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The synthesis and modification of aluminium phosphonates†

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Two synthetic approaches to the preparation of mixed aluminium phosphite–phosphonate solids have been made. First, the hydrothermal reaction of aluminium hydroxide (gibbsite) with mixtures of phosphorous and methylphosphonic acids under conditions that give microporous aluminium methylphosphonate-β (AlMePO-β) when methylphosphonic acid alone is used, and secondly, the reaction of AlMePO-β with increasing amounts of molten phosphorous acid. Under hydrothermal conditions there is no evidence that AlMePO-β can be prepared with phosphite groups randomly replacing methylphosphonate groups. Rather, the products are dominated over the intermediate phosphite/phosphonate compositional range by a novel phase that is thought, on the basis of ^{27}Al and ^{31}P MAS NMR and FTIR spectroscopies, to contain differing amounts of phosphite and methylphosphonate groups. Reaction of AlMePO-β with levels of molten phosphorous acid at 40% or more of the methylphosphonate content gives mixtures of AlMePO-β and a new phosphite phase, whereas reaction using lower amounts of the molten acid leaves AlMePO-β as the only X-ray visible phase. Extension of the melt method to the separate reaction of gibbsite with methylphosphonic and phosphorous acids yields, respectively, single crystals of a new aluminium methylphosphonate [$Al(O_3PCH_3)(HO_3PCH_3)\cdot H_2O$] and a known aluminium phosphite [$Al_2(O_3PH)_3\cdot 4H_2O$], the structure of which had only been solved from powder diffraction data. Single crystal diffractometry improved the accuracy with which the structural parameters of the phosphite are known and enabled structure solution of the new aluminium methylphosphonate [*Pnma*, $a=19.075(6)$ Å, $b=5.117(2)$ Å, $c=8.439(2)$ Å], which is made up of layers that contain isolated, octahedrally coordinated aluminium linked by methylphosphonate groups.

Introduction

The need for materials with specific properties has sustained a marked growth in synthetic studies of new solids in recent years. One family that has received considerable interest is the molecular sieves, where a great deal of current research is concerned with zeolites and aluminophosphates.[1] A number of important industrial processes are now dependent upon materials of this type, especially as catalysts where their microporous structure gives both a high surface area and the possibility of shape selectivity.

One of the most important features in the choice of a microporous catalyst is the nature of the internal surface presented to reactant and product molecules on their journey to, and from, the catalytic site. For zeolites and aluminophosphates this is mainly the van der Waals surface of oxygen ions, with, in some cases, charge balancing cations in low and asymmetrical co-ordination. In all but the highest silica zeolites this results in a hydrophilic environment, likely to hinder the migration of water and other polar molecules at temperatures associated with important reactions such as esterifications, hydrations, epoxidations and partial oxidations. Our major research goal is the preparation of new microporous catalysts with both inorganic and organic regions, which will permit us to tune the hydrophobicity/hydrophilicity of the catalysts. This will allow us to obtain the optimum environment for the migration of the reactant, product and solvent molecules through the pores of the material.

Metal organophosphonates (*i.e.* materials containing RPO_3 units where R is an organic group) show a wide range of structural architectures including chain, layered and microporous structures. A number of systems have been researched quite heavily, especially those of Zr, V and Zn, primarily with respect to their interesting intercalation,[2,3] ionic conduction[4] and charge storage properties.[5] These materials are layered in nature, with the organic functionality of the phosphonate anion pendant between the layers. In order to form microporous solids, diphosphonic acids may be used in the synthesis in order to create a covalently bonded 'bridge' between the inorganic layers.[6,7]

Divalent metal phosphonates have been reported in the literature with increasing frequency.[8–15] In general, they are again layered, but unlike the tetravalent phosphonates, there are examples in the literature of microporous materials, *e.g.* $Zn(O_3PCH_2NH_2)$[13] and β-$Cu(O_3PCH_3)$.[16] The organic functional groups line the inside of the microporous, inorganic part of the material, providing a surface with greatly different hydrophobicity than would a wholly inorganic analogue. Examples of tubular, microporous uranyl phenylphosphonates have also been reported in the literature.[17–19] In the case of these materials, however, the channel is hydrophilic and contains water molecules. The organic groups are arranged on the periphery of the channels, and it is their stacking forces which keep the channels intact in the lattice.[18]

Surprisingly, considering the possible chemical similarities between this type of material and the aluminium phosphates, studies of the organophosphonate chemistry of aluminium have only recently been initiated. A breakthrough in this area was made by Maeda and co-workers who synthesised two crystalline microporous aluminium methylphosphonate materials, AlMePO-β[20–23] and AlMePO-α,[24] with pore sizes in the same range as medium-pore zeolites such as ZSM-5. These solids have a number of interesting properties, including some unusual thermal behaviour,[20] and they are currently attracting interest for applications in catalysis and adsorption processes.

