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Capturing an Aluminophosphite Intermediate in the New Route of Synthesizing Zeolite-like Aluminophosphates

Niu Li,*,† Yanfeng Ma,‡ Shouhe Xiang,† and Naijia Guan†

Institutes of New Catalytic Material Science and Polymer, College of Chemistry, Nankai University, Tianjin 300071, P.R. China

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A new route for synthesizing zeolite-like aluminophosphates by using phosphorous acid (H_3PO_3) as the phosphorus source has been discovered. An important intermediate called NKX-2 has been captured in the crystallization of zeolite-like $AlPO_4$-5. NKX-2 is a microporous aluminophosphite with one-dimensional 12-member ring channels in its structure. It is acidic-stable in HCl solution and basic-stable under hydrothermal conditions at 200 °C for 15 days. An overview of this new route has been displayed by XRD patterns on the formation of $AlPO_4$-5 in a nonaqueous system. NKX-2 appeared first as an intermediate, and then reflections due to $AlPO_4$-5 appeared gradually with the time evolution. The conversion of P(III) species to P(V) species in the crystallization has been detected by Raman investigation. Besides, with use of NKX-2 as the starting material, by adding organic amine to the mixture of NKX-2 and water, $AlPO_4$-5, $AlPO_4$-41, and MeAPO-47 aluminophosphates have also been obtained hydrothermally.

Introduction

Significant advances in the past decades have been made to fabricate new porous materials with ordered structures. Within the domain of aluminophosphate, a large number of synthetic microporous frameworks with wealthy structural features[1] have been documented since their initial discovery by Flanigen et al.[2,3] In understanding the mechanisms of their formation, a few models have been proposed,[4,5] and many in situ techniques[6,7] have been employed to probe the process during crystallization. These investigations presuppose the component and structure of intermediates.[4] But some studies showed that zeolite-like $AlPO_4$-based molecular sieves such as $AlPO_4$-5 crystallizes directly from the reaction mixture[8,9] in the conventional synthesizing route by using H_3PO_4 as the phosphorus source, and no intermediate phases has been observed during the synthesis.

More recently, synthesis of metal phosphite materials[10,11] by incorporating the pseudo-pyramidal hydrogen phosphite group $[HPO_3]^{2-}$ into the desired structures[12,13] exhibits the diversity in crystal architectures and reserves much room for novel open-framework crystals.[14] On the basis of studying the synthesis and structures of aluminophosphites,[15,16] transformations of H_3PO_3-containing gel to zeolite-like aluminophosphates have also attracted our attention. Here, we report the pathway to the formation of zeolite-like aluminophosphates with H_3PO_3 as the phosphorus source. The route is identified by the isolation and structure refinement of a key intermediate called NKX-2, which is a microporous aluminophosphite with one-dimensional 12-member ring channels in the structure. It exhibits activity on transforming to zeolite-like aluminophosphate molecular sieves, such as $AlPO_4$-5, $AlPO_4$-41, and MeAPO-47. Transformation of P(III) species to P(V) in the framework during the crystallization process has been traced by Raman and FT-IR spectra.

Experimental Section

The intermediate called NKX-2 has been captured in both nonaqueous and aqueous systems. In a nonaqueous system, phosphorous acid (H_3PO_3), pseudo-boehmite (water loss at 600 °C: 34.75 wt %), and organic amine, such as triethylamine (TEA), dipropylamine, dibutylamine, *n*-propylamine, or citric acid, are used as the source materials and poly(ethylene glycol) 300 (PG300) as solvent. The molar ratio is $Al(OH)_3$:H_3PO_3:TEA:PG300 = 2.0:3.2:

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* To whom correspondence should be addressed.

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‡ Institute of Polymer.

