Thermal stability of hydroxy groups in dealuminated mordenites

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Results obtained by proton magnetic resonance and derivatographic measurements permitted the following conclusions regarding the thermal stability of OH groups in the framework of dealuminated mordenites:
(1) after vacuum pretreatment at room temperature, the adsorbed water molecules are removed. OH groups exist either in completely filled OH nests at the sites of aluminium vacancies, or as structural and terminal OH groups;
(2) the thermal stability of the OH nests is low, for after pretreatment at about 500 K, such nests could be detected neither with n.m.r., nor with derivatographic methods.

Keywords: Derivatography, nuclear magnetic resonance; dealuminated mordenites; OH groups; OH nests

INTRODUCTION
Aluminium ions removed from the zeolite framework leave behind a zeolite with a defect structure. It is assumed that an aluminium vacancy can be stabilized by the formation of hydroxylated nests or new $\equiv \text{Si}-\text{O}-\text{Si}$ linkages, depending on the dealumination procedure applied. From the results of i.r. studies the occurrence of both $\equiv \text{Si}^\text{OH}$ and $\equiv \text{Si}^\text{O-Si}$ bonds at former sites of aluminium in the framework can be substantiated.

It is generally accepted that dealumination is accompanied by an increase of acidity, though a detailed explanation of this is at present unknown. The proton magnetic resonance method allows determination of the absolute number of OH groups and may yield valuable information concerning their local arrangement.

For study of the thermal stability of zeolitic OH groups, thermal analysis is the most widely used method; by this means the dehydroxylation process can be followed quantitatively.

With a combination of the two methods, i.e. n.m.r. spectroscopy and derivatography, more detailed information can be obtained about the properties of OH groups in zeolitic structures.

This paper deals with experimental results of both proton magnetic resonance and derivatographic measurements concerning the thermal stability of OH groups in mordenites dealuminated with phosgene.

EXPERIMENTAL
Dealuminated synthetic mordenites were used in the experiments. The starting material were Na-mordenite and H-mordenite originating from the Norton Co. After dealumination with phosgene at selected temperatures, the samples were washed free of Cl$^-$ ions, dried and analysed. The aluminium contents of the samples are listed in Table 1.

A Derivatograph-Q instrument was used for the derivatographic measurements, which were carried out in the temperature range 298–1273 K.

Details of the proton magnetic resonance measurements can be found in ref. 16.

RESULTS
Figure 1 shows the t.g. and d.t.g. curves of untreated Na-mordenite (no. 1), H-mordenite (no. 2) and dealuminated mordenite (no. 3).

For sample no. 2, two weight loss processes can be observed. The first process reaches its maximum at about 370 K, whereas the second occurs at higher temperatures.

Dehydroxylation of dealuminated mordenite starts at lower temperature, as can be seen by comparing the t.g. and d.t.g. curves of Figure 1b and c. In the latter case there is no weight loss at 800 K, in contrast with H-mordenites. This behaviour is characteristic for de-aluminated mordenites, as observed first by Beyer.

Proton magnetic resonance spectra of dealuminated mordenite (no. 4), measured at a temperature of 120 K using a resonance frequency of 90 MHz, are shown in Figure 2. The peak doublet which gives rise to the
Table 2. Proton concentration in the dealuminated H-mordenite specimen no. 4 measured by n.m.r. Except the specimen denoted by an asterisk (293*) all other samples were evacuated for 24 h at the pretreatment temperature shown in the first column. For comparison the results of t.g. measurements (performed under normal pressure) are collected in the last column.

<table>
<thead>
<tr>
<th>Pretreatment temperature</th>
<th>Proton conc.</th>
<th>Proton per Al vacancy</th>
<th>Water content (mmol g⁻¹) n.m.r.</th>
<th>t.g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>293*</td>
<td>16.7</td>
<td>8.3</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>6.3 ± 0.3</td>
<td>4.3 ± 0.3</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>5.5 ± 0.3</td>
<td>3.9 ± 0.3</td>
<td>2.7</td>
<td>8.8</td>
</tr>
<tr>
<td>373</td>
<td>4.2 ± 0.3</td>
<td>2.3 ± 0.3</td>
<td>2.1</td>
<td>6.2</td>
</tr>
<tr>
<td>428</td>
<td>3.7 ± 0.3</td>
<td>1.6 ± 0.3</td>
<td>1.8</td>
<td>3.6</td>
</tr>
<tr>
<td>473</td>
<td>2.7 ± 0.3</td>
<td>0.4 ± 0.3</td>
<td>1.3</td>
<td>2.6</td>
</tr>
<tr>
<td>523</td>
<td>2.7 ± 0.3</td>
<td>0.4 ± 0.3</td>
<td>1.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Figure 1. T.g. (- - -) and d.t.g. (---) curves of (a) Na-mordenite, (b) H-mordenite and (c) dealuminated mordenite.

