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THERMAL BEHAVIOUR OF NATURAL STILBITE CRYSTALS

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ABSTRACT

Observations of the behaviour of natural stilbite crystals on dehydration are reported. Results of TG, DTA, static weight loss measurements, X-ray diffractometric analysis and IR studies are described and interpreted. It is established that the stilbite structure collapses at about 400°C. It is shown that around 300°C, stilbite changes into a mixture of epistilbite and heulandite, and that around 350°C, the resulting prominent phase is a mixture of heulandite and chabazite.

INTRODUCTION

During the last 25 years, interest in zeolites has increased at a remarkable rate. All commercial applications of natural zeolites make use of one or more of several physical or chemical properties, including (i) ion exchange, (ii) adsorption and related molecular sieve properties, (iii) dehydration and rehydration and (iv) siliceous composition. These properties are, of course, functions of the specific crystal structure of each individual zeolite species and of framework and cationic composition.

Stilbite, the first zeolite to be discovered by Cronstedt in 1756 [1], is commonly found as a vein mineral or locally as a replacement product in volcanogenic rocks in association with heulandite group minerals or laumontite. Sukeswala et al. [2,3] have described this variety of natural zeolite occurring in the Deccan Traps of Western India. The stilbite crystals used in the present study were collected from the quarries of the Pashan area, Poona, India. The present paper deals with a systematic study of the dehydration behaviour of these crystals.

EXPERIMENTAL

The stilbite crystals were first analyzed by TG and DTA. Known amounts of stilbite powder (2 g each) were heated at various temperatures, viz., 120, 150, 200, 250, 300, 350 and 400°C for 4 h in each case. Each sample was weighed as soon as possible after its removal from the furnace, and weighed again after overnight exposure to the atmosphere to determine the extent of rehydration.

X-Ray powder diffractographs were recorded for the natural stilbite samples (before dehydration), as well as for the same samples dehydrated at different temperatures. The IR spectra of the natural stilbite (before dehydration) and also of the dehydrated samples were recorded using the KBr wafer technique [4].

OBSERVATIONS

TG and DTA

The TG curve for stilbite (heating rate 10°C min^{-1}) is depicted in Fig. 1. A small step is observed at about 120°C. Most of the zeolite water is lost at about 350°C, as can be seen from Fig. 1.

The DTA curve of natural stilbite (heating rate 10°C min^{-1}) is shown in Fig. 2. A sharp endothermic peak is observed at 200°C. No other sharp peaks are observed except a small exothermic peak around 320°C and one broad exothermic peak around 580°C.

Static weight loss curve

The observed percentage weight losses of the samples heated at various temperatures were plotted against temperature, as shown in Fig. 3. The points indicated by × show the degree of rehydration of the samples at the corresponding temperatures.

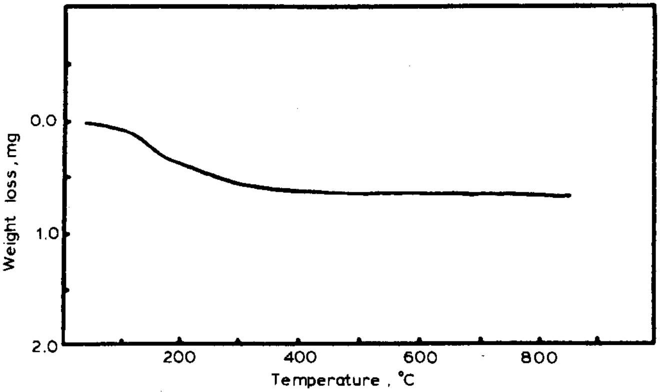

Fig. 1. TG of stilbite.

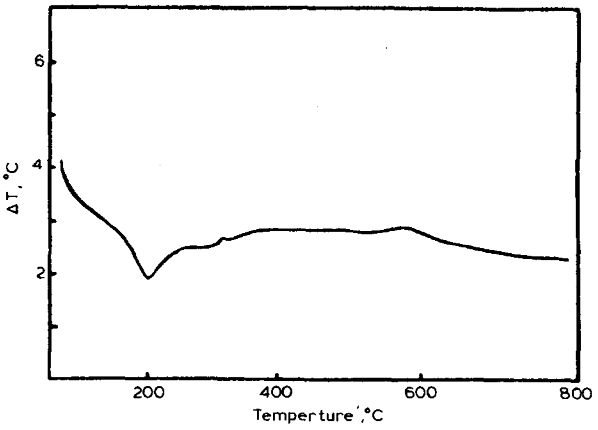

Fig. 2. DTA of stilbite.

