



FTIR STUDY OF DEHYDRATION DYNAMICS IN NATURAL ZEOLITES

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ABSTRACT

The dehydration behavior of naturally occurring zeolites (stilbite and scolecite) from deccan traps are investigated by the thermal induced variations of water bending (ν_2), and stretching (ν_3 and ν_1) modes; and corresponding second order modes in the wavenumber region 4000 – 8000 cm^{-1} . The observed spectral variations indicate that they partially dehydrate in the 450–500 K temperature range, triggered by the loss of half of its water molecules. A completely reversible spectral behavior of stilbite and scolecite indicate that they can be re-hydrated when heated up to 475 K and 575 K respectively. The rehydration is partial in the stilbite dehydrated to 630 K. Growth of a new mode around 4550 cm^{-1} in the temperature range 430–650 K is observed in stilbite. Similarly a new mode around 4485 cm^{-1} in temperature range 630–675 K is observed in scolecite. These modes indicate the presence of hydroxyl groups, created by the distortions in the framework, and breakage of T-O-T linkages. The mode around 4609 cm^{-1} (Al-OH) in scolecite decreased continuously and vanished at 500 K, indicating the expelled water molecules are hydrogen bonded to O atom of AlO_4 tetrahedra.

1. INTRODUCTION

Zeolites are the crystalline hydrates having a rigid aluminosilicate framework and the alkali and the alkaline-earth atoms as extra-framework cations. The water molecules of zeolites are able to dehydrate and rehydrate at low temperatures ($<400^\circ\text{C}$). The ion exchange, adsorption and molecular sieve properties of zeolites have wide spread applications, such as removal of heavy metal cations, radioactive cations, and ammonium from wastewater¹. The dehydration of zeolite induces a change in the co-ordination or migration of extra-framework cations. Some times the changes in co-ordination of the extra-framework cation with the framework oxygen and/or water molecules may cause structural variations during the dehydration². And on complete dehydration structural collapse occurs through the breakage of T-O-T bonds¹. The rehydration of zeolites may be in short intervals or in long intervals depending on structural changes induced by dehydration. However, rehydration may not be reversible if the induced structural changes break the T-O-T linkages¹.

The zeolites (stilbite and scolecite) commonly occur in wide range of geological formations, and samples used in the present study are from deccan traps, Poona region, India. The stilbite $\{(\text{Na}_2\text{Ca}_8)[\text{Al}_{18}\text{Si}_{54}\text{O}_{144}]\cdot 60\text{H}_2\text{O}\}$ is a common zeolite with the framework topology STI and the scolecite $\{\text{Ca}_8[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}]\cdot 24\text{H}_2\text{O}\}$ is fibrous zeolite with the framework topology NAT. Gottardi and Galli², Rykl and Pechar³, Rykl et al⁴ and Reeuwijk⁵ using experimental methods like thermal analysis, X-ray diffraction (XRD) and infrared spectroscopy have studied the thermal transformations of stilbite and scolecite. They reported stepwise dehydration in these samples. Cruciani et al⁶ have also studied the dehydration processes of stilbite using *in-situ* synchrotron powder XRD. They also reported stepwise dehydration mechanism and a change in the crystal symmetry (stilbite B) about 420 K. In the higher temperature range i.e., in stilbite B phase, a

continuous dehydration and breakage of T-O-T (T = Si or Al) bonding is also reported. Finally, above 720 K, the stilbite transforms into amorphous phase. Aumento⁷ studied the dehydration and rehydration behaviour of stilbite and where in he reported complete rehydration in the sample heated to a temperature below 573 K and partial rehydration in the sample heated to 573-873 K.

Stahl and Hanson⁸ studied the phase transformations in scolecite using real time synchrotron X-ray diffraction studies and reported that it transforms to metascolecite initially at 480 K by dehydrating the water co-ordinated with the Ca atom and then to amorphous phase at 625 K.

