

Dielectric Study of H-Mordenite

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Abstract— Zeolite Mordenite belongs to Group VII were collected near Ellora Ajanta belt. characterization was made using XRD,IR at NCL Pune.Dielectric study was made using LCR Bridge. Pellets of H-Mordenite 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— H- Mordenite,Characterization,Dielectric study

I. INTRODUCTION

Zeolites of the Mordenite group are stable to high temperature. Mordenite is one of the natural zeolites abandoned enough for commercial exploitation, and the synthetic varieties have been used for two decades. Zeolites structures have been classified on the bases of secondary building units. Structure types assigned to the Mordenite group can be built from 5-1 units consisting of the single 5 ring and attach tetrahedron. The structure of Mordenite was determined by Meier(1961) and consists of chains of 5 membered rings parallel to C axis connected through double eight membered rings in the AC plane . These are joined to give 12 ring channels in the Sea direction. With double 8 ring prisms lining the channel in the AC plane as adjacent 8 ring prisms are offset about 3.7 \AA in the sea direction ($C/2$), the path between the 12 ring channels is very distorted 8 ring having a minimum free diameter of about 2.8 \AA .Early studies of Mordenite showed that assist to the structure was limited to molecules having a diameter of less than 4.2 \AA .

Meier explained this by proposing that faulting occurs parallel to the $[001]$ plane in the $[010]$ direction. Such displacements replaces the 12 ring diffusion part by an 8 ring part and produces a structure consistent with much of the sorption data of the natural Mordenite. The compositions of the Mordenite fall within a narrow Si/Al range of 4.4 to 5.5 and generally have calcium and sodium as the major cations . The high Si/Al ratio make this one of the most thermally and acids stable zeolites. Mordenite can be readily deacidated and dealluminated by acid solutions which are of the particular interest as catalysts and catalytic promoters. To differentiate between Mordenite having 12 member ring channels and those having 8 channels sand (1968) proposed the generally accepted terms large port and small port. Natural mordenites are small port. Synthetic varieties may be either small or large port depending on synthesis conditions and washing procedures. Many small port varieties can be converted to large port form by acid treatments or ammonium exchange. Recent work on ammonium Mordenites indicates that these dealluminate like acid treated Mordenite .

Early sorption experiments on Mordenite show that the mineral rapidly sorbs NH_3 and CO_2 and O_2 , N_2 and Ar but sorption of CH_4 and C_2H_6 is very slow . Sorption capacity is generally increased in going from the sodium to H form. The high Silica to Alumina ratio of Mordenite make them interesting sorbents for acidic gases . Sodium and H Mordenite are good sorbents for HCL and NH_3 respectively. Several investigations have shown that Mordenite have the acid stability, selectivity and capacity to SO_2 and SO_3 from stack gases sorb NO_2 commercial availability of the synthetic large port Mordenite was a major stimulus to hydrocarbon sorption research on Mordenite.

Mordenite is a zeolite with an ideal composition $\text{Na}_8[(\text{AlO}_2)_8(\text{SiO}_2)_{40}]24\text{H}_2\text{O}$. It's structure is orthorhombic with unit cell parameters $a=18.11 \text{ \AA}$, $b=20.46 \text{ \AA}$ and $c=7.52 \text{ \AA}$ [1]. The aluminosilicate skeleton consists in parallel elliptical channels with 12 or 8 ring apertures. The main channels are interconnected by a small side channels. Mordenite is a naturally occurring silica rich zeolite (Si/Al ~ 5). The Si/Al ratio in a Mordenite is an important factor for it's thermal stability and reactivity [2].

Large deposits of Mordenite are present as sediments in the ocean and in saline alkaline lakes. In zeolitized tuffs Mordenite content sometimes reaches 70% and more. Si/Al – ratio is reasonably at the constant 4.5-5.5. Exchangeable cations are represented by the calcium and sodium in different ratios; potassium and magnesium are present in small amounts. This chapter deals with the dielectric properties of Mordenite.

II. SAMPLE PREPARATION

The zeolites under the study were collected from the quarries near Ajanta and Ellora caves. Ion exchange in zeolites is usually a relatively simple task. The alteration in the composition of the cations may produce some remarkable change in zeolite properties.

