AlMePO-β: inclusion and thermal removal of structure directing agent and the topotactic reconstructive transformation to its polymorph AlMePO-α

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The microporous aluminium methylphosphonate-β (AlMePO-β), prepared in the presence of 1,4-dioxane with the composition per formula unit of $Al_2(PO_3CH_3)_3 \cdot 0.25C_4H_8O_2$, loses dioxane molecules in two steps upon heating in an inert gas. Further heating in the presence of water vapour results in topotactic reconstructive transformation into the closely related α polymorph; under water vapour partial pressures of *ca.* 25 Torr, the transformation proceeds close to completion at temperatures in excess of 460 °C. Calculation of the lattice energies of the two AlMePO polymorphs shows the α form to be more stable by 12.6 kJ mol^{-1} per $Al_2(PO_3CH_3)_3$ formula unit, and confirms the thermodynamic reason for the transformation. Close comparison of the structures reveals that the main difference lies in the position of Al(4) in the β structure, and a mechanistic pathway is suggested and illustrated by which the aluminium migrates following Al—O—P bond hydrolysis and subsequent bond remaking to give rise to the α polymorph. The branching nature of the propagation step of the migration, which also results in methylphosphonate group rotations, explains how transformation might occur rapidly in a concerted fashion. A role for the water in catalysing the transformation is proposed.

Aluminium methylphosphonates (AlMePOs) can crystallise either as layered[1] or microporous framework structures, the latter being a logical extension to the aluminophosphate family of molecular sieves. Two framework structures have been reported and their structures solved.[2–4] These are polymorphs, termed AlMePO-α and -β, of stoichiometric formula $Al_2(PO_3CH_3)_3$ and possess hexagonal arrays of one dimensional pores, with free diameters of around 6.5 Å, that are lined partly with methyl groups (rather than by oxygen alone, as is the case in aluminophosphates). The hydrophobic natures of these materials promise useful applications in sorption and catalysis.

The β polymorph is the more readily prepared phase pure and its synthesis from an inorganic gel is strongly favoured by the presence of 1,4-dioxane, the incorporation of which into the as-prepared solid has been inferred from carbon content measurements on the bulk material.[2] In this work, we report direct evidence for the incorporation of the dioxane molecules within the channels and its stepwise removal upon heating.

The two polymorphs have extremely similar structures with a crystallographic relationship that has not yet been described explicitly in the literature. We have observed that thermal treatment in the presence of water vapour results in the topotactic reconstructive transformation of the β polymorph to the α polymorph. Such a transformation is rare in framework solids, where the usual response of such materials to elevated temperature is to lose crystallinity and transform to a denser phase. Examples include the conversion of microporous aluminium phosphates to the form of $AlPO_4$ isostructural with tridymite and the conversion of the zeolite Mg-B to cordierite.[5,6] Thermal transformations between structurally related polymorphs (such as the cubic and hexagonal stacking variants of zeolite Y) are rarely possible because even in these cases large-scale bond rearrangements are usually necessary, and when sufficient thermal energy is available to break bonds, more thermodynamically favourable recrystallisation is preferred. Some examples of solid-state transformations of microporous solids, usually facilitated by the presence of water, have been observed. One is the recrystallisation of VPI-5 to AlPO-8 at temperatures of around 100 °C.[7]

In addition to reporting the transformation, we discuss here the reasons why AlMePO-β is able to convert topotactically to AlMePO-α in terms of the structure, and postulate a mechanism. We also calculate the thermodynamic stabilities of the two polymorphs and confirm that the α polymorph is the more energetically stable.

Experimental and Results

Aluminium methylphosphonate-β was prepared according to published procedures[4] and its phase purity confirmed from the X-ray powder diffraction pattern. In general, $Al(OH)_3 \cdot xH_2O$ (Aldrich) and 1,4-dioxane (Aldrich) were added to a solution of methylphosphonic acid (Aldrich) and stirred for 30 min. The molar ratios of the components [$Al(OH)_3 : CH_3PO(OH)_2 : H_2O$: 1,4-dioxane] in the mixture were 1 : 1.5 : 40 : 0.5, respectively, and the pH was 3–3.5. To confirm the role of the organic molecule in structure direction, a preparation was performed in its absence, producing some AlMePO-β but mainly another polymorph of $Al_2(PO_3CH_3)_3$ without microporosity. In the case of the preparations performed in the absence of dioxane, all other reaction parameters were unchanged. The gel was sealed inside a Teflon-lined stainless steel autoclave and heated at 160 °C for 48 h. Needle shaped crystals of approximate dimensions 0.05–0.1 mm long by 0.005 mm across were formed in 69% yield (calculated w.r.t. phosphorus or aluminium theoretical yield). Heating experiments were performed either in commercial thermogravimetric equipment or, on a larger scale, in a silica glass tube in a tube furnace. Samples were heated at a rate of 10 °C min^{-1} in all cases. For the larger scale preparation the material was kept at the desired temperature and held for the reported period of time at that temperature (between 400 and 600 °C). The temperature measured at the sample, using a K-type thermocouple, was between 3 and 4 °C higher than the setpoint temperatures over the range used. EDX of samples before and after heating revealed, as expected, no significant change in the Al : P ratio. The effect of humidity was investigated by