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Table 1. Crystal Data for NKX-2

CSD number	415615
formula	H_6 Al_4 O_{18} P_6 (NKX-2)
formula weight	587.79
T (K)	291(2)
wavelength (Å)	0.71073
crystal system,	hexagonal
space group	$P6_3/m$ (No. 176)
a (Å)	7.8762(11)
b (Å)	7.8762(11)
c (Å)	7.1237(14)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	382.71(11)
Z	1
ρ_{calx} (Mg/m^3)	2.550
μ (mm^{-1})	1.036
F(000)	292
crystal size (mm)	0.20 × 0.10 × 0.10
θ range (deg)	2.99−27.52
limiting indices	$-8 \le h \le 10$, $-10 \le k \le 0$, $-9 \le l \le 9$
reflections collected/unique	1464/314 [$R_{int} = 0.0570$]
completeness to theta = 26.39	98.4%
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	314/ 1/29
goodness-of-fit on F^2	1.150
final R indices [$I > 2\sigma(I)$]	R1 = 0.0444, wR2 = 0.1159
R indices (all data)	R1 = 0.0504, wR2 = 0.1207
largest diff. peak and hole (e.Å^{-3})	0.872 and −0.568

5.9:14. This mixture is stirred for 2 h, then transferred into a stainless steel autoclave, and heated at 175−195 °C. The resulting solid products are recovered, washed with distilled water, and dried at ambient temperature. In an aqueous system, the molar ratio of the reacting mixture is 2.0:3.0:(50−100) $Al(OH)_3$:H_3PO_3:H_2O. This mixture is stirred for 30 min at room temperature, then transferred into a Teflon-lined stainless steel autoclave, and heated at 180 °C for 2−5 days.

The single crystal of NKX-2 with dimensions 0.20 × 0.10 × 0.10 mm^3 was carefully selected and glued to a thin glass fiber with superglue adhesive. The intensity data by X-ray diffraction were collected on a Bruker SMART 1000 CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source using monochromated Mo Kα ($\lambda = 0.71073$Å) radiation at a temperature of 19 °C. The final unit cell constants were determined by a least-squares fit of 1440 reflections in a θ range of 2.99−27.52°. The lattice parameters are as follows: $H_6Al_4O_{18}P_6$, crystallizes in the hexagonal space group $P6_3/m$ (No. 176), with $a = 7.876(11)$ Å, $b = 7.876(11)$ Å, $c = 7.1237(14)$ Å, $\gamma = 120°$, and $V = 382.71$ (11) Å^3. A total of 1464 reflections were collected, and these were merged to give 314 unique reflections ($R_{merg} = 0.0570$). The structure was solved in the space group $P6_3/m$ by direct methods and refined on $|F|^2$ by full-matrix least-squares using the SHELXTL97 program system.[17] The crystallographic data (CSD number 415615) are listed in Table 1.

The transformation of NKX-2 to zeolite $AlPO_4$-based molecular sieves, such as $AlPO_4$-5 and $AlPO_4$-41, is carried out in an aqueous system with NKX-2, organic amine such as triethylamine or dipropylamine, and H_2O as starting materials. When Zn^{2+} is added in the mixture, MeAPO-47 can be obtained. The mixture was stirred for 30 min at room temperature, then was transferred into a Teflon-lined stainless steel autoclave, and heated at 200 °C for 9−15 days.

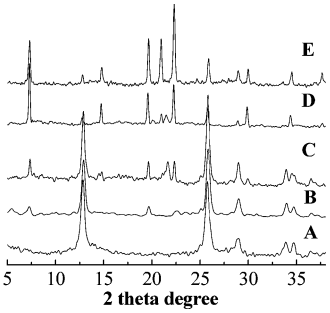

Figure 1. XRD patterns of crystalloid solids from the gels crystallizing for (A) 6 days, (B) 10 days, (C) 16 days, (D) 20 days, and (E) 26 days.

