Characterization and Dielectric study of Zeolite ZSM5

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Abstract:

ZSM-5 zeolites crystal was synthesized by the hydrothermal method. Sample were characterized by XRD,SEM,NMR Method at NCL Pune.Dielectric Study of ZSM-5 was studied in details. Dielectric study was made using LCR Bridge. Pellets of ZSM-5were prepared, variation of dielectric constant, dielectric loss, dielectric conductivity and relaxsession time were measured from 20Hz to 20KHz of parentZSM-5, and H-ZSM-5.Results were compared.

Keywords:Hydrothermal,Characterization,Dielectric Study

1 Introduction

ZSM-5 zeolites crystal was synthesized by the hydrothermal method. Growth and characterization on hydrothermaly grown zeolite crystals are studied in detail (1). Structure directing role, called templating, of organic quaternary species, ions, amines and the alcohol in the synthesis of aluminosilicate, molecular sieves has been reported (2). Among the synthetic zeolite ZSM – 5 (2) Intermediate pore zeolites having 10-membered ring, suppress all other zeolites on account of their unique catalytic selectivity, resistance to deactivation and resistance to aging. This pore high silica zeolites have been synthesized using try ethyl Butyl ammonium Bromide salts as templates (3,4).From their studies on the pore structure of these, Kokotailo and Meier (5) reported that ZSM-5 zeolite crystals contain two sets of intersecting channels both of which are formed by 10 member oxygen rings one of them is the almost circular (5.4x5.6A) and is Sinusoidal. It runs parallel to a-axis of the unit cell. The other one is straight and has elliptical opening (5.1x5.5 A). It is parallel to b-axis (6). The zeolite ZSM – 5 structure was originally prepared by Argauer and Landolt in 1972, when in addition to the needed sources of silicon, aluminum, hydroxide and Na+, the addition of TPA to the gel promotes crystallization of this unique structure (7). Study on the stability of hydrothermally grown zeolite crystals are presented (8).

2 Procedure for ZSM-5

The reagents used in the synthesis of ZSM-5 were sodium silicate (28%, SiO_2, 8% Na_2O and 64% H_2O.). Aluminum sulphate (15.8 % Al_2O_3.)., Sulphuric acid as (98%). Tri Ethyl Butyl Ammonium Bromide (99%) and distilled water.

The hydrothermal crystallization was carried out but at 170 °C under static condition. Initial gels comprising the molar composition 30 SiO_2:Al_2O_3:5.76 TEB A Br: 8.25 Na_2O: 2400 H_2O were prepared using

appropriate quantities of reagents in 35ml water was added into 22.23 gm sodium silicate diluted with 50 ml distill water under vigorous. Then aluminum source (2.23 gm aluminum sulphate dissolved in 50 ml water was added to the reaction mixture under vigorous stirring. The OH/SiO_2 molar ratio in initial gel mixture was adjusted to a value of 0.231 using appropriate quantities of desired sulphuric acid. The final homogeneous reaction mixture was distributed into a stainless steel autoclave. Which after being sealed were placed in, and air heated oven at 170°C. Autoclave was taken out of oven an advanced to room temperature. The solid products were separated by sanction filtering washed with water and then dried at 393 K in static air oven for 8 hrs. The samples were characterized by powder XRD, SEM technique.

3 Results & Discussion

XRD:- The X-ray diffractogrammes were recorded between 2θ value ranging from 5-50 with a chart speed of 1 /min on a Phillips X-ray diffractometer. (model PW 1710 based and Ni – filtered having wavelength CuKα radiation (λ= 1.54056 A) XRD is recorded for original as well as H-form of ZSM-5 sample .The relative intensities and 'd' values are compared with standard 'd' values and reported in table 1.1.

XRD spectra of parent ZSM-5 is shown in fig1.1 and XRD spectra of H-form ZSM-5 is shown in fig1.2 From both spectra we conclude that there is no change in structure of ZSM-5, after H-form. This indicates the stability of ZSM-5. Only change in intensity is observed.

SEM:- Scanning electron micrograph of ZSM-5 zeolite is shown in fig 1.3 from SEM we determine the size of ZSM-5 zeolite .The observed size is 10 μm. In the SEM the focused spot produced by the electron source or gun is scanned across the specimen with a television type of raster by means of an electrostatic deflection system. Information about the specimen is obtained by detecting secondary electrons emitted from the specimen using a solid state detector. A photo multiplier signal is amplified and used to modulate the intensity of a synchronously scanned display tube to form a specimen image.