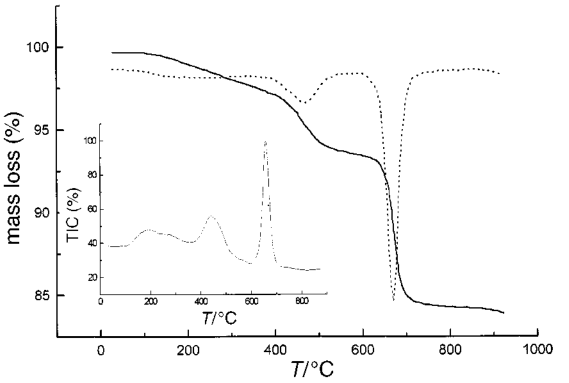


Fig. 1 Showing profile and its first differential for the TGMS experiment on AlMePO-β in helium. The inset shows the total ion count (TIC) from the MS for the same experiment.

saturating the nitrogen stream with vapour by bubbling through distilled water (this corresponds to approximately 20 cm^3 min^{-1} H_2O/500 cm^3 min^{-1} N_2 at 25 °C and 1 atm). X-Ray diffraction of products was performed on a STOE diffractometer with a linear position-sensitive detector covering 6° in 2θ and employing Ge-monochromated Cu-Kα_1 radiation ($\lambda = 1.540\ 56$ Å). Samples were prepared by mounting between two sheets of milar as rotating discs in the X-ray beam. ^{13}C, ^{31}P and ^{27}Al NMR were performed using magic angle spinning (MAS) on a Bruker 400 MHz spectrometer.

Thermogravimetric analysis of AlMePO-β in nitrogen (for which no special measures had been taken to remove trace amounts of water) and using a heating rate of 10 °C min^{-1} up to 600 °C revealed a small initial mass loss followed by two main mass loss peaks at *ca.* 190 and 460 °C. The first peak was broad and it is likely that it is formed by the combination of several peaks due to a range of sites with similar binding energies. The higher temperature peak is much more sharply defined, probably resulting from desorption from a single, more strongly binding site. X-Ray analysis subsequent to the experiment revealed the sample had completely transformed into AlMePO-α.

In order to determine the nature of the mass loss, a similar thermal treatment was applied under helium with on line mass spectrometric analysis (TGMS; Fig. 1) (although to ascertain the ultimate thermal stability of the sample the maximum temperature was increased to 850 °C with the same ramp rate). TGMS Fig. 1(insert) shows the two mass loss events with peaks at 190 and 450 °C and matching of the mass spectra at these times reveals these to be due to the removal of dioxane molecules. At temperatures of 600 °C and above, a mass loss of 8% is observed and this can be attributed mainly to the loss of methane as indicated by mass spectrometry. It is clear, however, that there are some higher hydrocarbons produced also, including C_2 and aromatic species. Comparison of thermal treatments in air and helium show a similar mass loss below 300 °C but the air-treated sample shows more mass loss at higher temperatures up to 600 °C, and less at temperatures greater than this. (Total mass loss: air treated = 11.7 mass% compared to He treated = 15.8 mass%.)

The TG results can be interpreted in the following way. As prepared (air dried at 60 °C) the chemical composition of AlMePO-β is $Al_2(PO_3CH_3)_3\cdot 0.25C_4H_8O_2$ (this corresponds to nine dioxane molecules per unit cell). Heating in an inert gas results in the removal of 33% of the dioxane in the first, broad event peak and the remainder in the second, sharper event. At elevated temperatures, assuming the process

$$4{-}CH_3 \rightarrow 3CH_4 + C$$

removal of the CH_3 group as methane only would permit a maximum mass loss of 10.7% of the AlMePO framework. A value of 9.8% mass loss is observed. Heating in air followed by XRD reveals AlMePO-β is air stable up to 350 °C. Although calcination at higher temperatures in air might be expected to remove all the CH_3 groups the observed mass loss is less than the theoretical maximum. The reduced mass loss observed must arise from the oxidation of the phosphonate units, involving take up of oxygen and, therefore, a mass gain offsetting that lost as methane.

