



Synthesis and Characterization of Architecturally Modified Mesoporous-Microporous MFI (Mobil Five) Zeolite with Enhanced Catalytic Activity

DHANJU MANI PATHAK^{1,*}, PANKAJ KUMAR GHOSH², KISHOR KR SHAH³ and ANUP KUMAR TALUKDAR⁴

¹Department of Chemistry, Nalbari College, Nalbari-781335, India

²Department of Chemistry, Mangaldai College, Darrang-784125, India

³Department of Chemistry, Anandaram Dhekial Phookan College, Nagaon-782002, India

⁴Department of Chemistry, Gauhati University, Guwahati-781014, India

*Corresponding author: E-mail: dhanjumani@gmail.com

Received: 2 June 2021;

Accepted: 3 August 2021;

Published online: 20 September 2021;

AJC-20517

Four samples of MFI zeolites with silica to alumina ratio of 100 and using different silica to carbon mass ratios (1:1, 1:4, 1:8 and 1:12) were synthesized by using carbon black particles. Silica-alumina molar ratio imposes the framework structure to the synthesized zeolites. In general with an increase in the silica-alumina molar gel ratio, the thermal stability, acid resistance and hydrophobicity of the product increases and ion-exchange capacity decreases. A higher molar ratio (as high as 100) of silica to alumina is considered. ZSM-5 zeolites being mainly microporous, their use as catalyst is restricted only to small molecules. So, by introducing mesopores in zeolite framework, we basically tried to overcome the limited use of ZSM-5 in reactions involving large molecules. Pore structure of ZSM-5 can be modified by using carbon black particles during synthesis. Such type of synthesis can be used to introduce the mesopore and to decrease the crystal size of ZSM-5 zeolite. Different silica to carbon mass ratio is used to study the pore structure and crystal size of ZSM-5 zeolites under autogeneous pressure without adding any promoter or organic solvent. The synthesized samples were characterized by different techniques such as X-ray diffraction, FTIR spectroscopy, scanning electron microscopy, TGA and N₂ adsorption-desorption isotherm. The samples exhibit high crystallinity (84-91%). The particle size ranged from 2.8 to 7.3 μm. Mesopore to micropore ratios was found to increase with increasing silicon to carbon mass ratio. These structurally modified meso-micro zeolite showed enhanced activity in the benzyl alcohol esterification reaction using acetic acid. The selectivity towards benzyl acetate in all the cases was found to be 100%.

Keywords: Mobil Five, Zeolites, Esterification, Benzyl alcohol.

INTRODUCTION

An approach for obtaining a crystalline, highly acidic material with an appreciable amount of mesoporosity has become the centre of zeolite research for last few years. Desilication and dealumination can create mesopore, but there is chance of structure damage when the treatments were applied to achieve the desired product. This is because desilication needs treatment of the zeolite sample with 1 M NaOH and dealumination needs treatment of the zeolite sample with 1 N HCl and heat them to ~ 100 °C. The hydrothermal synthesis of zeolite in the presence of a template with mesoscopic dimensions like carbon black, carbon rods, carbon spheres or carbon nanofibers [1-3] has been reported recently. Post synthesis combustion of the carbon template by calcination, results in the zeolite

crystal that consist of extra voids in mesoporous size range. This is because the pore structure of ZSM-5 can be modified by using carbon black particles during synthesis. Such type of synthesis can be used to introduce the mesopore in the zeolite framework. Jacobsen *et al.* [4] have reported that the MFI zeolite with carbon black particles can be synthesized in an autoclavation period of 72 h at 180 °C under autogeneous pressure. By the modification of synthesis method, Schmidt *et al.* [5] have reported that the autoclaving time can be reduced to 24 h at 175 °C.

In an attempt to reduce the synthesis time further, a two step method is used in the present study to prepare micropore-mesopore MFI zeolites by using carbon black particles under autogeneous pressure without adding any organic solvent, promoter or sulphuric acid. This procedure is successfully

employed for the synthesis of MFI zeolite using carbon black particles with different silica to carbon ratio. Such type of synthesis introduces mesopores in MFI zeolite and decreases its crystal size. The catalytic studies of the synthesized materials were carried out with the esterification reaction of benzyl alcohol by acetic acid. In organic synthesis esterification reaction is one of the fundamental reactions and has great use [6]. Most of the esterification reactions were carried out in presence of sulphuric acid, hydrochloric acid and toxic materials which are environmentally hazardous and unacceptable. Considering the impact of these chemicals on environment, zeolites are used as acid catalyst in organic transformation [7-10]. The use of zeolite has great advantage because it can be reused.

Further, zeolite is thermally and hydrothermally stable and more efficient catalyst for esterification reaction [11-13]. Microwave induced esterification was also carried out using ion-exchange resin which was compared with that of sulphuric acid [14]. In industries, different esterification of organic acid by different alcohol is used extensively for different purpose [6,15,16].

Benzyl acetate is the product of the reaction of benzyl alcohol and acetic acid in presence of conc. sulphuric acid [17]. MFI zeolites are more efficient catalyst for large number of organic reactions like esterification, hydroxylation of phenol [18], *etc.* Moreover, they are thermally quite stable and their properties can be modified by incorporating metals at the tetrahedral framework. Due to the porous nature, MFI zeolites can be used as molecular sieve as well. MFI zeolites being acidic in nature can substitute large number of hazardous inorganic acids in organic transformations to follow a green pathway for the desired transformation. Thus, in present study, the reaction of benzyl alcohol and acetic acid for esterification reaction is studied using modified ZSM-5 catalysts.

EXPERIMENTAL

The chemicals used in the synthesis process were tetrapropylammonium bromide (TPABr) (Lancaster), NaOH (Merck), sodium aluminate (Kemphasol), colloidal silica (National Chemicals) and deionized water.

Characterization: For the identification of phase and to determine crystallinity, the synthesized samples were analyzed by X-Ray powder diffraction using a Bruker D-8 Advance X-Ray Diffractometer with $\text{CuK}\alpha$ radiation with wavelength 1.5418 \AA operated at a voltage 40 kV and current 40 mA. The XRD patterns were taken in the 2θ ranges $5\text{-}50^\circ$ with step size 0.05° and step time 0.5 s. FTIR spectra were taken by using a Perkin-Elmer RX1 FT-IR Spectrophotometer by using KBr pellets in the mid IR region $4000\text{-}450 \text{ cm}^{-1}$. For the determination of particle morphology scanning electron micrograph of the synthesized MFI samples were taken by using LEO1430 VP; Carl Zeiss scanning electron microscope and Hitachi, S-3600 N scanning electron microscope.

