Aluminophosphate Molecular Sieves Comprised of Hydrated Triple Crankshaft Chains

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We report the first synthesis of pure aluminophosphate hydrate H2 ($AlPO_4$-H2) and its structure; $AlPO_4$-H2 is constructed exclusively from a hydrated chain building unit that also builds the 18-ring VPI-5 structure and has one-dimensional channels circumscribed by highly elliptical rings consisting of ten oxygen atoms, implications from the existence of this building unit for the synthesis of novel aluminophosphate molecular sieves and for the synthesis of aluminosilicate and silicate analogues of $AlPO_4$-H2 and VPI-5 are discussed.

In 1961, d'Yvoire[1] reported the synthesis of the aluminophosphate hydrates H1, H2, H3 and H4 (denoted here with prefix $AlPO_4$-). Only the structure of $AlPO_4$-H3 has been determined. Using single crystal X-ray diffraction methods, Pluth and Smith[2] found Al in $AlPO_4$-H3 coordinated to either four or six oxygen atoms. More recently, Keller *et. al.*[3] showed that $AlPO_4$-H3 reversibly dehydrates to $AlPO_4$-C which contains only four-coordinated aluminium. The increased coordination of aluminum above four in $AlPO_4$-H3 is due to bound water molecules. In 1982, workers at Union Carbide reported the synthesis of aluminophosphate molecular sieves with pore diameters below 8 Å.[4] Hundreds of aluminophosphates and heteroatom substituted aluminophosphates with approximately 27 topologies are now known. Most notably, the aluminophosphate VPI-5 contains the largest pore of all the tetrahedral frameworks.[5,6] In addition, the aluminophosphates $AlPO_4$-8[7] and JDF-20[8] (interrupted framework) and the gallophosphate cloverite[9] (interrupted framework) contain rings larger than those observed in non-phosphate-based molecular sieves, *e.g.*, zeolites. Thus, there is great current interest in synthesizing silica-based molecular sieves, with a pore size similar to VPI-5.

Early on, we recognized some similarities in the X-ray diffraction patterns of VPI-5 and $AlPO_4$-H1.[10] Since then, we have attempted to repeat d'Yvoire's work. In the course of this investigation, pure $AlPO_4$-H2 was synthesized for the first time (d'Yvoire[1] and others[11] have synthesized the hydrate $AlPO_4$-H2 in the presence of one or more other hydrated aluminophosphate phases, *e.g.*, $AlPO_4$-H1, $AlPO_4$-H3, $AlPO_4$-H4, variscite and metavariscite). Highly crystalline $AlPO_4$-H2 is synthesized at hydrothermal conditions from an aluminophosphate gel containing di-n-pentylamine (R). A phosphoric acid solution is added slowly to an alumina (Catapal B) slurry to form an aluminophosphate gel. The gel is aged for 8 h before addition of the amine. The molar composition of the final mixture is $R:Al_2O_3:P_2O_5:50\ H_2O$. The crystallization is carried out in Teflon-lined autoclaves at 393 K for one to two days. The amine does not function as a structure-directing agent since it is not present in the $AlPO_4$-H2 material after synthesis. The successful synthesis of pure $AlPO_4$-H2 enabled structure determination. Detailed discussions of the X-ray structure determination and refinement procedures will be given elsewhere.[12] $AlPO_4$-H2 is orthorhombic with $a = 16.184(5)$, $b = 9.914(3)$, $c = 8.134(4)$

