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The effect of Si/Al ratio of ZSM-5 zeolite on its morphology, acidity and crystal size

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ZSM-5 zeolite crystal with different Si/Al molar ratios in the range of 10-50 was synthesized using sodium silicate, aluminum sulfate and tetrapropylammonium bromide (TPA-Br) as the organic template. The produced samples were characterized using XRD, FT-IR, SEM and EDX techniques. All synthesized samples were found to be ZSM-5 zeolite as confirmed by XRD and supported by FT-IR. SEM results showed that ZSM-5 synthesized with different Si/Al molar ratios had different morphologies and particle sizes. It was found that the average ZSM-5 crystal size increased as Si/Al molar ratio increased. Thermogravimetric-difference thermal analysis (TG-DTA) technique was also used to measure the amount of template occluded inside the crystal pore. The synthesized Na-ZSM-5 was transformed into its acidic form, i.e., H-ZSM-5 using ion exchange method with ammonium nitrate solution. The H-ZSM-5 acidity was determined by NH_3-TPD. These results showed that different Si/Al molar ratios have effect on surface acidity of samples. The surface areas of the H-ZSM-5 were measured using BET method and the results showed that, decrease in Si/Al ratio, decreased the surface area.

1 Introduction

ZSM-5 zeolite is a high silica zeolite, which was first synthesized by Argauer and Landolt of Mobil Oil Corporation, in 1972 [1]. The most common method used to synthesize this material is the hydrothermal route using organic compounds such as tetrapropylammonium bromide, tetrapropylammonium hydroxide [2], tripropylamine, dipropylamine and etc. as template [3]. ZSM-5 is a medium pore (5.1-5.6 Å) zeolite with three-dimentional channels defined by 10-membered rings [4]. Due to its unique shape selectivity, solid acidity, ion exchangeability, pore size, thermal stability and structural network, ZSM-5 has been widely used as catalysts and sorbents in petroleum and petrochemical industry [5]. The catalytic and sorption properties of the zeolite are often influenced by their crystal size. The acidity of ZSM-5 zeolite used as a catalyst has significant effect on reaction path and product distribution in reaction.

The physicochemical properties of ZSM-5 zeolite is influenced by chemical composition and nature of the reagents, alkalinity, template, temperature, time of crystallization, water contents and other factors such as ageing and stirring [6-7]. Crystal size, on the other hand, is governed by the processes of ageing, stirring and temperature.

According to the important role of surface area and diffusional path in the catalytic behavior, zeolites with small crystal size having high external surface area and short diffusional path can have significant effect on product distribution in catalytic reaction. The morphology, crystal size distribution and Si/Al in the zeolite structure are influenced by different variables such as initial chemical composition [8-9], the silicon and

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aluminum source [10-11], the alkalinity [12-13], the presence of seeds [14-15], the OH/SiO_2 molar ratio [16] and dynamic of the system. The aim of the present work was to investigate the effect of Si/Al molar ratio of the as-synthesized ZSM-5 zeolite on its crystal size, morphology, surface area and acidity.

2 Experimental

Reagents The materials used in this work for the synthesis were aluminum sulfate, $(Al_2(SO_4)_3.18H_2O$, laboratory grade, Merck), silica gel (grade 923, 100-200 mesh, Aldrich), tetrapropylammonium bromide (TPA-Br, $C_{12}H_{28}BrN$, Merck), concentrated sulfuric acid (H_2SO_4, 98%, Aldrich), sodium hydroxide (flake, Merck) and ammonium nitrate (NH_4NO_3, laboratory grade, BDH)

Synthesis set-up A 500 cc high-pressure stainless steel autoclave reactor manufactured by Autoclave Engineers INC. (BURTON CORBLIN, 60101 NOGENT OISE), France, was employed for the synthesis of zeolite (Fig. 1).

