Synthesis and Characterization of Microporous Materials ZSM-5 and Mordenite

Durlov Saikia[1], Anup Kumar Talukdar*

[1]Assistant Professor,Department of Chemistry, University of Science and Technology, Meghalaya(USTM)
*Professor, Department of Chemistry, Gauhati University
Email id: durlovsaikia13@gmail.com, anup_t@sify.com

Abstract:

The Microporous materials ZSM-5 zeolite was synthesized with silica to alumina ratio 100 by one step synthesis systems. The required amount of sodium aluminate was added to a solution of NaOH in de-ionized water. The solution was kept under constant stirring tetrapropylammonium bromide (TPA-Br) was then added slowly. The calculated amount of colloidal silica was then added carefully to the stirred mixture to form a gel. The whole mass was then autoclaved in a teflon-lined stainless steel vessel. After cooled the products are filtered and washed, dried, calcined. and mordenite zeolites, and also synthesized following procedure. The synthesized samples were characterized with X-ray diffraction and FT-IR for phase identification, with TGA for thermal stability, with SEM for morphology and with N_2 adsorption-desorption for specific surface area, pore volume and pore size.

Key words: ZSM-5, TPA-Br, TGA, SEM, FT-IR etc.

Introduction
Synthesis of ZSM-5 and mordenite zeolites

Different synthesis routes are generally followed for the formation of ZSM-5 zeolite. The ZSM-5 zeolite was initially synthesized after about 7 day's autoclavation period of the mixing of gel within temperature range of 120-180 ^{0}C under autogeneous pressure [1]. Robson et al. [2] and Barrer et al. [3] have reported that by applying a nucleated gel method, the autoclaving time could be reduced to 48 h. By the modified synthesis technique, the autoclaving time was further reduced to 4-12 h in presence of promoters [4, 5]. Various problems like a decrease in the percentage of crystallinity, difficulty in the incorporation of metal ions in the framework tetrahedral positions, difficulty in controlling the Si/Al ratio, a low yield of product etc. arose in case of promoter induced ZSM-5 synthesis. Kulkarni et al. [6] have reported the synthesis of highly crystalline ZSM-5 with an autoclaving time of 4-10 h at 230-250 ^{0}C without

using promoter. However, these workers have used various organic solvents at high pressure and the overall synthesis period was 20-26 h, including the period of preparation of the seeding gel at 100 ^{0}C for about 16 h. Although the synthesis of ZSM-5 in 4-6 h has recently been reported by Ghiaci et al. [7], the procedure was limited to one silicon source and required sulfuric acid in the reaction gel. Although more than 190 types of zeolite framework structure have been identified and synthesized, only a few of them have found practical applications. Amongst them, mordenite (framework MOR) is one of the most important industrial catalysts for the conversion of hydrocarbons, for instance in hydroisomerization, alkylation, dewaxing, reforming and cracking [8-16], because it consists of parallel 12-membered ring (MR) channels (0.67 - 0.70 nm) with 8 MR side pockets (0.34 - 0.48 nm) [17]. Due

to the small size of the 8 MR, for most guest species, mordenite structure is generally considered as one-dimensional, which can induce diffusion limitations [13, 14]. Despite its superior performance, little is known about the molecular traffic properties inside the mordenite framework, since most synthetic methods yield mordenite with crystal sizes smaller than a few microns, which has impeded reliable intracrystalline diffusion measurements [18-20]. Sano et al. reported that addition of aliphatic alcohols had remarkable effects on the size and morphology of mordenite crystals [21, 22]. Needle-shaped crystals with size up to 60 nm can be obtained with ethanol additives. More recently, Lu et al. reported the synthesis of large mordenite crystals from a gel with low water content [23].

In the present we have reported one step synthesis of ZSM-5 following the green procedure of Kalita et al [24]. The synthesis of uniform large mordenite crystals is also attempted to systematically control their aspect ratios.