In this paper we report the results of our efforts to modify the structure and composition of the microporous aluminium methylphosphonates, in order to introduce some functionality into the materials. It is possible to speculate that this can be done in three ways, (i) by altering the organic functionality of the phosphonate group, either by preparing mixed phosphonate materials or by postsynthetic modification of the material,

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(ii) by substituting organophosphonate groups by phosphate groups, and (iii) by doping heteroatoms into the inorganic framework (*e.g.*, Mg^{2+}, Ti^{4+}, *etc.*). The postsynthetic modification of zirconium phosphonates based on α- and γ-zirconium phosphate has been demonstrated previously[22,23] and materials that have been topotactically exchanged with RSO_3H units are already under investigation as solid acid catalysts.[25–27] By varying the functionality of the solid we hope to prepare a new class of solid acid catalyst. We report here our attempts to prepare mixed phosphite–phosphonate materials according to method (i).

Apart from the two microporous[20–24] and one layered aluminium methylphosphonates,[28] the only functional groups which have been included in aluminium phosphonates have been hydrogen (phosphite),[29] and phenyl groups.[30] Whilst single crystal X-ray diffraction experiments have been performed on the three methylphosphonates, only powder diffraction has been carried out on the phosphite, the structure of which was solved from these data;[29] powder diffraction experiments on the phenylphosphonate have not resulted in solution of the structure.[30]

All the syntheses of methylphosphonates and phosphites reported to date have been hydrothermal in nature, and have been carried out in both the absence and the presence of organic molecules, which appear to have some structure-directing influence. The only reported aluminium phenylphosphonate was prepared by refluxing bayerite (a layered aluminium hydroxide) in a solution of phenylphosphonic acid.[30]

In the recent literature it was reported that nickel phosphonates[31] could be readily prepared by melting a phosphonic acid in the presence of nickel hydroxide. It was noted in this paper that the method had been used successfully in the synthesis of phosphonates of a number of divalent and trivalent metals. It has also been shown that the phosphate groups in α-zirconium phosphate can be exchanged for phenylphosphonate groups[26] and that phosphonate groups in nickel methylphosphonate can be replaced by phenylphosphonate groups[32] by contact with molten phenylphosphonic acid. In this work we report the application of this synthetic method to the synthesis of aluminium phosphonates. We also report the attempted synthesis of mixed phosphite–phosphonates, using this same method and also by hydrothermal syntheses. As well as producing phases thought to consist of both methylphosphonate and phosphite groups, during the course of these studies we have synthesised a new aluminium methylphosphonate phase and produced a new route to a previously known aluminium phosphite hydrate. Both these materials have been characterised by single crystal X-ray diffraction, the methylphosphonate using conventional laboratory four-circle diffractometry and the phosphite by synchrotron X-ray diffraction on a very small crystal.

Experimental

Synthesis of aluminium phosphite–phosphonates

Hydrothermal syntheses. The synthesis of a series of hydrogen-substituted AlMePO-β molecular sieves was attempted using a method adapted from Maeda *et al.*[21] from gels with compositions of $Al(OH)_3:CH_3PO(OH)_2:H_3PO_3:H_2O:$1,4-dioxane in the ratio $1:1.5-x:x:40:0.5$ (where $0 \leqslant x \leqslant 1.5$). Gels were stirred until homogeneous and heated in Teflon-lined stainless steel autoclaves of 24 ml volume at 160 °C for 120 hours. Immediately before heating the gels had a pH of 2–3.5 depending upon the ratio of phosphonic to methylphosphonic acid. Products were washed with distilled water and dried in air at 60 °C.

Exchange of methylphosphonate groups for phosphite groups. The attempted exchange of methylphosphonate groups for phosphite groups was carried out by mixing a pre-formed sample of AlMePO-β with increasing quantities of phosphorous acid, such that the molar ratio of methylphosphonate: phosphorous acid was increased in steps of 0.1 from 1:0.1 to 1:1. Products are labelled by the percentage of H_3PO_3 used in the synthesis with respect to the quantity of methylphosphonate groups in the AlMePO-β substrate, *i.e.* the label 100% means that the quantity of H_3PO_3 used in the synthesis was sufficient to completely replace the methylphosphonate groups. These mixtures were then placed in an oven at 110 °C for 48 hours. After this time the products were suspended in distilled water, recovered by filtration, thoroughly washed with distilled water in order to remove any methylphosphonic acid and unreacted phosphorous acid, then dried in air at 50 °C.

Two parallel series of experiments were carried out: one using AlMePO-β which contained 1,4-dioxane, and a second in which the 1,4-dioxane had been removed from AlMePO-β by heating to 370 °C for 10 hours in a stream of nitrogen.

Synthesis, by melt route, of aluminium phosphonates and phosphite

The aluminium methylphosphonate, $Al(HO_3PCH_3)(O_3PCH_3)\cdot H_2O$, was prepared in the following manner: methylphosphonic acid and aluminium hydroxide, such that $Al:P=2:3$, were ground together in a mortar and pestle. The mixture was placed in a thick glass tube that was sealed with a Teflon screw cap. The tube was then placed in an oven at 110 °C, which is slightly in excess of the melting temperature of methylphosphonic acid (102 °C), and left for 48 hours. After this time the products were suspended in distilled water, recovered by filtration, washed thoroughly with distilled water in order to remove any unreacted methylphosphonic acid and dried in air at 50 °C. Inspection of the recovered sample revealed the presence of small crystals amongst a polycrystalline phase. Some of these crystals were removed from the sample and used in a single crystal determination of the structure (*vide infra*).

