Synthesis, Structure and Adsorption of AlPO-21 Prepared by Co-template Method

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The phase of AlPO-21 was hydrothermally synthesized in the reactant system of diethylamine-RB-Al_2O_3-P_2O_5-H_2O-C_2H_5OH. The crystals of AlPO-21 growing in this system crystallizes in monoclinic system, space group $P2_1/n$ with $a = 0.8542(4)$ nm, $b = 1.7635(8)$ nm, $c = 0.9082(4)$ nm, $\beta = 108.234(5)°$, $V = 1.2993(10)$ nm^3, $Z = 4$, and the formula is $[C_4H_{10}NH_2]^+$-$[Al_3P_3O_{12}(OH)]^-$. The structure is resolved by the direct method and refined to $R_1 = 0.0767$ and $wR_2 = 0.1627$ based on 1719 observed reflections with $I > 2.0\sigma(I)$. An asymmetric unit consists of three PO_4 tetrahedra, one AlO_4 tetrahedron and two AlO_5 trigonal bipyramids. The framework is composed of 3-D uniform channels along [100], [001] and [101] with eight-membered oxygen ring windows. The powder sample of the MS was investigated with powder XRD, TG/DTG/DTA and the adsorption of water, methanol, *n*-hexane, ethylene, and ethane. The specific property for sieving molecules was observed on the adsorption isotherms, and proves the result of the single crystal structural analysis.

Keywords AlPO-21, co-template method, rhodamine B, diethylamine, Lowenstein rule

Introduction

AlPO-21 is a type of microporous aluminophosphate prepared by Flanigen and co-workers in 1982, and the structure was resolved by Smith *et al*.[1] in 1984. Almost at the same time Parise *et al*.[2] prepared AlPO-21 phase by another route and resolved the structure independently. In the next year, GaPO-21 phase was obtained as well.[3] Although Al(Ga)PO-21 phases prepared in different ways possess similar channel system, among them there are still some differences in lattice constants, indicating that different template molecules can affect locally the structure of AlPO-21. Compared with most AlPO molecular sieves (MS) *e.g.* AlPO-5, the structure of AlPO-21 shows a rather remarkable property, possessing the thermal stable framework with five coordinated aluminum Al(V) and linkage violating Lowenstein rule.

Generally, Al atom coordinates with four oxygen atoms and forms AlO_4 tetrahedron in the AlPO MS. In some micro-porous structures of alumino-phosphate (containing layered and 3-D structure), Al atom exhibit the ability to take five- and six-fold coordination and form AlO_5 trigonal bipyramid and AlO_6 octahedron, respectively. For instance, AlPO-12,[4] 17,[5] 40,[6] and UiO-13, 14[7] contain five-fold coordination aluminum atoms, and others including $Al_7P_7O_{28}(OH)_2 \cdot 2C_3H_7NH_3$[8] and UiO-26[9] contain six-fold coordination aluminum atoms (the framework of UiO-26 includes 4, 5 and 6 coordinated Al atoms). But the framework with AlO_5 or AlO_6 is not thermal stable enough in the most cases. On the other hand, Al- and P-containing polyhedra are linked in a strictly alternating manner, which is known as Lowenstein rule. Naturally, it benefits dispersing the charge furthest to obey the rule in the process of the framework forming. While the linkage of Al—O—Al is energetically unfavorable because it does not benefit the charge dispersion. The result of the calculation based on the lattice energy of an ionic model by Bell *et al*. shows that the energy loss caused by Al—O—Al linkage could be compensated by thermal energy.[10] Therefore, the Al—O—Al linkage can occur in some solid materials synthesized by high temperature methods, but usually does not appear in the framework prepared by hydrothermal route.