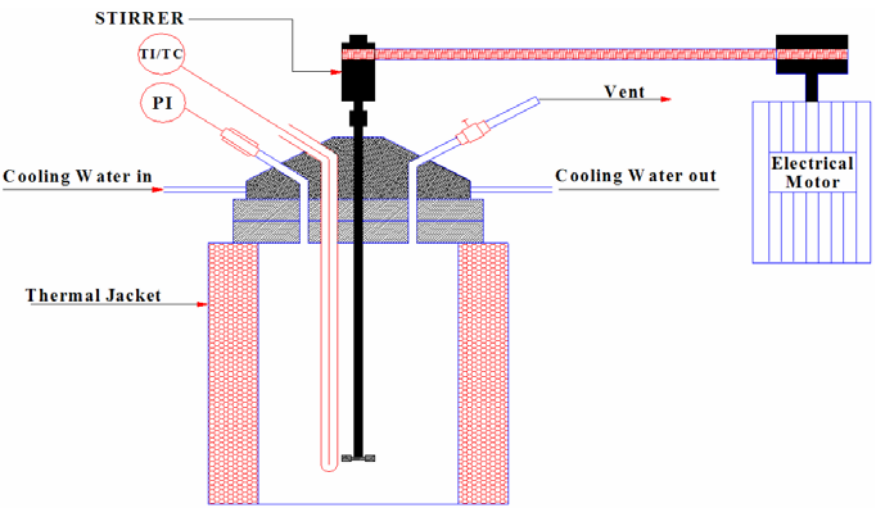

Fig. 1 Diagram of the autoclave reactor used for the synthesis. (online color at www.crt-journal.org)

Synthesize procedure ZSM-5 was synthesized from hydrogel mixture containing silicon, aluminum and template according to the following procedure:

Specified amount of aluminum sulfate was dissolved in de-ionized water and after complete digestion, the required amount of sulphuric acid solution was added to the solution and it was named as solution A (pH = 1). Sodium silicate solution with the composition of 29.50 wt% SiO_2, 10.50 wt% Na_2O was prepared by dissolving silica gel powder in an alkaline solution at 100 °C and the solution was named solution B. Solutions A and B were mixed together under vigorous agitation until a homogenous gel mixture was obtained. Tetrapropylammonium bromide solution was then added to the gel mixture and stirring was continued for about 2 h. The final gel mixture had a pH = 10.5.

The gel mixture was then put into the stainless-steel autoclave and synthesis was carried out under agitation speed of 700 rpm at 453 K for 24 h.

At the end of the synthesis time, the solid product was filtered and washed several times with warm de-ionized water. The solid product was dried at 393 K and then calcined at 823 K for 3 h under airflow in order to remove the organic template trapped in the zeolite pores.

Na-ZSM-5 transformation into H-ZSM-5 After calcinations, the Na-ZSM-5 was ion-exchanged for 24 h under stirring with 2 M solution of NH_4NO_3 with a zeolite-to-solution ratio of 1 g zeolite/10 cm^3 solution at 353 K under reflux to get NH_4^+-ZSM-5. After ion exchange the NH_4^+-ZSM-5 was filtered and washed with de-ionized water and the sample was calcined at 823 K for 3 h under airflow to decompose the ammonium ions to produce hydrogen form. The ion-exchange procedure was repeated twice for each sample.

Characterization of the product (ZSM-5) The ZSM-5 zeolite prepared was characterized for their crystallinity, chemical composition, morphology, crystal size and acidity. The samples were analyzed by X-ray diffraction (XRD) for phase identification using a Philips PW 1840 type equipped with a Cu tube working at a generator potential of 40 kV and a generator current of 30 mA with a nickle filter for phase identification.

The FT-IR spectra of the product were recorded using BRUKER Model IFS 88 Infrared Spectrophotometer in the range 4000-400 cm^{-1} on thin wafers of KBr in which 1 wt% of zeolite was dispersed.

The morphology and crystal size of the samples were examined using a Philips scanning electron microscope (SEM) model XL30. The aluminum and silicon ratio of the samples were analyzed using Energy Dispersive X-ray (EDX) microanalysis coupled with SEM and the sodium content of the sample was analyzed using a Perkin-Elmer Atomic Absorption Spectrometer, Model AAnalyst 200.

Thermal analyses to determine the amount of template trapped insides the crystals and the rate of their removal, were carried out using a Simultaneous Thermal Analyzer Model STA 1640. The temperature of the sample was raised at a rate of 10 $Kmin^{-1}$ from ambient to 973 K in airflow of 50 cm^3min^{-1}.

The surface area of the samples was determined using QUANTA CHROME physical adsorption series using a BET method and their acidity was measured by ammonia adsorption-desorption technique using a chemical adsorption instrument of AMERICAN micrometrics 2900.

3 Results and discussion

The gel composition and synthesis conditions for ZSM-5 synthesis with different Si/Al molar ratios are listed in table 1. The obtained samples were characterized using XRD, SEM, EDX, surface area, FT-IR, TG-DTA and NH_3-TPD techniques. These results are presented in this section.

