NMR AND IR STUDIES OF ZEOLITES OF THE ERIONITE TYPE

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ABSTRACT

Infrared spectroscopy (IR) and proton, aluminium and silicon magic-angle-spinning nuclear magnetic resonance spectroscopy (1H, 27Al and 29Si MAS NMR) yield information about the location and concentration of Brønsted acid sites, the distribution of aluminium in the framework and the concentration of non-framework species in erionite. Most of the bridging OH groups are formed on the O(1) oxygens located in the double-six-ring between two cancrinite cages. Other OH groups are in the large cavity at O(5) or O(6) oxygens as well as in the cancrinite cages. The differences of the Si/Al-ratios determined by different methods were explained in term of thermal decomposition of a parasite phase.

INTRODUCTION

Among the zeolite catalysts used on a larger scale in industry, erionite is unique with respect to the smallest available pore diameter (elliptical pore opening: 0.36 x 0.52 nm). A bifunctional Pt/H-erionite is applied for formselective reforming where n-alkanes are selectively hydrocracked in the feed. A study on the nature and location of hydroxyl groups influenced by the lattice structure may contribute to a better understanding of this process.

Figure 1 shows a model of the erionite structure. The cancrinite cages are linked to hexagonal prisms and single six-membered rings. In contrast to faujasite there are six crystallographically different oxygens in the erionite structure:

- O(1) - connecting the six-rings of the hexagonal prism,
- O(2) - shared among the four-ring of the hexagonal prism and the six-ring of the cancrinite cage,
- O(3) - shared among the four-ring of the hexagonal prism and the four-ring of the cancrinite cage,
- O(4) - shared among the four- and six-rings of the cancrinite cage.
Fig. 1 Model of the erionite structure

O(5) – oxygen of the single six-ring connecting two cancrinite cages, and
O(6) – shared among the single six-ring and the four-ring of the cancrinite cage.

Information about the Si/Al ratio and the aluminium distribution on nonequivalent tetrahedral T-sites is available from $^{29}$Si MAS NMR spectra. Based on such results Lillerud (ref. 1) made the assumption of a preferred occupation of the $T_2$-sites (see Fig. 1) by aluminium. For the best fit between the measured and calculated spectra he found 0.17 Al/$T_1$ in comparison to 0.35... 0.45 Al/$T_2$. Taking into account that for erionite $T_1/T_2=2$ it can be expected that nearly the same number of bridging OH groups must be formed in the environment of aluminium at $T_1$ and $T_2$ positions.

EXPERIMENTAL
The ammonium-exchanged erionite was prepared by repeated ion exchange of synthetic NaK-erionite with NH$_4$NO$_3$ solution at 363 K. The parent zeolite (Si/Al=3, by the chemical analysis) was obtained from VEB Chemiekombinat Bitterfeld, G.D.R. NMR measurements were performed on a Bruker MSL-300 spectrometer at resonance fre-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al determined by $^{27}$Al MAS NMR</th>
<th>$^{29}$Si MAS NMR</th>
<th>cations per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.0</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>NaK-erionite</td>
<td>3.6</td>
<td>2.3</td>
<td>6.9</td>
</tr>
<tr>
<td>0.77NH$_4$-erionite</td>
<td>3.6</td>
<td>2.4</td>
<td>8.2</td>
</tr>
<tr>
<td>0.91NH$_4$-erionite</td>
<td>4.5</td>
<td>2.4</td>
<td>8.4</td>
</tr>
<tr>
<td>0.93NH$_4$-erionite</td>
<td>4.5</td>
<td>2.4</td>
<td>8.4</td>
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</table>
frequencies of 300, 78 and 59.6 MHz for $^1$H, $^{27}$Al and $^{29}$Si NMR, respectively. The experimental error of intensities was 10%. For $^1$H NMR measurements shallow-bed activation conditions were used in a glass tube of 5.5 mm diameter containing a 10 mm layer of zeolite. The temperature was increased with a rate of 10 K/h. After maintaining the samples for 24 h at the final temperature of 670 K they were sealed. $^{27}$Al and $^{29}$Si MAS NMR measurements were generally carried out on rehydrated samples.

The infrared spectra were recorded on a UR-20 spectrometer (VEB Carl-Zeiss-Jena). The samples (thickness: 5-12 mg/cm$^2$) were also activated in-situ at 670 K and $10^{-1}$ Pa for 30 min. To increase the transmission all samples were deuterated by repeated treatment with D$_2$O at 373 K.