Aluminium phosphite was prepared in an identical manner using a mixture of phosphorous acid (melting point 78 °C) and gibbsite, such that the Al:P ratio was 2:3. The product was recovered as described for the methylphosphonate above. The product, viewed under a microscope, was seen to be made up from irregularly shaped microcrystals. These typically had dimensions $\leqslant 30$ μm, too small to allow a structural determination to be carried out using a conventional laboratory diffractometer. The structure of this material was determined, however, by single microcrystal diffraction at the synchrotron facility at Daresbury (*vide infra*).

AlMePO-β was prepared following the method of Maeda *et al.*[21] Aluminium hydroxide (1.81 g, 23 mmol), methylphosphonic acid (3.35 g, 34 mmol), water (14.2 ml) and 1,4-dioxane (0.8 ml) were stirred for 1–2 hours in order to form a homogeneous gel. The gel was transferred to an autoclave in which it was heated under autogenous pressure at 160 °C for a period of 48 hours. Products were recovered by filtration and thoroughly washed with distilled water prior to drying in air at 50 °C.

Scanning electron microscopy and energy dispersive X-ray analysis

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were performed on a JEOL JSM-35CF microscope fitted with a Link AN10000 EDX system using an accelerating voltage of 10 kV. Aluminium:phosphorus ratios were referenced with respect to AlMePO-β[21] (ratio 1:1.5) and give an Al:P ratio of 3.0(3):1 for the 33% H_3PO_3 sample.

Powder X-ray diffraction

Powder X-ray diffraction patterns were recorded on a STOE diffractometer with a position-sensitive linear detector covering 6° in 2θ and employing Ge-monochromated Cu-Kα_1 radiation ($\lambda = 1.54056$ Å). Samples were mounted in a glass capillary (in order to reduce any preferred orientation effects, where such are observed), or by mounting as rotating discs between two sheets of Mylar.

Single crystal X-ray diffraction

$Al(HO_3PCH_3)(O_3PCH_3)\cdot H_2O$. Single crystal X-ray diffraction data on a colourless block shaped crystal (dimensions $0.1 \times 0.1 \times 0.2$ mm) were collected on a Rigaku AFC7S four circle diffractometer using Mo-Kα radiation. The material crystallises in space group *Pnma* (no. 62) with unit cell dimensions $a = 19.075(6)$ Å, $b = 5.117(2)$ Å, $c = 8.439(2)$ Å, $V = 823.6(4)$ Å^3. The crystal structure was solved using the direct methods program SIR-92 and refined with a full matrix least-squares technique using the program SHELXL-97.[33] The final cycle of least-squares refinement included anisotropic displacement parameters for aluminium, phosphorus, oxygen and carbon atoms. The hydrogen atoms were placed in chemically sensible positions and their positions recalculated after each cycle of refinement. In all 808 integrated intensities were measured ($2.64° < \theta < 25.00°$), of which 615 were observed according to the criterion that $F^2 > 2\sigma(F^2)$. Final refinement of the 67 least-squares parameters converged to $wR(F^2_{\text{observed data}}) = 0.0995$, $wR(F^2_{\text{all data}}) = 0.11182$, $R(F_{\text{observed data}}) = 0.0384$, $S(F^2_{\text{all data}}) = 1.102$, max. residual electron density = 0.707 e Å^{-3}. Refinement on F^2 was carried out against all data. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/109.

Aluminium phosphite tetrahydrate. The crystals were too small (max. size $30 \times 30 \times 15$ μm) for single crystal X-ray data collection using a standard laboratory four circle diffractometer, so diffraction data were collected at low temperature (160 K) using a Bruker AXS SMART CCD area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, Cheshire, UK. The experiment used X-rays of wavelength 0.6849 Å selected by a horizontally focusing silicon (111) monochromator and vertically focused by a cylindrically bent palladium-coated zerodur mirror.[34] The data set covered more than a hemisphere of reciprocal space with several series of exposures, each series with a different crystal orientation and each exposure taken over 0.2° rotation. Corrections were made for the synchrotron beam intensity decay as part of standard inter-frame scaling procedures.[33]

The crystal structure of aluminium phosphite tetrahydrate was solved using the direct methods program SHELXS-97[33] and refined with a full matrix least-squares technique using the program SHELXL-97.[33] The final cycle of least-squares refinement included anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were placed in chemically sensible positions and their positions recalculated after each cycle of refinement against F^2. 1739 unique reflections ($2.73° < \theta < 28.13°$), of which 1652 were observed according to the criterion that $F^2 > 2\sigma(F^2)$. Final refinement of the 163 least-squares parameters converged to $wR(F^2_{\text{observed data}}) = 0.1413$, $wR(F^2_{\text{all data}}) = 0.1492$, $R(F_{\text{observed data}}) = 0.0556$, $S(F^2_{\text{all data}}) = 1.031$, max. residual electron density = 1.032 e Å^{-3}. Space group = $P2_1$, $a = 7.5784(3)$ Å, $b = 9.8909(3)$ Å, $c = 8.0313(3)$ Å, $\beta = 111.7380(10)°$, $V = 559.19(3)$ Å^3. CCDC 1145/109.

