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Research Article

Synthesis and Characterization of High Aluminum Zeolite X from Technical Grade Materials

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Abstract

Zeolites are widely used as ion exchangers, adsorbents, separation materials and catalyst due to their well-tailored and highly-reproducible structures; therefore, the synthesis of zeolite from low grade resources can be interested. In the present work, high aluminum zeolite X was prepared from mixing technical grade sodium aluminate and sodium silicate solutions at temperatures between 70°C and 100°C. The synthesized zeolite X was characterized by SEM and X-ray methods according to ASTM standard procedures. The results showed that aging of the synthesis medium at the room temperature considerably increased the selectivity of zeolite X formation. On the other hand, high temperature of reaction mixture during crystallization formed zeolite A in the product; therefore, it decreased the purity of zeolite X. In addition, it was found that increasing H_2O/Na_2O and decreasing Na_2O/SiO_2 molar ratios in the reaction mixture resulted product with higher purity.

Keywords: Zeolite X; Crystallization; Synthesis; Aging; Sodium silicate

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1. Introduction

Zeolites are porous crystalline alumino-silicates of regular skeleton structures formed by alternating silicon-oxygen and aluminum-oxygen tetrahedrons. Although only natural zeolites were initially used, synthetic zeolites, due to their well-tailored and highly-reproducible structures, have been used extensively as ion exchangers, adsorbents, separation materials and catalyst [1]. The negative charges of aluminum-oxygen tetrahedron, which are not rigidly fixed to the skeleton of zeolite, are compensated with cations, so they are capable of interchanging. Silicon-oxygen and aluminum-oxygen tetrahedrons in the zeolites of the type A, X and Y form a complex structural unit of cubooctahedron. The combination of such units forms the structure of type A, X and Y [1]. The difference between them consists in the fact that they are interconnected by means of different number of member rings (i.e., eight member rings (A), twelve member rings (X, Y)) (Fig. 1). The chemical difference of zeolites is defined by the ratio of Si/Al. For zeolite A this value is in the range of 0.95-1.05 and for faujasite (X, Y) 1-3. Zeolites A, X and Y are the most important ones to be used in industry.

Zeolites with different structure are known to be obtained by synthesis [2-7]. They are either synthesized from aluminosilicate hydrogel or by conversion of clay minerals. The hydrogel can be prepared

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from different sources of silica and alumina. But the types of starting materials and the method of mixing determine the structure of the resulting gel. Moreover, the nature of the gel influences the rate of the subsequent crystallization, which affects the particle size distribution, and the formation of impurities [8]. The general pathway for zeolite synthesis follows a specific temperature gradient at low temperatures (<60°C) where the sources of aluminium, silicon and water are placed in solution and mixed until a gel is formed. The temperature is then raised, and the gel is rearranged. Then the temperature is maintained until nucleation of the zeolite take place [9].

As a commercial material, zeolite X is used in many applications such as separation of gases in permanent gas-flow [10], aerobic digestion process [11], mild hydrocracking of naphthenic compounds [12], hydrocracking of vacuum gas oil [13] and especially in detergents as a water-softening builder [14].

In detergents as water softening agent, zeolite A is normally used in combination with another softening agent such as sodium tripolyphosphate (STPP). These softening agents are needed to remove hardness ions (calcium, magnesium and iron). Zeolite A is ineffective for removing large ions (magnesium) due to its small pore size. High aluminum (low silica) zeolite X that is called LSX has a larger pore size than zeolite A; therefore, it is suitable to remove large hardness ions from aqueous solution. It is also reported that the mixtures of zeolites A and X, containing an appropriate weight percent of each, exhibit a synergistic effect in the sequestering by ion exchange of calcium and magnesium ions in hard water [15]. By decreasing Si/Al ratio in the starting mixture, it is observed the region in which the crystallization of zeolites A and X is overlapped (Fig. 2).

Some works have reported for the synthesis of zeolites. Wazywoda et al. synthesized large crys-