To confirm the presence of the dioxane molecules and to attempt to locate two chemically distinct sites corresponding to the two TG events, ^{13}C and ^{31}P MAS NMR spectroscopies were performed on a sample of as-prepared AlMePO-β and on a sample heated at a temperature sufficient to remove the dioxane without effecting the β to α transformation. ^{13}C MAS NMR using cross-polarisation (CP), reveals a poorly resolved cluster of resonances at *ca.* δ 13.5, characteristic of $-CH_3$ groups attached to P. Also, there is one extremely sharp resonance at δ 67.65 corresponding to the carbon of the dioxane (Fig. 2). The ^{13}P MAS NMR spectrum of the sample containing dioxane (Fig. 3) shows broader resonances than does the sample from which dioxane has been removed. Taken together, these results indicate that the dioxane molecules are not well ordered with respect to the AlMePO framework, at least on the timescale of the NMR experiment.

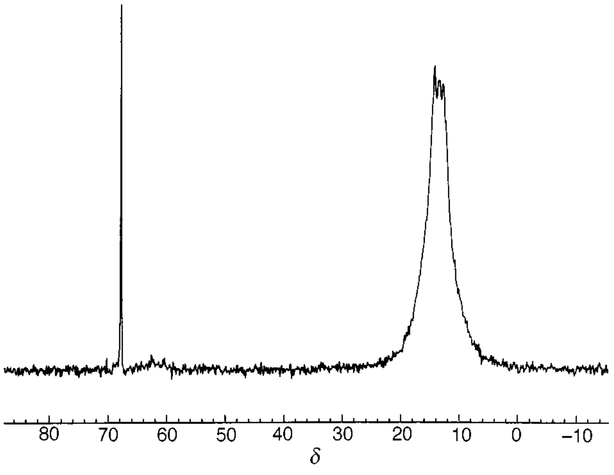


Fig. 2 ^{13}C CP MAS NMR spectrum of as-prepared AlMePO-β showing a cluster of peaks associated with CH_3 groups attached to P at *ca.* δ 13.5, and a single sharp resonance at δ 67.65 corresponding to 1,4-dioxane

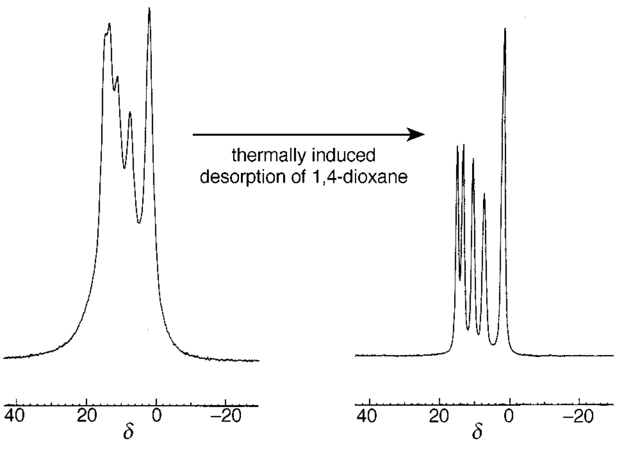


Fig. 3 Comparison of the ^{31}P MAS NMR spectra of AlMePO-β as-prepared and with 1,4-dioxane removed by heating (below the transformation temperature)

Topotactic transformation

A series of experiments was performed to establish the thermal stability over extended periods of AlMePOs in flowing nitrogen. This revealed that while AlMePO-β was stable after 8 h at 400 °C, a transformation started at *ca.* 450 °C and by 475 °C appreciable AlMePO-α had formed. After heating at 550 °C the sample was predominantly AlMePO-α with around 10% AlMePO-β remaining (as measured by XRD). As it was possible that the transformation was being catalysed by traces of water in the nitrogen this was investigated by controlling the humidity using a stream of nitrogen saturated with water vapour (*ca.* $20\ \mathrm{cm^3\ min^{-1}}$ $H_2O/500\ \mathrm{cm^3\ min^{-1}}$ N_2 at 25 °C and 1 atm) in the temperature range 450–525 °C. Typical results are given in Fig. 4. It was possible under these conditions to cause the complete conversion of AlMePO-β to the α form at 500 °C. (Heating at 525 °C or higher under these conditions caused the material to turn black and lose crystallinity.) Furthermore, the conversion could be followed by ^{27}Al MAS NMR spectroscopy, the signal for octahedral aluminium in AlMePO-β ($\delta -19.2$) decreasing as the signal for octahedral aluminium in AlMePO-α ($\delta -22.6$) increased. This procedure also resulted in a change in the N_2 adsorption capacity, at 77 K and $P_{N_2}/P_{N_2}{}^0 = 0.2$, from $2.6 \times 10^{-3}\ \mathrm{mol\ g^{-1}}$ for AlMePO-β to $4.6 \times 10^{-4}\ \mathrm{mol\ g^{-1}}$ for the product AlMePO-α. This reduction in adsorption capacity is presumably the result of defects produced during the transformation which act to block some of the channels in the structure. The original and the transformed materials were examined under cross-polars in an optical microscope for evidence of topotacticity. Each of the crystal fibres examined was found to go into extinction uniformly when it was parallel and perpendicular to the polarised direction of the incident light, indicating that the transformation is indeed topotactic.