FTIR Spectroscopy

IR spectra were recorded on a Perkin Elmer 1710 FTIR spectrometer. Samples were mounted as KBr pellets, which contained approximately 1% sample material, and the spectral resolution was 2 cm^{-1}.

Thermogravimetric analysis (TGA)

TGA experiments were carried out on a TA Instruments SDT 2960 Simultaneous DTA–TGA thermogravimetric analyser. Samples were heated in an alumina crucible, at a rate of 10 °C min^{-1}, to a maximum temperature of 1200 °C, in an atmosphere of flowing oxygen (100 ml min^{-1}). Recalcined alumina was used as the reference material.

Solid state NMR spectroscopy

^{27}Al and ^{31}P MAS NMR experiments were performed using a Bruker 400 MHz spectrometer. Chemical shifts are reported with respect to 85% H_3PO_4 and 1 mol dm^{-3} aqueous $AlCl_3$ respectively.

Results and discussion

Hydrothermal synthesis of aluminium phosphite–phosphonates

As the amount of H_3PO_3 in the synthesis gel is increased the crystallised material changes in composition. At 5% H_3PO_3, a low intensity XRD peak (6.8°) (Fig. 1) corresponding to a small amount (*ca.* 5–10%) of a material other than AlMePO-β is produced. This peak is not evident at substitutions of 15% and above. One might expect isomorphous substitution of the methylphosphonate groups in the structure by phosphite groups to occur most easily for the smallest amount of substituting material, hence the 5% H_3PO_3 synthesis should have had the highest probability of producing mixed CH_3P–HP AlMePO-β. However, even at such a small proportion of phosphonic acid, a single-phase aluminium phosphite–

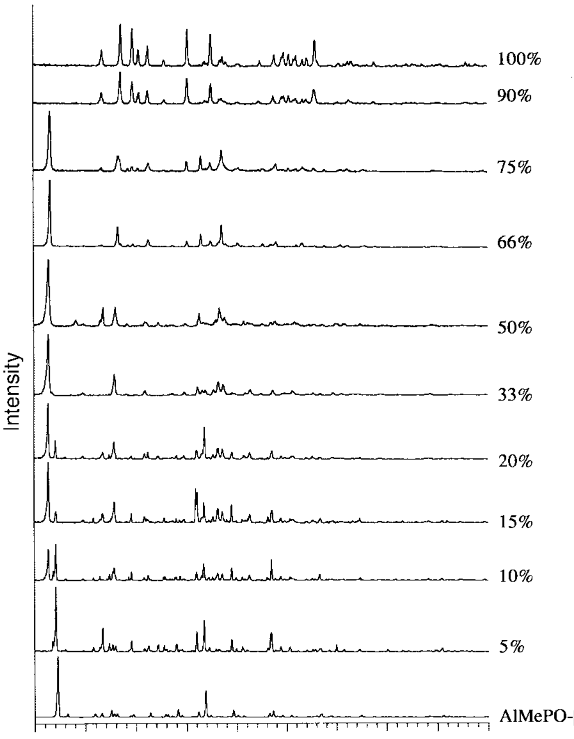

Fig. 1 Comparison of the X-ray diffractograms for syntheses using gels with a range of H_3PO_3 contents after 5 days at 160 °C.

phosphonate is not formed. The IR spectrum for the 5% H_3PO_3 sample shows the presence of P–H bonds (Table 1), but since the addition of the H_3PO_3 resulted in the formation of the impurity phase, it seems probable that this is where the P–H bonds are located.

At 10% substitution of phosphorous acid and greater, significant amounts of a second phase, other than AlMePO-β, are apparent in the XRD as a peak at 6.4° 2θ. The relative intensity of the new peak grows at the expense of the characteristic, low 2θ peak (7.1°) of AlMePO-β. This leads to the conclusion that the formation of AlMePO-β in which some of the methyl groups are randomly replaced by hydrogen atoms is unfavourable using this synthetic approach.

At 33–75% H_3PO_3 in the gel, the diffractograms show no AlMePO-β and the only major phase produced appears to be a new material. The XRDs for these samples are essentially the same, but do show small changes as the proportion of H_3PO_3 is increased, leading us to believe that the materials contain small quantities of unknown impurity phases. Optical and scanning electron microscopy support this, showing the samples to be predominately comprised of polycrystalline spheres (40–80 μm in diameter) with the only impurity phase being observed as a small number of needle-like crystals. The material is particularly interesting as its lowest 2θ peak corresponds to a *d*-spacing 1.6 Å greater than that for AlMePO-β(13.7 Å compared with 12.1 Å for AlMePO-β). At the present time we have been unsuccessful in attempts to index the XRD pattern.

