

Further Studies on Aluminophosphate Molecular Sieves

Part 1.— $\text{AlPO}_4\text{-H}_2$: A Hydrated Aluminophosphate Molecular Sieve

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Pure, highly crystalline $\text{AlPO}_4\text{-H}_2$ is synthesized from an aluminophosphate gel containing dipentylamine and characterized using X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, thermogravimetry and solid-state nuclear magnetic resonance spectroscopy. The $\text{AlPO}_4\text{-H}_2$ structure has orthorhombic symmetry with cell parameters of $a = 16.184(5)$ Å, $b = 9.914(3)$ Å and $c = 8.134(4)$ Å. It is constructed exclusively from hydrated triple crankshaft chains that also build the 18-membered ring VPI-5. $\text{AlPO}_4\text{-H}_2$ is a microporous, hydrated aluminophosphate with highly elliptical 10-ring channels (2.9 Å by 7.6 Å). One third of the framework Al atoms are octahedrally coordinated to two water molecules and four framework oxygens. Since $\text{AlPO}_4\text{-H}_2$ and VPI-5 share the same structural building unit, some of their physicochemical properties are similar. The existence of $\text{AlPO}_4\text{-H}_2$ and VPI-5 suggests that other molecular sieves with the same type of building unit can be synthesized.

In 1982, Wilson *et al.* announced the synthesis of a series of aluminophosphate molecular sieves ($\text{AlPO}_4\text{-}n$).¹ This new family of molecular sieves has greatly expanded the compositional and structural diversity of molecular sieve materials. Since then, hundreds of aluminophosphates and heteroatom-substituted aluminophosphates with more than two dozen structures have been synthesized.² The introduction of phosphate-based synthesis chemistries into molecular sieve science allowed a major breakthrough: the synthesis of molecular sieves with pore sizes greater than 10 Å. In 1988, VPI-5, an aluminophosphate molecular sieve containing extra-large pores (18-membered rings), was reported.³ Very recently, two other extra-large pore molecular sieves have been synthesized; cloverite (20-membered ring, interrupted gallophosphate framework)⁴ and JDF-20 (20-membered ring, interrupted aluminophosphate framework).⁵

In 1961, d'Yvoire⁶ reported the synthesis of several aluminophosphate hydrates, H1, H2, H3, H4, *etc.* (denoted with prefix $\text{AlPO}_4\text{-}$ in this work). These materials were prepared from dilute aqueous solutions of alumina and phosphoric acid with a $\text{P}_2\text{O}_5 : \text{Al}_2\text{O}_3$ ratio of 2.7. Of these aluminophosphate hydrates, only the structure of $\text{AlPO}_4\text{-H}_3$ has been determined. $\text{AlPO}_4\text{-H}_3$ contains PO_4 tetrahedra alternating between AlO_4 tetrahedra and $\text{AlO}_4(\text{H}_2\text{O})_2$ octahedra to form 4.8.8 and 6.6.6 sheets that construct a three-dimensional net.⁷ Recently, it was shown that $\text{AlPO}_4\text{-H}_3$ converts to $\text{AlPO}_4\text{-C}$ upon dehydration.⁸ $\text{AlPO}_4\text{-C}$ is a tetrahedrally linked framework without octahedral Al and contains pores of eight T-atoms (tetrahedral atoms). Early on, we noticed that $\text{AlPO}_4\text{-H}_1$ had X-ray diffraction (XRD) peaks similar to some of the XRD reflections of VPI-5.⁹ Further discussions on VPI-5, $\text{AlPO}_4\text{-H}_1$ and related materials are in our accompanying paper.¹⁰ Although XRD data for $\text{AlPO}_4\text{-H}_2$ are tabulated in d'Yvoire's report,⁶ the material was not synthesized as a pure phase. It co-crystallizes with one or more other aluminophosphate phases, *e.g.*, $\text{AlPO}_4\text{-H}_1$, $\text{AlPO}_4\text{-H}_3$, $\text{AlPO}_4\text{-H}_4$, variscite and metavariscite.^{6,11}

In this work, we report the synthesis of pure, highly crystalline $\text{AlPO}_4\text{-H}_2$ using an organic species in the reaction mixture. The structure and physicochemical properties of $\text{AlPO}_4\text{-H}_2$ are discussed, and to some extent, compared to those of VPI-5.