X-Ray diffractometric analysis

The observed *d* spacings for the natural stilbite samples are listed in Table 1. The samples dehydrated at 120, 150, 200 and 250°C do not undergo any appreciable changes in their *d* values. Appreciable changes are found in the *d* spacings for the samples dehydrated at and above 300°C. The observed *d* spacings for the samples dehydrated at 300°C and 350°C are also given in

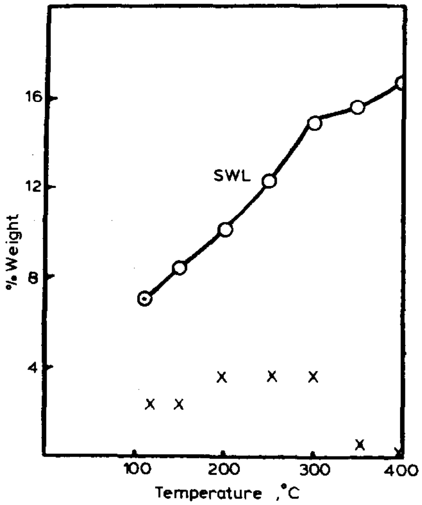

Fig. 3. Static weight loss curve of stilbite; × indicates the extent of rehydration.

TABLE 1

X-Ray powder data (*d* values) of natural stilbite and stilbite dehydrated at 300 and 350°C

d (Å)		
Natural stilbite at room temperature	Dehydrated at 300°C	Dehydrated at 350°C
9.007	9.025	10.281
5.630	8.117	9.213
5.296	7.762	8.192
4.599	7.668	7.830
4.506	7.499	7.499
4.413	7.081	6.916
4.250	6.948	6.809
4.062	6.810	6.371
3.720	6.326	6.237
3.480	6.151	5.867
3.376	5.906	5.539
3.175	5.246	5.438
2.984	4.671	5.340
2.858	4.270	5.215
2.763	4.033	5.126
	3.883	4.429
	3.818	4.353
	3.604	4.311
	3.484	4.270
	3.453	4.171
	3.427	4.114
	3.389	3.633
	3.022	3.479
	2.763	3.389
	2.549	3.255
		3.187

Table 1. No definite peaks are observed in the diffractograph of the samples dehydrated at 400°C, which indicates that the stilbite structure collapses at about 400°C, forming an unidentified product of low crystallinity.

IR studies

The IR spectrum of natural stilbite is illustrated in Fig. 4. Figures 5, 6 and 7 show the IR spectra of the samples dehydrated at 200, 300 and 400°C, respectively.

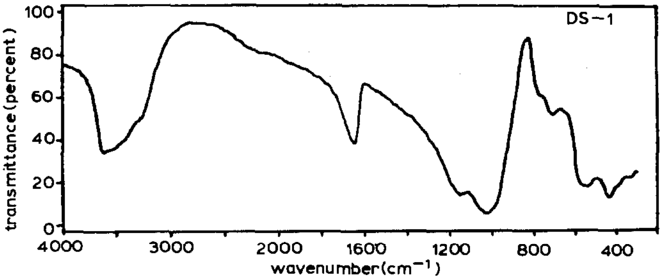

Fig. 4. IR spectrum of stilbite at room temperature.

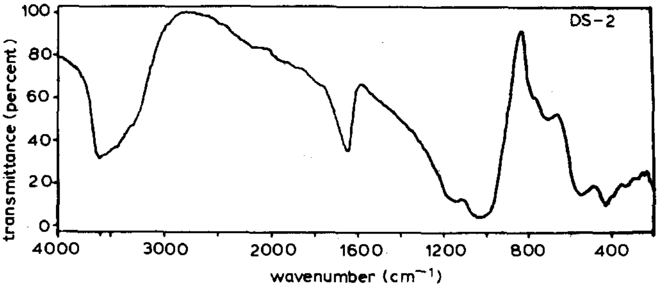

Fig. 5. IR spectrum of stilbite dehydrated at 200°C.

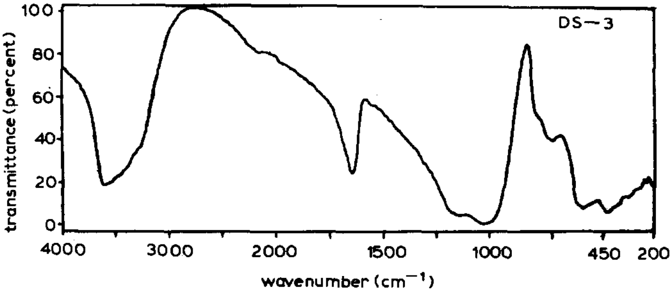

Fig. 6. IR spectrum of stilbite dehydrated at 300°C.

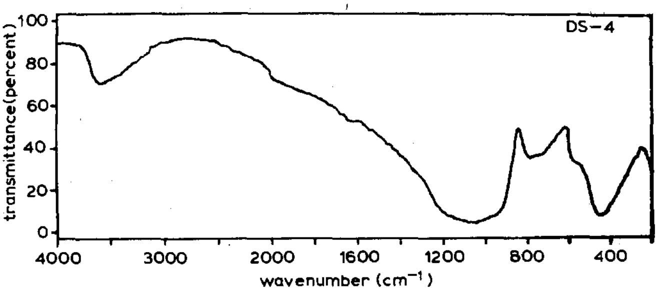

Fig. 7. IR spectrum of stilbite dehydrated at 400°C.

