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Topotactic synthesis of α-zirconium phenylphosphonate from α-zirconium phosphate

Gary B. Hix, Simon J. Kitchin and Kenneth D. M. Harris*

School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT

α-Zirconium phenylphosphonate has been synthesised by a reaction between α-zirconium phosphate and molten phenylphosphonic acid. The reaction produces a physical mixture of the 'pure' phases of α-zirconium phenylphosphonate and α-zirconium phosphate, with the ratio dependent on the ratio of phenylphosphonic acid to α-zirconium phosphate in the synthesis mixture. Detailed characterization of the reaction products has been carried out by powder X-ray diffraction, high-resolution solid-state ^{31}P NMR spectroscopy, thermogravimetric analysis and FT-IR spectroscopy, and by considering experiments involving the selective intercalation of *n*-butylamine.

Zirconium phosphate exists in two well characterised solid forms: α-zirconium phosphate[1] [$Zr(HPO_4)_2·H_2O$] and γ-zirconium phosphate[2] [$Zr(PO_4)(H_2PO_4)·2H_2O$]. Organic derivatives of α-zirconium phosphate, known as α-zirconium phosphonates [$Zr(RPO_3)_2·nH_2O$; usually $n = 1$], were first prepared[3] by direct synthesis, involving the use of the appropriate phosphonic acid, rather than phosphoric acid, in the synthesis procedure. These methods and some of the structural and chemical aspects of zirconium phosphonates have been discussed in recent review articles.[4,5] Several aspects of the chemistry of these α-zirconium phosphonates are well developed; for example, applications have been found as intercalation hosts for systems involving Brønsted and Lewis acidity,[6] and investigations have been carried out with regard to their ionic conductivity and ion exchange properties,[7–11] photochemical reactions[12,13] and catalysis.[14,15]

In contrast, there have been no reported preparations of organic derivatives of γ-zirconium phosphate by direct synthesis, but preparations employing topotactic reactions between pre-formed γ-zirconium phosphate and solutions of phosphonic acids[16,17] or solutions of propylene oxide[18,19] have been reported. Conversely, there have been no reports of the synthesis of α-zirconium phosphonates topotactically from pre-formed α-zirconium phosphate (we note, however, that a topotactic reaction of this type using α-titanium phosphate has been reported).[20]

α-Zirconium phosphonates are typically made using hydrothermal techniques or by refluxing solutions of zirconium salts in the presence of HF and a phosphonic acid. As shown recently,[21] layered metal phosphonates can be formed by reaction between layered metal hydroxides and molten phosphonic acids. The application of this synthetic method would remove the need to employ either extreme conditions or highly hazardous chemicals in the synthesis of α-zirconium phosphonates. The aim of the present paper has been to explore the synthetic strategy of using molten phosphonic acids in such preparations, particularly with a view to opening up new routes to metal phosphonate materials. In the present paper, we demonstrate the success of this approach for topotactic synthesis of α-zirconium phenylphosphonate by reaction between pre-formed α-zirconium phosphate and molten phenylphosphonic acid.

In principle, a synthetic procedure of this type may lead to a variety of possible products depending on the extent to which the phosphate groups in the α-zirconium phosphate precursor are replaced by phenylphosphonate groups. Some of the possible types of product are shown schematically in Fig. 1 (see also ref. 22). In addition to the case of a single product phase of α-zirconium phenylphosphonate [Fig. 1(c)], other possibilities include: (i) single phase mixed derivatives, containing both phenylphosphonate and phosphate groups 'interspersed' between the layers [an example of this type of product is shown in Fig. 1(b)]; (ii) single phase 'staged' products, comprising layers with only phenylphosphonate groups and layers with only phosphate groups [an example is shown in Fig. 1(d)]; or (iii) a physical mixture of the pure phase of α-zirconium phenylphosphonate [Fig. 1(c)] and the pure phase of α-zirconium phosphate [Fig. 1(a)]. Clearly the actual type of product obtained should be readily identified using diffraction techniques.

