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Influence of Aluminum Source on the Synthesis of Nanosized ZSM-5 Zeolite

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ABSTRACT

Aluminum sources have a great effect on ZSM-5 crystallization which leads to change in the properties of the final product. The crystallinity of nanosized ZSM-5 zeolite from precursor's mixtures containing different aluminum sources as sodium aluminate, aluminum chloride and aluminum nitrate has been studied. The produced samples were investigated using XRD, SEM, FT- IR, EDS and BET surface area. The average crystal size increased in the order; sodium aluminate <aluminum nitrate < aluminum chloride, whereas surface area increased as aluminum chloride < aluminum nitrate < sodium aluminate.

Keyword: ZSM-5; aluminum sources; Crystallinity; Crystal size, Surface area.

INTRODUCTION

Nano-compounds, especially zeolites, have great applications in the field of catalysis [1-6]. Zeolites are crystalline microporous aluminosilicates consisting of tetrahedral units producing open framework structures; which generates a system of pores and cavities having molecular dimensions. Different applications, particularly in petroleum refining and petrochemicals industries have been established [7,8]. However, the main applications are focused in the field of petroleum hydrocracking, isomerization, and alkylation and reforming [9,10]. Among all the zeolites, medium pore size ZSM-5 zeolite plays an important role in petrochemicals and fluid catalytic cracking processing. This molecular sieve with MFI structure is synthesized from hydro-gels containing precursors of silicon and aluminum at autogenously pressure and temperature above 100 $^{\circ}$C [11].The efficiency of the zeolites as catalysts is related to their morphological and particular properties (well- defined crystalline structure, high internal surface areas, uniform pores, good thermal stability, etc.).The zeolite catalysts can be used in shape selective reactions which can occur within the pores of the catalyst. Fraenkel et al. [12] have

expanded this concept to include reactions occurring near or on the zeolite surface. Additionally, Derouane and coworkers [13-15] proposed that each zeolite structure has a specific outer surface configuration that offers optimal interactions with adsorbed molecules. The pathway of the crystallization process as well as the morphology and singular properties of the MFI-type zeolite are influenced by variation of silicon and aluminum source [16], aluminum content [17-19], template/silicon ratio, the nature of the cations present in the synthesis medium [16, 20-22], the alkalinity [18, 23-25], the temperature of crystallization [17], presence of seeds [22-26], water contents [19], etc. Thus, it is well established that an increase in the SiO_2/ Al_2O_3 and OH/SiO_2 molar ratios as well as a decrease in the H_2O/SiO_2 molar ratio in the initial synthesis solution leads to a decrease in the final particle size. The control of the crystal size is crucial to monitor adequately the activity and selectivity of the ZSM-5 samples [27, 28].

The aim of the present study was to investigate the effect of different aluminum sources on the crystallinity of nano-size ZSM-5. The structural properties of the prepared ZSM-5 were also explored.

MATERIALS AND METHODS

2. Experimental

All chemicals used were of analytical grade and used without further purification.

2.1. Preparation of ZSM-5 using sodium aluminate

The hydro-gel solution was prepared by dissolving 0.055 gm of NaOH in 7.1 gm distilled water then 5 mL of 20 % tetrapropylammonium hydroxide was added drop wise to the sodium hydroxide solution with stirring for 30 min. Then 2.75 ml of tetraethyl orthosilicate was added drop wise and the resulting mixture was aged for one day at 30^{o}C then the temperature was raised up to 100 $^{\circ}$C and aged for another one day (Mixture I). A 0.405 gm of NaOH was dissolved in 5 gm of distilled water then added drop wise to sodium aluminate solution; prepared by dissolving 0.55 gm of sodium aluminate in 7.5 gm distilled water. A 98 mL of methanol was added to the sodium aluminate solution with stirring for 30 minute then 20.5 gm of tetraethyl orthosilicate was dropwisely added with stirring for one hour to the sodium aluminate solution and the resulting mixture solution is referred to as mixture (II). The mixture (I) was added drop wise to mixture (II) with stirring for one hr. Finally, the creamy gel was heated up in autoclave at 180 $^{\circ}$C for 5 days. At the end of the experiment the autoclave was quenched immediately with cold water. The solid product was filtered and washed with distilled water. The product was then dried at 110 $^{\circ}$C overnight then calcined in air at 550 $^{\circ}$C for 7 hr.