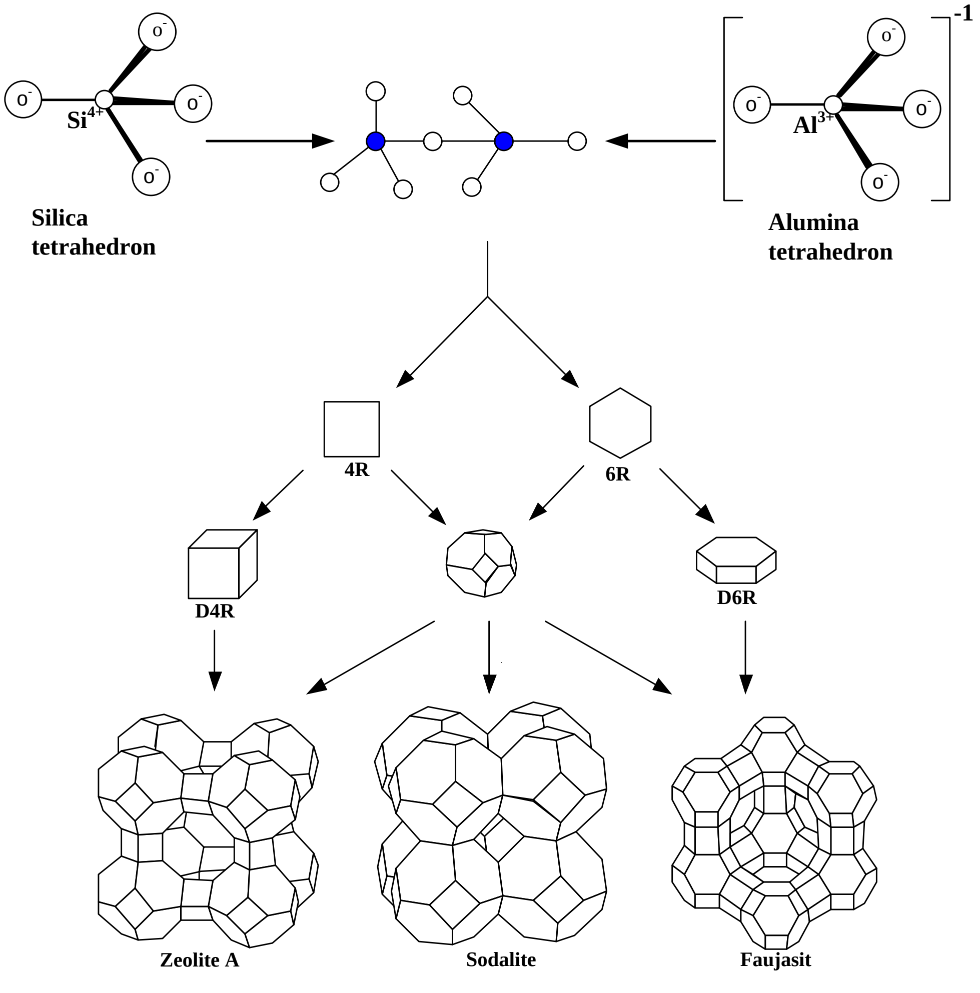

Fig. 1. Structural unit of zeolite A, sodalite and faujasite

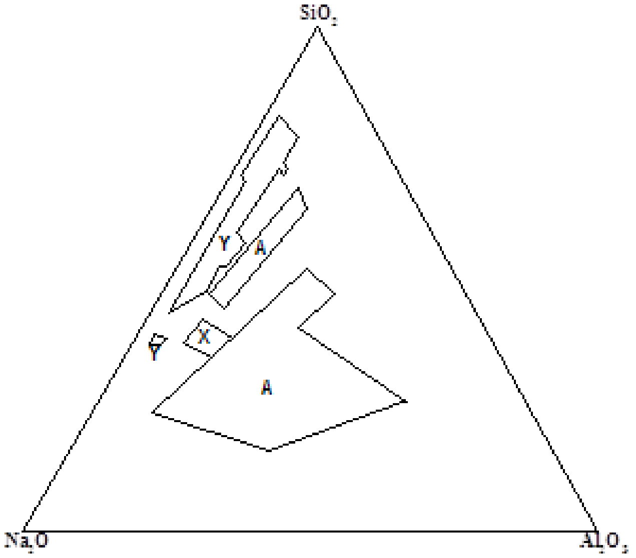

Fig. 2. Ternary compositional diagram for NaO_2-Al_2O_3-SiO_2 system for synthesis of zeolite A, X and Y [16]

