

Studies on Thermal Behaviour of Ca-Clinoptilolite Crystals from Marathwada, India

B.T. BHOSKAR† and S.D. GHAN*

Department of Physics, N.E.S. Science College, Nanded-431 602, India

The freshly extracted zeolite crystals collected from the Marathwada region of India were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), thermal analyses (TGA/DTA) and wet chemical analysis method as the Ca-clinoptilolite. The powder of the crystals was treated at various temperatures *viz.*, 50, 100, 150, 200, 250 and 300°C. At each stage the structural changes were studied by using mid-infrared spectroscopy. Thermogravimetric and differential thermal analysis were used to study the water loss at different stages and the corresponding structural changes. It has been inferred that the structural changes are temperature dependent and can be well studied with the help of infrared spectroscopy.

Key words: Thermal, behaviour, Ca-clinoptilolite, crystals.

INTRODUCTION

Clinoptilolite is a silica-rich zeolite that belongs to 7th group of platy zeolites¹. Heulandite, another platy zeolite of the same group and clinoptilolite are iso-structural but their thermal stability, Si/Al ratio and cation contents are different. Boles² investigated the relationship between chemical composition and thermal behaviour of these zeolites and proposed the name of the zeolite as clinoptilolite if Si/Al > 4 and if Si/Al < 4, the zeolite is termed as heulandite. There are two varieties of clinoptilolite, one silica-rich is called as simply clinoptilolite, whereas the low silica clinoptilolite is known as Ca-clinoptilolite³.

Clinoptilolite occurs as an alteration product of the acidic volcanic glass fragments in volcanoclastic sediments. They commonly co-exist with aluminous low cristoballite and smectite replacing glass⁴.

The framework structure of the clinoptilolite consists of a common unit which contains 10 nodes, known as the 4-4-1 unit⁵. These units are connected so as to share one or two nodes in zeolites. In clinoptilolite, they yield the important characteristics of two types of channels parallel of the 'a' and 'c' axes. The openings of these channels are formed by eight-membered rings (diameter 0.40 × 0.55 nm) and ten-membered rings (diameter 0.44 × 0.72 nm) respectively¹.

The clinoptilolite crystals used in the present investigation were collected from the Marathwada region of India. In the present study an attempt has been made to investigate the change in the structural properties of Ca-clinoptilolite treated at 50 to 300°C by infrared spectroscopy.

EXPERIMENTAL

The freshly extracted crystals were separated from the geodes. Then crushed

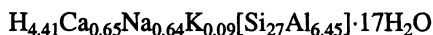
†Department of Physics, Nutan Mahavidyalaya, Sailu-431 503, India.

and sieved to get 150 μm sized crystals. The powdered sample was washed repeatedly with distilled water to remove soluble impurities and dried.

The characterization of the sample was carried out by X-ray diffraction, infrared spectroscopy, thermogravimetric and differential thermal analysis and by wet chemical analysis. A known amount of Ca-clinoptilolite powder (2 g) was heated at various temperatures, *viz.*, 50, 100, 150, 200, 250 and 300°C for a period of 2 h. The IR spectrum of each sample was recorded in the range 1300–400 cm^{-1} . The observed frequencies were correlated with the structural groups.

The X-ray diffraction of the sample was recorded by using Philips diffractometer, nickel filter, $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with chart speed of 4°/min in the 2θ values ranging from 5°–50°. The 'd' values and the peak intensities were compared with the reported data⁵.

The chemical contents of the sample were determined by wet chemical analysis method. The Na, K and Ca contents were obtained by atomic absorption spectroscopy employing a Hitachi-Z8000 instrument. From such analyses and by applying O_{72} formula the unit cell contents were determined as



with the Si/Al ratio of 4.14.

The TGA, DTG and DTA curves of the sample were recorded on 'Setaram 92' thermal analyzer from ambient temperature to 1000°C in air atmosphere at a heating rate of 10°C/min using calcined alumina as a reference material.

The infrared spectra of the sample were recorded on Shimadzu C-infrared spectrophotometer using Nujol Mull technique in the range 4000–400 cm^{-1} . The details of the frequencies are given in Table-1. For the thermally treated samples, the range was 1300–400 cm^{-1} . Observed spectral frequencies are given in Table-2.

RESULTS AND DISCUSSION

Thermal Studies

It has been realised that, for its zeolitic properties, studies on thermal stability of zeolites have got importance. Such studies on the thermal stability of heulandite and clinoptilolite have been reported⁶⁻⁸.

The TGA, DTG and DTA curves are depicted in Fig. 1. The TGA curve for the sample demonstrates the loss of water between 50 to 240°C which is supported by broad concave DTG curve over the same temperature. The amount of weight loss due to dehydration at this stage was 8%. Further, 3% weight being lost on heating the sample between 250 and 320°C. The total of 16% weight loss has been estimated when the sample was heated up to 900°C.