Synthesis of zeolites materials

Synthesis of ZSM-5 zeolites
Source of Chemicals

Materials used for the synthesis of ZSM-5 zeolites are tetrapropylammonium bromide (Lancaster), sodium aluminate (Kemphasol), sodium hydroxide (Merck), deionized water and silica source, colloidal silica (National Chemicals).

A sample of ZSM-5 zeolite was synthesized with silica to alumina ratio 100 by one step synthesis systems. The required amount of sodium aluminate was added to a solution prepared by dissolving 0.0325 mol of NaOH in 135 mL of de-ionized water. The solution was kept under constant stirring conditions for 15 minutes and 0.0142 mol of tetrapropylammonium bromide (TPA-Br) was then added slowly. The calculated amount of colloidal silica was then added carefully to the stirred mixture to form a gel. Finally, the mixture was stirred at a pH of about 8 for one hour to obtain a homogeneous mass. The whole mass was then autoclaved in a teflon-lined stainless steel vessel maintained at 473 K inside an oven. After 17 h the autoclave was quenched and the resultant solid product was separated from mother liquor by centrifugation. The product was washed several times using de-ionized water and dried at room temperature overnight and at 383 K for 6 h. The sample was calcined at 753 K to remove the template.

Table 1.1 Molar ratios of the components in the gel and other conditions

maintained during the synthesis of the ZSM-5 zeolite sample

Sample	Si : Al	TPA-Br : SiO$_2$	H$_2$O: SiO$_2$	Autoclavation time (hr)	pH of the gel
ZSM-5	100	0.07	80	17	8

Synthesis of mordenite
Source of chemicals

Silicon source employed was colloidal silica (Ludox AM30, 30% suspension in H$_2$O, Sigma–Aldrich). Sodium aluminate (NaAlO$_2$, technical grade, Merk) was used as the aluminum source, and sodium hydroxide (Merck, >99%) was used as the base. Deionised water was used as solvent.

For synthesis of mordenite 0.34 g of NaAlO$_2$ and 0.56 g of NaOH were added to 8.0 g of colloidal silica solution (Ludox AM30). The resultant mixture was thoroughly mixed in a mortar for 10 min. The uniform white gel thus formed was transferred into a Teflon bottle and aged at room temperature for an additional 50 min. The pH values of obtained gel were measured to be 12 and 12.6, respectively at 30 and 60 min, after the addition of the silica precursor. The autoclave was heated in a preheated oven at 170 ^{0}C under static conditions for 4 days. The autoclave was afterwards quenched with tap water. The precipitated product was washed four times with batches of 100 mL of hot water (75– 80 ^{0} C). The powder product was filtered, dried at 60 ^{0}C for 14 h, and followed by calcination in static air at 550 ^{0}C for 10 h (ramp 2 ^{0}C / min).

Table 1.2 Molar ratios of the components in the gel and other conditions

maintained during the synthesis of the Mordenite zeolite sample

Sample	Si : Al	Al$_2$O$_3$: Na$_2$O	H$_2$O: SiO$_2$	Autoclavation time (days)	pH of the gel
Mordenite	100	0.16	79.5	4	12

Characterization procedure and instruments

The synthesized samples were characterized by using the following techniques-

X-ray diffraction

X-ray powder diffraction patterns were obtained for the identification and the determination of crystallinity of the ZSM-5, mordenite samples using a Bruker D-8 Advance X-ray diffractometer with CuK$_\alpha$ radiation of wavelength 1.5418 Å operated at voltage = 40 kV and current = 40 mA. The XRD data were collected in 2θ

