(2v_{L})\) for \(I = 1\) and \(\eta = 0\) yielding 0.1 ppm for \(C_{\text{qcc}} = 220\ kHz\) and \(v_{L} = 76.775\ MHz\). The residual linewidth (FWHM for \(I = 1\), \(\eta = 0\)) caused by a deviation from the magic angle between the rotation axis and the external magnetic field is more significant: \(\delta_{\text{MAS}} = (3/8) C_{\text{qcc}} (3 \cos^{2}\theta - 1)/v_{L}\). It yields 1 ppm in our case for a deviation of 0.02° from the magic angle. Thus an instability of the rotor axis or a static deviation from the magic angle can limit the resolution in the \(^{2}H\) MAS NMR spectra. Another explanation of the decreased resolution compared with the \(^{1}H\) MAS NMR spectra may be the mobility of the OH groups. The mean residence time of a hydrogen atom on one oxygen site must be much greater than the reciprocal frequency difference between the two lines (b) and (c). The latter value increases by a factor of 6.6 going from \(^{1}H\) to \(^{2}H\) NMR. The ability to resolve lines (b) and (c) and relatively short acquisition times are still the advantage of the \(^{1}H\) MAS NMR.

The \(^{2}H\) MAS NMR technique reveals a new dimension for the study of surface hydroxyl groups, which can be used in two ways: Firstly, it is evident from Fig. 2B that the quadrupole dimension increases the resolution of signals having similar positions in the \(\delta\)-scale but different values in the \(v_{Q}\)-scale. Signals of residual ammonium ions or of residual adsorbed molecules (not shown here) appear predominantly close to \(v_{Q} = 0\ kHz\). Secondly, in addition to the values of chemical shifts, the quadrupole coupling constants \(C_{\text{qcc}}\) can be studied in order to characterize the hydroxyl groups. The values of \(C_{\text{qcc}}\) of the bridging hydroxyl groups (see table 1) increase with the framework aluminium content of the zeolite from 208 kHz (H-ZSM-5) to 235 kHz (H-X 50 and H-Y 85) due to the decreased acid strength of the bridging OH groups. Relations between the proton chemical shift and the corresponding deuterium quadrupole coupling constant can be found in literature: Rosenberger et al. [18] derived the equation \(\delta_{\text{ppm}} = c_{1} - c_{2} \times C_{\text{qcc}}/kHz\) with the constants \(c_{1} = 18.88\) and \(c_{2} = 0.05\) for polycrystalline trihydrogen selenites. Sternberg and Brunner [19] have predicted for hydroxyl groups in solids values of 26 and 0.095 for the constants \(c_{1}\) and \(c_{2}\), respectively. Using this correlation, it follows from our values of \(C_{\text{qcc}} = 208\ kHz\) and 235 kHz that the values of \(\delta\) should be 6.24 ppm and 3.68 ppm, respectively. The absolute value is well predicted.
for the $^1$H MAS NMR signal of zeolite H-X. But the average chemical shift of bridging hydroxyl groups in the zeolites H-Y (lines (b) and (c)) is very close to the value of 4.3 ppm measured for the zeolite H-ZSM-5, whereas from the theoretical prediction [19] a difference of 2.56 ppm should follow from our experimental values of $C_{qcc}$.

The quadrupole dimension of the signals of defect hydroxyl groups shows signals reduced in the FWHM in comparison with those of the bridging hydroxyl groups. For the Al hydroxyl groups the signal shows two singularities; the fitting procedure yields $C_{qcc} = 67$ kHz, $\eta = 0.2$. The signal of the silanol groups has only one maximum, the FWHM is 65 kHz and the fit yields $C_{qcc} = 75$ kHz and $\eta = 0.6$. The simple explanation of the quadrupole coupling constant predicts a decrease of $C_{qcc}$ for the weakening of the oxygen-hydrogen bond. But bond weakening of the defect hydroxyl groups in comparison to bridging hydroxyl groups is in disagreement with the explanation of the corresponding values of the chemical shift. A motional narrowing of the spectral width due to fast jumps between oxygen atoms can also be excluded. If the spinning sideband pattern exists, the jump frequency must be small in comparison with the rotation frequency, which is small in comparison with the spectral width. But a fast rotational diffusion of the hydrogen around the Si-O or Al-O axis reduces the static linewidth by a factor of $(1/2) (3 \cos^2 \beta - 1)$. Ernst [20] has determined an angle of $\beta = 40^\circ \pm 5^\circ$ between the Si-O and O-H axes of silanol groups. The fast rotation around the Si-O (Al-O) axis with an Si-O-H angle in the corresponding range reduces the static linewidth by a factor of $0.25 - 0.5$. This effect and a distribution of an additional electrostatic interaction between defect hydroxyl groups and framework oxygen atoms can explain the quadrupole lineshape of the $^2$H MAS NMR spectra of defect hydroxyl groups.