NMR Spectra :-

NMR is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of a nuclei of molecule. The magnetic levels are created by keeping the nuclei in a magnetic field. Frequency of radio wave is 10^7 and 10^8

$E = h \nu$

$h = 6.6 \times 10^{-27}$ ergsec

$E = 6.6 \times 10^{-19}$ ergs

The quantity of energy involved in r.f. radiation is very small which is too small to vibrate rotate or excite on atoms or molecules. But this energy is sufficient to affect the nuclear spin of the atoms of a molecules when a nucleus is placed in a system where it absorbs energy, it comes excited. It then loses energy to return to the unexcited state. This nucleus which alternately becomes excited and unexcited is said to be in a state of resonance. As the field H_o is increased so that processional frequency of the nucleus increases and when this frequency becomes equal to the frequency of oscillation field, transitions occur between nuclear energy states. The energy absorbed in this process produces a signal at the detector and this signal is amplified and recorded as a brand in the spectrum.

Fig 1.4 shows the Si MAS NMR spectra of ZSM-5 zeolite. This indicates that 116.4 ppm is assigned to Si(O Al). The values 112.4 ppm is assigned to Si (1 Al), -1-4 ppm is assigned to (3 Al) and –106.8 ppm corresponds to Si(2 Al).

All 29Si Mas NMR spectra were recorded in a 47 KG field at 59.627 MHz with the pulse width 2 μs and repetition time 3s, on a Bruker. Physik (CXD – 20 /300) solid state high resolution NMR spectrometer equipped with

a wide bore super conducting magnet and an Aspect 2000 data system Reference for 29Si is taken to be tetraethyl ortho silicate.

For 27Al MAS NMR spectra reference is aluminum Nitrate. The spectra were recorded at 78.205 MHz. The Pulse length is 1 μs with repetition time 200 ms.