Table 1 Synthesis conditions* and properties of the synthesized ZSM-5 zeolite with different Si/Al molar ratios. (*Temperature and synthesis time are 453 K and 24 h)

Sample	Gel Compositions (mol) TPA-Br:Na_2O:Al_2O_3:SiO_2:H_2O	Products		
		Si/Al molar ratio	BET surface area ($m^2 g^{-1}$)	Crystal size μm
ZSM-5(10)	9.15:8.0:1.0:60:2137.5	10	355	1
ZSM-5(20)	9.64:8.0:1.0:90:3206.3	20	368	1.2
ZSM-5(25)	9.95:8.0:1.0:100:3562.5	25	371	2
ZSM-5(30)	10.5:8.0:1.0:105:3740.6	30	381	4
ZSM-5(40)	10.6:8.0:1.0:115:4096.9	40	386	7
ZSM-5(50)	10.5:8.0:1.0:125:4453.1	50	392	9

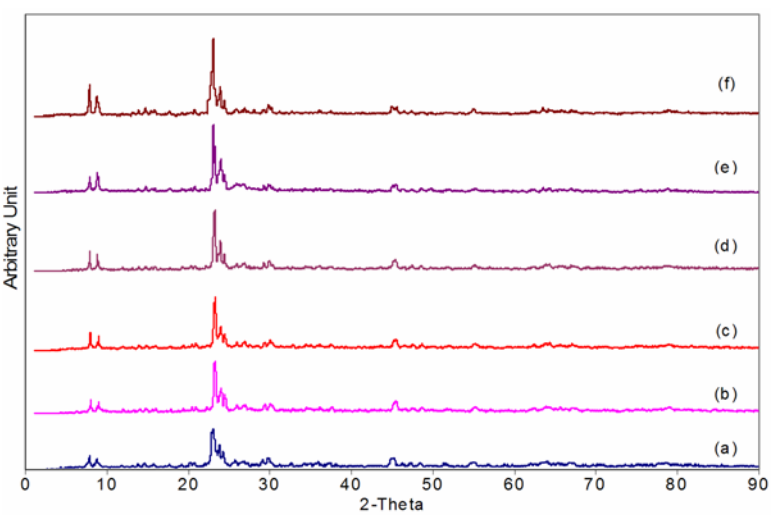

Fig. 2 XRD patterns of the as-synthesized zeolites with different molar ratios of Si/Al (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50. (Online color at www.crt-journal.org)

X-ray diffraction The only crystalline phase obtained within the range of experimental conditions used in this work, i.e., gel mixture, temperature and synthesis time, was ZSM-5 crystals. This is confirmed using X-ray analysis. Figure 2 shows the X-ray diffraction (XRD) patterns of the as-synthesized samples prepared with different Si/Al molar ratios. All samples gave similar XRD patterns, which agree well with those reported in

the reference [17]. No other phase apart from ZSM-5 was found for all of the samples. Purity of the product (i.e. presence of the amorphous phase) was examined by studying the pattern obtained using IR.

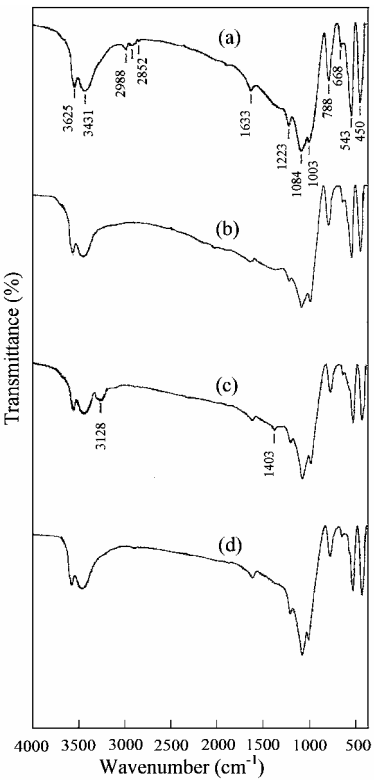

Fig. 3 FT-IR spectra of zeolite having Si/Al molar ratio of 25: (a) as-synthesized, (b) calcined, (c) ion-exchanged and (d) calcined after ion exchanging.

