

Controlled Crystallization of LTA Zeolitic Nanoparticles from a Clear Solution Using Organic Template

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ABSTRACT: *LTA Zeolite nanoparticles was successfully synthesized from clear solution under controlled conditions using hydrothermal method using tetramethyl ammonium hydroxide as a structural directing agent. The as-synthesized LTA zeolite particles were characterized by powder X-ray Diffraction (XRD) analysis, Scanning Electron Microscopy (SEM), Fourier Transform InfraRed (FT-IR) spectroscopy, Energy Dispersive X-ray (EDX) analysis and surface area measuring technique of Brunauer, Emmett and Teller (BET). XRD patterns and FT-IR spectra were ascertained the formation of pure crystalline phase of 4A (i.e. LTA) zeolite. SEM micrograph was shown particles size in the range of 60 -170 nm with uniform morphology. The Si/Al ratio of the as-synthesized zeolite nanoparticles was 1.66 with a BET surface area of 421 m²/g.*

KEY WORDS: *LTA zeolite, Nanoparticle, Hydrothermal synthesis, Controlled crystallization.*

INTRODUCTION

Aluminosilicate zeolitic materials are crystalline compounds having highly regular and open microporous structure made of a three-dimensional network of SiO₄ and AlO₄ tetrahedra [1]. Extraordinary adsorption, catalysis, and ion exchange properties of zeolitic materials have led to numerous industrial and research applications as bulk powder form [2–4]. The reduction of particle size from the micrometer to the nanometer scale leads to substantial changes in the properties of

the materials, which have an impact on the performance as catalysis and separation comparing to comparing to micron sized zeolites. By decreasing the particle size, external surface area will be increased. Consequently, ratio of external to internal number of atoms increases remarkably resulting higher surface activity. The external surface acidity is of importance when a zeolitic material use as a catalyst in reactions involving bulky molecules. In addition, smaller zeolite crystallites have reduced

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diffusion path lengths relative to conventional micrometer-sized zeolites [5]. The synthesis of zeolite crystallites with narrower particle size distribution requires controlled and homogeneous nucleation in the crystallization system. Therefore, having a homogeneous starting gel and controlling of all the parameters leading to the formation of precursor gel, and their transformation into a crystalline phase are very important [6].

In order to prepare nano sized zeolite crystallites, the precursors gel using for the synthesis should have a high degree of super saturation, because higher super saturation tends to result in high nucleation rates, larger numbers of nuclei, and thus smallest particle sizes [7]. In general, much diluted systems containing abundant amounts of tetraalkylammonium hydroxides have been used in the synthesis of zeolite nanocrystals with narrow particle size distribution. The alkaline cation concentration in such systems has to be very limited in order to avoid the flocculation of gel particles. Moreover, the crystallinity of the manufactured nano sized zeolites is typically very low and rarely exceeds a few percent.

LTA is one of the well known zeolitic materials in terms of the performed research studies and large scale commercial production and applications [8]. LTA is described in terms of sodalite cages linked by 4 membered Rings (4R). The connection of the sodalite cages results in a central large cavity known as supercage. This central cavity is connected to six similar cavities by an 8-ring window with an opening diameter of 4.2 Å. The Si/Al ratio of synthetic LTA zeolite is generally about one although somewhat higher ratios (up to 1.7) are possible when Tetra Methyl Ammonium (TMA) is used in the synthesis mixture [9-11]. Several authors have already reported on the synthesis of nanocrystalline zeolite LTA [6, 7, 12-18].

In continuation of our group research activities on developing new approaches for effective manufacturing of various zeolitic nano materials, in which we have synthesized several zeolites including LTA [19], B-ZSM-5 [20], ZSM-5 [21, 22], sodalite [23], LTL [24], T zeolite [25], NaY [26], in this paper a successful synthesis of the LTA zeolite nanoparticles under a controllable condition using organic compounds as Si and Al precursors as well as structural directing agent will be reported. The basis of the idea was to obtain LTA zeolite phase with narrower particle size distribution by shortening crystallization time.

EXPERIMENTAL SECTION

Synthesis of zeolite NaA nano particles

The materials used in this research were Tetra Ethyl Ortho Silicate (TEOS) (Merck 98%), Tetra Methyl Ammonium Hydroxide (TMAOH) (Merck 25% solution in water), Aluminium isopropoxide (Merck 98%), Sodium hydroxide (NaOH) (Merck 98%), Ethanol (Merck 96%) and De-Ionized (DI) water. All of the chemicals were used as received without further purification.