range 5-50° for the two zeolites and in the 2θ range of 1 to 10 for mesoporous materials. The crystalline size is determined by using Scherrer relation $D_{hkl} = K\lambda / (\beta \times Cos\theta)$ **Relation 1**
It was used to determine the crystallite dimension ($D_{hkl)}$ of the identified crystalline phase [64]. β is the full width at half maximum; K is the shape factor (taken to be 0.9); θ_{hkl} is the Bragg angle and λ is the wave length of $CuK\alpha_1$ (1.5418 Å). The factor 5.73 is used to convert the value of β from degree to radian to obtain D_{hkl} in nanometer unit.
The % of crystallinity is determined by using following relation
$$(\%C) = 100 \times I_{hkl} / (I_b + I_{hkl})$$
Relation 2
For a particular crystallographic plane (hkl) where, I_{hkl} is the corrected integral XRD peak intensity and I_b is the integral background intensity for the same plane.
(step size 0.05°, step time 0.5 s).

Fourier-Transform Infrared (FTIR) Spectroscopy
A Perkin Elmer RX1 FT-IR Spectrophotometer was used for recording the FT-IR spectra of the samples in the form of KBr pellets in mid-IR region of 4000-500 cm^{-1} (resolution 8 cm^{-1}).

Scanning Electron Microscopy (SEM)
Scanning electron micrographs of the samples were taken for investigation of the particle morphology and crystallite size.

Adsorption measurements
The N_2 adsorption–desorption isotherms of the samples were obtained using nitrogen as adsorbate at 77.15 K on a Micromeritics Tristar 3000 analyzer. For this purpose previously calcined sample was out gassed at 383 K for 3 h and then gradual heating to 623 K in continuous flowing N_2 and maintained at that temperature for 12 h. The samples were then slowly cooled down to 383K under N_2 atmosphere and the anhydrous weight of the samples was taken prior to N_2 adsorption–desorption measurement. Finally, the samples were chilled to 77.15 K using liquid nitrogen and the adsorption of nitrogen was carried out at different equilibrium pressures.

Thermal analysis (TG-DTA)
Thermal Gravimetric Analysis (TGA) of the samples were done on Mettler Toledo TGA/DSC 1, STAR^e System analyzer in the temperature range 313-1173 K with heating rate of 10 K/min in N_2 gas atmosphere.
Characterization of synthesized materials
X-Ray diffraction