Selected area analysis (EDX) (using AlMePO-β as a standard) indicates an Al : P ratio of approximately 3 : 1. The ^{27}Al MAS NMR spectrum (Fig. 2) shows that the aluminium in the material is divided approximately equally between tetrahedral and octahedral environments with little variation in this ratio throughout the range 33–75% H_3PO_3. The chemical shifts of the both the aluminium species are very close to those present in AlMePO-β, but become less negative with increasing H_3PO_3 levels.

The ^{31}P MAS NMR spectra (Fig. 3) of samples in the range 33–75% show three environments with a fourth observed in the spectrum in the 33% sample. It is possible that the extra peak corresponds to some residual methylphosphonic acid trapped within the matrix (this sample contained the greatest PCH_3 : PH ratio of all the preparations resulting in the new phase). There is a marked increase in the intensity of the peaks at *ca.* -10 and *ca.* -20 ppm as the amount of H_3PO_3 is increased. ^{13}C MAS NMR shows that the samples (33%, 66% and 75% H_3PO_3) contain no 1,4-dioxane; each spectrum contains a single broad resonance in the range 13.5–14.8 ppm, *i.e.* in the methyl region. Considering this, along with the FTIR data (Table 1) which indicate that the material contains substantial amounts of P–H bonds (increasing with the fraction of H_3PO_3 in the synthesis gel), one comes to the conclusion that we have been successful in making a new mixed phosphite–phosphonate phase.

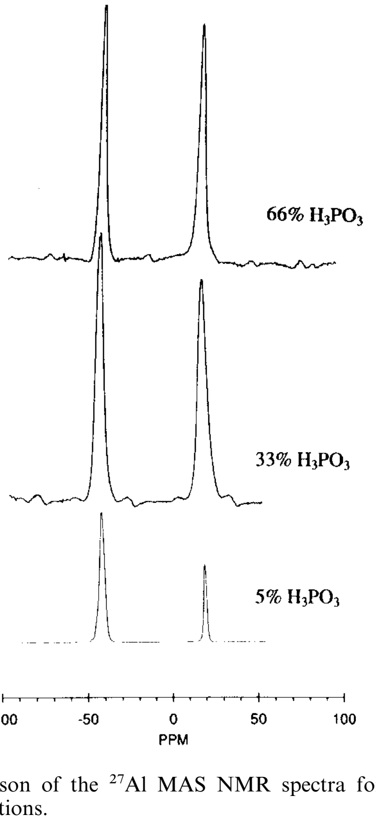

Fig. 2 Comparison of the ^{27}Al MAS NMR spectra for a range of H_3PO_3 substitutions.

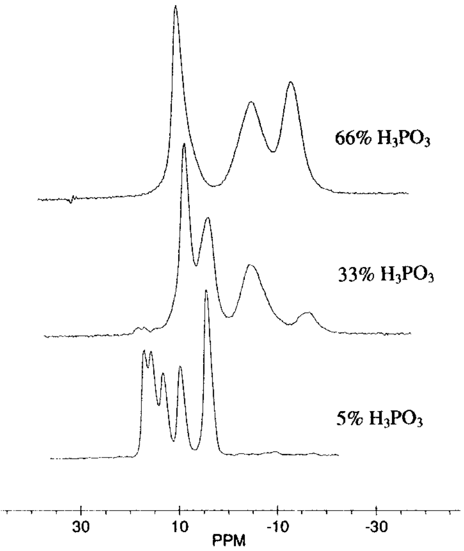

Fig. 3 Comparison of the ^{31}P MAS NMR spectra for a range of H_3PO_3 substitutions.

At greater than 75% H_3PO_3, the pure aluminium phosphite structure, $Al_2(O_3PH)_3 \cdot 4H_2O$,[29] is produced. It is very unlikely that the phosphite material could contain any methylphosphonate groups, as the structure would have to distort a great deal to accommodate the methyl groups.

Synthesis of aluminium phosphite–phosphonate materials by modification of existing phosphonate phases

Characterisation of the materials produced using AlMePO-β that contained the 1,4-dioxane template, and AlMePO-β from which it had been removed, showed that the samples were very similar. The following discussion will cover both series of products, with particular reference being made to any significant differences.