The FTIR spectroscopy is a powerful technique particularly to investigate the behaviour of water molecules. We investigate the thermal stability of zeolites upon dehydration using the spectral variations in NIR (4000-8000 cm^{-1}) region. The present investigations are aimed at understanding short term or long term rehydration behaviour and the breakage of T-O-T linkages induced by the dehydration in zeolites.

2. EXPERIMENTAL

2.1 Materials and methods

The samples were collected from naturally occurring zeolite around Poona region, India. These samples were used without further purification. Suitable samples were cut from a larger crystal for near infrared (NIR) studies; whereas, powdered samples were used for sample characterisation and mid infrared (MIR) studies. The X-ray diffraction (XRD) patterns were obtained using Philips PW-1830 powder diffractometer with Ni-filter. The radiation used was Cu-K α and the 2θ scan was from 5° - 80° . The angle variation was at a rate of $3^\circ/\text{min}$. The DSC patterns were recorded on 2010 TA-instruments. The sample was weighed using Metler AE 163 balance. Aluminum pans were used to place the samples. The weight of the sample used was 8 mg and the rate of heat flow was 10°C per minute.

2.2. Infrared Spectroscopy

FTIR studies were carried out on a NEXUS FTIR spectrometer from Thermo-Nicolet, using a thermo electrically cooled deuterated triglycene sulphate (DTGS) detector, extended range KBr (XT-KBr) beam splitter, and a dual source, capable of working in the wavenumber range 375 – 12500 cm^{-1} . The samples were placed in a specially fabricated environmental chamber. This chamber can be used to increase the temperature of the sample under study up to about 950 K with an accuracy of $\pm 2^\circ$. Running tap water is used to cool the outer jacket of the chamber, which house the infrared transparent windows. The conventional KBr pellet method has been followed to study the rehydration behaviour of fundamental modes in the wavenumber range 400 to 4000 cm^{-1} , using NEXUS Ever-Glo source. The spectra were recorded in the wavenumber region 2000 to 8000 cm^{-1} using a white light source (tungsten halogen) and each spectrum is an average of 256 scans and with 2 cm^{-1} resolution.

3. RESULTS

3.1. Characterisation

The spectra of zeolites in the mid-IR (MIR) region are collected with KBr pellet method. Figure 1 shows the MIR spectra of stilbite (A) and scolecite (B) collected at ambient temperatures and they match well with those reported by Gottardi and Galli² and Rykl and Pechar³. The water molecules of stilbite have three bands in the stretching region at 3260, 3426 and 3587 cm^{-1} and a band in the bending region at 1653 cm^{-1} . The corresponding spectra of scolecite has a complex structure with five bands in stretching region at 3589, 3507, 3409, 3327 and 3232 cm^{-1} and three

bands in bending region at 1665, 1649 and 1591 cm^{-1} . Figure 2 shows the DSC recorded profiles of stilbite (—) and scolecite (----). It is evident that the transition temperatures for stilbite are at 488 K and 560 K. The same for scolecite are at 567 K and 650 K. The DSC results are compared with reported thermal analysis data of Gottardi and Galli². The X-ray diffraction patterns of virgin samples are collected and matched with the reported data of Gottardi and Galli² confirming further that the samples are stilbite and scolecite, with minor (<3%) impurities.