Experimental

Preparation of α-zirconium phosphate

α-Zirconium phosphate was prepared by the sol–gel method of Benhamza *et al.*[23] An aqueous solution of phosphoric acid (85%) and a solution of zirconium propoxide in propan-1-ol (1 mol dm^{-3}) were mixed, leading to the formation of a gelatinous white precipitate which was kept in the mother-liquor at 60 °C for 10 d. The semi-crystalline α-zirconium phosphate was recovered by centrifugation, washed with propan-1-ol and water, and finally dried in air at 60 °C.

Reaction of α-zirconium phosphate and molten phenylphosphonic acid

α-Zirconium phosphate (*ca.* 1 g) was mixed with phenylphosphonic acid; different ratios of these reagents were used, as specified in Table 1. The mixture was ground thoroughly and placed in a thick pyrex tube (volume *ca.* 35 cm^3) capable of withstanding pressures up to 200 psi (≈1379 kPa). The tube was sealed with a Teflon screw cap. The reaction mixture was then kept at 166 °C (the melting point of phenylphosphonic acid) for 3 d. Following this period, the products of the reaction were suspended in deionised water, recovered by filtration, and then washed thoroughly to remove any unreacted phenylphosphonic acid. The solid products were then dried in air at 60 °C for about 30 min. The products obtained from the reactions with different ratios of α-zirconium phosphate and α-zirconium phenylphosphonate are denoted samples A–G (see Table 1).

Procedure for intercalation of *n*-butylamine

The procedure for attempted intercalation (see below) of *n*-butylamine within samples A–G was to place the sample

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* E-Mail: K.D.M.Harris@bham.ac.uk

Table 1 Ratio of reactants in the reactions carried out between molten phenylphosphonic acid ($H_2O_3PC_6H_5$) and α-zirconium phosphate [$Zr(HPO_4)_2{\cdot}H_2O$]

Sample	Mass of phenylphosphonic acid/g	Molar ratio $H_2O_3PC_6H_5 : Zr(HPO_4)_2{\cdot}H_2O$
A	0.1	0.38
B	0.2	0.77
C	0.3	1.1
D	0.4	1.5
E	0.5	1.9
F	1.0	3.8
G	2.0	7.6

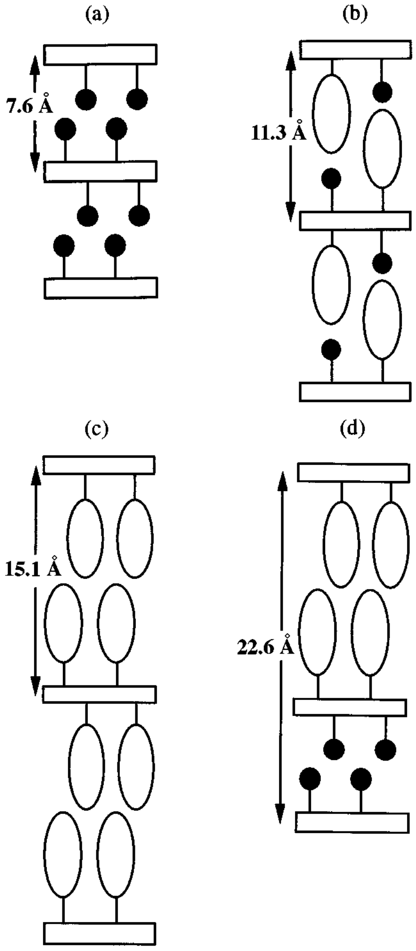

Fig. 1 Possible arrangements of phosphate (filled circles) and phenylphosphonate (open ellipses) groups on the internal layer surfaces of a phosphate/phenylphosphonate material. See text for discussion. The pure phosphate phase is represented in (a) and the pure phenylphosphonate phase is represented in (c).

together with an open vessel containing *n*-butylamine inside a closed desiccator. After 24 h the sample (which in some cases was visibly swollen) was removed, washed briefly with deionised water, and allowed to dry under ambient conditions.