Melting H_3PO_3 in the presence of AlMePO-β results in the formation of a phase containing phosphite groups, evident from the band seen at 2466 cm^{-1} in the IR spectra. The intensity of this band increases with the quantity of H_3PO_3 used in the synthesis, indicating the presence of increasing

Table 1 Frequencies of P–H stretching frequencies for various degrees of phosphonic acid substitution

Amount of H_3PO_3 substitution (%)	Frequency of band/cm^{-1}			Ratio of peaks
5	2463	2446	2407	2 : 1 : 3
33	2489	2442	2410	2 : 1 : 2
50	2494	2448	2415	1 : 1 : 2
66	2497	2454	2417	1 : 1 : 2
100	2478	2454	2416	1 : 4 : 4

quantities of the phosphite phase. As the intensity of this band increases there is a concomitant decrease in the intensity of bands associated with the methyl group at 2985, 2966, 2933 and 2860 cm^{-1}. The bands at 2966 and 2933 cm^{-1} are not observed in the samples where 1,4-dioxane was removed, and must therefore arise from C–H stretching in this molecule. Additionally, the band arising from the P–C stretch at 1323 cm^{-1} is seen to decrease in intensity as the phosphite content increases. The bands associated with methylphosphonate groups do not, however, disappear entirely, even when the quantity of H_3PO_3 used in the synthesis is sufficient to completely replace all of the methylphosphonate groups. This may indicate that there is an equilibrium between the formation of aluminium phosphite and aluminium methylphosphonate.

There are also distinct changes in the spectral region associated with P–O vibrational modes. Peaks at 1165 and 1187 cm^{-1} decrease as the phosphite content increases, whilst peaks at 1114 and 1027 cm^{-1} become increasingly evident. The latter two peaks arise from a P–H deformation mode and a ν_{symm} H–P–O_3 stretching mode respectively. The P–O stretching mode at 1215 cm^{-1} remains visible in all sample spectra.

The XRD profiles of the materials formed show a steady decrease in the intensity of reflections arising from AlMePO-β. Beginning at the 40% sample (50% where 1,4-dioxane was removed from AlMePO-β), reflections are observed that arise from the phosphite phase, which increase in intensity as the quantity of H_3PO_3 used in the synthesis increases (Fig. 4). The profile of the 100% sample shows that it contains no AlMePO-β whatsoever. There are no other apparent impurity lines evident in the diffraction profiles. This implies that below 40% (or 50%) the material may be a single phase that contains both phosphite and methylphosphonate groups, or that the phosphite phase is X-ray amorphous. Above this level the materials are simple mechanical mixtures of AlMePO-β and an aluminium phosphite. The X-ray profile of the phosphite phase does not correspond to any known aluminium phosphite phase, and work is currently in hand to solve the structure.

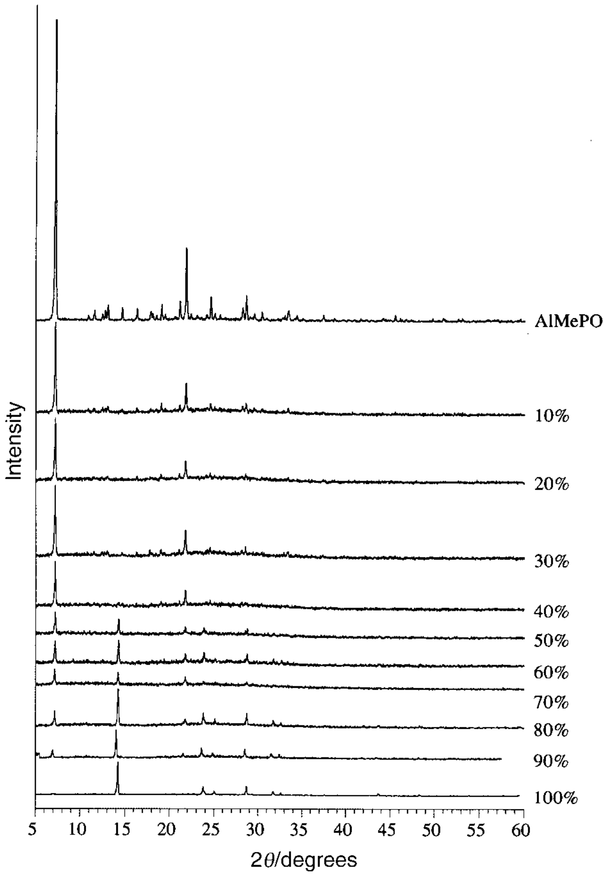

Fig. 4 Comparison of powder X-ray profiles for materials made by reaction with AlMePO-β (without 1,4-dioxane) and molten H_3PO_3.

Thermogravimetric analysis curves of the two series of materials synthesised differ slightly from one another. Both sets of curves have features in common: a water loss at temperatures in the region of 90–110 °C, the exothermic removal of the methyl group at around 580 °C, a slight weight gain as the phosphite groups are oxidised to phosphate in the region of 800–900 °C, and finally the dehydration of the phosphate (presumably to form pyrophosphate) at 950–1000 °C. The most noticeable differences between curves for analogous samples from the two series are the mass losses at 220 °C and 400 °C that appear in the curves recorded for the sample made from AlMePO-β that still contained 1,4-dioxane. This is consistent with observations reported regarding the removal of 1,4-dioxane template molecules from pure AlMePO-β.[20]

Synthesis of new materials

Aluminium methylphosphonate: $Al(O_3PCH_3)(HOPCH_3)\cdot H_2O$. The sample recovered from the melt procedure involving methylphosphonic acid was a white polycrystalline material, which contained small colourless crystals. Comparison of a powder profile generated from the single crystal data with the powder X-ray diffraction of the sample as a whole shows that there are in fact two phases present. The nature of the polycrystalline phase has not been determined at this point.