3.2. In-situ fourier transform infrared studies

We have investigated dehydration behaviour and structural modifications of the zeolites by probing the second order modes (combination and overtones) of water molecules occurring in the wavenumber range 4000 – 8000 cm^{-1} . *In-situ* NIR spectra are collected at different temperatures in the range 300-850 K. The spectra of stilbite collected at different stages of dehydration, i.e. at 300, 430, 450, 650 and 850 K temperatures, are shown in figure 3A. The spectrum at 300 K has a band around 5233 cm^{-1} in the water combination region, and other bands at 6825 and 7057 cm^{-1} in the overtone region of water. These are similar to that reported by Cloutis et al⁹. The spectra of scolecite, shown in figure 3B, are collected at different stages of dehydration i.e. at 300, 430, 495, 675 and 875 K temperatures. The spectrum at 300 K of scolecite is vastly complex compare to stilbite, behaviour similar to the fundamental modes in MIR region (fig 1B). The spectrum has two intense peaks at 5139, 5064 cm^{-1} and three shoulder peaks at 5219, 4912 and 4838 cm^{-1} in the combinations region of water. Other bands at 6998, 6923, 6825, 6733 and 6490 cm^{-1} are the overtones of water molecules. As the temperature is increased all these modes gradually became weaker and completely disappeared, indicating complete dehydration. The spectrum of stilbite at 650 K in figure 3A clearly shows a new mode around 4550 cm^{-1} which initially observed at 450 K. This band at 4550 cm^{-1} is assigned to Si-OH bond¹⁰⁻¹¹. Besides water modes the spectrum of scolecite at 300 K in figure 3B has band at 4609 cm^{-1} which is assigned to Al-OH bond¹⁰. The spectrum at 675 K in figure 3B clearly shows a new mode around 4485 cm^{-1} and is also attributed to Si-OH bond¹⁰⁻¹¹. The variations in the integrated peak areas of water modes are the better represent of water loss/gain¹². The thermal variations in the integrated peak areas of stilbite and scolecite in the wavenumber region 6310-7500 cm^{-1} and 4585-5845 cm^{-1} are plotted in figure 4 and 5 respectively. Solid circles and open triangles represent the combinations and overtones respectively. The inset in figure 4 shows the evolution and thermal variations of the mode at 4550 cm^{-1} of stilbite. The inset in figure 5 shows the thermal variations of Al-OH bond around 4609 cm^{-1} and evolution of Si-OH bond around 4485 cm^{-1} .

4. DISCUSSION

The dehydration and rehydration properties of zeolites are applicable in the purification of wastewater by removal of ammonium ion, heavy metal ions and radioactive cations¹. Thus, it becomes important to understand the thermal stability and the molecular linkages during the dehydration and rehydration processes.

On the basis of thermal behaviour, zeolites are classified in to the following categories. (1) Reversible dehydration with little or no modifications in the framework and cell volume; (2) reversible dehydration accompanied by a large distortions in the framework and significant decrease in the cell volume; and (3) partially irreversible dehydration accompanied by breakage of T-O-T bonds¹. In the stilbite the decrease in the cell volume is marginal up to 420 K and rather sharp by -3.24% at 420 K. Further decrease about -3.81% in the temperature range 430-520 K is reported, and the phase with in the temperature range is called stilbite 'B'⁶. The transition namely stilbite A to B is clearly observed around 450 K in our case with a almost sudden drop in water modes (see Fig 4), and the discrepancy in the temperature we attribute to different heating rates and chemical compositions. We observed no modifications in the structural modes during the dehydration of stilbite A phase. Upon cooling from 475 K, the stilbite rehydrated completely

within a short interval of five hours. Reversible dehydration of stilbite with in it's A phase (300-450 K) with no modifications in framework (as seen from the thermal induced variations of network IR modes – see ref 11) indicate that it belongs to the first class of zeolites classified by Bish and Carey¹.

Stahl and Hanson⁸ reported that the initially expelled water in scolecite is hydrogen bonded to an O atom in AlO_4 tetrahedra. Besides the water modes in our spectra of scolecite at 300 K (Fig 3B) has a band at 4609 cm^{-1} . This band is assigned to Al-OH bonding¹⁰. The variation in the total peak area of this band is shown in the inset of figure 5. This mode decreased continuously with temperature and vanished at 500 K corroborating the studies of Stahl and Hanson⁸. Stahl and Hanson⁸ reported a change in the crystal symmetry on initial dehydration, transforming scolecite to metascolecite phase at 480 K. A large variation in the water concentration around 495 K (figure 5) and collapse of Al-OH bond implies change in the crystal symmetry. Thus, the dehydration behaviour observed in the water modes of scolecite is different to that in stilbite. Our detailed investigations on scolecite indicate that the dehydration is reversible when the samples are heated upto 575 K. As seen in fig 5 inset disappearance of mode at 4609 cm^{-1} as the temperature increased to 500 K, indicates a considerable decrease in Al-OH type bonds. This could occur during the dehydration process involving distortions around Ca (extra-framework cation). These observations corroborate the mechanism proposed by Stahl and Hanson⁸. A completely reversible dehydration of scolecite with slight modifications in the framework structure during the dehydration, the temperature range 300-575 K, indicates that it belongs to second type of zeolites classified in Bish and Carey¹.