The XRD pattern of the synthesized ZSM-5 samples is shown in **Fig 1.1**. The prominent characteristic peaks are observed in 2θ values nearly 7 and 23 with a few additional shoulder peaks for the ZSM-5 sample. The crystallite size and % crystallinity of the materials were found to be 52 nm and 94.2 % respectively. The XRD patterns for standard samples are shown in the inset diagram of **Fig 1.1**. The XRD patterns of the synthesized mordenite are depicted in **Fig 1.2** which includes the XRD patterns of standard mordenite samples as inset. By comparing the peak position of the XRD patterns of standard and synthesized samples it is confirmed that well crystallized mordenite phase is prepared in the present investigation. Crystalline size and percentage of crystallinity with respect to characteristic peaks are found to be 54 nm (average) and 94 %.
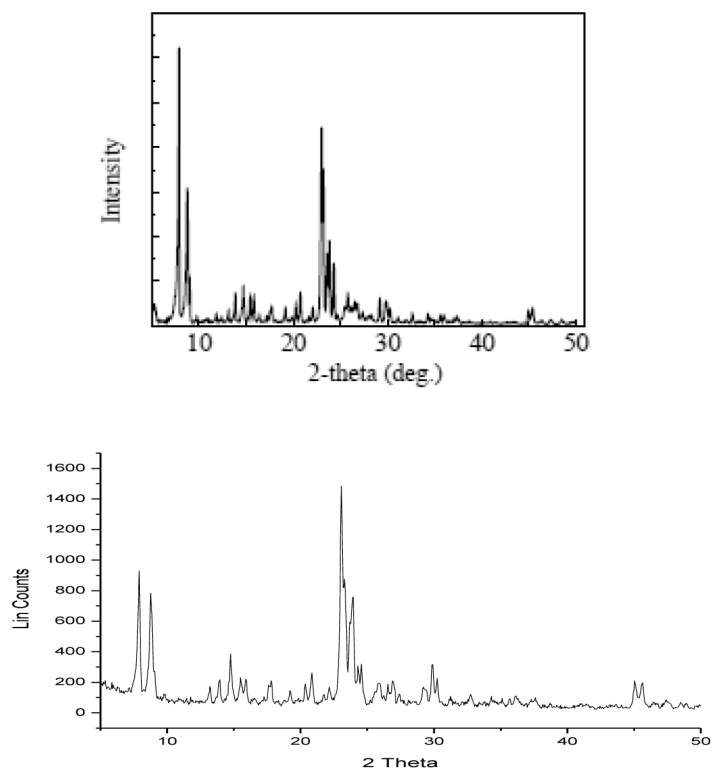
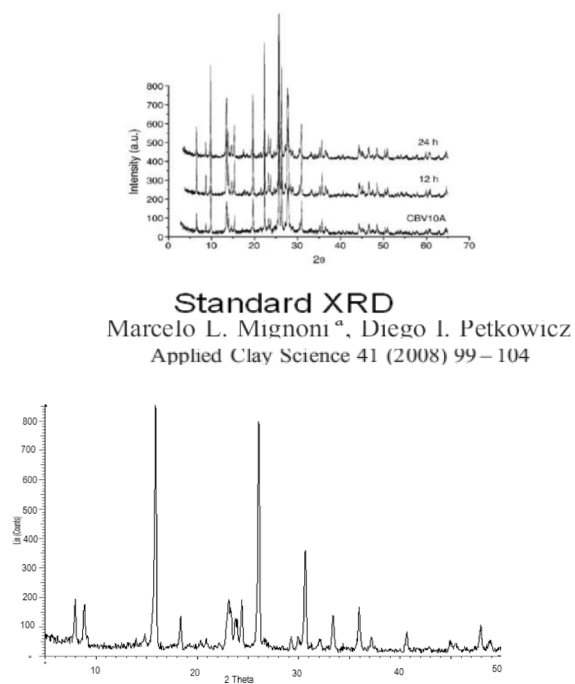**Fig. 1.1 XRD of ZSM-5 (in set XRD of standard ZSM-5)**

Standard XRD
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Fig. 1.2 XRD of mordenite (in set XRD of few samples of standard mordenite)

Fourier Transform Infra Red (FT-IR)

As FT- IR spectroscopy is complementary to X-ray structural analysis of this type of materials. The FT-IR spectra of ZSM-5, mordenite, samples are shown in **Figures 1.3, 1.4** respectively in the mid infrared region (400-1500 cm^{-1}) for ZSM-5 and in the 500-4000 cm^{-1} region for the other material.

