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Synthesis and characterization of Nanocrystalline ZSM-5 molecular sieve from Ethylene diamine template

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ABSTRACT

Nanocrystalline ZSM-5 zeolite from ethylene diamine template have been prepared and characterized using XRD, TEM, TG/DTA, FT-IR, Nitrogen adsorption, XPS, MASNMR techniques and methanol to olefin reaction. Synthesis were carried out using a standard gel composition for 2,4 and 6th day. X-ray diffraction pattern of fourth day sample did not show any peaks, like 6th day sample. However its FT-IR spectra of framework region shows similarity with 6th day sample. TEM image of 4th day sample show the presence of nanoparticle which is lower than 10 nm size. 6th day samples are platelets of micron range. However 4th day sample properties are similar to 6th day samples. Its selectivity towards methanol to olefin conversion is higher than X-ray crystalline ZSM-5 samples.

Key words: ZSM-5, X-ray amorphous, XRD, TEM, TG/DTA, N_2 adsorption, XPS, MASNMR, Methanol to olefin.

INTRODUCTION

ZSM-5 zeolites have been used to prepare some unique catalysts for a variety of processes[1,2]. It has been shown that these zeolites may be modified in various ways to monitor reaction selectivity[2]. One ways of doing so depends on the variation of the crystal size[3]. In an effort to reduce the crystal size of these zeolites, a family of ZSM-5 materials has been discovered which is amorphous when studied by X-ray diffraction (XRD/ZSM-5). The zeolites were prepared by interrupting the crystallization during the synthesis. Experimental evidence is presented which indicates that the material contains very small zeolite nuclei, the sizes below the X-ray detection limit.

Recently a high alumina containing ZSM-5 was synthesized from ethylene diamine template[4,5]. Besides an organophosphate similar to ZSM-5 also reported[6]. Further by shortening the crystallization time, X-ray active nanocrystals are reported[7]. Here we have modified the ZSM-5 synthesis procedure and prepared X-ray inactive nanocrystals and characterized the material by various physicochemical techniques.

EXPERIMENTAL

Synthesis

In a typical procedure to synthesize ZSM-5 using ethylene diamine template, 0.825g of sodium aluminate (99%, s.d.fine, India) was mixed well with 0.7g of sodium hydroxide (99%, s.d.fine, India) and 129g of distilled water. This mixture was stirred well until all the solid is dissolved. This was taken as solution A. Another solution B was made by thorough mixing of 46.47g of silica sol (30%, s.d.fine, India) and Ethylene diamine (18.3g, 99%, Aldrich, U.S.A). Solution A and B were mixed well to make clear mixture of the following chemical composition: $1.85Na_2O$: Al_2O_3: $15.2SiO_2$: $592H_2O$:

19.7C_2DN was allowed to react at 177°C in a teflon lined steel autoclave. Crystallization times varied between 0.25 and 10 days. The materials were then air-dried, calcined at 550°C, and ammonium exchanged.

Characterization

X-ray diffraction patterns were recorded on a Rigaku (D/MAX III VC) instrument in the 2θ region of 5-45°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope: Chemical analysis was carried out by XRF using a Rigaku 3070 X-ray Spectrometer. Carbon and nitrogen were estimated by microanalysis. The framework IR spectra were recorded in the diffuse reflectance mode using 300 : 1 ratio sample in KBr (Nicolet 60SXB). Crystallinity was studied by both I.R. spectroscopy and X-ray