shoulders (arrows) in curve 'a' is due to adsorbed water molecules firmly bound to the framework at 120 K. Its intensity decreases strongly after evacuation (= 10⁻² Pa) at room temperature (curve 'b'), and it disappears completely at 323 K (curve 'c'). This behaviour complements the finding of Bosák et al. in that dealuminated Y-zeolites become completely dehydrated following evacuation for 12 h at 333 K.

Table 2 contains values of the concentrations of protons in dealuminated mordenite (no. 4) following treatments at increasing temperatures. Pretreatment involved evacuation for 24 h at temperatures between 293 and 523 K (first column), except the sample marked with an asterisk. The values in the second column were derived from the second moments (M₂) of the n.m.r. signals.

Table 3 reflects the effect of dealumination on the proton concentration in the case of Na-mordenites dealuminated to various extents: the second column gives the second moments of the n.m.r. signals (M₂), and the last one the computed proton concentrations. Measurements of M₂ at room temperature and the temperature of liquid nitrogen (77 K) resulted in the same values. An additional experiment with Hahn's echo showed that in sample no. 1, half of the protons can be attributed to bridging OH groups, like the structural OH groups in decationated zeolites, characterized by a strong proton-aluminium dipole-dipole interaction. The other half of the protons in sample no. 1 (∼0.4 mmol g⁻¹) can be assigned to terminal OH groups and to OH groups at lattice defects. The values $M₂ = 0.8 \cdot 10^{-8} T^2$ measured for sample nos. 5 and 6 are comparable with the value $M₂ = 1.0 \cdot 10^{-8} T^2$ measured for structural OH groups in dealuminated zeolites. If we subtract the concentration of non-structural OH groups (0.4 mmol g⁻¹) in the Na-mordenite sample no. 1 from the proton concentrations given in Table 3, and divide the difference by the aluminium content given in Table 1, we obtain the number of protons per lattice aluminium. The resulting values for sample nos. 5 and 6 are 0.92 and 0.74, respectively, and support the assumption that these protons are in structural OH groups, for which the value should be one. Only sample no. 7, the most strongly dealuminated Na-mordenite, contains significantly more than one proton per aluminium. Hence, there should be non-negligible number of protons due to lattice defects in this sample.
Table 3 Values for the second moment $M_2$ of the n.m.r. signals and proton concentration in Na-mordenites dealuminated to various extents. All samples were evacuated (--- 10^-2 Pa) at 673 K for 24 h

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_2$ x 10^-4 T²</th>
<th>Proton conc. (mmol g^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.42 ± 0.05</td>
<td>0.78 ± 0.08</td>
</tr>
<tr>
<td>5</td>
<td>0.82 ± 0.05</td>
<td>2.9 ± 0.3</td>
</tr>
<tr>
<td>6</td>
<td>0.74 ± 0.05</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>7</td>
<td>0.65 ± 0.05</td>
<td>2.5 ± 0.2</td>
</tr>
</tbody>
</table>

The proton concentration in sample no. 4 is given in Table 2 as a function of the pretreatment temperature. Sample no.4 was derived from the original Na-mordenite (sample no. 1) by decationization and dealumination. In order to find the proton concentration following dealumination, 0.4 mmol g^-1 must first be subtracted from the concentrations given in column 2 for the non-structural OH groups, followed by the concentration corresponding to one proton per aluminium, which takes account of the structural OH groups caused by decationization (2.0 mmol g^-1). The result divided by the concentration of aluminium vacancies in this sample (0.8 mmol g^-1, cf. Table 1) is shown in column 3, Table 2. We find about 4 OH groups per vacancy in the sample evacuated at room temperature, half of this value after vacuum pretreatment at 373 K and an insignificant amount of OH groups in OH nests after vacuum pretreatment at 473 K.

