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Fabrication and characterization of $AlPO_4$-5 nanozeolites : Effect of hydrothermal temperature and duration

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Molecular sieves and zeolites are materials whose crystalline frameworks form nanometre or subnanometre pores. A variety of different crystal structures are known having a range of pore sizes. Because the pore sizes are usually smaller than 2 nm, they are classified as microporous materials. Although microporous materials have ordered structures over the nanometre scale, they do not typically have ordered structures at larger dimensions. Crystals with a well-defined morphology and a small size distribution can be used as building blocks for generating complex structures by particle assembly techniques. Synthesis of microporous materials is usually conducted by a high temperature treatment (80-200 °C) of aqueous synthesis gels. The process of heating aqueous mixtures to elevated temperatures for crystallization is typically described as hydrothermal synthesis. The raw materials for synthesis of microporous materials include silicon and aluminum containing precursors, an organic structure directing agent (SDA), and a fluoride-containing mineralizing agent. $AlPO_4$-5 nano-zeolite has been synthesized via a hydrothermal technique. The crystals have been structurally characterized using X-ray diffraction (XRD), a scanning electron microscope (SEM), and energy dispersive X-ray analysis (EDAX). The effect of crystallization temperature and duration on morphology of the powder have been studied.

Key words: Nano-Zeolite, $AlPO_4$-5, Synthesis, Characterization, Temperature, Duration.

Introduction

Zeolites have crystalline structures with uniform, molecular-sized pores. These inorganic structures have been used extensively as catalysts and adsorbents. More recently, continuous polycrystalline zeolite layers have been deposited on porous supports and used as zeolite membranes [1]. $AlPO_4$-5 has a hexagonal open framework structure with a = 13.827 Å, b = 13.827 Å, c = 8.580 Å and $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 120^o$. The structure is composed of alternating alumina and phosphate tetrahedra with the main porosity along the [001] plane as seen in Fig. 1. The pore size of $AlPO_4$-5 is 7.3 Å. The space group is P6/mcc (mass centered cubic), and the largest ring size is 12 atoms. Bulk $AlPO_4$-5 has the powder X-ray diffraction pattern shown in Fig. 2, which is taken from the database of zeolite structures of the International Zeolite Association [2]. It has typical unit cell composition is $|(C_{12}H_{28}N)\ (H_2O) \times (OH)|\ [Al_{12}P_{12}O_{48}]$ [3].

In this study, we prepared nano-sized $AlPO_4$-5 crystals by an aging process of a gel and a hydrothermal as synthesis method.

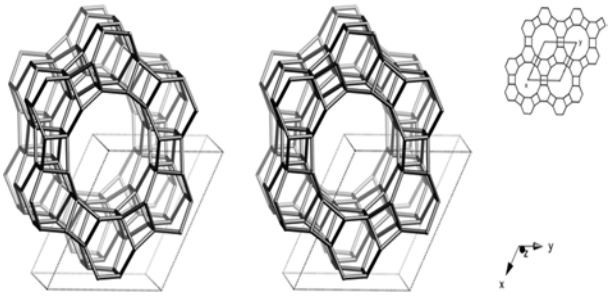

Fig. 1. Framework viewed along [001] (upper right: projection down [001]).

Experimental

Aluminum triisopropylate ($Al(C_3H_7O)_3$) has been used as source of the Al, orthophosphoric acid (H_3PO_4) has also been used as the source of P. $AlPO_4$-5 was hydrothermally synthesized with different initial solutions with a com-

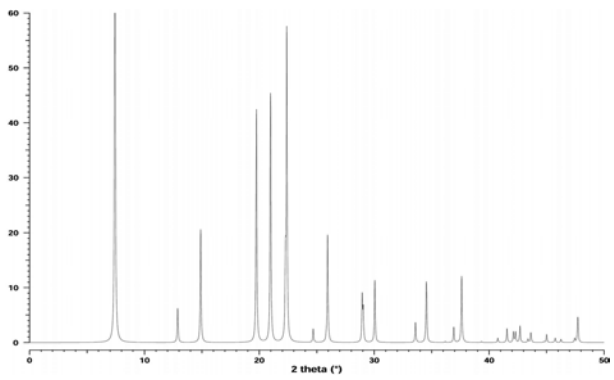

Fig. 2. The standard XRD pattern of AFI [2].

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position Al_2O_3 : 1.3 P_2O_5 : 1.6 TEA : 1.3 HF : 425 H_2O : 6 C_3H_7OH and conditions of hydrothermal crystallization are as follow :

The reactants were phosphoric acid (H_3PO_4 85 wt%), triethylamine (TEA, 99.5%) $(C_2H_5)_3N$ and hydrofluoric acid (HF, 40 wt%). First, H_3PO_4 was added to deionized water. Aluminum triisopropylate was put in the beaker containing the mixture at 0 °C then the mixture stirred at room temperature for 2 hour to homogenize. TEA was added to the mixture dropwise into the reaction mixture while stirring. In a parallel process, another solution was prepared by pulting HF in deionized water. The first solution was then added to the latter rapidly and left to homogenize by stirring for 2 h at room temperature. The prepared gel was transferred to a Teflon-lined steel autoclave. The autoclave putted into a preheated oven, and maintained at a temperature of 180 °C for 6 h without agitation; after crystallization, the autoclave was cooled to room temperature. The product was obtained by a Buchner vacuum filtration funnel, washed with deionized water to gain a pH under 10 and dried at 353 K overnight. The product was washed and dried, calcined at 600 °C for 4 h. The gel was crystallized in four conditions at 180 °C and 165 °C, and for 6 h and 10 h.