The DTA studies of the sample showed the presence of an endothermic peak located at 190°C and of a second endothermic peak at 320°C. An exothermic peak centered at 510°C indicated the collapse of the structure within this temperature range.

The two endotherms in the DTA curve can be attributed to the two types of combined water in the voids of the zeolite. One corresponds to the water coordinated along the cations in the ten and eight membered rings. However, the

dehydration causes the deformation of the framework with the flattening of the ten and eight membered ring channels. In the second type the water is contained in the channels and cavities.

There are two exotherms in DTA curve, one at 300°C and another one at 510°C. The first one may be due to the structural rearrangements. However, the second exotherm may indicate the structural collapse.

TABLE-1
IR DATA (cm^{-1}) FOR Ca-CLINOPTILOLITE SAMPLE

<i>Internal tetrahedra:</i>	
Asymmetric stretch	1018
Symmetric stretch	667
T-O bend	450
<i>External linkages:</i>	
Asymmetric stretch	1150
Symmetric stretch	772
Double ring	520
<i>Water bands:</i>	
OH stretch	3383
H ₂ O bend	1622

Infrared Studies

Infrared spectral studies (Table-1) give information about the polyhedral framework structure and composition of zeolites. Such a study can be used to find a systematic change in the framework structure and composition by various treatments of zeolite. This type of study has been reported earlier by Joshi *et al.*^{9, 10}

The mid-infrared region of 1300-400 cm^{-1} contains the fundamental vibrations of the Si, AlO_4 units in the zeolite frameworks and, therefore, may be expected to contain useful information on the structural characteristics of the zeolite frameworks. Miezownikowski *et al.*¹¹ applied mid infrared spectroscopy to a study of the framework of zeolites as a function of framework Si/Al ratio, cation type and state of hydration.

Fig. 2 depicts the IR spectra of thermally treated samples and the observed frequencies are given in Table-2. From 50 to 150°C the structure insensitive band 1022 cm^{-1} (asymmetric stretch) remains constant with minor change, but at 200°C this band shifts toward high frequency 1105 cm^{-1} which suggests the weakening in crystallinity of the Ca-clinoptilolite. Similar results have been observed in crystallization sequence for sodium zeolite (NaX) from aluminosilicate gel by Flanigen *et al.* The structure sensitive bands at 1150 cm^{-1} (T-O band) and 770 cm^{-1} (symmetric stretch) remain with minor change, whereas a band 520 cm^{-1} (double ring D4R) disappears at 300°C.

A strong band at 667 cm^{-1} becomes weaker and weaker from 250 to 300°C and almost disappears above 300°C. The 667 cm^{-1} band is in the region where the absorption band is observed for aluminosilicates formed by the isomorphous