Before the discovery of the family of alumino-phosphate micro-porous structure, only a natural micro-porous mineral, cacoxenite $[Al(Al,Fe)_3Fe_{21}O_6(OH)_{12}(PO_4)(H_2O)_{24}] \cdot \sim 51H_2O$, possesses the framework with the linkage violating Lowenstein rule.[11] Now, several micro-porous alumino-phosphate structures, particulatly layered alumono-phosphate structure have been found to involve the linkage violating the rule, such as UiO-18-200,[12] UiO-15-225,[13] $Cs_2Al_2P_2O_9$,[14] and $[C_2N_2H_{10}][Al_2(OH)_2H_2O(PO_4)_2]H_2O$.[15] In 3-D open framework of alumino-phosphate, only a few structures contain Al—O—Al linkage. As a typical example, JDF-2, a micro-porous aluminophosphate discovered by Chippindale *et al*.,[16] is found to possess the framework containing Al—O—Al linkage and five-fold coordination Al atom synchronously. AlPO-21 has similar structural features to JDF-2, while it shows thermal stability in some sense. Smith *et al*. attributed it to the hydrogen bonding across 5-ring.[1]

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In this paper, AlPO-21 phase was synthesized by co-template method. Here, diethylamine (DEA) and Rhodamine B (RB) are used as template molecules. The single crystal XRD shows that no RB molecules are in the framework. But it is believed that RB must play an important role in the process of the framework forming, because AlPO-21 phase cannot be obtained under the condition of DEA as the template alone. The comparisons between the as-synthesized AlPO-21 and AlPO-21 reported are listed in Table 1.

Experimental

Preparation of AlPO-21

AlPO-21 was hydrothermally synthesized in the reactant system of Al_2O_3-P_2O_5-H_2O-C_2H_5OH using rhodamine B (RB) and diethyl amine (DEA) as the co-template. The initial reactant mixture included reagent grade aluminum iso-propoxide, phosphoric acid (85 wt%), diethyl amine (DEA), RB and distilled water. In order to increase the solubility of RB, reagent grade ethanol was added, and the molar ratio of the reactant is 1.0 (Al_2O_3): 1.0 (P_2O_5):0.618 (DEA):0.382 (RB):60 (water):40 (ethanol). In a typical preparation, 2.042 g of aluminum iso-propoxide, 1.830 g of RB, 1.080 g of distill water, 1.840 g of ethanol and 0.452 g of DEA were mixed. Then 1.153 g of phosphoric acid was dropped under vigorous stirring for 24 h at room temperature to form a homogeneous red sol. The sol was sealed and hydrothermally reacted in 20 mL stainless steel autoclaves lined with Teflon at 170 ℃ for 10 d in an oven under autogenous pressure. The product was washed with distilled water and ethylene for many times until no suspension species was observed and the color of crystalline products turned into white. Then the product was dried at 100 ℃ for 2 h.

Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D MAX/II A X-ray powder diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) in the 2θ range of 5°—35° at a scanning speed of 8 (°)/min. TG/DTG/DTA curves were measured on a Rigaku-PTC10A thermal analyzer in the temperature range of 25—500 ℃ at a rate of 10 ℃/min in nitrogen flow. The adsorption isotherms were determined with a Sartorius 7012 super-micro electron balance in vacuum. The sample was pre-heated at 350 ℃ for 5 h to remove water and organic template before measuring. About 60 mg sample was used for each test. Reagent grade methanol and *n*-hexane, and deionized water were used as the adsorbate in vapor adsorption. Ethane and ethylene with the purity of 99.99% were used as the adsorbate in gas adsorption.

Table 1 Comparisons of AlPO-21 prepared with different routes

	AlPO-21(DEA)[a]	AlPO-21(TMPD)[b]	AlPO-21(en)[c]	AlPO-21(py)[c]
Formula	$[C_4H_{10}NH_2]^+[Al_3P_3O_{12}(OH)]^-$	$Al_3P_3O_{12}OH\cdot 1.33N_2C_7H_{21}$	$Al_3(PO_4)_3\cdot C_2H_8N_2\cdot H_2O$	$Al_3(PO_4)_3\cdot C_4H_9N\cdot H_2O$
Reaction temperature (K)	443	473	473	423
Reaction time	7 d	7 d	68 h	93 h
Template	RB and DEA[d]	TMPD[e]	EN[f]	PY[f]
M_r	454.99	462.50	444.0	455.0
a (nm)	8.542(1)	10.3307(10)	8.472(3)	8.668(1)
b (nm)	17.634(9)	17.5241(13)	17.751(6)	17.558(2)
c (nm)	9.081(5)	8.6757(10)	9.062(3)	9.186(2)
β (°)	108.23(4)	123.369(7)	106.73(3)	107.751(1)
Z	4	4	4	4
V (nm^3)	1.2993(10)	1.3117	1.305(1)	1.3337(5)
Space group	$P2_1/n$	$P2_1/a$	$P2_1/n$	$P2_1/n$
T (K)	293(2)		298	298
F(000)	920		914	920
μ (mm^{-1})	0.743	0.67	0.721	0.707
No. of unique reflections	1719	2184	2612	2112
R	0.0767	0.046	0.045	0.071

[a] Sample synthesized in our laboratory; [b] synthesized by Smith, J. V.; [1c] synthesized by Parise, J. B.; [2d] RB = Rhodamine B; DEA = diethylamine; [e] TMPD = *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine; [f] EN = ethyldiamine; PY = pyrrolidine.