Experimental

Sample Preparation

A typical synthesis procedure used to produce pure, highly crystalline $\text{AlPO}_4\text{-H}_2$ is given below. An aluminophosphate gel is prepared by slowly adding diluted phosphoric acid solution (85%, from Fisher) to an alumina slurry (Catapal B, from Vista Co.) with stirring (each mixture contains *ca.* one-half of the total water used for synthesis). This gel is then aged without stirring at room temperature for *ca.* 8 h before an organic amine, *e.g.* dipentylamine (DPeA), is added dropwise with stirring. The molar composition of the final mixture is $\text{R} : \text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : x\text{H}_2\text{O}$, where R represents the organic amine and x can range from 40 to 50. The entire reaction mixture is stirred at room temperature for an additional 15 min, sealed in Teflon-lined autoclaves, and heated statically at 393 K for a time period ranging from 15 h to a few days. The solid product is diluted with distilled water before filtration. The filtered product is dried in air at room temperature.

VPI-5 is prepared by a procedure reported earlier¹² which involves the use of a reactive aluminophosphate gel and a mixture of triisopropanolamine (1,1',1''-nitritotripropan-2-ol) and tetramethylammonium hydroxide.

Characterization Techniques

Synchrotron X-ray powder diffraction data were collected at the Brookhaven National Laboratory using a wavelength of $\lambda = 1.15063$ Å. X-Ray powder diffraction (XRD) data were collected on a Scintag XDS 2000 diffractometer equipped with a liquid-nitrogen-cooled germanium solid-state detector and using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178$ Å). Infrared spectra were obtained on a Nicolet System 800 Fourier-transform infrared (FTIR) spectrometer by scanning KBr pellets which contained 2 wt.% of sample. Thermogravimetric (TG) analyses were performed in air on a DuPont 951 thermogravimetric analyser. The scanning electron micrograph (SEM) was taken on a JEOL 840-A scanning electron microscope.

The magic-angle-spinning (MAS) NMR spectra were recorded on a modified Bruker 300 AM NMR spectrometer. The ^{27}Al NMR spectra were collected at 78.2 MHz, with a

pulse length of 4 μ s, a pulse interval of 1 s, a spinning rate of 6 kHz, while for ^{31}P MAS NMR spectra these parameters are 121.5 MHz, 4 μ s, 4 s and 6 kHz, respectively. ^1H - ^{27}Al and ^1H - ^{31}P cross-polarization, magic-angle-spinning (CP MAS) NMR spectra were collected at an optimum contact time of 2 ms and ^1H 90° pulse of 4 μ s. The chemical shifts for ^{27}Al and ^{31}P are reported relative 1 mol dm $^{-3}$ $\text{Al}(\text{NO}_3)_3$ solution and 85% H_3PO_4 , respectively.

Results and Discussion

Synthesis

Many syntheses were carried out following the exact procedures described by d'Yvoire. In our hands, these procedures do not lead to the formation of $\text{AlPO}_4\text{-H}_2$ or $\text{AlPO}_4\text{-H}_1$. It is well known that organic amines and/or quaternary ammonium salts can direct the crystallization of aluminosilicate and aluminophosphate molecular sieves. The organic species may play roles as structure-directing agents and/or pH moderators.¹² Here we have synthesized pure $\text{AlPO}_4\text{-H}_2$ from a reactive aluminophosphate gel and dipentylamine (DPeA). The as-synthesized $\text{AlPO}_4\text{-H}_2$ does not contain DPeA in its channels (*vide infra*) indicating that the amine does not serve as a structure-directing agent during the crystallization process. Once $\text{AlPO}_4\text{-H}_2$ is formed, the crystals are stable in the mother liquor and do not transform to other phases under hydrothermal conditions even after a period of two weeks. Ageing the synthesis gel at room temperature is a necessary step for the synthesis of $\text{AlPO}_4\text{-H}_2$; otherwise $\text{AlPO}_4\text{-H}_3$ is formed as the final product. Other linear secondary amines, such as dipropylamine (DPA), dibutylamine (DBA) and dihexylamine (DHA) cannot be substituted for DPeA. Thus, $\text{AlPO}_4\text{-H}_2$ can be synthesized in the absence (ref. 6, 11; although not pure) or presence (this work; pure) of an organic species.