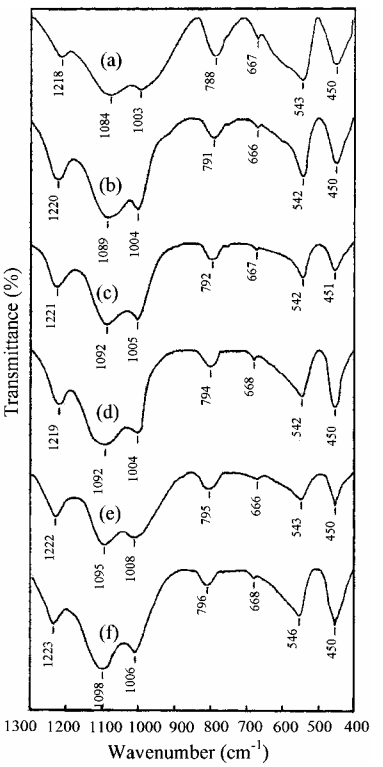

Fig. 4 FT-IR spectra of the as-synthesized zeolite having different molar ratios of Si/Al : (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50.

Fourier transform infrared spectroscopy The FT-IR spectra of the zeolite ZSM-5 (25) in different forms, the as-synthesized (a), calcined (b), ion-exchanged (c) and calcined after ion-exchanging (d) were recorded in the range 4000-400 cm^{-1}. Figure 3 shows appearance and disappearance of different absorption band during the pretreatment procedure. The spectra of the as-synthesized zeolite ZSM-5 (25) shows weak C-H stretching absorption bands in the region 2988-2852 cm^{-1} due to presence of the template together with two broad bands at 3625 and 3431 cm^{-1} assigned to tetraalkylammonium O-H stretching modes [18]. Calcination results in elimination of absorption bands corresponded to the template. Following ion-exchange with aqueous solution of ammonium nitrate, new bands appeared at 3128 and 1403 cm^{-1} due to N-H stretching and bending modes. When the ammoniated zeolites were calcined to produce the hydrogen form of the zeolite, the bands at 3128 and 1403 cm^{-1} eliminated.

Figure 4 shows the infrared absorption spectra of the as-synthesized zeolite with different molar ratios of Si/Al in the region of 1300-400 cm^{-1}. The absorption bands near 788, 1084 and 1218 cm^{-1} are characteristic of SiO_4 tetrahedron units [19]. The strong absorption band in the region 1000-1200 cm^{-1} has been assigned to the internal vibration of SiO_4, AlO_4 tetrahedra for ZSM-5, and also for silica and qartz [20]. The graph shows that the asymmetric stretching vibration frequencies at 1218 and 1084 cm^{-1} generally shift to higher wavenumbers with an increase in the Si/Al ratio. The bands near 1218 and 543 cm^{-1} provide information on the differences between these zeolites (ZSM-5) and other zeolite types. The external asymmetric stretching vibration near 1218 cm^{-1} was assigned to the presence of structures containing four chains of 5-membered rings arranged around a two-fold screw axis, as in the case ZSM-5 structure [21] . The band around 1084 cm^{-1} is attributed to the internal asymmetric stretching vibration of Si-O-T linkage and is observed to shift towards higher wavenumbers with increasing Si/Al ratio of the zeolite. This shift is due to the slightly lower mass of aluminum as compared to that of silicon [22]. The band near 788 cm^{-1} is assigned to the symmetric stretching

of the external linkages, and the strong band near 543 cm^{-1} is attributed to the double five-ring lattice vibration of the external linkages [23]. The absorbance at around 450 cm^{-1} is due to the T-O bending vibrations of the SiO_4 and AlO_4 internal tetrahedral. The absorption bands around 543 and 450 cm^{-1} are characteristic of the ZSM-5 crystalline structure [24] and the ratio of the intensities of these two peaks provides an approximate estimate of the degree of crystallinity of a given zeolite sample. The ratio of the absorbance of these two bands falls between 0.74-0.85 for as-synthesized forms of zeolites. These value compare to a literature value of 0.8, suggested for pure ZSM-5 zeolites [25]. FT-IR confirmed that, the as-synthesized zeolites exhibit good crystallinity. This is in agreement with the results of XRD.

Scanning electron microscopy The morphology of the ZSM-5 crystals with different molar ratios of Si/Al are shown in figure 5. The synthesized samples had different crystal morphologies, from ellipsoidal to cuboidal and a very uniform size distribution and do not contain amorphous substances or other crystalline impurities.

In case with Si/Al molar ratio of 10, highly intergrowth and twinning with highly aggregation had occurred. Also, it is seen that by increasing the aluminum content of the sample, crystal size will decrease. The crystal sizes are in the range from 1 to 10 μm. The electron micrographs show convincingly that the size and morphology of the crystals depend on the Si/Al molar ratio used.

