A novel aluminophosphate precursor that transforms to $AlPO_4$-5 molecular sieve at high temperature

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A novel aluminophosphate microporous compound, denoted UHM-5, synthesized from an aqueous aluminophosphate gel at 150 °C in the presence of cyclohexylamine as the template, transforms upon calcination above 300 °C into $AlPO_4$-5 molecular sieve.

Hydrothermal synthesis of microporous materials using organic structure directing templates normally leads to a crystalline solid (precursor) that possesses a three dimensional framework of TO_4 tetrahedra, where T is a tetrahedral atom, and the subsequent elimination of the template by calcination occurs without significant structural variation. Surprisingly, this is not the case for the precursor reported in this work. However, partial removal of the organic species from the precursor by calcination above 300 °C leads to the AFI type structure. A similar behavior has been reported recently in the structural transformation of JDF-20, an extra large pore molecular sieve with a 20-membered ring, to $AlPO_4$-5.[2] JDF-20 has been reported to be crystallized from a predominantly non-aqueous synthesis medium using triethylamine which is also a template for $AlPO_4$-5. Although both UHM-5 and JDF-20 exhibit similar transformation to $AlPO_4$-5, these materials differ significantly in their structural and compositional details. From various characterization results on UHM-5, we believe that this is a new member of the extra-large pore molecular sieve family.

Synthesis of UHM-5 was achieved from an aqueous aluminophosphate gel using cyclohexylamine (CHA) as the structure directing template. UHM-5 was prepared by a modification of a synthesis procedure which would otherwise yield $AlPO_4$-5 molecular sieve. Typically the molar composition of the gel was: 1 CHA : 1 Al_2O_3 : 1 P_2O_5 : 50 H_2O. In a typical synthesis procedure aluminium isopropoxide (Aldrich, 98+%) was slurried in deionized water. While stirring, orthophosphoric acid (Merck, 85%) diluted with water was added. After stirring for 10 min, cyclohexylamine (Aldrich, 99%) was added slowly. The mixture was then heated at 70 °C for 30 min using a water-bath. The final gel was crystallized at 150 °C for 74 h.

Fig. 1 shows the X-ray powder diffraction patterns of a sample in the as-synthesized form and after heating this sample in O_2 at 300 °C. The observed crystalline pattern for the as-synthesized material is novel. The very low 2θ value (d = 17.96 Å) of the most intense line in the XRD pattern is indicative of an extra-large pore molecular sieve. The weak line at 2θ 7.57° is probably due to a very small amount of $AlPO_4$-5 which can probably crystallize along with UHM-5. After heating the sample at 300 °C, the structure changes to that of well crystallized $AlPO_4$-5 as also shown in Fig. 1. This structural transformation is brought about by the partial removal of the organic template. There is an extra line at 2θ 21.80° in the XRD pattern which does not belong to $AlPO_4$-5. Note that a line at 2θ 21.85° is also present in the XRD pattern of the as-synthesized sample. Thus, we believe that this extra line is possibly due to a small amount of a dense impurity phase present in the sample. By considering the first 15 lines after excluding the lines due to $AlPO_4$-5 (2θ 7.57°) and the impurity phase (2θ 21.85°) the powder pattern of UHM-5 has been indexed as a tetragonal unit cell with lattice parameters of a = 18.15, c = 20.59 Å and U = 6786.3 Å^3.

To remove the organic template without effecting structural transformation, ion-exchange with NH_4Cl was attempted. As in the case of thermal treatment, this procedure also leads to transformation of UHM-5 to $AlPO_4$-5 with significant loss in crystallinity. This suggests strong interaction between cyclohexylamine and the framework of UHM-5. The interaction between template and framework is further evidenced from thermal analysis results. Thermogravimetry (TG) and differential thermal analysis (DTA) of the material (Fig. 2) show two exothermic mass losses; a sharp loss at *ca*. 300 °C and a gradual loss between 300 to 500 °C due to the desorption and decomposition of the organic template. The total mass loss of 34 mass% observed on UHM-5 is significantly higher than the mass loss reported for any of the extra large pore molecular sieve materials and indicates the very high internal volume confined by the aluminophosphate framework. For example, both JDF-20 and VPI-5 show about 25% mass losses.[2,3] Interestingly, the material contains a very low amount of water as only < 1% of the total mass loss is accounted for by water desorption.