2.2. Preparation of ZSM-5 using aluminum chloride

The hydro-gel solution was prepared by dissolving 2.15 g sodium hydroxide pellets and 2.16 g aluminum chloride in 83.73 g distilled water. After that 5 ml of 20% tetrapropylammonium hydroxide was added drop wise to the previous mixture with stirring for 30 min .Then 50 ml tetraethyl orthosilicate was added drop wise with vigorous stirring for 2 hr. Prior to being transferred to the autoclave, the above synthesis solution was aged for 20 hr at room temperature and then hydrothermally treated for 5 days in an oven at a temperature of 180 $^{\circ}$C. At the end of the experiment, the autoclave was quenched immediately with cold water. The solid product was

filtered and washed with distilled water. The product was then dried at 110^{o}C overnight then calcined in air at 550 $^{\circ}$C for 7 hr.

2.3. Preparation of ZSM-5 using aluminum nitrate

The hydro-gel was prepared by dissolving 2.15 g sodium hydroxide pellets and 3.36g aluminum nitrate in 99.3 g distilled water. After that, 5 ml of 20% tetrapropylammonium hydroxide was added drop wise to the previous mixture with stirring for 30 min. Then 50 ml tetraethyl orthosilicate was added drop wise with vigorous stirring for 2 hr. Prior to being transferred to the autoclave, the above synthesis solution was aged for 20 hr at room temperature and then hydrothermally treated for 5days in an oven at a temperature of 180 ^{0}C. At the end of the experiment the autoclave was quenched immediately with cold water. The solid product was filtered and washed with distilled water. The product was then dried at 110^{o}C overnight then calcined in air at 550 ^{o}C for 7 hr.

2.4. General characterization

X- ray diffraction (XRD) patterns and average crystal size were collected with Brukeraxs, D8 Advance. Surface areas were recorded using Nova2000 series, Chromatech. The FT- IR spectra were recorded using Jasco FT- IR- 460 plus, Japan; the zeolite samples were also characterized by scanning electron microscopy (SEM) model JSM5410. Elemental analysis was carried out using link, ISIS-300, Oxford EDS (energy dispersion spectroscopy) detector. The crystallinity was determined from the peak area between 2 θ = 22–25° using a highly crystalline ZSM-5 sample (ZSM-5 820NAA supplied by Mobil company Japan) as reference. Average crystal size measured by Scherer's equation from XRD peak between 2θ =7-10.

RESULTS AND DISCUSSION

3.1. X-ray diffraction studies

XRD patterns of synthesized Zeolites (ZSM-5) obtained using sodium aluminate, aluminum chloride and aluminum nitrate are shown in figure1 (A, B and C respectively). The peaks at ranges of 2Θ =7–9° and 23–25° confirmed ZSM-5 Zeolite [29]. The crystallinity of sample, which prepared using sodium aluminate, showed the highest crystallinity (100%). This means that Aluminum sources can influence different aspects of ZSM-5 crystallization which leads to change in the final properties of the final product. Moreover, the acidic radical of aluminum source shows a great effect on the crystallization of ZSM-5. The average crystal size increased in the order; sodium aluminate (78.56nm) <aluminum nitrate (104.87nm) <aluminum chloride (112.3nm), whereas degree of crystallinity increased in the order; aluminum nitrate (85.58%) <aluminum chloride (90.29%) <sodium aluminate (100%) .

3.2. Surface area measurements studies

The different surface characteristics of various investigated ZSM-5 materials were determined from N_2 adsorption /desorption isotherms conducted at 77 k. These characteristics include surface area data, Pore volume data and Pore size data and are summarized in table 1. BET surface area increased in the following order; aluminum chloride (153.1m^2/g) <aluminum nitrate (212.4m^2/g) <sodium aluminate (290.1m^2/g).

3.3. IR studies

The FT-IR transmission spectra for nanosized ZSM-5 samples prepared by using sodium aluminate, aluminum chloride and aluminum nitrate are shown in figure 2 (A, B and C respectively). The findings emerge that the bands near 1080 cm^{-1} (internal asymmetric stretch), 790 cm^{-1} (external symmetric stretch), 550cm^{-1} (double ring vibration) and 450 cm^{-1} (T-O bending vibration of the SiO_4 and AlO_4 internal tetrahedral) were appeared for all samples, due to formation of only ZSM-5 phase [30,31]. Additional evidence for the nanosized ZSM-5 zeolite was the asymmetric stretch vibration of the band at 1225 cm^{-1}, which has been assigned to external linkages (between TO_4 tetrahedral) and is a structure-sensitive IR band of ZSM-5 zeolite [32].