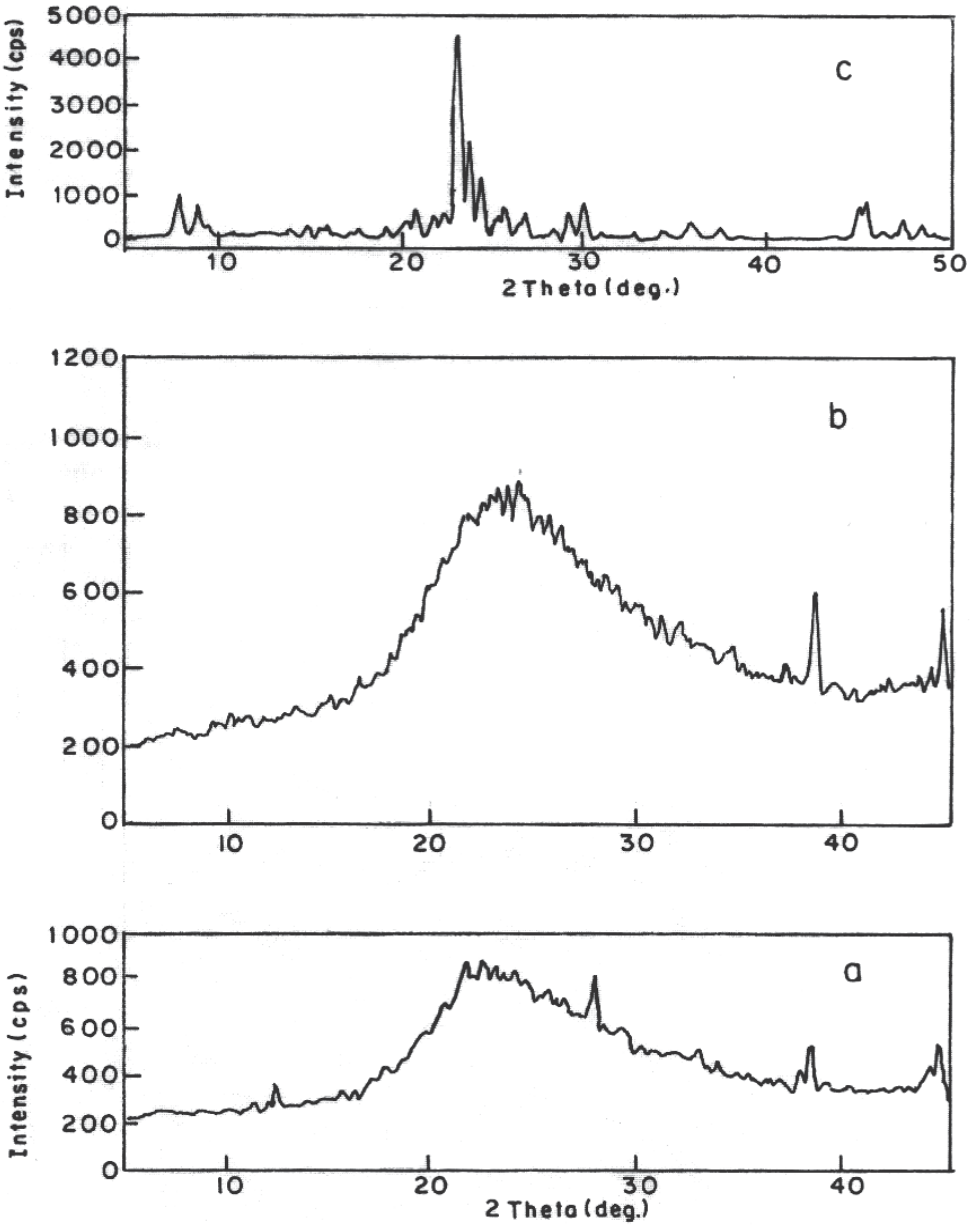

Fig. - 1: X-ray diffraction pattern of ZSM-5 synthesized at a)2 days, b) 4 days and c) 6 days.

diffraction using a highly crystalline laboratory preparation as the 100% standard. For I.R. crystallinity the absorbance of a typical ZSM-5 skeleton vibration[5] at 550 cm^{-1} was followed. This band has been assigned to highly distorted double six-rings, present in the ZSM-5 structure[8]. The KBr pellet technique was used with KCN as internal standard (reference peak at 2200 cm^{-1}). To study the nature of the surface hydroxyl groups in the transmittance mode, self-supported wafers (~10mg/cm^{-2}) and an IR cell with controlled environment chamber were used. The sample was activated in situ at 673K under vacuum (10^{-6} torr) for 4h and then cooled to 323K before recording the spectrum (4cm^{-1} resolution, averaged over 500 scans). XPS measured at 10^{-8}mm using Vg Scientific, ESCA-II MK3 instrument. MASNMR spectra were recorded in the solid state with a Bruker DRX 500 spectrometer operating at a field of 11.7 Tesla. ^{27}Al spectra were recorded at a frequency of 130.3 MHz, with a pulse length of 2ms and a spinning speed of 3-5 KHz. ^{29}Si NMR spectra were recorded at 99.3 MHz, 2ms (45°) pulse width and repetition time of 2s. Tetramethylsilane (for silicon), 1M $Al(NO_3)_3$ solution (for aluminium) were used as standards. Methanol to olefin reaction was carried out using a fixed bed reactor, with the following conditions. WHSV(h^{-1}) = 6.0, N_2/methanol (mole) = 1.5, TOS = 2h, catalyst = 2g, and Temperature = 673K.