The molar composition of initial synthesis gel was 0.86 NaOH: 5 TMAOH: 3.4 SiO₂: 1.0 Al₂O₃: 370 H₂O: 19.6 EtOH [27]. Aluminate and silicate solution were prepared according to the following procedure. NaOH pellets and approximately half of the required amount of TMAOH were dissolved in de-ionized water, in which aluminum isopropoxide was added later. The resulting mixture was stirred until a clear solution was formed (solution A). Separately, TEO was added to the rest of the required amount of TMAOH and ethanol solution. The resulting mixture initially formed an emulsion-like state under stirring. However, after 2h of continuous stirring, a homogeneous and clear solution was formed (solution B). Mixing of solutions A and B under stirring was resulted the initial clear solution for synthesis. In order to assure the formation of initially clear solutions free from cloudy particles of gel, the solutions were typically stirred for 3h at room temperature. Then, hydrothermal crystallization of the zeolite was carried out at 98 °C for 50h. Finally, zeolite nanoparticles were recovered from the mother liquor by centrifuge at 13000 rpm for 30min. In order to remove un-reacted materials, the powder was dispersed in DI water by sonication and centrifuged again. This procedure was repeated until the pH of the supernatant decreased to lower than 8. Then the powder was dried at 65 °C overnight. The as-synthesized nanozeolitic powders were calcined in oven at 500 °C in 4h with the heating and cooling rate of 1 °C/min to remove TMAOH molecules.

Characterization

X-Ray Diffraction (XRD), using a Philips X'pert diffractometer with CuK α radiation and a power operating at 40 kV and 40 was used to determine the crystallinity. FT-IR (Shimadzu 8400s, Japan) was used to analyze sample structures. The morphology and particle size of the solid product was examined using SEM instrumental technique (VEGA2-TESCAN).

Table 1: Chemical composition of the as-synthesized nano zeolite of LTA by means of the Energy-Dispersive X-ray Spectroscopy (EDXS).

Element	Atomic Concentration [at.%]	Un-normalized Concentration [wt.%]	Normalized Concentration [wt.%]
Oxygen	59.62	43.29	46.92
Sodium	8.12	8.47	9.18
Aluminium	12.42	15.21	16.48
Silicon	19.84	25.30	27.42
Si/Al	--	--	1.66
Total	100	92.27	100.05

Elemental analysis of the samples was conducted by an Energy Dispersive X-ray Spectrometer (EDXS) attached to the scanning electron microscope. Nitrogen adsorption-desorption experiments were carried out at 77 K on a Brunauer-Emmett-Teller (BET) technique (MicrometricsBELSORP-MINI II) to determine the sample surface area, pore size distribution (i.e. Barrett-Joyner-Halenda; BJH method). The total pore volume, was evaluated from the desorption branch of the isotherm at $P/P_0 = 0.99$, assuming complete pore saturation.

RESULTS AND DISCUSSION

XRD pattern of the as-synthesized nanozeolite along with a simulated pattern of the LTA zeolite single crystal [28] are shown in Fig.1 (A) and (B) respectively. It is clear that the patterns are completely compatible, which ascertain the successful synthesis of high purity LTA zeolitic phase. According to Scherrer equation, $D_{hkl} = K\lambda/(\beta \times \cos\theta_{hkl})$, decreasing of the crystallites sizes were resulted a remarkable broadening of the peaks' width. The identification peaks for zeolite LTA are at $2\theta = 7.18, 10.17$ and 12.46 degrees [28].

FT-IR spectrum of the sample is illustrated in Fig.2. The vibrations of zeolites structure in infra red spectroscopy are located in the wave number ranges from 300 to 1400 cm^{-1} [29]. This spectrum also can be used to indicate the secondary building units of zeolitic structures such as double rings and pore opening [30]. The vibration of T-O bending in 475.42 cm^{-1} , double ring in 576.68 cm^{-1} , and TO_4 asymmetric stretch in 1035.7 cm^{-1} resulted from FT-IR analysis ascertain the formation of zeolitic structure [29]. The SEM image of the particles is shown in Fig. 3, which shows uniform particle morphology and small particle size in range of 60 - 170 nm . Chemical composition of the as-synthesized nano zeolite can be found in Table 1.