Characterization

Powder X-ray diffraction patterns were recorded using Cu-Kα1 radiation on a Siemens D5000 diffractometer, operating in transmission mode with a primary beam germanium monochromator. Fourier-transform IR spectra were recorded using a Perkin-Elmer Paragon 1000 FT-IR spectrometer for materials dispersed in KBr pellets. Thermogravimetric analysis (TGA) was carried out using a Stanton Redcroft 870 instrument referenced against re-calcined alumina; the samples were heated in air (at 10 °C per min) to a maximum temperature of 1000 °C. High resolution solid-state ^{31}P NMR spectra were recorded at 121.16 MHz on a Chemagnetics CMX-Infinity 300 spectrometer, using a Chemagnetics double resonance probe with magic angle sample spinning (frequency *ca.* 8 kHz; rotor diameter 3.2 mm) and high-power ^1H decoupling. All spectra were recorded at ambient temperature, with the recycle delay (120 s) estimated to be greater than $5 \times T_1$ (to ensure quantitative spectral intensities). Chemical shifts are given relative to the ^{31}P resonance in aqueous H_3PO_4 solution (42%) as an external standard.

Table 2 Total mass losses, determined by TGA, for samples A–G obtained in the synthesis involving α-zirconium phosphate and phenylphosphonic acid, and for the materials formed following the *n*-butylamine intercalation procedure on these samples. The corresponding data for α-zirconium phosphate (denoted α-ZrP) are also given

Sample	Total mass loss (%)	Total mass loss for *n*-butylamine intercalate (%)
α-ZrP	15.0	40.4
A	19.7	39.6
B	22.5	38.9
C	28.4	37.8
D	30.8	37.3
E	31.3	37.2
F	31.9	37.1
G	34.1	36.5

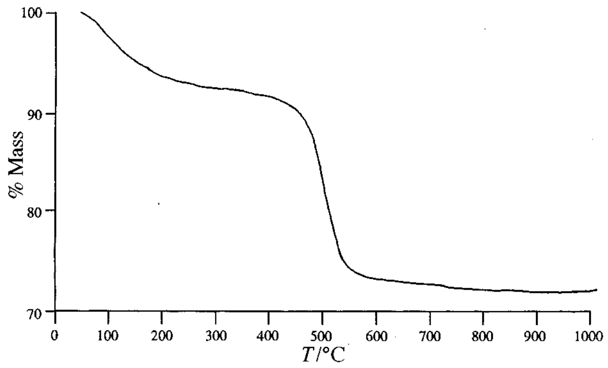

Fig. 2 Typical TGA curve for samples obtained in the synthesis involving α-zirconium phosphate and phenylphosphonic acid. The TGA curve shown is for sample C

Results and Discussion

Thermogravimetric analysis (TGA) was carried out for all samples A–G in air, and stepwise mass losses are observed in all cases. A representative TGA curve is shown in Fig. 2, and total mass losses for all samples studied are reported in Table 2. The first step occurs between ambient temperature and 120 °C and is ascribed to the loss of water. The second step in the region 400–550 °C involves oxidation of the organic portion and dehydration to yield zirconium pyrophosphate. These observations are in agreement with results reported previously for mixed phosphate/phosphonate derivatives of zirconium[24] and titanium.[20] The stoichiometries of samples A–G determined from the TGA data are given in Table 3. As the materials are mixtures of the pure phases of α-zirconium phosphate and α-zirconium phenylphosphonate, the composition is specified as $[Zr(O_3POH)_2{\cdot}H_2O]_x[Zr(O_3PC_6H_5)_2]_y$ rather than $Zr(O_3POH)_x(O_3PC_6H_5)_{2-x}{\cdot}{}^x/_2H_2O$ (which is how a single phase of a mixed derivative phase would be represented). The stoichiometries determined from the TGA data indicate that the synthesis method is successful in producing α-zirconium phenylphosphonate. In order to achieve a complete exchange, however, an excess of phenylphosphonic acid must be employed in the synthesis. Sample G was prepared using a four-fold excess of

Table 3 Stoichiometry $[Zr(O_3POH)_2{\cdot}H_2O]_x[Zr(O_3PC_6H_5)_2]_y$ of samples A–G determined from TGA data and high-resolution solid-state ^{31}P NMR data