tals of zeolite X from gels with the composition of 4.76 Na_2O, 1Al_2O_3, 3.5 SiO_2, 454H_2O, 5–8.5TEA [17]. The syntheses were conducted using aqueous slurries of Cab-O-Sil M-5 or Aerosil 200 fumed silica, and sodium aluminate solutions containing triethanolamine made with sodium hydroxide and sodium aluminate powder. Yan et al. synthesized 4A zeolite by mixing 5–15 wt% bauxite with kaolin and calcination at high temperature, followed by reaction with sodium hydroxide, filtration, and drying [18]. Wajima et al. [19] synthesized zeolites from waste sandstone cake using the alkali fusion method. In that work, the siliceous minerals in the cake were converted into soluble material by alkali fusion, and zeolite X, zeolite P, hydroxysodalite, tobermorite, and nepheline were obtained. It was found that the best fusion conditions for the synthesis of zeolite X were the mixed ratio of NaOH to the cake of 1.6, fusion temperature of 600°C, and heating time of 80°C for less than 12 h. Hiraki et al. described the synthesis of zeolite X from waste metals [20]. In their study, silicon sludge and $Al(OH)_3$ from aluminum dross were separately solved in NaOH solution, leading to the generation of hydrogen, and then mixed with the desired molar ratio to synthesize zeolite X. The product showed the Si/Al molar ratio (1.0–1.5), and BET surface area (500–600 m^2/g) as a commercially available product. Wang et al. [1] synthesized zeolite X from low-grade bauxite by a two-step synthesis method: alkali fusion activation and hydrothermal reaction. The solubility and activity of the aluminium and silicon of bauxite in alkali solution were significantly improved after fusion with sodium hydroxide. Sodium silicate solution (water glass) was added as supplementary silicon to adjust the SiO_2/Al_2O_3 ratio.

In this work, attempt was made to selectively synthesis zeolite X from domestic resources with technical grade materials, not previously reported in the literature. Furthermore the effects of factors such as: i) aging; ii) crystallization temperature, and iii) composition of starting reaction mixture on the purity of zeolite X were investigated.

2. Experimental

2.1 Reagents

Reagents used in this work were domestic low grade sodium silicate (water glass) with the Na_2O/SiO_2 molar ratio of 2.9, aluminum hydroxide (57.7 wt% Al_2O_3, 1.65 wt% Na_2O) and sodium hydroxide (98%). The sodium, silica and aluminum content of the reagents were analyzed by following methods: (a) Silica and sodium in water glass (UOP - method 627-85); (b) Aluminum in molecular sieves or catalysts (UOP - method 633-82)

2.2 Zeolite synthesis

The reaction mixture was prepared by adding the sodium silicate solution (5.23 wt% Na_2O, 8.67 wt% SiO_2) to the sodium aluminate solution (4.11 wt% Na_2O, 2.46 wt% Al_2O_3) under vigorous agitation. The hydrogel was stirred vigorously for 30 minutes to produce a homogeneous mixture. The mixture was then aged for 4 hours at room temperature. Then, the mixture was transferred into an autoclave and kept in an oven at temperature 75°C. After completing the crystallization, the crystalline solid product was filtered, washed with plenty of distilled water until the pH of the filtrate was below 10. The solid sample was left in an oven at temperature of 120°C over night.

2.3 Characterization

Philips X-ray diffractometer model PW 1840 (Cu K_α, APD - software package and JCPDF - search files) were used for the qualitative phase analysis, determinations of the degree of crystallinity and until-cell dimensions. The data obtained were evaluated by ASTM D3942 and D5357 test methods using reference samples [21,22]. Scanning electron micrographs (SEM) were taken using a Cambridge Stereoscan scanning electron microscope model 360 according to ASTM E- 986-04 test procedure [23]. Particle size analysis of the same samples was done by Cambridge Image Analyzer model Quantimet 570. Ion exchange capacity was also measured by the standard ASTM D1782 test method [24].

3. Results and Discussion

3.1 Composition and Structure

Pure high aluminum X zeolite with the Si/Al molar ratio of 1.08 and with a unit cell parameter of 2.499 nm was obtained from the reaction mixture with the following ratio:

$$Al_2O_3 : 4.5Na_2O : 3SiO_2 : 315H_2O$$

The XRD patterns of the commercial zeolite X and the synthesized zeolite are shown in Fig.3. From this figure, higher crystallinity of the synthesized product than that of the commercial one is detected. The scanning electron micrograph of the synthesized zeolite is shown in Fig.4. It can be found that the final product has a mean particle size of 5.9 µm. Moreover, it has a narrow crystal size distribution with well defined morphology. Additionally, the measurement showed that the ion exchange capacity of the sample was 140 mg CaO/g of zeolite.