RESULTS AND DISCUSSION

Fig. -1 shows the X-ray diffraction pattern of ZSM-5 synthesized at different time intervals (2, 4 and 6th day). On 6th day full fledged crystal appears. Before it all the samples were X-ray amorphous. However, when studied these materials by FT-IR spectroscopy, the framework region spectra is similar to XRD crystalline ZSM-5 samples. This samples other property also similar (in following text). Using the Scherrer formula[9], it is calculated that in order to observe an X-ray diffraction peak (Fig. -1) at $2\theta = 10^{o}$ with half band width of 1° crystallite sizes of 8.0 nm are needed. In other words, the XRA/ZSM-5 materials must have crystals which contain less than 4 unit cells. We studied the pore structure of Nanocrystalline ZSM-5 by high resolution transmission electron microscopy of fourth day sample (Fig. -2). The periodic arrangement of the inorganic structure is also confirmed by direct TEM imaging. Transition electron micrographs only show ill defined

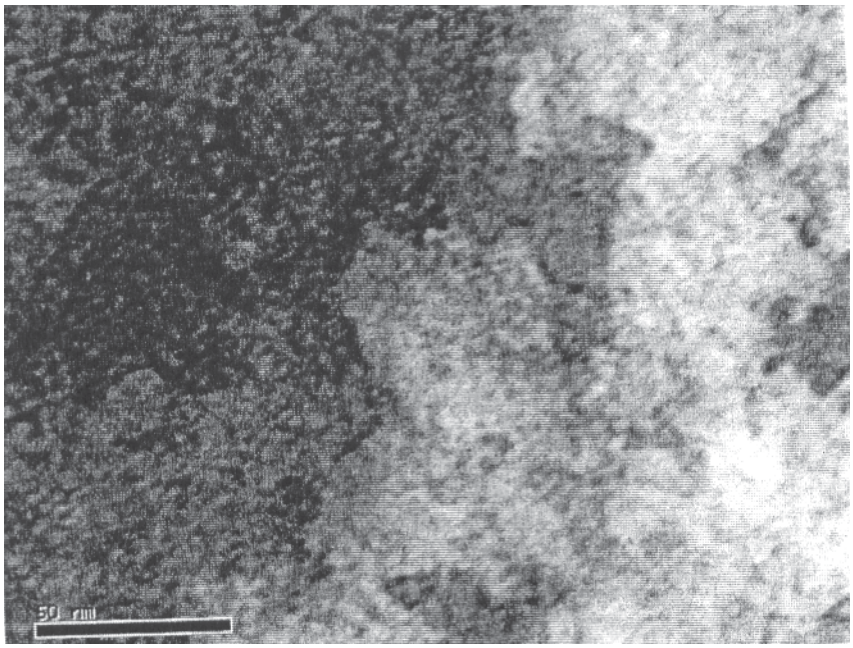

Fig. - 2: Transition electron microscopic picture of 4th day sample, scale 50 nm.

amorphous agglomerates without any trace of crystalline material. In this respect, the existence of amorphous zeolite of type A has been reported[10].

The process of template removal by calcinations was monitored by using a TGA and DTA technique (Fig. -3). The presence of two stage weight loss 25-191.7 (2.09%) and 191.7 – 664.2°C (22.29%) were observed. The first stage weight loss is due to the loss of physisorbed water. The second stage weight loss is due to the loss of oxidative decomposition of the template. The higher temperature to eliminate the template shows that the strong interaction of template with the aluminosilicate structure. Carbon and Nitrogen analysis of the sample give Carbon = 14.07% and Nitrogen = 2.46%. The number of template molecule present as per nitrogen calculation 0.175 and as per carbon calculation 0.195.

FT-IR spectra in the framework region (Fig. -4) shows the peaks at 470(s), 550(m), 795(m), 1089(vs), 1200(wsh) cm^{-1} for pore opening, bending, double ring, symmetric and asymmetric T-O-T vibrations. The peak at 795 is due to Si-O-Si vibrations. FT-IR spectrum in the –OH region shows six prominent peaks (Fig. -5). Peaks at 3545, 3584, 3630 and 3666 cm^{-1} bands for due to the silanol groups (Si-OH-Al) situated in different crystallographic positions. Peaks at 3728 and 3773 cm^{-1} peaks are due to Al-OH and Si-OH groups present in aluminosilicate structure.

