Solvothermal Synthesis and Characterization of a New 3-D Open Framework Aluminophosphate $[Al_2P_3O_{12}][C_4N_3H_{16}]$

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The synthesis of microporous aluminophosphates ($AlPO_4$-*n*) by Wilson et al.[1,2] opened a new chapter in the history of zeolite field. Within the past few years, a number of papers have been reported on organically templated aluminophosphates (AlPOs) especially AlPOs with an Al/P ratio lower than unity. These materials not only show rich compositional and structural varieties with 1-D chain, 2-D layered, and 3-D open-frameworks, but also provide insight on the formation mechanism of microporous aluminophosphates.[3] This further assists in the rational design and synthesis of target materials.[4]

So far, the stoichiometry of AlPOs with an Al/P ratio lower than 1 are found to be $AlP_2O_8^{3-}$ (1-D chains[5−8] and 2-D layers[9−11]), $Al_2P_3O_{12}^{3-}$ (2-D layers),[12−14] $Al_3P_4O_{16}^{3-}$ (2-D layers),[9,15−24] $Al_4P_5O_{20}^{3-}$ (2-D layer[25] and 3-D AlPO−HDA[26]), and $Al_5P_6O_{24}^{3-}$ (3-D JDF-20).[27,28] These materials are normally synthesized in an organic solvent system, instead of an aqueous system, with the presence of organic amines as the templates. Alcohols (ethylene glycol, triethylene glycol, butanol, etc.), pyridine, dimethyl formamide, and acetone are often used as the organic solvents in solvothermal synthesis.[29] It has been noticed that the type of organic solvents has a significant effect on the product.[30] In this work, we, for the first time, use phenol as an aromatic and acidic solvent in the solvothermal synthesis. We think that its difference in properties such as polarity, viscosity, phenolysis, and H-bonding abilities, etc. from other solvents will directly affect the balance of interactions among the solvent, the template agent, and the framework species in determining a specific structure, although phenol is solid at room temperature (melting point is 41 °C). We are able to make a uniform gel at 50 °C and have successfully synthesized the first 3-D open framework aluminophosphate $[Al_2P_3O_{12}][C_4N_3H_{16}]$ (denoted AlPO-DETA) with an Al/P ration of $^2/_3$. The structure of AlPO-DETA is built up through connecting 2-D 3-connected 4.8-nets via $PO_2(=O)_2$ tetrahedra to form 3-D open framework, which contains parallel 12- and 8-membered ring (MR) channels along the [001] direction.

Large single crystals of AlPO-DETA were synthesized in a solvothermal system in which phenol (PhOH) is used as a solvent and diethylenetriamine (DETA) as a template. Typically, 1.0 g of aluminum triisopropoxide was first dispersed in 30 g of phenol at 50 °C under reflux condition with stirring, and then 0.6 mL of H_3PO_4 (85 wt % in water) was added dropwise to form a gel. Finally, 4.0 mL of DETA was added to the above mixture. The reaction mixture was further stirred until homogeneous and then was sealed in a Teflon-lined stainless autoclave and heated at 185 °C for 15 days under autogenous pressure. The resulting product containing large platelike single crystals of up to 1 mm was filtered, washed thoroughly with ethanol and deionized water, and dried at ambient temperature. AlPO-DETA can be crystallized in the gel mixture with molar