Crystal structure determination

A transparent flake single crystal (200 μm × 100 μm × 20 μm) was selected and fixed on the top of a glass thread for measurement. The crystal structure determination by X-ray diffraction was performed on a Bruker SMART CCD area-detector with monochromatic Mo Kα radiation (λ = 0.071069 nm) by graphite. The exact data were collected at a temperature of 293(2) K using the ω-φ technique. The refinement of all non-hydrogen atoms [except O (13)] with anisotropy was made with Bruker SHELXTL 97 program. The atom of O(13) is refined with isotropy because of no positive definition. Refining on F_o^2 gave $wR_2 = 0.1672$ and the conventional $R_1 = 0.0767$.

Results and discussion

Description of crystal structure

An asymmetric unit of AlPO-21 crystal structure contains three phosphorus atoms, three aluminum atoms, thirteen oxygen atoms and one hydrogen atom (Fig. 1). The atomic coordinates of all non-hydrogen atoms are listed in Table 2. Each of the three phosphorus atoms [P(1), P(2) and P(3)] is coordinated with four oxygen atoms to form a tetrahedron. The atom of Al(2) is coordinated with four oxygen atoms. Each of the other two aluminum atoms Al (1) and Al(3) is coordinated by five oxygen atoms and form AlO_5 trigonal bipyramids. The AlO_n polyhedra and PO_4 tetrahe-dra are connected with oxygen atoms constructing the 3-D framework. Remarkably, oxygen atoms in the framework, particularly those belonging to AlO_5 groups, are all shared to form oxygen-bridge bond. Therefore, there is no terminal oxygen in the framework of AlPO-21, which would have impact on the thermal stability of AlPO-21 framework. A secondary structure unit of the framework is composed of three oxygen-membered (3-) ring and four-oxygen membered (4-) ring. These rings connect with each other to form eight-oxygen membered (8-) ring. Each 3-ring is formed by one PO_4 tetrahedron and two AlO_5 trigonal bipyramids, and each 4-ring is formed by two PO_4 tetrahedra, one AlO_4 tetrahedron and one AlO_5 trigonal bipyramid as shown in Fig. 1. The whole framework exhibits the channels with 8-ring window with size of 0.31 nm × 0.44 nm along [001], 0.28 nm × 0.54 nm along [101] and 0.31 nm × 0.44 nm along [100] directions (Fig. 2), respectively.

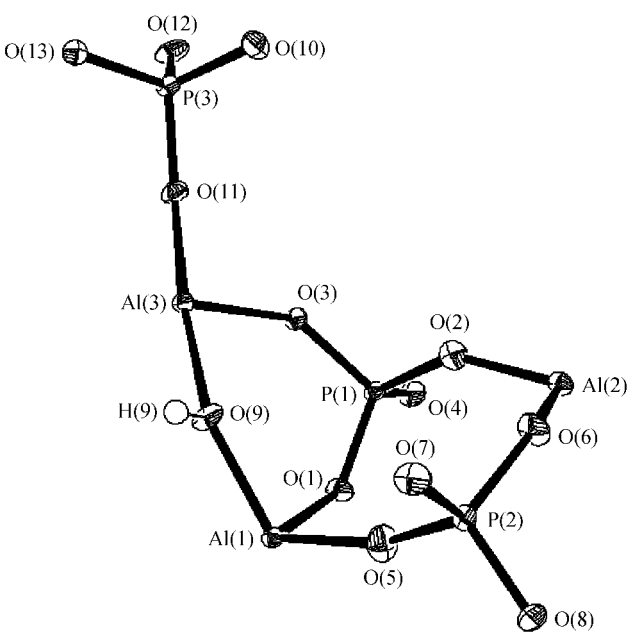

Fig. 1 Asymmetric unit for as-synthesized AlPO-21 (ORTEP package, thermal ellipsoids at 50% probability level). Number of coordination for Al(1), Al(3) is 5 and for Al(2) is 4. The 3-ring and 4-ring formed by MO (M = Al or P) polyhedra can be seen in the asymmetric unit of as-synthesized AlPO-21.