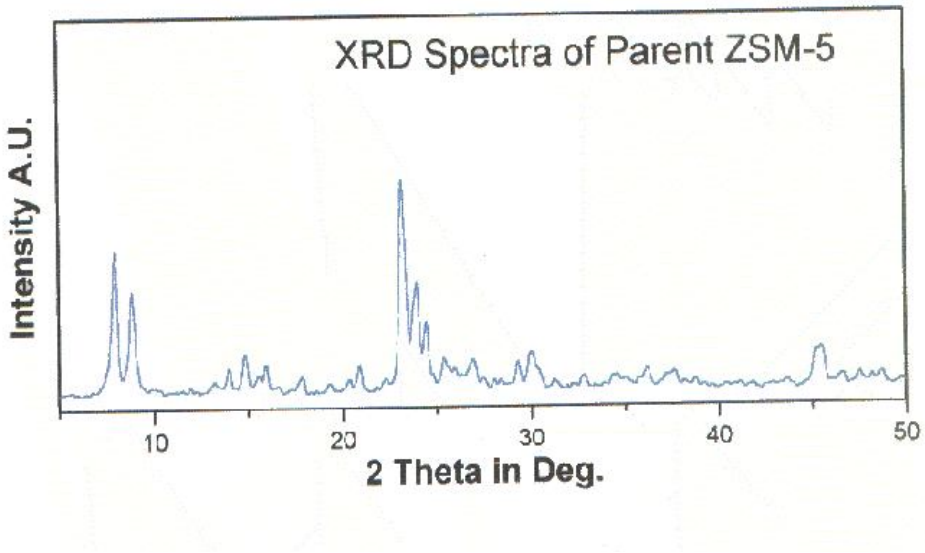


Fig 1.1 XRD spectra of parent ZSM-5

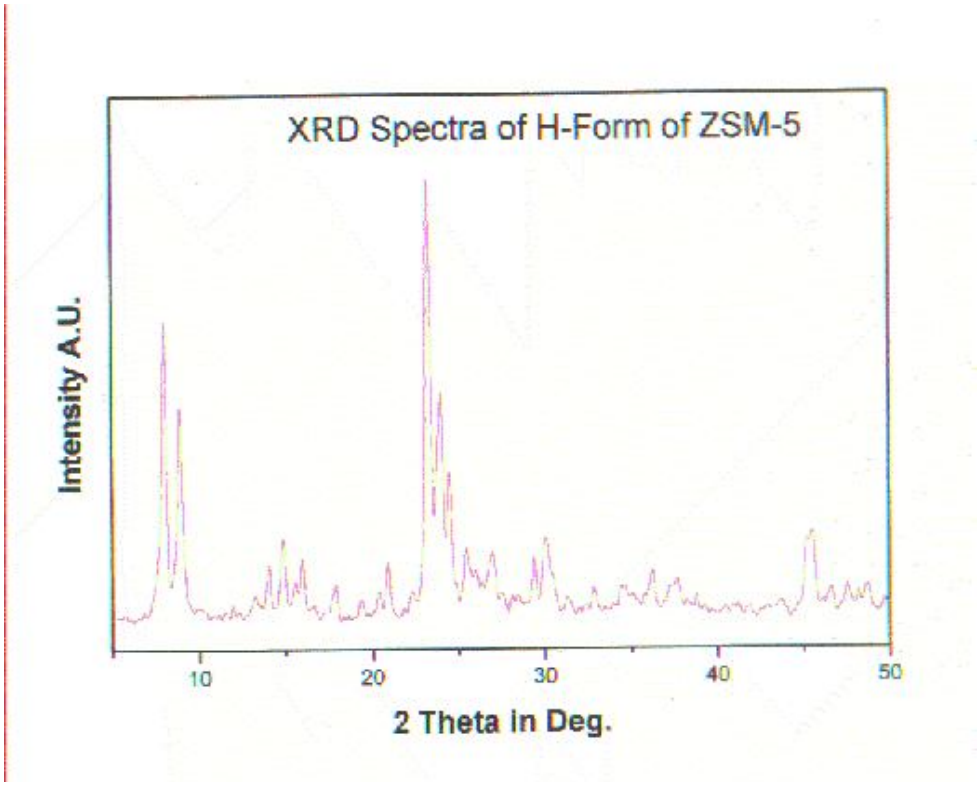
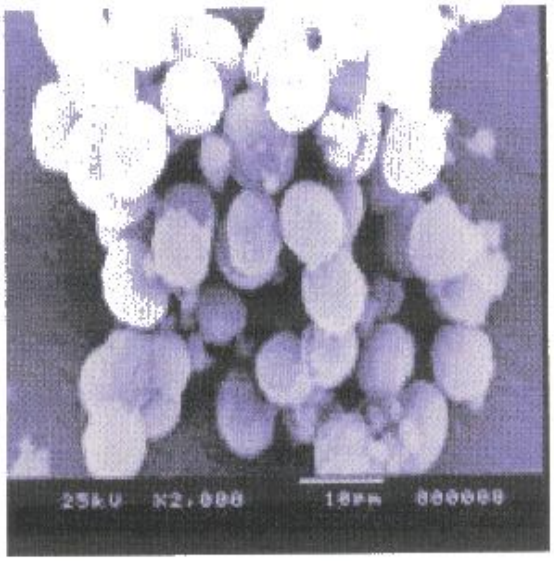