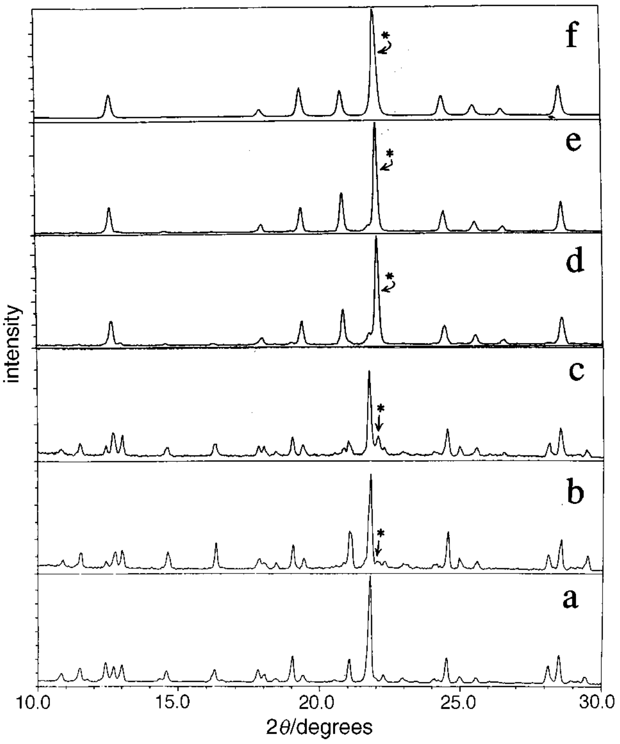


Fig. 4 X-Ray powder diffraction patterns for (a) pure, as-synthesised AlMePO-β, (b) AlMePO-β heated at 450 °C for 8 h under flowing nitrogen saturated with water vapour, (c) AlMePO-β heated at 460 °C for 8 h under flowing nitrogen saturated with water vapour, (d) AlMePO-β heated at 480 °C for 8 h under flowing nitrogen saturated with water vapour, (e) AlMePO-β heated at 500 °C for 8 h under flowing nitrogen saturated with water vapour, (f) AlMePO-α (simulated pattern for the pure phase). The position of the (1 0 2) reflection of AlMePO-α is marked with an asterisk illustrating the increase in relative amount of this phase as the temperature is raised. Note also the great change in degree of transformation over the temperature range 460–480 °C (c,d).

Computational studies

Since the materials are very similar and the heating experiments suggest that AlMePO-α is the more stable, we have attempted to confirm this using computational methods. While interatomic potential methods have been successfully used to model aluminophosphate structures and relative energies,[8] they are not readily amenable to the AlMePOs because of having to blend a shell model for the inorganic component with a covalent model for the methyl groups. Hence we have decided to use a new periodic implementation of the semi-empirical quantum mechanical Hamiltonian AM1[9] as implemented in the program GULP.[10]

In order to handle the long range summation of the Coulomb terms in this approach the integrals are evaluated exactly out to 12 Å, beyond which the integral formula is expanded as a power series in inverse powers of the distance. These terms become negligible after the fifth power and so the series is truncated here. Each term in the series can be summed by a partial transformation into reciprocal space in the same fashion as for the Ewald summation.[11] In the long range limit the integrals are evaluated in a point multipole approximation and the exact integrals are tapered to the approximate region to avoid discontinuities. All overlap integrals can be truncated similarly at the 12 Å cut-off as they become negligible.

Given the large unit cells involved, the wavefunction is sampled at the gamma point of the Brillouin zone only as this should be sufficent. All structures are minimised fully with respect to the cell strains and the fractional coordinates using analytical first derivatives and a BFGS update of the hessian which is initialised as a unit matrix. See work by Gale[12] for further details.

While semi-empirical methods, including AM1, are generally known to have a weakness for the prediction of the relative energies of different coordination numbers, particular for hypervalent compounds, they should be far more reliable in this case as we are comparing two structures which are closely related and have the same connectivities and enviroments for all atoms.