Interpretation of these spectra was based on the assignment of the infrared bands to the structural groups in the framework. Absorption bands at around 1225 cm^{-1} (external asymmetric stretch), 1150-1050 cm^{-1} (internal asymmetric stretch), 795 cm^{-1} (external symmetric stretch) and 455 cm^{-1} (T-O-T bending) are typical for highly silicious materials. While the framework vibration at ~ 550 cm^{-1} (double ring) is characteristic of ZSM-5 type zeolites.
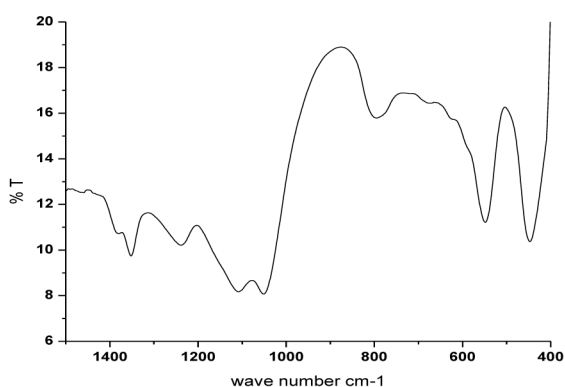
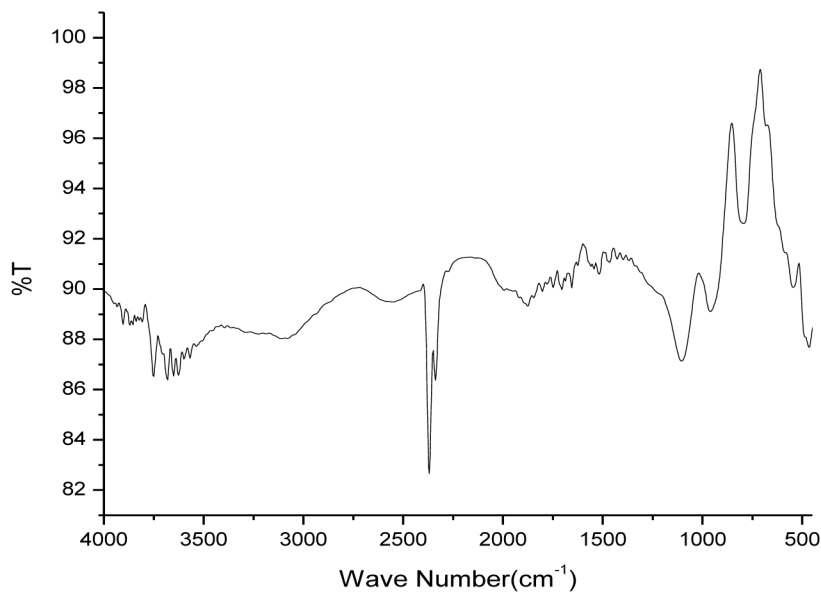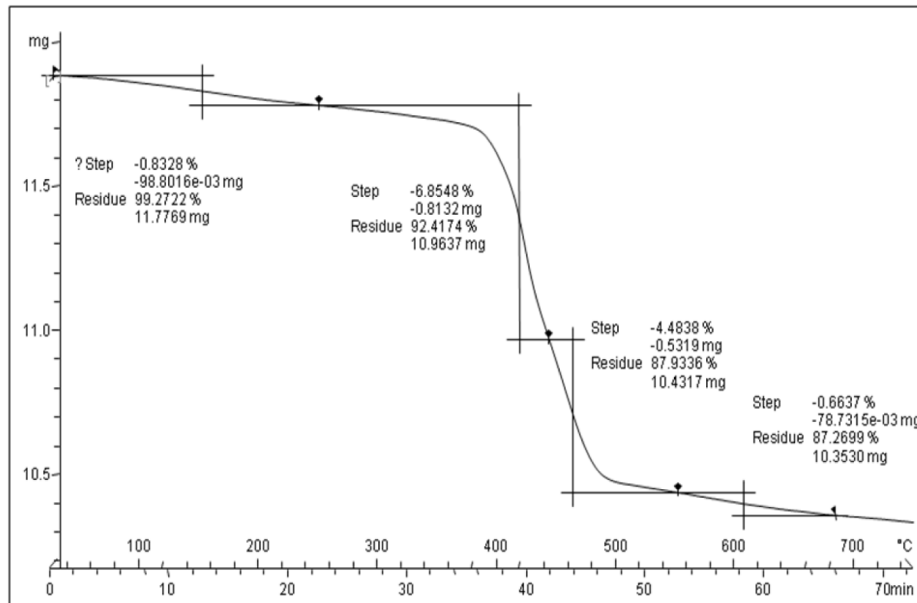**Fig. 1.3 FT-IR spectrum of ZSM-5**