Thermogravimetric analysis (TGA) of all the synthesized samples were done by using Mettler Toledo TGA/DSC 1, STAR[®] System analyzer in the temperature range $313\text{-}1173 \text{ K}$ with heating rate of 10 K min^{-1} in N_2 gas atmosphere. The BET

surface areas of the synthesized MFI samples and value of pore size were obtained from N_2 -adsorption technique. Nitrogen adsorption-desorption measurements were carried out by using surface area and porosity analyzer instrument (Micromeritics; Tristar-3000). Prior to the experiments, all the samples were activated at 673 K for 2 h in high vacuum. After this treatment, liquid nitrogen was used to cool the samples to 74 K. The samples were allowed to adsorb nitrogen gas and complete isotherm was obtained. BET surface area were calculated using t-plot method and pore size distribution (PSD) were calculated using Barrett-Joyner-Halenda (BJH) formula.

Synthesis of MFI zeolite with and without carbon black particles: Four samples of MFI zeolites were synthesized with silica-alumina molar ratio of 100 and using different silica to carbon mass ratios by using carbon black particles (Merck). One sample of MFI zeolite without using carbon black particles but with same silica to alumina molar ratio was also synthesized.

A typical two step procedure for the synthesis of MFI zeolite is stated below:

Preparation of seeding gel (step 1): Sodium hydroxide (0.2018 g) was dissolved in 36 mL of distilled water followed by the addition of 3.771 g TPABr with continuous stirring. The mixture was then stirred for another 0.5 h. After that 3.889 g colloidal silica was added slowly to the mixture with continuous stirring. The mixture was again stirred for another 1 h to get a homogeneous gel. The entire synthesis process was carried out at room temperature.

Preparation of second gel (step 2): About 1.099 g NaOH was dissolved in a solution of 26 mL distilled water and 0.410 g NaAlO_2 followed by the addition of distilled water (72 mL) and the mixture was stirred for 0.5 h. To the solution, 11.131 g colloidal silica was added with continuous stirring and then the mixture was stirred for 1 h to get a homogeneous gel.

Finally, the seeding gel prepared in the step 1 was added slowly and with continuous stirring to the second gel and the mixture was stirred for 1 h to get a homogeneous mixture. The pH of the final gel was maintained at 11.3. The gel was transferred into an autoclave and then heated at $200 \text{ }^\circ\text{C}$ for 16 h in an oven. The solid product thus obtained was filtered, washed with distilled water and dried at room temperature overnight and then the product was heated in an oven at $110 \text{ }^\circ\text{C}$ for 6 h. Finally, the sample was calcined at $480 \text{ }^\circ\text{C}$ in a muffle furnace for 6 h. The synthesized product was in sodium form.

For the synthesis of ZSM-5 with carbon black particles, the same procedure as discussed in step-1 and step-2 was followed, only difference in this case was the addition of carbon black in desired proportion in the second step. Four samples of MFI using different SiO_2 to carbon ratios were synthesized. The designation and gel composition of the synthesized samples are shown in Table-1. During synthesis, the following gel compositions were maintained: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$, $\text{OH}^-/\text{SiO}_2 = 0.15$, $\text{H}_2\text{O}/\text{SiO}_2 = 30$, $\text{TPABr}/\text{SiO}_2 = 0.05$ and $\text{SiO}_2/\text{C} = 1:1, 1:4, 1:8$ and $1:12$.

Preparation of catalyst (ion exchange method)

Preparation of NH_4 -MFI and H-MFI: A definite amount of sodium form of MFI and 120 mL of 15% NH_4NO_3 solution

TABLE-1
DESIGNATION AND GEL COMPOSITION OF DIFFERENT SYNTHESIZED MFI SAMPLES

Sample designation	SiO ₂ /Al ₂ O ₃	OH ⁻ /SiO ₂	H ₂ O/SiO ₂	TPABr/SiO ₂	SiO ₂ /C
ZP	100	0.15	30	0.05	–
ZC1	100	0.15	30	0.05	1:1
ZC2	100	0.15	30	0.05	1:4
ZC3	100	0.15	30	0.05	1:8
ZC4	100	0.15	30	0.05	1:12

was refluxed in an oil bath with constant stirring with the help of a magnetic stirrer at 90 °C for 6 h. The solution was decanted and the residue was treated again with 15 % NH₄NO₃ solution and the above procedure was repeated for another time. The solution was filtered, washed with distilled water, dried at room temperature for overnight and then at 110 °C for 6 h. The NH₄-MFI was calcined at 480 °C to get the H-MFI (Scheme-I).

Esterification of benzyl alcohol by acetic acid over parent and modified MFI zeolite: The esterification reaction of benzyl alcohol by acetic acid using parent and modified MFI were carried out under different reaction time. The reactions were carried out in glass batch reactor under atmospheric pressure. The temperature of the reaction was controlled by a temperature controller and stirring was done by a magnetic stirrer. Before the use of catalysts in the reaction they were activated at 373 K for 4 h. The product and the unreacted reactants of the reaction were collected at different time intervals and

analyzed by gas chromatography (Perkin-Elmer, Clarus 500, Elite 501 column) to calculate the percentage of conversion under different reaction conditions.

RESULTS AND DISCUSSION

XRD studies: The synthesized samples were identified from their XRD patterns. The XRD patterns of the MFI zeolite samples match with those of standard sample obtained from literature [19] and found that all the samples were highly crystalline. Fig. 1 shows the XRD patterns of MFI samples synthesized without and with carbon black particles except ZC4 for which the same is shown in Fig. 2. In XRD patterns, the prominent peaks were observed at 2θ values ~ 7, ~ 23.2 and ~ 45, which are the characteristic peaks for the formation of ZSM-5 zeolites. From Fig. 2, it is not clear whether MFI phase was really materialized or not, although IR spectra show the formation of required T-O bonds and basic units. The variation of

