



Molecular engineering of microporous crystals: (VII) The molar ratio dependence of the structure-directing ability of piperazine in the crystallization of four aluminophosphates with open-frameworks

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ABSTRACT

The crystallization fields of initial mixtures with compositions of $\text{Al}_2\text{O}_3 \cdot 3.0 \text{P}_2\text{O}_5 \cdot x \text{pip} \cdot 277 \text{H}_2\text{O}$, where $x = 2.4\text{--}12$ and pip = piperazine, were investigated. Pure and highly crystalline three-dimensional (3D) AIPO-CJB2, two-dimensional (2D) AP2pip, 3D AIPO-JU88, and 2D AIPO-CJ9 were obtained when $x = 3, 3.4, 6.5,$ and $12,$ respectively. Along with the increase in the ratio of piperazine to Al_2O_3 in the initial mixture, the density of piperazine in the final structure as well as the non-bonding interaction between the inorganic framework and the protonated piperazine increased. The crystallization processes of AIPO-CJB2, AP2pip, and AIPO-JU88 were investigated using multiple techniques. In the crystallization of AIPO-CJB2, a pure and highly crystalline AP2pip intermediate phase was first formed and then dissolved. A species that may promote the dissolution of AP2pip and the formation of AIPO-CJB2 was identified. Under the synthetic condition of AP2pip, however, this species was not formed; thus, the transformation of AP2pip to AIPO-CJB2 was not observed even for significantly prolonged crystallization times. Additionally, the crystallization rate of AP2pip was significantly accelerated by an increased molar ratio of the reactants with respect to the aluminum source. The results indicate that the type and concentration of the species in the liquid phase were the governing factors in determining the final products and that the formation of particular structures is energy-directed.

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1. Introduction

Since the discovery of microporous aluminophosphate molecular sieves (denoted AIPO_{4-n}) by Wilson et al., a significant number of aluminophosphate-based structures with open-frameworks have been hydro/solvo/ionothermally synthesized and characterized [1–10]. Their preparation typically involves heating a mixture containing phosphoric acid, aluminum oxide in the form of (pseudo)boehmite or alkoxide, organic amine or quaternary ammonium species (denoted the template- or structure-directing agent), and solvent. During the crystallization process, the synthesis medium involves three interacting phases, including a liquid phase, an amorphous gel, and a crystalline solid. The ionic species present in the liquid phase are expected to be in equilibrium with the amorphous and crystalline phases. System equilibrium is con-

trolled by the pH of the system and maintained by (1) dissolution of the amorphous phase and/or the crystalline phase to form soluble species (i.e., oligomers or fragments); (2) the re-organization or assembly of the soluble species around the template or structure-directing agent to form a specific composite that can be developed into the final open-framework; and (3) re-precipitation of the soluble species on the surface of that composite to complete the crystallization process. It is highly agreed that the template- or structure-directing agent plays an important role during the open-framework formation process.

In the synthesis of aluminophosphates with open-frameworks, some structures can only be obtained with a specific structure-directing agent, such as JDF-20, which has only been synthesized with triethylamine as the template thus far [6]. However, in some cases, one structure-directing agent can direct several different microporous structures, depending on the synthesis conditions, which is called the “one-template/multiple-structure” phenomenon [8]. Therefore, the ability of an organic amine to direct the formation of a certain structure type depends strongly on the specific synthesis conditions.

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Given the importance of these materials, it is necessary to study their crystallization process and to understand further the structure-directing effect for synthesis by rational design.

In past decades, significant effort has been made in studies on the crystallization process of aluminophosphates and other microporous materials using *ex situ* or *in situ* characterization techniques [11–54]. However, our current level of understanding of the crystallization process, particularly with respect to the most important factor in the synthesis of these materials, i.e., the structure-directing effect, is still very limited [32,55].

In this study, we systematically investigated the crystallization field of the initial mixture with compositions of $\text{Al}_2\text{O}_3:3.0 \text{ P}_2\text{O}_5:x$ ($x = 2.4\text{--}12$) piperazine:227 H_2O . Four crystalline aluminophosphates with open-frameworks, i.e., 3D AIPO-CJB2 [56,57], 2D AP2pip [58], 3D AIPO-JU88 [59], and 2D AIPO-CJ9 [60], were obtained. The crystallization processes of AIPO-CJB2, AP2pip, and AIPO-JU88 were characterized with XRD, NMR, pH, and elemental analyses. The molar ratio dependence of the structure-directing ability of piperazine was studied. A species promoting the dissolution of layered AP2pip and the formation of 3D AIPO-CJB2 was identified.

