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Synthesis of AlPO-5 at Low Temperature by Controlling the Kinetics of Conversion of Aluminophosphate Phases

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We found that AlPO-5 crystals can be synthesized at relatively low temperature (120 °C) by hydrothermal reaction. The critical requirement was the adjustment of the gel composition to control the crystallization rates of aluminophosphate phases. The obtained products showed almost the same pore characteristics compared with the reference products synthesized at high temperature.

Zeolitic aluminophosphate series, AlPO-*n*, were first reported by Wilson et al. in 1982.[1] They are classified as microporous crystals, and the framework of AlPO-*n* crystals consists of AlO_4 and PO_4 tetrahedra. AlPO-5 is one of such aluminophosphates, containing one-dimensional 12-ring pores (7.3 Å in diameter). Similar to the aluminosilicate zeolites, AlPO-*n* has potential applications in industry, because of their unique framework structures and high thermal stability.[2,3]

AlPO-5 has been a model material to understand the crystallization mechanism of zeolitic aluminophosphate. A model indicates that the structure results from the transformation of ladder-structured chains with sharing the corner of Al_2P_2 four-membered rings.[4] Recently, the detailed synthesis mechanism of AlPO-5 was characterized by several in situ methods.[5] At the same time, crystal growth of AlPO-5 has been controlled by several methods.[6–10] Because of one type of straight pores, the morphology control of AlPO-5 crystals, such as the preparation of *c*-oriented AlPO-5 membrane, has been investigated,[3,10–12] and the synthesis of millimeter-sized crystals has been achieved.[13]

Synthesis of aluminosilicate zeolites at lower temperature by hydrothermal reaction has several advantages; not only they can reduce cost or energy, but also they have a potential to alter the properties of products, such as crystal morphology and size. Especially, the low-temperature synthesis has already been applied on the synthesis of nanosized crystals.[14] However, few reports focused on the synthesis of zeolitic aluminophosphate materials at low temperature. In particular, AlPO-5 has been synthesized at relatively high-temperature range (150–190 °C). Although microwave synthesis successfully achieved the synthesis of AlPO-5 at 120 °C,[6,13,15] there are no reports on the synthesis of AlPO-5 under 150 °C by conventional heating as far as we know.

Here we report the synthesis of AlPO-5 crystals at relatively low temperature (120 °C), and its crystallization range is investigated. In the synthesis of AlPO-5, VPI-5 phase tends to appear as by-product, and, to avoid this, the gel composition is adjusted based on the crystallization kinetics of zeolitic aluminophosphate phases. The obtained products were compared with reference products synthesized at high temperature. The product showed the characteristic crystal morphology and pore characteristics, which are almost the same as the reference sample.

Table 1. Chemical compositions of the initial aluminophosphate gel, synthesis conditions, and characteristics of the products

Sample No.	Al_2O_3/P_2O_5[a]	TPAOH/P_2O_5[a]	Temp /°C[b]	Phase	Crystallinity /%[c]
1	1	1.5	120	AlPO-5 + boehmite	20
2	0.8	1.5	120	AlPO-5 + boehmite	20
3	0.7	1.5	120	AlPO-5 + boehmite	30
4	0.6	1.5	120	AlPO-5 + boehmite	100
5	0.5	1.5	120	AlPO-5	100
6	0.4	1.5	120	AlPO-5	100
7	0.3	1.5	120	Dense	—
8	0.2	1.5	120	Dense	—
9	1	1	190	AlPO-5	100
10	1	1	120	VPI-5 + Impurity	—

[a]Chemical composition of the initial reaction gel. [b]Operation condition of the hydrothermal reaction. [c]Relative crystallinity of the AlPO-5 phase.

The synthesis gels were prepared with the following chemical composition (P_2O_5:$x$$Al_2O_3$:$y$TPAOH:100$H_2O$), where x and y were varied from 0.2 to 1.0 and 1.0 to 1.5, respectively (see Table 1 for details). The gels were prepared by adding pseudoboehmite (Catapal C, Sasol) to a solution of phosphoric acid (Wako) and stirred for 24 h. Then, tetrapropylammonium hydroxide (TPAOH, Merck) was added to the mixtures and stirred for 24 h. The resulting gels were introduced into 23-mL Parr Teflon-lined, stainless steel autoclaves and heated at a specific temperature for different periods of time under rotating at 20 rpm. The resulting solids were collected, washed by centrifugation with water, and dried at 80 °C. The obtained products were characterized by powder X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and nitrogen adsorption-desorption measurements.

The synthesis compositions, synthesis conditions, and the details of the obtained products are summarized in Table 1. The highly crystalline AlPO-5 phase could be synthesized at 120 °C with the initial gel compositions range in $Al_2O_3/P_2O_5 = 0.4$–0.6 and $TPAOH/P_2O_5 = 1.5$. The chemical composition of zeolitic aluminophosphate is fixed as Al, P, O_4 to balance the charge of aluminum and phosphorus, so that the Al_2O_3/P_2O_5 ratio of synthesis gel compositions is also fixed to 1 in usual. However, as shown in Table 1, the Al_2O_3/P_2O_5 ratio was quite different in our cases.

