CHARACTERIZATION OF ZEOLITES BY MAGIC-ANGLE-SPINNING NMR

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ABSTRACT

Magic-angle-spinning nuclear magnetic resonance (MAS NMR) has been used to study structure defects in TPA/ZSM-5, the dealumination process caused by hydrothermal treatment and acid leaching of zeolites, the influence of Lewis sites upon water as a probe molecule, the boron incorporation into the ZSM-5 framework, and the acid sites and structure defects in SAPO-5. The nuclei under study are $^1$H, $^{11}$B, $^{27}$Al, $^{29}$Si, and $^{31}$P.

INTRODUCTION

Studies on zeolites take advantage of nearly all NMR techniques developed during the forty-year-history of this branch of rf-spectroscopy. With the advent of superconducting magnets and the development of the magic-angle-spinning (MAS) solid state MAS NMR became one of the most important analytical methods for zeolite research. It is capable of probing local atomic environments in zeolites in unrivalled detail.

Since the pioneering work of Lippmaa et al. (ref. 1) the resolution of $^{29}$Si MAS NMR spectra was improved by more than an order of magnitude (ref. 2). Following the early $^{27}$Al MAS NMR study on zeolites (ref. 3) the nucleus became number two for the determination of the structure of zeolites by MAS NMR. $^1$H MAS NMR of zeolites in sealed samples (ref. 4) helped to elucidate the nature of catalytic acidity. Gabelica et al. proved by $^{11}$B MAS NMR that the substituted boron atoms are present in the framework (ref. 5), and Müller et al. demonstrated that $^{31}$P in AIPO zeolites is in tetrahedral coordination (ref. 6).

The principal technique used in this work is $^1$H MAS NMR. While $^1$H samples have to be activated (to remove adsorbed water) and sealed, hydrated samples for MAS NMR studies of $^{11}$B, $^{27}$Al, $^{29}$Si, and $^{31}$P are used without special treatment. The aim of this paper is to demonstrate the potential of MAS NMR for obtaining high-resolution spectra and thus establishing the local environment of framework and non-framework atoms, acidic and non-acidic hydroxyl groups, and to study the nature of defects in the zeolite framework.
METHODS

Sample preparation

Samples for $^1$H NMR were activated under conditions similar to the shallow bed activation in a glass tube of 5.5 mm inner diameter with the zeolite layer 10 mm thick. Temperature was increased at a rate of 10 K/hr. After maintaining the samples for 24 hrs. at the final activation temperature of 400 °C under a pressure below $10^{-2}$ Pa, the samples were cooled and sealed. MAS NMR of other nuclei was carried out on non-activated samples.

NMR measurements

All measurements were conducted in an external magnetic field of 6.3 or 7 Tesla using a single excitation pulse. Samples were spun at the magic angle at 3 - 6 kHz. As a reference for $^{27}$Al intensity measurements a well characterized sample of ZSM-5 with a framework Si/Al ratio of 15 was used. The total concentration of OH groups in the activated samples was determined by comparison of the maximum amplitude of the free induction of the samples with those of a capillary with an aqueous solution in a probe with a short ring-down time. To separate quantitatively the relative intensities of different lines in an $^1$H MAS spectrum, the signals of the spinning sidebands were added to the main signal.

RESULTS AND DISCUSSIONS

OH groups in ZSM-5 synthesized with TPA

The zeolites of ZSM-5 type synthesized with TPA and calcined at 600 °C have an extremely high concentration of non-acidic hydroxyl groups created by the decomposition of the template (ref. 7). Deeper insight into the origin of these silanol groups could be obtained by ammonium exchange, acid treatment and steaming of the calcined zeolite.

![Fig. 1. $^1$H MAS NMR spectra of ZSM-5 synthesized with TPA after calcination, ammonium exchange, acid treatment and steaming.](image-url)
Fig. 1 shows the $^1$H MAS NMR spectra of a zeolite with Si/Al = 90 and a crystallite diameter of 0.025 μm calcined for 10 hrs. at 600 °C. The four samples were treated at 400 °C in the shallow-bed and sealed. The first spectrum in Fig. 1 contains only the signal of silanol groups. From the intensity it follows a value of 2 OH groups per unit cell. While ammonium exchange does not affect the concentration of SiOH groups, treatment with 0.1n HCl doubles their concentration and shifts the $^1$H NMR line from 1.4 ppm to 2.2 ppm.

