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ORIGINAL RESEARCH

# Hydrothermal synthesis of $AlPO_4$-5: Effect of precursor gel preparation on the morphology of crystals

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**Abstract** This paper reports on the effect of precursor gel preparation on the microstructural formation of aluminophosphate-5 ($AlPO_4$-5) molecular sieves in the hydrothermal synthesis. The morphology of $AlPO_4$-5 crystal changed from sphere to ellipse with two symmetrical craters when the aluminophosphate precursor gel was prepared via dropwise addition of acid and TEA under strong stirring, and continuous stirring overnight during the gel aging process. The results also showed that both of well-crystallized spherical and elliptical $AlPO_4$-5 crystals covered by the fibrous crystals could be hydrothermally synthesized at 150 °C for 4 h or longer. The average particle size of spherical $AlPO_4$-5 samples was about 35–45 μm in diameter, whereas the elliptical $AlPO_4$-5 exhibited approximately 13 μm in width and 15 μm in length.



## 1. Introduction

Aluminophosphate $AlPO_4$-5 with an AFI structure is composed of alternating $AlO_4$ and $PO_4$ tetrahedrons, which form a framework with one-dimensional, electrically neutral cylindrical pores of uniform cross-section (7.3 Å) that are extended parallel to the long (*c*) axis of the crystal [1–3]. It is an important material in shape-selective catalysis [4], separation technology [5–7], and nonlinear optics [8]. Similarly to other types of molecular sieves, $AlPO_4$-5 crystals can be synthesized *via* different routes, such as hydrothermal synthesis [9–14] and microwave heating [2,15–18]. Some synthesis parameters, including the initial composition of precursor solutions, temperature and crystallization time, are crucial in controlling the morphology of resulting $AlPO_4$-5. Jiang et al. concluded that HF content, crystallization temperature and duration were essential in obtaining optically clear hexagonal rods [19]. The results in Utchariyajit's research showed that the morphology could be controlled by varying the composition of reaction mixture, the addition of HF acid, the crystallization time

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and temperature [16]. They successfully synthesized mesoporous $AlPO_4$-5 with a perfect rod-like AFI structure *via* a microwave heating technique. Without adding HF in the synthesis gel, Mintova et al. synthesized nanosized AFI crystals and in some cases the crystal size could be substantially decreased to 50 nm by varying the composition ratio of $Al_2O_3$:triethylamine (TEA):-$P_2O_5$:$H_2O$ under microwave heating [2,17]. Fiber-like, hexagonal rod (barrel), pencil-like, hexagonal plate and cross-like $AlPO_4$-5 aluminophosphate were prepared by systematically changing the initial composition of precursor solution at 150 °C for 6 h [9]. $AlPO_4$-5 with novel morphologies of brooms and nano-fibers (about 3.8 μm and 70–200 nm in width, respectively) were hydrothermally synthesized by varying the precursor compositions [20]. Non-doped and 11 (Si, Co, Mg, Zn, Mn, Sn(II), Sn(IV), Cr, Fe, V and Zr) heteroatom-doped $AlPO_4$-5 samples were crystallized using *N*-methyldicyclohexylamine as a structure-directing agent. The particles were cylindrical or spherical agglomerates composed of needle- or rod-like crystals [13]. Very recently, Zhang et al. prepared silica-$AlPO_4$-5 with bullet-, flower-like and disk-shaped morphologies from neutral or alkaline hydrogels using acetic acid or HCl at 180 °C for 48 h [21]. However, there has been no report on the effect of precursor gel preparation process, e.g. controlling reagent addition and stirring [22], on the morphology of aluminophosphate molecular sieves.

In this work, we report our finding on controlling the morphology of $AlPO_4$-5 by varying the precursor gel preparation conditions. Two different morphologies including well-crystallized spherical aluminophosphate $AlPO_4$-5 particles and elliptical $AlPO_4$-5 crystals with two symmetrical craters were successfully obtained.