	TGA		^{31}P NMR	
Sample	*x*	*y*	*x*	*y*
A	1.43	0.57	1.37	0.63
B	1.20	0.80	1.17	0.83
C	0.65	1.35	0.67	1.33
D	0.40	1.60	0.43	1.57
E	0.34	1.66	0.36	1.67
F	0.28	1.72	0.25	1.75
G	0.02	1.98	0.05	1.95

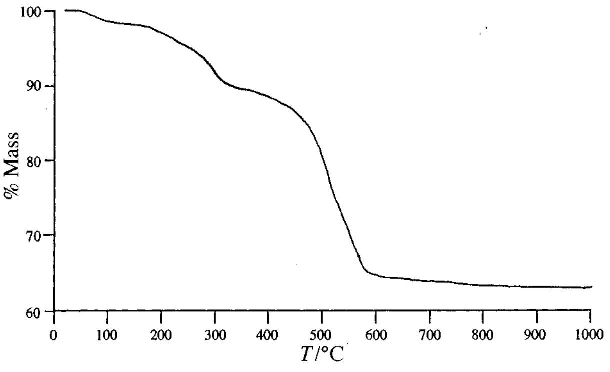

Fig. 3 Typical TGA curve for the materials obtained following the *n*-butylamine intercalation procedure for samples A–G. The TGA curve shown is for sample D

phenylphosphonic acid over that required for a stoichiometric exchange of the phosphate groups, and this sample was indeed the one closest to pure α-zirconium phenylphosphonate (representing 98% exchange of the phosphate groups). Increasing the quantity of phenylphosphonic acid used in the synthesis, or re-immersing the sample in a fresh sample of molten phenylphosphonic acid may be successful in producing a pure phase of α-zirconium phenylphosphonate. When lower molar ratios of phenylphosphonic acid to α-zirconium phosphate are used (samples A–D), there is an almost stoichiometric exchange of phosphate groups by phenylphosphonate groups. Clearly it becomes progressively less easy to replace the final phosphate groups, and a significant excess of phenylphosphonic acid is required.

For the materials obtained following the *n*-butylamine intercalation procedure for samples A–G, the TGA curves again exhibit stepwise mass losses. A representative TGA curve is shown in Fig. 3, and total mass losses for all samples studied are reported in Table 2. The first step occurs between ambient temperature and 150 °C and is due to the loss of water. The second step, from 150 to 360 °C, involves desorption/decomposition of the intercalated *n*-butylamine molecules. The third step, in the region 420–570 °C, is due to oxidation of the phenyl moiety and dehydration to yield zirconium pyrophosphate. These observations are again in agreement with observations for corresponding materials containing titanium.[20]

The powder X-ray diffraction patterns of samples A–G are shown in Fig. 4. All materials have a reflection at $2\theta \approx 5.9°$ (corresponding to *d* spacing 15.1 Å), assigned as the {002} reflection of α-zirconium phenylphosphonate. This reflection is not present in the powder X-ray diffractogram of α-zirconium phosphate and is in good agreement with results reported previously[3,25] for α-zirconium phenylphosphonate synthesized by other methods. The relative intensity of this reflection increases as the ratio of phenylphosphonic acid to α-zirconium phosphate in the reaction mixture increases (samples A to G), with a concomitant decrease in the relative intensity of the reflection at $2\theta \approx 11.7°$ and the pair of reflections in the range $2\theta \approx 25$–$26°$ which are assigned to the pure phase of α-zirconium phosphate [the peak at $2\theta \approx 11.7°$ (corresponding to *d* spacing 7.56 Å) is the {002} reflection of α-zirconium phosphate]. However, when the ratio of phenylphosphonic acid to α-zirconium phosphate in the reaction mixture is greater than 1.5 (samples E–G), no further decrease in the intensity of the peak at $2\theta \approx 11.7°$ is observed. This is because, by coincidence, the {004} reflection for α-zirconium phenylphosphonate also occurs at $2\theta \approx 11.7°$, and therefore overlaps the {002} reflection for α-zirconium phosphate.