Structure

The synchrotron XRD pattern of the as-synthesized $\text{AlPO}_4\text{-H}_2$ is shown in Fig. 1(a). The reflections are deconvoluted using a profile-fitting program. Table 1 compares the synchrotron XRD data of the $\text{AlPO}_4\text{-H}_2$ material synthesized in this work with those reported by d'Yvoire.⁶ It is surprising that all the peak positions match extremely well between the two data sets, even though d'Yvoire never synthesized pure $\text{AlPO}_4\text{-H}_2$. The successful synthesis of pure $\text{AlPO}_4\text{-H}_2$ allowed for structure determination. Detailed discussions of the structure determination and refinement procedures will be given elsewhere.¹³ The symmetry of the $\text{AlPO}_4\text{-H}_2$ structure is orthorhombic with unit cell parameters of $a = 16.184(5)$ Å, $b = 9.914(3)$ Å and $c = 8.134(4)$ Å. Fig. 2(a) illustrates the projection of the $\text{AlPO}_4\text{-H}_2$ structure along the c crystallographic axis. It contains fused four-rings which circumscribe highly elliptical 10-membered rings (2.9 Å by 7.6 Å) parallel to the c axis. The dots adjacent to the centre of the fused four-rings indicate two water molecules (*vide infra*). The framework density (FD, number of T-atoms per nm 3) of $\text{AlPO}_4\text{-H}_2$ is 18.4 and the pore volume for the 10-ring channels is around 0.14 cm 3 g $^{-1}$. This structure is constructed exclusively of a simple building unit depicted in Fig. 3(a), i.e. the hydrated triple crankshaft chains that extend indefinitely in the c directions with the centre chain cranking in the opposite direction from the two side chains. X-Ray structural analysis shows that the Al atoms located in the centre chain are octahedrally coordinated by bonding two water molecules in addition to four framework oxygens. The calculated XRD powder patterns in the presence and absence of bonded water molecules at the Al atoms are also plotted in Fig. 1 for

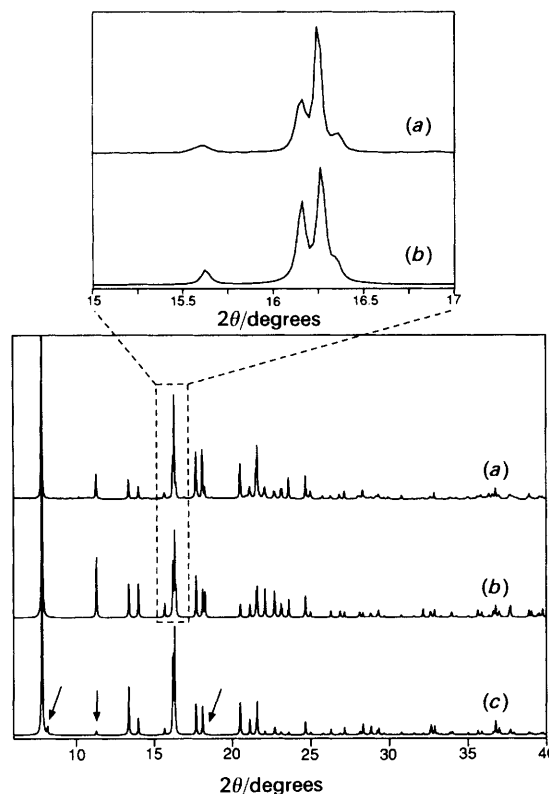


Fig. 1 Synchrotron X-ray powder diffraction patterns of $\text{AlPO}_4\text{-H}_2$: (a) experimental ($\lambda = 1.15063$ Å), (b) calculated based on a DLS model with two H_2O molecules bonded to Al atoms at the centre of the fused four-rings, and (c) calculated based on a DLS model in the absence of H_2O

comparison with the experimental pattern. The calculated XRD powder pattern is in good agreement with the experimental one only if there are two water molecules bonded to Al atoms at the centre of the triple crankshaft chains.¹³ If the water molecules are absent or are placed on the Al atoms other than at the centre of the triple crankshaft chains (not shown in the figure), the calculated patterns do not agree with the experimental one. The projection of the dehydrated triple crankshaft chains along the c axis shows fused four-rings [Fig. 3(b)]. Fused four-rings in the *cis* conformation [Fig. 3(c)] have been found in 22 known zeolite structures.¹⁴ The *trans* conformation of the fused four-rings [Fig. 3(d)], which is observed in the $\text{AlPO}_4\text{-H}_2$ structure, does not occur in any aluminosilicate zeolite. Most likely it is the water molecules that stabilize the building unit of $\text{AlPO}_4\text{-H}_2$ and play an important role during the crystallization process.

Fig. 2(b) illustrates the [001] projection of the VPI-5 topology. From the view along the c axis, $\text{AlPO}_4\text{-H}_2$ is comprised of four- and 10-rings only, while VPI-5 has four-, six- and

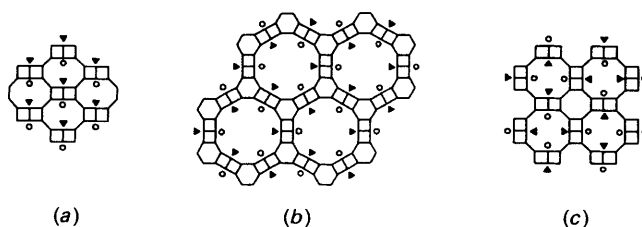


Fig. 2 Schematic [001] projections of hydrated structures. The symbol adjacent to the centre of fused four-rings represents two water molecules bonded to Al, ○ and ▲ indicative water molecules at different layers due to the alternation of Al and P: (a) $\text{AlPO}_4\text{-H}_2$, (b) VPI-5, and (c) net 39(1) (derived from ref. 16).