In accordance with the results of Lippmaa et al. (ref. 8) the increased chemical shift points to a reduced OH-OH distance as in geminal (≥Si(OH)$_2$) or vicinal (≡Si-OH HO-Si≡) silanol groups. From the absence of the ≥Si(OH)$_2$ signal at c. -90 ppm in the $^{29}$Si CP MAS NMR spectrum of this sample the existence of geminal silanol groups can be ruled out and the following reaction scheme of defect sites in as-synthesized TPA ZSM-5 is suggested:

\[
\begin{array}{c}
\text{Na TPA} \\
\text{Na H} \\
\text{Si Si} \\
\end{array}
\quad \text{calcination} \quad \begin{array}{c}
\text{Na H} \\
\text{Si Si} \\
\end{array}
\quad \text{acid treatm.} \quad \begin{array}{c}
\text{H H} \\
\text{Si Si} \\
\end{array}
\quad \text{steam} \\
\begin{array}{c}
\text{Si-O-Si} \\
\end{array}
\]

Hydroxyl groups and non-framework aluminium in dealuminated zeolites

We denote an OH group chemically bonded to a non-framework aluminium as AlOH. The dissociation of a water molecule on a Lewis site can create an AlOH group and a bridging OH group similar to the bridging OH groups in H-type zeolites. Hydroxyl groups on framework defects including the external surface of the crystallite are denoted as SiOH.

Scherzer (ref. 9) reviewed the infrared bands due to OH groups caused by the dealumination process on zeolite Y. Two additional bands appear at about 3700 cm$^{-1}$ and at about 3600 cm$^{-1}$. Lohse and Hunger (ref. 10) carried out a combined IR and $^1$H MAS NMR study of dealuminated zeolites Y and discovered an NMR signal at 2.6 ppm denoted as line (e) in addition to the lines corresponding to SiOH and bridging OH groups. In the $^1$H MAS spectra of zeolites we were able to separate the following signals (c.f. ref. 4):

- Line (a) at 1.8 - 2.3 ppm is caused by SiOH groups.
- Line (b) at 3.8 - 4.4 ppm is assigned to bridging OH groups.
- Line (c) at c. 5.2 ppm is assigned to bridging OH in 6-membered rings.
- Line (d) at 6.5 - 7.0 ppm is due to residual ammonium ions.
- Line (e) at 2.6 - 3.6 ppm represents AlOH groups.
- Line (f) at 6.5 ppm can be found after water adsorption on Lewis sites.

In the present paper we have studied samples of zeolite Y, mordenite, and H-ZSM-5 hydrothermally treated and with or without acid leaching. From $^1$H and $^{27}$Al NMR intensity measurements the total amount of $^1$H and the observable
amount of $^{27}$Al nuclei in the samples could be determined. The MAS spectra allow a line separation according to the contribution of the different hydroxyl groups and aluminium species.

The parent zeolites Na-Y, Na-mordenite, and H-ZSM-5 were produced by VEB Chemiekombinat Bitterfeld, GDR. The Si/Al ratio of these zeolites was 2.4, 5.8, and 15, respectively. ZSM-5 was prepared by template-free synthesis.Dealumination procedures were: for H-ZSM-5 hydrothermal treatment at 500 °C for 1.5, 3, 6, or 24 hrs. and acid leaching with 1n HNO$_3$ for one portion of the zeolites; for zeolites Y hydrothermal treatment at 770 °C for 3 hrs. and leaching with 0.001n HCl; for mordenites heating for 3 hrs. at 600 °C in air and leaching with 6n HNO$_3$ if denoted as Ex. The total Si/Al ratio was determined by chemical analysis.