Fig. 1.4 FTIR spectrum of mordenite
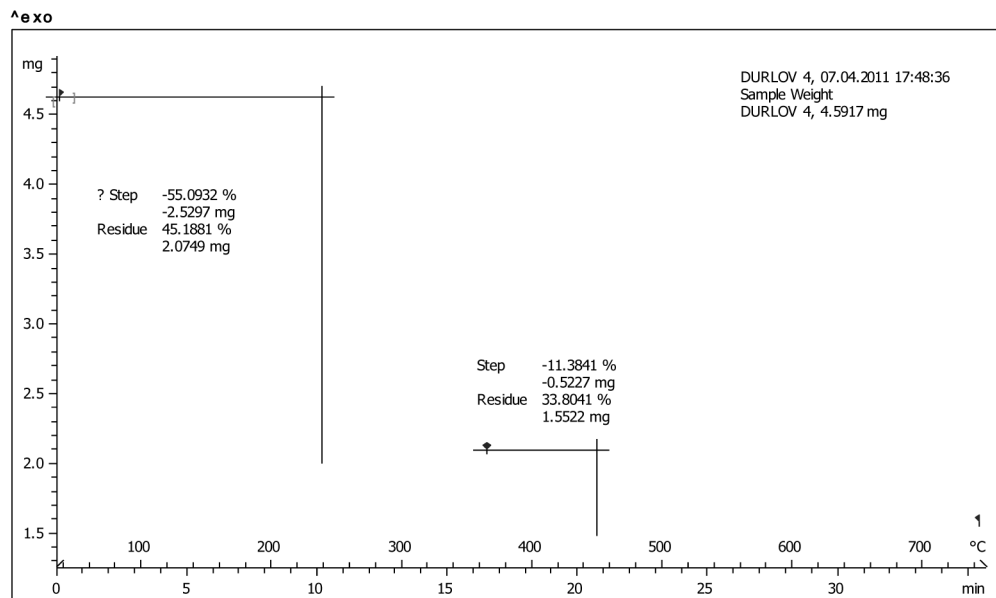
Thermogravimetric Analysis

The TGA of the samples ZSM-5, mordenite are shown in the **Figs 1.5, 1.6** respectively. The first loss below 150 ^{0} C is due to primarily loss of occluded water. The loss above 150 ^{0} C is attributed to the thermal decomposition of template species.

Fig. 1.5 TGA of ZSM-5

Fig. 1.6 TGA of mordenite

N₂ adsorption-desorption isotherm

The N₂ adsorption desorption isotherms for ZSM-5, mordenite, are shown in **Figs 1.7, 1.8** respectively. The surface area of zeolite ZSM-5 and mordenite was found to be 366 and 307 m^2g^{-1} which is well within the range of zeolite. The pore volume and BET surface area of different synthesized materials are shown in **Table 1.3.**