Table 1 X-Ray powder diffraction data

AlPO ₄ -H ₂ ^{a,b}		AlPO ₄ -H ₂ ^c		dehydrated AlPO ₄ -H ₂ ^{a,d}		AlPO ₄ -E ^{c,e}	
d/Å	I/I ₀ (%)	d/Å	I/I ₀ ^f	d/Å	I/I ₀ (%)	d/Å	I/I ₀ ^f
8.463	100	8.48	FFF	7.88	44	7.72	FF
5.867	15	5.87	m	7.24	1	7.02	ff
4.960	12	4.96	mf	5.91	10	6.29	fff
4.737	8	4.74	f	5.68	16	5.76	m
4.537	<1	4.55	fff	4.79	1	5.68	f
4.237	3	4.25	f	4.57	2	5.18	f
4.095	24	4.09	m	4.45	2 (sh)	4.97	fff
4.071	71	4.06	FF	4.38	25	4.76	mf
4.044	7	4.04	ff	4.10	100	4.52	mf
3.752	29	3.75	F	4.00	5	4.29	F
3.668	30	3.66	F	3.94	36	4.17	FFF
3.637	6	3.64	f	3.87	13	3.96	mf
3.239	21	3.24	m	3.63	21	3.85	F
3.147	5	3.14	f	3.55	34	3.67	m
3.087	14	3.08	F	3.42	1	3.58	mf
3.076	31						
3.011	5	3.01	f	3.37	5	3.51	mF
2.932	3	2.933	ff	3.27	9	3.46	mf
2.877	5	2.875	f	3.16	1	3.37	f
2.818	13	2.819	mf	3.05	4	3.19	mf
2.696	14	2.697	mf	3.03	15	3.04	mf
2.664	4	2.666	ff	3.00	21	2.99	mF
2.585	1	2.581	fff	2.95	13	2.87	m
2.535	1	2.533	fff	2.93	18	2.82	m
2.483	2	2.482	ff	2.89	1	2.78	mf
2.454	4	2.453	f	2.84	16		
2.371	1	2.373	ff	2.81	6		
2.355	4	2.352	f	2.78	3		

^a This work. ^b Synchrotron X-ray diffraction data ($\lambda = 1.15063 \text{ \AA}$). ^c From ref. 6. ^d X-Ray diffraction data ($\lambda = 1.54178 \text{ \AA}$); sample dehydrated at room temperature under vacuum. ^e Dehydration of AlPO₄-H₂ at 293 K over P₂O₅. ^f F = strong; m = medium; f = weak; sh = shoulder.

18-rings. The view perpendicular to the *c* axis is comprised entirely of six-rings for both AlPO₄-H₂ and VPI-5. The same network of six-rings is found in the view perpendicular to the *c* axis of the AlPO₄-5, AlPO₄-11 and AlPO₄-tridymite structures. We now recognize that AlPO₄-H₂ and VPI-5 structures are constructed exclusively of the same building unit, *i.e.* the hydrated triple crankshaft chains. As shown in Fig. 2, if the fused four-rings are aligned in the same direction (following a two-fold axis), an elliptical 10-rings system (AlPO₄-H₂) is formed. If three sets of such fused four-rings are linked following a three-fold axis, a six-ring is formed;

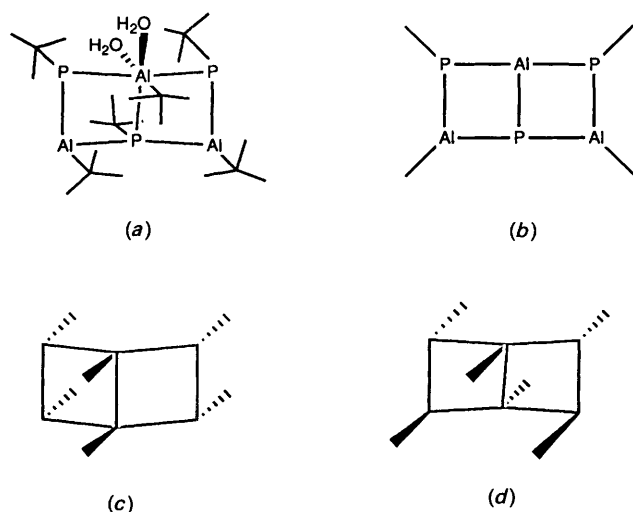


Fig. 3 Building units for AlPO₄-H₂, VPI-5 and net 39(1): (a) hydrated triple crankshaft chains, (b) projection of triple crankshaft chains along the chain axis, (c) fused four-rings in *cis* conformation, and (d) fused four-rings in *trans* conformation