![Fig. 2. $^1$H MAS NMR spectra of dealuminated zeolites spun at 3 kHz.](image)

![Fig. 3. $^{27}$Al MAS NMR spectra of dealuminated zeolites spun at 6 kHz.](image)
TABLE 1
Concentration of aluminium species and hydroxyl groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number per 24 framework tetrahedra</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
<th>(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total framew.</td>
<td>n.oct.</td>
<td>n.tetr.</td>
<td>total SiOH bridging</td>
<td>AlOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5/1.5</td>
<td>1.36</td>
<td>0.48</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.22</td>
<td>0.13</td>
<td>0.55</td>
<td>0.54</td>
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</tr>
<tr>
<td>ZSM-5/1.5 Ex</td>
<td>1.19</td>
<td>0.42</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ZSM-5/3</td>
<td>1.36</td>
<td>0.36</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.20</td>
<td>0.14</td>
<td>0.40</td>
<td>0.66</td>
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<tr>
<td>ZSM-5/3 Ex</td>
<td>0.94</td>
<td>0.33</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.10</td>
<td>0.39</td>
<td>0.35</td>
<td>0.36</td>
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<tr>
<td>ZSM-5/6</td>
<td>1.36</td>
<td>0.32</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.15</td>
<td>0.15</td>
<td>0.33</td>
<td>0.67</td>
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<td>ZSM-5/6 Ex</td>
<td>0.73</td>
<td>0.28</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.08</td>
<td>0.46</td>
<td>0.31</td>
<td>0.31</td>
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<tr>
<td>ZSM-5/24</td>
<td>1.36</td>
<td>0.19</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.12</td>
<td>0.18</td>
<td>0.25</td>
<td>0.69</td>
<td></td>
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<tr>
<td>ZSM-5/24 Ex</td>
<td>0.53</td>
<td>0.18</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>0.72</td>
<td>0.35</td>
<td>0.17</td>
<td>0.20</td>
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<tr>
<td>Y</td>
<td>7.06</td>
<td>0.89</td>
<td>0.25</td>
<td>0.8</td>
<td>2.15</td>
<td>0.85</td>
<td>0.74</td>
<td>0.56</td>
<td></td>
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<tr>
<td>Y Ex</td>
<td>1.75</td>
<td>0.77</td>
<td>0.28</td>
<td>\leq0.1</td>
<td>2.18</td>
<td>1.12</td>
<td>0.79</td>
<td>0.27</td>
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<tr>
<td>Mordenite</td>
<td>3.53</td>
<td>1.04</td>
<td>0.33</td>
<td>1.0</td>
<td>2.44</td>
<td>0.31</td>
<td>1.05</td>
<td>1.08</td>
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<tr>
<td>Mordenite Ex</td>
<td>0.60</td>
<td>0.55</td>
<td>\leq0.05</td>
<td>\leq0.1</td>
<td>1.55</td>
<td>0.94</td>
<td>0.42</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>

Values for the concentration of OH groups and aluminium in all samples under study are given in Tab. 1. The experimental error for all values is 0.1 species per 24 framework T-atoms. The unit "Number of species per 24 framework T-atoms" corresponds to the unit "Number of species per channel intersection" in the case of ZSM-5 and to "Number per cavity" for zeolites Y. The columns in Fig. 1 can be explained by:

1. Total concentration of Al determined by chemical analysis.
2. Framework Al determined by the intensity of the narrow line at 60 ppm.
3. Octahedrally coordinated non-framework Al giving a narrow line at 0 ppm.
4. Tetrahedral non-framework Al giving a broad line at about 50 ppm.
5. Total conc. of protons determined from the maximum amplitude of the FID.
6. SiOH groups obtained from the intensity of line (a) in the spectrum.
7. Intensity of line (b) which is due to bridging OH groups.
8. Intensity of line (e) which is due to ALOH groups.

$^{27}$Al spectra consist in general of three signals corresponding to three kinds of aluminium. If the sum of intensities of these lines gives a value for the concentration which is less than the total concentration of aluminium determined by chemical analysis, the deficit is caused by the presence of the so-called "NMR invisible" aluminium. Framework aluminium gives a relatively narrow line at c. 60 ppm. Octahedrally coordinated non-framework aluminium
resonates at about 0 ppm referred to the aluminium hexaaquo complex. The third kind of aluminium is described in ref. 4 as tetrahedrally coordinated non-framework aluminium, which gives a broad line at c. 50 ppm.

