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DEHYDRATION BEHAVIOUR OF SCOLECITE CRYSTALS

M.S. JOSHI, A.L. CHOUDHARI, P. MOHAN RAO and R.G. KANITKAR

Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat (India)

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ABSTRACT

Dehydration and rehydration behaviour of natural scolecite crystals are studied using DTA, TG, X-ray and IR techniques. Before structure collapse, the structure sensitive bands are found to change with temperature. No changes in OH stretch and H_2O bend are observed up to 300°C. The changes in these two modes are observed above 300°C. From the appearance of the new bands above 500°C, it is concluded that the samples have transformed into some new form. Rehydration behaviour is also studied by a static weight-loss method.

INTRODUCTION

Zeolites form a well-defined group of hydrated aluminosilicates of the alkali or alkaline earth metals. In most of the naturally occurring zeolites the main cations present are Ca, Na and K. These cations are loosely bound with the framework. Water molecules, present within the channels, are also loosely bound with the framework and cations.

On heating, the water in the zeolites is given off, either continuously or in stages at certain temperatures. On the other hand, on exposure to water vapour, completely or partially dehydrated zeolites can absorb it, without significant changes in the framework up to a certain temperature.

Scolecite belongs to a class of zeolites under the natrolite group. It is widely available as a fibrous zeolite, occurring in the cavities of the basaltic rocks and in contact zones.

Chemical analysis of scolecite has been reported by Hey [1] and Sukeshwala et al. [2]. Its structure has been proposed by Pauling [3], Taylor et al. [4], Ileva and Gabuda [5] and by Fäth and Hanseen [6]. The oxide formula and unit cell formula of scolecite are $CaO \cdot Al_2O_3 \cdot 3\ SiO_2 \cdot 3\ H_2O$ and $Ca_8[(AlO_2)_{16}(SiO_2)_{24}] \cdot 24\ H_2O$, respectively.

Eight out of twenty-four water molecules in the unit cell occupy vacant cation sites, and the remaining sixteen molecules are coordinated to oxygen in the framework and calcium ions in the channels.

For the present studies scolecite crystals were collected from quarries in the Pashan area, Poona, India. Their dehydration behaviour was investigated using a static weight-loss (SWL) method, TG, DTA, IR spectroscopy and X-ray diffraction. The results obtained are reported in this paper.

EXPERIMENTAL DETAILS

Scolecite crystals were cleaned with double distilled water. They were then coated with gold and examined by EDAX. The crystals were also examined by electron probe micro-analysis.

Two grams of powdered (200 mesh) scolecite were placed in a crucible and heated in an electric furnace at 200°C for 4 h. Soon after its removal from the furnace the sample was weighed. It was then exposed to the atmosphere overnight, and then weighed again. This procedure was repeated at 250, 300, 350, 400, 450, 500 and 550°C. From these observations percentage weight loss and percentage weight gain were estimated. Thermogravimetric and differential thermal analyses were carried out at a heating rate of 10°C min^{-1}. Infrared spectroscopy was used to investigate the framework changes of the samples. X-Ray powder diffractograms (using Cu K_α radiation and a speed of 5′ min^{-1}) were taken at each stage to check the crystallinity of the sample.

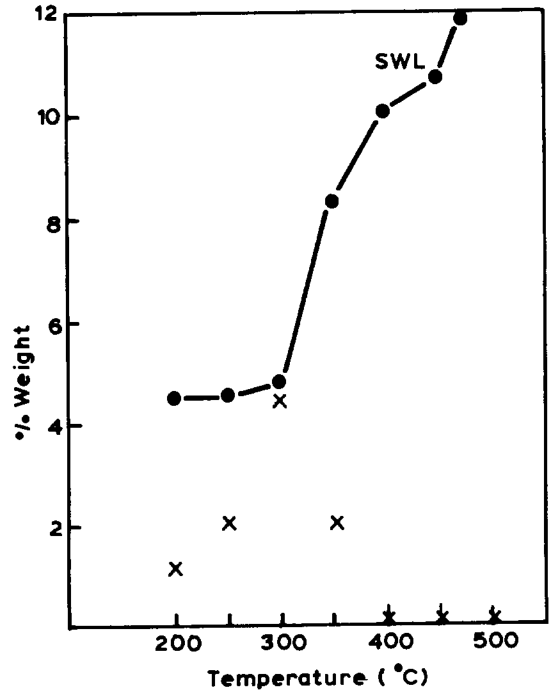

Fig. 1. SWL curve. Points X indicate the degree of rehydration.