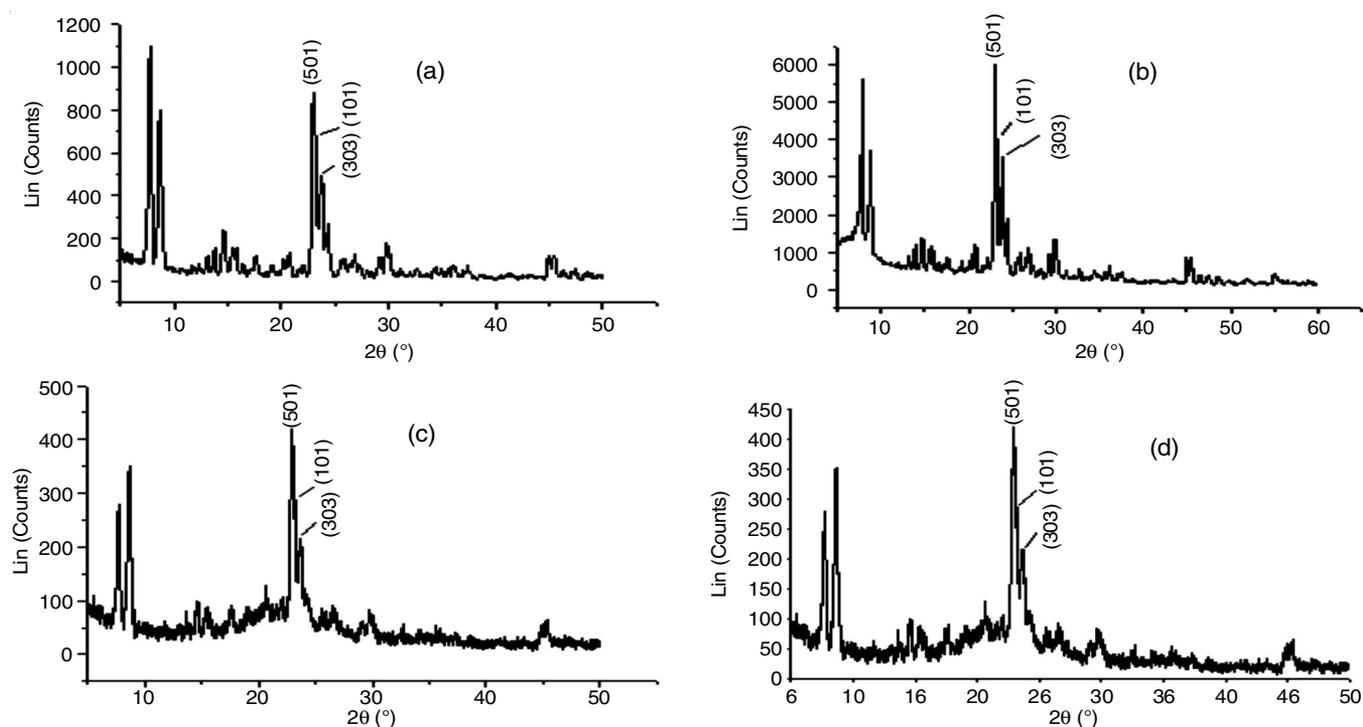
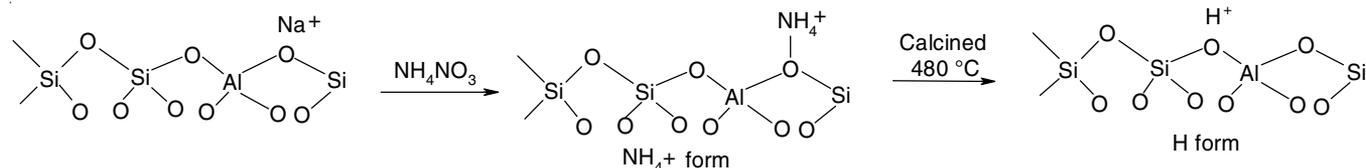
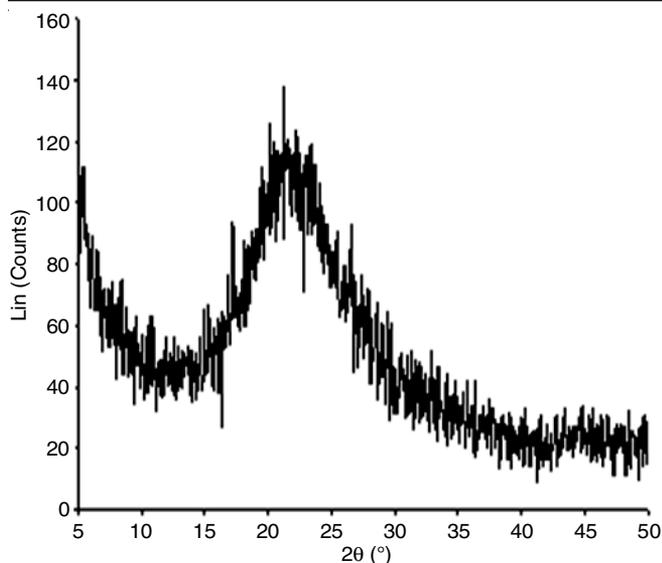
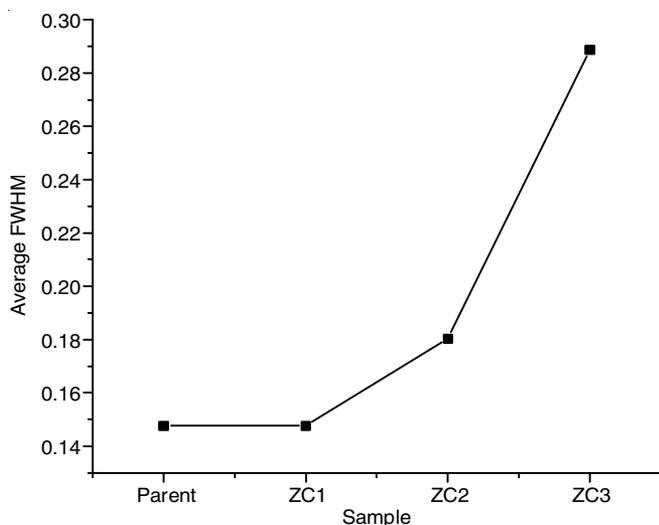


Fig. 1. XRD pattern of (a) MFI (ZP) samples without carbon black particles with SAR 100 (b) ZC1, (c) ZC2 and (d) ZC3

Fig. 2. XRD of MFI (ZC4) in 1:12 SiO₂/carbon ratio

full width at half maxima (FWHM) value with different SiO₂/carbon ratio is given in Fig. 3. It is clear that with the increase in carbon content in the synthesized gel the FWHM value increases.

Fig. 3. Variation of FWHM value for different SiO₂/C

For a particular crystallographic plane (hkl), the crystallinity of MFI samples were calculated by using eqn. 1 [20]:

$$C (\%) = 100 \times \frac{I_{hkl}}{I_b + I_{hkl}} \quad (1)$$

where I_{hkl} is the corrected integral XRD peak intensity and I_b is the integral background intensity for the same plane. The

percentage of crystallinity of the samples with respect to one of the most significant peaks *i.e.* (501) is shown in Table-2. All the samples were found to be highly crystalline (84-91%), which is the average % of crystallinity found from the three significant peaks 101, 303 and 501 of XRD data. The average crystallite size of the samples were found in the range from 28.71-58.85 nm.