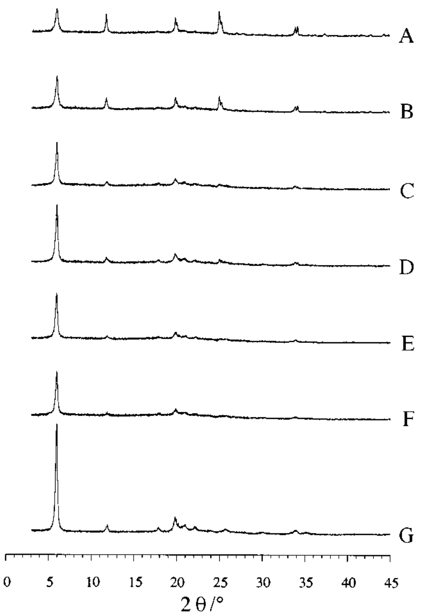

Fig. 4 Powder X-ray diffractograms of the samples A–G obtained in the synthesis involving α-zirconium phosphate and phenylphosphonic acid. The different samples were prepared from different initial ratios of phenylphosphonic acid to α-zirconium phosphate in the reaction mixture (as detailed in Table 1). The absolute intensities for the different samples are not normalized

The powder X-ray diffractograms provide no evidence for the production of a single-phase mixed derivative, for which a peak corresponding to a *d* spacing of about 11.3 Å may be expected {corresponding, for example, to a single phase containing both phenylphosphonate and phosphate groups 'interspersed' between the layers [Fig. 1(b)] or to a single phase with phenylphosphonate and phosphate groups occupying layer faces opposite each other}. There is also no evidence for 'staged' products [Fig. 1(d)], for which a peak corresponding to *d* spacing in the range 22.5–25.4 Å would be expected (the actual value would depend on the level of hydration of the material).[24] In summary, the powder X-ray diffraction data suggest that the materials formed in our preparation procedure are mixtures of the pure phases of α-zirconium phosphate and α-zirconium phenylphosphonate.

To further confirm this conclusion, samples A–G were subjected to the conditions for intercalation of *n*-butylamine. *n*-Butylamine is preferentially intercalated into regions of a host material in which there are opportunities for acid–base interactions, and should therefore be included preferentially into α-zirconium phosphate rather than α-zirconium phenylphosphonate. Following this attempted intercalation procedure on samples A–G, the powder X-ray diffractograms (Fig. 5) of all materials have an additional reflection at $2\theta \approx 4.7°$, corresponding to a *d* spacing of about 18.8 Å. This observation is consistent[26] with intercalation of an extended bimolecular layer of *n*-butylamine within α-zirconium phosphate (with the longitudinal axes of the *n*-butylamine molecules inclined at *ca.* 59° with respect to the plane of the layer). Thus, following the *n*-butylamine intercalation procedure, samples A–G (assigned above as mixtures of α-zirconium phosphate and

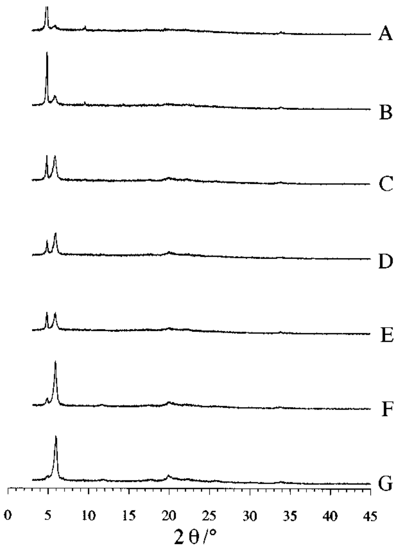

Fig. 5 Powder X-ray diffractograms of the materials obtained following the *n*-butylamine intercalation procedure for samples A–G

