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Synthesis and characterization of a new open-framework aluminophosphate $C_4N_3H_{16}\cdot Al_4P_5O_{20}(H_2O)_2$ (AlPO-CJ31)

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Abstract

A new three-dimensional (3-D) open-framework aluminophosphate (denoted AlPO-CJ31), with an Al/P ratio of 4/5, has been synthesized hydrothermally in the presence of diethylenetriamine (DETA) as the structure-directing agent (SDA). Its structure is determined by single-crystal X-ray diffraction and further characterized by X-ray powder diffraction, ICP, TG analyses and solid-state NMR techniques. The alternation of AlO_4 tetrahedra, $AlO_5(H_2O)$ octahedra and PO_4 tetrahedra gives rise to an interrupted open-framework structure with parallel 8-membered ring (MR) and 12-membered ring channels along the [0 0 1] directions. Crystal data: $C_4N_3H_{16}\cdot Al_4P_5O_{20}(H_2O)_2$, orthorhombic *Pbcn* (No. 60), $a = 24.7293(16)$ Å, $b = 8.9442(4)$ Å, $c = 9.9806(5)$ Å, $V = 2207.5(2)$ Å^3, $Z = 4$, $R_1 = 0.0720$ ($I > 2\sigma(I)$), and $wR_2 = 0.1669$ (all data).

Keywords: Aluminophosphates; Hydrothermal synthesis; Structure; Open-framework

1. Introduction

Following the first discovery of the aluminophosphate family of molecular sieves ($AlPO_4$-*n*, where *n* denotes the structure type) by Wilson et al. in 1982 [1], a large number of new microporous aluminophosphates have been successfully synthesized under hydrothermal or solvothermal conditions [2–7], because of their potential applications in sorption, catalysis, and host–guest assembly chemistry [8]. Comparing to neutral framework $AlPO_4$-*n* built up from strict alteration of AlO_4 and PO_4 tetrahedra through corner-sharing vertex oxygen atoms, a large variety of anionic aluminophosphates including 1-D chain, 2-D layer and 3-D open-framework structures, with the Al/P ratio of less than unity have been synthesized [9–17]. The framework structures of these compounds are constructed from the alternation of Al-centered polyhedra (AlO_4, AlO_5, and AlO_6) and P-centered tetrahedra (PO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$, PO_bO_{3t} with b representing bridging oxygens and t terminal oxygens), and their Al/P ratios are 1:2, 2:3, 3:4, 3:5, 4:5, 5:6, 11:12, 12:13, and 13:18. These materials exhibit rich framework compositions and structural varieties, which provide insight on the formation mechanism of microporous aluminophosphates.

So far, five unique structural architectures with an Al/P ratio of 4/5 have been known as 2-D layer structure Mu-4 [16], 3-D open-framework structures AlPO-HDA [9], AlPO-DETA [10], SIZ-1 [13] and AlPO-CJ19 [14]. It has been noticed that the type of solvents has a significant effect on the product [15]. These compounds are all prepared in the solvothermal conditions by using diethylformamide, ethylene glycol, phenol, ionic liquid, pyridine as the solvent, respectively. In this work, we present a new open-framework aluminophosphate $C_4N_3H_{16}\cdot Al_4P_5O_{20}(H_2O)_2$ (denoted AlPO-CJ31) with an Al/P ratio of 4/5 prepared in an aqueous system. Its interrupted open-framework is built up from the double 2-D 4.8-net sheets connected by PO_4 tetrahedra, resulting parallel 8-MR and 12-MR

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channels along the [0 0 1] directions. The structure of AlPO-CJ31 resembles to gallophosphate JGP-8 reported by Wenqin Pang and co-workers [18].

2. Experimental section

2.1. Synthesis and characterization

AlPO-CJ31 was prepared under hydrothermal conditions by using diethylenetriamine (DETA) as the structure-directing agent (SDA). Aluminium triisopropoxide and the oxalic acid were first dispersed into distilled water, followed by addition of the orthophosphoric acid (85 wt%). The mixture was stirred for 30 min and DETA was added to give a gel with overall composition of $1.0Al(OPr^i)_3$:$3.6H_3PO_4$:$1.0H_2C_2O_4$:4.0DETA:$920H_2O$. The gel was stirred until it was homogeneous, and then was sealed in a Teflon-lined stainless steel autoclave, and heated under autogenous pressure at 180 °C for 6 days. The resulting product, containing colorless plate-like single crystals, washed with deionized water, and dried in the air at room temperature.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Inductively coupled plasma (ICP) analysis was performed on a Perkin–Elmer Optima 3300Dv spectrometer. Elemental analyses were conducted on a Perkin–Elmer 2400 elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA 7 unit in air with a heating rate of 20 °C/min. Solid-state NMR experiments were performed with magic angle spinning (MAS) on an Infinity Plus-400 spectrometer operating at frequencies of 104.20 MHz and 161.88 MHz for ^{27}Al and ^{31}P, respectively. Chemical shifts were referenced to an external standard of $Al(H_2O)_6^{3+}$ for ^{27}Al and 85% H_3PO_4 for ^{31}P.