Scherrer formula, shown in eqn. 2, was used to determine the crystallite dimension of crystallite phase of the synthesized samples [21].

$$D_{hkl} (\text{crystallite dimension}) = \frac{K\lambda}{\beta \times \cos\theta} \quad (2)$$

where β is the full width at half maximum (FWHM); K is the shape factor (taken to be 0.9); θ_{hkl} is the Bragg angle and λ is the wavelength of CuK α (1.5418 Å). The factor 5.73 is used to convert the value of β from degree to radian in order to obtain D_{hkl} value in nanometer unit. The average crystallite size ranges from 28-58 nm. The crystallite size and percentage of crystallinity (%C)_{hkl} of the synthesized samples is shown in Table-2. The crystallite size of the parent as well as the modified ZSM-5 were calculated with reference to three significant peaks at 101, 303 and 501 planes [18]. The conversion(%) were calculated using peaks in all the three above mentioned planes and are presented in Table-2 as average conversion(%). It was found that as the carbon content in the gel increases, the crystallite sizes of the MFI zeolites decreases. Crystal size of zeolite decreases with increase in mesoporosity. In mesoporous substance, the pore size is greater than that in the microporous substance. When the mesoporosity is increased, a portion of the crystal size is converted in to pores, thereby resulting in the decrease of crystal size. According to Thangaraj *et al.* [22], crystal size of zeolite decreases with increase in mesoporosity. In present study, the mesoporosity of the synthesized samples increases as the carbon content increases (Table-2).

FT-IR studies: FT-IR spectra of parent (ZP) MFI and MFI samples synthesized in presence of C (ZC) are shown in Fig. 4. FT-IR results also confirmed the formation of MFI zeolites in all cases showing distinct absorption bands near 1080 cm⁻¹ (internal symmetric stretching), 790 cm⁻¹ (external symmetric stretching), 540 cm⁻¹ (double ring vibration) and 450 cm⁻¹ (O-T-O bending) [23]. The absorption bands near 550 cm⁻¹ have been assigned to the presence of double five-membered rings in the structure [24]. The external asymmetric stretching vibration around 1225 cm⁻¹, present in the spectra, were assigned to four chains of five-membered rings arranged around a two-fold screw axis.

SEM studies: The size and shape of the crystalline MFI zeolites were investigated by SEM analysis. From the micro-

TABLE-2
CRYSTALLITE SIZE, PERCENTAGE OF CRYSTALLINITY (%C)_{hkl}

Sample	Crystallite size (nm)			(%C) ₅₀₁ from XRD	Average (%C) from XRD	Average crystallite size (nm)
	(101)	(501)	(303)			
Parent	40.49	55.27	80.80	92.52	85.13	58.85
ZC1	40.52	54.97	41.29	94.28	91.83	45.59
ZC2	40.53	41.25	50.09	95.84	89.26	43.96
ZC3	33.76	29.44	22.93	84.75	84.75	28.71

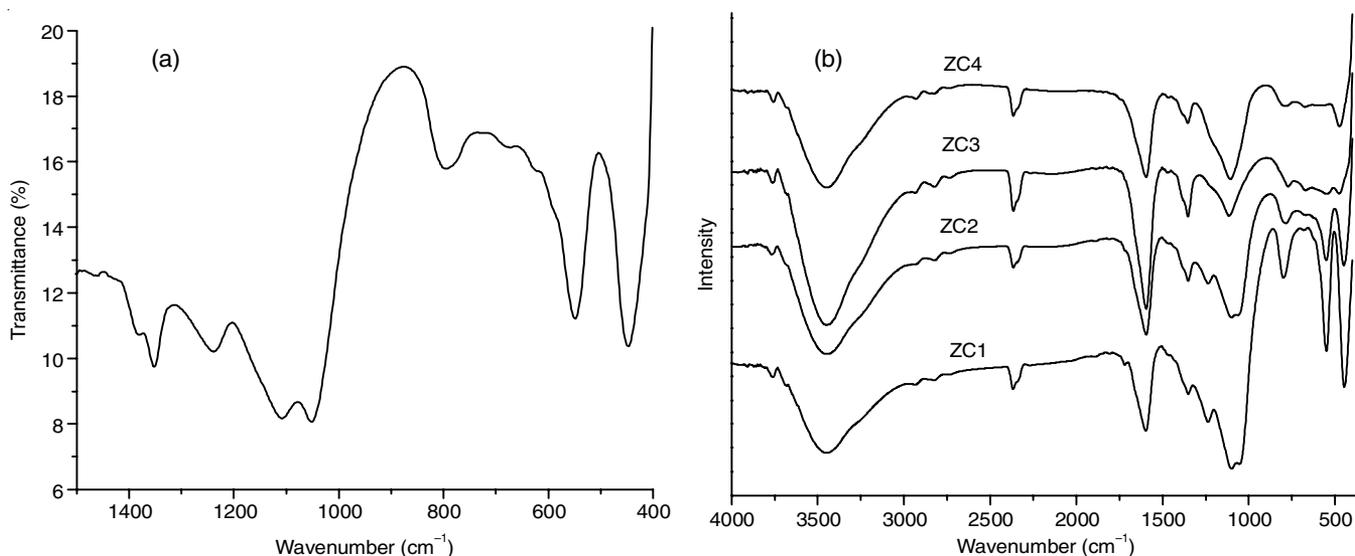


Fig. 4. FT-IR spectra of (a) parent (ZP) and (b) modified (ZC) MFI samples

graphs (Fig. 5), it is seen that the particles are cubic in shape and particle sizes ranges from 2.8 to 7.3 μm (Table-3). The particle size of the parent ZSM-5 sample, calculated from the SEM image was found to be 2.8 μm . The particle size of the samples increased significantly when carbon black was used

during the synthesis of the samples. Some cracks were seen in the particle as the carbon content increases. Moreover, it was found that the particle size increases with the increase in carbon content from 3.4-7.3 μm . The samples synthesized without using carbon black and using carbon black did not show any