Fig 1.2 XRD Spectra of H-form of ZSM-5



Scanning electron micrograph of ZSM-5 Zeolite

Fig. 1.3 SEM of ZSM - 5

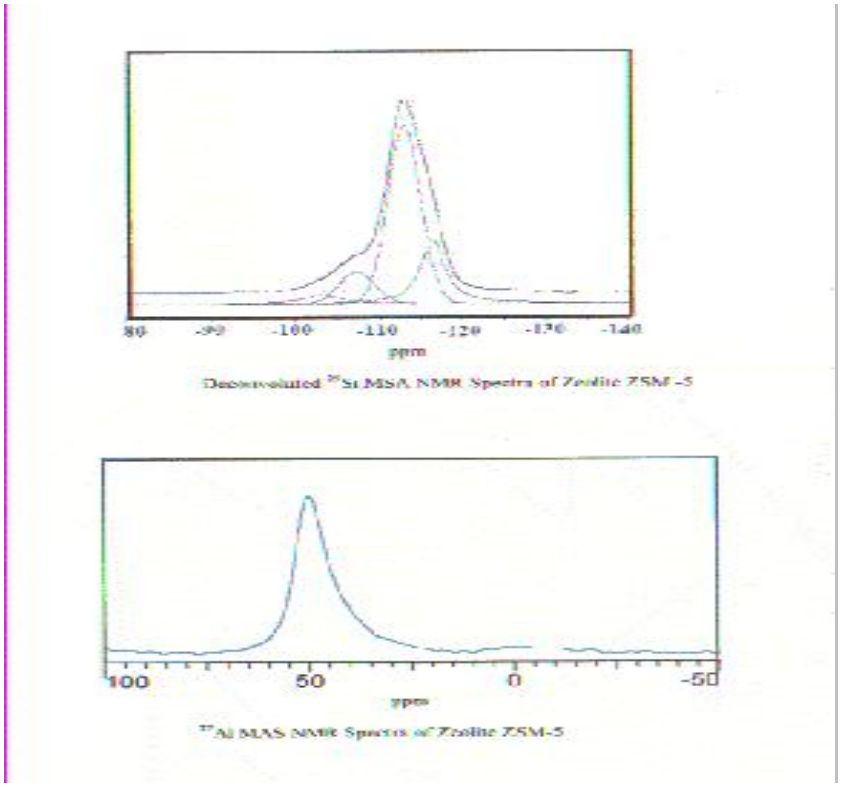


Fig 1.4 & 1.5 NMR Spectra of ZSM - 5

2 Theta	d-Value	Peak Width	Intensity (I/I_0)
08.06	10.96	0.42	15
08.94	09.88	0.44	13
12.04	07.34	0.35	8
14.04	06.30	0.30	7
14.82	05.97	0.23	7
15.56	05.69	0.28	6
16.04	05.52	0.32	6
19.04	04.57	0.28	4
20.44	04.34	0.35	7
20.94	04.23	0.37	8
22.36	03.97	0.25	6
23.30	03.81	0.37	100
23.98	03.70	0.30	39
24.50	03.63	0.28	28
26.02	03.42	0.42	11
26.92	03.30	0.32	12
29.36	03.03	0.32	9
30.10	02.96	0.37	11
34.50	02.59	0.30	5
36.08	02.48	0.23	7
37.56	02.39	0.21	5
45.34	01.99	0.37	19
45.50	01.99	0.14	17
47.60	01.90	0.47	6
48.84	01.86	0.18	5

Table 1.1 - ***XRD Data For ZSM –5 (After Background Subtraction)***

NMR spectra gives information on changes of atomic nucleus surroundings. 27AlMAS NMR spectra provides information on the environment of aluminum atoms in the structure (9). When aluminum atoms occur in tetrahedral coordination and create the three dimensional frame work, the peak showing the chemical shift of 60 ppm (10-12) in the spectra can be observed. If the extra frame work aluminum occurs in the structure, then it is present in octahedral coordination and simultaneously , the peak at about 0 ppm in the spectra is observed . In the present case in ZSM-5 Shift is at 50 ppm (in fig 5.5). This indicates the tetrahedral co-ordination of Al (13)

4 Dielectric studies of ZSM-5 parent form

Dielectric constant (Є):- Fig 1.6 shows the variation of dielectric constant against frequency. Initially Є' goes on decreasing up to 6000 KHz Є' increases as thickness increases.

Dielectric Loss (Є''):- Є'' decreases as frequency increases. Decrease is slow up to frequency 6000 KHzs slowly increases then decreases.

Relaxation Time (т) :- Fig 1.8 shows the frequency against relaxation time. Graph shows that there is decrease in т as frequency increases.

A.C. Conductivity (б):- Fig. 1.9 shows the variation of б against frequency. This shows that increase in б with increase in frequency is observed.

ZSM – 5 H-Form

Dielectric Constant (Є') :- Fig 1.10 shows the variation of dielectric constant against frequency . This shows that there is decrease in Є' up to frequency 6000 KHz. Then Є' increase slowly or remain constant.

Dielectric Loss (Є''):- Fig 1.11 shows the dielectric loss against frequency. There is decrease in Є'' with increase in frequency in H-form of ZSM-5 zeolite.

Relaxation Time (τ):- Fig 1,12 shows the Relaxation Time against frequency. Decrease in τ observed with increase in frequency.