RESULTS AND DISCUSSION

The synthesis of erionite is normally accompanied by the formation of other aluminosilicates (ref. 2). X-ray studies on the parent NaK-erionite have shown a contribution of zeolite P (ref. 3). Since the H-form of zeolite P is thermally unstable, a comparison of the $^{27}$Al NMR spectra of the fresh and 720 K calcined samples must indicate intensity changes of the line at 60 ppm assigned to tetrahedrally coordinated framework aluminium. This assumption is supported by the results shown in Table 2 (see columns 5 and 6). The Si/Al ratio of NaK-erionite before and after calcination remains constant and corresponds to the value obtained by wet chemical analysis. However, the calcined ammonium-exchanged erionites lost approximately 30% of their framework aluminium. Unlike NMR spectra, the framework vibration bands observed by infrared spectroscopy were not shifted, i.e. the Si/Al ratio of erionite was not changed. Both results can only be explained in terms of thermal decomposition of the zeolite P. The calculated amounts of zeolite P agree with the calculations based on NH$_3$-t.p.d. and H/D-isotopic exchange (ref. 3).

TABLE 2

Concentrations of different species /in $10^{19}$ per gramme/ in the erionite calculated from $^1$H and $^{27}$Al MAS NMR

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Chem. shift /ppm/</th>
<th>SiOH or AlOH</th>
<th>SiOHA l</th>
<th>residual NH$_4^+$</th>
<th>framework Al before/after calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.9-2.6</td>
<td>3.9</td>
<td>6.7</td>
<td>60$^1$</td>
</tr>
<tr>
<td>NaK-erionite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.37 H-erionite</td>
<td></td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>246</td>
</tr>
<tr>
<td>0.77 H-erionite</td>
<td></td>
<td>18</td>
<td>54</td>
<td>0</td>
<td>234</td>
</tr>
<tr>
<td>0.91 H-erionite</td>
<td></td>
<td>25</td>
<td>95</td>
<td>0</td>
<td>214</td>
</tr>
<tr>
<td>0.93 H-erionite</td>
<td></td>
<td>23</td>
<td>100</td>
<td>17</td>
<td>214</td>
</tr>
<tr>
<td>0.93 H-erionite2</td>
<td></td>
<td>28</td>
<td>105</td>
<td>56</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52</td>
<td>95</td>
<td>5</td>
<td>123</td>
</tr>
</tbody>
</table>

$^1$Chemical shift of $^{27}$Al MAS NMR.
$^2$Calcined at 720 K.
In zeolite structures, where each silicon has four nearest-neighbour silicon or aluminium atoms, the $^{29}\text{Si}$ NMR chemical shift falls into five ranges which can be correlated with the number of aluminium neighbours surrounding a given silicon (ref. 4):

- $\text{Si(4Al)}$: -80 to -89 ppm
- $\text{Si(3Al)}$: -88 to -97 ppm
- $\text{Si(2Al)}$: -94 to -103 ppm
- $\text{Si(1Al)}$: -98 to -107 ppm
- $\text{Si(0Al)}$: -103 to -114 ppm

The ion-exchanged erionites activated at 720 K for 2 h show a complex $^{29}\text{Si}$ MAS spectra (Fig. 2) for different reasons:

(i) superposition of signals from the erionite phase and phases of crystalline impurities mainly zeolite P,

(ii) different lines for different number $n$ ($n=0...4$) of aluminium atoms in the first silicon's coordination sphere $\text{Si(nAl)}$, and

(iii) different lines for $T_1$ and $T_2$, i.e. for $\text{Si(nAlT}_1)$ and $\text{Si(nAlT}_2)$ (ref. 5).

Unfortunately, for erionite the effect of the site inequivalence (5.3 ppm) is almost exactly the same as the effect of aluminium in the first coordination sphere (5.5 ppm) (ref. 5). Using a line fit, Lillerud (ref. 1) demonstrated a favourite occupation of $T_2$ positions for aluminium atoms in erionite. Nevertheless, the splitting procedure dividing the signal into two (or three) parts is very problematic. Our experiments prove the result of Lillerud (ref. 1) that aluminium atoms occupy preferably $T_2$ positions in NaK-erionite. In case of H-erionite no reliable information can be derived when we take into account a 10% error in measurement. The difference between the spectra of NaK- and H- erionite can be explained by thermal decomposition of zeolite P which contributes a broad unresolved $^{29}\text{Si}$ MAS NMR signal.

