



THERMAL BEHAVIOUR OF NATURAL STILBITE

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ABSTRACT

Crystals collected from the Ajantha, Aurangabad, Maharashtra, India, have been characterized as stilbite by X-ray diffraction, IR spectroscopy and chemical analyses. The thermal behaviour was studied using thermogravimetric/differential thermal analysis (TG/DTG/DTA). The sample was exchanged at reflux temperature with NH_4Cl and NaCl . The sample exchanged with NH_4Cl was further transformed to the H-form of stilbite by heating at 823 K for 2 h. Investigations suggest that thermal stability of zeolite framework can be varied due to ion exchange.

Key words: Zeolite, Thermal behaviour, Stilbite.

INTRODUCTION

The zeolites classified in group 7 include morphologically lamellar zeolites; heaulandite, stilbite and clinoptilolite. Occurrence of this type of zeolite in the Antrim basalt of Ireland has been reported¹. It has also been reported that the formation of stilbite from the lake took place as the result of the reaction of meteoric water heated from below or partly from exothermic hydration reaction.

Investigation on stilbite has been reported by Gottardi and Galli², Slaughter³ and later refined by Galli⁴. According to these workers, the stilbite is characterized by large intersecting relatively open channels of 10 and 8 membered tetrahedral rings. All the channel cavities and channel openings are occupied by cations. Dehydration studies of stilbite have been reported by Barrer and Vanghan⁵. A study of dehydration of zeolites from India has also been reported by many workers^{6–8}.

In the present investigation, the crystals collected from hills of Ajantha caves, Aurangabad, MS, India, has been studied for its thermal behaviour.

EXPERIMENTAL

Materials

The as grown sample of stilbite was crushed and sieved to get 5–10 μm sized crystals, was treated three times at 368 K for 2 h in 0.1 M solution of NH_4Cl with a solid/solution ratio of 1 :

10 with stirring. After washing with distilled water, filtering and drying at 353 K for several hours, the ion exchanged sample is obtained.

This sample was further calcinated at 823 K for 2 h under N₂ flow and then cooled naturally to get H form of stilbite. The H form was treated three times at 368 K for 2 h in 0.1 M NaCl solution with a solid/solution ratio of 1 : 10 with stirring. The sample was washed with distilled water, filtered and dried at 353 K for several hours.

The samples so prepared were designated as follows: The as grown stilbite as P – Sti; The NH₄⁺ exchanged stilbite as NH₄ – Sti; the H form of stilbite as H – Sti and the Na⁺ exchanged with H form of stilbite as Na – Sti

Characterization

X-ray diffraction studies

The X-ray powder diffractograms were recorded on a Rigaku (Model D-max/III VC) diffractometer using CuK ($\lambda = 1.5404 \text{ \AA}$) radiation, scanning at a chart speed of 1°/min in the range of 2θ values from 5° to 65° at room temperature. The relative intensities and 'd' values were compared with the standard 'd' values. All the characteristics peaks of stilbite were found to be present in the X-ray diffract organ, thus confirming its identity. XRD's of P – Sti, H – Sti and Na – Sti we also recorded at 723 K, 823 K and 923 K, respectively to study the crystallinity of the samples. They are shown in Fig. 1 (a), (b) and (c).

Chemical analysis

The chemical analyses were carried out by wet chemical analysis methods. Atomic absorption spectroscopy (Hitachi-Z8000) was used to obtain contents of cations of the sample. The chemical formula derived on the basis of oxygen 72 is



IR Studies

IR spectra were recorded on Pye-Unicam sp-300 spectrometer using Nujol mull technique. The details of the observed IR bands are given in Table 1.

Table 1. IR Data of P-Sti, NH₄-Sti, H-Sti, Na-Sti

Sample Name	External Linkage (cm ⁻¹) (Structure Sensitive)		Double Ring (cm ⁻¹)	Internal Tetrahedra (cm ⁻¹) (Structure insensitive)			Water Bands (cm ⁻¹)	
	Asym. Stretch	Sym. Stretch		Asym. Stretch	Sym. Stretch	T-O Bend	Hydroxyl Stretch	H ₂ O Bend
P-Sti	1032	775	555	1277	698	439	2923	1636
NH ₄ -Sti	1035	775	568	1276	715	439	2926	1636
H-Sti	1068	772	582	1276	654	474	2922	1653
Na-Sti	1066	772	580	1276	655	470	2926	1655