Table 1
Crystal data and structure refinement for AlPO-CJ31

Empirical formula	$C_4N_3H_{16}\cdot Al_4P_5O_{20}(H_2O)_2$
Formula weight	720.98
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *Pbcn*
Unit cell dimensions	$a = 24.7293(16)$ Å $\alpha = 90°$ $b = 8.9442(4)$ Å $\beta = 90°$ $c = 9.9806(5)$ Å $\gamma = 90°$
Volume	2207.5(2) Å^3
Z, calculated density	4, 2.181 mg/m^3
Absorption coefficient	0.688 mm^{-1}
$F(000)$	1472
Crystal size	$0.25 \times 0.26 \times 0.15$ mm
Theta range for data collection	2.42–28.37°
Limiting indices	$-32 \leqslant h \leqslant 22$, $-11 \leqslant k \leqslant 11$, $-13 \leqslant l \leqslant 13$
Reflections collected/unique	13,520/2554 [R(int) = 0.1187]
Completeness to $\theta = 28.37°$	92.5%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2554/0/157
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0720$, $wR_2 = 0.1540$
R indices (all data)	$R_1 = 0.1104$, $wR_2 = 0.1711$
Largest diff. peak and hole	1.490 and −0.970e Å^{-3}

$R_1 = \sum(\Delta F/\sum(F_o))$;
$wR_2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$.

Table 2
Bond lengths [Å] for AlPO-CJ31

Al(1)–O(2)	1.714(5)	P(1)–O(1)	1.493(6)
Al(1)–O(3)#1	1.741(4)	P(1)–O(2)	1.530(5)
Al(1)–O(5)	1.751(4)	P(2)–O(3)	1.546(4)
Al(1)–O(7)#2	1.757(4)	P(2)–O(4)	1.498(4)
Al(2)–O(4)#3	1.838(4)	P(2)–O(5)	1.552(4)
Al(2)–O(6)	1.881(4)	P(2)–O(6)	1.517(4)
Al(2)–O(8)#3	1.889(4)	P(3)–O(7)	1.540(4)
Al(2)–O(9)#4	1.947(4)	P(3)–O(8)	1.509(4)
Al(2)–O(10)	1.880(4)	P(3)–O(9)	1.527(4)
Al(2)–O(11)	1.950(4)	P(3)–O(10)	1.537(4)
H Bond			
N–H···O	d(N···O)	<(NHO)	
N(1)–H(1B)···O(1)#10	2.835(12)	158.3	
N(1)–H(1C)···O(1)#5	2.899(11)	149.5	
N(2)–H(2D)···O(1)#5	2.944(14)	134.9	

Symmetry transformations used to generate equivalent atoms: #1: $x, -y, z - 1/2$; #2: $-x + 1/2, y - 1/2, z$; #3: $-x + 1/2, y + 1/2, z$; #4: $-x + 1/2, -y + 1/2, z + 1/2$; #5: $-x + 1, y, -z + 3/2$; #6: $x, -y, z + 1/2$; #7: $-x + 1/2, -y + 1/2, z - 1/2$.

2.2. Structure determination

A suitable single crystal of dimensions $0.25 \times 0.26 \times 0.15$ mm^3 was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at a temperature of 20 ± 2 °C. Data processing was accomplished with the SAINT processing program [19]. Direct methods were used to solve the structure using the SHELXL crystallographic software package [20]. All framework Al, P and O atoms could be unambiguously located. C and N atoms were subsequently located from difference Fourier map suggested as triprotonated DETA cations by charge balance and elemental analysis and C and N atoms are disordered. The H atoms in DETA molecules were added geometrically and refined in a riding model. The non-hydrogen atoms were refined anisotropically. Structure details and selected bond lengths are listed in Tables 1 and 2, respectively.

3. Results and discussion

3.1. Synthesis and characterization of the AlPO-CJ31

Pure single crystals of AlPO-CJ31 can be prepared in an aqueous system with the gel compositions of $1.0Al(OPr^i)_3$:$3.6H_3PO_4$:$1.0H_2C_2O_4$:4.0DETA:$920H_2O$ at 180°C for 6 days. It is found that many factors influence the synthesis of AlPO-CJ31, as seen in Table 3. The pH value is an important factor, and the optimum pH value is 8. Moreover, the small size crystals of AlPO-CJ31 can be obtained