Figure 1 shows the XRD patterns of the products synthesized for various heating periods. The gel compositions and synthesis conditions of Figures 1a, 1b, and 1c correspond to the

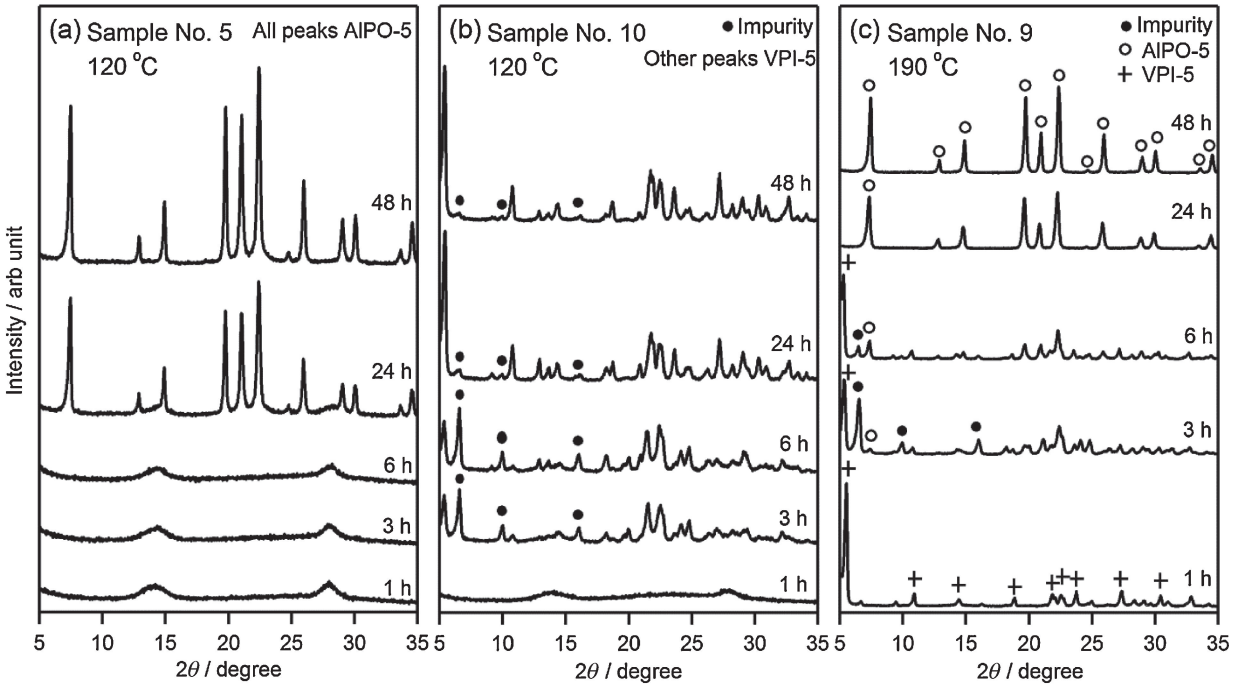

Figure 1. XRD patterns of the products synthesized for various heating periods.

sample Nos. 5, 10, and 9, respectively. As shown in Figures 1a and 1b, XRD patterns of aluminophosphate at the early stage of heating showed broad diffraction peaks at 14 and 28°, indicating that the products contains boehmite (aluminum oxide hydroxide). After the hydrothermal reaction long enough for crystallization, the products showed sharp diffraction peaks. In the case of the sample No. 5, the diffraction peaks due to AlPO-5 appeared after the 24 h of hydrothermal reaction (Figure 1a). The product synthesized for 24 h showed small peaks due to boehmite, so that the unreacted aluminum species remained. After 48 h of hydrothermal reaction, the crystallization was completed and the peak intensities of the product were similar to those of product obtained in 72 h (data not shown). It is noteworthy that when the reactant gel that have the same gel composition as sample No. 5 was exposed to the hydrothermal reaction at 190 °C, AlPO-5 was successfully obtained in ca. 12 h, which is shorter than the conventional case (sample No. 9, Figure 1c). On the other hand, in the case of sample No. 10, the diffraction peaks due to VPI-5 appeared just after 3 h (Figure 1b). As the crystallization time was prolonged, the product became rich in VPI-5, and the peaks due to impurity gradually decreased after 24 h of hydrothermal reaction (Figure 1b).

Kinetically, VPI-5 usually crystallizes faster than AlPO-5, although AlPO-5 is more thermodynamically stable phase. In the conventional case at high temperature (sample No. 9), we observe well-crystallized VPI-5 phase after only 1 h of hydrothermal reaction (Figure 1c). AlPO-5 appeared after 3 h of hydrothermal reaction, followed by the gradual decrease of VPI-5. The temperature has significant influence on the crystallization rate. Therefore, the crystallization of VPI-5 and AlPO-5 at high temperature started much faster than at low temperature. After 24 h of hydrothermal reaction, the phase of product was only AlPO-5 (Figure 1c). Thus, the dissolution of VPI-5 crystal or Ostwald ripening could occur at high temperature. On the other hand, in the case of low-temperature synthesis (Sample No. 10), we could see only VPI-5 phase not AlPO-5 phase, throughout the 48 h of hydrothermal reaction (Figure 1b).