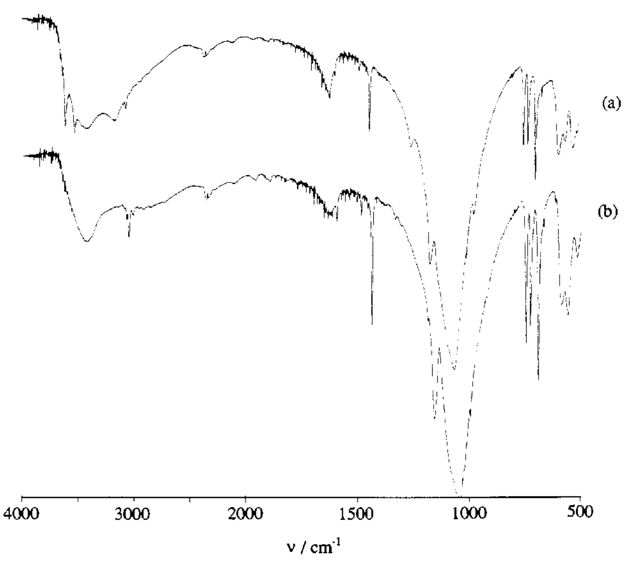

Fig. 6 Fourier-transform IR spectra for samples obtained in the synthesis involving α-zirconium phosphate and phenylphosphonic acid: (a) sample A, (b) sample G

α-zirconium phenylphosphonate) are converted into mixtures of α-zirconium phosphate intercalated with *n*-butylamine and α-zirconium phenylphosphonate (essentially unaltered by the intercalation procedure). This conclusion is further supported by the fact that the relative intensity of the new peak at $2\theta \approx 4.7°$, following the *n*-butylamine intercalation procedure, decreases from sample A to sample G (*i.e.* as the amount of α-zirconium phosphate decreases). Consistent with our suggestion that the α-zirconium phenylphosphonate does not intercalate *n*-butylamine is the fact that the peak at $2\theta \approx 5.9°$ remains unchanged following the *n*-butylamine intercalation procedure. In summary, all the evidence from our powder X-ray diffraction studies suggests that samples A–G are physical mixtures of the pure phases of α-zirconium phenylphosphonate and α-zirconium phosphate, rather than single phases containing both phosphate and phenylphosphonate groups.

The FT-IR spectra of samples A–G (Fig. 6) confirm that they contain both phosphate and phenylphosphonate groups. Thus, characteristic bands[27] for α-zirconium phenylphosphonate and α-zirconium phosphate at 1438 [phenyl ν(C=C)], 748 and 692 [δ out of plane], 3440 [ν(O–H)], 3055 [aromatic ν(C–H)], 1156 [ν(P–C)] and 1044 cm^{-1} [ν(P–O(H))] are all present. It is interesting to note that the sharp bands at 3593 and 3510 cm^{-1} decrease in intensity as the ratio of phenylphosphonic acid to α-zirconium phosphate in the synthesis mixture increases (*i.e.* from sample A to sample G). These bands are attributed to the asymmetric and symmetric stretching modes of the interlayer water molecule of α-zirconium phosphate.

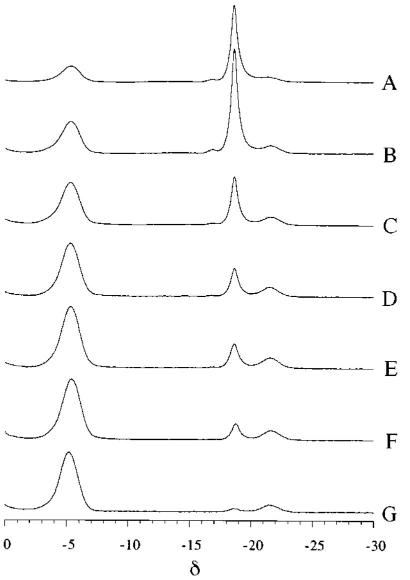

Fig. 7 High-resolution solid-state ^{31}P NMR spectra for samples A–G obtained in the synthesis involving α-zirconium phosphate and phenylphosphonic acid