The freshly extracted crystals were separated from the geodes. Then crushed and sieved to get $106 \mu\text{m}$ sized crystals. The powdered sample was washed repeatedly with distilled water to remove soluble impurities and dried. The as grown sample was treated at 95°C for six hours in 1 M solution of Ammonium Nitrate (NH_4NO_3) with a solid solution ratio of 1:15 with stirring. After washing with distilled water filtering and drying at 80°C for the several hours the ion exchanges sample were obtained. The samples so obtained were used to study the Physicochemical properties.

NH_4 ion exchange form of Mordenite is heated at 250°C for 48 hours & obtained H- Form of Mordenite.

III. CHARACTERIZATION

3.1 X-ray Diffraction :- The X-ray diffraction were recorded between 2θ values ranging from $5^\circ - 50^\circ$ with a chart speed of 1 /min on a Phillips x- ray diffractometer (model PW 1710 BASED) and Ni filtered having wavelength $\text{CuK}\alpha$ radiation ($\lambda= 1.54056 \text{ \AA}$). Continuous scan type was

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used for the analysis of the samples. The x-ray diffractograms are recorded for parent Mordenite, NH₄ exchanged Mordenite and H-form Mordenite in fig 1 the relative intensities and 'd' values compared with standard 'd' values reported and are given in table 1

3.2 Infrared Studies:- The IR spectra of parent Mordenite, NH₄ form and H form of Mordenite were recorded on a Perkin – Elmer – 221 spectrophotometer in the frequency range 400 to 4000 cm⁻¹ using Nujol Mill technique. The parent Mordenite at the temperature 100, 150 and 200 °C were recorded on the same model

The observed infrared bands and assignment are given in table 2. Structure sensitive, structure insensitive and the water bands are compared with the reported data (3) which confirms the framework structures of these zeolites.

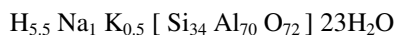
IV. CHEMICAL FORMULA

The chemical analysis was carried out by wet chemical analysis method. The chemical formula obtained from chemical analysis of Mordenite is as follows:

In parent form



In H – form



V. DIELECTRIC STUDIES

For the dielectric studies, Mordenite of H –form was taken in pellets form of different thickness. Pellets are formed under the pressure of 8 tones. The electrode polarization could be reduced greatly by improving the electrode contacts with the silver pest pressed on the pallets. The powder samples of H Mordenite were treated with Polyvinyl Alcohol (PVA) and then pelletized at a pressure of 8 tones. The dielectric properties were measured on pellets (Coated with Ag Paste as electrodes). Using the observation were close to each other and the values were averaged.

Frequency range 75KHz to 30 MHz is applied between two sides of pellets and measure the capacity value and by knowing this value we calculate Dielectric Constant. Dielectric Loss, A.C. Conductivity and Relaxation Time of Parent form, NH₄ ion exchanged form and H- form of Mordenite.

VI. RESULTS AND DISCUSSION

The physical perfection is equally important after the identity and quantity of the atoms present in a crystal, for crystal characterization. The beginning of such work is the accurate determination of structure of crystals with X-rays. These techniques, based on monochromatic X-radiation are generally more important because the d-spacing can be calculated from the observed diffraction angles. For natural zeolites and synthetic zeolites, x-ray powder diffraction methods are commonly used for the structural investigations and also for the purpose of identification.

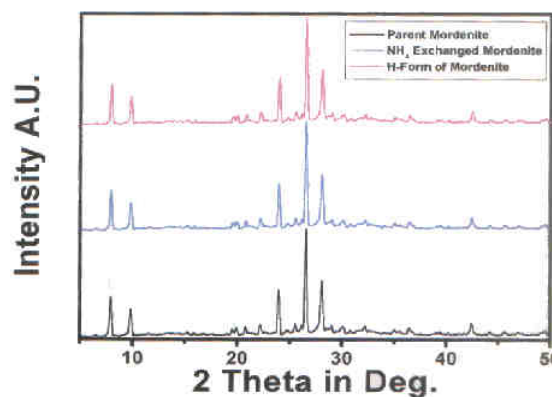


Fig 1 XRD Pattern of H-mordenite

In the present investigation, the bragg diffractometer arrangement is used. The specimen in the form of micro crystalline powder is mounted in the sample holder, which is then placed at the center of the diffractometer and rotated by an angle θ around on axis in the sample plane. The counter is attached to an arm rotating around the same axis by angles twice as large as those of the specimen rotation only (hkl) planes of the microcrystals parallel to the sample plane contribute to the diffracted intensity.