Whereas a detailed discussion exists about the correlation between proton chemical shift values (cf. [1, 4]) or deuteron quadrupole coupling constants (cf. [18, 19]) with the weakening of the oxygen-hydrogen bond, which describes the property of the Brönsted site, the correlation between the aluminium quadrupole coupling constant of the Brönsted site with its acidic properties is unknown until now. In the present study first experimental values are given for $C_{qcc}$ of the aluminium atom in a SiOHAl site. Experiments with hydrated zeolite samples could not give information about this site, because the hydroxyl proton is involved in the formation of hydroxonium ions [17]. The values of $C_{qcc}$ in Fig. 4 demonstrate that the electric field gradient at the position of the aluminium atom increases by a factor of 2.3 or 3.4 for the zeolites Y or ZSM-5, respectively, going from the dehydrated sodium form to the dehydrated hydrogen form of the zeolite. This proves the influence of the acidic proton upon the EFG tensor at the position of the framework aluminium atoms. A comparison between the samples under study yields the higher value of $C_{qcc}$ for the Brönsted site in the zeolite H-ZSM-5, which is supposed to have the strongest polarized O-H bond. The higher rotational symmetry of the EFG tensor for zeolite H-ZSM-5 can be explained by an isolated Brönsted site, whereas in zeolites of faujasite type the Brönsted sites in the neighbourhood or aluminium cations can destroy the symmetry of the tensor. Further experiments and also calculations of the EFG tensor are necessary in order to correlate the field gradient tensor at the site of the $^{27}$Al nucleus in the SiOHAl group with the properties of the Brönsted site.

Values of the $^{27}$Al NMR chemical shift can be determined with a high accuracy for the hydrated zeolites. The value for the 4-coordinated framework aluminium is ca. 60 ppm for the hydrogen and sodium forms of the zeolites Y and ZSM-5, whereas a narrow signal of 6-coordinated extra-framework aluminium appears at ca. 0 ppm. In the case of dehydrated hydrogen zeolites one Al-O bond in the bridging groups (≡Si-OH-Al≡) is weakened or broken, commonly denoted by a dotted line instead of a solid line in the picture of the structure. This can be understood as an intermediate case between 4- and 3-coordination. Consequently the chemical shift values of these nuclei should be expected to be higher than those in hydrated samples. The values of $\delta = 105\pm 20$ ppm for the dehydrated zeolites H-Y and $\delta = 82\pm 20$ ppm for the zeolite H-ZSM-5 obtained for the first time in this study support this suggestion.
Figure 5 shows that also the extra-framework aluminium in the dehydrated sample can be observed now. The signal assigned to extra-framework aluminium is narrower compared with that of the bridging SiOHAl positions. Therefore, the quadrupole broadening of the extra-framework aluminium species is smaller corresponding to a higher symmetry of these positions.

4.2. Methanol Conversion

The results presented in Figs. 6 and 7 show that the methanol conversion starts immediately after the reaction temperature was switched from room temperature to 200 °C by the laser beam. The concentration of methanol and dimethylether goes through a minimum and maximum, respectively, until chemical equilibrium is approached after 40 minutes. This equilibrium corresponds to values measured with method (B) and is different from that at room temperature [method (A)], as was shown by a room temperature measurement after the conversion at 200 °C. It is important to note that CO₂ is observed as a reaction product in our experiment.

The in situ ¹H MAS spectra (cf. Fig. 8) show broad lines, with peaks at 9 ppm and 8 ppm after a reaction time of 25 minutes and 40 minutes, respectively. Anderson et al. observed at room temperature the signal of the methanol hydroxyl at 9.1-10.5 ppm, the latter value for a methanol loading similar to that used in our study. They explain the strong low field shift by hydrogen bonding or protonation of the methanol molecules in the zeolite H-ZSM-5. The chemical shift of water is 4.78 ppm, that of the bridging hydroxyl group is 4.3 ppm, and a signal of a hydroxonium ion is supposed to have a chemical shift of ca. 10 ppm (cf. [17]). A fast chemical exchange of the ¹H nuclei between these species gives a mean value of the chemical shift, which increases with mean degree of polarization of the O-H bond. From the intensity of the line at 8-9 ppm it can be concluded that the concentration of protons in the species with stronger polarized O-H bonds increases during the reaction up to 60% at equilibrium. The nature of the species is not yet clear and further time-resolved in situ MAS NMR experiments could be helpful to solve this question.

Literature