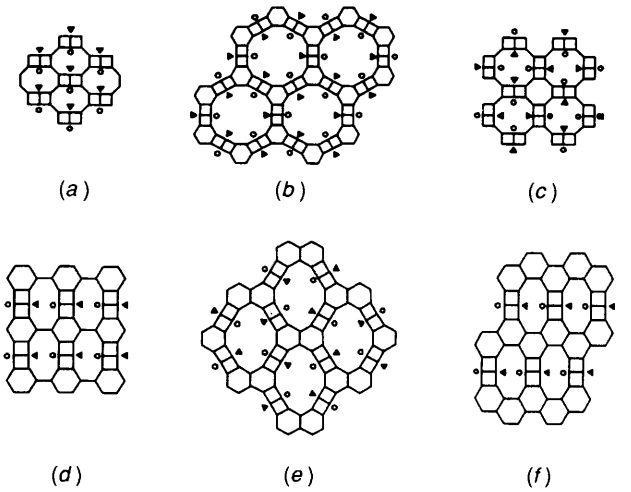

Fig. 1 The [001] projections of framework structures. (Each symbol adjacent to the centre of fused four-rings represents two water molecules bonded to an Al atom; ○ and ▲ indicate water molecules at different layers due to the alternation of Al and P in the $AlPO_4$ framework.): (*a*) $AlPO_4$-H2; (*b*) VPI-5; (*c*) hydrated Net 39(1) (derived from ref. 19); (*d*)–(*f*) hypothetical structures constructed with hydrated triple crankshaft chains and other building units.

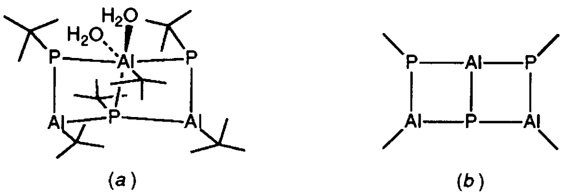

Fig. 2 Building unit for $AlPO_4$-H2, VPI-5 and hydrated net 39(1): (*a*) hydrated triple crankshaft chains; (*b*) [001] projection of the triple crankshaft chains showing the fused four-rings

Å and a maximum topochemical symmetry of $Cmc2_1$ (allows the strict alternation of Al and P atoms throughout the framework). Fig. 1(*a*) illustrates the [001] projection of the $AlPO_4$-H2 framework which has fused four-rings and highly elliptical ten-ring channels (2.9 by 7.6 Å). The view perpendicular to the *c*-axis shows only six-rings. The framework of $AlPO_4$-H2 is constructed from the simple building unit depicted in Fig. 2(*a*). This unit consists of hydrated triple crankshaft chains that extend indefinitely in the *c* direction with the the centre chain cranking in the opposite direction from the two outside chains [the triple crankshaft chain (not hydrated) was originally proposed by Richardson *et al.*[13]]. The projection of the triple crankshaft chains along the chain axis shows fused four-rings [Fig. 2(*b*)]. X-Ray diffraction and ^{27}Al NMR data indicate that the Al atoms in the centre chain are octahedrally coordinated with two water molecules and four framework oxygens. The X-ray powder diffraction pattern of as-synthesized $AlPO_4$-H2 agrees well with the calculated pattern from a distance least square[14] (DLS) refined model (Fig. 3). Notice that two water molecules must be placed on the Al atoms at the centre of the fused four-rings for the calculated pattern to match the experimental data. The structure of $AlPO_4$-H2 is dramatically distorted when water is removed by evacuation,[12] and upon heating transform to $AlPO_4$-tridymite (Fig. 4). By comparing the structures of $AlPO_4$-H2 and $AlPO_4$-tridymite (Fig. 4), it is easy to envision the transformation. The bonds between Al and P in the centre of the fused four-rings break and reconnect to form new bonds that yield the tridymite structure. This transformation is analogous to that which occurs when VPI-5 transforms to $AlPO_4$-8.[15]

