CHAPTER 8

THERMAL BEHAVIOUR OF ION-EXCHANGED FORMS OF
STILBITE AND HEULANDITE

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CHAPTER 8

THERMAL BEHAVIOUR OF ION-EXCHANGED FORMS
OF STILBITE AND HEULANDITE

8.1 Introduction

In this chapter results of thermal analysis (TGA and DTA) of the various ion-exchanged forms of stilbite and heulandite have been described over the temperature range 25 - 1000°C. From these studies the water contents, the hydroxyl group concentrations and the thermal stabilities of each of these ion-exchanged forms are obtained.

8.2 Experimental

The various cation-exchanged forms of stilbite and heulandite are prepared as described in section 5.2. Thermoanalytical measurements are carried out using a derivatograph (MOM, Hungary) wherein the thermogravimetric and differential thermal analytic curves could be obtained simultaneously. The heating rate used is 10°C/min. Equal amounts (500 mg) of samples are taken in each case.
8.3 Results and discussion

The TG and DTA curves for some of the ion-exchanged forms of stilbite and heulandite are shown in Figs. 8.1 to 8.12.

8.3.1 Water contents in various ion-exchanged forms of stilbite and heulandite

The water contents of various cation-exchanged forms of stilbite and heulandite as obtained from the corresponding TG curves are listed in Tables 8.1 and 8.2.

It can be seen from these tables that the water content in both stilbite and heulandite increases with decrease in the cationic radius. Also, the water content is comparatively greater in the divalent cationic forms of these zeolites than in their monovalent cationic forms. The size and number of cations in the unit cell obviously affect the number of water molecules which can be contained in the unit cell. These observations are in accordance with the earlier discussion regarding the crystal structures of stilbite and heulandite (chapters 4, 5 and 6). The water molecules in stilbite
### Table 8.1 Water contents of some ion-exchanged forms of stilbite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cation radius £</th>
<th>No. of water molecules per unit cell</th>
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</thead>
<tbody>
<tr>
<td>Ca-stilbite</td>
<td>0.99</td>
<td>28.6</td>
</tr>
<tr>
<td>Li-stilbite</td>
<td>0.60</td>
<td>30.9</td>
</tr>
<tr>
<td>X-stilbite</td>
<td>1.33</td>
<td>26.8</td>
</tr>
<tr>
<td>Cs-stilbite</td>
<td>1.69</td>
<td>20.4</td>
</tr>
<tr>
<td>Ag-stilbite</td>
<td>1.26</td>
<td>22.6</td>
</tr>
<tr>
<td>NH₄-stilbite</td>
<td>1.40</td>
<td>32.4</td>
</tr>
<tr>
<td>Mg-stilbite</td>
<td>0.65</td>
<td>28.5</td>
</tr>
<tr>
<td>Sr-stilbite</td>
<td>1.13</td>
<td>28.4</td>
</tr>
<tr>
<td>Ba-stilbite</td>
<td>1.35</td>
<td>28.3</td>
</tr>
</tbody>
</table>
Table 8.2  
Water contents of some ion-exchanged forms of heulandite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cation radius</th>
<th>No. of water molecules per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-heulandite</td>
<td>0.99</td>
<td>25.2</td>
</tr>
<tr>
<td>Li-heulandite</td>
<td>0.60</td>
<td>25.9</td>
</tr>
<tr>
<td>K -heulandite</td>
<td>1.33</td>
<td>21.7</td>
</tr>
<tr>
<td>Cs-heulandite</td>
<td>1.69</td>
<td>17.6</td>
</tr>
<tr>
<td>Ag-heulandite</td>
<td>1.26</td>
<td>23.1</td>
</tr>
<tr>
<td>NH₄-heulandite</td>
<td>1.40</td>
<td>27.5</td>
</tr>
<tr>
<td>Sr-heulandite</td>
<td>1.13</td>
<td>26.0</td>
</tr>
<tr>
<td>Ba-heulandite</td>
<td>1.35</td>
<td>27.0</td>
</tr>
</tbody>
</table>
and heulandite are associated with the cations. As the number of size of the cations increase, there will remain less space to be filled in by the water molecules and hence the water content in such cases will decrease. Similar results have been obtained for zeolites X and Y\(^1\) and for chabazite\(^2\).

8.3.2 Thermal stability of zeolites

The resistance to collapse at elevated temperatures was one of the first recognized manifestation of zeolite stability. The discovery that these materials could be heated past the point of dehydration without collapse attracted wide spread attention. Literature references to this phenomenon are numerous\(^2-4\) but only recently has the thermal stability of zeolites been reported in any detail\(^5,6\). Some of the factors affecting the structural stability of zeolites at elevated temperatures are briefly discussed in what follows.