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(1) Wilson, S. T.; Lok, B. M.; Messian, C. A.; Cannon, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.
(2) Wilson, S. T.; Lok, B. M.; Flanigen, E. M. U.S. Patent 4 310 440, 1982.
(3) Oliver, S.; Kuperman, A.; Ozin, G. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 46.
(4) Zhou, B.; Yu, J.; Li, J.; Xu, Y.; Xu, W.; Xu, R. *Chem. Mater.* **1999**, *11*, 1094.
(5) Jones, R. H.; Thomas, J. M.; Huo, Q.; Xu, R.; Cheetham, A. K. Bieber, D. *J. Chem. Soc., Chem. Commun.* **1990**, 1170.
(6) Wang, T.; Yu, L.; Pang, W. *J. Solid State Chem.* **1990**, *89*, 392.
(7) Chippindale, A. M.; Turner, C. *J. Solid State Chem.* **1997**, *128*, 318.
(8) Williams, I. D.; Yu, J.; Gao, Q.; Chen, J.; Xu, R. *Chem. Commun.* **1997**, 1273.
(9) Yu, J.; Williams, I. D. *J. Solid State Chem.* **1998**, *136*, 141.
(10) Morgan, K. R.; Gainsford, G. J.; Milestone, N. B. *Chem. Commun.* **1997**, 61.
(11) Leech, M. A.; Cowley, A. R.; Prout, K.; Chippindale, A. M. *Chem. Mater.* **1998**, *10*, 451.
(12) Chippindale, A. M.; Powell, A. V.; Bull, L. M.; Jones, R. H.; Cheetham, A. K.; Thomas, J. M.; Xu, R. *J. Solid State Chem.* **1992**, *96*, 199.
(13) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. *Chem. Commun.* **1996**, 1761.
(14) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. *Chem. Mater.* **1996**, *8*, 2391.
(15) Jones, R. H.; Thomas, J. M.; Cheetham, A. K.; Powell, A. V. *J. Chem. Soc., Chem. Commun.* **1991**, 1266.
(16) Thomas, J. M.; Jones, R. H.; Xu, R.; Chen, J.; Chippindale, A. M.; Natarajan, S.; Cheetham, A. K. *J. Chem. Soc., Chem. Commun.* **1992**, 929.
(17) Chippindale, A. M.; Natarajan, S.; Thomas, J. M.; Jones, R. H. *J. Solid State Chem.* **1994**, *111*, 18.
(18) Jones, R. H.; Chippindale, A. M.; Natarajan, S.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 565.
(19) Kuperman, A.; Nadimi, S.; Oliver, S.; Ozin, G. A.; Garces, J. M.; Olken, M. M. *Nature* **1993**, *365*, 239.
(20) Morgan, K.; Gainsford, G.; Millestone, N. *J. Chem. Soc., Chem. Commun.* **1995**, 425.
(21) Barrett, P. A.; Jones, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1979.
(22) Williams, I. D.; Gao, Q.; Chen, J.; Ngai, L.; Lin, Z.; Xu, R. *Chem. Commun.* **1996**, 1781.
(23) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. *Inorg. Chem.* **1996**, *35*, 6373.
(24) Gao, Q.; Li, B.; Chen, J.; Li, S.; Xu, R.; Williams, I. D.; Zheng J.; Barber, D. *J. Solid State Chem.* **1997**, *129*, 37.
(25) Vidal, L.; Gramlich, V.; Patarin, J.; Gabelica, Z. *Eur. J. Solid State Chem.* **1998**, *35*, 345.
(26) Yu, J.; Sugiyama, K.; Zheng, S.; Qiu, S.; Chen, J.; Xu, R.; Sakamoto, Y.; Terasaki, O.; Hiraga, K.; Light, M.; Hursthouse, M. B.; Thomas, J. M. *Chem. Mater.* **1998**, *10*, 1208.
(27) Huo, Q.; Xu, R.; Li, S.; Ma, Z.; Thomas, J. M.; Jones, R. H.; Chippindale, A. M. *J. Chem. Soc., Chem. Commun.* **1992**, 875.
(28) Jone, R. H.; Thomas, J. M.; Chen, J.; Xu, R.; Huo, Q.; Li, S.; Ma, Z.; Chippindale, A. M. *J. Solid State Chem.* **1993**, *102*, 204.
(29) Xu, R.; Huo, Q.; Pang, W. In *Proceedings of the Ninth International Zeolite Conference*; Ballmoos, R. V., Higgins, J. B., Treacy, M. M. J., Eds.; Montreal, 1992; p 271.
(30) Shelddrick, S.; Wachhold, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 206.