Results and Discussion

The accuracy of the prepared $AlPO_4$-5 was established using XRD and SEM analysis. Fig. 3 shows XRD patterns of the powder product. The pattern corresponds to the XRD of the standard sample shown in Fig. 2. Using calculations done on the basis of the XRD data the Scherrer equivalent particle size of the synthesized $AlPO_4$-5 is estimated as 52 nm (Eq. 1) :

$$D = 0.9\lambda / \beta_{sample} \cos(\theta) . \quad (1)$$

The effect of the hydrothermal duration on the morphology of $AlPO_4$-5 crystals has been studied. A longer hydrothermal duration in the synthesis affected the size of the crystals. The crystals which were synthesized for 10 h are larger than crystals synthesized for 6 h as shown in Fig. 4. The XRD patterns of the samples which were synthesized for 10 h indicate a higher level of crystallinity than those synthesized for 6 h (Fig. 3).

The morphology of the crystals changed by increasing the crystallization temperature. Increasing the temperature from 165 °C to 180 °C led larger crystals to be formed which have less crystallinity. SEM micrographs shown in Fig. 4 and the XRD patterns of products are similar to perfect $AlPO_4$-5 crystals.

Conclusions

The synthesis and characterization of $AlPO_4$-5 powder were investigated. Crystals were obtained from crystallization of a precursor gel with sizes as small as 38-52 nm. A

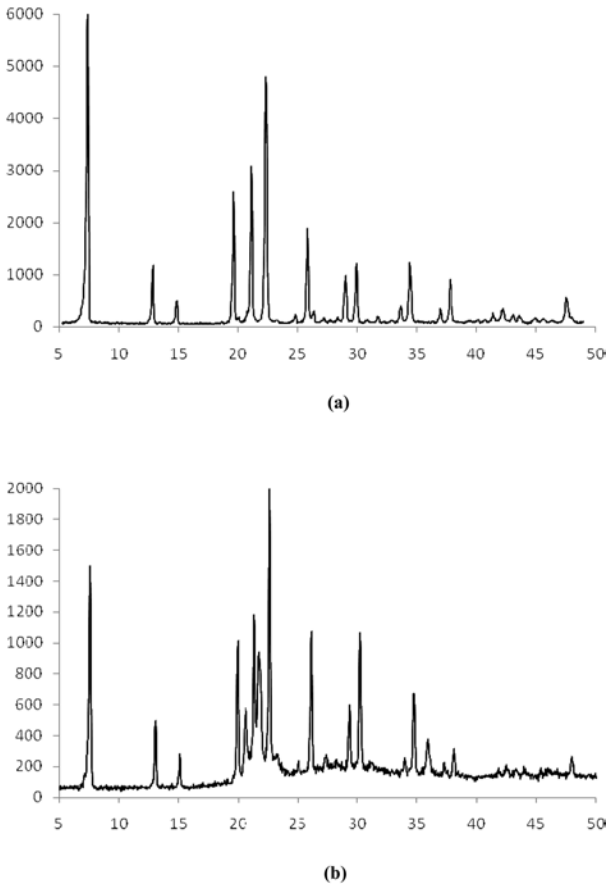

Fig. 3. XRD patterns of the prepared $AlPO_4$-5 crystals : a. 10 h and b. 6 h.

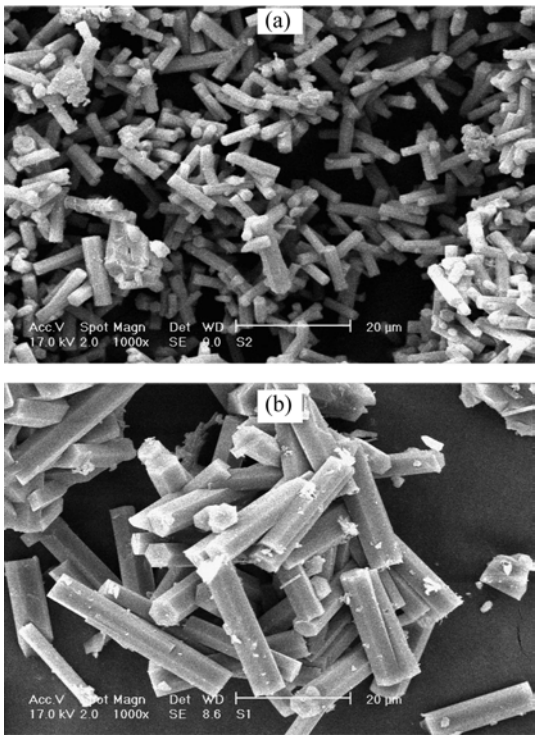

Fig. 4. SEM images of the prepared $AlPO_4$-5 crystals : a. 10 h and b. 6 h.

template-free hydrothermal treatment was used in this study, so post-treatment calcinations have been omitted. XRD patterns of the powders obtained in Fig. 3 showed a high-crystallinity $AlPO_4$-5 phase. The SEM images and Scherrer equation showed that the nano-size of the $AlPO_4$-5 powder was approximately 38-52 nm. And, according to the EDAX results, the P/Al ratio in prepared $AlPO_4$-5 powder was 2. Crystals with sizes ranging from 2 μm to about 20 μm along the hexagonal c-axis can be better synthesized with good yields when the crystallization temperature was increased and the heating time decreased.

References

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