Results from the calculations on the energy minimised structures indicate that AlMePO-α is *ca.* $12.6\ \mathrm{kJ\ mol^{-1}}$ per formula unit $[Al_2(CH_3PO_3)_3]$ more stable than AlMePO-β, supporting the experimental observations. The calculated fractional coordinates of the two materials show excellent agreement with the experimentally determined values and the calculated cell parameters [AlMePO-α: a(calc.) = 14.188 Å, c(calc.) = 8.6532 Å; AlMePO-β: a(calc.) = 24.7701 Å, c(calc.) = 25.9097 Å] are all within *ca.* 2% of the published observed values.[2,3]

Discussion

These studies of the behaviour of as-prepared aluminium methylphosphonate-β when heated are best treated in two sections: firstly the removal of 1,4-dioxane molecules entrained during synthesis and secondly the topotactic transformation to AlMePO-α.

Magic angle spinning ^{13}C NMR shows the presence of 1,4-dioxane as a single sharp resonance, indicating that the molecules are mobile on the NMR timescale and do not occupy distinct sets of crystallographic sites. This is supported by the ^{31}P MAS NMR because the ^{31}P resonances, arising from different crystallographic environments, are broadened, rather than split. Combined thermogravimetry and mass spectrometry, however, reveal that dioxane molecules are evolved in two steps. We suggest that these steps correspond to the removal of dioxane molecules that exist in two kinds of environment at different distances from the framework, but that can exchange between these positions. Continued heating in the presence of water vapour in an inert gas results in the transformation to the α polymorph. The methyl groups are removed from the framework, largely as methane, at temperatures of 500 °C and above, depending on the partial pressure of water vapour.

The transformation between the polymorphs is observed by X-ray diffraction and optical microscopy reveals it to be topotactic. The thermodynamic driving force for the reaction is revealed by the higher thermal stability of α polymorph and confirmed by computational energy minimisations that indicated that the α form is more stable per $Al_2(PO_3CH_3)_3$ unit than the β form by 12.6 kJ mol^{-1} (2.52 kJ mol^{-1} per framework cation). The significance of this energy difference is best seen in comparison with the energies of aluminophosphate polymorphs. The difference in the lattice enthalpies between highest and lowest energy structures in the series AlPO-5, -11, -42, VPI-5 is 4.5 kJ mol^{-1} per tetrahedral atom (experimental)[13] and 7.6 kJ mol^{-1} (computed).[8] The value of 2.52 kJ mol^{-1} per framework cation calculated for the AlMePO polymorphs is around a half of the difference between VPI-5 and AlPO-8, computed value = 4.6 kJ mol^{-1} and experimental value = 4.3 kJ mol^{-1}, which also undergo a topotactic interconversion (from VPI-5 to AlPO-8).

To understand how such a topotactic transformation is possible the structures are compared in Fig. 5 and 6. The materials have the same composition, $Al_2(CH_3PO_3)_3$, and have channels, lined with methyl groups, of almost exactly the same dimensions. In both structures the phosphorus is exclusively tetrahedral and the coordination around the aluminium atoms is octahedral and tetrahedral in the ratio 1 : 3. The crystal structure of AlMePO-α is conventionally described in the trigonal space group *P*31*c*, with unit-cell parameters $a = 13.995$ Å and $c = 8.531$ Å. However, the structure can be described using the space group *R*3*c* with $a' = \sqrt{3}a = 24.240$ Å and $b' = 3b = 25.293$ Å. This is equivalent to the conventional description of AlMePO-β in space group *R*3*c* with unit cell $a = 24.650$ Å and $c = 25.299$ Å, allowing direct comparison of atomic positions in the two structures. The orientations of the unit cells are shown in Fig. 5. Ensuring that the origins of both structures are fixed with respect to the octahedrally coordinated aluminium atoms (in space group *R*3*c* the origin is not fixed by symmetry and can lie anywhere along the threefold axis), it can be seen that the major difference in the two structures lies in the position of one of the tetrahedrally coordinated aluminium atoms [labelled Al(4) in the atomic numbering scheme of Maeda *et al.*[4]]. Al(4) is shifted by *ca.* 2.4 Å in AlMePO-β relative to its position in AlMePO-α, while the other two tetrahedral aluminium atoms are shifted by only very small amounts ($\Delta < 0.4$ Å). The structures of both AlMePO-β and AlMePO-α can conveniently be described in terms of columns of cage-like building units having aluminium-centred (AlO_6) octahedra as vertices that are linked parallel to the channels along the ***c***-direction (these are seen in Fig. 5). The cages are made up of four 4-, one 6- and one 8-ring in β [Fig. 8(a)] and of three 4- and three 6-rings in the more symmetrical α [Fig. 8(b)]. The columns of cages are joined in the *xy* plane by 'channel walls' comprising 4-, 6- and 8-rings in β and 6-rings only in α [Fig. 7(a), (b)].