We also observed a new band around 4550 cm^{-1} with the on-set of stilbite B phase. This band is assigned due the presence of silanol groups¹⁰⁻¹¹. This band became prominent at a temperature around 650 K (Fig 3A). The variations in the total peak area of this band are shown in the inset of figure 4. Similarly in scolecite we observed the evolution of a new band around 4485 cm^{-1} . The thermal variations of this band are plotted and shown in the inset of figure 5. This band appeared at 630 K and became prominent at 675 K. This band arises due to the distortions created in the framework of zeolite during the dehydration and causing breakage of T-O-T linkages. And the hydroxyl groups attach the Si forming silanol bond. The above results corroborate our previous results¹¹ and the reported data of cruciani et al⁶. The rehydration behaviour of stilbite heated to 630 K is observed. The stilbite rehydrated partially with in a period of one day. Partially reversible dehydration with modifications in the framework of this stilbite dehydrated with in a temperature range 450-630 K indicate that it belongs to the third kind of zeolites classified in Bish and Carey¹. These zeolites when heated to elevated temperatures (around 800-850 K) became amorphous.

In summary, we studied the dehydration and rehydration of naturally occurring zeolites (stilbite and scolecite) using FTIR spectroscopy. We investigated thermal induced variations of second order modes of water molecules in zeolites. The observed variations indicate that the transition of stilbite is at around 450 K and scolecite around 495 K. The stilbite and scolecite rehydrated completely within short interval of five hours upon cooling from 475 and 575 K respectively. The rehydration of the stilbite is partial in the sample heated to 630 K. Growth of silanol bonds in stilbite (4550 cm^{-1}) and scolecite (4485 cm^{-1}) is observed in the temperature range of 430-650 K and 630-675 K, respectively, indicating the breakage of T-O-T bonds, which trigger the destruction of zeolite network structure. At elevated temperature the structure of zeolites collapsed completely.

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FIGURES

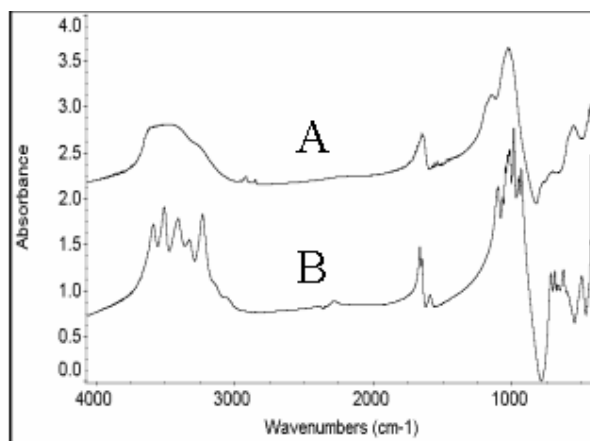


Fig 1: Back ground corrected Mid IR spectra of stilbite (A) and scolecite (B).

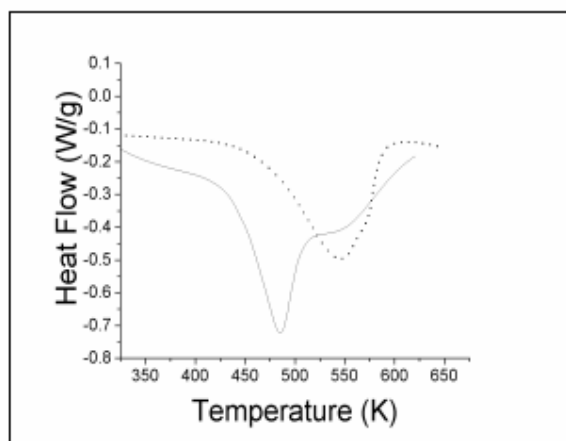


Fig 2: Differential Scanning Calorimetry of stilbite (—) and scolecite (---).