and eventually an 18-rings structure (VPI-5) is constructed. Recently, McCusker *et al.*¹⁵ refined the structure of hydrated VPI-5 and revealed that the Al atoms in the fused four-rings are octahedrally coordinated (two bonded water molecules and four framework oxygens). In addition to AlPO₄-H₂ and VPI-5, the hydrated fused four-rings can be linked by following a four-fold axis to construct a network with eight- and 12-rings channels [Fig. 2(c)]. The dehydrated version of this 8/12-ring system is the framework denoted net 39(1), which was proposed by Smith and Dytrych some years ago.¹⁶ In the same paper,¹⁶ they also proposed net 81(1) (now re-numbered as 520), which is the topology of the dehydrated VPI-5. The existence of VPI-5 and AlPO₄-H₂ indicates that a hydrated aluminophosphate material with the framework illustrated in Fig. 2(c) can probably be synthesized at hydrothermal conditions.

Infrared Analysis

Fig. 4 shows the infrared spectra in the structural vibration region for AlPO₄-H₂ and VPI-5. Since these two materials are constructed from the same building units, their infrared spectra are expected to be similar. Indeed, the infrared spectra of AlPO₄-H₂ and VPI-5 show analogous structural vibration modes that are unique and more complicated than those of zeolites and other AlPO₄-*n* molecular sieves.^{3b} In the region between 1200 and 1000 cm⁻¹, four peaks are observed for AlPO₄-H₂ and VPI-5 (although some peak positions are slightly different between the two spectra), whereas only a broad band is found in this region for AlPO₄-5 and AlPO₄-11.^{3b,17} The splitting of this broad band in AlPO₄-H₂ and VPI-5 is probably due to the different internal stretching modes of the PO₄ tetrahedra, AlO₄ tetrahedra and AlO₄(H₂O)₂ octahedra. The sharp peak around 1270 cm⁻¹ is unusual for aluminophosphate materials. Such an IR peak

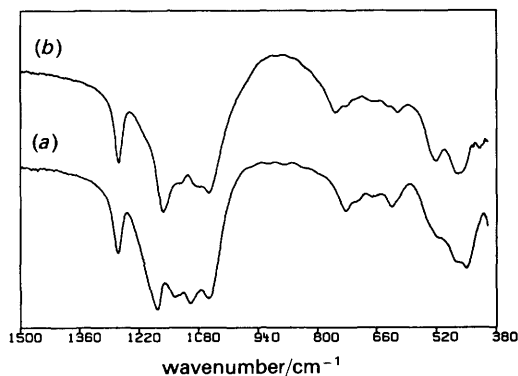


Fig. 4 Mid-infrared spectra of structural vibrational region for $\text{AlPO}_4\text{-H}_2$ (a) and VPI-5 (b)

may be an exclusive feature for aluminophosphate molecular sieves that contain the hydrated triple crankshaft chains.

Particle Morphology

Fig. 5 shows the SEM of $\text{AlPO}_4\text{-H}_2$. Both VPI-5¹⁸ and $\text{AlPO}_4\text{-H}_2$ show needle-like crystals. The needle-like crystals of VPI-5¹⁸ are more closely packed than those of $\text{AlPO}_4\text{-H}_2$ and form larger aggregates. It is not surprising that $\text{AlPO}_4\text{-H}_2$ and VPI-5 have similar shaped needle-like bundles since they crystallize from similar gel compositions and they are constructed of the same building units.

Thermal Analysis

Fig. 6 illustrates the TG curves for $\text{AlPO}_4\text{-H}_2$ and VPI-5. Although organic amines are employed in the synthesis of $\text{AlPO}_4\text{-H}_2$ and VPI-5, the TG results show that the organic species do not reside in these materials. There are two stages of water loss for $\text{AlPO}_4\text{-H}_2$ as well as for VPI-5.^{3b} This indicates that water molecules are located in different environments. $\text{AlPO}_4\text{-H}_2$ contains ca. 18 wt.% H_2O , which is close to the amount reported by d'Yvoire.⁶ According to the structural analysis ($\text{Al}_{12}\text{P}_{12}\text{O}_{48} \cdot 8\text{H}_2\text{O}$ per unit cell),¹³ water that is chemically bonded to the aluminium accounts for ca. 8 wt.% of the sample. The remainder of the water molecules are not well located. They must be distributed in both the unidimensional 10-ring pores and in the six-rings lined along the *c* axis, since the pore volume for the 10-rings channels is