The results for the zeolites Y and mordenites collected in Tab. 1 show in accordance with further samples studied in ref. 11 a significant difference: In dealuminated mordenites all aluminium is visible in the NMR spectrum, which means that all non-framework aluminium is located in sites of a cubic symmetry. However, in zeolites ZSM-5 and Y the whole or the majority of non-framework aluminium is present on sites of lower symmetry and consequently cannot be observed by NMR.

Tetrahedrally coordinated non-framework aluminium which gives rise to a relatively broad line at c. 50 ppm can be observed in dealuminated samples of zeolite Y and mordenite. Klinowski et al. (ref. 12) measured a broad line on this position in dealuminated samples but did not assign it. In ref. 4 we concluded that the line at 50 ppm is caused by tetrahedrally coordinated non-framework aluminium and that a quadrupole correction of 10 - 30 ppm should be added to this value. The range of tetrahedral Al-O-coordination is 40-80 ppm (ref. 13). The assignment of this line to tetrahedrally coordinated non-framework aluminium was supported by Bosáček und Mastikhin (ref. 14) and by Samoson et al. (ref. 15). Parise et al. (ref. 16) gave evidence for 4-coordinated Al species in the center of the sodalite unit in dealuminated zeolite Y by neutron powder diffraction techniques. Gilson et al. (ref. 17) assigned a broad line at c. 30 ppm to five-coordinated non-framework aluminium. However, the linewidth of spectra given in ref. 17 is so great that the quadrupole correction must be applied. This amounts to 10 - 30 ppm and therefore, the true chemical shift of the line is 40 - 60 ppm, which is characteristic of 4-coordination.

All non-framework aluminium can be observed by $^{27}$Al MAS NMR directly, i.e. through the signals occurring at 0 and 50 ppm, only in dealuminated mordenites. For dealuminated zeolites ZSM-5 and Y all or the majority of the non-framework Al exists in non-cubic symmetry, which is presumably due to the condensation of non-framework aluminium species. Since these species are "NMR invisible" only their amount (the NMR deficit in Tab. 1) but not their nature can be studied. Because our spectra of ZSM-5 spun at 6 kHz do not show signals due to non-framework aluminium we cannot confirm the finding of tetrahedral non-framework aluminium in dealuminated zeolite ZSM-5 (ref. 15).

Now the question arises about the nature of tetrahedrally coordinated non-framework aluminium species.

We explain our two lines of non-framework aluminium at 0 and 50 ppm by two types of isolated non-framework aluminium complexes, which are already discussed in the review paper of Scherzer (ref. 9): $\text{Al(H}_2\text{O)}_6^{3+}$ and $\text{AlOOH}$. The
former is 6-coordinated and the latter may be 4-coordinated. We propose that the AlOOH molecule is associated with two framework oxygens giving a tetrahedral Al-O-coordination and that the proton weakly interacts with a further framework oxygen.

AlOOH is still present in dehydrated samples. The concentration of OH groups connected with non-framework aluminium measured by $^1$H MAS NMR are in reasonable agreement with the values for the concentration of tetrahedrally coordinated non-framework aluminium (Al$^{n.tetr.}$) for zeolites Y and mordenites. This supports the proposal of AlOOH as non-framework species for these zeolites.

Tab. 1 shows that the concentration of SiOH groups does not change upon hydrothermal dealumination. It remains constant at 0.2±0.1 OH groups per 24 framework T-atoms for the non-leached samples (one exception is sample DY). This value is too large to be attributed to terminal OH groups on the external surface of the crystallites (ref. 7). Structural defects which can be healed by thermal treatment must also be excluded. Only the presence of an amorphous aluminosilicate and/or non-healing crystal imperfections can explain this constant concentration of silanol groups.

Acid leaching increases the number of SiOH groups. One explanation of this effect is that non-cubic extra framework aluminium is bonded to oxygen at framework defects. Then new SiOH groups are created by the removal of non-framework Al.

Concerning the concentration of bridging OH groups we found that before and after dealumination of the hydrogen zeolites the number of bridging OH groups is equal to the number of framework Al atoms.