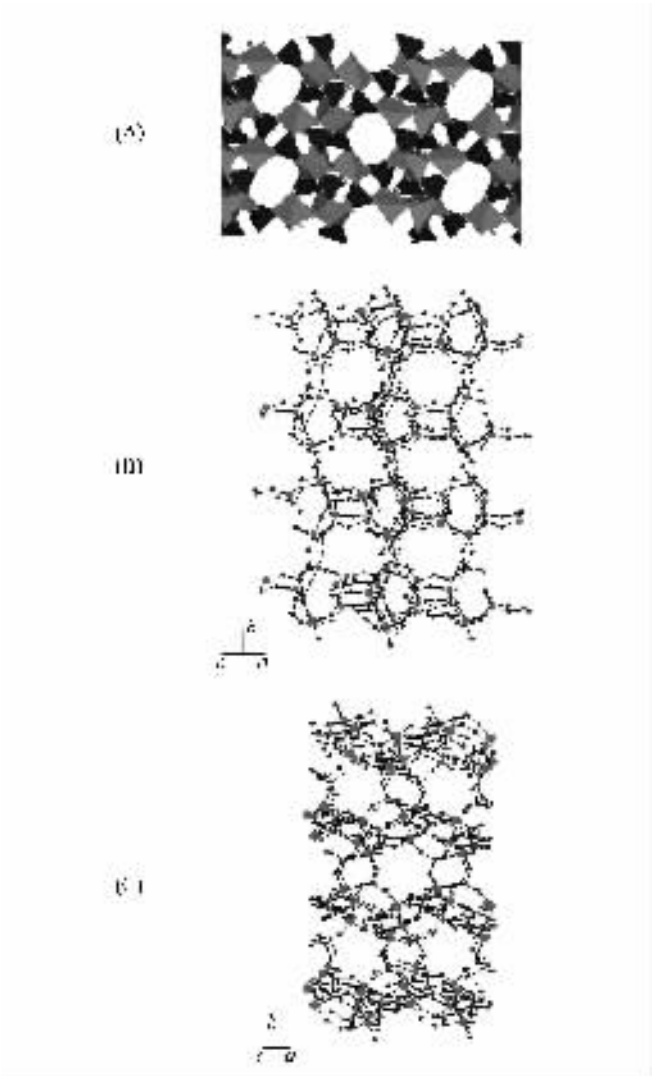

Fig. 2 8-Membered channels system of as-synthesized AlPO-21 along the [100] (A), [101] (B) and [001] (C) directions. The size of windows of channel along [100] and [001] direction is 0.31 nm × 0.44 nm, along [101] direction is 0.28 nm × 0.54 nm. The template DEA molecules are not shown for clarity.

Table 2 Atomic coordinates, site occupancy fractor (s.o.f) and isotropic displacement parameters U_{eq}(nm^2) for as-synthesized AlPO-21

