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Preparation of $AlPO_4$-5 nano-pore crystals: Effect of alteration in precursor gel preparation on the morphology of crystals

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ABSTRACT

Aluminophosphate-5 ($AlPO_4$-5) nano-pore zeolite was synthesized. The effect of alteration in precursor gel preparation on the morphology of zeolite was studied. The effect of variety of synthesis conditions on the purity, crystal and pore size, and crystallinity of $AlPO_4$-5 zeolite been studied. A hydrothermal synthesis has been used to produce nano-pore Aluminophosphate-5 crystals. The crystals were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM). The morphology of crystals was changed by alteration on precursor gel. The size of crystals decreased from 10 to 2 micrometer when the aging time of precursor gel was changed from 2 to 12 h. The results also showed that the aluminum triisopropylate, as Aluminum source, has been affected the crystals morepure than the crystals were synthesized by aluminum hydroxide. The Al source was changed affected factors such as the pH precursor gel and then changed the morphology of crystals. The SEM analysis and Debye-Scherrer equation showed that the average particle size is about 58 nm.

Keywords: *Nano-pore; $AlPO_4$-5; Precursor gel; Preparation; Morphology.*

INTRODUCTION

The study of molecular sieves, their structures and properties have been an interesting subject, recently. $AlPO_4$-5 is one of the aluminophosphates that have one-dimensional channels. $AlPO_4$-5 with high purity and crystallinity has been synthesized by hydrothermal method [1-3]. Zeolites can also be shown using the following formulation: $M_2/n.Al_2O_3.xSiO_2.yH_2O$

The aluminophosphates is used in many studies in catalysis [4], separation technology [5], and adsorption process [6, 7]. $AlPO_4$-5 has a hexagonal framework structure with a=13.827 Å, b=13.827 Å, c=8.580 Å and $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$ [8]. The $AlPO_4$-5 framework structure is shown in Figure 1 [9].

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This structure consisted of AlO_4 and PO_4 tetrahedrons, which is formed a framework with one-dimensional, pores that diameter of pores is 7.3 Å [10]. In this structure, T_{12} rings are connected (T=Al or P) strict alternation (Figure 1a), then 12-Rings are connected parallel by O-bridges (Figure 1b). Sheets are linked via O-bridges along c (Figure 1c) and the channels are formed, ultimately (Figure 1d) [9]. $AlPO_4$-5 nano-pore crystals can be synthesized via 2 methods as hydrothermal synthesis [11] and microwave heating [12].

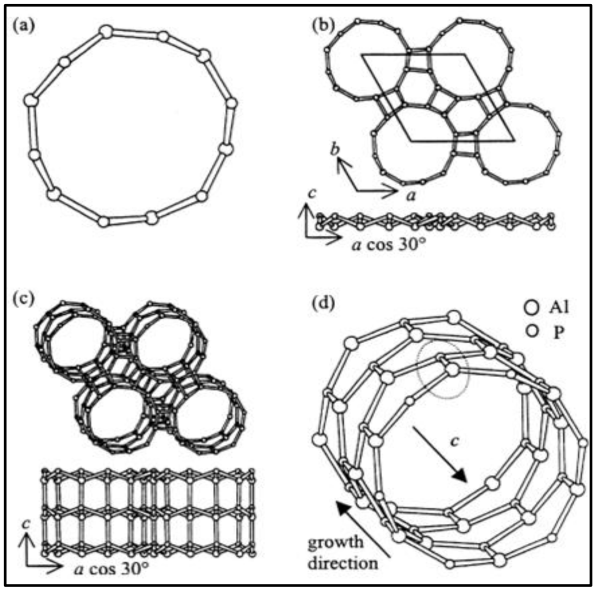

Fig. 1. Hexagonal AFI framework viewed along [001].

The AFI type molecular sieves are synthesized by using various templates. In this study, we prepared nano-pore $AlPO_4$-5 crystals by aging process of gel and hydrothermal as synthesis method. Triethylamine (TEA) is used as template to synthesize crystalline porous of Aluminophosphates. Also, various Aluminum sources are used to analyzing the affection of these sources. Some synthesis parameters, such as the initial composition of precursor solutions, crystallization temperature and time, are controlled to achieving pure morphology of resulting $AlPO_4$-5.

EXPERIMENTAL

Synthesis materials

The $AlPO_4$-5 nano-pore crystals were obtained by these materials: Aluminum triisopropylate ($Al(C_3H_7O)_3$) or Aluminum hydroxide ($Al(OH)_3$), and Orthophosphoric acid (H_3PO_4) (85%, Aldrich) as aluminum and phosphorus sources, respectively. Triethylamine ($(C_2H_5)_3N$) (TEA, 99%, Aldrich) used as structure-direction agent. The Hydrofluoric acid (HF) (40%, Aldrich) and deionized water were another materials where used in this study. The most salient experimental details are summarized in Table 1.