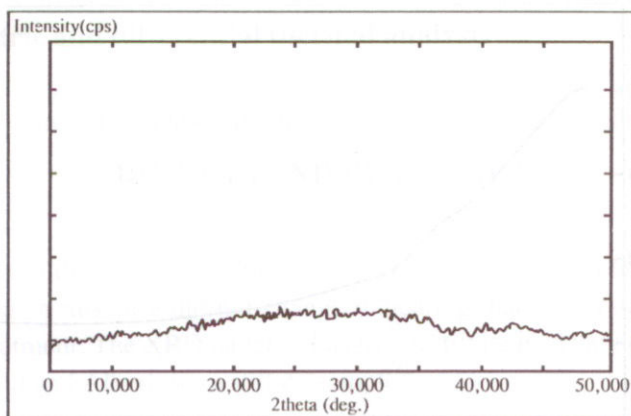


Fig.1 (a) : X-Ray Diffractogram of P-Sti Calcinated at 723 K

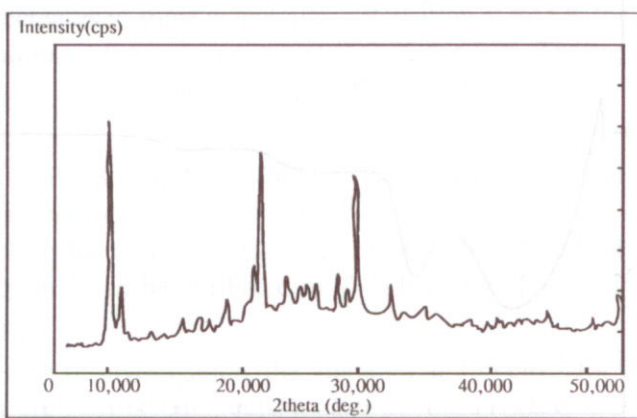


Fig.1 (b) : X-Ray Diffractogram of H-Sti Calcinated at 823 K

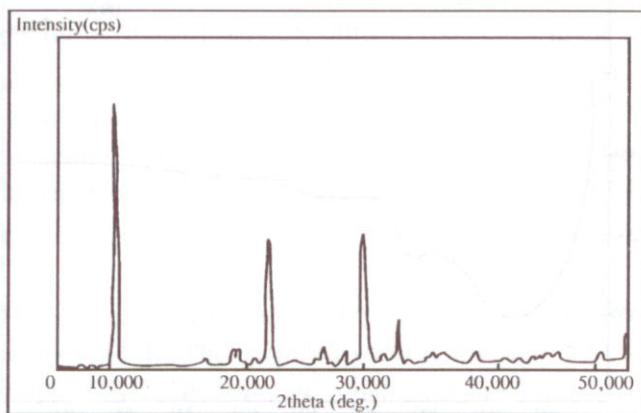


Fig.1 (c) : X-Ray Diffractogram of Na-Sti Calcinated at 923 K

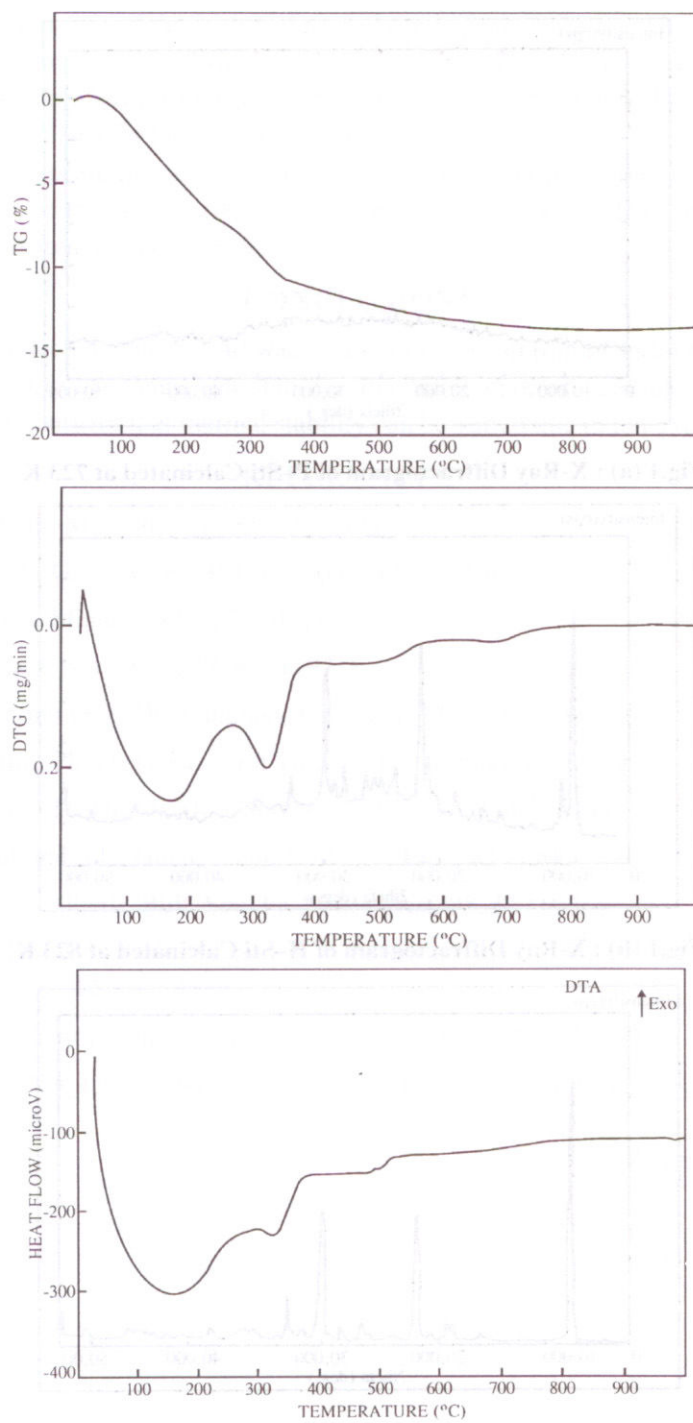


Fig.2 (TG/DTG/DTA) Curves of P-Sti

Thermogravimetric and differential thermal analysis

The TG/DTG/DTA curves for natural stilbite were recorded on a Setaram 92 thermal analyzer in air using pre-calcinated α -alumina as reference material as shown in Fig. 2.

RESULTS AND DISCUSSION

XRD Patterns

In XRD patterns of the as grown stilbite and its exchanged forms, it has been observed that the number of peaks in this case did not change indicating that no crystalline transformation occurred during treatment. The XRD pattern of asgrown stilbite is in very good agreement with that reported by Galli and Alberti for a stilbite sample⁹.

The XRD patterns of calcinated samples show that structure of P – Sti is seriously degraded after calcination at 723.K. On the other hand structure of sample H – Sti stays intact though crystallinity of it decreases to some extent after calcination at 823 K for 2 h. Sample Na – Sti retains high crystallinity after calcinations at 923 K for 2 h. Thermal stability of zeolite framework in our case is in the order: Na – Sti > H – Sti > P– Sti.

IR Spectra

The IR spectra of P – Sti and NH_4 – Sti are very similar. The vibration 1636 cm^{-1} can be assigned to deformation band of adsorbed water^{10, 11}. According to Maxwell and Baks¹⁰, cation can exert remarkable influence on the frequency of adsorption. Bands in the range of $440\text{--}490\text{ cm}^{-1}$ and $540\text{--}590\text{ cm}^{-1}$ can be attributed to T–O bending (T = Si or Al) and double ring vibration respectively.