A.C. Conductivity (б):- Fig 1.13 indicates A.C. Conductivity against the frequency .б goes on increasing with increase in frequency.

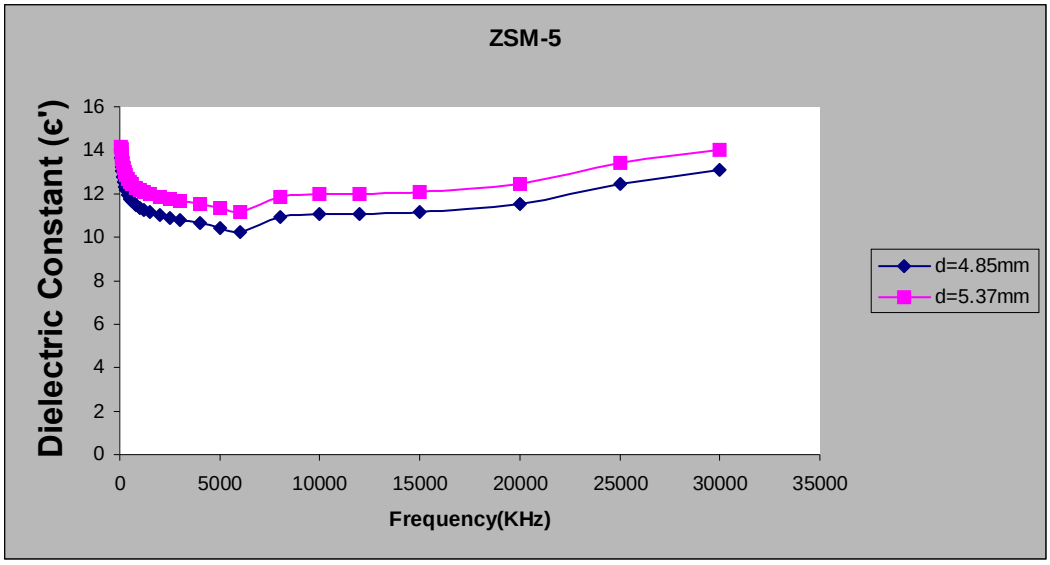


Fig1.6 variation of dielectric constant in ZSM –5

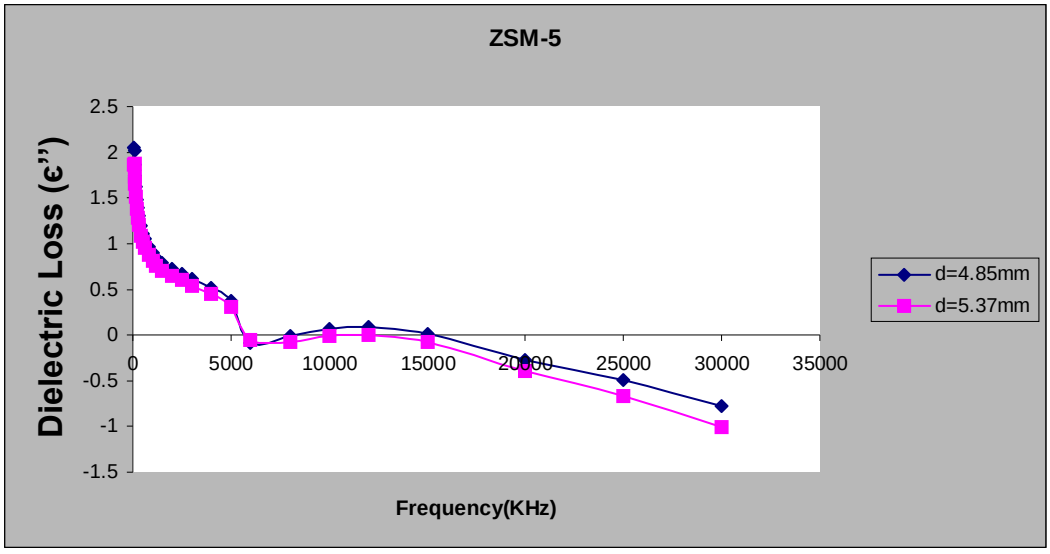


Fig 1.7 *variation of dielectric loss in ZSM –5*

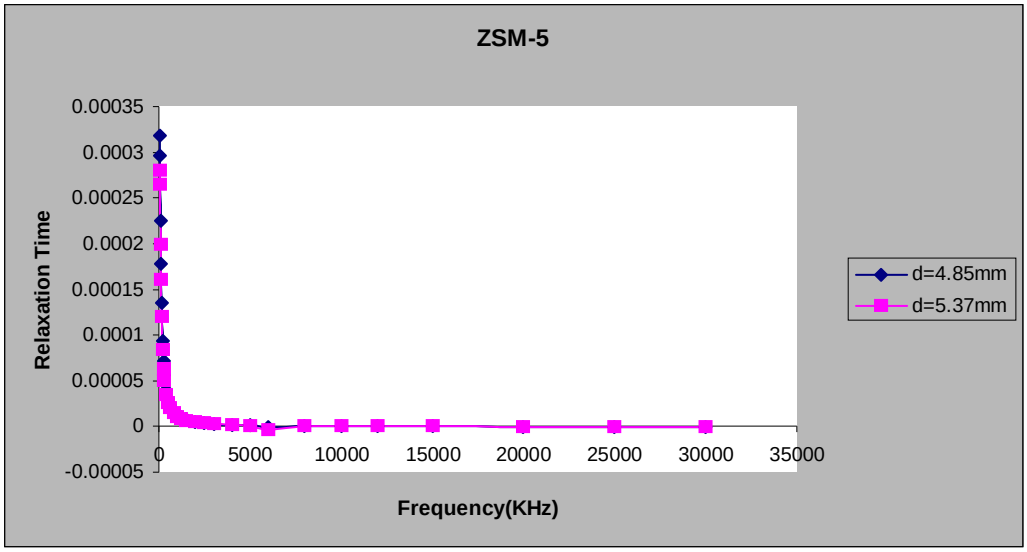