Table 1.3 Pore volume and surface area of ZSM-5, mordenite

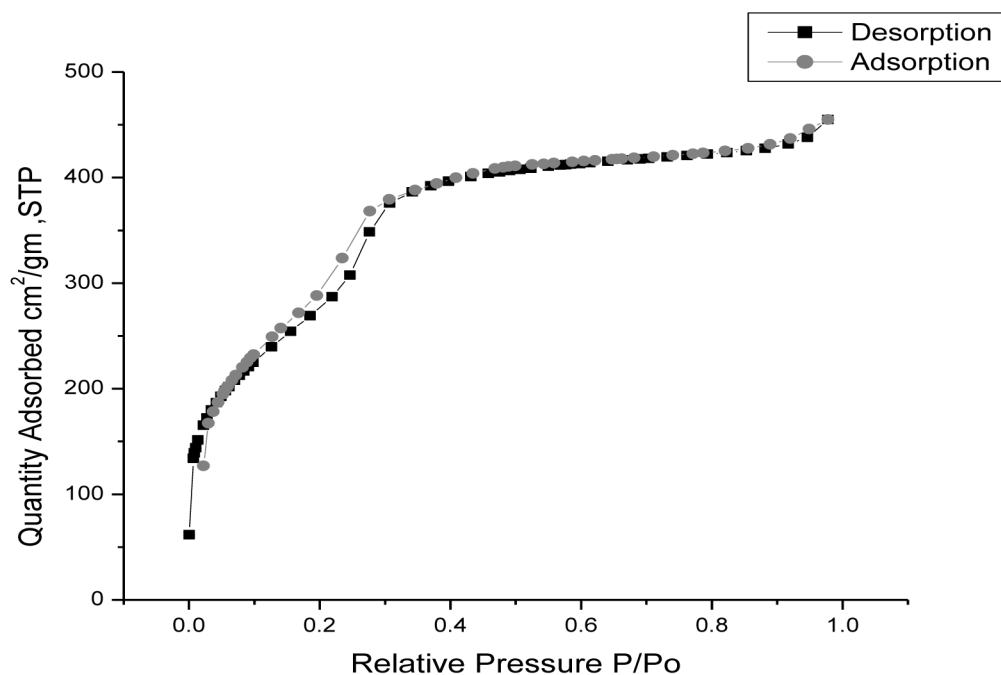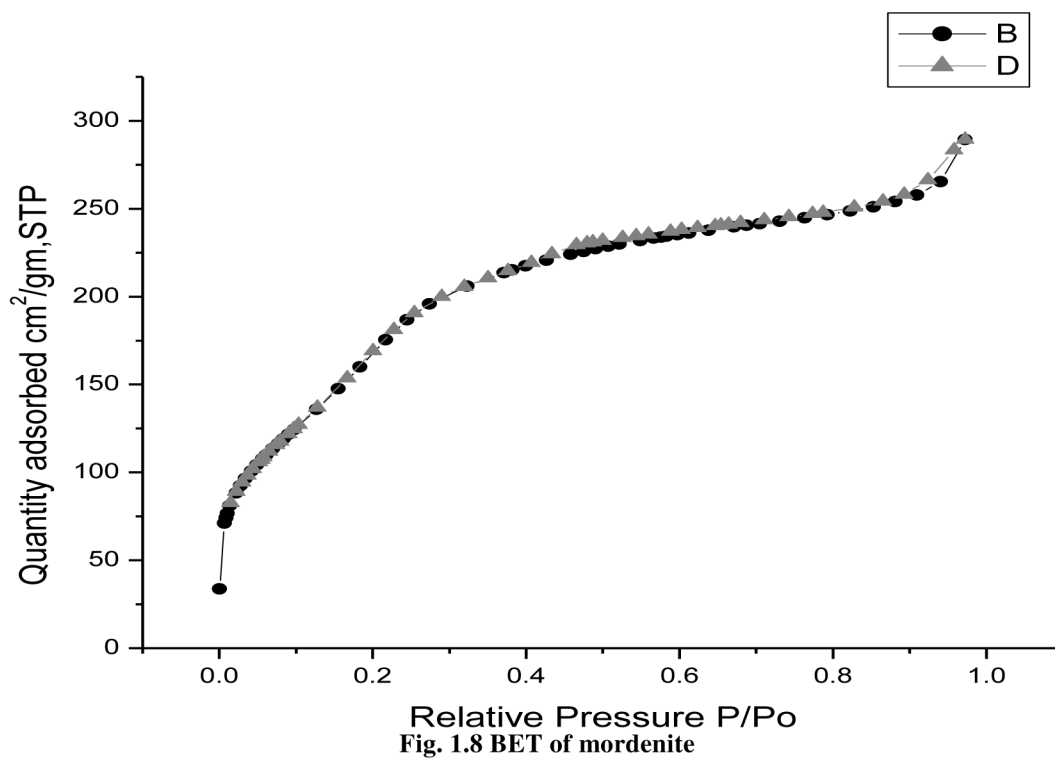| Materials	Pore volume (cm^3/g)	BET surface area (m^2/g)
MFI	0.189	365.67
Mordenite	0.979	306.98