RESULTS AND DISCUSSION

Energy dispersion analysis of X-rays (EDAX) indicated the presence of Si, Al and Ca in the samples under study. The Si/Al ratio computed by this method turns out to be in the range 1.6–1.7, which is in close agreement with values reported [2] on the basis of chemical analysis.

The results of the SWL method are shown in Fig. 1. Between 200 and 300°C the weight loss increases very slowly. There is a rapid increase above 300°C. The points marked "X" indicate the degree of rehydration. It is clearly seen that rehydration gradually increases with temperature (above 200°C), reaches a maximum (at 300°C) and then decreases. Rehydration is negligible at and above 400°C.

DTA and TG curves of the scolecite samples are depicted in Fig. 2. Of the three endothermic peaks in the DTA curve, only two (at 280°C and 470°C) have corresponding steps in the TG curve. The DTA curve exhibits a third endothermic peak at 540°C. X-Ray analysis of these samples indicates structure collapse of scolecite around 500°C. One more endothermic peak is observed in the DTA curve at 980°C. This leads to transformation into a possibly new form.

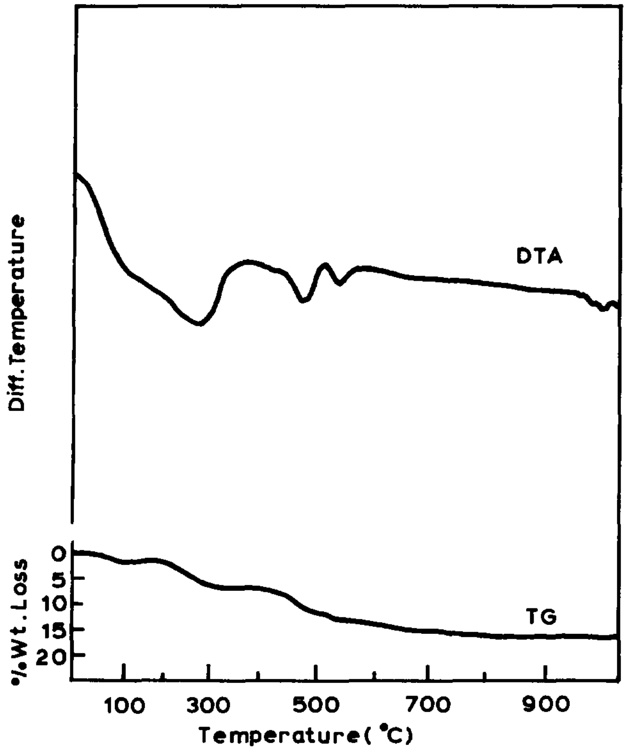

Fig. 2. DTA and TG curves.

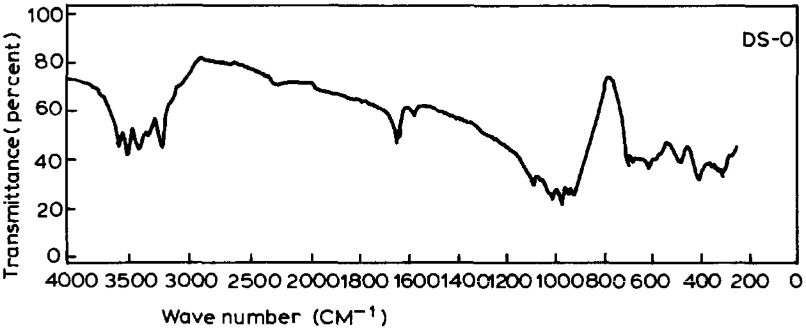

Fig. 3. IR spectrum of as-found scolecite.

In the DTA curve a step at 280°C corresponds to a water loss of 6.5% and that at 470°C gives a water loss of 11.5%. The remaining amount of water is lost continuously on further heating. The total water loss is estimated at 16% as evidenced by the graph. In the TG curve ten H_2O molecules are lost at the first stage and eight at the second.

Infrared spectral studies give useful information about the constitution and surface properties of zeolites, and also how these are modified by various treatments to the samples. Zhdanov et al. [7,8] and Flanigen et al. [9] have used infrared spectroscopy to study major structural information such as framework Si/Al composition, structural changes, etc. during dehydration and dehydroxylation. Their studies were mainly on synthetic zeolites.

Infrared spectra of scolecite samples, dehydrated at the temperatures cited and consequently rehydrated, were recorded at room temperature using a Perkin Elmer 180 IR spectro-photometer using the KBr technique. Out of the infrared spectra recorded in the present study only three spectra are shown, one in Fig. 3 for as-found scolecite and two in Fig. 4, for scolecite treated at 500 and 550°C. Tables 1 and 2 show the frequency assignment of bands in the spectra.