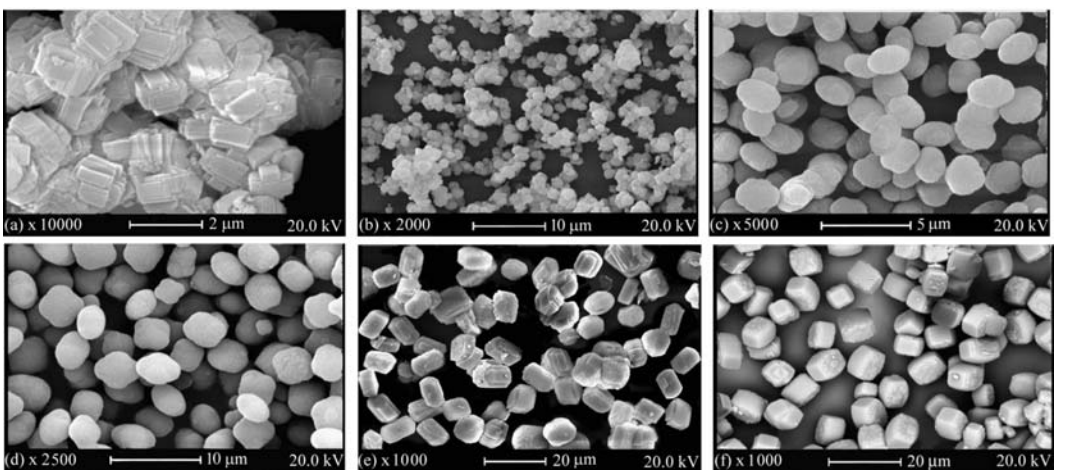

Fig. 5 Scanning electron micrographs of the as-synthesized zeolites with different molar ratios of Si/Al (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50.

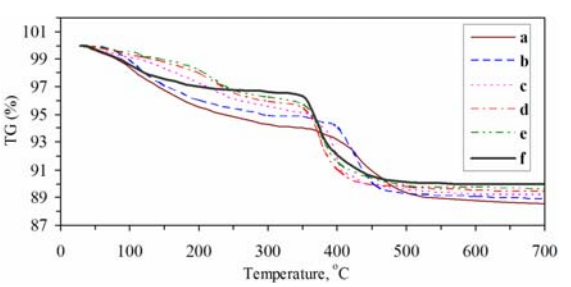

Fig. 6 TGA curves of the as-synthesized zeolites having different Si/Al molar ratios (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50. (Online color at www.crt-journal.org)

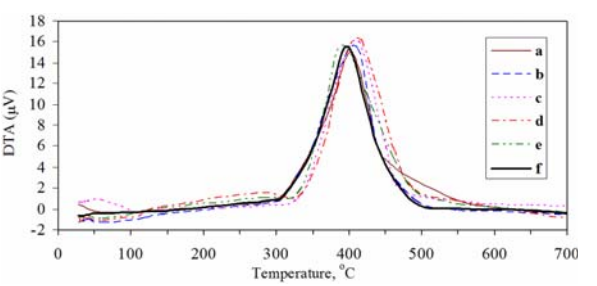

Fig. 7 DTA curves of the as-synthesized zeolites having different Si/Al molar ratios (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50. (Online color at www.crt-journal.org)

Surface area Surface area of the samples is shown in table 1. The results show that, the surface areas increase with increasing the Si/Al molar ratios of the samples.

Thermogravimetric-difference thermal analysis Thermogravimetric analysis was carried out to determine the removal rate of water and template content of the zeolites. TGA and DTA curves of the samples are shown in figure 6 and 7. The observed exotherms are due to the decomposition of the TPA cations trapped in the channels of ZSM-5. Endotherms representing water loss are overshadowed by the exotherms due to combustion of the template. The total percent weight losses in the temperature range 20-600 °C represent water

loss as well as loss of template. These two losses are overlapped in the thermogram and thus provide an approximate estimation. Dehydration occurred below 300 °C. The weight loss in the temperature ranges of 20-300 °C represented by a broad region in the thermogram is believed to be due to water loss and was found decreasing with increasing Si/Al ratio of the zeolites (Fig. 8). This is because the acidity of the zeolite decreases with increasing Si/Al ratio, thus increasing its hydrophobic nature. Therefore, less water is present in the zeolites with low aluminum content. The weight loss in the temperature range of 300-600 °C can be attributed to TPA cation and increase with increasing Si/Al ratio of the zeolites.