From the diffractogram of parent Mordenite, NH₄ exchanged Mordenite and H –form of Mordenite there is no change except intensity. This shows the stability of material 'd' values are compared with standard 'd' values (4) .This confirms the Mordenite zeolite. Change in intensity is due to the difference in scattering factor of cations (5).

2 Theta	d – Value	Peak width	Intensity
05.41	16.34	0.48	44
9.97	8.88	0.12	58
13.85	6.40	0.48	2
19.67	4.51	0.16	13.5
20.05	4.43	0.16	18.4
20.82	4.27	0.40	6.5
22.26	4.00	0.20	17.5
24.12	3.69	0.12	40
24.92	3.57	0.20	9.4
25.73	3.46	0.12	12.8
26.67	3.34	0.12	100
28.17	3.17	0.08	64
29.08	3.07	0.08	7.5
30.05	2.97	0.48	7
30.98	2.89	0.24	6
32.31	2.77	0.16	2.8
35.25	2.55	0.48	4.2
36.52	2.46	0.16	6.5
39.02	2.31	0.16	15
42.03	2.15	0.48	2
44.34	2.04	0.64	1.5
45.79	1.98	0.12	6.5

Table 1- XRD Data for H-Mordenite (After Background Subtraction)

The d values from the X-ray powder diffraction patterns for zeolite samples are given in table 1. It was found that in most

of the cases the d values agree fairly well with the standard d values given in ASIM data cards. From the lattice parameters this confirms the orthorhombic structure of mordenite.

2)Infrared Studies :-

By an extension of the infrared studies, it may be possible to deduce structural information on a new zeolite for which x-ray structural analysis is not complete. The object of this study is to apply mid-infrared spectroscopy to zeolite structural problems with the help of using infrared, as a tool to characterize the frame work structure and to detect the presence of polyhedral building units present in zeolite frameworks.

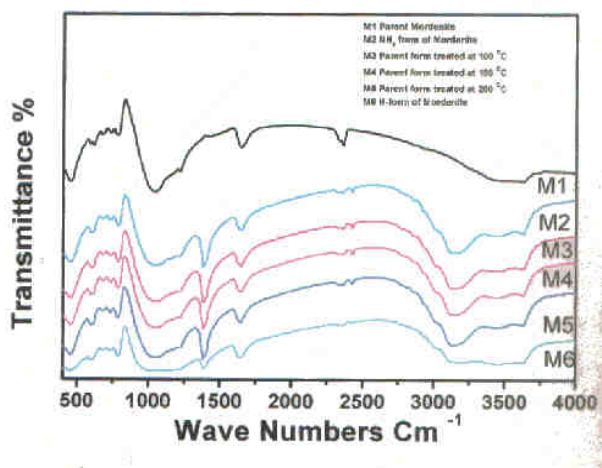


Fig 2 IR of H-mordenite

Infrared spectrum in the region 400 to 4000 cm⁻¹ is sensitive tool indicating structural features of zeolite frame works. It can also be said that the major structural group present in zeolites can be detected from their infrared pattern. There are often general similarities among the spectra of zeolites with the same structural type and in the same structural group. The infrared spectra of zeolites in the region 1300 – 200 cm⁻¹ appears to consists of two classes of vibrations. Those due to internal vibrations of the TO₄ tetrahedron which is the primary unit of structure. These vibrations are not sensitive to variations in framework structure

Vibrations which may be related to the linkages between tetrahedra. are sensitive to the framework structure and to the presence of some SBU and building block polyhedra such as double rings and the large pore openings.