The structure refinement yielded a stoichiometry of $Al(O_3PCH_3)(HOPCH_3)\cdot H_2O$. To the best of the authors' knowledge this is the first aluminium phosphonate reported to have an Al:P ratio of 1:2; in AlMePO-α,[24] AlMePO-β[21] and $Al_2(O_3PPh)_3\cdot 4H_2O$[30] this ratio is 2:3, and in $[Al(OH)PO_3Me\cdot H_2O]_4$[28] it is 1:1.

The phosphorus atoms in the phosphonate anions of $Al(HO_3PCH_3)(O_3PCH_3)\cdot H_2O$ show the usual tetrahedral coordination geometry of three oxygens and a methyl group (Fig. 5). There are, however, two different types of phosphonate groups: one in which all three of the oxygens are coordinated to aluminium atoms (P1), and another in which only two of the oxygens are coordinated to aluminium atoms (P2). The third oxygen is part of a P–O–H group, which is directed into the interlayer region. The methyl groups of the P1 phosphonate groups are directed into the interlayer region with the P–C bond perpendicular to the layers, whilst those of the P2 anions are directed such that the P–C bond lies parallel with the layer.

The aluminium atoms are coordinated by an octahedral arrangement of oxygen atoms. Five of these come from phosphonate groups (three from P1, and two from P2). A water molecule supplies the sixth oxygen, which is coordinated to the metal centre.

Layers are made up from chains of AlO_6 octahedra, in which aluminium atoms are bridged by two oxygens from each type of phosphonate anion. The third oxygen of the P1 phosphonate group crosslinks these chains to form the layers; the third oxygen of the P2 phosphonate anion is the –OH group, which projects into the interlayer region. The layers are held together by hydrogen bonds between the P–O–H groups in the interlayer region. This hydrogen bonding forms a chain, which lies parallel to the [010] axis (Fig. 6). The outcome of this is the formation of an elliptical channel, lined with methyl groups, which runs parallel to the [010] axis (Fig. 5). The shortest distance (H–H) across these channels is 2.81 Å.

Aluminium phosphite. Examination, under a microscope, of the sample recovered from the experiment in which phosphorous acid had been melted in the presence of gibbsite revealed

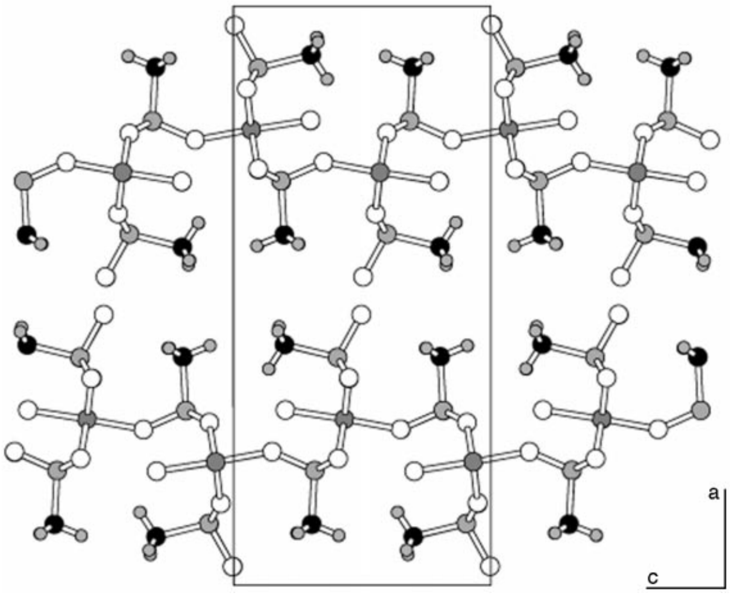

Fig. 5 Structure of $Al(O_3PCH_3)(HO_3PCH_3)\cdot H_2O$, viewed along the [010] axis; P atoms are shown as large light grey circles, H as small light grey circles, C as black circles, Al as dark grey circles and O as white circles.

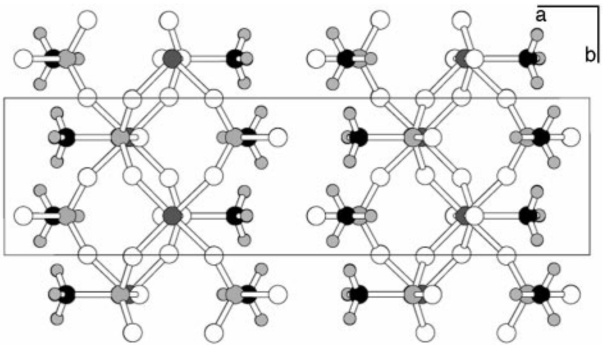

Fig. 6 Structure of $Al(O_3PCH_3)(HO_3PCH_3)\cdot H_2O$, viewed along the [001] axis, highlighting the chain of hydrogen bonding P–O–H groups; P atoms are shown as large light grey circles, H as small light grey circles, C as black circles, Al as dark grey circles and O as white circles.

that the sample contained small crystals, *ca.* 20 μm maximum dimension. Single, microcrystal diffraction carried out at the synchrotron source at Daresbury showed that the crystals had the same structure as a previously reported aluminium phosphite, $Al_2(HPO_3)_3\cdot 4H_2O$[29] (and a gallium analogue[35]). The two earlier studies solved the structure *ab initio* from powder diffraction data; this is the first single-crystal diffraction study of this material.