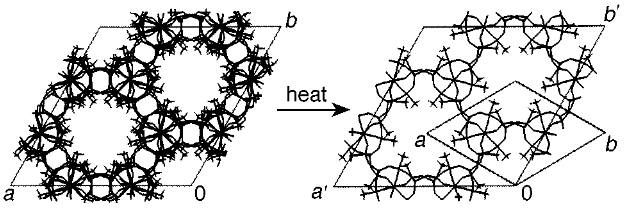


Fig. 5 Views of AlMePO-β (left) and AlMePO-α (right) down the crystallographic [001] axis. The relationship between the unit cells of AlMePO-β and the conventional (*abc*) and unconventional (*a'b'c'*) descriptions of AlMePO-α is shown. One can also see the columns of cage-like building units (parallel with the channels) and the difference in the way they are linked in the two polymorphs.

In order to understand what occurs during the transformation detailed consideration of the structure is necessary. Possibly the most informative section to examine is the cage-like building unit between two aluminium octahedra. This is represented by a ball and stick diagram in Fig. 8 where a large sphere has been chosen to show Al(4). If the aluminium coordinations are shown as polyhedra (Fig. 9) we can more readily appreciate the overall nature of the reaction and the greater symmetry of the product. To summarise the transformation—the first stage consists of the breaking of two of the Al—O bonds of Al(4) (the two furthest from the arrow on the diagram), leaving it free to move. This process leaves two phosphonate tetrahedra with an unattached oxygen vertex

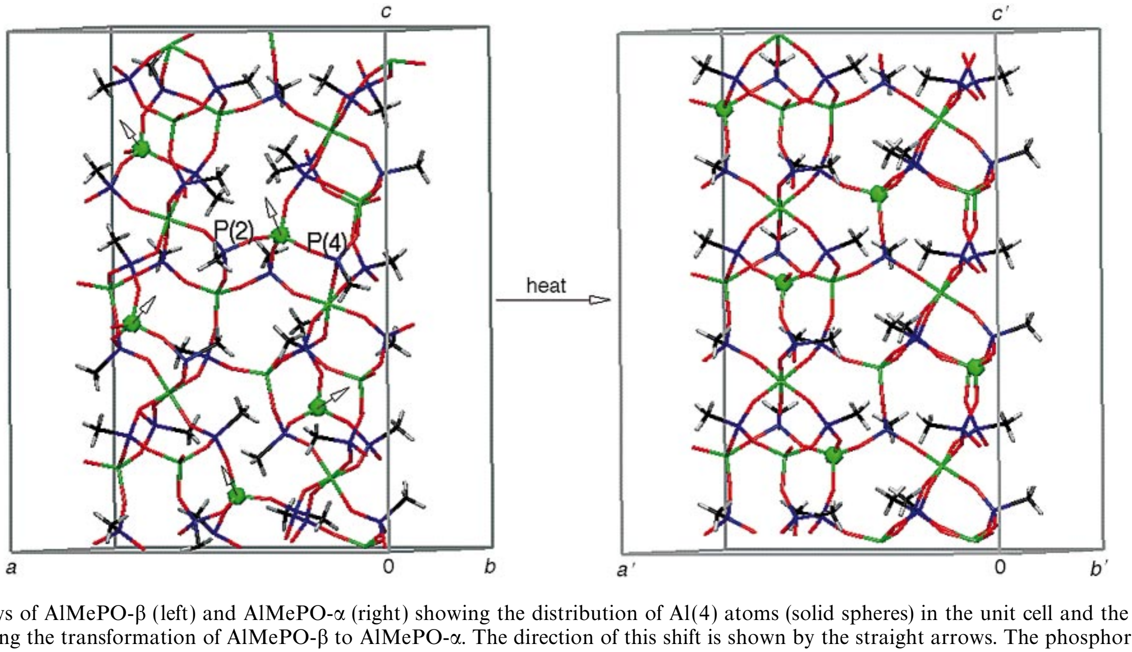
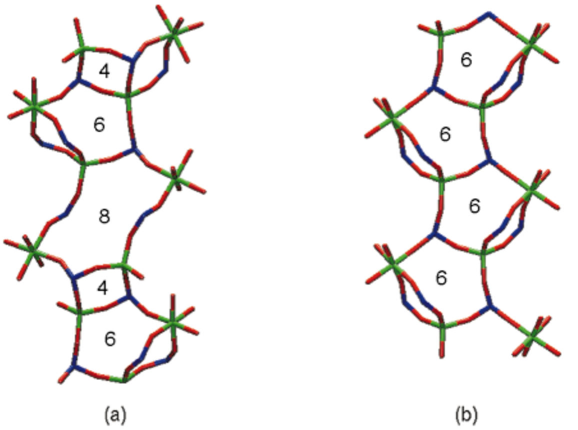
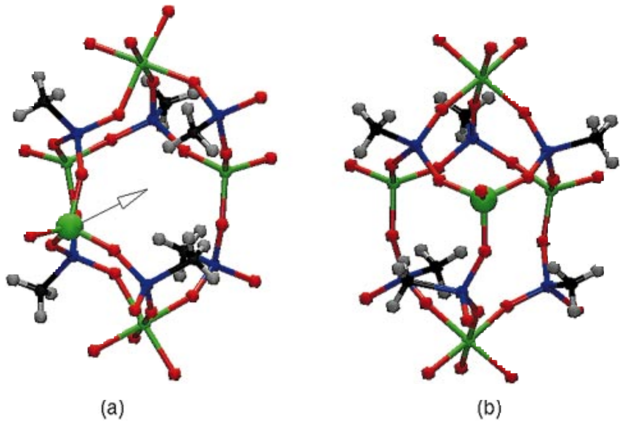