## 2. Experimental section

### 2.1. Synthesis of $AlPO_4$-5 crystals

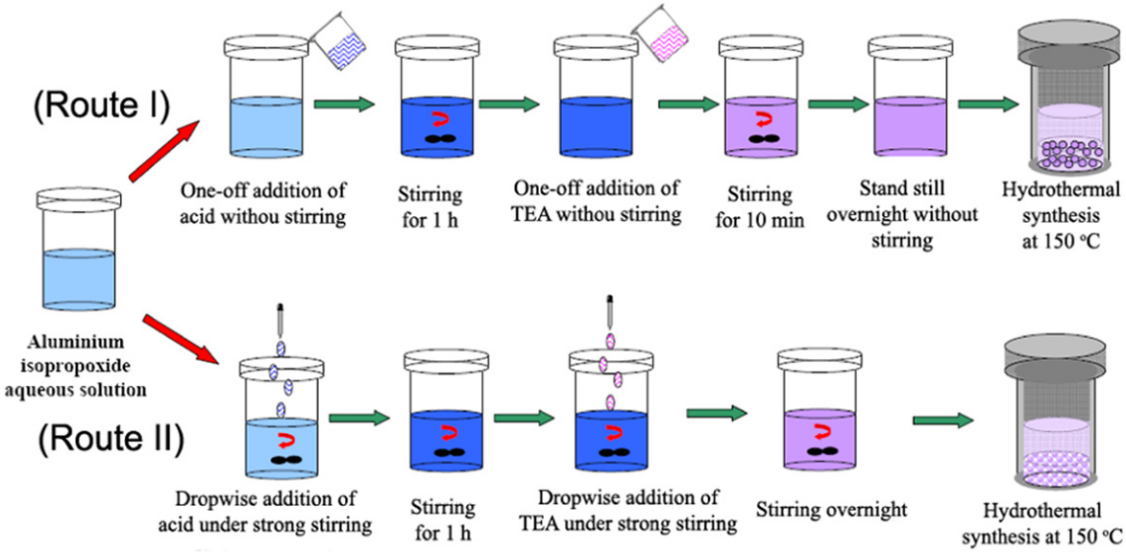
The synthesis procedures are summarized in Scheme 1. Two different preparation routes were used to synthesize $AlPO_4$-5 crystals.

*Route I:* In a typical synthesis, 4.1 g of aluminum isopropoxide (98%, Aldrich) was hydrolyzed in 18 g of deionized water for 3–4 h under magnetic stirring. An amount of 3 g of phosphoric acid (85%, Aldrich) was then added without stirring, and the resulting solution was stirred and allowed to homogenize for 1 h. The structure-directing agent (triethylamine, 99%, Aldrich) was added into the above solution under no stirring, and then stirred for 10 min. The molar composition of the synthesis gel was 1.00 $Al_2O_3$:1.33 $P_2O_5$:1.20 TEA:205 $H_2O$. The precursor gel was allowed to stand still for 12 h at 25 °C, followed by transferring into Teflon-lined autoclave and heating for different periods (0.5, 1, 2, 4, 6 and 8 h). After the hydrothermal reaction, the samples were collected by washing with sufficient deionized water and drying at 80 °C overnight. In order to remove the organic template TEA, the samples were calcined in oxygen at 600 °C for 6 h with a heating rate of 1 °C/min. The samples were denoted as S-0.5, S-1, S-2, S-4, S-6 and S-8 on the basis of the hydrothermal synthesis time, 0.5, 1, 2, 4, 6 and 8 h, respectively.

*Route II:* The recipe in Route II was exactly the same as that in Route I. The addition method of phosphate acid and TEA in Route II was changed to the dropwise addition instead of one-off addition in Route I (Scheme 1). The resulting samples were calcined in oxygen to 600 °C for 6 h to remove the organic templates, and they were denoted as H-0.5, H-1, H-2, H-4, H-6 and H-8 when the hydrothermal synthesis time was 0.5, 1, 2, 4, 6 and 8 h, respectively.

### 2.2. Characterization

Scanning electron microscopy (SEM) images were taken with a JSM-6300 F microscope (JEOL). X-ray diffraction (XRD) patterns were measured on a Philips PW1140/90 diffractometer with Cu $K_\alpha$ radiation (25 mA and 40 kV) at a scan rate of 1°/min with a step size of 0.02°. Thermogravimetric analysis (TGA, Perkin Elmer, Pyris 1 analyzer) was performed




**Scheme 1** Synthesis of $AlPO_4$-5 crystals *via* two different routes: one-off addition of reagents (acid and TEA) without stirring and no stirring in the aging process (Route 1); and dropwise addition of reagents with stirring, and continuous stirring in the aging process (Route 2).