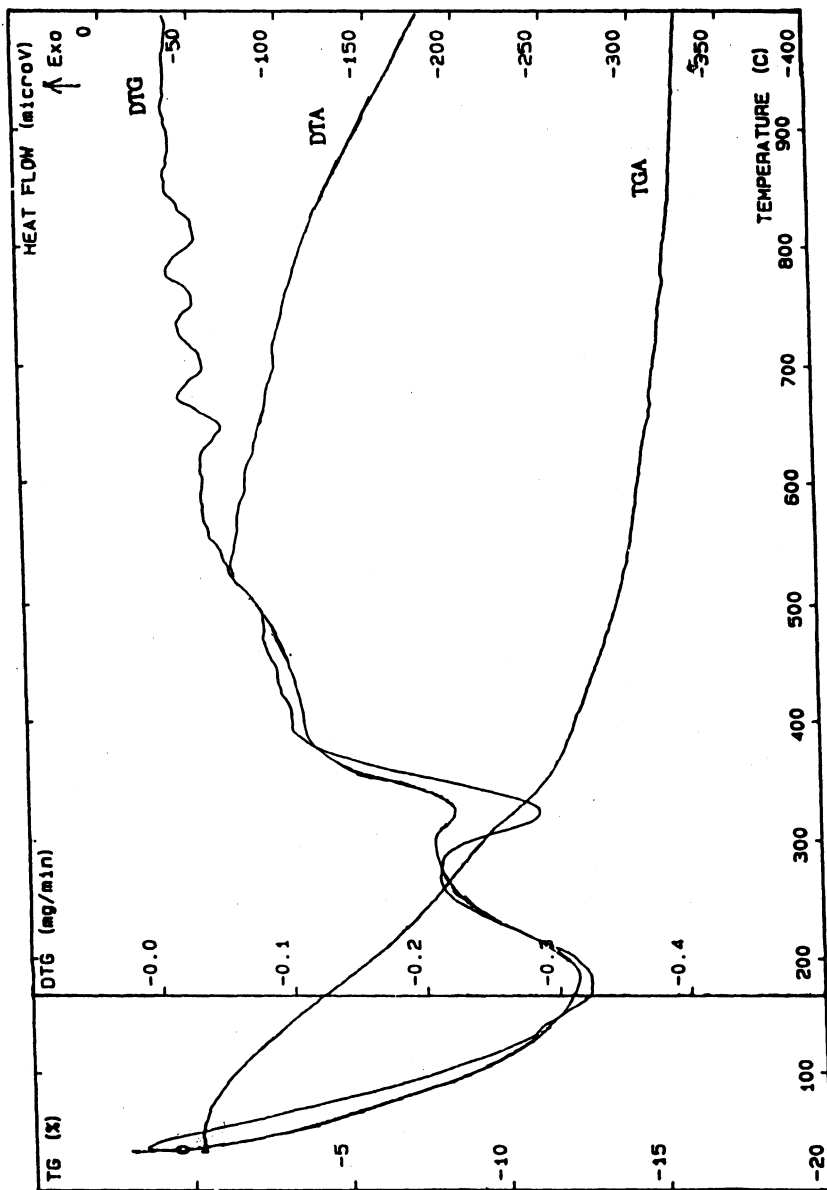


Fig. 1. TGA/DTA curves of Ca-clinoptilolite sample

TABLE 2
IR DATA FOR THERMALLY TREATED Ca-CLINOPTILOLITE SAMPLE

Temp (°C).	IR spectra	Structure insensitive bands (cm ⁻¹)			Structure sensitive bands (cm ⁻¹)		
		Asymmetric stretch	Symmetric stretch	Double ring	Asymmetric stretch	Symmetric stretch	Double ring
50	A	1018	667	450	1150	772	520
100	B	1020	667	460	1150	772	516
150	C	1022	667	446	1150	770	516
200	D	1105	667	450	1220	770	516
250	E	1105	667	450	1220	770	515
300	F	1107	667	450	1220	770	-

very weak

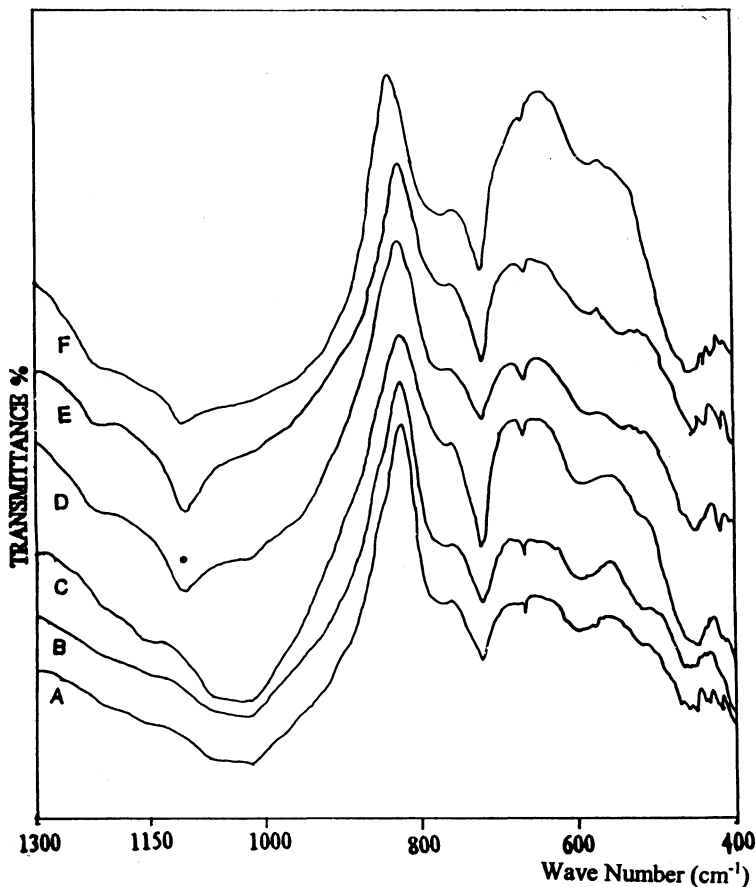


Fig. 2. IR spectra of thermally treated Ca-clinoptilolite:
A. 50°C, B. 100°C, C. 150°C, D. 200°C, E. 250°C, F. 300°C

substitution of Al^{3+} for Si^{4+} . This band has been assigned to the vibration of the Al—O bond. It has been found that in case of synthetic faujasite, the intensity of such type of band at 758 cm^{-1} diminishes with decreasing Al content in the faujasite, which indicates that it is a band belonging to the vibration of Al—O bond inside the AlO_4 tetrahedra. The absence of this band 667 cm^{-1} indicates that there is considerable distortion in framework structure and the Si/Al ratio in the residual framework is not the same as that in the original sample.

Conclusion

The occurrence of Ca-clinoptilolite crystals in Marathwada area has been recorded. The zeolitic nature of this sample has been confirmed with the help of X-ray diffraction, infrared spectroscopy, chemical analysis and DTA/TGA studies. From DTA/TGA and IR studies it can be inferred that the structural stability gets disturbed above 200°C and structural collapse at about 500°C . Thus it is possible to deduce the information about the framework structure of zeolite from the recorded IR frequencies.

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