2. Experimental sections

2.1. Synthesis of AIPO-CJB2, AP2pip, and AIPO-JU88

Boehmite (Catapal B, 72.7% Al_2O_3 , Sasol) and phosphoric acid (85 wt.% H_3PO_4) were used as the aluminum and phosphorus sources, respectively. Piperazine hexahydrate ($\text{C}_4\text{H}_{10}\text{N}_2 \cdot 6\text{H}_2\text{O}$, denoted pip hereafter) was used as the structure-directing agent. A typical procedure for the preparation of a reaction mixture for AIPO-CJB2 (AP2pip and AIPO-JU88) was conducted as follows: 41.4 g (20.7 g for AP2pip and AIPO-JU88) of 85% phosphoric acid was stirred with 300 g (150 g for AP2pip and AIPO-JU88) of water, and 8.4 g (4.2 g for AP2pip and AIPO-JU88) of boehmite was added. The mixture was thoroughly stirred for 1 h, and then 34.2 g (19.38 g for AP2pip and 37.05 g for AIPO-JU88) of piperazine hexahydrate was added with continuous stirring. The gel was further stirred for 1 h at ambient temperature to ensure homogeneity. While stirring, the same pre-calculated amount (15 mL) of the reaction mixture with a molar ratio of $\text{Al}_2\text{O}_3:3.0 \text{ P}_2\text{O}_5:3.0$ (3.4 for AP2pip and 6.5 for AIPO-JU88) pip:277 H_2O was loaded into each of several Teflon-lined autoclaves (volume: 45 mL) using a 25-mL pipette. The autoclaves were then placed in a pre-heated oven at 180 °C. The heating records were started when all of the autoclaves were loaded into the oven. The autoclaves were heated for different periods of time and then were quenched in cold water. The pH of the liquid phase in each autoclave was measured. The produced liquid and solid phases were separated by centrifugation (9500 rpm or 8475 g), and the solid phase was dried under vacuum at ambient temperature without any further washing in water. To obtain a pure and highly crystalline sample for NMR analysis, one product crystallized for three days was washed with water several times and is marked as “final” in the NMR spectra. The dried samples were sealed for later characterization.

2.2. Characterization

All NMR experiments were performed on a Varian Infinity-plus 400 spectrometer operated at a magnetic field strength of 9.4 T. The resonance frequencies in this field strength were 161.9 and 104.2 MHz for ^{31}P and ^{27}Al , respectively. A Chemagnetics 5-mm triple-resonance MAS probe with a spinning rate of 8 kHz was employed to acquire ^{31}P and ^{27}Al NMR spectra. The ^{27}Al MAS spectra were acquired using a single pulse sequence with a short radio-frequency (rf) pulse of 0.5 μs (corresponding to a $\pi/15$ flip angle) and

a pulse delay of 1.0 s. The pulse length for ^{27}Al was measured using a 1 M $\text{Al}(\text{NO}_3)_3$ solution. Single-pulse ^{31}P MAS NMR experiments with ^1H decoupling were performed with a 90° pulse width of 4.6 μs , a 180 s recycle delay, and a ^1H decoupling strength of 42 kHz. 2D $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS heteronuclear correlation (HETCOR) experiments were performed using a method previously reported in the literature [61]. The chemical shifts were referenced to a 85% H_3PO_4 solution for ^{31}P and a 1 M $\text{Al}(\text{NO}_3)_3$ solution for ^{27}Al .

Powder XRD patterns were recorded on a Rigaku diffractometer equipped with a graphite monochromator using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The pH values of the liquid phases were measured with a Sartorius PB-10 pH meter. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed on a Perkin–Elmer Optima 3300Dv spectrometer.

2.3. Simulation

The non-bonding interaction between the inorganic host and the guest species was modeled using the force field of DREIDING [62]. Periodic boundary conditions (PBCs) were applied. The electrostatic terms were calculated using the Ewald summation. The atomic charges of the protonated piperazine cations were calculated by density functional theory (DFT) studies at B3LYP/6–31G (d, p) levels using the GAUSSIAN 03 W program [63,64]. The QEq method was used to equilibrate and redistribute the overall charge on the guest molecules and atoms of the framework [65]. The non-hydrogen atoms of the frameworks were fixed for all subsequent calculations. Simulated annealing calculations were performed using Materials Studio to obtain the best configuration and location of the guest species [66]. To find the configuration with the lowest energy, geometry optimization of guest molecules was performed while fixing the atoms of the framework. Thirty annealing cycles were carried out for each model. In each annealing cycle, the structure model was heated from 300 K to 400 K in temperature increments of 2 K (50 ramps), and then the structures were cooled down in the same way. Five hundred NVT steps were run in each ramp.

3. Results and discussion

During preparation of the initial mixture, the ratios of $\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5$ and $\text{Al}_2\text{O}_3:\text{H}_2\text{O}$ were fixed at 1:3 and 1:227, respectively. The crystallization temperature was 180 °C. The only variable was the ratio of pip/ Al_2O_3 , which was varied from 2.4 to 12. The pH values of the initial mixtures with the various pip/ Al_2O_3 ratios and the corresponding products crystallized for 3 days at 180 °C are listed in Table 1. The simulated XRD patterns of the corresponding structures and the experimental XRD patterns of the corresponding as-synthesized products are shown in the Supplementary Data. When the ratio of pip to Al_2O_3 was 2.4, a dense phase of AlPO_4 -cristobalite and a trace amount of AIPO-CJB2 were obtained. The pH of the initial mixture was 3.0. Increasing this ratio to 2.6 and then further to 3.0 resulted in the formation of a pure 3D anionic aluminophosphate AIPO-CJ11/AIPO-CJB2. The pH values of the initial mixtures reached 3.3 and 4.51, respectively. With a further increase of this ratio to 3.2, layered anionic aluminophosphate AP2pip appeared in addition to AIPO-CJB2. The pH of the initial mixture was 4.78. When this ratio was increased to 3.4, the pH of the initial mixture was increased to 4.81, and pure AP2pip was obtained. The pH of the initial mixture was in the range of 4.99–6.27 when this ratio fell in the range of 3.8–5.4. In addition to layered AP2pip, a 3D anionic aluminophosphate AIPO-JU88, which is a new, recently reported aluminophosphate structure, first appeared as a minor phase when this ratio reached 3.8. The percentage of AIPO-JU88 in the product was gradually increased with increasing ratio of

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