The structure (Fig. 7) is made up of sub-units, which consist of two AlO_6 octahedra, linked by three phosphite groups *via* shared oxygens. These units are then connected, by sharing of oxygens with other units and hydrogen bonding, to form a three-dimensional structure. The manner in which the three-dimensional structure is made up produces two types of elliptical channels, which are parallel to the [010] direction. One of these channels contains the water molecules; the other is lined with hydride groups. The narrowest part of the hydride-lined channels is 2.75 Å (the shortest H–H distance), a distance which would make intercalation of a substrate species impossible.

Conclusions

The attempt to isomorphously replace methylphosphonate moieties with phosphite in AlMePO-β by hydrothermal methods was not successful. At low $HP(O)(OH)_2$: $CH_3P(O)(OH)_2$ ratios the phosphite seemed to form a separate, additional phase to the AlMePO-β and at higher ratios a completely new material is produced. Although we have not as yet been able to solve the structure of the new material, it nevertheless possesses several interesting features. The fact that the *d*-spacing of the lowest 2θ peak is considerably larger than that for AlMePO-β together with evidence indicating that the material contains water raises the possibility of the new phase being microporous. Attempts to characterise the phase further will continue.

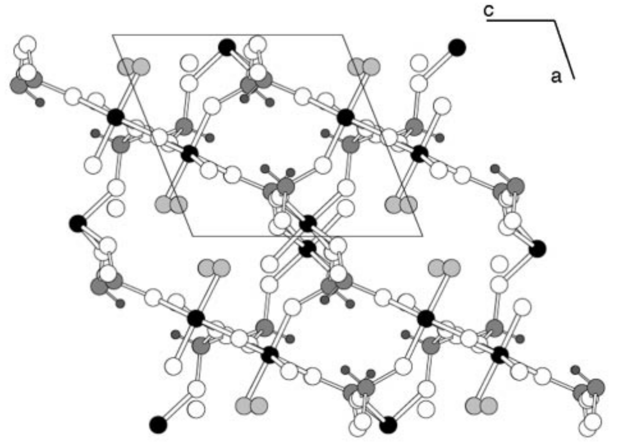

Fig. 7 Structure of $Al_2(O_3PH)_3\cdot 4H_2O$ viewed along the [010] axis; H atoms are shown as small shaded circles, P as large dark grey circles, O atoms as white circles, O(water) as large light grey circles and Al as black circles.

The attempted modification of AlMePO-β to include phosphite groups by contacting it with molten phosphorous acid, $>40\%$ with respect to the quantity of methylphosphonate groups on the AlMePO-β substrate, results in the formation of a mechanical mixture of AlMePO-β and an aluminium phosphite phase. The XRD profile of the phosphite phase does not correspond to any previously published in the literature. The structure of this phase is in the process of being solved. Samples prepared with less phosphorous acid contain phosphite groups, but it is unclear whether this indicates the replacement of methylphosphonate by phosphite in AlMePO-β, or the formation of an amorphous phosphite phase. It is thought that the aluminium substrate is, at least partially, soluble in the molten acid. Whether crystallisation occurs at higher temperatures or as the mixture is cooled is unknown, but there is clearly a preference for the formation of the phosphite over formation of a methylphosphonate (be it AlMePO-β, or otherwise).

Synthesis of aluminium phosphonates and phosphites has been shown to be viable using the method of melting a phosphonic acid in the presence of a suitable substrate material, demonstrated by the preparation of $Al(HO_3PCH_3)(O_3PCH_3){\cdot}H_2O$ and $Al_2(O_3PH)_3{\cdot}4H_2O$. It is thought that $Al(OH)_3$ dissolves in the molten acid and the aluminium phosphonate crystallises out of the 'solution'. As an additional bonus, single crystals can readily be produced allowing relatively simple structure determinations to be carried out. The indications are that this method might successfully be applied to the synthesis of aluminium phosphonates that contain other functional groups, and this is currently being explored in the laboratory.

With different phosphites being formed when gibbsite and AlMePO-β are reacted with molten phosphorous acid, it is clear then that the choice of aluminium-containing substrate in melt syntheses has some effect upon the reaction product. The success in the synthesis of novel materials shows some promise and remains an area for more in-depth investigation.

Correct choice of the phosphonic acid used means that the acidic functional groups, required for catalytic applications, might easily be included in an aluminium phosphonate. Further, we are not restricted to using a single phosphonic acid in the synthesis of these materials, and the preparation of mixed phosphite–phosphonates, and mixed phosphonates using mixtures of phosphonic acids with aluminium substrates is an area which remains to be explored in detail.

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