Table 1. Experimental details of samples.

Sample	Aluminum Source	Template	Crystallization Temp	Crystallization Time	Aging Time
1	Aluminum triisopropylate	TEA	180	8	12
2	Aluminum triisopropylate	TEA	180	8	2
3	Aluminum hydroxide	TEA	180	8	12
4	Aluminum hydroxide	TEA	180	8	2

Preparation of $AlPO_4$-5 nano-pore crystals

The $AlPO_4$-5 nano-pore crystals were synthesized by two different routes to prepare precursor gel. In the first route, Orthophosphoric acid (H_3PO_4) (85%, Aldrich) was dissolved in deionized water by magnet stirrer. The source of aluminum was added to the mixture at 0 °C then the resulting solution was stirred at room temperature for 2 h to homogenize. Triethylamine ($(C_2H_5)_3N$) (TEA, 99%, Aldrich) was added dropwise to playing a role of structure-direction agent while stirring. Simultaneously, hydrofluoric acid (HF) (40%, Aldrich) and deionized water were mixed together in other beaker. Eventually, second solution was added to first solution and allowed the precursor gel stirring 2 h at room temperature to be homogenized. The final pH of gel was about 5.5. This gel was transferred to a Teflon-lined steel autoclave. Autoclave placed into preheated oven and preserves it at 180 °C for 6 h. After the crystallization reaction, the autoclave placed at room temperature until slightly cooled to avoid getting into shock. Samples were washed with deionized water by Buchner vacuum filtration funnel and collected after drying at 70 °C overnight. The products were calcined at 600 °C for 8 h to remove the organic template.

The second route is similar the first route with the only difference. The difference is in aging time of the precursor gel. The prepared solution left 12 h to be homogenized at room temperature.

Characterization

As-synthesized $AlPO_4$-5 nano-pore crystals were characterized by X-ray powder diffraction (XRD) through PHILIPS PW1800 diffractometer via CuKa radiation. The morphology and shape of crystals studied by scanning electron microscopy (SEM) using a PHILIPS scanning electron microscope.

RESULTS AND DISCUSSION

Many experiments have been done to study the influence of the synthesis parameters on the size of crystals, pores size, purity and quality of synthesized $AlPO_4$-5 zeolites.

Gel composition

In order to investigate the effect of gel composition on the synthesis of $AlPO_4$-5 nano-pore crystals, the following some parameters were kept constant. The crystallization temperature and time were set at 180 °C and 12 h, respectively. The molar composition of crystals fixed as follow: 1.0 Al_2O_3: 1.3P_2O_5: 1.6 TEA: 1.3 HF: 425 H_2O: 6 C_3H_7OH. Two batches of $AlPO_4$-5 nano-pore crystals were synthesized to study the affect of the aging time, and Aluminum sources, respectively. Figure 2 shows the XRD a pattern of as-synthesized nano-pore crystals which is indicates that the crystals formed in pure AFI structure. The particle size of produced crystals was measured by calculations on the base of XRD data in Scherer equivalent (Eq. 1). The particles size is calculated about 58 nm.

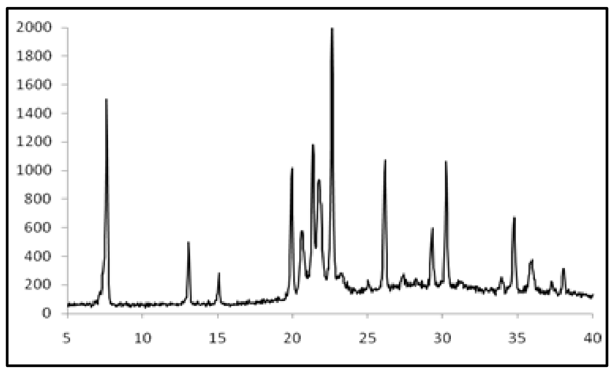

Fig. 2. XRD pattern of the as-synthesized $AlPO_4$-5 crystals.

$$D = 0.9\lambda / \beta_{sample} Cos(\theta) \qquad (1)$$

Where:

- D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;
- 0.9 is a dimensionless shape factor. The shape factor has a typical value of about 0.9 and also shown in other references by K symbol;
- λ is the X-ray wavelength;
- β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as Δ(2θ);
- θ is the Bragg angle.

Figure 3 shows SEM image of the nano-sized crystal of $AlPO_4$-5. The image confirmed that the particles size of the produced $AlPO_4$-5 zeolite is into the nanometer range.