Fig 1.8 variation of relaxation time in ZSM –5

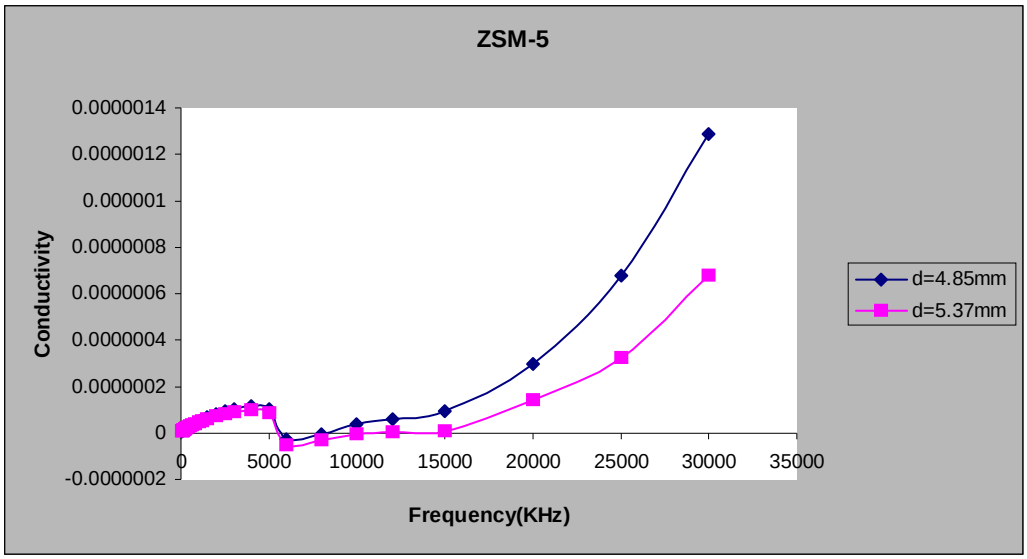


Fig 1.9 ***variation of conductivity in ZSM –5***

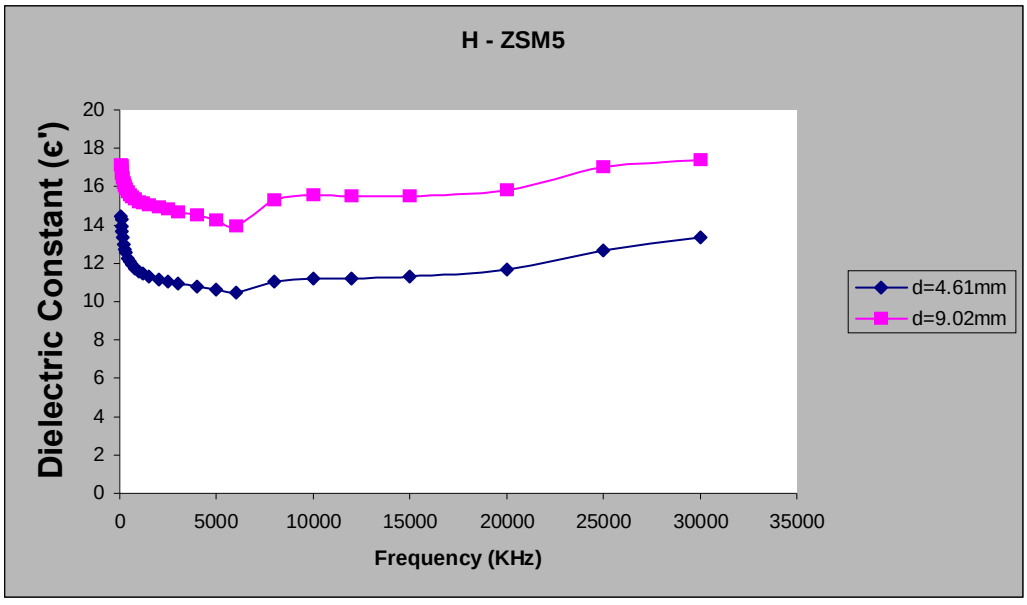


Fig 1.10. variation of dielectric constant in H ZSM – 5

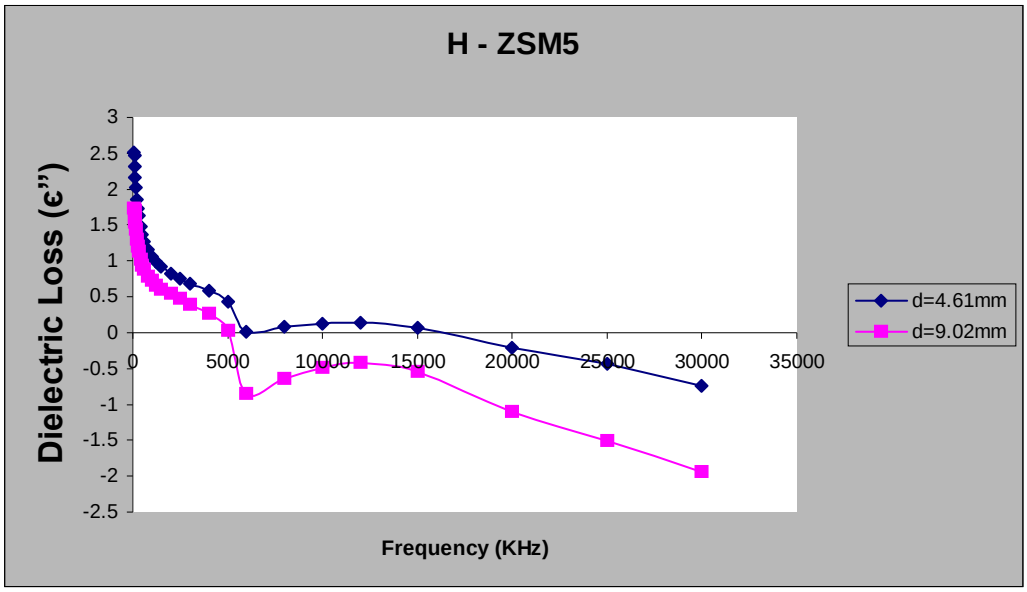


Fig 1.11 ***variation of dielectric loss in H ZSM –5***

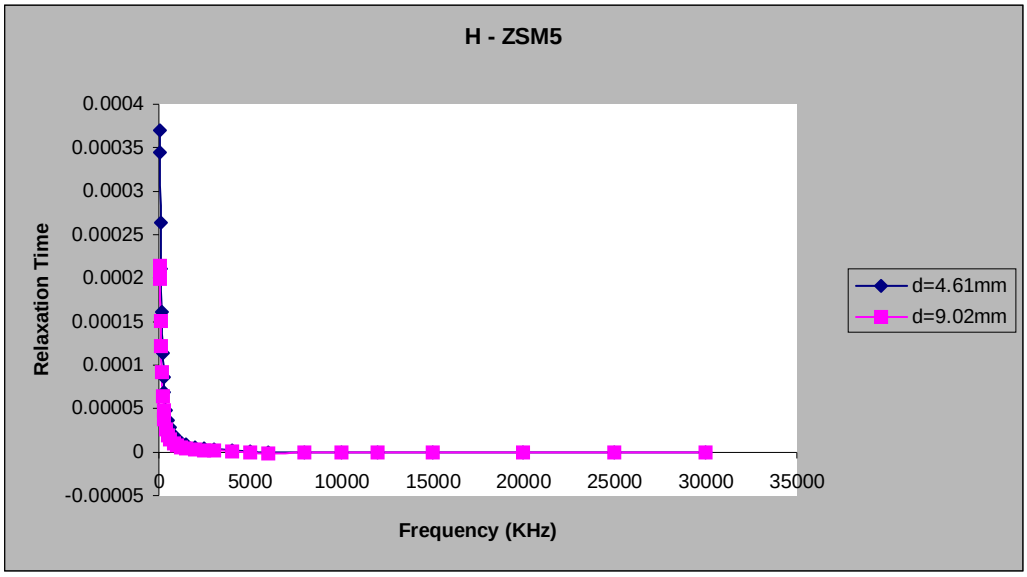


