

Dielectric study of Natural Zeolite NH₄- Clinoptilolite

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Abstract— Natural Zeolite Clinoptilolite belonging to group VII Zeolite were obtained from the quarries near Ajanta caves, Marathwada (Maharashtra). Characterization was made using XRD,IR at NCL Pune. Dielectric study was made using LCR Bridge. Pellets of NH₄ Clinoptilolite were prepared, variation of dielectric constant, dielectric loss, dielectric conductivity and relax session time were measured from 20Hz to 20KHz .Results were compared.

Index Terms— NH₄ Clinoptilolite, Characterization, Dielectric study

I. INTRODUCTION

Clinoptilolite belonging to group VII Zeolite (1)were obtained from the quarries near Ajanta caves, Marathwada (Maharashtra).The use of the zeolite crystals has been explored in the many scientific disciplines. The realization that the zeolite crystals have potential applications in the numerous areas of the scientific, industrial and agricultural technology has provided impetus for the research and development program that have been carried out in several countries. Clinoptilolite is a silica rich zeolite that belongs to 7th group of platy zeolites. Heulandite, another platy zeolite of the same group and Clinoptilolite are isostructural but their thermal stability, Si /Al ratio and the cation contents are different. Boles₍₂₎investigated the relationship between the chemical composition and thermal behavior 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.

The unit cell parameter of Clinoptilolite is
a= 17.62Å°, b=17.91Å°, c=7.39Å°, β=116°, 18'

Clinoptilolite has been utilized intensively in environmental applications such as treatment of waste water from nuclear factories (5), remediation of radioactive soils (6), the treatment of sewage and agricultural effluents (7) etc. In such environmental applications, Clinoptilolite is valued for it's high cation exchange selectivity for Cs , Sr and NH₄⁺ during ion exchange

As the Si/Al ratio increases for a group of zeolites ,the stability to acid attack also increases. The blocking effects of the cations in Clinoptilolite can therefore be minimized by the acid treatment, which reduces the cation exchange capacity by leaching Al⁺⁺⁺ from framework positions and substitutes H⁺ into the few remaining cation positions. Exchangeable cations are first replaced by hydrogen, followed by the hydroxylation of the Al-O bonds in the frame works, and the removal of ammonium from the framework into solutions . Acid

treatment of several high silica natural zeolites produces a range of improved or modified sorbents both via , the mechanism of Dactionation and deallumination , and by dissolving any silica blocking channels in the structures by acid treatment on Clinoptilolite. surface area could be increased and effective pore size could be enlarged to allow the sorption of the benzene and isopentane . It also sorbs Kr, CO₂ and H₂O.

II. SAMPLE PREPARATION

Clinoptilolite were collected from the quarries of Ajanta caves , Marathwada (Maharashtra). Sample was crushed and sieved to get 106 μm sized crystals for the ion exchanged. The sample is treated with 1 M solution of Ammonium Nitrate with stirring at 95°C. for the six hours. NH₄ ion exchanged form of Clinoptilolite is heated at 250°C for 48 hours for getting H – Clinoptilolite.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns were recorded between 2θ values from 5° to 50° on Phillips model (PW 1710)with Cu Kα wavelength= 1.54056 Å°. Diffractogram are recorded for the parent Clinoptilolite , NH₄ – exchanged Clinoptilolite and H – form Clinoptilolite. D values & intensities are recorded in table 1

XRD – Pattern of the parent Clinoptilolite, NH₄ – exchanged Clinoptilolite and H – form Clinoptilolite is shown in fig.1. From diffractogram we determine the crystalline nature of Clinoptilolite d- values are compared with standard 'd' values. This confirms the Clinoptilolite structure. There is no major change in diffractograms of these three forms. The intensity in NH₄ – Clinoptilolite and H – form Clinoptilolite increases.

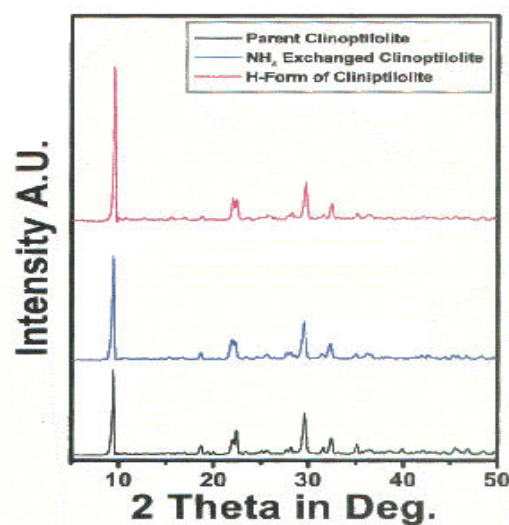


Fig 1 XRD pattern of clinoptilolite

2 Theta	d-Value	Peak Width	Intensity
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09.91	08.93	0.12	100
16.64	05.33	0.06	1.3
19.11	04.65	0.06	6.4
19.83	04.48	0.12	1.9
22.28	03.99	0.16	3.7
22.75	03.91	0.16	3.8
23.84	03.73	0.24	0.9
25.46	03.50	0.16	1.2
28.54	03.13	0.16	1.5
29.95	02.98	0.12	15
30.23	02.96	0.16	7.3
31.95	02.80	0.16	1.8
32.89	02.72	0.28	2.7
35.52	02.53	0.20	1.6
40.28	02.24	0.16	2.6
42.47	02.13	0.24	1.1
44.67	02.03	0.64	0.4
45.97	01.97	0.24	1.5
47.27	01.92	0.32	0.6
48.96	01.86	0.40	0.4