High-resolution solid-state ^{31}P NMR spectra (Fig. 7) of samples A–G contain two main peaks at δ −5.3 and −18.6, assigned to phenylphosphonate and phosphate groups respectively, in line with results reported previously.[24,28] (We note that the ^{31}P NMR spectra contain other peaks of low intensity, suggesting that the samples also contain small amounts of other phosphorus-containing species, perhaps at the surfaces of the crystallites or in less well ordered regions of the samples. At present, a definite assignment of the identity of these minor components of the samples has not been made.) As the ratio of phenylphosphonic acid to α-zirconium phosphate in the synthesis mixture is increased (*i.e.* from sample A to sample G), the relative intensity of the peak at δ −5.3 increases and the relative intensity of the peak at δ −18.6 decreases. However, the peak at δ −18.6 due to α-zirconium phosphate is always present, even when a large excess of phenylphosphonic acid is used in the synthesis. This observation is in agreement with our conclusions from powder X-ray diffraction discussed above. Integration of the peaks at δ −5.3 and −18.6 provides an estimate of the ratio of α-zirconium phenylphosphonate to α-zirconium phosphate (see Table 3) and the stoichiometries determined in this way are in good agreement with those determined from the TGA data.

Conclusion

In summary, the topotactic synthesis procedure described in this paper has been used successfully to produce α-zirconium phenylphosphonate by reaction of α-zirconium phosphate with molten phenylphosphonic acid. It is clear from powder X-ray diffraction that the materials formed are not single phases containing both phenylphosphonate and phosphate groups, but rather they are physical mixtures of the pure phases of α-zirconium phosphate and α-zirconium phenylphosphonate. The TGA data and high-resolution solid-state ^{31}P NMR data indicate clearly that the quantity of α-zirconium phenylphosphonate formed increases as the ratio of phenylphosphonic acid to α-zirconium phosphate in the reaction mixture is increased. However, all the materials synthesized contain some amount of α-zirconium phosphate, even when a large excess of phenylphosphonic acid is used in the synthesis procedure.

The production of mixtures of pure α-zirconium phosphate and pure α-zirconium phenylphosphonate, rather than a single phase containing both phosphate and phenylphosphonate groups, is interesting {although we note that the synthesis of a staged material [Fig. 1(d)] has been reported[24] using hydrothermal methods}. Evidently for the synthetic method reported here, the phenylphosphonate groups become preferentially incorporated into certain layers, arising from the mobility of the phenylphosphonate anions in the interlayer region, which ultimately become pure phenylphosphonate layers in the α-zirconium phenylphosphonate phase of the product.

The results reported here have several parallels with a previous report[20] of the topotactic formation of α-titanium phenylphosphonate from α-titanium phosphate. This reaction involved repeated contact of α-titanium phosphate with an aqueous solution of phenylphosphonic acid, and resulted in the formation of mixtures of α-titanium phosphate and α-titanium phenylphosphonate. The extent of formation of α-titanium phenylphosphonate was found to be related to the contact time between solid and solution. The incomplete replacement of the phosphate groups by phenylphosphonate groups was attributed to the establishment of an equilibrium between the α-titanium phosphate and α-titanium phenylphosphonate. It is plausible that a similar equilibrium may be set up during the reaction reported here between α-zirconium phosphate and molten phenylphosphonic acid. Thus, α-zirconium phosphate may be partially hydrolysed under the conditions of the experiment to give phosphoric acid and Zr^{IV}, which then reacts with the phenylphosphonic acid to form α-zirconium phenylphosphonate. Equilibrium (1) between the α-zirconium phenyl-

$$Zr(HPO_4)_2 + 2\,RPO_3H_2 \rightleftharpoons Zr(RPO_3)_2 + 2\,H_3PO_4 \quad (1)$$

phosphonate and α-zirconium phosphate phases may then be established. Clearly the position of this equilibrium will be altered by changing the ratio of phenylphosphonic acid to α-zirconium phosphate in the initial reaction mixture. Although the results presented here would be consistent with the existence of such an equilibrium, they do not prove that this is actually the mechanism that operates.

Further investigations are clearly required to understand in detail, from both chemical and thermodynamic viewpoints, the mechanism of the synthetic reaction for the preparation of α-zirconium phenylphosphonate reported here. Ultimately, such an understanding may be applied to determine the conditions required to produce a single pure phase of α-zirconium phenylphosphonate *via* this synthetic procedure.

Acknowledgements

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