The geometry of the crystalline net work is undoubtedly a major factor in stability. However, the quantitative relationship has not been determined and we are still unable to predict the stability of a given
structure. Even empirical co-relations between stability and structure are difficult because other factors make simultaneous contributions.

In general, there is a relation between the silica to alumina ratio of a zeolite and its thermal stability; the more siliceous zeolites tend to be more stable. Many authors attribute the relatively high stability of zeolites such as mordenite, clinoptilolite and erionite to their high silica content.

The nature and number of metal cations that are present contribute significantly to the stability exhibited by a particular zeolite structure. The examples of natural zeolite chabazite\(^7\) and the synthetic analogs of faujasite\(^8\) in various cationic forms typify the behaviour of other zeolites.

In summary, thermal stability increases with silica content and is greatly influenced by the choice of cation, with some ionic series appearing to have a fairly systematic influence while others exhibit complex behaviour.

8.3.3 Differential thermal analysis

Properties like X-ray diffraction, surface
area, electrical conductivity, infrared spectra and thermal behaviour have been used to indicate the thermal stability of zeolites. Thermal collapse of a zeolite crystal is usually accompanied by liberation of heat. Magnitude of this exothermic reaction and the temperature at which it occurs can often be determined by DTA. Consequently, the position of this exothermic peak has often been used as an indication of thermal stability. Thermal stabilities of various cation-exchanged forms of stilbite and heulandite are discussed below. Since the ammonium-exchanged zeolites represent a class having complex and unique behaviour, these materials are considered separately.

8.3.4 Thermal stabilities of various metal cationic forms of stilbite and heulandite

It has been confirmed from the studies on dehydration behaviour of stilbite (chapter 4) that the structure collapses above 400°C. The DTA curve of Ca-exchanged stilbite (Fig. 8.1) shows a sharp exothermic peak around 460°C corresponding to this framework collapse. The DTA curve for Mg-exchanged stilbite (Fig. 8.2) is almost similar to that for its Ca-exchanged form (Fig. 8.1). There are no considerable differences in the DTA curves of other divalent cation-exchanged forms of
When Ca$^{2+}$ in the original sample of stilbite is exchanged with alkali metal cations the exothermic peak corresponding to the structural collapse becomes broader (see DTA of Cs-exchanged stilbite in Fig. 8.3). These results can be explained by assuming that the increase of the number of cations reduces the chance of sudden lattice collapse. Instead, there occurs a gradual loss in the crystallinity or the structural collapse occurs more sluggishly in these samples.

A more significant result is obtained in the case of Ag-exchanged stilbite. Figure 8.4 shows no pronounced exothermic peaks except one around 950°C. This observation indicates the possibility of using Ag-exchanged stilbite as an industrial catalyst. However, more detailed studies on the acidity and catalytic activity of Ag-exchanged stilbite are needed before giving due significance to this observation.

In the case of heulandite, it is known that when this zeolite is dehydrated at 300-400°C, a partial collapse of the framework occurs, yielding a new crystal phase, heulandite - $\beta^9,10)$. The DTA curves of heulandite exchanged with Ca$^{2+}$, Ba$^{2+}$, Li$^+$ and Cs$^+$...
(Figs. 8.5 to 8.8) are similar in nature. The exothermic peak corresponding to the structure collapse becomes broader in case of Ag-exchanged and K-exchanged heulandite (Figs. 8.9 and 8.10) indicating an increase in thermal stability of these samples.

8.3.5 Thermal behaviour of NH₄-exchanged stilbite and heulandite

The thermochemical properties of NH₄-exchanged zeolites have been investigated due to their extensive use as catalysts. The decomposition reactions which take place during the thermal treatment of different NH₄-exchanged zeolites are similar. Ammonia is desorbed and the hydrogen form of the corresponding zeolite is produced. At higher temperatures "dehydroxylation" occurs, resulting in elimination of acidic surface hydroxyl groups (Bronsted sites) as water and formation of Lewis acid sites. Despite this common feature, the deammoniated and dehydroxylated forms of the different zeolites show considerable differences in thermostability in acidity and in catalytic behaviour.