Lewis sites can be detected via their interaction with a small amount of water molecules. The signal of isolated water molecules in the adsorbents without Lewis sites appears at 1.1 ppm in Aerosil (ref. 8) and at 1.5 ppm for silicalite. Bulk water molecules have a chemical shift of 4.8 ppm. Fig. 4 (a) shows the $^1$H MAS NMR spectrum of a template-free synthesized H-ZSM-5, which was calcined for 2 hrs. at 500 °C and extracted by 1n HNO$_3$ at 100 °C for 2 hrs. The concentrations of both the bridging OH groups and the framework aluminium atoms correspond to one species per channel intersection (c.i.). The adsorption of 0.15 water molecules per c.i. effects besides a weak increase of the line of isolated water molecules at 1.5 ppm the appearence of a narrow line (f) at 6.5 ppm (see Fig. 4 (b)). Up to 0.45 H$_2$O/c.i. the intensity of line (f) does not change. The intensity of the line at 1.5 ppm however increases by a factor of up to 3 and the signal of bridging OH groups decreases due to the fast proton exchange between these hydroxyl groups and adsorbed water molecules (see Fig. 4 (c),(d)). In fully hydrated zeolites finally all lines merge into a single narrow line caused by a fast proton
exchange between proton-bearing species. It is suggested that the intensity of the line (f) occurring at weak hydration may be taken as a measure for the concentration of Lewis sites.

\[ \text{Intensity of line (f)} \]

- **unloaded**
- **0.15 H}_2O per c.i.**
- **0.3 H}_2O per c.i.**
- **0.45 H}_2O per c.i.**

Fig. 4. \(^1H\) MAS NMR spectra of calcined and acid leached H-ZSM-5 after loading with different amounts of water.

**Zeolites SABO-5**

\(^{11}B\) MAS NMR measurements were conducted at a Larmor frequency of 96 MHz and a spinning rate of c. 4 kHz. The chemical shift is referred to BF\(_3\).OEt\(_2\). Three spectra are presented in Fig. 5. The spectrum (a) of RASOTHERM glass is plotted for comparison and shows the superposition of a single line (at c. -3 ppm) and typical quadrupolar pattern due to the tetrahedrally and the trigonally oxygen coordinated boron atoms, respectively. Spectrum (b) has lower signal-to-noise-ratio because of its small concentration of boron. We measured this type of spectra which is similar to the spectrum (a) for partially rehydrated samples. Scholle and Veeman (ref. 18) first showed for boron substituted ZSM-5 the superposition of a single line and typical quadrupolar pattern. Spectrum (c) contains a single narrow line at -3.1 ppm. Fully rehydrated samples show only this narrow line. The full-width-at-half-maximum (FWHM) is 0.6 ppm and much less than for for the single lines in spectra (a) and (b). The maximum difference between the values of the chemical shift for the single lines in all spectra is only 0.8 ppm. Thus, the FWHM seems to be more significant for boron incorporation than the chemical shift which was used by Gabelica et al. (ref. 5). The tetrahedral oxygen coordination in the zeolite framework gives relatively narrow lines for \(^{11}B\) at T-positions due to the relatively small value of the electric quadrupole moment of \(^{11}B\).

Measurements of the intensity of the narrow line at -3.1 ppm for the as-synthesized SABO and for the zeolite after calcination, ammonium exchange, and ammoniation gave the following important result: Only for samples with a content of more than 0.5 boron atoms per c.i. is the loss of boron in the framework during the above mentioned procedure small. On the samples with a
lower concentration (after synthesis) the majority of boron is washed out during the treatment. Thus, samples with a boron content comparable with the aluminium content (Si/Al=30 - 40) show a relatively stable boron incorporation (for acidity, catalytic activity and shape selectivity see ref. 19).

Fig. 5. $^{11}$B MAS NMR spectra of RASCTHERM glass (a), of SABO with 0.4 boron atoms per c.i. (b), and of SABO with 0.8 boron atoms per c.i. (c).