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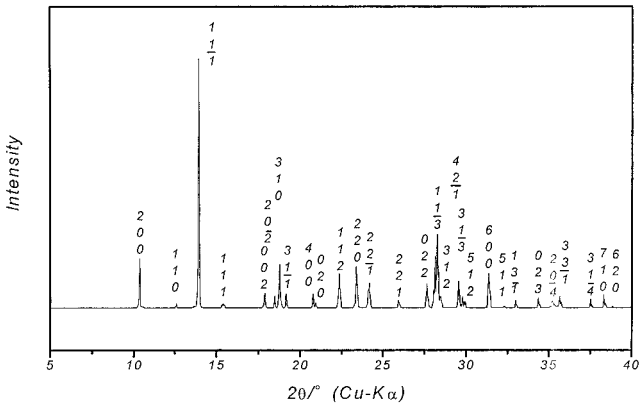

Figure 1. Experimental X-ray powder diffraction pattern of AlPO-DETA with indices.

Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters *U*(eq) (Å^2 x 10^3) for AlPO-DETA

atom	*x*	*y*	*z*	*U*(eq)[a]
P(1)	0.2906(1)	0.6021(1)	0.8852(1)	17(1)
P(2)	0.5000	0.2333(1)	0.7500	19(1)
Al(1)	0.3292(1)	0.3506(1)	0.6832(1)	15(1)
O(1)	0.3018(1)	0.4495(2)	0.8121(2)	26(1)
O(2)	0.2061(1)	0.6576(2)	0.8222(2)	21(1)
O(3)	0.4293(1)	0.3440(2)	0.7159(2)	30(1)
O(4)	0.3486(1)	0.7268(2)	0.8817(2)	30(1)
O(5)	0.2905(1)	0.5508(2)	1.0316(2)	21(1)
O(6)	0.4951(2)	0.1316(3)	0.8680(3)	44(1)
N(1)	0.3836(2)	0.0477(3)	0.9988(3)	31(1)
C(1)	0.4502(2)	0.2674(4)	1.1414(4)	41(1)
C(2)	0.3768(2)	0.1802(4)	1.0892(4)	40(1)
N(2)	0.4783(3)	0.2000(6)	1.2913(5)	30(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

composition of 1.0 Al_2O_3:1.8 P_2O_5:8.0 DETA:65.1 PhOH. Under similar conditions, while using other solvents, such as ethylene glycol or triethylene glycol, instead of phenol, no crystalline products were obtained.

A suitable single crystal with dimensions of 0.2 × 0.1 × 0.06 mm^3 was selected for single-crystal X-ray analysis.[31]

Powder X-ray diffraction (XRD) pattern of AlPO-DETA, recorded on Siemens D5005 X-ray diffractometer, is shown in Figure 1, which is in good agreement with the simulated XRD pattern based on single-crystal structure analysis. This proves that the as-synthesized product is a single phase.

(31) A single crystal of the AlPO-DETA with dimensions of 0.2 × 0.1 × 0.06 mm^3 was glued to a fine glass fiber and mounted on the three-circle fixed Siemens diffractometer fitted with a Bruker SMART CCD detector. Cell dimensions and intensity data were collected on a Bruker SMART system using graphite monochromatic Mo Kα radiation generated by a rotating anode X-ray tube (λ = 0.71073 Å) at 298 K. The lattice constant was determined by the least-squares procedure applied to the θ values for 25 reflections (2.37−23.20 °). [Intensity data of 1531 independent reflections ($-18 \le h \le 16$, $-8 \le k \le 9$, $-4 \le l \le 11$) were collected in the ω scan mode, among which 969 [R(int) = 0.02861] reflections meet the condition $I > 2\sigma(I_{obs})$.] Measured intensity data were corrected for Lorentz and polarization effects together with an absorption correction by means of a φ and ω scan algorithm. The structure was solved by directed methods and refined using a least-squares program package (SHELXL-97; Sheldrick, University of Göttingen, Germany, 1997). During the isotropic refinement for framework atoms and non-hydrogen atoms of the diethylene triamine molecule, the protonation of the DETA molecule is suggested so as to achieve the charge balance of the present compound. All H atoms are geometrically placed. AlPO-DETA: $Al_2P_3O_{12}{\cdot}C_4N_3H_{16}$, Mr = 446.08, Z = 4, D_c = 1.970 Mg/m^3, F(000) = 916. The refinement converged to give a final R = 2.86% for $I > 2\sigma(I_{obs})$ and ωR2 = 8.14%.