Table.1- XRD Data For Clinoptilolite (After Background Subtraction)

Infrared Studies:

The infrared spectra of Clinoptilolite was recorded on perkin – Elmer – 221 Spectrophotometer in the frequency range 400 – 4000 cm⁻¹ of NH₄ – form, H – form & parent form at 100°C, 150°C and 200°C. The observed IR bands and assignments are given in table 2

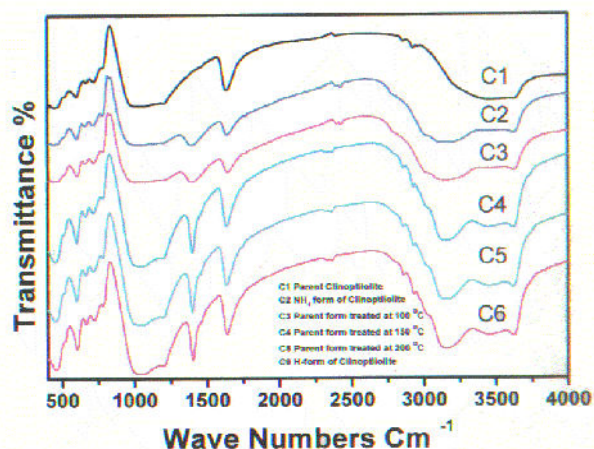


Fig. 2 IR of clinoptilolite from 400-4000

Sample Name	External linkage cm ⁻¹ Str. sensitive		Double ring	Internal Tetrahedral Str Insensitive cm ⁻¹		T – 0 Bend	Water Bands	
	Asymmetric Stretch	Symmetric stretch		Asymmetric Stretch	Symmetric stretch		OH-stretch	H ₂ O Bands
Clinoptilolite	1391	772	598	1250	750	490	3625	1630
Heulandite	1200	795	599	1095	750	490	3740	1655
Stilbite	1417	833	616	1045	816	443	3605	1659

Table2 . IR assignments in Cm⁻¹

IR spectra of heat treated zeolites provide new data concerning their dehydration and rehydration, the state of water, and the existence of hydroxyl groups and hydronium ion. The IR of Clinoptilolite and their ion exchange forms shows that depending on the radius, atomic number and valence of the exchange cations, change in the position of maxima and the intensities of high frequency bands takes place in the range of 400 to 4000 cm⁻¹

IR bands for Clinoptilolite are shown in table 2. in external linkage, asymmetric stretch is observed at 1391 cm⁻¹ & symmetric stretch is at 795 cm⁻¹, OH- stretch is at 3625 cm⁻¹ and the water bands are 1630 cm⁻¹. Double ring is observed at 598 cm⁻¹. Zeolite structure is insensitive to the asymmetric stretch at 1250 and symmetric stretch at 750 cm⁻¹ bands at 490 is observed due to the vibration of Si – O or Al – O bond. As we heat the parent sample at 100°C, 150°C, 200°C & H – form Clinoptilolite there is no major change in IR spectrum this confirms the stability of the Clinoptilolite. Only water bands become more intense and OH – stretching is more intense than the parent form of Clinoptilolite.

Dielectric constant (ε'): The variation of Dielectric constant to frequency of NH₄ - Clinoptilolite is shown in fig 3. Decrease in dielectric constant is observed up to frequency 5000 KHz. Then ε' increases slowly or nearly remain constant. Also observed that dielectric constant increases with increase in thickness of the sample

Dielectric Loss (ε'') : Fig 4 shows that the variation of ε'' against frequency decrease in ε'' with increase in frequency is observed

Relaxation Time :- Fig 5. shows the variation of relaxation time against the frequency. There is decrease in (τ) as the frequency increases.

A.C. Conductivity:- Fig.6 shows the variation of conductivity against frequency as frequency increases the conductivity goes on increasing, initially σ increases up to 5000 (KHz). Then decreases up to 6000 (KHz). Then increase linearly as thickness increase the σ goes on increasing.