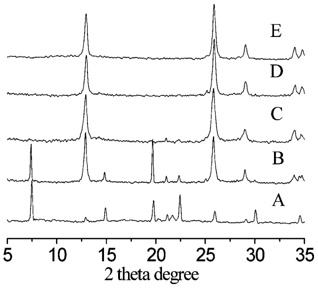

Figure 2. X-ray diffraction patterns of remaining solids when phase D in Figure 1 was soaked in 0.2 N HCl solution for (A) 0 h, (B) 4 h, (C) 6 h, (D) 12 h, and (E) 36 h.

The Renishaw inVia spectroscopy system was used to explore the transformation of P(III) species to P(V) species. The laser used was an argon ion laser with a 514.5 nm excitation source with a power output of 20 mW. Elemental analysis was performed on an Elementar Varioel element analyzer. Thermal analysis was performed on a Netzsch STA 409 PC thermal analyzer at a heating rate of 10 °C/min in nitrogen.

Results and Discussion

With use of H_3PO_3 as the phosphorus source, a series of zeolite-like aluminophosphates have been synthesized hydrothermally. The gel compositions and crystallization conditions of crystallization of several zeolite-like $AlPO_4$-based materials are listed in Table 2. For example, $AlPO_4$-41 and SAPO-41 can be prepared in aqueous solution with DPA as the organic structure-directing agent (SDA).

The intermediate NKX-2 was first captured in our efforts from a nonaqueous system (to crystallize $AlPO_4$-5). The starting mixture is formed by reacting phosphorous acid with pseudo-boehmite in poly(ethylene glycol) 300 with triethylamine as the SDA. From the XRD pattern showed in Figure

Table 2. Gel Compositions and Crystallization Conditions of Several Zeolite-like $AlPO_4$-Based Materials

reactant composition[a] (mole ratio)	crystallization conditions	product
2.0:3.2:3.5:95 $Al(OH)_3$:H_3PO_3:TEA:H_2O	195 °C for 4 days	$AlPO_4$-5
2.0:2.0:1.5:95 $Al(OH)_3$:H_3PO_3:DPA:H_2O	130−195 °C for 9 days[c]	$AlPO_4$-11
2.0:2.0:4.0:95 $Al(OH)_3$:H_3PO_3:DPA:H_2O	200 °C for 9 days	$AlPO_4$-41
0.20:0.85:2.0:3.0:95 SiO_2:Al_2O_3:H_3PO_3:DPA:H_2O	185−200 °C for 10 days[b]	SAPO-31
0.30:1.70:2.0:3.5:95 SiO_2:$Al(OH)_3$:H_3PO_3:TEA:H_2O	195 °C for 2 days	SAPO-47
0.30:1.70:2.0:1.5:95 CoO:$Al(OH)_3$:H_3PO_3:CHA:H_2O	180 °C for 3 days	CoAPO-44
0.10:2.0:2.4:10.0:20 FeO:$Al(OH)_3$:H_3PO_3:DPA:H_2O	195 °C for 4 days	FeAPO-39

[a] TEA: triethylamine; CHA: cyclohexylamine; DPA: dipropylamine. [b] Heating at 185 °C for 3 days and then at 200 °C for 7 days. [c] Heating at 130 °C for 3 days and then at 195 °C for 7 days.