DISCUSSION

In the t.g. curve of the dealuminated mordenite (see Figure 1c) the weight loss processes relating to dehydration and dehydroxylation are not separated. It is therefore difficult to find out how many protons form an OH nest near to the aluminium ion removed. It is even more difficult to judge whether these OH nests exist at all in the zeolite after heat treatment at temperatures above 700 K, i.e. those generally used for the activation of zeolite catalysts.

In spite of various speculations concerning the origin, structures and features of the OH nests presumed to be formed in the dealumination process, structures exhibiting 4 OH groups/nest have never been observed in proton magnetic resonance experiments, although this is the best method of determining the absolute number and arrangement of OH groups in zeolites.

If the OH nests are built up from 4 OH groups formed in the dealumination process, they should be of low thermal stability and should decompose by dehydroxylation at relatively low temperatures. According to Beyer, the OH nests dehydroxylate at a temperature lower than 473 K. Water and new $\equiv$Si-O-Si$\equiv$ bonds are formed as a result of this process.

Though under quite different conditions (at 873 and 1473 K), Moulson and Roberts, studying the penetration of water in silica glass, found that the equilibrium

$$H_2O + \equiv$Si-O-Si$\equiv$ $\rightarrow$ $\equiv$Si-OH

lies well to the left, which again shows the limited stability of hydrated nests.

This view is supported by the silanation experiments of Barrer et al. as well. It was found that partially dealuminated, wetted and outgassed mordenites never reacted with SiH₄, as might have been expected on the basis of the nests having 4 OH groups.

$$\equiv$Si-OH + SiH₄ $\rightarrow$ $\equiv$Si-O-Si-O-Si$\equiv$ + H₂

The low ratio of 2.28 OH groups/nest found by monitoring the H₂ evolved strongly suggests that the hydrated nests have already reacted to give at least one new $\equiv$Si-O-Si$\equiv$ bond/nest and one molecule of water during the outgassing, which at 630 K is in agreement with our n.m.r. data.

As can be seen in Figure 3, the d.t.g. curve of the dealuminated mordenite sample no. 4 runs parallel to the temperature axis between about 570 and 1270 K, indicating a constant weight loss in this temperature range. This also follows from the t.g. curve, which decreases linearly between these temperatures. The temperature relating to the maximum of the d.t.g. curve of the dealuminated mordenite (=370 K) is smaller than that for Na-mordenite (400 K) or H-mordenite (390 K). From this result we conclude that the water is more loosely bound in dealuminated mordenite structures.

From the proton concentration data determined by n.m.r. measurements it was possible to determine the water content, including the OH groups (2 OH groups are equivalent to one water molecule), for sample no. 4. The data are shown in Figure 3. The agreement between

Figure 2 Proton magnetic resonance signals of a dealuminated mordenite (no. 4) measured at 120 K: (a) before evacuation at room temperature; (b) after an evacuation (--- 10^-2 Pa) for 24 h at room temperature; (c) after an evacuation (--- 10^-2 Pa) for 24 h at 323 K
the results of the derivatographic and n.m.r. investigations is quite good for the non-evacuated sample (filled circle in Figure 3).

From the line shapes of the n.m.r. signals in Figure 2 it follows that after evacuation ($\approx 10^{-2}$ Pa) for 24 h at room temperature the zeolite sample contains only negligible amounts of molecular water.

It is evident from Table 2 that the water contents of the evacuated samples, determined by n.m.r. (open circles in Figure 3), are lower than the water contents of the non-evacuated samples (filled circle and t.g. curve in Figure 3).

From the n.m.r. intensities due to aluminium vacancies (column 3 in Table 2) it must be concluded that each aluminium vacancy is filled with about 4 OH groups/OH nest at room temperature. Heat treatment above 373 K causes their destruction, and no OH nests exist above 473 K. Hence, on the basis of the n.m.r. measurements, the t.g. curve can be explained by the loss of adsorbed water and dehydration of OH nests up to a temperature of about 500 K. At about 500 K and above, water is released by the loss of structural and terminal OH groups. In other words, this means that no OH nests remain in the framework after heat treatment at 500 K.

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