The N_2 adsorption isotherms of Nanocrystalline ZSM-5 (Fig. 6) are characteristics of micropore materials with uniform pore size[11]. These isotherms show an inflection near p/p_o 0.72 - 0.96, indicating capillary condensation within the pores. The presence of hysteresis, characteristic of multilayer adsorption dominating the process of filling and emptying the voids, indicates the pore size[12]. The BET surface area, is 300 m^2/g, the average pore diameters is 38 Å and cumulative adsorption pore volume (184.39 cc/g) as calculated using the BJH[13] model.

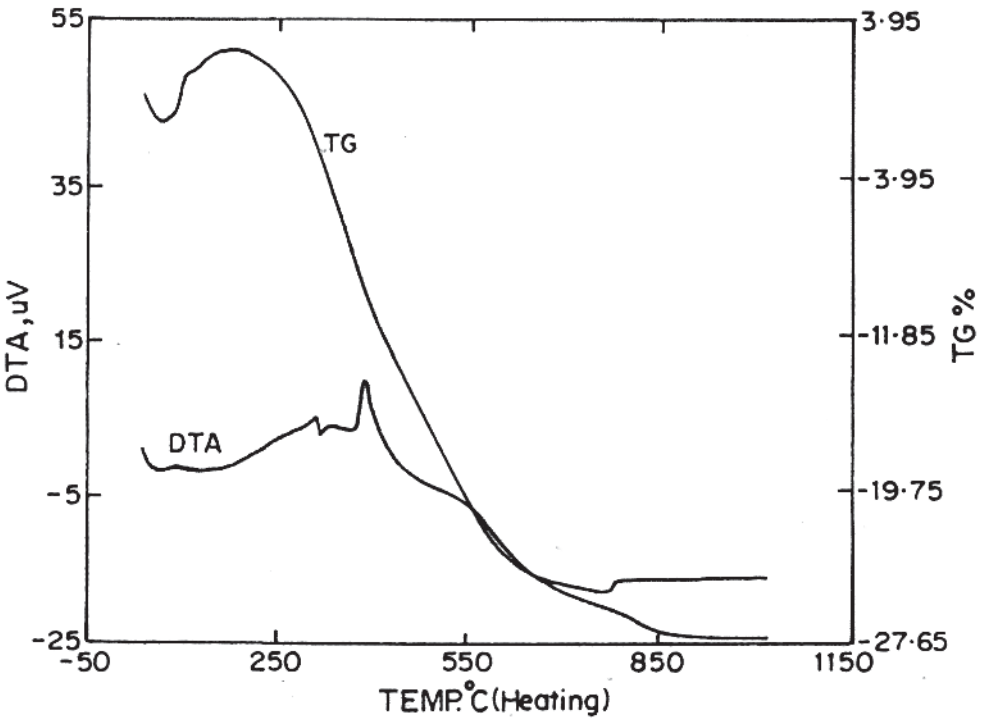

Fig. - 3: TG(a)/ DTA (b) curves of 4th day sample.