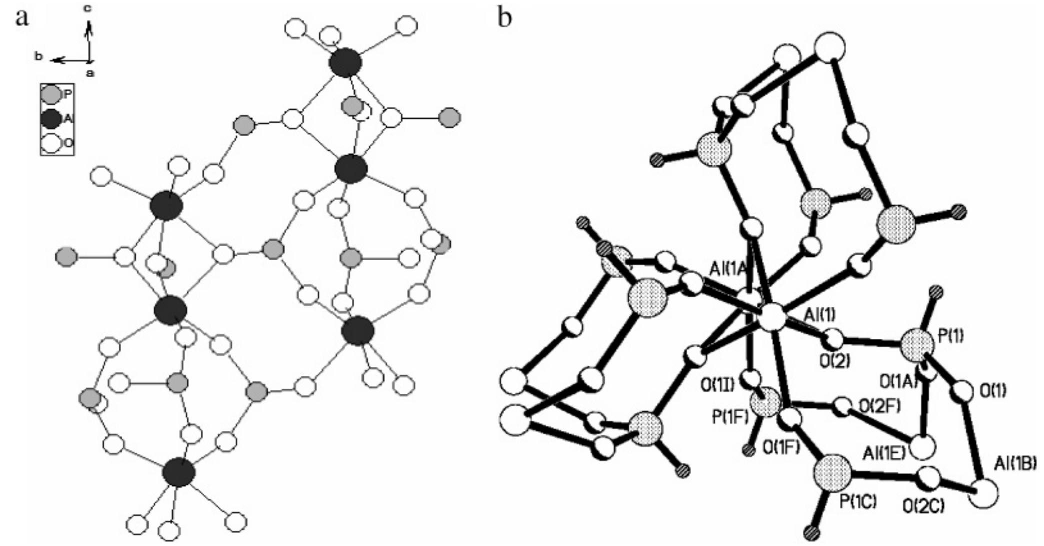

Figure 3. Building units in the structure of NKX-2. (a) A bunch of cages along the *c*-axis containing two cages (hydrogen atoms have not been labeled); (b) Clover-like units on the vertical plane of the *c*-axis.

1A, it can be seen that crystallization at 195 °C for 6 days gave a crystalloid phase with two main reflections ($d = 6.82$ Å, $d = 3.45$ Å). This phase shows a simple XRD pattern with high symmetry and has been called NKX-2. Following the time evolution of the crystallization process, as shown in Figure 1B−D, it can be seen that the reflections due to the NKX-2 phase decreased gradually; at the same time, reflections due to the $AlPO_4$-5 phase appeared and grew gradually. In the end, after reacting at 195 °C for 26 days, $AlPO_4$-5 molecular sieve formed, and single-crystal refinement has proved it to be $AlPO_4$-5. These results suggest that the transformation of phosphite(III) species to phosphates(V) occurs in the crystallization process.

Further investigation has been carried out to discover the correlation among these crystalloid solids in Figure 1. They were soaked in 0.2 N HCl solution for a period of time. $AlPO_4$-5 dissolved completely after only half an hour, whereas NKX-2 was insoluble in 0.2 N HCl solution even after 36 h. The other crystalloid solid phases were partly dissolved in acid solution, and the unsolvable part proved to be NKX-2, which was a reminder that phases B−D were partly transformed from NKX-2 to $AlPO_4$-5. Take phase D in Figure 1 as an example, which is closely related to $AlPO_4$-5 in XRD patterns with only small differences in the diffraction of the (002) plane. When it was soaked in 0.2 N HCl solution for 4 h, two reflections due to NKX-2 increased with the lines due to $AlPO_4$-5 decreasing (Figure 2). After 6 h, only NKX-2 reflections could be seen, suggesting that the phases correlated with $AlPO_4$-5 dissolved and only the phase of NKX-2 remained as a solid. These results showed that NKX-2 was an important intermediate in the synthesis of $AlPO_4$-5 from aluminophosphite gel, and the transformation from NKX-2 to $AlPO_4$-5 went along gradually. To find the intrinsic relationship between NKX-2 and $AlPO_4$-5, it is necessary to know the structure of NKX-2.

