Aluminophosphate Molecular Sieves Comprised of Hydrated Triple Crankshaft Chains

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We report the first synthesis of pure aluminophosphate hydrate H2 (AlPO4-H2) and its structure; AlPO4-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 AlPO4-H2 and VPI-5 are discussed.

In 1961, d’Yvoire1 reported the synthesis of the aluminophosphate hydrates H1, H2, H3 and H4 (denoted here with prefix AlPO4-). Only the structure of AlPO4-H3 has been determined. Using single crystal X-ray diffraction methods, Pluth and Smith2 found Al in AlPO4-H3 coordinated to either four or six oxygen atoms. More recently, Keller et. al.3 showed that AlPO4-H3 reversibly dehydrates to AlPO4-C which contains only four-coordinated aluminium. The increased coordination of aluminum above four in AlPO4-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 AlPO4-87 and JDF-208 (interrupted framework) and the gallolphosphate cloverite9 (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 AlPO4-H1.10 Since then, we have attempted to repeat d’Yvoire’s work. In the course of this investigation, pure AlPO4-H2 was synthesized for the first time (d’Yvoire1 and others11 have synthesized the hydrate AlPO4-H2 in the presence of one or more other hydrated aluminophosphate phases, e.g., AlPO4-H1, AlPO4-H3, AlPO4-H4, variscite and metavariscite). Highly crystalline AlPO4-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 successful synthesis of pure AlPO4-H2 enabled structure determination. Detailed discussions of the X-ray structure determination and refinement procedures will be given elsewhere.12 AlPO4-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; O and $\alpha$ indicate water molecules at different layers due to the alternation of Al and P in the AlPO$_4$ framework): (a) AlPO$_4$-H$_2$; (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$_4$-H$_2$, 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.

Fig. 3 X-Ray powder diffraction patterns of AlPO$_4$-H$_2$: (a) experimental (synchrotron X-ray powder diffraction, $\lambda = 1.15063$ Å); (b) calculated based on a DLS model with H$_2$O 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$_2$O molecules (arrows point out main differences from the experimental pattern).

Fig. 4 Schematic illustration of the framework transformation of AlPO$_4$-H$_2$ 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, Brunner 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, the water molecules could not be located with this technique. Recently, McCusker et al. 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$_4$-H$_2$. 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. If the bonded water is removed from the
structure of VPI-5, then net 81(1) (now renumbered to net 520) is obtained and was also proposed by Smith and Dytrych. The existence of AlPO₄-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 [AlPO₄-H₂, VPI-5 and hydrated net 39(l)], 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 AlPO₄-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 AlPO₄-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 AlPO₄-H₂ and VPI-5 will be synthesized at hydrothermal conditions.

Support of this work was provided by the NSF Alan T. Waterman Award to M. E. D. H. X. L. thanks Akzo America, Inc. for financial support. The synchrotron X-ray data were collected at X7A beam line, National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the US Department of Energy, Division of Material Science and Division of Chemical Science.

Received, 23rd October 1992; Com. 205667D

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