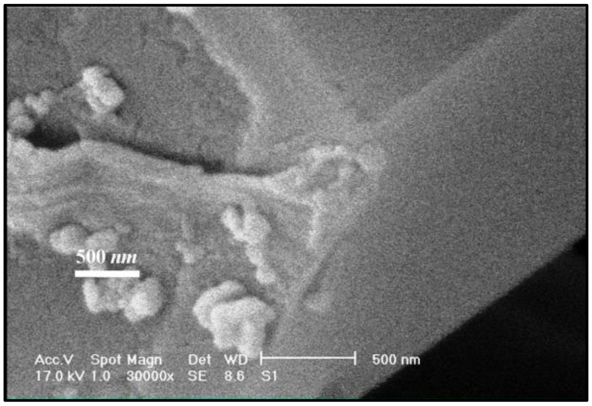

Fig. 3. SEM image of the as-synthesized $AlPO_4$-5 crystal (30000x).

- ***Effect of Aluminum source***

According to XRD schemes and by comparison of precursor gels with different Al sources this result was obtained that the aluminum triisopropylate (Figure 4a) is better that aluminum hydroxide (Figure 4d) to synthesized $AlPO_4$-5 nano-pore zeolite. It was found that the source of Al changed the pH value of the starting gel and plays an important role in forming the crystalline phase. While the Al source changed from aluminum triisopropylate to aluminum hydroxide, the pH value increased from 5.5 to 7.5, and the crystallinity and purity of prepared crystals were decreased respectively (Figure 4a, 4c and Figure 4b, 4d).

The purity of sample 1 and 2 is more than sample 3 and 4. The homogenization of precursor gel was more convenient when the aluminum triisopropylate used as Al source. On the other hand, the other phases that are not considered to form were grown when the aluminum hydroxide used as Al source (Figure 4b, 4c). The morphology of crystals was changed by alteration on aging time of precursor gel. The size of crystals decreased from 10 to 2 micrometer when the aging time of precursor gel was changed from 2 to 12 h.

- ***Effect of the aging time***

Figure 4b, 4c demonstration that the crystal quality increased by increasing precursor gel aging time. Whatever the precursor gel aging time was higher, the quality of the crystals improved: the surface of the crystals became flat and soft, and the crystals were shaped better. This reason of the crystal formation can be attributed to the solubility of raw materials together which is caused homogenized precursor gel. The dissolved raw materials can take a place into the AFI crystals, leading to the crystals forming an inappropriate morphology and caused the amorphous phase arise in the structure of nano-pore zeolite. On the other hand, the behavior of size and purity of crystals were opposite of each other. The size of crystals was decreased and the purity of synthesized zeolites improved by increasing the time of homogenize of precursor gel.

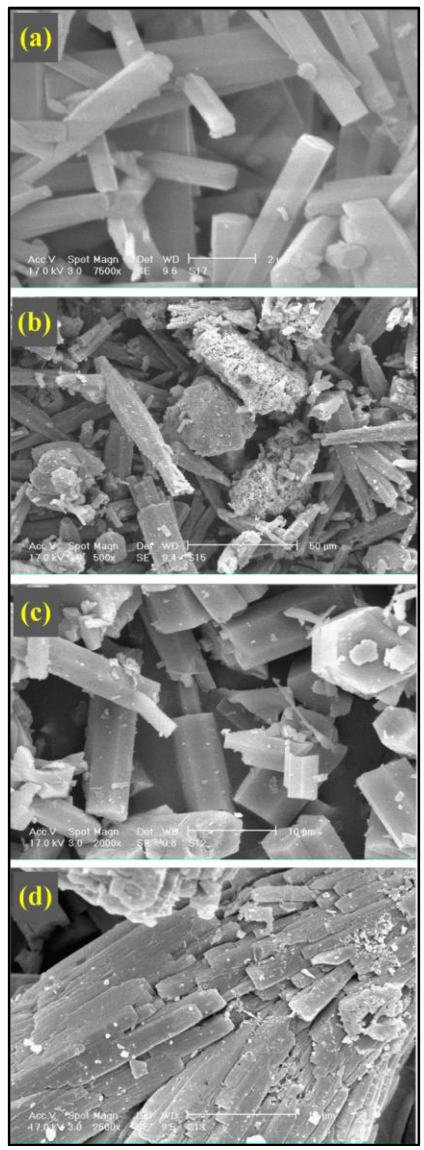

Fig. 4. SEM image of the prepared $AlPO_4$-5 crystals a) sample 1, b) sample 2, c) sample 3, d) sample 4.

CONCLUSIONS

In this study, the Synthesis and characterization of $AlPO_4$-5 nano-pore crystals were investigated. The particles size of Crystals was obtained as small as 58 nm. The hydrothermal treatment used in this study. It was observed that Al sources have strongly influenced both the crystallinity and purity of the resulting $AlPO_4$-5 crystals. Results show that aluminum tri-isopropoxide is the best source to form the pure $AlPO_4$-5 structure. The XRD pattern of crystals showed high crystallinity and purity in samples that was synthesized by aluminum triisopropylate as Al source. The more aging time of precursor gel for homogenization was lead to more production of more pure crystals.

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