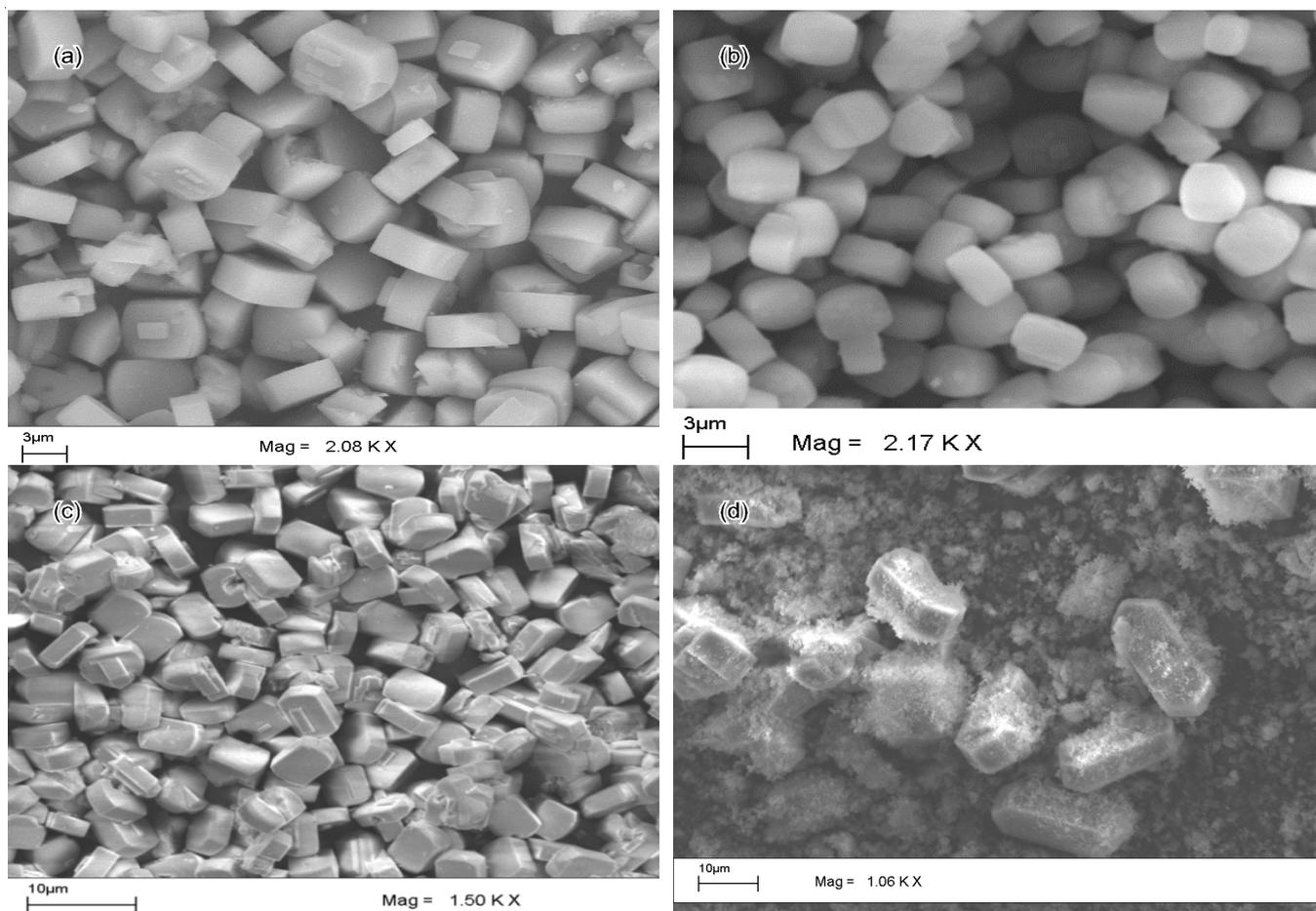


Fig. 5. SEM image of (a) MFI (parent); (b) MFI (ZC1) with $\text{SiO}_2/\text{carbon} = 1:1$; (c) MFI (ZC2) with $\text{SiO}_2/\text{carbon} = 1:4$; (d) MFI (ZC3) with $\text{SiO}_2/\text{carbon} = 1:8$

Sample	Particle size (μm)
Parent	2.8
ZC1	3.4
ZC2	4.4
ZC3	7.3

distinct difference in morphological features among themselves.

Thermal studies: Thermal curves show the initial mass loss up to 423 K (Fig. 6). This may be due to adsorbed water in the porous materials, which means that the endothermic peak in the region 373-423 K can be assigned to the desorption of water from zeolite [25]. This weight loss is common for all the samples. The second and third weight loss is due to the degradation of TPA⁺ cations inside the zeolite structure [26]. The percentages of mass loss in the different regions of temperature are given in Table-4. With the increase in carbon content, the

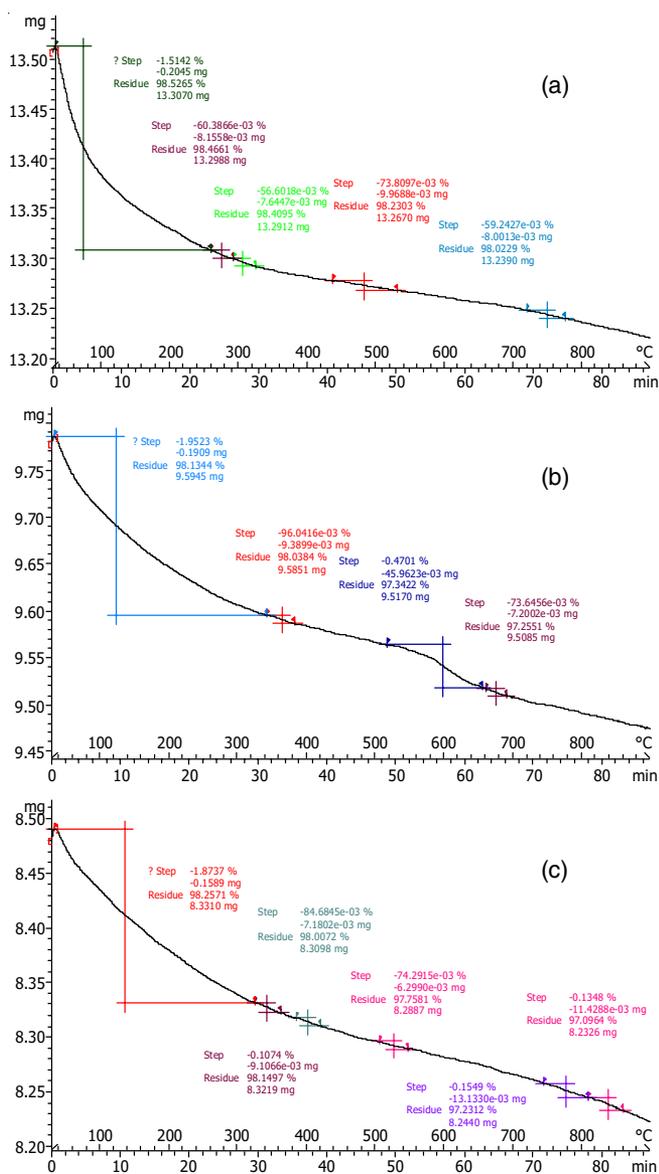


Fig. 6. TGA of sample (a) ZC1; (b) ZC2; (c) ZC3

mass loss in the temperature range 323-573K was found to be increased, while for temperature ranges 573-773 and 773-1073 K, no such trend in the mass loss was observed.