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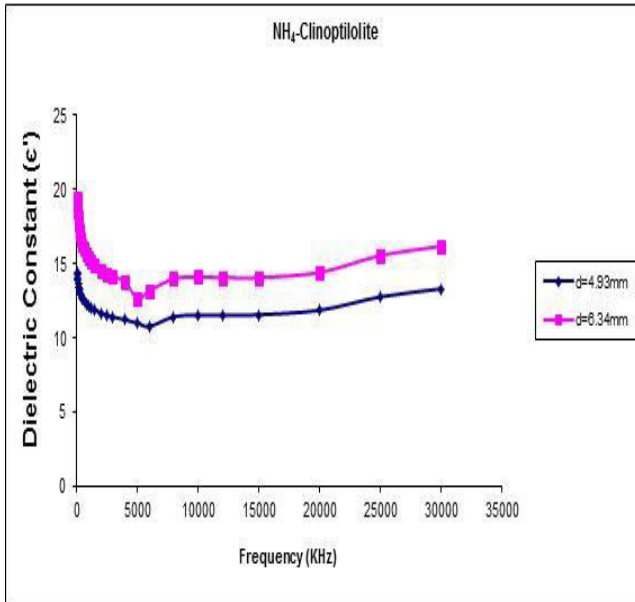


Fig. 3 Variation of dielectric constant as a frequency in NH_4 clinoptilolite

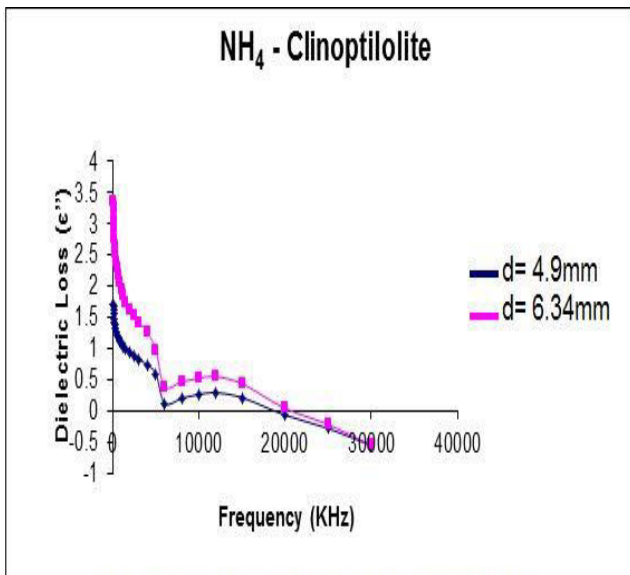


Fig. 4. Variation of dielectric loss as a frequency in NH_4 clinoptilolite

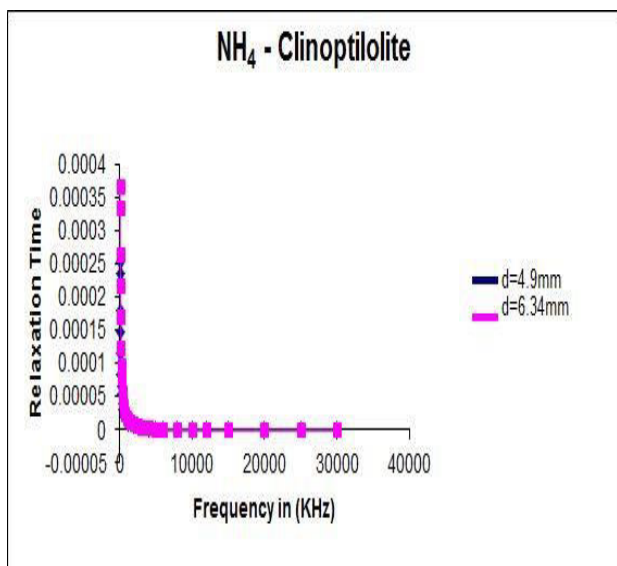


Fig. 5 Variation of relaxation time as a frequency in NH_4 clinoptilolite

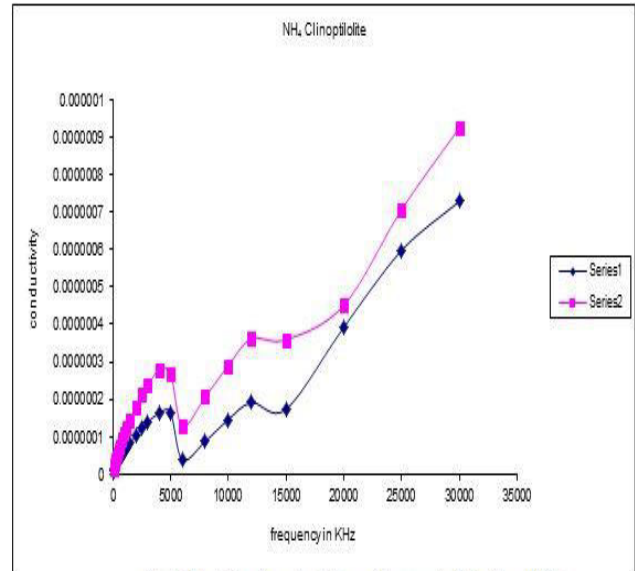


Fig. 6 Variation of conductivity as a frequency in NH_4 clinoptilolite

CONCLUSIONS

There is no major change in XRD Pattern of three forms of Clinoptilolite. IR bands confirm the stability of Clinoptilolite, Dielectric study of NH_4 Clinoptilolite plays an important role in stating the nature of zeolite. From chemical analysis we conclude that there is no structural change in zeolite by ion exchange of zeolite except cation exchange.

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