Fig1.12 variation of relaxation time s in H ZSM –5

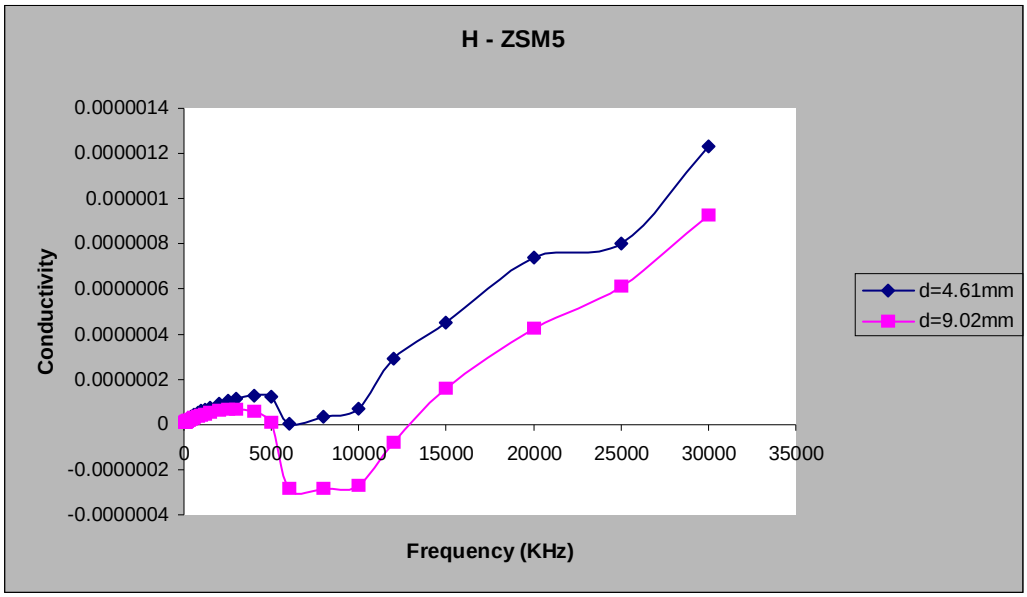


Fig 1.13 ***variation of conductivity in H ZSM –5***

5 Conclusions

1) Zeolite ZSM-5 is synthesized hydrothermally.
2) Intensity variation is observed in XRD may be due to difference in scattering factor of cations
3) From Fig. 1.5 the Aluminum mass NMR shows the peak at 50 ppm This shows that aluminum is situated at the tetrahedral co-ordination.
4) Dielectric properties of zeolite ZSM-5 play an important role in stating the nature of zeolite.

Acknowledgements

Auther is thankful to Director of NCL for Characterization help and Director of CEDTI Aurangabad.

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