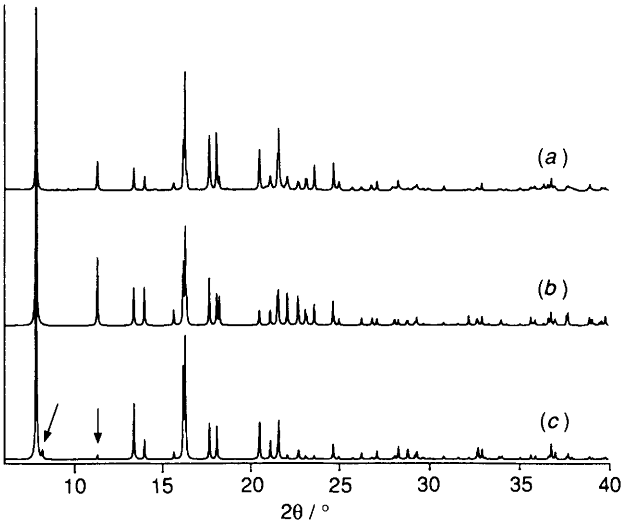

Fig. 3 X-Ray powder diffraction patterns of $AlPO_4$-H2: (*a*) experimental (synchrotron X-ray powder diffraction, $\lambda = 1.15063$ Å); (*b*) calculated based on a DLS model with H_2O molecules bonded to Al at the centre of fused four-rings (however, no physically adsorbed water is taken into account); (*c*) calculated based on a DLS model in absence of H_2O molecules (arrows point out main differences from the experimental pattern)

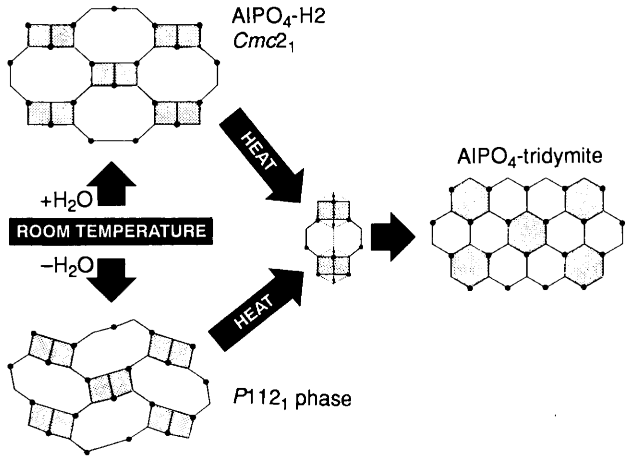

Fig. 4 Schematic illustration of the framework transformation of $AlPO_4$-H2 to $AlPO_4$-tridymite

The existence of the hydrated triple crankshaft chains suggests possibilities for the synthesis of new molecular sieves. After publication of the VPI-5 topology,[5,6] Brunner[16] questioned the feasibility of this framework. He considered the VPI-5 structure highly unlikely because the fused four-rings are in the *trans*-conformation rather than the well-known *cis*-conformation (observed in 22 zeolite frameworks). Although both tetrahedral and octahedral Al sites in VPI-5 have been detected with high-resolution double-rotation ^{27}Al NMR,[17] the water molecules could not be located with this technique. Recently, McCusker *et. al.*[18] determined the structure of hydrated VPI-5 and showed that the Al atoms in the fused four-rings are octahedrally coordinated (two bonded water molecules in addition to four framework oxygens). We now recognize that as-synthesized VPI-5 [Fig. 1(*b*)] is constructed exclusively from the hydrated triple crankshaft chains that build $AlPO_4$-H2. The hydrated triple crankshaft chains can be used to construct a third three-dimensional net with 12-membered rings [Fig. 1(*c*)]. In the absence of octahedral Al, this framework is net 39(1) originally proposed by Smith and Dytrych.[19] If the bonded water is removed from the structure of VPI-5, then net 81(1) (now renumbered to net 520[12]) is obtained and was also proposed by Smith and Dytrych.[19] The existence of $AlPO_4$-H2 and VPI-5 suggests that a material with the topology illustrated in Fig. 1(*c*) can be synthesized.

In addition to nets comprised entirely of the hydrated triple crankshaft chains [$AlPO_4$-H2, VPI-5 and hydrated net 39(1)], the hydrated triple crankshaft chains can be linked with other building units to yield a broad spectrum of novel nets. Several examples are illustrated in Fig. 1 (*d*)–(*f*).

The hydrated triple crankshaft chains are unique to $AlPO_4$-H2 and VPI-5. In addition, both materials can be synthesized in the presence of organic molecules yet the organics do not ultimately reside within the framework void spaces as is common with all other microporous aluminophosphates. These results suggest that water and octahedral Al play important roles in the synthesis of $AlPO_4$-H2 and VPI-5. Since the formation of octahedral, framework aluminium or silicon is not observed in zeolites and microporous silicas, it is unlikely that phosphate-free materials with structures analogous to $AlPO_4$-H2 and VPI-5 will be synthesized at hydrothermal conditions.

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