In the present case of investigation, the vibration at 555 cm^{-1} for the double ring in the spectrum of P – Sti shifts to 568 cm^{-1} in NH_4 – Sti. But the T–O bending vibration at 439 cm^{-1} does not shift obviously. The symmetrical stretching at 698 cm^{-1} in the spectrum of P–Sti shifts to 715 cm^{-1} in that of NH_4 –Sti. The strong vibration at 1032 cm^{-1} in the spectrum of P–Sti, which corresponds to the asymmetric stretch, shifts to 1035 cm^{-1} in the spectrum of NH_4 –Sti.

The vibration of asymmetric stretch at 1035 cm^{-1} and vibration of symmetric stretch at 775 cm^{-1} shifts to 1068 cm^{-1} and 772 cm^{-1} , respectively, from NH_4 – Sti to H – Sti. The vibration of double ring, which shifts from 568 cm^{-1} to 582 cm^{-1} for NH_4 – Sti. and H – Sti. These facts indicate that dealumination of stilbite framework occur in the process of deammoniation during calcination of NH_4 – Sti¹².

TG/DTG/DTA

The TG and DTA curves show that most of the water is lost upto 620 K. The structure of the stilbite is stable upto 599 K. The occluded water is lost upto 599 K and structural water continues to be lost upto 829 K. The structure collapses at 794 K.

A sharp endothermic peak is observed at 438 K, which corresponds to dehydration without change in structure. The second endothermic peak is observed at 599 K, which corresponds to

structural rearrangement on dehydration. An exothermic peak is observed in the range (1003 K to 1051 K) shows that remaining water molecules are lost. Broad endotherm denote chemical reactions. A sharp endotherm is indicative of crystalline rearrangements. In the present case of investigation, 7.097% weight loss is observed in the temperature range 351 K to 473 K as most of the water molecules are lost in this range. 1.61% weight loss in the range 594 K–620 K and 0.48% weight loss in the range 1003 K–1052 K is also observed. The total weight loss in sample of stilbite is found to be 13.54%.

CONCLUSION

The sample collected from Marathwada region of Deccan trap of India is a stilbite with a high crystallinity. Ion exchange can stabilize the framework of zeolites. Investigations of thermal behaviour confirms that thermal stability can be varied due to ion exchange.

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