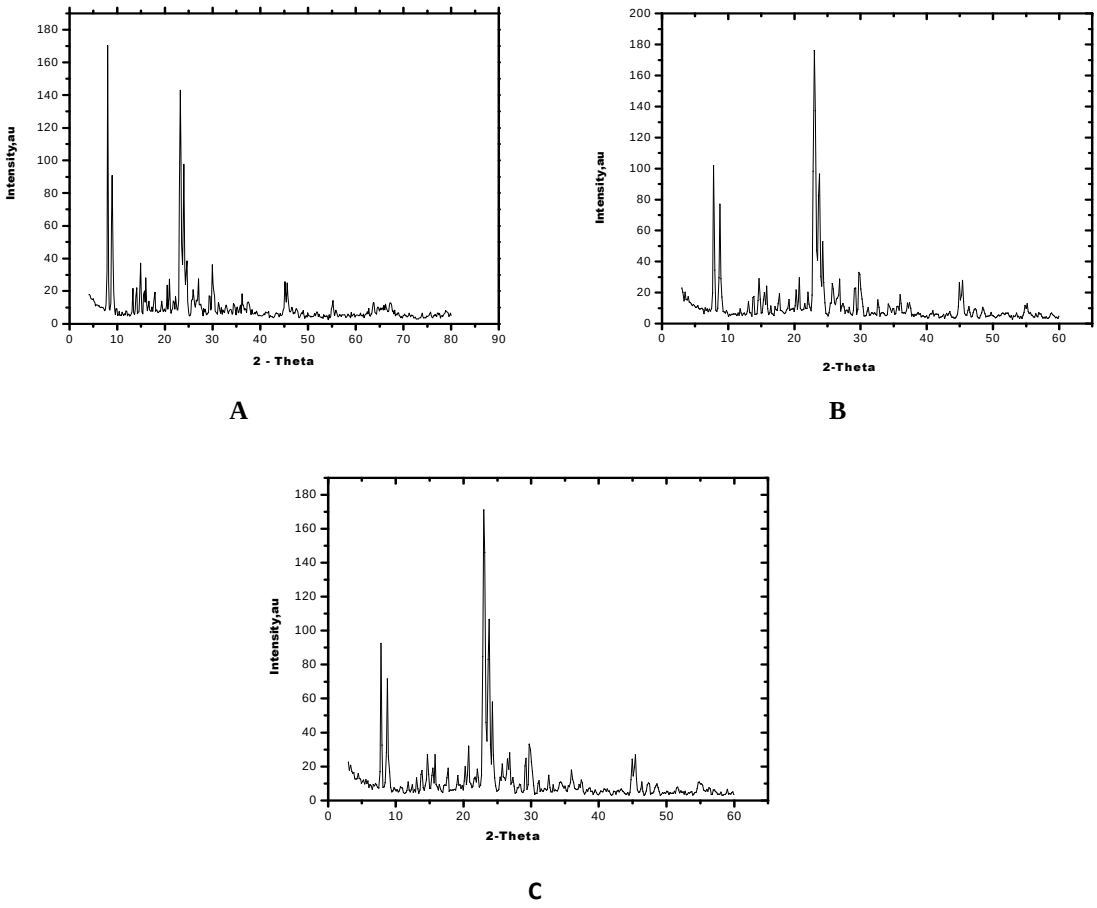

Figure (1): XRD of the prepared ZSM-5 samples using, (A) sodium aluminate, (B) aluminum chloride and (C) aluminum nitrate.