The product composition was estimated from electron microprobe analysis and TG results as 0.36 CHA $(Al_{0.5}P_{0.5})O_2{\cdot}x\,H_2O$. The observed Al/P ratio of unity in UHM-5 is characteristic of three dimensional microporous solids with

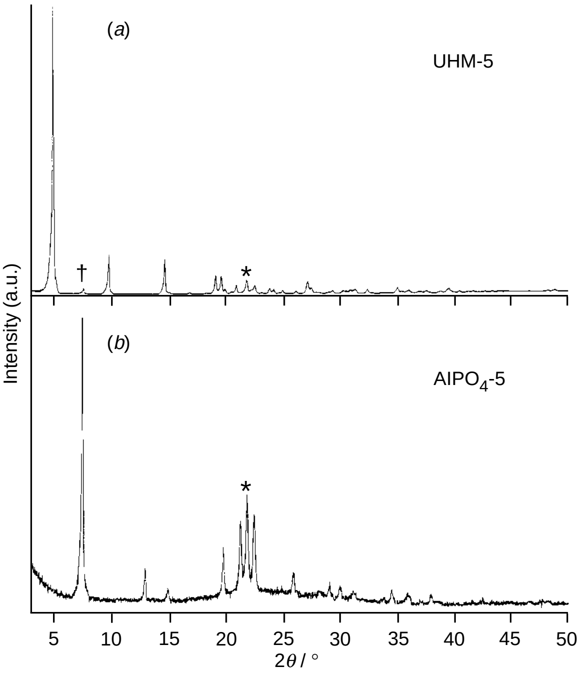

Fig. 1 X-Ray powder diffraction patterns of (*a*) as-synthesized UHM-5 and (*b*) $AlPO_4$-5 obtained after calcination of UHM-5 at 300 °C in oxygen. In the as-synthesized sample the line marked with † is due to a small amount of $AlPO_4$-5 phase present. In both the as-synthesized and calcined samples, the lines marked by * are due to an impurity phase.

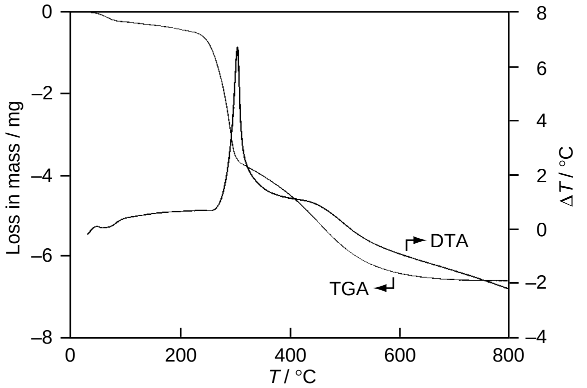

Fig. 2 Thermogravimetry (TG) and differential thermal analysis (DTA) results on UHM-5. The data were recorded with a heating rate of 5 °C min^{-1} in O_2 atmosphere. The initial mass of the sample was 17.418 mg.

alternate Al and P in the framework and is not observed in layered aluminophosphate materials. Previously synthesized layered aluminophosphates have a framework Al/P ratio of 0.75 and consist of vertices sharing AlO_4 and PO_4 tetrahedra with all of the vertices of the AlO_4 units being shared but only three-quarters of the PO_4 units being shared thus leaving formally a P=O group. It has been shown that these structure types can be related to two dimensional nets with the inclusion of a capping PO_4^{3-} group.[4]