Fig. 6 Views of AlMePO-β (left) and AlMePO-α (right) showing the distribution of Al(4) atoms (solid spheres) in the unit cell and the shift that occurs during the transformation of AlMePO-β to AlMePO-α. The direction of this shift is shown by the straight arrows. The phosphorus atoms, P(2) and P(4), which show the largest reorientation during the transformation are also labelled.



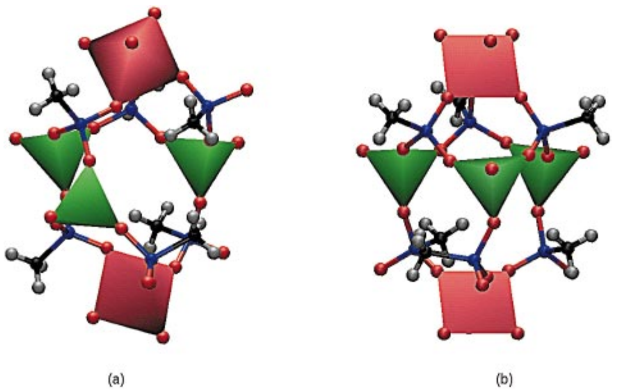
(a) (b)

Fig. 7 Diagram comparing the different rings connecting the columns of cage-like building units in the two polymorphs, (a) AlMePO-β linked by 4-, 6- and 8-rings, (b) AlMePO-α linked by 6-rings only. Green denotes Al, blue denotes P, red denotes O.



(a) (b)

Fig. 8 Diagram showing the cage-like building units and the movement of Al(4) (large sphere) during the transformation (a) AlMePO-β and (b) AlMePO-α. Note that only half of β's cage-like units are shown as there are also mirror image cages to consider. One should also note the inversion of the phosphonate group in the top right of the diagram. Green denotes Al, blue denotes P, red denotes O, black denotes C and grey denotes H.



(a) (b)

Fig. 9 Diagram showing the cage-like building units and the overall rearrangement of the two polymorphs showing the aluminium coordination as polyhedra, (a) AlMePO-β and (b) AlMePO-α. One can see the overall change in geometry of the cages and the greater symmetry of the product. The green polyhedra are tetrahedral AlO_4 units, the red are octahedral AlO_6 units, blue denotes P, red denotes O, black denotes C and grey denotes H.

each. The second stage is the movement of Al(4), which retains its two Al—O—P bonds and moves to form two new bonds to two oxygens of different phosphonate groups. The phosphonate tetrahedra thus bonded to that Al(4) must have broken their bonds with Al(4) atoms further on in the structure to have been able to rotate and form the new bonds. It is interesting to note that during this process the phosphonate group involved [top right of Fig. 8(a) and (b)] undergoes inversion (the $-CH_3$ orientation is greatly different).