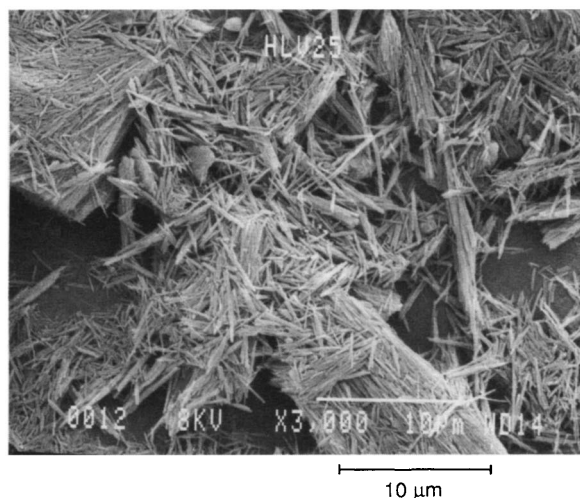


Fig. 5 Scanning electron micrograph of $\text{AlPO}_4\text{-H}_2$

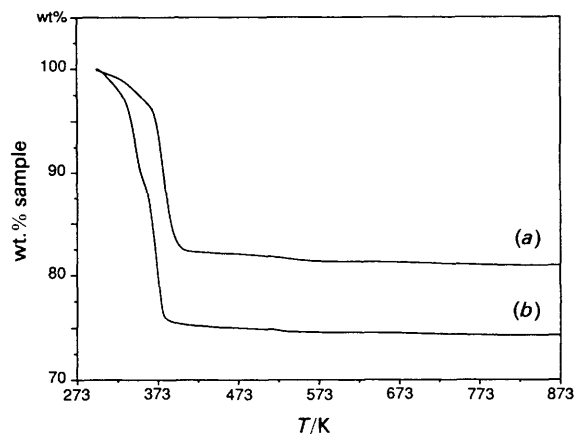


Fig. 6 TG curves of $\text{AlPO}_4\text{-H}_2$ (a) and VPI-5 (b); heating rate 1 K min^{-1} to 573 K, then 10 K min^{-1} to 873 K

only $0.14 \text{ cm}^3 \text{ g}^{-1}$ [$0.19 \text{ g}^{-1} \text{ g}$ (total water) in $\text{AlPO}_4\text{-H}_2$ according to adsorption measurements].

$\text{AlPO}_4\text{-H}_2$ is not thermally stable. Upon heating to 873 K, $\text{AlPO}_4\text{-H}_2$ transforms to $\text{AlPO}_4\text{-tridymite}$. In fact, this transformation occurs at temperatures around 373 K. When the structures of $\text{AlPO}_4\text{-H}_2$ and $\text{AlPO}_4\text{-tridymite}$ are compared, it is easy to envision the transformation. Upon heating, the bonds between Al and P located at the centre of the fused four-rings break and reconnect to form new bonds that yield the stable $\text{AlPO}_4\text{-tridymite}$ structure. This transformation is analogous to that which occurs when VPI-5 transforms to $\text{AlPO}_4\text{-8}$.¹⁹

^{27}Al and ^{31}P NMR

The ^{31}P and ^{27}Al MAS NMR spectra of as-synthesized $\text{AlPO}_4\text{-H}_2$ are illustrated in Fig. 7(a) and (b), respectively. The ^{27}Al MAS NMR spectrum shows a resonance at 36.7 ppm that corresponds to tetrahedral aluminium and twin peaks at -13.8 and -17.2 ppm due to octahedral aluminium species (two water molecules and four framework oxygens). The two-peak at high field is probably due to the second-order quadrupolar interaction of the octahedral aluminium, which cannot be completely removed by using the MAS technique and thus gives a resonance with a powder pattern.

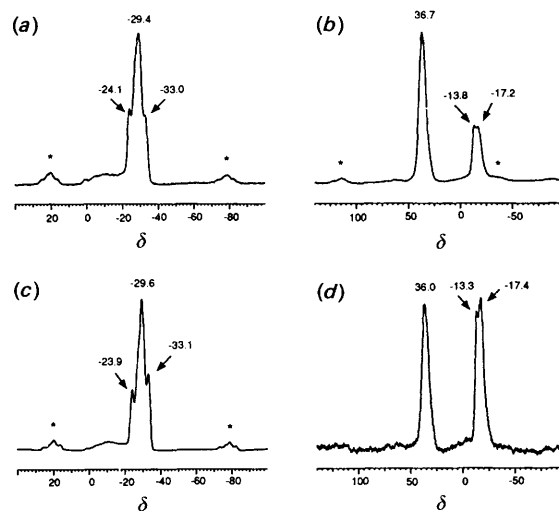


Fig. 7 Solid-state ^{31}P and ^{27}Al NMR spectra of as-synthesized $\text{AlPO}_4\text{-H}_2$ (asterisks denote spinning side bands). MAS NMR: (a) ^{31}P , (b) ^{27}Al . CP MAS NMR: (c) ^{31}P , (d) ^{27}Al .