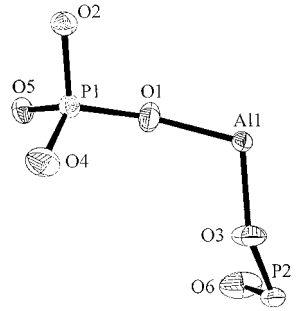

Figure 2. The asymmetric unit of AlPO-DETA.

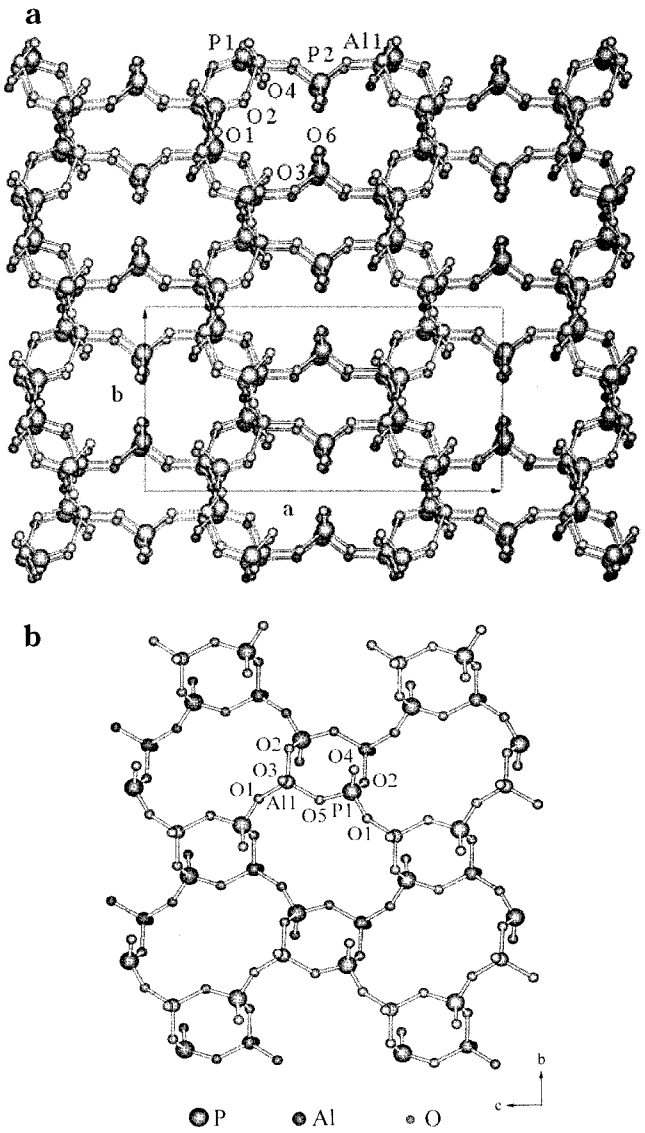

Figure 3. (a) The framework structure of AlPO-DETA viewed along the [001] direction and (b) the 3-connected 4.8-nets parallel to the (*bc*) plane.

Single-crystal analysis indicates that AlPO-DETA crystallizes in the monoclinic space group *C*2/*c* (no. 15) with lattice parameters a = 17.669(4) Å, b = 8.537(2) Å, c = 10.252(3) Å, and β = 103.42(3)°. Table 1 lists the final atomic coordinates and temperature factors for AlPO-DETA.

Figure 2 shows the asymmetric unit, which contains one crystallographically distinct Al atom and two crystallographically distinct P atoms. Al(1) shares four oxygens with adjacent P atoms. The Al−O bond lengths

(1.721−1.760 Å) are within the typical range for AlPO materials. P(1) has three bridging oxygens to adjacent Al atoms (the P−O bond lengths are in the range of 1.539−1.563 Å) and one terminal oxygen (P═O(4) bond length: 1.484 Å). P(2) atom, located in the 2-fold axis, shares two oxygens with adjacent Al atoms with P−O(3) bond length of 1.541 Å, whereas other two oxygens are terminal with a shorter P═O(6) bond length of 1.508 Å. The structure of AlPO-DETA consists of macroanion $[Al_2P_3O_{13}]^{3-}$, which is charged balanced by triprotonated DETA molecule $^+H_3N(CH_2)_2NH_2^+(CH_2)_2NH_3^+$. The framework of AlPO-DETA is constructed from strictly alternating AlO_4 and PO_4 tetrahedra via oxygens, with partial oxygens attached to the PO_4 tetrahedra being terminal.