Samples	Mass % loss		
	323-573 K	573-773 K	773-1073 K
ZC1	1.53	0.23	0.21
ZC2	1.96	0.71	0.08
ZC3	1.99	0.25	0.67

Adsorption-desorption studies: Nitrogen adsorption-desorption isotherms of parent, ZC1, ZC2 and ZC3 samples are shown in Fig. 7. Significant changes in the N₂ adsorption-desorption isotherms were observed for ZC1, ZC2 and ZC3 samples. The adsorption-desorption isotherms of N₂ of each sample show the typical type IV isotherm. The materials showing type IV isotherm are the mesoporous materials with strong adsorbate-adsorbent interactions. At high pressure capillary condensation, loops were observed for carbon containing samples ZC1, ZC2 and ZC3. Correspondingly bimodal pore systems were suggested for ZC1, ZC2 and ZC3 as there are mesopores in these samples. The first capillary loops on the isotherms at p/p_0 nearly in the ranges 0.2-0.5, which is the characteristics of framework confined mesoporosity [27,28]. The second loops at $p/p_0 = 0.6-1.0$ in the isotherm indicates the presence of secondary mesopores arising from intracrystalline voids in the packing of smaller crystals [29]. The carbon black particles produce mesoporosity in the MFI samples. The BET surface area and the average pore diameter of the synthesized MFI samples in different solvent are listed in Table-5. For parent ZSM-5 sample, the BET surface area was found to be 341.39 m² g⁻¹. On the other hand, the BET surface area of the samples were found to decrease from 232.066 m² g⁻¹ to 123.25 m² g⁻¹, with the increase in carbon content in the gel. As the carbon content increases in the gel, the micropore volume decreases from 0.15 to 0.05 cm³ g⁻¹ (Table-5) and total pore diameter increases from 20.64 to 27.51 Å. On the contrary, mesopore volume was found to increase from 0.07-0.18 cm³ g⁻¹. This may be due to the conversion of some micropores into mesopores. The variation of BET surface area with the amount of SiO₂/carbon ratio is shown in Fig. 8. It is clear that with the increase in the carbon content in the gel, the BET surface area decreases significantly.

Esterification: Esterification of benzyl alcohol by acetic acid was carried out over parent ZSM-5 and samples ZC1,

Sample	BET surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)	Pore diameter (Å)
Parent	341.39	0.1509	0.0720	20.64
ZC1	232.066	0.0985	0.1191	20.53
ZC2	233.54	0.0956	0.1249	21.39
ZC3	123.25	0.0544	0.1848	27.51

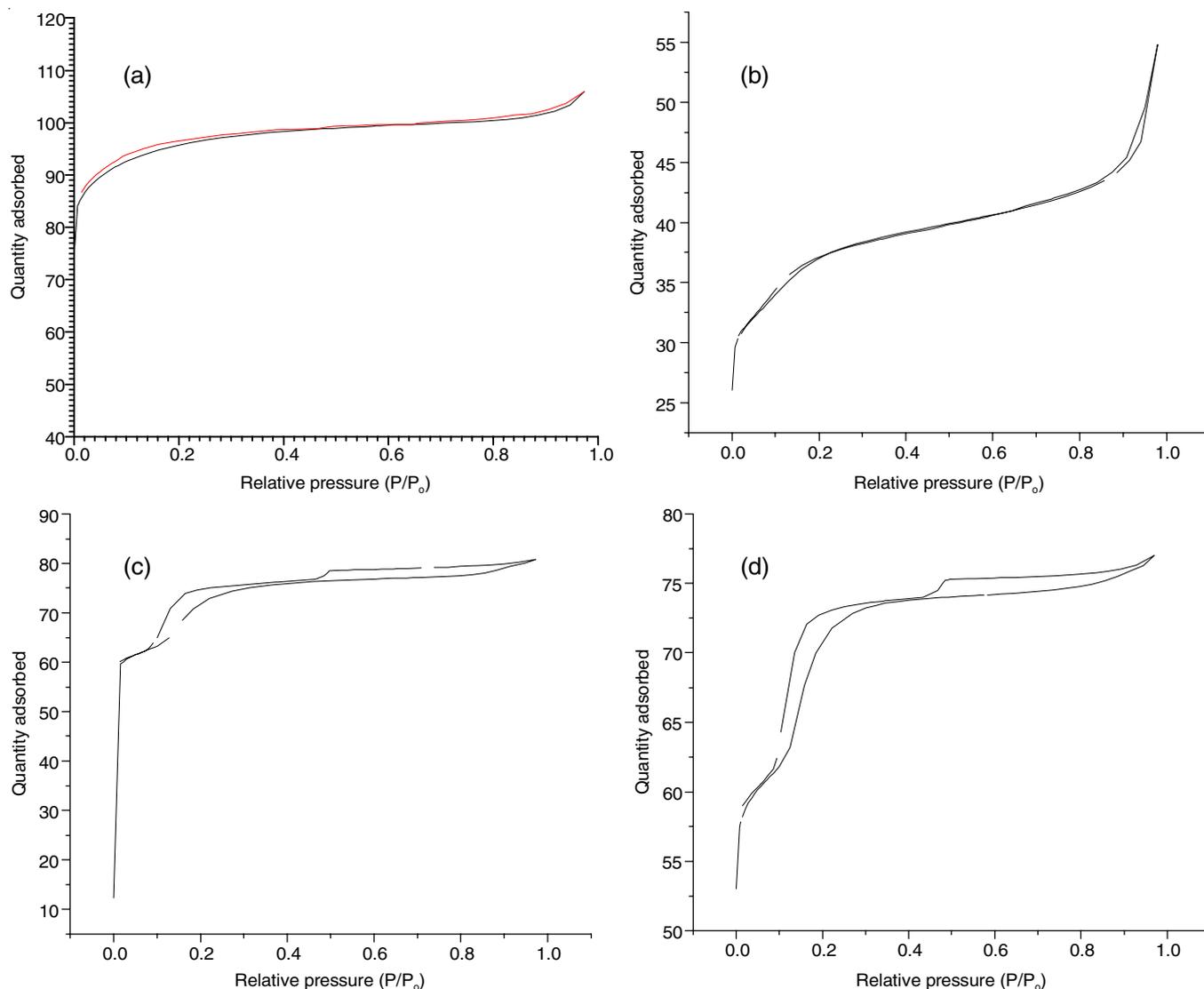


Fig. 7. N₂ Adsorption-desorption isotherm of (a) parent MFI sample; (b) ZC1; (c) ZC2; (d) ZC3

