The hydrolysis of divalent cations in alkaline earth cation-exchanged zeolite Y is studied by proton magic-angle-spinning (1H MAS) NMR. Ca2+ and Mg2+ dissociate about one water molecule per cation giving rise to a Brønsted proton and a non-acidic MOH+ cation (M=Ca or Mg); two 1H MAS NMR signals appear in the spectra. The chemical shift of the bridging OH group is 4.0±0.2 ppm while the signal of the metal-bound OH groups lies between -0.5 and 3.0 ppm. The concentration of OH groups decreases with increasing temperature of activation. As a result of the so-called Plank mechanism the samples contain less than 0.1 bridging hydroxyl group per cavity after activation at 400°C.

1. Introduction

Plank [1] 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" can be represented as follows [2-5]:

\[
\text{M}^{2+} + \text{H}_{2}\text{O} \rightarrow \text{H}^+ + \text{MOH}^+.
\]

Numerous infrared studies of zeolite Y containing Ca2+ and Mg2+ and a small amount of adsorbed water have reported [2-9] five hydroxyl stretching vibrations at about 3740, 3690, 3650, 3600 and 3540 cm\(^{-1}\). The band near 3740 cm\(^{-1}\) represents silica-type hydroxyl groups on framework defects and on the external surface of the crystallites. The 3650 and the 3540 cm\(^{-1}\) bands were attributed to bridging OH groups in the neighbourhood of framework aluminium atoms on \(\text{O}_1\) and \(\text{O}_2\) positions, respectively. Uytterhoeven et al. [8] and Ward [9] observed in zeolite Ca-Y a band at \(\approx 3600 \text{ cm}^{-1}\), which increases significantly after readsoption of water. This band does not react with pyridine and was attributed to CaOH+ groups [8]. In samples exchanged with various cations except Ca2+ Ward [4], Hall and co-workers [5] and Angell and Schaffer [10] observed a band at \(\approx 3690 \text{ cm}^{-1}\). This is generally attributed to metal OH groups similar to AlOH in alumina. The adsorption of ammonia resulted in a decrease in intensity of the 3650 and 3540 cm\(^{-1}\) bands, but not the 3690 cm\(^{-1}\) band [8].

The catalytic significance of hydroxyl species formed by the dissociation of water at divalent cations was shown by cracking [1,11] and alkylation [12]. The increase in activity on readdiation 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 [13] in alkaline earth cation zeolites. The aim of the present work is to establish a quantitative description of Plank's mechanism using 1H MAS NMR.
2. Experimental

Zeolite Na–Y (Si/Al = 2.6) purchased from VEB Chemiekombinat Bitterfeld was exchanged at 343 K using an aqueous solution of 0.1 M Ca(NO₃)₂ or Mg(NO₃)₂ to give a degree of exchange of 83%, i.e. 2.77 divalent cations per cavity. After the exchange the zeolite was washed and dried at 100°C. For activation the zeolite batches were heated in a glass tube with 6 mm inner diameter and 10 mm height of zeolite under vacuum at a heating rate of 10 K/h. After keeping the samples for 2 h at 400°C they were evacuated to a pressure below 0.01 Pa for 20 h. One portion of the sample was partially rehydrated at room temperature with doubly distilled water and, if stated, reactivated (RA) for 24 h under vacuum at 200, 300 or 400°C. Some samples were activated after partial rehydration, loaded with fully deuterated pyridine and then sealed.

NMR measurements were carried out on a Bruker MSL-300 spectrometer. Sealed samples were spun in a home-made MAS probe at 3 kHz. Using external standards, the accuracy of the chemical shifts is given to ±0.2 ppm, the accuracy of concentrations is ±10%.

3. Results and discussion

The spectrum of the activated zeolite MgNa-Y (fig. 1A) contains a line due to silanol groups at ≈ 1.6 ppm and a weak shoulder at 4.0 ppm. After loading with 0.5 H₂O molecules per cavity (H₂O/c) an additional line at ≈ 0 ppm appears, and a separate signal due to bridging OH groups at 4.0 ppm (figs. 1B and 1C for 0.5 and 1.0 H₂O/c, respectively). The line at ≈ 0 ppm has weak spinning sidebands in comparison to those of bridging OH groups. As shown in table 1, the intensity of the latter signal increases simultaneously with that of the bridging OH groups. As shown in table 1, the intensity of the latter signal increases simultaneously with that of the bridging OH groups. As shown in fig. 1D is a hint 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. A reactivation of the sample at 200°C removes the broad line and in fig. 1E a spectrum similar to that in fig. 1C (1.0 H₂O/c) can be observed. Fig. 1F 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. As is known from studies on zeolites H–Y [14], the high acid strength of bridging OH groups protonates adsorbed pyridine molecules and gives rise to a line at 15 ppm. The line at ≈ 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.