Fig. 1.7 BET of ZSM-5

Fig. 1.8 BET of mordenite

Scanning Electron Microscopy

The SEM images of the materials ZSM-5, mordenite are shown in **Figs 1.9, 1.10** respectively. From the SEM analysis it is seen that ZSM-5 interwinned particles of uniform size were formed. For mordenite two different morphologie were obtained one with an acicular form size of ZSM-5, mordenite, were found to be 8, 14 µm respectively.
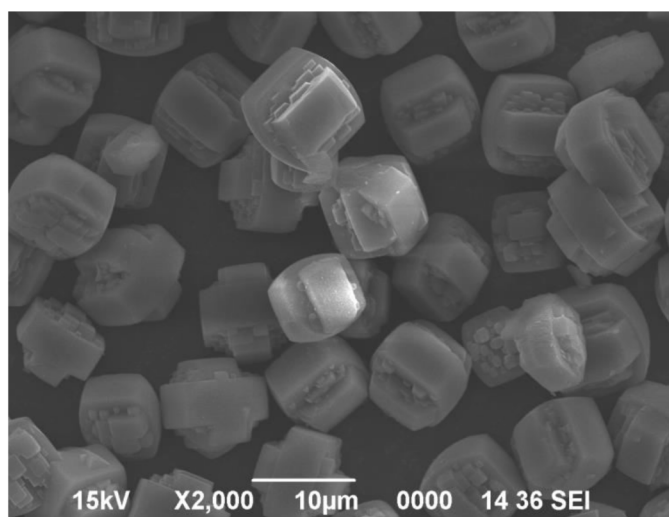

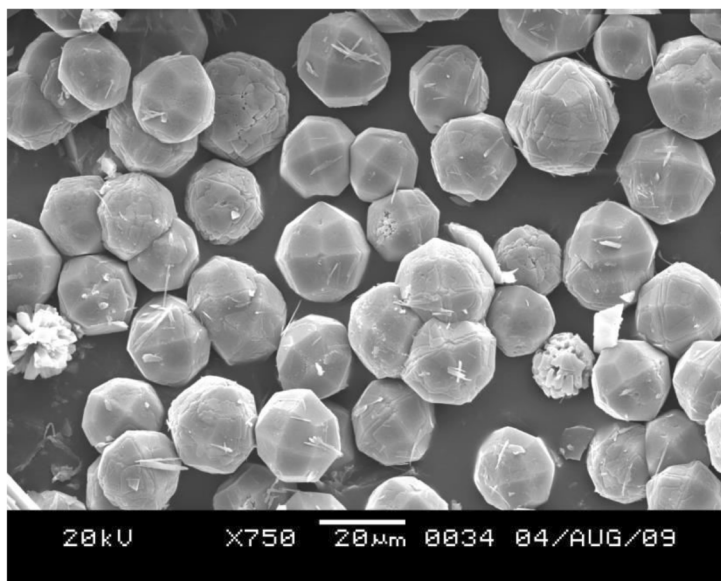**Fig. 1. 9 SEM micrograph of ZSM-5**

Fig. 1.10 SEM micrograph of mordenite

Conclusions

Samples of ZSM-5, mordenite were successfully synthesized. The basic principle for all these synthesis procedures is based on the fact that the surfactant molecules self organize and interact with the inorganic species to form nanoporous structure. Different synthetic parameters like gel composition, silica source, temperature, ageing time, pH etc. assist in manipulating synthesis time for the formation of these materials.

The synthesized samples were characterized with X-ray diffraction and FT-IR for phase
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identification, with TGA for thermal stability, with SEM for morphology study.

From the N_2 adsorption-desorption study of the synthesized samples the specific surface area (BET) were found to be 365.67 m^2/g for ZSM-5 , 306.98 m^2/g for mordenite. The pore volumes were found to be 0.189 cm^3/g for ZSM-5, 0.979 cm^3/g and for mordenite.

From the SEM analysis it is seen that ZSM-5 interwinned particles of uniform size were formed. For mordenite two different morphologies were obtained. The average particle sizes of ZSM-5, mordenite, were found to be 8 and 14 µm respectively

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