Of course, the description above ignores the role of the water vapour in the reaction. As described the transformation would be very unlikely as there are many unstable species generated as transition states, *i.e.* $P-O^-$ and three-coordinate aluminium. A more likely scenario is that water coordinates to Al(4), hydrolyses the Al—O bond, protonating the $P-O^-$ and leaving a hydroxy attached to the metal (aluminium is known to be able to be five- and six-coordinate in aluminophosphates). Al(4) can migrate to its new position as a stabilised intermediate and form a new bond with a phosphonate by condensation. In this way, water would act in a catalytic role, permitting Al(4) and the relevant phosphonate groups to move into a more stable configuration, that of AlMePO-α, with a reduced activation energy. It might appear, therefore, that Al(4)—O bonds have a greater vulnerability to hydrolysis than those of the other tetrahedral Al. However, it is likely that it is Al(4) rather than the other Al atoms that migrates because for that ion there is a more stable configuration into which it can move whereas the other two tetrahedral aluminiums have no other favourable position into which to migrate even though bond hydrolysis might have freed them to do so. There is relatively little to distinguish the tetrahedral aluminium species on the basis of their bond valence sums [Al(2) = 3.19, Al(3) = 3.23, Al(4) = 3.21 as calculated by the procedure of Brown *et al.*[14]], but there is slightly higher degree of distortion around Al(4) [mean deviation from tetrahedral: Al(3) − 1.63°, Al(2) − 2.0° and Al(4) − 2.6°]. As a consequence, the 5Q MAS NMR results of Rocha *et al.*[15] show Al(2) and Al(3) at $\delta_{iso} = 42.8$ and 42.3, respectively, and Al(4) at $\delta_{iso} = 45.0$, indicating a small difference in the local environments of these atoms.

A further consideration in understanding this phase transformation is the way in which the reaction spreads through the crystal. For every Al(4) that migrates, two phosphonate tetrahedra are left with unattached vertices (possibly OH groups), and another two form bonds with the migrating aluminium. This forces them to break bonds and rotate leaving two more Al(4) atoms in low coordination, probably stabilised by the action of water. Thus, every time an aluminium migration takes place the possible progress of the transformation can take two directions, both of which can occur at the same time. Owing to this branching effect, one can imagine the reaction fanning out through the structure with ever increasing velocity if the transition states are sufficiently stabilised by the adsorption of water molecules. A possible result of this is that either the conditions are favourable and an entire crystal domain transforms very quickly or they are not and nothing happens. This observation is borne out by the narrow temperature gap between parts (c) and (d) of Fig. 4 (460 and 480 °C, respectively). Over this temperature range the transformation goes from a very low conversion to almost complete. Indeed, during all our investigations of this phenomenon we found very few samples that had transformed approximately half-way. In addition, the peak width of the product, AlMePO-α, is always narrow (even in the early stages of the transformation), indicating domains > 1000 Å, whereas some broadened X-ray diffraction peaks would result if domain size were growing slowly.

The reconstructive transformation of AlMePO-β to AlMePO-α is a rare type of structural change in a novel class of solids. It will be important to consider this transformation when using AlMePO-β in applications in adsorption and catalysis when reduction of adsorption capacity might result as a consequence of channel blocking due to defect formation. In principle though, under suitable conditions, it should be possible to transform the β form to the α form without loss of adsorption capacity. In that case changes in adsorption and, for appropriately substituted materials, catalysis, would result from differences in the accessible framework topology (see, for example, Fig. 7). This would not only enable differences in physical properties of the solids to be examined purely as a function of structure (and not particle size), but would also offer an alternative preparative route to the AlMePO-α polymorph which is the more difficult of the two materials to synthesise by direct hydrothermal methods.

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References

1 L.-J. Sawers, V. J. Carter, A. R. Armstrong, P. G. Bruce, P. A. Wright and B. E. Gore, *J. Chem. Soc., Dalton Trans.*, 1996, 3159.
2 K. Maeda, Y. Kiyozumi and F. Mizukami, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2335.
3 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1199.
4 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *J. Chem. Soc., Chem. Commun.*, 1995, 1033.
5 M. A. Subramanian, D. R. Corbin and U. Chowdry, *Bull. Mater. Sci.*, 1993, **16**, 665.
6 G. Sankar, P. A. Wright, S. Natarajan, J. M. Thomas, G. N. Greaves, A. J. Dent, B. R. Dobson and R. H. Jones, *J. Phys. Chem.*, 1993, **97**, 9550.
7 J. W. Richardson and E. T. C. Vogt, *Zeolites*, 1992, **12**, 13.
8 N. Henson, A. K. Cheetham and J. D. Gale, *Chem. Mater.*, 1996, **8**, 664.
9 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
10 J. D. Gale, General Utility Lattice Program (GULP) Version 2.0, Imperial College, London, 1996.
11 D. E. Williams, *Cryst. Rev.*, 1989, **2**, 3.
12 J. D. Gale, *Faraday Discuss.*, 1997, **106**, in press.
13 A. Navrotsky, I. Petrovic, Y. Hu, C.-Y. Chen and M. E. Davis, *Microporous Mater.*, 1995, **4**, 95.
14 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
15 J. Rocha, Z. Lin, C. Fernandez and J.-P. Amoureux, *Chem. Commun.*, 1996, 2513.

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