Zeolite CaNa-Y shows, in comparison with MgNa-Y, a similar behaviour for the bridging OH...
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:</th>
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<tbody>
<tr>
<td></td>
<td>$\approx 0$ ppm</td>
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<tr>
<td>MgNa-Y</td>
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<tr>
<td>MgNa-Y, 0.5 H$_2$O/c</td>
<td>0.8</td>
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<tr>
<td>MgNa-Y, 1.6 H$_2$O/c</td>
<td>0.8</td>
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<tr>
<td>MgNa-Y, 2.5 H$_2$O/c</td>
<td>1.8</td>
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<tr>
<td>MgNa-Y, 2.5 H$_2$O/c, RA 200°C</td>
<td>0.8</td>
</tr>
<tr>
<td>MgNa-Y, 2.5 H$_2$O/c, RA 300°C</td>
<td>0.3</td>
</tr>
<tr>
<td>MgNa-Y, 2.5 H$_2$O/c, RA 400°C</td>
<td>0.2</td>
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<tr>
<td>CaNa-Y</td>
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<tr>
<td>CaNa-Y, 0.4 H$_2$O/c</td>
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<tr>
<td>CaNa-Y, 1.0 H$_2$O/c</td>
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<tr>
<td>CaNa-Y, 2.0 H$_2$O/c</td>
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<tr>
<td>CaNa-Y, 2.0 H$_2$O/c, RA 200°C</td>
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<td>CaNa-Y, 2.0 H$_2$O/c, RA 300°C</td>
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<td>CaNa-Y, 2.0 H$_2$O/c, RA 400°C</td>
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groups but a different behaviour for OH groups associated with the metal. The spectrum of the activated zeolite CaNa-Y (fig. 2A) consists of only one line due to silanol groups at 1.6 ppm appears, and a 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. 2B). 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 (figs. 2C and 2D). 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. 2E). Fig. 2F 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 concerning the assignment of the different metal OH groups giving rise to two signals in the $^1$H MAS NMR spectra paralleling the stretching vibrations at 3600 and 3690 cm$^{-1}$ in the infrared spectra. Costenoble et al. [15,16] 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 S II, 2.28–2.68 cations at site S I' and 0.2 cations at site S I (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 non-framework oxygen species could also be found at S II' positions. The number of those oxygen species equals the number of divalent cations at S I' positions [15]. They observed S I'–S II' distances of 0.238–0.245 nm in good agreement with the Ca–O bond length of 0.239 nm [16]. This suggests the existence of CaOH$^+$ groups in the sodalite cages.

Yesinowski et al. [17] gave an empirical relation for the dependence of the isotropic chemical shift of hydroxyl protons on the oxygen–oxygen (OH...O) distances of hydrogen bonds in hydroxyapatites. According to this, the shift of the line from 0.5 to 2.8 ppm can be explained by 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 as being due to 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).

The spectra of zeolites MgNa–Y and CaNa–Y partially rehydrated and then reactivated at 200, 300 and 400°C are shown in figs. 1, 2E, 2G and 2H. Table 1 demonstrates that the number of metal OH groups
Fig. 2. $^1$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) loaded with 1.0 H$_2$O/c; (D) loaded with 2.0 H$_2$O/c; (E) loaded with 2.0 H$_2$O/c, reactivated at 200°C; (F) loaded with 2.0 H$_2$O/c, reactivated at 200°C and loaded with two molecules pyridine per cavity; (G) loaded with 2.0 H$_2$O/c, reactivated at 300°C; (H) loaded with 2.0 H$_2$O/c, reactivated at 400°C. Asterisks denote spinning sidebands.

Fig. 3. Concentration of bridging OH groups in zeolites MgNa-Y (●) and CaNa-Y (○) as a function of the reactivation temperature.

Acknowledgement

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References