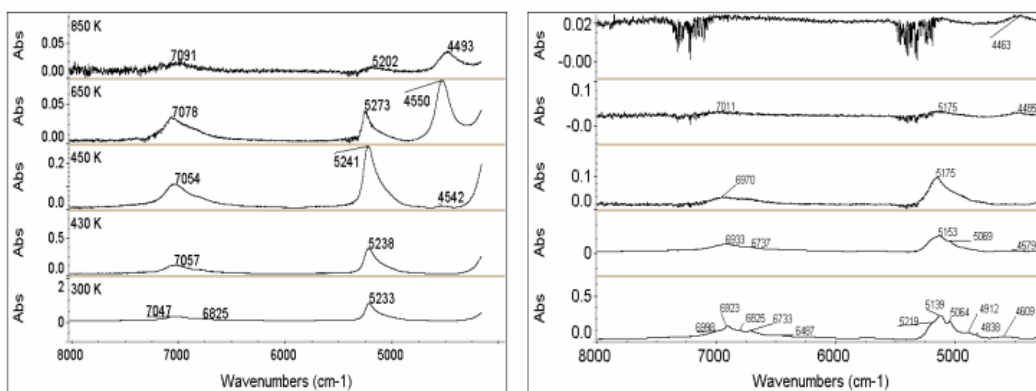


Fig 3: A: Background corrected spectra of stilbite at different temperatures (300, 430, 450, 650, 850 K) in the wavenumber region 4000-8000 cm^{-1} . B: Background corrected spectra of scolecite at different temperatures (300, 430, 495, 675, 875 K) in the wavenumber region 4000-8000 cm^{-1} .

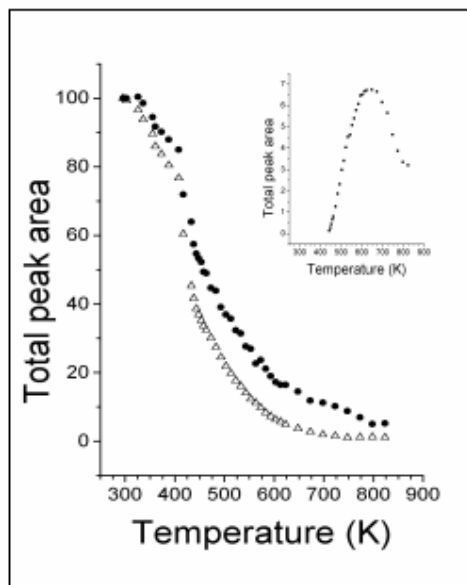


Fig 4: The variations in the normalised peak areas for the combinations (solid circles) and overtones (open triangles) of water molecules in stilbite. The inset in the figure is the variations in peak area of mode at 4550 cm^{-1} .

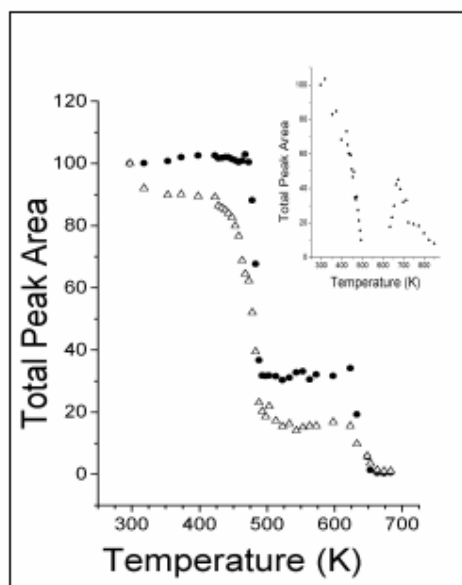


Fig 5: The variations in the normalised peak areas for the combinations (solid circles) and overtones (open triangles) of water molecules in scolecite. The inset in the figure is the variations in peak area of mode at 4485 cm^{-1} (solid triangles) and mode at 4609 cm^{-1} .