Zeolites SAPO-5

Multinuclear MAS NMR studies were performed on zeolites of SAPO-5 type synthesized with 20% SiO₂. Fig. 6 shows the $^1$H spectrum of the activated sample which consists of three well resolved lines. Loading with NC₅D₅ quenches the lines at 3.9 and 4.9 ppm and gives a new line at 16.5 ppm due to the pyridinium ion. Thus, the lines at 3.9 and 4.9 ppm must be assigned to acidic hydroxyl groups, whereas the lines at c. 1.5 ppm represent non-acidic OH groups. A spectrum of a zeolite AlPO-5 shows only lines at c. 1.5 ppm.

Fig. 6. $^1$H MAS NMR spectrum of SAPO-5. * denotes spinning side bands. The total intensity is c. 0.5 OH groups per c.i.

We assign the lines at 3.9 and 4.9 ppm to bridging Si-O-Al groups. This parallels the high frequency band (≈3627 cm⁻¹) assigned to bridging hydroxyls
pointing towards the main channel, and the low frequency band ( \( \approx 3510 \text{ cm}^{-1} \)) assigned to hydroxyls in the sex-membered ring in an IR study by Lercher et al. (ref. 20). The difference of 1 ppm between the two lines is the result of an additional electrostatic interaction of the proton in the six-membered ring with the nearest oxygen atoms. Comparing with zeolites H-Y, the 3.9 and 4.9 ppm lines are the lines (b) and (c), respectively.

Using Sanderson's concept of intermediate electronegativity Jacobs and Mortier (ref. 21) related the acid strength of bridging OH to the compound composition. The average electronegativity of AlPO\(_4\) compounds is intermediate between those of HAlSiO\(_4\) and SiO\(_2\) (ref. 22). We therefore expect to find the chemical shift of the large channel bridging OH in SAPO-5 between the values of bridging hydroxyl groups in H-X (3.8 ppm) and H-ZSM-5 (4.3 ppm, c.f. ref. 4).

The total intensity of bridging OH groups is c. 0.4 OH per c.i. That means, that only 0.4 silicon atoms per c.i. (1.6 Si/u.c.) are incorporated in the framework (20% SiO\(_2\) in the synthesis).

Further information about the incorporation of silicon into the zeolite framework gives the \(^{29}\text{Si}\) spectrum. Fig. 7 (a) shows two lines at -92 and -112 ppm. The line at -92 ppm we assign to silicon 4-coordinated with O-Al (c.f. ref. 23). The line at -112 ppm must be explained with a portion of SiO\(_2\) in the sample. The single line at -92 ppm appears if we use cross polarization (CP). This is due to the fact that bridging OH groups are in the neighbourhood of the silicon incorporated in the framework on P-sites. The spectra show no evidence for the incorporation of silicon pairs for Al+P.

The aluminium spectra show two lines: The 38 ppm line must be ascribed to aluminium tetrahedrally OP-coordinated. The line at -12 ppm is due to 6-coordinated non-framework aluminium. The increase of this line in the cross polarization spectrum confirms the assumption, that it is due to Al\(_2\)(OH\(_2\))\(_2\) complexes which arise in a non-ideal synthesis.

The asymmetry of the 38 ppm line in the \(^{27}\text{Al}\) spectrum may be caused by second order quadrupole interaction. However, in the \(^{31}\text{P}\) spectrum the asymmetry must be explained by different positions of phosphorus in the framework. Further work is in progress to characterize zeolite of SAPO type by multi-nuclear MAS NMR (see also ref. 24).

ACKNOWLEDGEMENT

We wish to thank Dr. E. Jahn (Berlin) for providing the zeolites SAPO-5, Dr. W. Reschetilowski and Dr. B. Unger (Merseburg) for the zeolites SABO-5, Dr. H.-G. Jerschkewitz and Dr. U. Lohse (Berlin) for the dealuminated zeolites, and Dr. J. Klinowski (Cambridge) for helpful remarks.
Fig. 7. MAS NMR spectra of the non-activated zeolite SAPO-5, (a) $^{29}$Si, (b) $^{29}$Si with cross polarization, (c) $^{31}$P, (d) $^{27}$Al, (e) $^{27}$Al with CP.

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