Atom	*X*	*Y*	*Z*	s.o.f	U_{eq}($\times 10^{-2}$ nm^2)
P(1)	0.2564(2)	0.33406(11)	0.5008(2)	1	0.0093(4)
P(2)	−0.2062(2)	0.21186(11)	0.4712(2)	1	0.0094(4)
P(3)	0.1617(2)	0.57000(10)	0.1331(2)	1	0.0095(4)
Al(1)	0.0682(3)	0.20485(12)	0.2904(2)	1	0.0084(5)
Al(2)	0.0094(3)	0.32723(13)	0.6908(2)	1	0.0105(5)
Al(3)	0.1370(3)	0.39057(12)	0.1628(2)	1	0.0088(5)
O(1)	0.2375(6)	0.2517(3)	0.4436(5)	1	0.0133(11)
O(2)	0.1219(7)	0.3552(3)	0.5722(6)	1	0.0189(12)
O(3)	0.2409(6)	0.3898(3)	0.3681(5)	1	0.0121(11)
O(4)	0.4252(6)	0.3449(3)	0.6195(5)	1	0.0155(12)
O(5)	−0.0665(7)	0.1975(3)	0.4071(6)	1	0.0201(13)
O(9)	0.0399(6)	0.2939(3)	0.1787(5)	1	0.0145(12)
O(6)	−0.1674(6)	0.2796(3)	0.5817(6)	1	0.0168(12)
O(7)	−0.3665(6)	0.2298(3)	0.3417(6)	1	0.0168(12)
O(8)	−0.2284(6)	0.1417(3)	0.5588(6)	1	0.0146(11)
O(10)	0.0533(6)	0.5918(3)	0.2340(6)	1	0.0179(12)
O(11)	0.2182(6)	0.4883(3)	0.1641(5)	1	0.0130(11)
O(12)	0.3140(6)	0.6193(3)	0.1756(6)	1	0.0168(12)
O(13)	0.0632(6)	0.5813(3)	−0.0372(5)	1	0.0124(11)
N(1A)	0.270(3)	0.0435(15)	0.853(3)	0.5	0.087(8)
N(1B)	0.197(4)	0.0870(13)	0.763(3)	0.5	0.113(10)
C(1)	0.035(2)	0.0107(10)	0.9513(18)	1	0.093(5)
C(2)	0.120(3)	0.0714(12)	0.883(3)	1	0.164(10)
C(3)	0.165(3)	0.0075(14)	0.709(2)	1	0.169(10)
C(4)	0.028(3)	0.0214(14)	0.556(2)	1	0.148(9)

Because of the existence of 3-ring, Al—O—Al linkage [Al(1)—O(9)—Al(3)], appears in the open-framework of AlPO-21. The selected data of bond lengths and bond angles are listed in Table 3. From the data listed, the following features should be noticed. Al(1)O_5 trigonal bipyramid takes on obvious asymmetry and Al(1) atom is almost located at the side of the triangle, not at the center of the polyhedron as usual according to 170.2° of O(1)-Al(1)-O(4) angle. On the other hand, the bond lengths of Al(1)—O(9) (0.1844 nm) and Al(3)—O(9) (0.1921 nm) are longer than those of other Al—O with 0.177 nm in average, implying that the two bonds are unsaturated. Since the primary chemical formula of $[Al_3P_3O_{13}]^{2-}$ for AlPO-21 is not able to meet charge balance, a hydrogen atoms may connect with O atoms in this situation. In order to confirm the deduction, bond valence sums (BVS) for oxygen atoms in the framework have been calculated and the results are listed in Table 4. The calculation of BVS is an empirical theory based on the parameters of bond length. The relationship between the bond valence (s) and the bond length (r) can be described as: $s = \exp[(r_0 - r)/B]$. Here s refers to bond valence for selected atom, r_0 means the standard bond length for selected bond and r is bond length measured. B is the empirical parameter and the value is determined to be 0.37. The details about BVS theory can be seen in the references.[17,18] The bond valence of O(9) is 1.073 and others are all around 2. Therefore, we can conclude that there is indeed a hydrogen atom connected with O(9) atom. However, the asymmetric unit of AlPO-21 still has an excess negative charge even the hydrogen is bonded. To obtain charge balance, it is proposed that each DEA molecule is protonized and exists in the form of $C_2H_5NH_2^+C_2H_5$. Hence the chemical formula can be written as $[C_4H_{10}NH_2]^+[Al_3P_3O_{12}(OH)]^-$.

Although there is a little disorder for the site of nitrogen atom, the atomic coordinates of DEA molecule in the framework of AlPO-21 can be obtained. The nitrogen atoms in the cell have two possible sites with site occupancy factor of about 50% and the exact site of nitrogen should be between the two sites. The data of the bond length imply a structure feature. The distance between two adjacent DEA molecules is 0.128 nm [C(1)—C(1)] or 0.124 nm [C(4)—C(4)], which is much shorter than the bond length of C—C (about 0.15 nm) in the same molecule of DEA. This abnormal phenomenon could be caused by disorder of the site for the DEA molecule. The arrangement of DEA molecule (parallel with [001] direction) in the 8-ring channel of AlPO-21 is shown in Fig. 3.