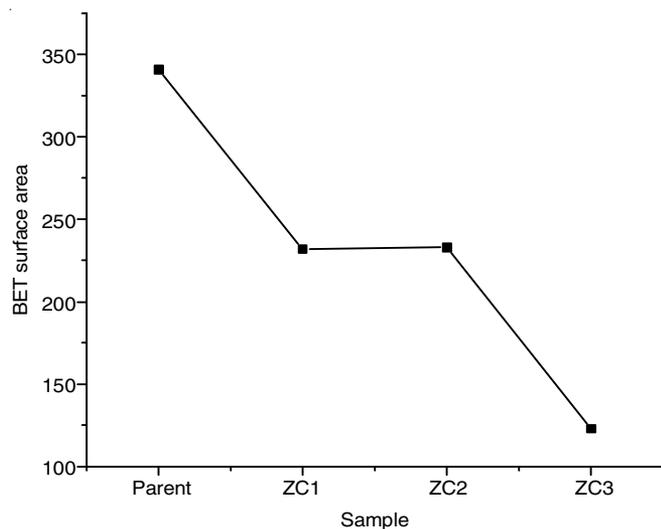
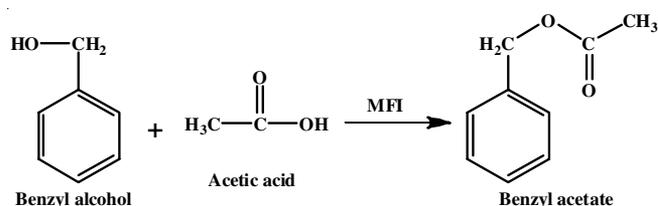


Fig. 8. Variation of BET surface area with carbon content

ZC2 and ZC3 under 373 K and up to duration of 10 h. Benzyl alcohol reacts with acetic to produce benzyl acetate (**Scheme-**

II). The samples were collected at different time intervals such as 2 h, 4 h, 6 h, 8 h and 10 h. The results for esterification of benzyl alcohol on different catalysts under similar conditions at 373 K are summarized in Table-6. When the progress of the reaction was studied in different time intervals, it was observed that the conversion of the reactant increased in all cases with increase of reaction time. It has been observed that the conversion increases from 20.5 to 33.9%, from 20.7 to 50.4%, from 21.3 to 54.3% and from 23.2 to 56.9% for the catalysts ZP, ZC1, ZC2 and ZC3 respectively (Fig. 9). When time of reaction is increased from 2 to 4 h, there is a difference of pattern in



Scheme-II: Reaction of benzyl alcohol and acetic acid to produce benzyl acetate

Time (h)	Conversion (%)			
	ZP	ZC1	ZC2	ZC3
2	20.5	20.7	21.3	23.2
4	28.4	28.9	28.9	30.5
6	31.2	45.2	47.1	50.7
8	33.7	50.1	54.1	56.5
10	33.9	50.4	54.3	56.9

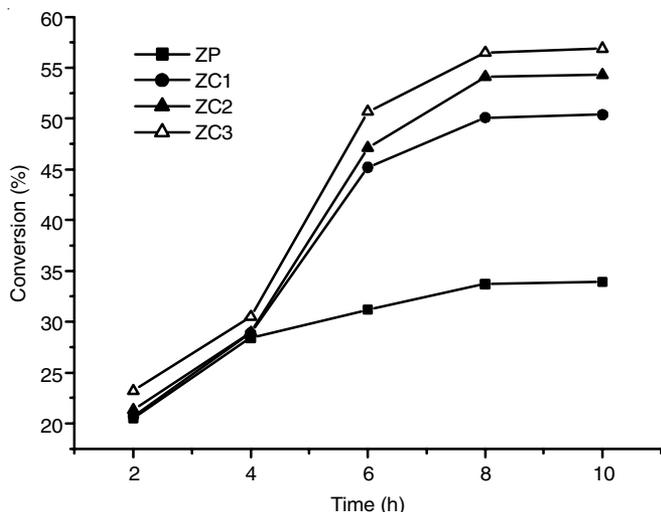


Fig. 9. Comparison of conversions (%) of esterification of benzyl alcohol with acetic acid over different catalysts at different time

increase of conversion in case of catalyst ZP than other catalysts for increase of time of reaction from 4 to 6 h under similar conditions. It also appears that the reaction tends to equilibrate after 8 h of reaction. Reaction conditions maintained in the reaction are temperature = 373 K, catalyst amount = 0.2 g, benzyl alcohol: acetic acid = 1:2 (molar ratio) and substrate volume 16 mL. It was found that with the increase in carbon content, the % conversion of the samples also increases. This may be due to increase in pore volume with the increase in carbon content. With the increase in the carbon content in the synthesis gel, the % conversion was found to increase from 20.5-23.2, 28.4-30.5, 31.2-50.7, 33.7-56.5 and 33.9-56.9 for time of reaction 2,4,6,8 and 10 h respectively. Hence, it can be concluded that with the increase in the carbon content in the synthesis gel, the catalytic activity of the ZSM-5 formed also increases.

Conclusion

In present study, MFI zeolites were synthesized successfully using silica to alumina ratio of 100, in presence of carbon black particles with different silica to carbon ratio and also without carbon black particles. The entire synthesis process was completed in 16 h duration time without using any promoter and organic solvent. The formation of MFI zeolites were confirmed by the XRD patterns of the synthesized samples. The formation of MFI zeolites were further confirmed by the FT-IR results. The average crystallite sizes of the MFI zeolites were found within the range 28.71-58.85 nm, which were

calculated based on the three significant peaks 101, 303 and 501 plane of XRD data. The crystal size of the MFI zeolites were found to decrease with the increase in the amount of carbon black in the gel used for the synthesis of the said zeolites. The decrease in crystal size is an indication of formation of mesopores in the zeolite crystals. The formation of mesopores in the zeolite crystals were confirmed by the nitrogen adsorption-desorption studies. The mesopore volume and pore diameter of the synthesized MFI zeolites were found to increase whereas micropore volume were found to decrease as the carbon content increases in the synthesized gel. From the above results, it may be concluded that some mesopores were introduced in the MFI zeolite materials. From the SEM images, the particle sizes of the synthesized samples were found in the range from 2.8 to 7.3 μm . From SEM analysis, it was found that the particle size of the samples increased significantly when carbon black was used during the synthesis of the samples. By analyzing the data of the esterification reaction, it can be concluded the MFI samples prepared by using higher amount of carbon black in the synthesis gel, show higher catalytic activity in the conversion of benzyl alcohol to benzyl acetate. This may be due to increase in pore volume with the increase in carbon content. The selectivity towards benzyl acetate in all the cases was found to be 100%. The purpose of the experiment was to introduce mesopore in zeolites framework to overcome the limited use of ZSM-5 in reactions involving large molecules, because of its small pore diameter. The purpose was achieved successfully by using carbon black in the gel used for the synthesis of MFI zeolites.