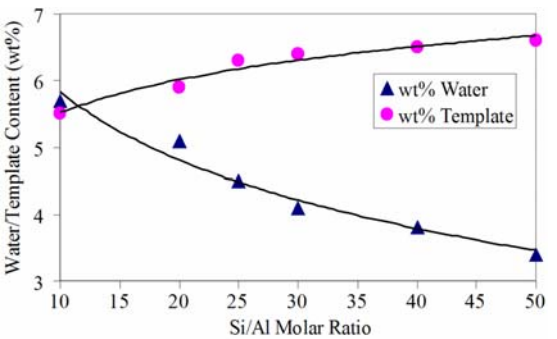

Fig. 8 Water and template contents as a function of Si/Al molar ratio of the as-synthesized zeolites. (Online color at www.crt-journal.org)

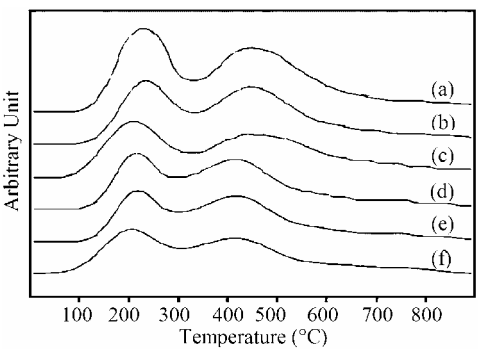

Fig. 9 NH_3-TPD profile of ZSM-5 samples with different Si/Al molar ratios (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50.

Acidity of samples The acidity of the samples with different Si/Al molar ratios was determined by NH_3-TPD. Figure 9 shows a typical acid site distribution as obtained by TPD of ammonia. All samples exhibit two well resolved desorption peaks: the low-temperature peak (LTP) at 210-255 °C and the high-temperature peak (HTP) at 420-465 °C. Generally, LTP and HTP correspond to weak and strong acid sites, respectively.

As shown in figure 9, the peak intensity at 420-465 °C increased as the Si/Al ratio decreased. This is primarily due to the increase in extra-framework aluminum content as well as the in the framework. Figure 9 also shows that the desorption temperature of ammonia from the strong acid sites shifted to higher temperature as the Si/Al ratio decreased, strongly suggesting the existence of aluminum in extra-framework positions.

The amount of NH_3 adsorbed weak and strong acid sites for ZSM-5 with different molar ratio of Si/Al is shown in table 2. This table shows that the total acid sites of ZSM-5 dearease with increasing of Si/Al molar ratio, which agree well with those, reported in the literature [26]. The results showed that the molar ratio of Si/Al of the initial gel mixture has a significant effect on chemical and physical properties of the final products.

Table 2 TPD-NH_3 adsorption for ZSM-5 with different molar ratio of Si/Al.

Sample	Total Acidity (mmole NH_3/g catalyst)
ZSM-5(10)	27.02
ZSM-5(20)	23.03
ZSM-5(25)	21.38
ZSM-5(30)	20.76
ZSM-5(40)	19.93
ZSM-5(50)	19.93

4 Conclusion

Parameters such as molar ratios of Si/Al, acidity and crystal size of the ZSM-5 zeolite are highly important in their application for catalysis in industry. In this work, ZSM-5 zeolites with different molar ratios of Si/Al in the range of 10-50 were synthesized. Calcination of the zeolites to remove the template was carried out by heating the zeolites in airflow for 3 h at 823 K temperature. The zeolites were ion exchanged with a 2.0 M aqueous solution of ammonium nitrate solution at 353 K for 24 h. All synthesized samples as confirmed by their X-ray diffraction and IR patterns, were pure ZSM-5.

SEM images of the samples showed that, the morphology of the synthesized zeolites was of cubical, hexagonal and ellipsoidal in shape. In case with Si/Al molar ratio of 10, highly intergrowth and twinning with highly aggregation had occurred. The BET specific surface areas of the synthesized zeolites increase with increasing Si/Al molar ratio. The particle size of the sample also, changed with the change in Si/Al molar ratios of the gel mixture used for synthesis of ZSM-5. The water content of the sample was found to decrease, while the template concentration was observed to increase with increasing Si/Al molar ratios of the zeolite. NH_3-TPD profiles showed that different Si/Al molar ratios affect the acidity of the samples and the total acid sites of ZSM-5 decreased with increasing the Si/Al molar ratio.

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