In Particular, zeolite structures have been studied by IR spectroscopy (6). For natural zeolites, spectroscopic data are more scanty, although some Japanese workers have examined the IR spectra of the eight natural zeolites. These investigations have yielded information on structural properties, the state of the adsorbed phase and effects of various types of treatment. Structural characteristics of zeolite lattice obtained by IR studies of certain zeolites in the range of aluminosilicate skeleton frequencies (200 – 1300 cm⁻¹) have been reported (7). Oscillations of the zeolite frame work in the range 200 to 1200 cm⁻¹ have been classified as being either structure sensitive oscillations of external tetrahedral bonds or structure insensitive oscillations of individual tetrahedra on the basis of this classification and with wide ranging experimental evidence, the bands were described to modes: antisymmetric stretches (1250 – 950cm⁻¹) Symmetric stretches (720 – 650 cm⁻¹) and deformations (490 – 500 cm⁻¹) modes involving the external bonds include double ring (650 – 500 cm⁻¹) poreopening (300 – 420 cm⁻¹) symmetric (750 – 820 cm⁻¹) and antisymmetric stretching frequencies (1050 – 1150 cm⁻¹). Studies of the IR spectra of Mordenite showed that they are characterized by the absorption bands at 550 – 650 , 650 – 720 , 750 – 820, 850 – 900 , 1000 – 1100 and 1150 – 1250 cm⁻¹ (8). These bands arise from vibrations of the Si-O (Al) and Al-O(Si) bonds in tetrahedral combined in the aluminosilicate oxygen frame work vibrations of the Si-O (Al) bond caused by the internal deformations (symmetric and antisymmetric) are revealed at 650-720 , 780-820 and 900-1250 cm⁻¹. The most intense bands are observed at 1040-1100. The band at 750-820 cm⁻¹ is clearly caused by symmetric vibration of the Si-O bond. The adsorption bands at 550-650-cm⁻¹ relate to oscillations of chain of aluminosilicate oxygen tetrahedral.

IR of Mordenite from 400 to 4000 cm⁻¹ are recorded for different conditions i.e. parent form (M1) NH₄ form (M2) parent form at 100 °C (M3) parent form at 150 °C (M4) parent form at 200 °C (M5), H – form (M6) and assignment of bands are shown in table 3.2.

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
Mordenite	1227	785	625	1057	773	459	3625	1625

Table 2 IR Assignment of H-Mordenite

In the external linkage (structure sensitive) Asymmetric stretch is observed at 1227 cm⁻¹ and symmetric stretch is observed at 785 cm⁻¹, Hydroxyl stretch is observed at 3625 cm⁻¹ and the water bands are 1625 cm⁻¹. Double ring is observed at 625 cm⁻¹. Zeolite structure in internal tetrahedral structure (insensitive) , asymmetric stretch is at 1057 cm⁻¹ and symmetric stretch is at 773 cm⁻¹, bands at 459 cm⁻¹ are present due to vibration of Si-O or Al-O bond after NH₄ treatment to the parent zeolite and heating the sample at 100 °C, 150 °C, 200 °C & H – form of zeolite not major change in the bands which confirms the stability of Mordenite after ion exchange and heating up to H-form band at 3615 cm⁻¹ is due

to the OH – stretch this band is more intense in H-form than original form bands at 2846 cm⁻¹, 3000 cm⁻¹ & 3115 cm⁻¹ are observed due to hydroxyl stretching bands in the region 900 cm⁻¹ to 1200 cm⁻¹ are observed due to skeleton vibration of Si-O , O-Al-O bond.

Dielectric Study of H- mordenite :

1) **Dielectric constant ϵ'** :-Fig3 shows the variation in dielectric constant against frequency. The dielectric constant goes on decreasing in H – Mordenite up to 6000 KHz. Then increases slowly or remain constant.

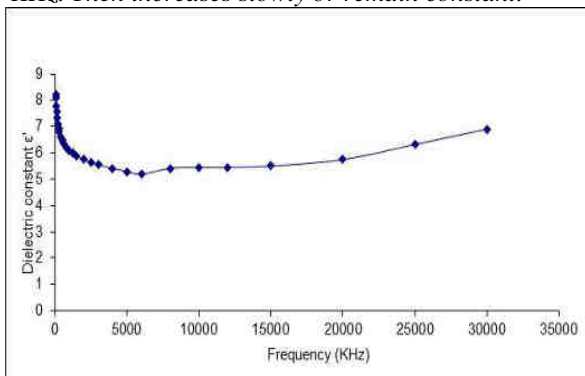


Fig.3 Variation of dielectric constant as frequency in H-mordenite

2) **Dielectric Loss (ϵ'')**Fig 4 shows the variation in dielectric loss against frequency in H-form of Mordenite. Dispersion in dielectric loss is due to the space charge polarization a peak in ϵ'' also occurs at one frequency since the most energy is dissipated at that point This shows that Dielectric loss decreases with increase in frequency decrease in loss up to 600 KHz is rapid then it remain constant up to 30 MHz.

