UiO-6: a novel 12-ring AlPO₄, made in an inorganic–organic cation system

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A new molecular sieve type material UiO-6 is prepared and its structure solved through a combination of simulated annealing, used to isolate the framework topology, and Rietveldt refinement, to verify the suggested topology; the structure has been approved and given the IUPAC code OSI by the Structure Commission of the International Zeolites Association.

One of the goals in the hydrothermal synthesis of zeolites and metalloaluminophosphates is the identification of new synthetic parameters that result in novel phases which may be then isolated in a pure form. The introduction of fluoride into known synthetic recipes[1] has opened up new possibilities, and the synthesis method has now been developed further using combinations of fluoride and alkali-metal cations. This approach has resulted in the formation of a new aluminophosphate UiO-6, the structure of which has been solved through a combination of recent methods based on simulated annealing, used to isolate the framework topology, and Rietveld refinement, to verify the suggested topology.

The synthesis of UiO-6 is unusual in that the aluminophosphate gel containing the organic amine tetraethylammonium hydroxide (TEAOH) has to be modified with both fluoride and alkali-metal cations. In the absence of the fluoride, only AlPO₄-5[2] is formed and in the absence of cations, a mixture of AlPO₄-5 and UiO-6 is obtained, with the latter only in a small amount. The synthesis was carried out using both sodium and potassium modified gels. The optimum gel ratios are: 1 Al₂O₃ : 1 P₂O₅ : 0.5 HF : 0.2 KF : 1 TEAOH : 40 H₂O and 1 Al₂O₃ : 1 P₂O₅ : 0.4 HF : 0.1 NaF : 1 TEAOH : 50 H₂O, in the sodium and potassium cation systems, respectively.

The synthesis gels were made as follows: pseudobohemite alumina (VISTA) was mixed with water and phosphoric acid (85 mass%, KEBO), to this mixture was added a solution consisting of HF (40 mass% in water), TEAOH (tetraethyl-ammonium hydroxide, 40 mass%, Aldrich), and KF (Fluka) or alternatively NaF (Merck).

The reaction mixtures were heated in Teflon-lined stainless-steel autoclaves, under static conditions, and autogenous pressure. The synthesis temperature was 150 °C, and the crystallisation time was 24 h

The phases obtained were identified by their XRD patterns, using a Siemens D500 diffractometer. All samples were analysed by SEM equipped with EDX, selected highly crystalline samples were further characterised by ³¹P and ²⁷Al MAS NMR, thermal analysis (TG–DSC–MS) and adsorption measurements.

High-resolution powder diffraction data were collected at the Swiss Norwegian beamline (D1) at the European Synchrotron Radiation Facility (ESRF).

The materials synthesized from both sodium and potassium gels incorporate fluoride and cations in the as-synthesized materials. Typical compositions derived from TG–MS and EDX analysis are: potassium system {(NEt₄)₁.₅K₁.₅F₃}[Al₁₆-P₁₆O₃₂]·6H₂O, sodium system {(NEt₄)Na₀.₅F₁.₅} [Al₁₆P₁₆O₃₂]·3H₂O.

The diffraction pattern of the as-synthesized material (Fig. 1) is unusual in that there are only a few strong, non-overlapping

peaks and the intense reflection at 2θ 20.5 dominates. This peak is very close to the main peak in the dense tridymite AlPO phase, we initially assumed that the material was contaminated by this dense phase; this combination of a few weak peaks and the possible presence of an impurity phase thus posed a problem in the identification of the unit cell.

An extended data collection of the calcined, more regular material was necessary to index the diffraction pattern.[3] Finally, we identified a tetragonal cell with parameters $a = 18.38$, $c = 5.06$ Å. Comparison of diffraction patterns obtained for the calcined, as-synthesized and high-temperature forms then allowed indexing of the as-synthesized material which has an orthorhombic unit cell; $a = 18.34$, $b = 18.44$, $c = 10.10$ Å, where the c-axis is doubled compared to the more regular calcined material. A study of systematic absences in the calcined diffraction patterns indicated six possible space groups: $I4$, $I\bar{4}$, $I4/m$, $I422$, $I\bar{4}2m$ and $I4/mmm$.

The size of the cell along the short c-axis (5.06 Å) gave a strong indication that the only possible T-atom linkage in this direction is zigzag chains. This essentially reduced the problem of determining the topology to a two-dimensional level.

The topology of the framework was determined through the simulated (SA) annealing method[4] in which series of frame-
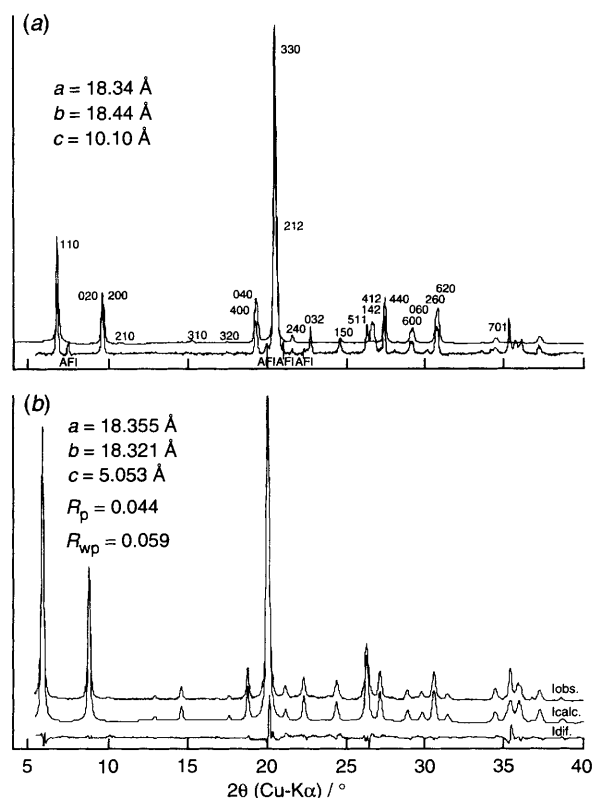