Table 3 Selected bond lengths (nm) and angles (°) for as-synthesized AlPO-21

Atoms	Distances (nm)	Atoms	Angles (°)
Al(1)—O(5)	0.1796(6)	O(12)-Al(1)-O(9)	141.7(3)
Al(1)—O(12)	0.1786(5)	O(12)-Al(1)-O(5)	105.5(3)
Al(1)—O(9)	0.1844(5)	O(5)-Al(1)-O(9)	112.8(3)
Al(1)—O(1)	0.1857(5)	O(12)-Al(1)-O(1)	89.0(2)
Al(1)—O(4)	0.1867(5)	O(5)-Al(1)-O(1)	94.7(2)
		O(9)-Al(1)-O(1)	88.3(2)
		O(12)-Al(1)-O(4)	86.2(2)
		O(5)-Al(1)-O(4)	94.8(2)
		O(9)-Al(1)-O(4)	90.2(2)
		O(1)-Al(1)-O(4)	170.2(3)
		Al(1)-O(9)-Al(3)	144.3(3)
Al(3)—O(8)	0.1794(5)	O(8)-Al(3)-O(3)	110.8(2)
Al(3)—O(3)	0.1796(5)	O(8)-Al(3)-O(13)	113.0(2)
Al(3)—O(13)	0.1803(5)	O(3)-Al(3)-O(13)	136.1(3)
Al(3)—O(11)	0.1856(6)	O(8)-Al(3)-O(11)	89.9(2)
Al(3)—O(9)	0.1921(5)	O(3)-Al(3)-O(11)	86.4(2)
		O(13)-Al(3)-O(11)	91.6(2)
		O(8)-Al(3)-O(9)	96.9(3)
		O(3)-Al(3)-O(9)	90.0(2)
		O(13)-Al(3)-O(9)	86.9(2)
		O(11)-Al(3)-O(9)	173.1(2)
N(1A)—C(2)	0.1477(10)	C(2)-N(1A)-C(3)	89.1(18)
N(1A)—C(3)	0.1477(10)	C(2)-N(1B)-C(3)	89.5(19)
N(1B)—C(2)	0.1462(10)	N(1)-B(2)-C(1)	145(2)
N(1B)—C(3)	0.1482(10)	N(1A)-C(2)-C(1)	113.0(19)
C(1)—C(1)	0.128(3)	N(1A)-C(3)-C(4)	145(2)
C(1)—C(2)	0.1529(10)	N(1B)-C(3)-C(4)	99(2)
C(3)—C(4)	0.1525(10)	C(1)-C(1)-C(2)	151(2)
C(4)—C(4)	0.124(4)	C(4)-C(4)-C(3)	130(3)

Table 4 Results of bond valence sums (BVS) calculation for O in the framework of as-synthesized AlPO-21

Number of O	Bond length of P—O (nm)	Bond length of A—O (nm)	BVS for O
1	0.1533	0.1858	1.826
2	0.1532	0.1726	2.075
3	0.153	0.1797	1.939
4	0.1519	0.1868	1.860
5	0.1505	0.1797	2.027
6	0.153	0.1742	2.047
7	0.1534	0.1762	1.992
8	0.1516	0.1795	1.991
9	0.1845	0.1922	1.072
10	0.1543	0.1739	2.010
11	0.1519	0.1857	1.876
12	0.1512	0.1857	1.901
13	0.1526	0.1804	1.940

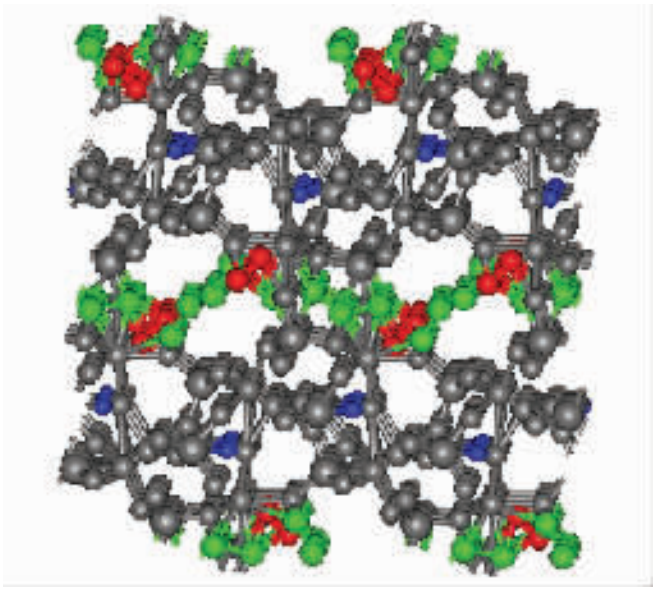

Fig. 3 Arrangement of template molecule chains parallel to [100] direction in the channel of as-synthesized AlPO-21. Red : N atoms ; green : C atoms ; grey : framework atoms (include P and Al atoms) ; blue : H atoms.