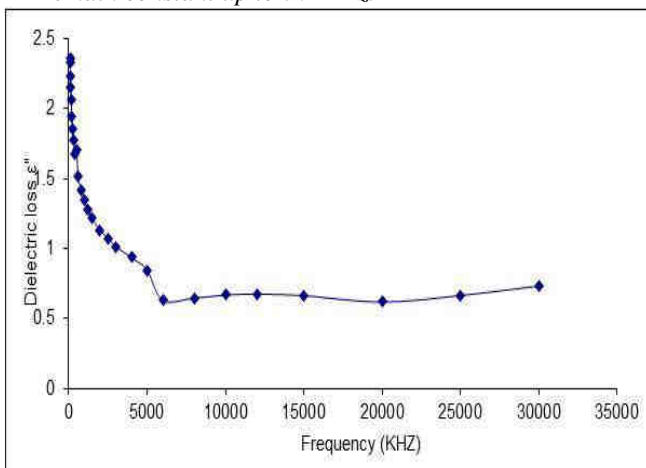


Fig. 4 Variation of dielectric loss as frequency in H-mordenite

3) **Relaxation Time (m)**:- Fig 5 shows the frequency versus Relaxation Time, this shows that m goes on decreasing with increase in frequency.

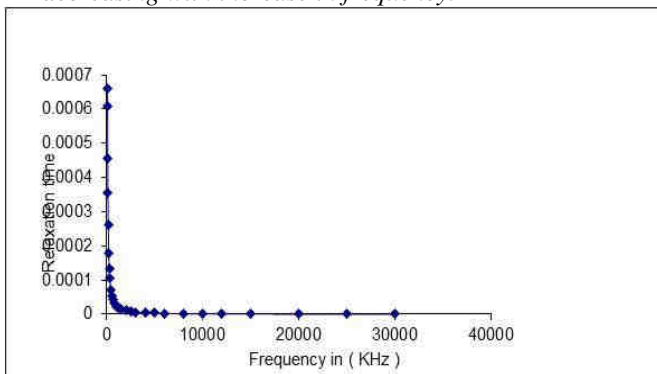


Fig. 5 Variation of relaxation time as frequency in H-mordenite

4) **A.C. Conductivity**:- Fig 6 shows the variation in A.C. Conductivity with increase in frequency. The A.C. conductivity goes on increasing with increase in frequency. As the frequency increases relaxation time goes on decreasing, which increases the A.C.conductivity.

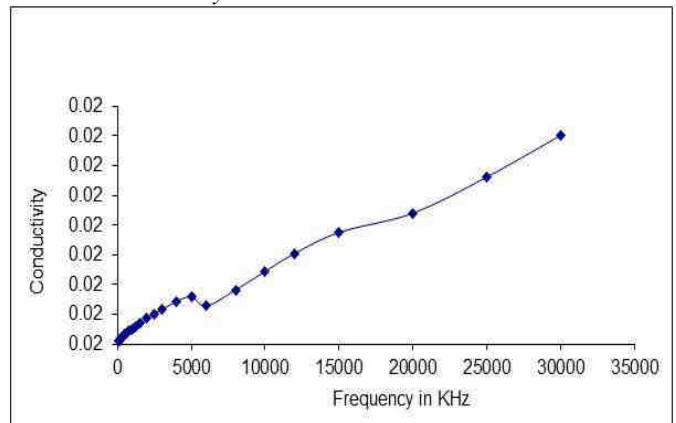


Fig.6 Variation of conductivity as frequency in H-mordenite

CONCLUSIONS

Intensity variation is observed in XRD patterns of as grown Mordenite, NH_4 ion exchange form and H-form. The variation in the intensities may be due to difference in scattering factor of cations. IR bands & XRD of Mordenite do not change with temperature of H – form . This Confirms the stability of Mordenite. Dielectric study of Mordenite plays an important role in stating the nature of zeolite.

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