Fig. 1 (a) Diffraction pattern of the as-synthesized UiO-6 material, upper line diffractometer data, lower line synchrotron data; (b) diffraction patterns from Rietveld refinement of calcined UiO-6

work topologies are generated within the symmetry of the space group according to a figure of merit based on deviations from prescribed connectivities, bond lengths and angles. This method requires as input, in addition to the cell and symmetry, the total numbers of T atoms in the cell and the number of unique T atoms.

The total number of tetrahedral atoms (N_T) of the framework was determined as 33, from the correlation of the water absorption in the micropore volume (0.11 cm^3 g^{-1}) and the framework density.[5]

The largest organic molecule absorbed by UiO-6 is 1,3,5-trimethylbenzene, indicating a 12-ring channel system. The total absorption of trimethylbenzene is 70% of that of AlPO-5, in accord with the suggested structure.

The number of unique T sites in the asymmetric unit (N_U) was estimated as 3 P sites or 6 Al + P sites from the deconvoluted ^{31}P solid-state MAS NMR spectra of the calcined material. The three different T atom positions are indicated in the drawing of the [001] projection of the structure in Fig. 2. One T atom position is located in the planar 4-ring next to two 6-rings, while T-(2) and T-(3) are both located next to the 12-ring, in accord with the 1:2 ratio observed in the NMR spectrum. The NMR spectrum of the as-synthesized material is more complicated. Three peaks are resolved with area ratio 1:1:4 but the large peak is very broad and a deconvolution with three or four gaussian peaks was not able to produce satisfactory results. A deconvolution into six peaks appeared more reasonable, reflecting the six P-atom positions in the as-synthesized cell that is double compared to the calcined material.

From the possible space groups, starting with $I4$, it is expected that the number of T atoms should be a multiple of 8. From absorption measurements the number of T atoms was estim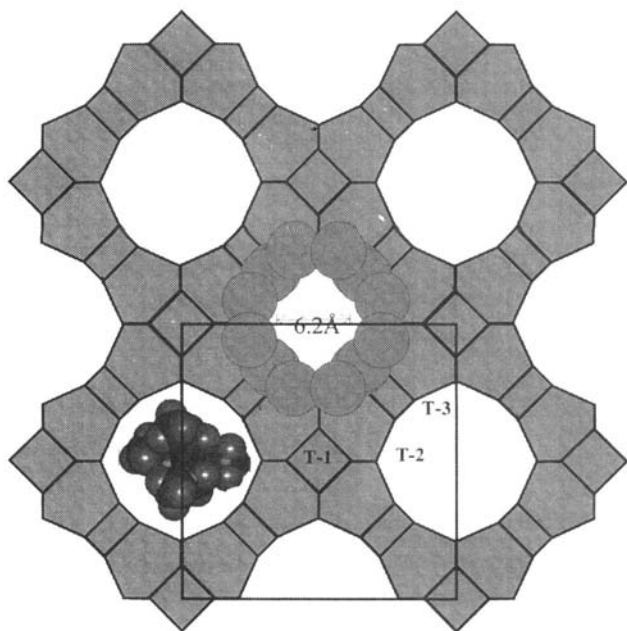ated as 33; 32 is the closest number divisible by 8. This results in four unique T atoms, but from NMR three unique T atoms were expected (Al and P equivalent) resulting in only 24 T atoms in the cell. If the strong peak in the diffraction pattern was due to a tridymite impurity then density measurements from absorption would be systematically too high. This possibility could therefore not be excluded. A series of SA computations with subsequent geometry optimization[6] within the calcined unit cell was therefore performed going systematically through all possible combinations of space groups and framework density. This resulted in the generation of three topologies that gave a simulated powder diffraction pattern that agreed reasonably well with the observed data. Refinement[7] of all the possible solutions gave one reasonable solution (wR_p = 0.059, R_p = 0.044) [Fig. 1(b)]. The final structure solution shows that the strong peak at 2θ 20.5° belongs to the structure and not an impurity. Increasing the symmetry from $I4$ (no. 79) to the highest possible symmetry for the T atom lattice, $I4/mmm$ (no. 139) reduces the number of unique T atoms from 4 to 3 which is in agreement with the NMR results. However, in order to take account of the Al/P ordering in the framework, the symmetry must be reduced to orthorhombic $Imm2$ (no. 44).

As is clear from the [100] projection of the framework (Fig. 2), UiO-6 contains a narrow one-dimensional 12-ring channel system, with a free aperture of 6.2 Å.

A detailed structural analysis including location of the non-framework atoms is not possible with the present diffraction data, however, collection of high-resolution PXRD data is underway.

The discovery of UiO-6 shows the continued potential for the preparation of novel phases through modification of known gel systems by the introduction of new synthesis variables, such as inorganic cations. The solution of the structure by simulated annealing shows the potential for new methods in the solution of complex structures from powder data.

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Fig. 2 The framework of UiO-6 showing the [001] projections of the framework along the 12-ring channels