The large crystal of NKX-2 has been obtained in the absence of any organic molecules, though it can be synthesized in aqueous or nonaqueous solutions in the presence of a template such as triethylamine, di-*n*-propylamine, propylamine, or citric acid. Single-crystal refinement in the Supporting Information showed that the symmetric unit of NKX-2 contains only one crystallographically distinct Al atom and P atom. Its structure is built up from AlO_6 octahedra and slightly distorted HPO_3^{2-} tetrahedra. Each AlO_6 octahedron shares three Al−O(2) (1.994 Å) corners with three HPO_3^{2-} tetrahedral and three Al−O(1) (1.825 Å) with one adjacent AlO_6 octahedron. Each HPO_3^{2-} tetrahedron has a terminal P−H bond and shares its two corners (O1) with two adjacent AlO_6 octahedra; the other corner links to O2 in the Al−O2−Al to form a three-linkage O atom. The basic building unit of NKX-2 consists of an AlO_6 octahedron linked to another AlO_6 octahedron via three equivalent bridging HPO_3^{2-} groups as Al−O−P−O−Al bridges (Figure 3a), just like the basic building unit of $Sc_2(SeO_3)_3 \cdot 3H_2O$.[18] These $[Al_2(HPO_3)_3]$ units link with each other through three Al−O−Al bridges along the polar [001] direction as shown in Figure 3a, forming a cage with three Al^2O^2 windows. And in turn, these $[Al_2(HPO_3)_3]$ units are cross-linked in the (001) plane by the P−O−Al links to similar $[Al_2(HPO_3)_3]$ units. It can be seen from the (001) plane that the second building unit of NKX-2 is a clover-like unit (Figure 3b) made up of AlO_6 octahedra and HPO_3 tetrahedra. Adjacent clover-like units link from each other through P−O−Al or Al−O−P to construct a three-dimensional framework of NKX-2. Its 12-member ring (MR) channel is constructed by 6 adjacent clover-like units with pore diameter (the distance of H−H) of 4.9 Å (Figure 4 a1).

Both NKX-2 and $AlPO_4$-5 crystallize in the hexagonal system, $P6_3/m$ and $P6/\ mcc$ space group, respectively, with the same prism-like morphology and have a one-dimensional 12-MR channel system along the *c*-axis direction.[1] In a comparison with the 12-MR channels in $AlPO_4$-5, which are limited by 12 alternative PO_4 and AlO_4 tetrahedra, 12-MR channels in NKX-2 are limited by the HPO_3^{2-} tetrahedra

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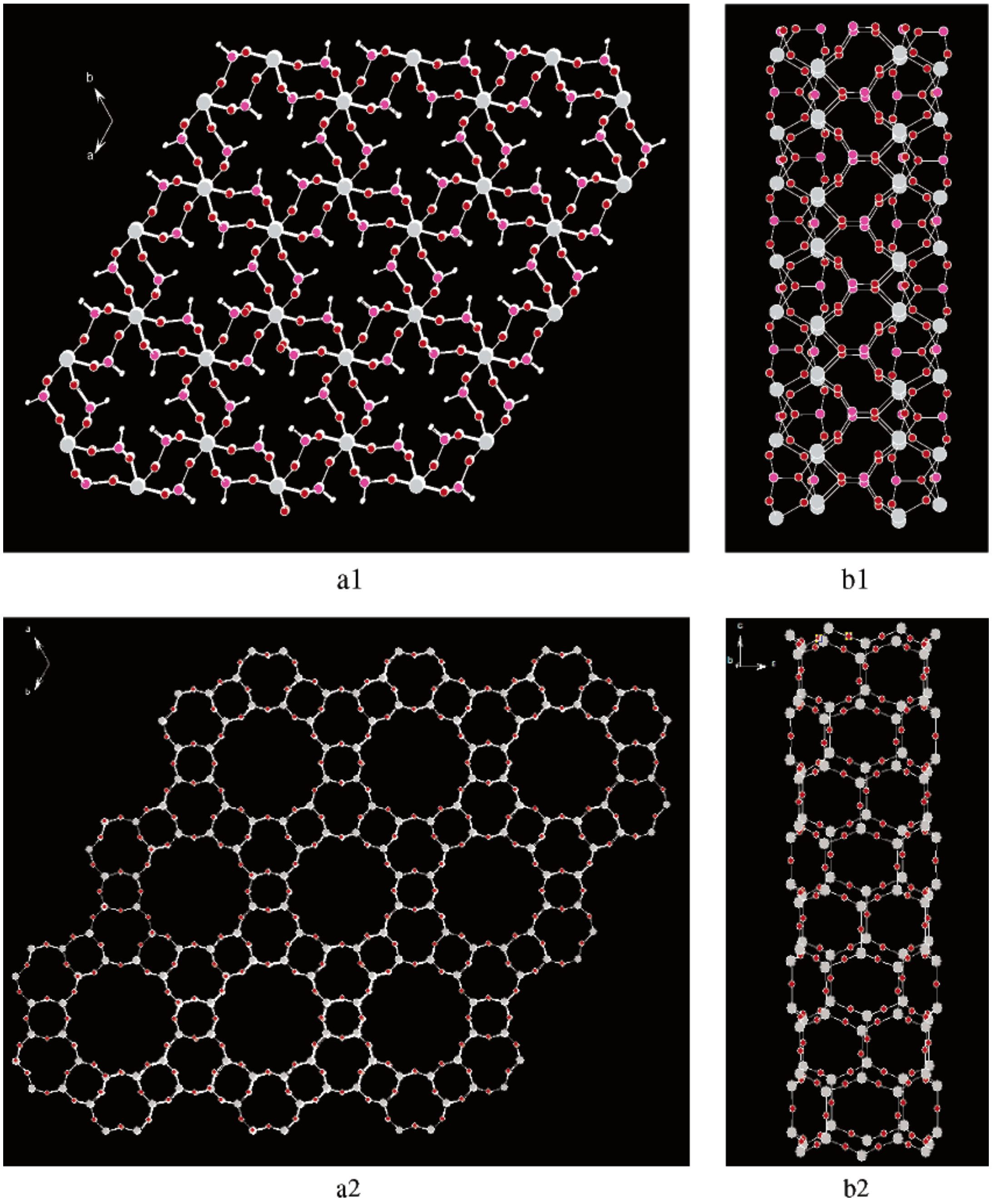