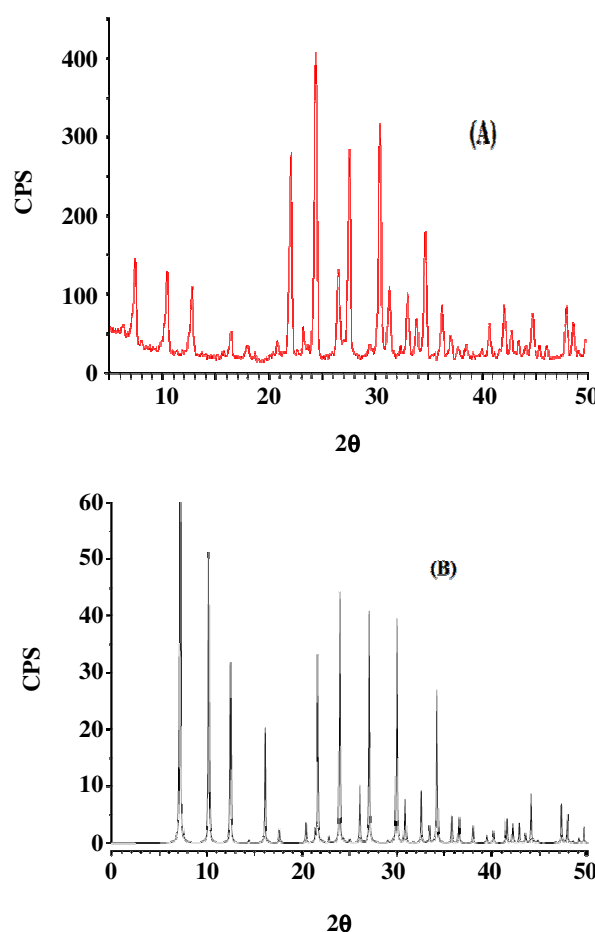


Fig. 1: A) XRD pattern of the as-synthesized LTA zeolite nanoparticles, B) Simulated XRD pattern of LTA zeolite [28].

The Si/Al ratio of the as-synthesized zeolite determined by Energy-Dispersive X-Ray Spectroscopy (EDXS) was 1.66, which is in the reported range of zeolite NaA compositions. Using of template in the synthesis of zeolites tends to change the Si/Al ratio of the final products. For example, zeolite A, synthesized

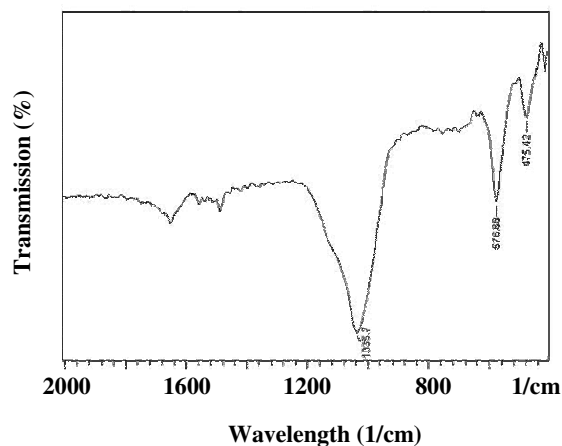


Fig. 2: FT-IR spectra of as-synthesized LTA zeolite nanoparticles.

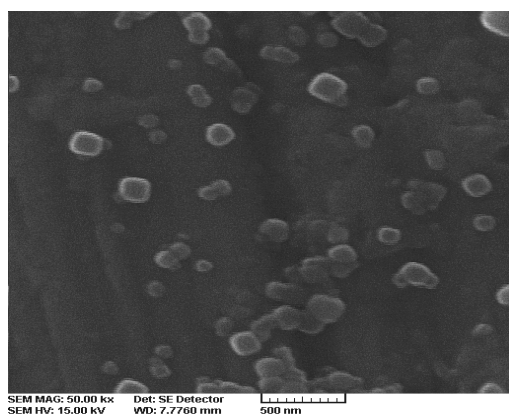


Fig. 3: SEM image of as-synthesized LTA zeolite nanoparticles (scale bar = 500 nm).