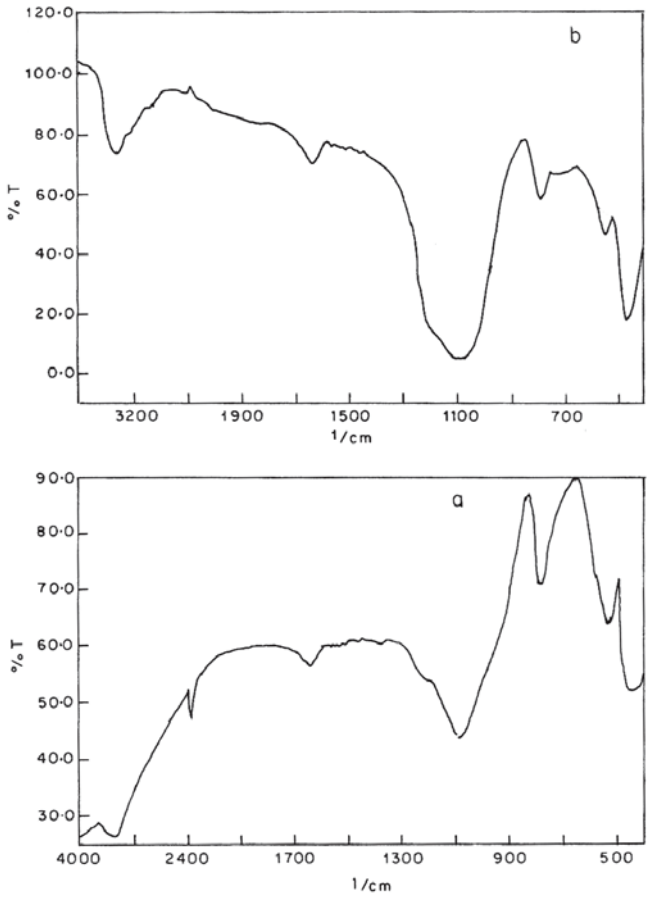

Fig. - 4: FT-IR spectra of a) 6th day sample and b) 4th day sample.

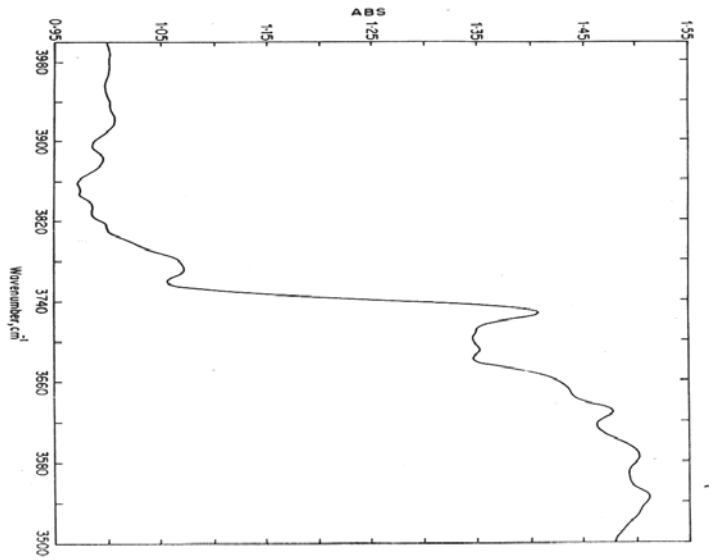

Fig. - 5: FT-IR spectra of 4th day sample in the hydroxyl region.