3.2 Aging

It was found that a preliminary aging of the reaction mixture at temperatures ranging from 20 to 50 °C followed by subsequent crystallization at higher temperature improved the crystallization process [25]. Before starting the crystallization process, the effect of aging was studied by keeping the gel at the room temperature. Therefore, in the first experiment, without any preliminary aging, the crystallization was performed at 100°C for 20 hours. It was observed that percent amount of zeolite A was high. In the second experiment, the preliminary aging was performed at 25°C for 1 hour, and the reaction temperature was increased to

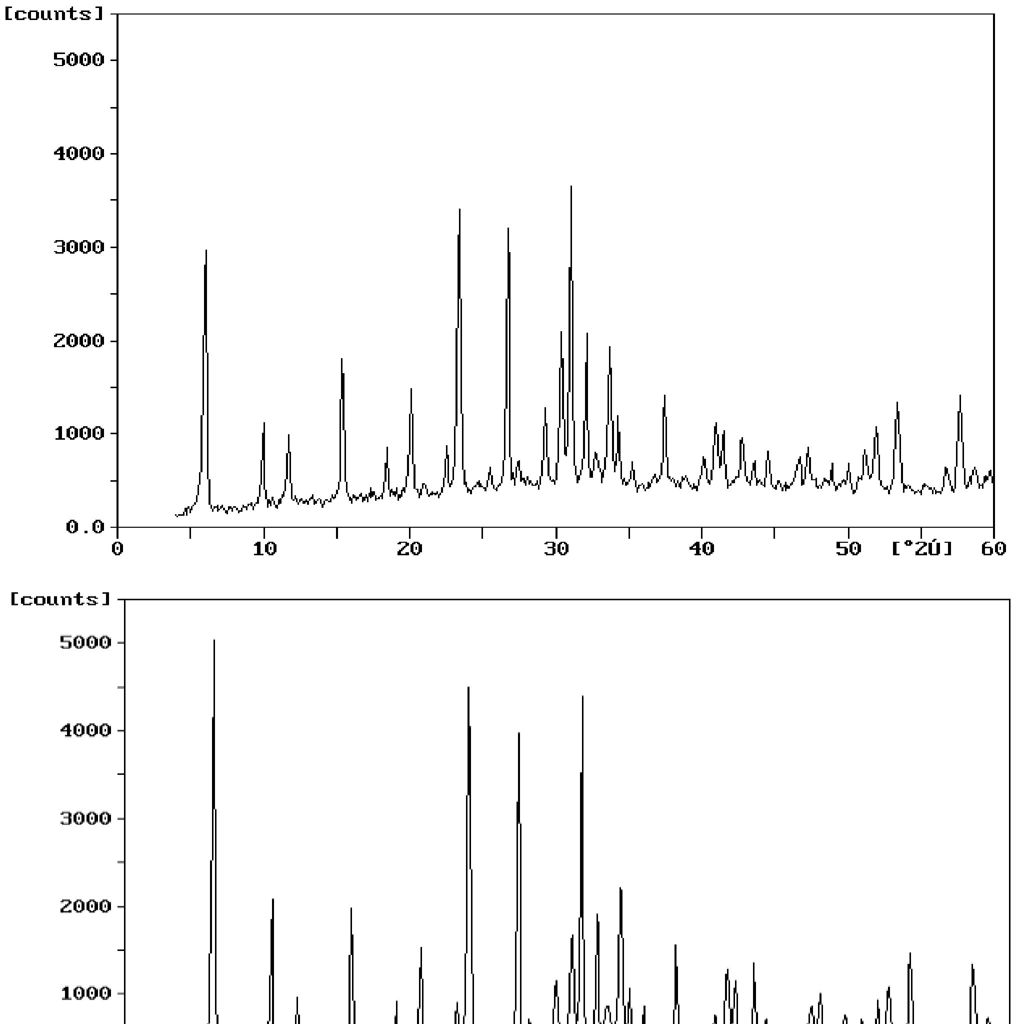

Fig. 3. The XRD Patterns, (Top): Commercial zeolite X; (Bottom): Synthesized product