TG/DTG/DTA *and thermal stability*

There are two regions for the weight loss in the TG/DTG/DTA curves (Fig. 4). A slight weight loss is in the temperature range of 60—120 ℃ for de-water. A major weight loss is in the temperature range of 120—350 ℃, accompanied with a visible endothermic effect for de-template. The total weight loss for AlPO-21 is 10.6 wt%. It should be emphasized that the framework keeps intact after calcination at 350 ℃ for 5 h in air for removing the water and the template. The powder XRD patterns for the samples obtained from the calcination at 250 ℃ and at 350 ℃ possess almost the same fashion compared with that of the as-synthesized sample (Fig. 5). The thermal stability should only be attributed to the special linkage in the framework of AlPO-21. Generally, AlO_5 trigonal bipyramid and AlO_6 octahedron can lead to forming terminal oxygen atoms, which must link to H^+ or other cations for compensating the excess charges in the framework. The formed terminal OH or other groups would release from the framework when being heated. Therefore, the frameworks of alumino-phosphate with AlO_5 trigonal bipyramid or AlO_6 octahedron are usually unstable. In the framework of AlPO-21, each oxygen atom in all AlO_5 trigonal bipyramids is shared and forms oxygen bridge bond, leading to the thermal stability improved greatly. It should be pointed out that AlPO-25 phase appears with the temperature increasing, although the as-synthesized sample shows the thermal stability to some degree. The splitting of the peak at $10.02°/2\theta$ in the pattern of the calcined sample implies a trend of conversion from AlPO-21 to AlPO-25.

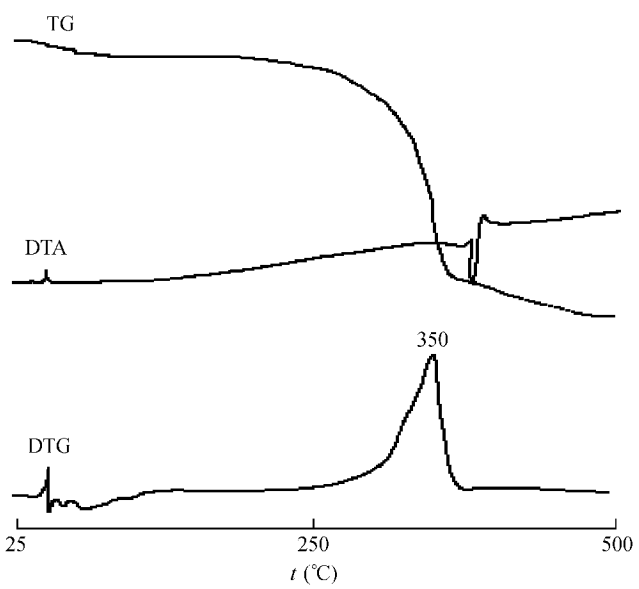

Fig. 4 TG/DTA/DTG curves of as-synthesized AlPO-21, the start mass is 13.98 mg, and the end mass is 12.50 mg. The weight lose is 10.6%.

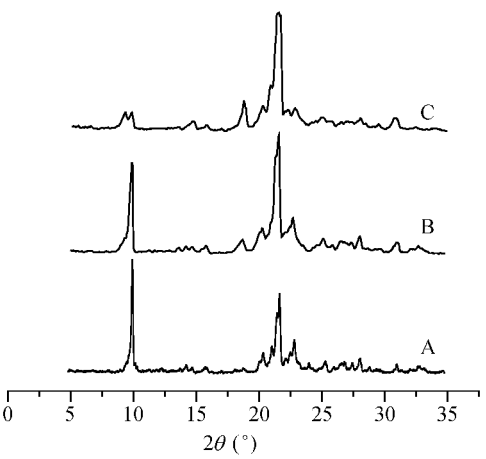

Fig. 5 XRD patterns for calcinated sample of as-synthesized AlPO-21. A : uncalcinated ; B : calcinated at 250 ℃ ; C : calcinated at 350 ℃.