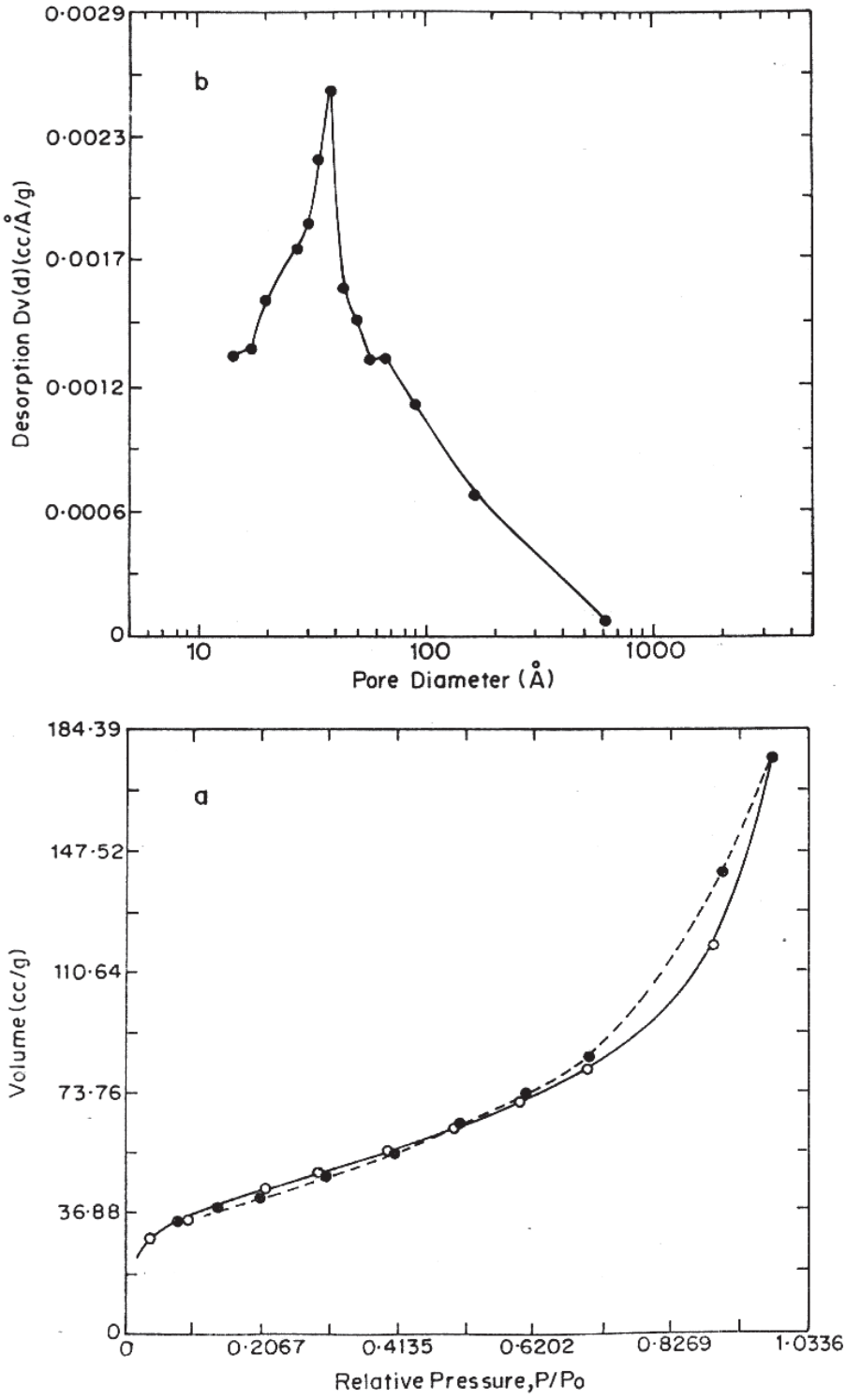

Fig. - 6: Adsorption isotherm of sample b,
a) Relative pressure vs Volume and b) Pore diameter vs Desorption plot.

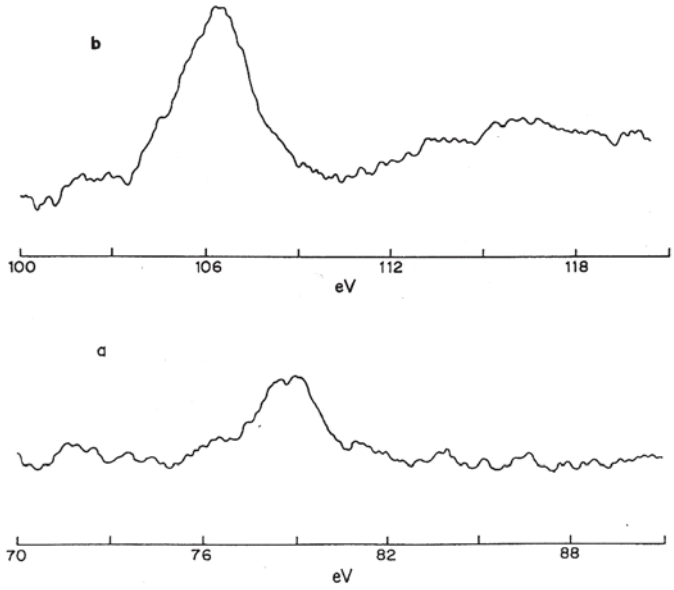

Fig. - 7: XPS spectra of a) Al^{3+} and b) Si^{4+} in 4th day sample.

XPS spectra of X-ray amorphous ZSM-5 (Fig. -7) for various metal ions shows peaks at Si = 106.48, Al = 78.52, 79.00 and C = 289.6 eV. The Silicon spectra shows a single peak. How ever MAS NMR of ^{29}Si shows multiple peaks. This shows that the different silicon environment cannot be identified by XPS. However the splitting in aluminium spectra shows the presence of two environmentally different aluminium.

The ^{27}Al and ^{29}Si MAS NMR spectra of X-ray amorphous ZSM-5 are presented in Fig. -8. The ^{27}Al NMR spectra for the as-synthesized samples show a single symmetrical ^{27}Al line at 7.925 along with small peak at 53.156 for environmentally different tetrahedrally co-ordinated aluminium atoms. ^{29}Si MASNMR of the sample shows that the presence of Si: [3Al:Si] (-89.2, -92.5 and –94.7 ppm), Si: [2Al:Si] (-98.8 and –101.8 ppm) and Si: [3Al:Si] (-107.0) species.