a1 b1

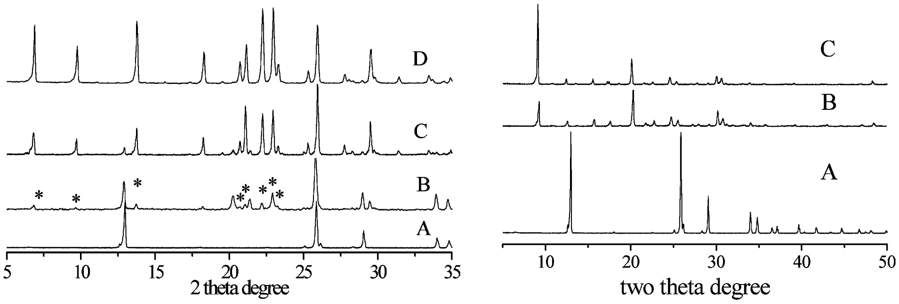
a2 b2

Figure 4. (a1) 1D 12-MR channel system of NKX-2; (b1) wall of the 1D 12-MR channel in NKX-2 (hydrogen atoms have not been labeled); (a2) 1D 12-MR channel system of $AlPO_4$-5; (b2) wall of the 1D 12-MR channel in $AlPO_4$-5.

and AlO_6 octahedra (Figure 4). So the structural similarities of NKX-2 and $AlPO_4$-5 may arouse our speculation on the formation of $AlPO_4$-5 from the transformation of NKX-2 accompanying the conversion of P(III) to P(V) species. During the crystallization, while the P(III) species converted into P(V) species, HPO_3^{2-} tetrahedral transformed to PO_4 tetrahedral with one-third of HPO_3^{2-} departing from the framework, and at the same time, AlO_6 octahedra transformed to AlO_4 tetrahedra. These result in the structure changes from aluminophosphite NKX-2 to aluminophosphate $AlPO_4$-5, as detected by XRD patterns in Figure 1.