The ^{31}P MAS NMR spectrum of the as-synthesized $\text{AlPO}_4\text{-H}_2$ shows three peaks at -24.1 , -29.4 and -33.0 ppm, respectively. The peak positions are similar to those observed for VPI-5,^{3b} whereas the relative intensities of the peaks are very different. The ^{31}P spectrum of $\text{AlPO}_4\text{-H}_2$ is quite complicated since the resonances are not as well resolved as those for VPI-5. Like VPI-5, the peak at -33.0 ppm for $\text{AlPO}_4\text{-H}_2$ can be assigned to the P atoms at the centre of the fused four-rings. The remainder of the peaks cannot be assigned (such is the case for VPI-5 as well). According to the structure of $\text{AlPO}_4\text{-H}_2$, the ratio of P atoms at the corner of the fused four-rings to the ones at the centre is 2:1. Similar to VPI-5, the observation of more than two ^{31}P peaks for $\text{AlPO}_4\text{-H}_2$ suggests that the water molecules probably affect the framework sites to generate different shielding environments for the P atoms. Full understanding of the NMR spectra of $\text{AlPO}_4\text{-H}_2$ and VPI-5 requires further investigation.

Fig. 7(c) and (d) show the ^1H - ^{31}P and ^1H - ^{27}Al CP MAS spectra, respectively, of the as-synthesized $\text{AlPO}_4\text{-H}_2$ sample. The peak positions in the ^{31}P CP MAS NMR spectrum are nearly identical to those observed in the MAS spectrum. The enhancement of all the signals in the ^{31}P CP MAS spectrum is indicative of water molecules having an effect on all the phosphorus sites. The ^{27}Al CP MAS NMR spectrum shows that the resonance associated with octahedral aluminium species is more enhanced than the one for tetrahedral aluminium. This is expected since water molecules are chemically bonded to the octahedral aluminium.

Dehydration of $\text{AlPO}_4\text{-H}_2$

Since $\text{AlPO}_4\text{-H}_2$ irreversibly transforms to $\text{AlPO}_4\text{-tridymite}$ upon heating, dehydration of $\text{AlPO}_4\text{-H}_2$ can only be carried out at room temperature. In order to study the dehydration, $\text{AlPO}_4\text{-H}_2$ was loaded into a sealed chamber on an X-ray diffractometer which can be evacuated. Fig. 8 displays the XRD patterns of $\text{AlPO}_4\text{-H}_2$ before evacuation, after evacuation for 8 h, and after the return to ambient conditions for 8 h. Dehydration of $\text{AlPO}_4\text{-H}_2$ under vacuum dramatically changes the XRD pattern. This XRD pattern does not match the XRD data described by d'Yvoire for $\text{AlPO}_4\text{-E}$ (see Table 1) that was obtained by dehydration of $\text{AlPO}_4\text{-H}_2$ over P_2O_5 at 293 K. The indices of the XRD reflections for dehydrated $\text{AlPO}_4\text{-H}_2$ indicate that dehydration distorts the original $\text{AlPO}_4\text{-H}_2$ framework and changes the crystallographic sym-

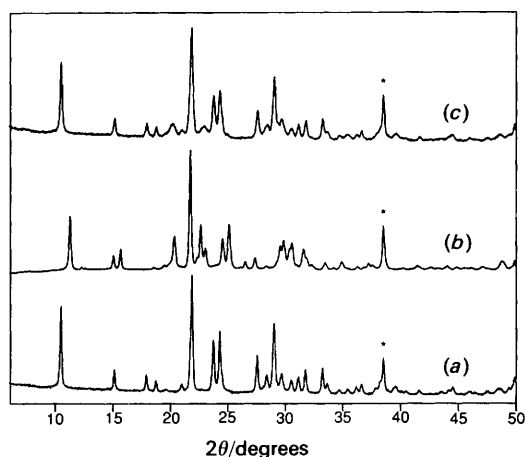


Fig. 8 X-Ray powder diffraction patterns of $\text{AlPO}_4\text{-H}_2$ in a sealed chamber (asterisks indicate reflections from tantalum sample holder): (a) before evacuation, (b) after evacuation for 8 h, and (c) after vacuum release and exposure to ambient conditions for 8 h

metry.¹³ After the vacuum is released, the original XRD pattern is nearly recovered except that there are two broad humps at 20° and 23° (2θ), which are most likely due to incomplete rehydration. After the dehydrated sample is exposed to air for several days, the XRD pattern returns exactly to the original pattern for $\text{AlPO}_4\text{-H}_2$. Although $\text{AlPO}_4\text{-H}_2$ shows significant changes in the XRD pattern when water is removed by vacuum, the dehydration and rehydration of $\text{AlPO}_4\text{-H}_2$ at room temperature is a completely reversible process.