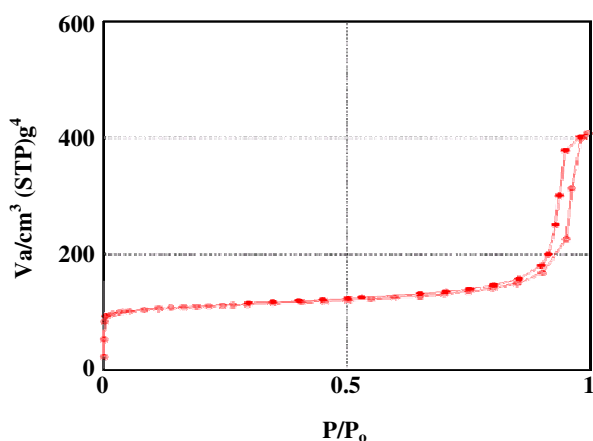


Fig. 4: N_2 adsorption/desorption isotherm of as-synthesized LTA zeolite nanoparticles.

by using template (tetramethylammonium), has a Si/Al ratio about 2. In contrast, template-free synthesis leads to Si/Al = 1 [10, 11]. As results of increasing of Si/Al ration, thermal and chemical stability of the product will be improved remarkably. Enhancing the zeolite stability is of a great interest of industries in various commercial applications. According to the BET analysis; surface area of the as-synthesized zeolites was $421 \text{ m}^2/\text{g}$. The nano LTA sample shows mesoporosity characteristics as it is evident in the adsorption/desorption isotherm, which is shown in Fig.4. There is a steep jump and a large desorption loop in the isotherm. The hysteresis loop of zeolite appears at a high relative pressure ($P / P_0 = 0.9-1.0$), and it reflects intercrystalline voids in the packing of the smaller crystals. Thus, in nano particles, a large share of surface can be assigned to the external ones, namely the super micropore as well as mesopore. This is also evident from Fig. 5, the BJH pore size distribution curve of the as-synthesized LTA nanozeolite shows increased micro porosity, and also that there is a pecking order of porosity which can only be due to intercrystalline space. It also means heterogeneity in crystal size and their aggregation though all crystals are in nano range.

CONCLUSIONS

Nano-sized LTA zeolite particles were successfully synthesized by means of a controlled hydrothermal crystallization technique using organic precursors of Si and Al as well as organic template. The XRD pattern and FT-IR spectrum were ascertained the formation of high purity zeolite LTA phase. The SEM micrograph indicated that the LTA zeolite particle were in range of 60-170 nm with uniform morphology and narrow distribution size. EDXS analysis determined that the Si/Al ratio of the as-synthesized LTA zeolite was 1.66 showing the positive effect of TMAOH organic template in increasing the Si/Al ratio. As a results of increasing the Si/Al ratio from 1 to 1.66, the thermal and chemical stability of the product will be enhanced remarkable. The BET plot showed the surface area of the sample was relatively high (i.e. $421 \text{ m}^2/\text{g}$). The nano LTA sample showed mesoporosity. There was a steep jump and a large desorption loop in the isotherm. The hysteresis loop of zeolite appeared at a high relative pressure ($P / P_0 = 0.9-1.0$) and it reflected intercrystalline voids in the packing of the smaller crystals.

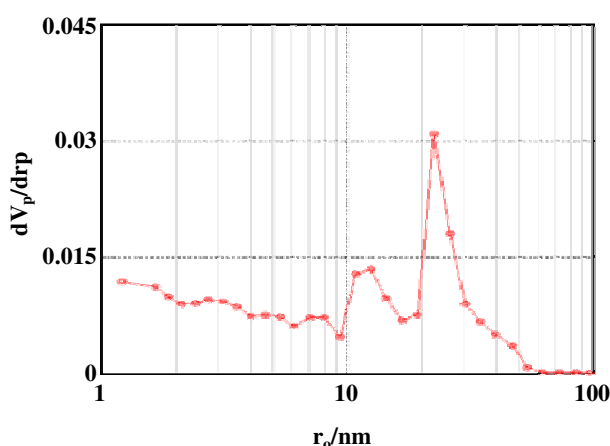


Fig. 5: BJH pore size distribution curve of the as-synthesized LTA nanozeolite

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