Generally, zeolite-like aluminophosphates are synthesized using phosphoric acid (H_3PO_4) and aluminum oxide (pseudo boehmite) as the starting materials. The Al−O−Al linkages in the mineral are broken, and phosphate ions are covalently bonded with aluminum atoms through bridging oxygen atoms.[5] Through dissolution of the mineral structure, molecular species of aluminophosphate are leached into supernatant. In contrast, NKX-2 is acidic-stable microporous aluminophosphite and is also basic-stable under hydrothermal conditions at 200 °C for 15 days. But in the presence of organic amine molecules, the transformation of NKX-2 to aluminophosphate does occur under hydrothermal conditions. Further investigations have been carried out to confirm the transformation process by using the pure phase of NKX-2 as the starting material to prepare aluminophosphate molecular sieves in the presence of organic amine molecules.

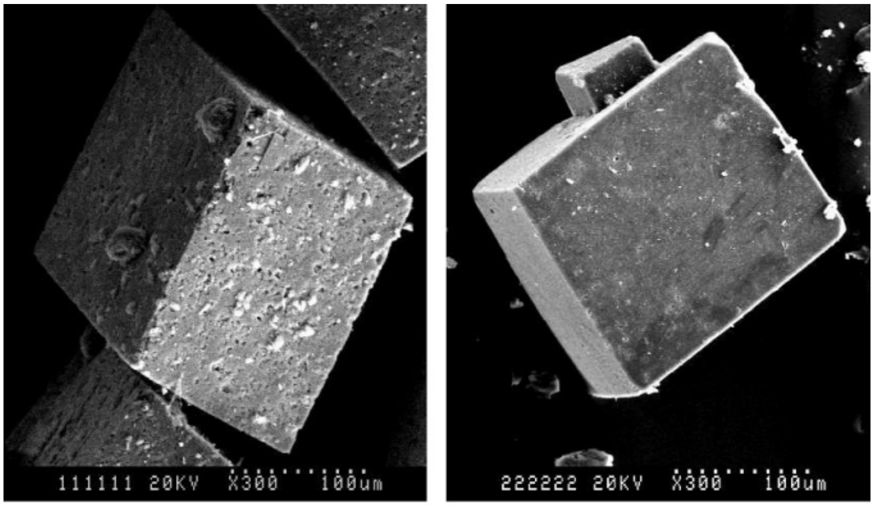
With TEA (triethylamine) as the structure-directing agent (SDA), and the molar ratio being 1.0:2.0:90 NKX-2:TEA:H_2O, $AlPO_4$-5 phase appeared when the reaction mixture was heated at 200 °C for 9 days. When the time increased to



left

right

Figure 5. XRD patterns of NKX-2 and its transforming products. (Left) (A) As-synthesized NKX-2; (B) heating the mixture of NKX-2 and DPA in water at 200 °C for 10 days (* indicates the typical lines of $AlPO_4$-41); (C) heating the mixture for 15 days; (D) $AlPO_4$-41 separated from the solid product in C. (Right) (A) As-synthesized NKX-2; (B) heating the mixture of NKX-2, $Zn(CH_3COO)_2$, and DPA in water at 200 °C for 7 days; (C) MeAPO-47 obtained by heating the mixture for 10 days.



a

b

Figure 6. SEM images of the two types of solid products from the transformation of NKX-2 to MeAPO-47.

15−20 days, more $AlPO_4$-5 phase formed. The XRD pattern of the solid separated from the transformed product showed pure diffraction lines of $AlPO_4$-5 phase. When the mixture was heated for more than 22 days, prism-like $AlPO_4$-5 phase disappeared with the dense tridymite forming.

With DPA (di-*n*-propylamine) as the SDA, the molar ratio being 1.0:2.0:90 NKX-2:DPA:H_2O, this mixture was heated at 200 °C for 10 days and $AlPO_4$-41 phase appeared (Figure 5B, left). For 15 days, more $AlPO_4$-41 phase formed. The XRD pattern of the solid separated from the transformed product showed the pure diffraction lines of $AlPO_4$-41 phase (Figure 5D, left).