An $\text{AlPO}_4\text{-H}_2$ sample was dehydrated under vacuum at room temperature and immediately transferred to an NMR rotor in a glove box. ^{27}Al and ^{31}P NMR spectra were collected on the dehydrated material and are shown in Fig. 9. The resonances for the octahedral framework aluminium disappear in the ^{27}Al MAS NMR spectrum of the dehydrated sample indicating that chemically bonded water has been removed by vacuum. The ^{31}P NMR spectrum of dehydrated $\text{AlPO}_4\text{-H}_2$ shows two major resonances at -24.5 and -29.1 ppm, respectively, in a ratio of ca. 2:1. The peak at higher field may be associated with the P atoms at the centre of the fused four-rings. The peak at ca. -14 ppm in the ^{31}P NMR spectrum of dehydrated $\text{AlPO}_4\text{-H}_2$ is probably due to P-OH. The enhancement of this signal in the ^{31}P CP MAS spectrum indicates that some P-OH species are generated upon dehydration of $\text{AlPO}_4\text{-H}_2$ under vacuum. Presumably, some of the P-O-Al bonds are broken when the structure is dramatically distorted from that of hydrated $\text{AlPO}_4\text{-H}_2$. This may be the reason why $\text{AlPO}_4\text{-H}_2$ very easily transforms to $\text{AlPO}_4\text{-tridymite}$ upon heating even under vacuum. In the case of VPI-5, dehydration causes slight changes in unit cell dimensions²⁰ and the structure is stable when the temperature is slowly ramped to 823 K under vacuum^{3b} or quickly increased to 923 K in ambient air.²⁰

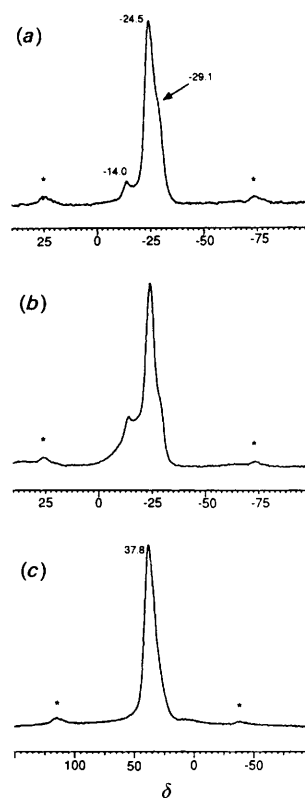


Fig. 9 Solid-state ^{31}P and ^{27}Al NMR spectra of dehydrated $\text{AlPO}_4\text{-H}_2$ (asterisks denote spinning side bands): (a) ^{31}P MAS, (b) ^{31}P CP MAS, (c) ^{27}Al MAS

Conclusions

Pure $\text{AlPO}_4\text{-H}_2$ is synthesized from an aluminophosphate gel containing dipentylamine (DPeA). DPeA is not occluded within the void space of $\text{AlPO}_4\text{-H}_2$. Thermal analysis shows two stages of water loss for $\text{AlPO}_4\text{-H}_2$ and the material transforms to AlPO_4 -tridymite upon heating. $\text{AlPO}_4\text{-H}_2$ is a microporous material with highly elliptical 10-ring channels (2.9 Å by 7.6 Å). One third of the framework aluminium atoms are chemically bonded with two additional water molecules to form octahedral coordination. $\text{AlPO}_4\text{-H}_2$ and VPI-5 share the same building units and to some extent have similar physicochemical properties such as crystal morphologies, IR vibrational modes and ^{27}Al and ^{31}P NMR spectra. $\text{AlPO}_4\text{-H}_2$ irreversibly transforms to AlPO_4 -tridymite upon heating, while vacuum dehydration and rehydration of $\text{AlPO}_4\text{-H}_2$ at room temperature is a reversible process. The successful syntheses of VPI-5 and $\text{AlPO}_4\text{-H}_2$ suggest that a material with net 39(1) topology may be synthesized hydrothermally.

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