In the synthesis of zeolitic aluminophosphate, the reaction proceeds under acidic condition, and phosphoric acid provides protons as mineralizer. It should be concerned that the acidity of mixture is being lost along with the crystallization, because the phosphorus is incorporated into the aluminophosphate framework. Thus, after the crystallization of a certain aluminophosphate phase, the crystallization of other phases becomes more difficult. However, because of the high temperature, the conversion of aluminophosphate phase from VPI-5 to AlPO-5 proceeded at 190 °C to form the more thermodynamically stable phase, even if the concentration of phosphoric acid is not high enough for crystallization (Figure 1c). On the other hand, the conversion did not proceed at low temperature with the same gel composition (Figure 1b). Thus, problems of the low-temperature synthesis of AlPO-5 are the following; VPI-5 crystallizes faster than AlPO-5 and conversion from VPI-5 to AlPO-5 does not proceed at low temperature.

On the basis of the results as well as the above discussions, the requirement of the successful synthesis of AlPO-5 at low temperature is proposed as follows. First, crystallization rate was controlled by selecting the amount of TPAOH. Usually, organic amines are used as structure-directing agents not to hinder the work of proton, although aluminophosphate can be synthesized with either organic amines or ammoniums.[16] In the present work, organic ammonium hydroxide was added intentionally to increase the pH to control the crystallization rate.[16] One and a half times amount of TPAOH was required to obtain the AlPO-5 for hindering the formation of VPI-5 (sample No. 1). Second, the crystallinity was controlled by selecting the amount of aluminum source. In the sample No. 1, the crystallinity of

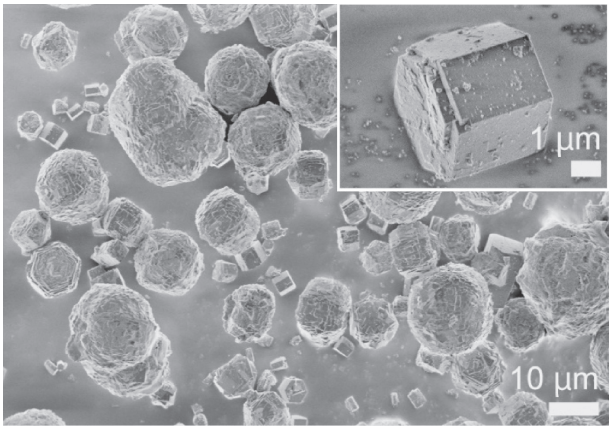

Figure 2. FE-SEM image of the products synthesized by the low-temperature hydrothermal reaction.

Table 2. Pore characteristics of AlPO-5

Sample No.	BET surface area /$m^2\,g^{-1}$	Micropore volume /$cm^3\,g^{-1}$
5	403	0.107
9	393	0.093

AlPO-5 was low, and much amount of boehmite remained. In the synthesis of sample Nos. 2 to 8, the amount of boehmite was varied, and well-crystallized AlPO-5 was obtained with $Al_2O_3/P_2O_5 = 0.4$–0.6. At the smaller Al_2O_3/P_2O_5 ratio under 0.3, a dense phase is formed (sample Nos. 7 and 8). We also challenged the synthesis of AlPO-5 at 100 °C with the same strategy, but only the dense phase that is the same one as obtained in sample Nos. 7 and 8 was obtained (data not shown).

Figure 2 and Table 2 show the morphology and pore characteristics of AlPO-5, which were synthesized by low- and high-temperature hydrothermal reaction corresponding to the sample Nos. 5 and 9, respectively. Two types of crystal morphology was observed, round-shaped aggregates ca. 10–30 μm in size and hexagonal cylinder-like single crystal with well-defined morphology ca. 5 μm in size (extended in Figure 2). Compared to the conventional crystal (sample No. 9), the crystal synthesized at low temperature showed much short and thick morphology, although we could not conclude that the difference was caused only by the low temperature. The BET surface area and micropore volume of AlPO-5 synthesized at low temperature (sample No. 5) are 403 $m^2\,g^{-1}$ and 0.107 $cm^3\,g^{-1}$, respectively. The values of pore characteristics are comparable to that of reference sample synthesized at high temperature (sample No. 9).

In conclusion, the highly crystalline AlPO-5 crystals were synthesized by hydrothermal reaction at 120 °C, which would be the lowest temperature as far as we know. It was found that the crystallization of AlPO-5 at low temperature proceeded in a specific aluminophosphate gel composition. The critical requirement was kinetic control of aluminophosphate phases to hinder the formation of VPI-5 and to complete the crystallization of AlPO-5. The obtained crystals synthesized at 120 °C had almost the same pore properties as the crystal synthesized by conventional temperature at 190 °C.

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