On heating the mixture of NKX-2, Zn^{2+}, and DPA in water (NKX-2:$Zn(CH_3COO)_2$:DPA:H_2O = 1:0.2:4:90) at 200 °C for 10 days, we also carried out the hydrothermal transformation of NKX-2 to MeAPO-47 (Figure 5, right). In the procedure, two types of solids were obtained. One is an opaque cubelike solid (Figure 6 a, denoted as solid A), and there exist many holes on the surface of this solid. The other is a cubelike but transparent solid (Figure 6b, denoted as solid B), the surface of which is smoother than the former. Their Raman spectra were determined and are shown in Figure 7. The band in the region of 2400−2500 cm^{-1} is attributed to P−H vibration mode in HPO_3^{2-}, and the P−H vibration mode of NKX-2 is at 2480 and 2492 cm^{-1} (Figure 7A). Clearly, the P−H vibration mode appears in the Raman spectra of solid A, but does not appear in that of solid B. This means that, in solid B, the P(III) species has converted to P(V) species completely, but in solid A the P(III) species still exists. The single crystal of solid B has proved to be MeAPO-47. The P−H vibration mode of solid A has shifted to 2401 and 2460 cm^{-1}, which indicates that the chemical environment of the P element has changed.[19,20] Also, the

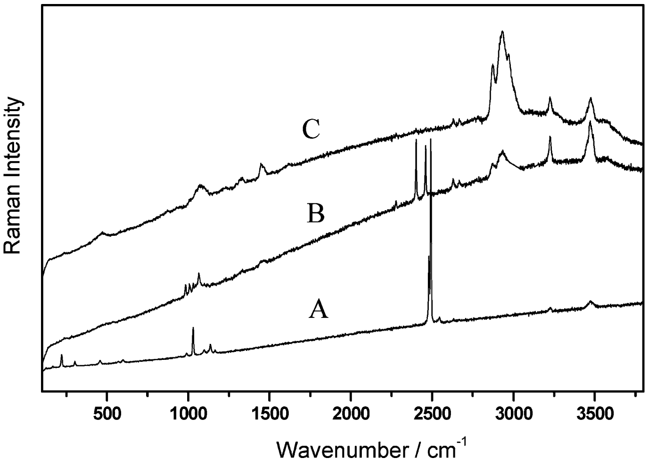


Figure 7. Raman spectra of NKX-2 and its transformation product: (A) NKX-2, (B) solid A in Figure 6a, and (C) solid B in Figure 6b.

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P−O vibration mode of solid A in the region of 1000−1200 cm^{-1} shows some similarity and difference from NKX-2. And the vibration mode of C−H in DPA appears in the Raman spectra of solid A in the region of 2800−3000 cm^{-1}. These suggest that solid A may be an intermediate phase partly transformed from NKX-2 to MeAPO-47. Under the direction of DPA, NKX-2 transforms to MeAPO-47 via a cubelike intermediate, while the transformation of P(III) to P(V) species takes place within.

Conclusions

A new route to synthesize zeolite-like aluminophosphates by using H_3PO_3 as the phosphorus source was reported. The route is identified by the isolation and structure refinement of a key intermediate named NKX-2. The key intermediate is an acidic-stable microporous aluminophosphite with one-dimensional 12-member ring channels in the structure. The formation of $AlPO_4$-5 may undergo the transformation from aluminophosphite to aluminophosphate accompanying the conversion of P(III) to P(V) species. With use of NKX-2 as the starting material, $AlPO_4$-5, $AlPO_4$-41, and MeAPO-47 aluminophosphates can be synthesized in the presence of organic amine. This further proves the intermediate role of NKX-2 in the route of synthesizing aluminophosphate molecular sieves by using H_3PO_3 as the phosphorus source.

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Supporting Information Available: CIF file for $H_6A_{14}O_{18}P_6$ and Table 1 showing bond distances and angles for NKX-2. This material is available free of charge via the Internet at http://pubs.acs.org.

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