DISCUSSION

Based on their dehydration behaviour, zeolites may be classified as (a) those which show no major structural changes during dehydration and which exhibit continuous weight loss curves as a function of temperature, and (b) those which undergo major structural changes during dehydration and which exhibit discontinuities in their weight loss curves. The latter group includes those zeolites whose structures collapse on heating to elevated temperatures. Stilbite belongs to the latter category, as is evident from the present study.

The crystal structure of stilbite has been determined by Slaughter [5] and later refined by Galli [6]. Accordingly, the crystal structure of stilbite is characterized by large intersecting relatively open channels of 10- and eight-member tetrahedral rings. All channel cavities and channel openings are occupied by cations. The main cation site, the Ca, Na-site, is located in the centre of the largest part of relatively large cage or cavity in the silica–alumina framework. Each Ca, Na-site is surrounded by eight water molecules. With all eight sites filled, the unit cell would contain 32 water molecules. Gabuda et al. [7] have investigated the positions of water molecules in stilbite using NMR.

Using X-ray powder method, Coombs et al. [8] have reported that the Ca-rich stilbite transforms into a mixture of epistilbite and wairakite at about 250°C. The decomposition products of Hungarian stilbite were wairakite and heulandite [9]. Stilbite from Iceland and Strzegom (Poland) seem to give clinoptilolite as the decomposition product [9]. The present X-ray diffraction studies on Indian stilbite indicate that around 300°C, stilbite changes into a mixture of epistilbite and heulandite. However, around 350°C, the prominent phase seems to be a mixture of heulandite and chabazite (another Ca-rich zeolite with almost the same Si/Al ratio). It is also found that at all stages the different decomposition products are present together. The transformation from one phase to another is gradual and never complete.

The sluggish nature of these structural changes occurring in stilbite due to dehydration is also endorsed by the DTA curve. No sharp exothermic peaks are observed other than the small peak around 320°C and one small broad peak at 580°C. The sharp endothermic peak at 200°C corresponds to dehydration.

Infrared spectroscopy was employed by Zhdanov et al. [10,11], Flanigen et al. [12] and several other workers to study zeolites of a variety of crystalline structures, and of various compositions (Si/Al ratios) and various degrees of dehydration and decationization, and various cation-exchanged forms.

The influence of dehydration of dehydration on the IR spectrum depends on the degree of framework distortion effected by the dehydration reaction.

Figures 4, 5 and 6 show no appreciable changes in the spectra. This means the framework distortion is minimal on dehydration up to 300°C. On the other hand, considerable changes are observed in the IR spectrum of the sample dehydrated at 400°C (Fig. 7).

The hydroxyl (O–H) bond near 3600 cm^{-1} has become weaker, and the strong peak around 1650 cm^{-1} (assigned to H_2O bending mode) has turned into a weak shoulder. This is attributed to the structural collapse of stilbite at 400°C. Even though some rehydration may occur, the water molecules are of non-zeolitic type.

The absorbance of the structure-sensitive bands near 1140 cm^{-1} (asymmetric T–O stretch), 775 cm^{-1} (symmetric T–O stretch), 550 cm^{-1} (secondary building units) and 330 cm^{-1} (pore opening) are found to decrease gradually in Figs. 6 and 7. This must be due to a reduction in crystallinity of the sample. Similar results were obtained by Flanigen et al. [12] for zeolites Y, A, X and L. The internal tetrahedral vibrations around 1030 cm^{-1} (asymmetric stretch) and near 440 cm^{-1} (T–O bending mode) remain, with minor changes, in breadth and position. On the other hand, the strong band near 700 cm^{-1} (Figs. 4, 5 and 6) is noticeably absent in Fig. 7. The 700 cm^{-1} band is in the region where the absorption band is observed for aluminosilicates formed by the isomorphous substitution of Al^{3+} for Si^{4+}. This band has been assigned to the vibration of the Al–O band [13]. Kiselev and Lygin [14] have found that in the case of synthetic faujasites the intensity of a similar band around 758 cm^{-1} diminishes with decreasing Al content in the faujasites, which suggests that it is a band belonging to the vibrations of the Al–O bond inside the aluminium–oxygen (AlO_4) tetrahedra. The absence of the band near 700 cm^{-1} in Fig. 7 indicates that there is a considerable distortion in the framework structure of stilbite due to dehydration at 400°C, and the Si/Al ratio in the residual framework is not the same as that in the original sample. The absence of any new band indicates that there is no formation of octahedral Al or layer-type structure.

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