Adsorption

The adsorption isotherms of the vapor of water, methanol and *n*-hexane at 25 ℃ are shown in Fig. 6. The isotherms with typical Langmuir type indicate that the molecules of water (0.28 nm), methanol (0.42 nm) are adsorbed into the micro-pores of AlPO-21. The loading for water, methanol and *n*-hexene calculated from the isotherms is 0.109, 0.068 and 0.011 $mL \cdot g^{-1}$, at $p/p_0 = 0.65$, respectively. The adsorption with very low loading at $p/p_0 = 0.9$ for the molecule of *n*-hexane (0.53 nm) indicates that AlPO-21 actually refuse *n*-hexane molecules at room temperature. Fig. 7 shows the adsorption isotherms of ethane and ethylene at −40 ℃ in gaseous state. Both isotherms are Langmuir type. Remarkably, the volumes of the adsorption for the molecule of ethylene (0.39 nm) and ethane (0.43 nm) are 24.7 and 31.1 $cm^3 \cdot g^{-1}$, respectively at $p = 6.13 \times 10^3$ Pa. The ad-

sorption data confirm that AlPO-21 adsorbs the molecules with size < 0.50 nm. The fact strongly supports that the framework of AlPO-21 possesses open channels with 8-ring window, in agreement with the result of single crystal structure analysis, and showing the character of molecular sieve.

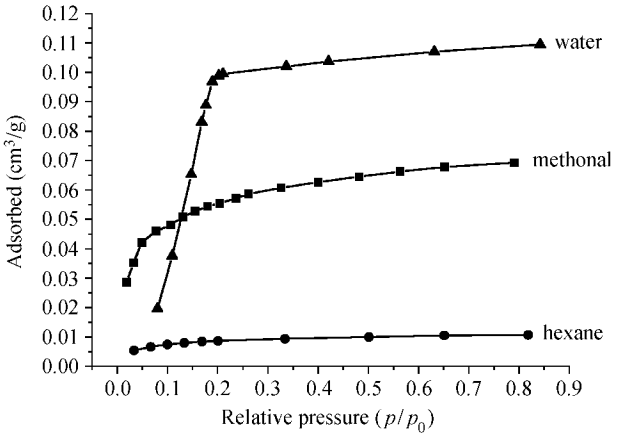

Fig. 6 Adsorption isotherms of water, methanol and *n*-hexane on as-synthesized AlPO-21 at 25 ℃.

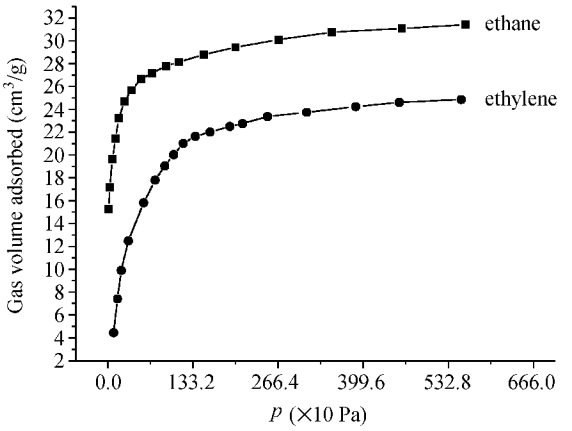

Fig. 7 Adsorption isotherms of hexane and ethylene on as-synthesized AlPO-21 at −40 ℃.

Evidently, The adsorption of water is lower than that of methanol at $p/p_0 < 0.10$, implying a slight hydrophobic character of the MS. On the other hand, the saturation adsorption of water and methanol is 0.11 and 0.07 mL·g^{-1}, respectively. The difference of the adsorption volume between water and methanol can be interpreted as follows. The window size of the channels along [001] and [100] are all 0.31 nm × 0.44 nm, which can adsorb both the molecules of water and methanol. The window size of the channels along [101] is 0.28 nm × 0.54 nm which is too narrow to adsorb methanol molecule. It means that all the channels can adsorb water molecule but only two channels adsorb methanol molecule. As a result, the saturation adsorption volume for methanol is lower than that for water.

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Supporting information available

An X-ray crystallographic file (CIF) is available free of charge via Internet at http://pubs.acs.org.

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