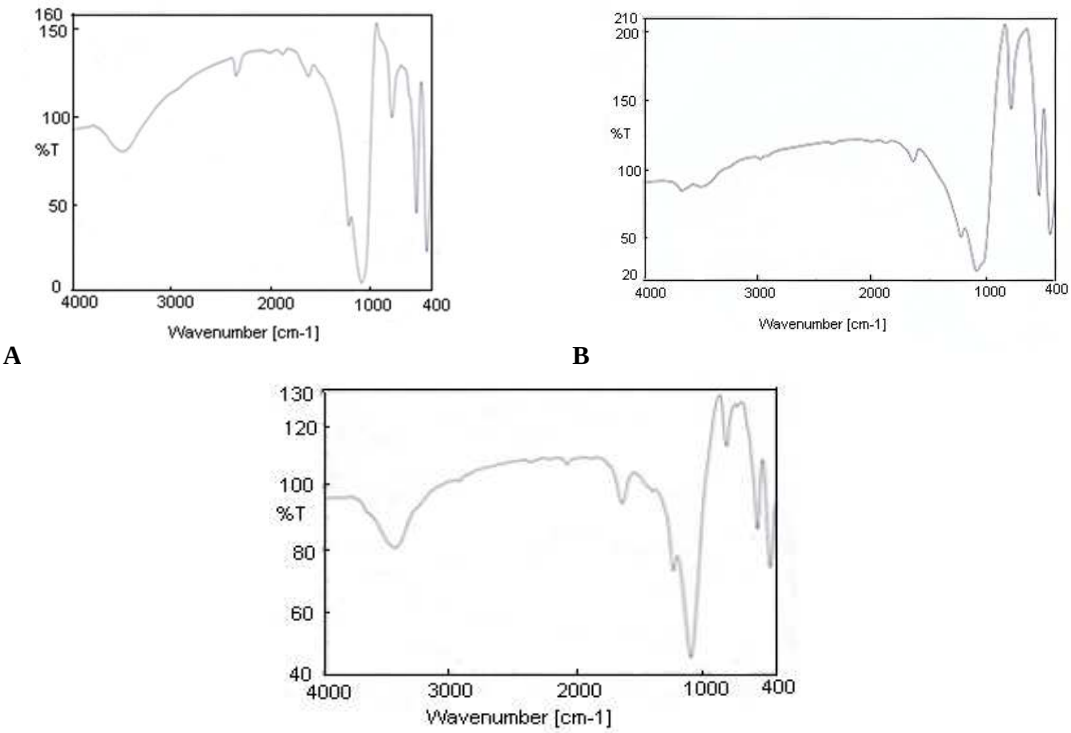

Figure (2): IR spectra of the prepared ZSM-5 samples using; (A) sodium aluminate, (B) aluminum chloride and (C) aluminum nitrate.

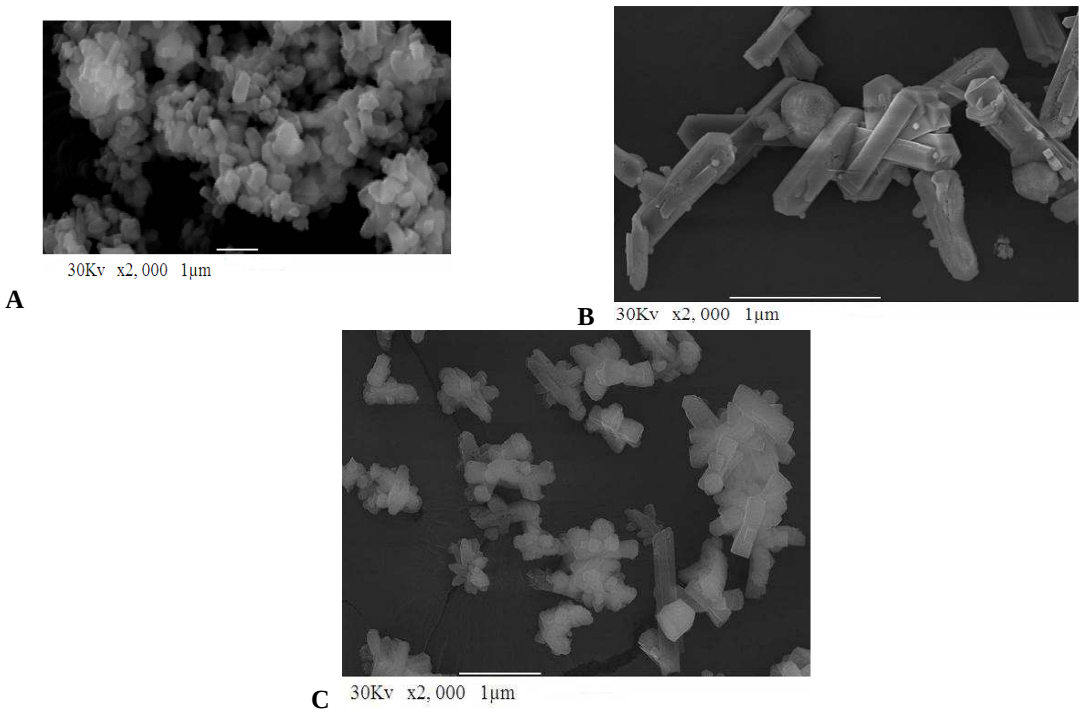

Figure (3): SEM images of the prepared ZSM-5 samples using; (A) sodium aluminate, (B) aluminum chloride and (C) aluminum nitrate.