Methanol to Olefin reaction results were given in Table -1. Although the activity over X-ray amorphous ZSM-5 is lower to ZSM-5, the selectivity is similar. Propene is the major product in ZSM-5 and butene is the major product in Nanocrystalline ZSM-5. Also in ZSM-5 the aromatics were formed but which is not formed in Nanocrystalline ZSM-5.

Table - 1: Methanol to Olefin reaction products over X-ray amorphous ZSM-5

Sample	Conversion	C_1+C_2	C_3	C_4	C_5+ Aliphatics	C_6-C_8 aromatics	>C_8 aromatics
4th day	70	18.110	24.045	35.001	23.021	-	-
6th day	100	15.859	37.701	11.736	20.702	4.430	7.001

Conditions: WHSV(h^{-1}) = 6.0, N_2/methanol (mole) = 1.5, TOS = 2h, catalyst = 2g, and Temperature = 673K.

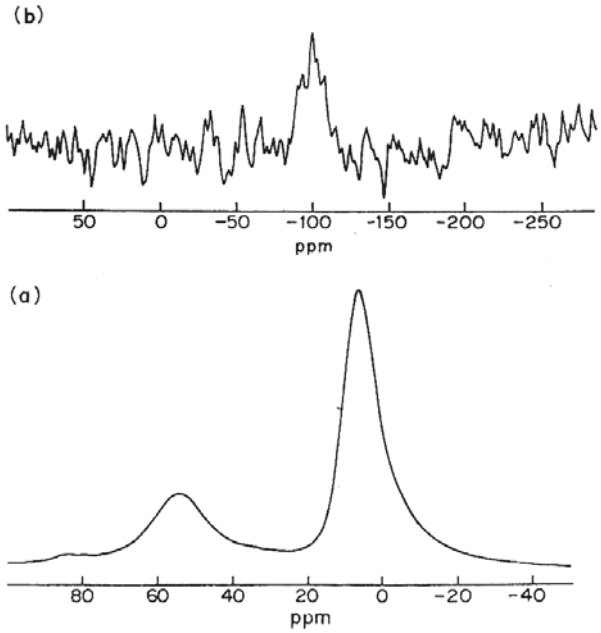

Fig. - 8: ^{27}Al (a) and ^{29}Si (b) MASNMR spectra of 4th day sample.

Conclusions

Nanocrystalline ZSM-5 zeolite from ethylene diamine template have been prepared and characterized using different physicochemical techniques. Most of the Al is in tetrahedral coordination in two different locations and pore size distribution is very narrow and centered in the micropore region. Silicon are present in multiple environment viz. Si: [Al: 3Si], Si: [2Al: 2Si] and Si: [3Al: Si]. There are six type of hydroxyl groups are found which includes four types of silanol groups, Al-OH and Si-OH groups.

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REFERENCES

1. Rabo, J.A., Bezman, R.D. and Poutsma, M.L., *Acta Phys. Chem.*, **24**, 39 (1978).
2. Weisz, P.B., *Proc. 7th Int. Congr. Catalysis*, Tokyo, P1 (1980).
3. Haag, W.O. and Olson, D.H., *U.S. Pat.*, 4,117,026.
4. N. Venkatathri, *Orient. J. Chem.*, **21,** 195 (2005).
5. N.Venkatathri, *Bull. Catal. Soc. Ind.,* **5,** 17 (2006).
6. N. Venkatathri, *Bull. Catal. Soc. India*, **5**, 146 (2006).
7. N. Venkatathri, *Stud. Surf. Sci. Catal.,* **154,** 189 (2004).
8. Valyon, J., Mihalyfi, J., Beyer, H. K. and Jacobs, P. A., *Proc. Workshop on Adsorption*, Berlin, DDR, (1979).
9. Cullity, B.D., *Elements of X-ray diffraction*, Addition-Wesley, Reading, Massaachusetts, 99 (1967).
10. Thomas, J. M. and Bursill, L.A., *Angew. Chem.*, **92**, 755 (1980).
11. Yuan, Z.Y., Liu, S.K., Chen, T. H., Wang, J.Z. and Li, H.X., *J. Chem. Soc., Chem. Commun.*, 973 (1995).
12. Rathousky, J., Zukal, A., Franke, O. and Schulz-Euloff, G., *J. Chem. Soc., Faraday Trans.*, **91**, 937 (1995).
13. Gregg, S.J. and Sing, K.S.W., in *Adsorption Surface Area and Porosity*, Academic Press, London, Ch. IV (1982).