Fig. 3 shows the ^{27}Al and ^{31}P NMR spectra recorded on UHM-5 and after heating at 300 °C. The as-synthesized UHM-5 exhibits a single asymmetrical resonance in the ^{27}Al MAS NMR spectrum at δ 41.2 (reference: aqueous aluminium nitrate) characteristic of tetrahedral aluminium.[5] After the solid state transformation an additional peak is detected at δ 36.8. As-synthesized and calcined $AlPO_4$-5 is reported to exhibit a single resonance centered at δ *ca.* 35.[5] The fact that the line at δ 41.2 did not completely disappear during the transformation indicates that only a fraction of the Al sites undergo changes in environment during the transformation. The ^{31}P MAS NMR spectrum of as-synthesized UHM-5 exhibits a single sharp line at δ −4.6 and an additional broad line at δ −30 (reference 85% H_3PO_4). After the transformation, the line at δ −4.6 completely disappears while the line at δ −30 increases substantially. A ^{31}P line at δ −28.1 has been determined for $AlPO_4$-5.[6] Tetrahedral phosphorus in microporous materials generally exhibits resonances in the range δ −25 to −35 range characteristic of $P(OAl)_4$ environments.[5] The resonance at δ *ca.* −30 in UHM-5 is clearly due to tetrahedral phosphorus as found in several other microporous materials. The fraction of $AlPO_4$-5 present in the original as-synthesized sample is very small. Thus, the relatively strong NMR signal at δ *ca.* −30 in an as-synthesized sample cannot be fully accounted for by an $AlPO_4$-5 phase, although a small contribution of this phase to the observed signal is obvious. In $AlPO_4$-based materials, the interaction of the framework phosphorus with extraframework species such as water or organic molecules can modify or shift the resonance signal considerably.[7] A wide range of chemical shifts spanning from δ 30 to −85 has been reported for five-coordinate phosphorus compounds.[8] A framework P/Al ratio of unity in UHM-5 implies an alternate arrangement of Al and P units in the framework. The observed resonance at δ −4.6 could be due to five-coordinate phosphorus of the form $P(OAl)_4(OH)$ formed by coordinating with four framework Al and an extraframework species such as a hydroxyl group. The presence of hydroxyl groups was observed in UHM-5 by FTIR measurements which show an intense sharp band at 3650 cm^{-1} normally assigned to hydroxyl stretching vibrations.[9] The disappearance of the resonance at δ −4.6 after heating above 300 °C can be viewed as a consequence of phase transformation where the five-coordinated phosphorus transforms to tetrahedral to form $AlPO_4$-5 molecular sieve. Associated with each $P(OAl)_4(OH)$ unit one would expect a protonated template species. $AlPO_4$ units in which both Al and P are in tetrahedral coordination are neutral and do not require amine to balance any framework charge. From the observed chemical composition of UHM-5, it can be seen that for every ten P atoms there are about seven CHA species. This suggests that out of ten P atoms of the framework, roughly seven are in five-coordination and three in tetrahedral coordination consistent with the two ^{31}P NMR signals.

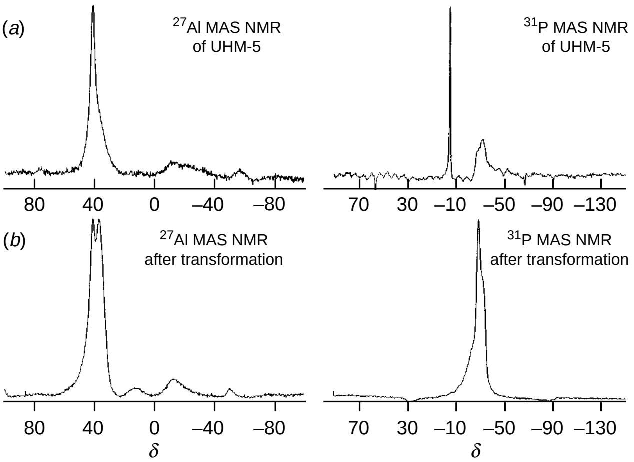

Fig. 3 ^{27}Al and ^{31}P MAS NMR spectra recorded (*a*) for as-synthesized UHM-5 and (*b*) after heating UHM-5 at 300 °C in oxygen

The observations made above suggest that the framework of UHM-5 probably consists of both $AlPO_4$ and $(AlPO_4)OH$ units. The framework structure of UHM-5 is stable in the presence of the organic species and transforms upon heating to the $AlPO_4$-5 structure. UHM-5 crystallizes in small 4–6 μm platelets bunched together to form large clusters of *ca.* 100 μm as revealed by scanning electron microscopy. Because of the small crystal size, single crystal analysis would be difficult. All the characterization results so far obtained on UHM-5 indicate an extra large pore material. Additional experiments are necessary for a better understanding of the transformation mechanism and work is in progress to determine the structure of UHM-5.

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Footnote and References

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