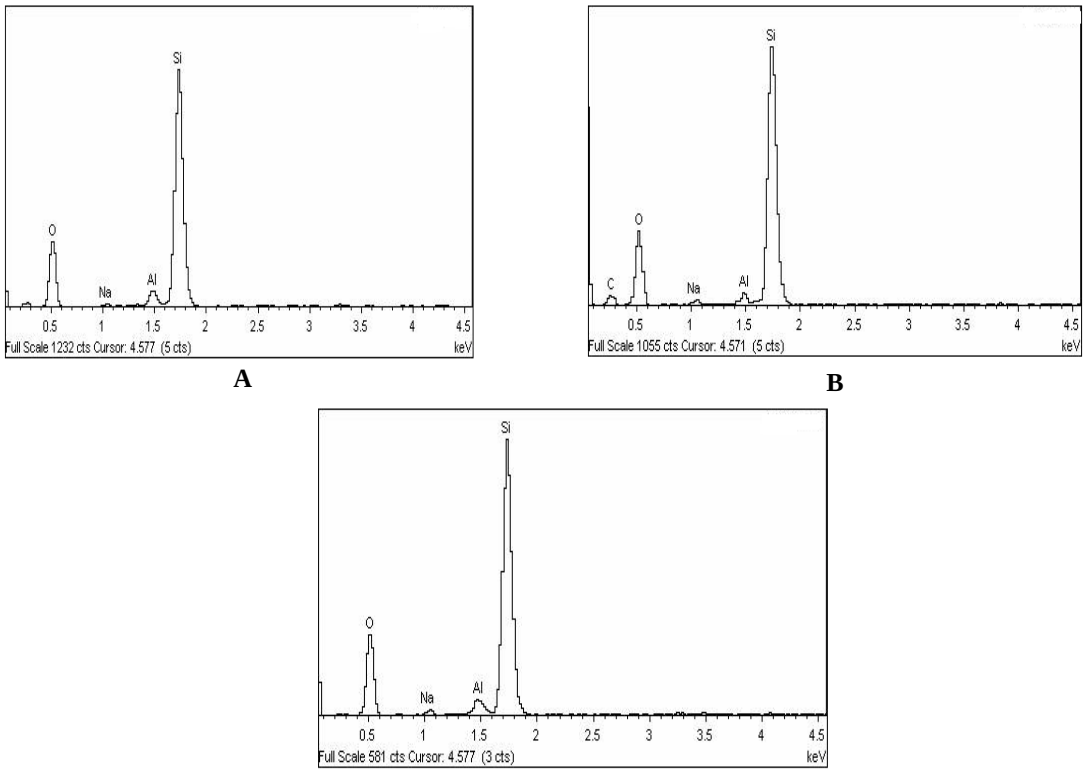

Figure (4): EDS of the prepared samples using; (A) sodium aluminate, (B) aluminum Chloride and (C) aluminum nitrate

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Table (1): Surface area data of the prepared samples

Aluminum source	**BET surface area (m^2/g)**	**External surface area (m^2/g)**	**Micro pore volume (cc/g)**	**Micro pore width(Å)**	**Average pore diameter (Å)**	weight %				
						Si	Al	Na	O	C
Sodium aluminate	290.10	35.39	0.163	114.60	20.31	36.33	2.37	0.82	60.48	0.00
Aluminum chloride	153.10	21.40	0.09	122.80	21.18	22.72	0.90	1.05	54.30	21.03
Aluminum nitrate	212.40	11.48	0.12	75.50	20.47	35.60	2.19	1.76	60.45	0.00

3.4. SEM

Figure 3 (A, B and C) shows SEM images of the prepared samples using sodium aluminate, aluminum chloride and aluminum nitrate, respectively. The results show that the samples, which prepared using sodium aluminate, crystallized in cubical shape crystals. Whereas, the sample prepared using aluminum chloride crystallized in both of hexagonal and spherical shape crystals. However, the sample prepared using aluminum nitrate crystallized in orthorhombic shape crystals.

3.5. EDS

Figure 4(A, B and C) shows EDS of the samples prepared using sodium aluminate, aluminum chloride and aluminum nitrate, respectively. The results show that the prepared samples are chemical compounds of Si-O-Al-Na composition. The weight % of elements (Si, Al, Na, O and C) of the prepared samples is summarized in table 1.

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