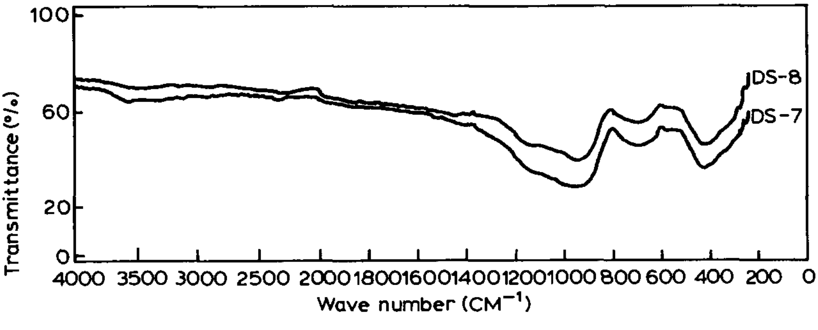

Fig. 4. IR spectrum of scolecite samples treated at 500 and 550°C.

TABLE 1

Frequency assignments for bands found in the IR spectra of scolecite samples

Sample	Temperature (°C)	Pore opening (cm^{-1})	T–O bend (cm^{-1})	Symmetric stretch, sensitive (cm^{-1})	Symmetric stretch, insensitive (cm^{-1})	Symmetric stretch, sensitive (cm^{-1})	Internal tetrahedra asymmetric stretch (cm^{-1})
DS0	As-found	305 ms, 405 ms	470 ms	590 vvw, 620 w	680 w	710 w	920 w, 940 w, 980 ms, 1010 w
DS1	200	305 ms, 405 ms	470 ms	590 vvw, 620 w	680 w	710 w	920 w, 940 w, 980 ms, 1010 w
DS2	250	305 w, 405 ms	470 ms	590 wb, 620 w	680 w	710 w	920 w, 940 w, 980 ms, 1010 w
DS3	300	305 w, 405 ms	470 ms	590 wb, 620 w	680 vw	710 vw	920 w, 940 w, 980 ms, 1010 w
DS4	350	305 vvw, 405 wb	470 sh	590 wb, 620 vw	680 vvw		920 w, 940 sh, 980 w, 1010 sh
DS5	400	305 vvw, 405 wb		590 wb, 620 sh	680 vvw		920 vvw, 940 sh, 980 w, 1010 sh
DS7	500	430 vvb			680 b		950 b, 1010 sh
DS8	550	430 vvb			680 b		950 b, 1010 sh

s, strong; ms, medium strong; w, weak; vw, very weak; sh, shoulder; wsh, weak shoulder; b, broad.

TABLE 2

Frequency assignments for bands found in the IR spectra of scolecite samples

Sample	Temperature (°C)	External linkage asymmetric stretch (cm^{-1})	H_2O bend (cm^{-1})	OH stretch (cm^{-1})
DS0	As-found	1060 sh, 1095 ms	1580 ms, 1640 s, 1660 s	3050 sh, 3140 sh, 3220 s, 3320 w, 3400 s, 3500 s, 3580 ms
DS1	200	1060 sh, 1095 ms	1580 ms, 1640 s, 1660 s	3050 sh, 3140 sh, 3220 s, 3320 w, 3400 s, 3500 s, 3580 ms
DS2	250	1060 sh, 1095 w	1580 w, 1640 s, 1660 s	3050 sh, 3140 sh, 3220 s, 3320 w, 3400 s, 3500 s, 3580 ms
DS3	300	1060 wsh, 1095 w	1580 w, 1640 ms, 1660 ms	3050 sh, 3140 wsh,3220 ms, 3320 w, 3400 s, 3500 s, 3580 ms
DS4	350	1060 wsh, 1095 sh	1640 w, 1660 w	3050 sh, 3220 w, 3320 sh, 3400 w, 3500 w, 3580 w
DS5	400	1095 wsh		3220 wb, 3320 wsh 3400 sh,
DS7	500			
DS8	550			

s, strong; ms, medium strong; w, weak; vw, very weak; sh, shoulder; wsh, weak shoulder; b, broad.

Structure-sensitive bands are found to change (showing an intensity reduction) before structure collapse, whereas, structure-insensitive bands are unaffected. Structure-sensitive bands in Tables 1 and 2 provide information on the decrease in crystallinity of the samples. No changes in OH stretch and H_2O bend are observed up to 300°C. Only above 300°C are there changes in these two modes. These bands are absent in the infrared spectra at 500 and 550°C, indicating stages of structure collapse and post structure collapse. From the appearance of the new bands above 500°C, it is concluded that the samples have transformed into some new form.

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