The structure of AlPO-DETA, see Figure 3a, consists parallel 12- and 8-MR along the [001] direction, with terminal oxygens O(4) (attached to P(1)) and O(6) (attached to P(2)) protruding into the channel in a manner as in JDF-20[27,28] and AlPO−HDA.[26] The framework of AlPO-DETA is built up from connecting the 4.8-net sheets parallel to the *bc* plane through P(2) tetrahedra. Figure 3b shows the 3-connected 4.8-nets, in which Al(1) and P(1) atoms share three oxygens with adjacent P(1) and Al(1) atoms, respectively. The forth oxygen O(4) of P(1) tetrahedra is terminal as described before, whereas the forth oxygen O(3) of Al(1) tetrahedra is bridged to P(2) atom along the [100] direction to form a 3-D open framework. According to the building regularity of AlPO-DETA, a variety of theoretical 3-D open frameworks with $Al_2P_3O_{12}^{3-}$ stoichiometry can be generated by connecting 66 kinds of 2-D 3-connected nets described by Smith through a $PO_2(=O)_2$ tetrahedra.[32] On the other hand, the structure of AlPO-DETA further implies that a 3-D open framework structure can possibly be condensed from 2-D layers.

DETA molecules are trapped in the main 12-MR channels. Figure 4 shows two triprotonated DETA molecules $^+H_3N(CH_2)_2NH_2^+(CH_2)_2NH_3^+$ in the 12-member ring channels with the middle N atoms disordered. The template molecules interact with the terminal oxygens attached to the framework through H-bondings. One end of the $-N(1)H_3^+$ group supplies two H-bonds to the terminal atoms attached to opposite P(2) atoms, with N(1)···O(6) separation of 2.716 Å, while another end of $-N(1)H_3^+$ group supplies one H-bond to terminal O(6) separation of 2.716 Å. The middle $N(2)H_2^+$ group tends to form H-bonds to the terminal oxygens

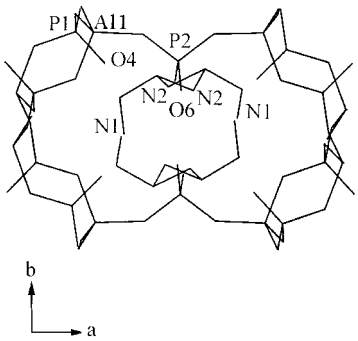

Figure 4. The diethylenetriammonium cations trapped in the 12-MR opening.

O(6) protruding into the channel and terminal oxygen O(4) attached to P(1). This may be the reason causing the disorder of the template. The N(2)···O(6) and N(2)···O(4) H-bond distances are 2.696 and 2.949 Å, respectively.

Thermogravimetric analysis shows only one major mass loss of about 22% in the region 330−500°C, which is correlated to the decomposition of the occluded DETA (the theoretical weight loss is 23%). Elemental analysis gives C 11.0; H 3.6 and N 9.3% in AlPO-DETA, which is in good agreement with the theoretical calculation (Calcd C 10.8; H 3.9; N 9.4%). The template molecules can be removed upon calcination in the air at 300−330 °C. Powder XRD study indicates that the structure of AlPO-DETA is stable up to 350 °C, and collapses to amorphous phase above 400 °C.

In conclusion, phenol has been used for the first time as a solvent to facilitate the crystallization of a new aluminophosphate $[Al_2P_3O_{12}][C_4N_3H_{16}]$ (AlPO-DETA). AlPO-DETA is the first 3-D open-framework compound with $Al_2P_3O_{12}^{3-}$ stoichiometry, which is distinctly different from the previously reported $Al_2P_3O_{12}^{3-}$ compounds that all exhibit a 2-D layered structure. The structure of AlPO-DETA highlights the structural change from 2-D sheets to 3-D framework. This work will further inspire us to investigate the crystallization mechanism of microporous aluminophosphates with tailor-made structures and properties through utilizing some other potential solvents and template agents.

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(32) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.