ACKNOWLEDGEMENTS

The authors acknowledge the Centre for Nanotechnology and CIF of IIT, Guwahati and Department of Instrumentation and USIC, Gauhati University, Guwahati, India for the characterization of the samples.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. C.H. Christensen, K. Johannsen, I. Schmidt and C.H. Christensen, *J. Am. Chem. Soc.*, **125**, 13370 (2003); <https://doi.org/10.1021/ja037063c>
2. Y. Tao, K. Kanoh and K. Kaneko, *J. Am. Chem. Soc.*, **125**, 6044 (2003); <https://doi.org/10.1021/ja0299405>
3. A.H. Janssen, I. Schmidt, C.J.H. Jacobsen, A.J. Koster and K.P. de Jong, *Micropor. Mesopor. Mater.*, **65**, 59 (2003); <https://doi.org/10.1016/j.micromeso.2003.07.003>
4. C.J.H. Jacobsen, C. Madsen, J. Houzvicka, I. Schmidt and A. Carlsson, *J. Am. Chem. Soc.*, **122**, 7116 (2000); <https://doi.org/10.1021/ja000744c>
5. I. Schmidt, A. Boisen, E. Gustavsson, K. Ståhl, S. Pehrson, S. Dahl, A. Carlsson and C.J.H. Jacobsen, *Chem. Mater.*, **13**, 4416 (2001); <https://doi.org/10.1021/cm011206h>
6. R.C. Larock, *Comprehensive Organic Transformations*, VCH Publishers: New York, Chap. 9 (1989).
7. R.A. Sheldon and R.S. Downing, *Appl. Catal. A Gen.*, **189**, 163 (1999); [https://doi.org/10.1016/S0926-860X\(99\)00274-4](https://doi.org/10.1016/S0926-860X(99)00274-4)

8. S.E. Sen, S.M. Smith and K.A. Sullivan, *Tetrahedron*, **55**, 12657 (1999); [https://doi.org/10.1016/S0040-4020\(99\)00747-4](https://doi.org/10.1016/S0040-4020(99)00747-4)
9. A. Pandey and A.P. Singh, *Catal. Lett.*, **44**, 129 (1997); <https://doi.org/10.1023/A:1018964722746>
10. U. Freese, F. Heinrich and F. Roessner, *Catal. Today*, **49**, 237 (1999); [https://doi.org/10.1016/S0920-5861\(98\)00429-5](https://doi.org/10.1016/S0920-5861(98)00429-5)
11. Y. Ma, Q.L. Wang, H. Yan, X. Ji and Q. Qiu, *Appl. Catal. A Gen.*, **139**, 51 (1996); [https://doi.org/10.1016/0926-860X\(95\)00328-2](https://doi.org/10.1016/0926-860X(95)00328-2)
12. A. Corma, H. Garcia, S. Iborra and J. Primo, *J. Catal.*, **120**, 78 (1989); [https://doi.org/10.1016/0021-9517\(89\)90252-2](https://doi.org/10.1016/0021-9517(89)90252-2)
13. M. Lasperas, P. Graffin and P. Geneste, *J. Catal.*, **139**, 362 (1993); <https://doi.org/10.1006/jcat.1993.1031>
14. K.G. Kabza, B.R. Chapados, J.E. Gestwicki and J.L. McGrath, *J. Org. Chem.*, **65**, 1210 (2000); <https://doi.org/10.1021/jo990515c>
15. G. Sartori and R. Maggi, *Chem. Rev.*, **106**, 1077 (2006); <https://doi.org/10.1021/cr040695c>
16. A. Zaidi, J.L. Gainer and G. Carta, *Biotechnol. Bioeng.*, **48**, 601 (1995); <https://doi.org/10.1002/bit.260480607>
17. A.I. Vogel, Text book of Practical Organic Chemistry, Longmans: London, Ed: 3, p. 783 (1956).
18. K.K. Shah, M. Nandi and A.K. Talukdar, *Mater. Res. Bull.*, **66**, 101 (2015); <https://doi.org/10.1016/j.materresbull.2015.01.018>
19. H. Robson, Ed.: K.P. Lillerud, Verified Synthesis of Zeolitic Materials, Elsevier: Amsterdam, Ed.: 2 (2001).
20. K.K. Shah, J. Saikia, D. Saikia and A.K. Talukdar, *Mater. Chem. Phys.*, **134**, 43 (2012); <https://doi.org/10.1016/j.matchemphys.2012.02.012>
21. B.D. Cullity, Elements of X-Ray Diffraction, Addison Wesley Publishing Company Inc.: London, p. 286 (1978).
22. A. Thangaraj, R. Kumar, S.P. Mirajkar and P. Ratnasamy, *J. Catal.*, **130**, 1 (1991); [https://doi.org/10.1016/0021-9517\(91\)90086-J](https://doi.org/10.1016/0021-9517(91)90086-J)
23. E.M. Flanigen, H. Khatani and H.A. Szymanski, Molecular Sieve Zeolites, Advan. Chem. Series 101, American Chemical Society, Washington, DC, p. 201(1971).
24. R. Szostak, Molecular Sieve, Blackie-Academic & Professional: London, Eds: 2, p. 306, 310, 311 (1998).
25. M.A. Cambor, A. Corma and S. Valencia, *Micropor. Mesopor. Mater.*, **25**, 59 (1998); [https://doi.org/10.1016/S1387-1811\(98\)00172-3](https://doi.org/10.1016/S1387-1811(98)00172-3)
26. J. El Hage-Al Asswad, N. Dewaele, J.B. Nagy, R.A. Hubert, Z. Gabelica, E.G. Derouane, F. Crea, R. Aiello and A. Nastro, *Zeolites*, **8**, 221 (1988); [https://doi.org/10.1016/S0144-2449\(88\)80311-7](https://doi.org/10.1016/S0144-2449(88)80311-7)
27. X. Chen, L. Huang, G. Ding and Q. Li, *Catal. Lett.*, **44**, 123 (1997); <https://doi.org/10.1023/A:1018968823654>
28. B.X. Chen, L. Huang and Q. Li, *J. Phys. Chem. B*, **101**, 8460 (1997); <https://doi.org/10.1021/jp9705333>
29. Y.H. Chou, C.S. Cundy, A.A. Garforth and V.L. Zholobenko, *Micropor. Mesopor. Mater.*, **89**, 78 (2006); <https://doi.org/10.1016/j.micromeso.2005.10.014>