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![Fig. 2. $^{29}\text{Si}$ MAS NMR spectra of NaK- and 0.91 H-erionite.](image-url)
Information on the nature and location of hydroxyl groups is available from infrared spectroscopy. In the spectra of a deuterated 0.91 H-erionite activated at 670 K, bands remain at 2640, 2670, 2710 and 2760 cm\(^{-1}\) (Fig. 3a). The band at 2760 cm\(^{-1}\), also observed for ion-exchanged Y zeolites and silica, is assigned to terminal hydroxyl groups located on the external surface or on lattice defects. When the activated erionite is exposed to ammonia at 130 Pa and room temperature (Fig. 3b), the intensity of the band at 2670 cm\(^{-1}\) decreases, the shoulder at 2640 cm\(^{-1}\) vanishes completely, while the bands at 2710 and 2760 cm\(^{-1}\) remain as in the unloaded sample. To confirm the location of the hydroxyl groups, a H-erionite calcined in air was ion-exchanged with 0.1 M CsCl solution at room temperature. Comparing the spectra of H- and CsH-erionite deuterated (Fig. 3a and 3c) the shoulder at 2640 cm\(^{-1}\) is completely eliminated and the intensity of the band at 2670 cm\(^{-1}\) is drastically reduced.

It is known that the Cs\(^+\) ion is too large (d=0.338 nm) to enter the hexagonal prism and cancrinite cages through the six-ring windows (d=0.26 nm). Taking into account these results we can conclude that the bands at 2640 and 2670 cm\(^{-1}\) represent acidic bridging OH groups located in the large cavity (gmelinite cage). The similarity in structure between erionite and Y zeolite allows the assignment of the most intensive band at 2670 cm\(^{-1}\) to O(1)H groups. Hence the band at 2640 cm\(^{-1}\) represents perturbed acidic OH groups vibrating in 6-membered rings [compare ref. 6], i.e. they were formed, perhaps, on O(5) and/or O(6) oxygens in the large cavity. Furthermore, the 2710 cm\(^{-1}\) band should be assigned to hydroxyl groups in the cancrinite cage (O(2)H, O(3)H and/or O(4)H groups) inaccessible for large cations or hydrocarbons (ref. 7).

The \(^1\)H MAS NMR spectra of ammonium-exchanged erionites (Fig. 4) contain information about both the nature and the concentration of hydroxyl species (Table 1). In agreement with earlier studies on zeolites H-Y (ref. 8,9), mordenite and ZSM-5 (ref. 10), the following assignment is made: the line at 1.9 ppm is caused by non-acidic SiOH groups at the external surface or at lattice defects; the line at 2.6 ppm represents hydroxyl groups associated with non-framework aluminium; the line at 3.9 ppm is ascribed to acidic bridging OH groups and the line at 6.7 ppm is due to residual
amounts of ammonium ions.

The amount of SiOH and AlOH groups (Table 2, column 2) is a measure of the lattice defects formed by decomposition of the zeolite P and by dealumination. The intensity of the line at 3.9 ppm depends on the degree of ion exchange (Table 2). However, the intensity of the line was not changed in the range of ion exchange between 77 and 93 %, i.e. the OH species formed at higher values of ion exchange have a lower concentration. Indeed, the intensity of the band at 2970 cm⁻¹ in the IR spectra assigned to acidic O(1)H groups was not drastically increased for ammonium exchange higher than 77 %. In this range the intensity of the band at 2710 cm⁻¹ due to OH groups located in the cancrinite cage increases (ref. 3). The amount of bridging OH groups of the calcined erionite determined by ¹H MAS NMR is more than 20 % lower than the amount of lattice aluminium determined by ²⁷Al MAS NMR. Besides the residual ammonium, the existence of non-framework aluminium could cause this difference. Furthermore, the acidity of H-erionite is comparable with zeolite Y, taking into consideration the chemical shift of the unperturbed bridging OH groups at 3.9 and 4.2 ppm (ref. 10), respectively. However, the relatively large amount of residual ammonium ion in H-erionite activated in vacuum at 670 K indicates the presence of strong acidic sites as shown by t.p.d. of ammonia (ref. 3).

CONCLUSION

(i) During the synthesis of erionite an parasite phase (zeolite P) was formed. Its thermal decomposition causes changes in the ²⁹Si MAS NMR spectra.

(ii) Different Si/Al ratios determined by ²⁹Si, ²⁷Al MAS NMR and chemical analysis can be explained in terms of thermal de-
composition of the zeolite P and erionite.

(iii) Three different bridged hydroxyl groups are detected upon deammonization of NH₄-erionite.

(iv) Acidic OH groups located in the large cavity are preferentially formed at ion exchange degrees up to 77%.

(v) Potassium ions located in the cancrinite cages are only substituted by multiple ammonium-exchange and intermediate calcination. Furthermore, stronger acidic sites are formed as indicated by the presence of ammonium ions in the erionite activated 670 K.

(vi) The existence of OH groups associated with non-framework aluminium was shown.

REFERENCES