The derivatographs of NH₄-exchanged heulandite are depicted as shown in Figs. 8.11 and 8.12. The thermogravimetric traces of NH₄-stilbite and NH₄-heulandite
indicate a continuous weight loss over the whole temperature region. The corresponding DTA curves show an intense exothermic peak around 480°C which is attributed to the oxidation of exchanged ammonia according to the reaction

\[ \text{NH}_4^+ Z \downarrow \rightarrow \text{H}_2 \uparrow + \text{NH}_3 \uparrow \]

The broad endotherms between 200 and 400°C show that dehydration, deammoniation and dehydroxylation overlap. Absence of any other exothermic peak in these DTA curves (Figs. 8.11 and 8.12) establishes that \(\text{NH}_4^+\)-exchanged forms of stilbite and heulandite are thermally more stable as compared to their other metal cationic forms.

It is a general rule that the alkali and alkaline earth metal forms of zeolites are more stable than their hydrogen forms. An example to this effect is recent studies on thermal stability of natural gmelinite and some of its ion-exchanged forms\(^1\))\(^6\)). In the present investigation it is observed that the hydrogen forms of stilbite and heulandite are more stable.

Mechanisms involved in the high temperature collapse of zeolites are still not completely clear. DTA provides some interesting insight concerning the
mechanism of thermal collapse. As described above collapse of the framework is accompanied by liberation of heat or an \textit{exo}thermic peak, whereas the usual melting of a crystalline material is an \textit{endo}thermic reaction. The exothermic nature of the crystal collapse has been attributed to the large amount of surface energy associated with the zeolite. At the temperature of collapse the surface area decreases and the energy associated with the lost surface appears in the form of liberated heat\textsuperscript{17}. 

Role of the cation in thermal stability of stilbite and heulandite also suggests a complex mechanism. Influence of the cation in zeolite stability has been attributed to its size and consequently to its space-filling capacity by Barren\textsuperscript{17} and to its distorting effect on the lattice by Bremer\textsuperscript{13}. Increase in thermal stability of K-exchanged heulandite is similar to the results obtained with that for chabazite and gmelinite\textsuperscript{16}. The greater stability of Ag-exchanged forms of stilbite and heulandite shows the complex nature of the influence of cations on the thermostability of these zeolites.

Observation of a greater thermal stability of hydrogen forms of stilbite and heulandite indicates that
the mechanism of framework distortion (or collapse) is related to the presence of cations. The positions of cations and the exchangeable cationic sites in these zeolites are discussed in the earlier part of this thesis (chapters 5 and 6). The cations at the main Ca, Na-site in stilbite and at the site referred earlier as Ca 1 in heulandite exert a strongly attractive force on the framework oxygens, drawing them closer to achieve the best possible coordination environment. As a result, the frameworks of these zeolites distort or collapse. Mortier and Pearce\(^{18}\) have recently reported the studies on thermal stability of the heulandite-type framework. According to these studies, the two-dimensional channels in stilbite and heulandite are severely occluded as a result of the thermal collapse of stilbite and heulandite structures, rendering them almost useless as industrial catalysts or dehydrating agents. Results obtained in the present investigations indicate the possibility of stabilizing the frameworks of stilbite and heulandite and of producing industrially useful materials by reducing the number of exchangeable cations.

8.4 Summary and conclusions

Thermal behaviour of various cation-exchanged
forms of stilbite and heulandite are studied for the first time using TGA and DTA. For all forms of stilbite and heulandite (despite some irregularities) there is a tendency for the number of water molecules per unit cell to decrease with increasing number of cations and with increasing cation radius.

Role of cation in deciding thermal stability of stilbite and heulandite suggests a complex mechanism of thermal collapse of these two zeolites. Ag-exchanged forms of stilbite and heulandite show greater thermal stability. Similarly the thermostability increases in the case of K-exchanged heulandite and alkali metal forms of stilbite.

\( \text{NH}_4 \)-stilbite does not show phase transformations of higher temperatures. This is one of the rare cases where the H-form of a zeolite is thermally more stable than its ion-exchanged forms. The ammonium form heulandite also behaves similarly; it is thermally more stable than the natural Ca-rich heulandite. It seems possible to stabilize the frameworks of these two zeolites and hence to produce industrially useful materials (for catalysis and dehydration) by reducing the number of cations.
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17 F. Freund  

18 W. J. Mortier and J. R. Pearce  
Captions of the figures

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<th>Figure</th>
<th>Description</th>
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<td>TGA and DTA of Ca-stilbite</td>
<td>Ca-stilbite</td>
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<td>Fig. 8.2</td>
<td>&quot;</td>
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<tr>
<td>Fig. 8.3</td>
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<td>Fig. 8.4</td>
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<td>Fig. 8.5</td>
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