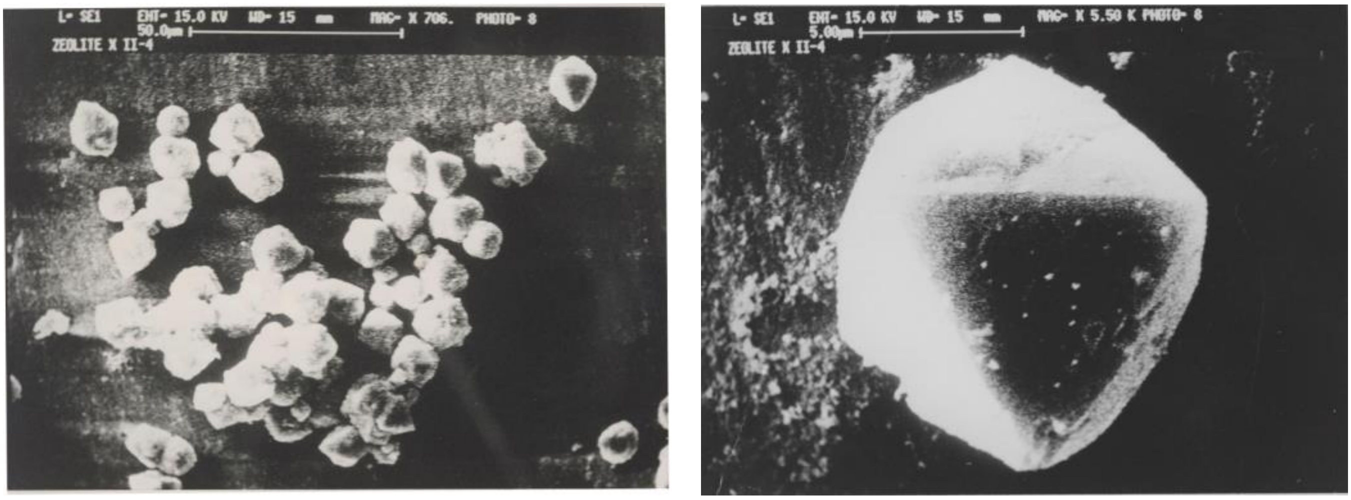

Fig. 4. Scanning electron micrograph of synthesized zeolite X

Table 1. Composition of the reaction mixture for the zeolite X production

Run No.	**Composition (mol)**				**Aging**		**Crystallization**	
	Al_2O_3	**SiO_2**	**Na_2O**	**H_2O**	**T (°C)**	**Time (h)**	**T (°C)**	**Time (h)**
1	1	3.95	5.1	200	25	1	75	4
2	1	4	5	315	25	1	75	4
3	1	3	4.5	315	25	1	75	4
4	1	3	2.3	161	25	1	75	4

100°C for 20 hours. Results indicated that zeolite X was formed in the product, but considerable amount of amorphous product was also detected in the mixture. In the final experiment, it was found that aging of the gel at 25°C for 20 hours and then crystallization at 75°C for 4 hours prevented the formation of zeolite A. Therefore, zeolite x with high purity and crystallinity was obtained.

3.3 Crystallization Temperature

To study this effect, a reaction mixture with the composition of: Al_2O_3, $3.5SiO_2$, $5Na_2O$, $200H_2O$ was prepared. Then, it was aged at 25°C for 20 hours, and crystallization was performed at 110°C during a period of 40 hours. For this experiment, some zeolite A was observed in the final product.

At the other experiment, a reaction mixture with the same composition was aged at 25°C for 20 hours; but in this experiment, the crystallization process was carried out at 75°C for 40 hours. Now, high pure zeolite X was easily detected in the final product. It seems that the structure of zeolite X was more open with larger intra-crystalline pore volume than that of zeolite-A and this fact justified why zeolite X could be easily formed at lower temperatures.

3.4 Composition of the Starting Reaction Mixture

To study the effect of SiO_2/Al_2O_3 and H_2O/Na_2O molar ratios, the reaction mixtures with the specified molar compositions were prepared (Table 1). According to the results, it was observed that increasing H_2O/Na_2O molar ratio in the reaction mixture from 39.2 to 63 (Runs 1 and 2) decreased the formation of zeolite A. So zeolite X with higher purity could be obtained. On the other hand, the comparison of the experiments 3 and 4 revealed that decreasing Na_2O/SiO_2 molar ratio from 1.5 to 0.77 increased the purity of the zeolite X.

4. Conclusion

In this study, pure zeolite X was synthesized by adding sodium silicate (5.23 wt% Na_2O, 8.67 wt% SiO_2) to the sodium aluminate solutions (4.11 wt% Na_2O, 2.46 wt% Al_2O_3). At first the reaction mixture aged at the room temperature for 4 h, and then the crystallization was performed at 75°C. The SEM and X-ray results showed that the final product had a mean particle size of 5.9 μm and ion exchange capacity of 140 mg CaO / g of zeolite. Moreover, its relative crystallinity was higher than that of commercial one.

Then the effect of the operating factors i.e. preliminary aging, crystallization temperature and reaction composition on the purity of zeolite X were studied. It was found that with the preliminary aging of reaction mixture at 25°C, the formation of zeolite A could be prevented, and so zeolite-X with high purity and crystallinity could be obtained. Moreover, at higher temperature, zeolite A was formed in the final product. So it was confirmed that crystallization temperature considerably affected the purity of zeolite X. Finally, it was confirmed that increasing H_2O/Na_2O molar ratio in the reaction gel from 38.6 to 63, and decreasing Na_2O/SiO_2 molar ratio from 1.5 to 0.77 improved the purity of the synthesized zeolite X.

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