A direct access to layered zirconium-phosphonate materials from dialkylphosphonates

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Reaction of dialkylphosphonates with zirconium salts in acidic aqueous media provides a facile route to crystalline hybrid zirconium phosphonate materials.

Since the first synthesis of a layered zirconium phosphonate,[1] many other layered materials involving different metals [M(IV) or M(II)] have been synthesised. Some of these materials may have practical applications as supported catalysts,[2] protonic conductors[3] and molecular sieves.[4] These materials which possess a well ordered structure, are synthesised by reaction of a phosphonic acid with a metal(IV) or a metal(II) source in water or sometimes with an organic co-solvent. In order to increase the crystallinity of these materials, the addition of a mineralising agent (HF) or the use of hydrothermal conditions[5] can be employed.

Phosphonic acids, which form the necessary precursor to synthesise metal phosphonate materials, are generally obtained by reaction of a phosphonate with either a hydrogen halide (HCl, HBr) in aqueous medium or by using the method of McKenna *et al.*[6] These phosphonates are easily obtained by the Arbusov reaction[7] or by a palladium or nickel assisted phosphonation when aromatic phosphonates are required.[8] It is worth noting that, unlike dialkylphosphonates, the purification of phosphonic acids can not be readily achieved using chromatographic or distillation methods. Owing to their strong polarity and the formation of strong intermolecular hydrogen bonds.

With the aim of avoiding the prior synthesis of phosphonic acids, we report here an easy method to synthesise hybrid metal phosphonate materials by using phosphonates instead of phosphonic acids as precursors.

In a preliminary result (entry 1, Table 1) zirconium bis(methylphosphonate) **5** was obtained in quantitative yield from the reaction of dimethyl methylphosphonate **1** with zirconyl chloride **4** in an acidic aqueous solution (9 M HCl) under reflux for 24 h . This first result indicates that methyl phosphonic acid, which is progressively produced *in situ* by hydrolysis of phosphonate **1**, reacts immediately with zirconyl chloride **4** to yield **5** in quantitative yield.† Analyses of material **5** (microanalyses, XRD powder diffraction pattern, IR), as synthesised from phosphonate **1** or from phosphonic acid **2** (Alberti's method) are identical.‡ It is interesting that the microanalysis of material **5** does not show any increase in carbon content that might come from the phosphonate function. This observation indicates that the hybrid material does not contain any product resulting from monohydrolysis of phosphonate **1**.

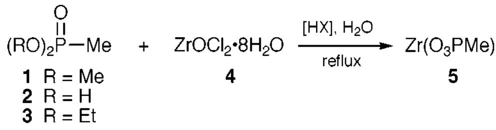
Taking into account this interesting result, the influence of experimental conditions on crystallinity of **5** has been studied. Powder XRD patterns and surface area data (BET) were used to obtain information about the degree of crystallinity of the materials. In particular, BET analysis is an interesting indicator of the crystallinity and granulometry of resulting materials. In a previous study, concerning zirconium bis(methylphosphonate) **5**, a direct relationship between the crystallinity and specific area was demonstrated (greater crystallinity leads to a smaller surface area).[9]

The use of HBr (entry 2, Table 1) instead of HCl (entry 1) affords after refluxing for 24 h, a poorly crystalline sample of material **5** (S_{BET} = 378.1 $m^2 g^{-1}$). This observation may be explained by the well known difference in the affinity of chloride and bromide ions for Zr(IV) (Cl > Br).[10] Furthermore, bromide is a better nucleophile than chloride and this property enhances the kinetics of the hydrolysis of phosphonate to phosphonic acid. Both factors, *i.e.* the greater affinity of HCl towards Zr and the slower hydrolysis of phosphonate by use of HCl, contribute to a decrease in the rate of reaction between phosphonic acid and Zr(IV), leading to more crystalline hybrid materials.

In order to compare the influence of the substrate (phosphonate or phosphonic acid), on the crystallinity of the resulting material, **5** was synthesised from both precursors dimethyl methylphosphonate **1** (entry 1) and methylphosphonic acid **2** (entry 3) under identical experimental conditions. The materials obtained from both experiments exhibit the same characteristics (IR, microanalyses) with the exception of their specific area. The use of phosphonate **1** leads to a slightly more crystalline material (S_{BET} = 96.6 $m^2 g^{-1}$) compared to the material obtained from the corresponding phosphonic acid **2** (S_{BET} = 119.0 $m^2 g^{-1}$).

Using diethyl methylphosphonate **3** (entry 4) in a 24 h reflux experiment leads to a sample of **5** that is less crystalline compared to that prepared using dimethyl methylphosphonate **1** (entry 1). From these results it appears that dimethylphosphonate is the best choice when short refluxing times are required.

Table 1 Reaction of phosphonates **1–3** or phosphonic acid **2** with zirconyl chloride **4** leading to compound **5**



$(RO)_2P(O)Me + ZrOCl_2\cdot 8H_2O \xrightarrow[\text{reflux}]{[HX],\ H_2O} Zr(O_3PMe)_2$

Entry	Substrate	[HX]/M	*t*/h	Mole ratio **1**, **2** or **3**/Zr	S_{BET} (**5**)/$m^2 g^{-1}$
1	**1**	9[a]	24	3	96.6
2	**1**	9[b]	24	3	378.1
3	**2**	9[a]	24	3	119.0
4	**3**	9[a]	24	3	249.2
5	**1**	12.2[a]	24	3	86.0
6	**1**	12.2[a]	24	1.66	38.4
7	**2**	12.2[a]	24	1.66	26.0
8	**1**	12.2[a]	112	1.66	27.6
9	**1**	9[a]	112	1.66	28.8
10	**1**	3[a]	112	1.66	62.3
11	**1**	0[c]	112	1.66	203.4

[a] HCl. [b] HBr. [c] Water was used as solvent.

Since it is often the aim to synthesise hybrid materials possessing functionalised pendant organic groups (chiral molecules[11] or ligands), it is worth considering the effect of using an excess of metal salt, in order to avoid the loss of costly organic substrate. By using an excess of zirconyl chloride we observed that the phosphonate/Zr ratio has a great influence on the crystallinity of the resulting material. Indeed, a slight excess of zirconyl chloride (1.2 equiv.) yields a more crystalline sample of material **5** (entry 6, $S_{\mathrm{BET}} = 38.4\ \mathrm{m^2\ g^{-1}}$) when compared to the use of an excess of phosphonate (entry 5, $S_{\mathrm{BET}} = 86.0\ \mathrm{m^2\ g^{-1}}$). By using the same excess of zirconyl chloride, it appears that the use of phosphonic acid leads to a material **5** with a slightly better crystallinity (entry 7, $S_{\mathrm{BET}} = 26.0\ \mathrm{m^2\ g^{-1}}$) compared to the use of dimethyl methylphosphonate **1** (entry 6, $S_{\mathrm{BET}} = 38.4\ \mathrm{m^2\ g^{-1}}$).

Finally the effect of HCl concentration upon the crystallinity of **5** was investigated. When **5** was synthesised by using a high concentration of HCl ($>$ 9 M) the same surface areas ($S_{\mathrm{BET}} = 28\ \mathrm{m^2\ g^{-1}}$) were obtained (entry 8 and 9) while the use of a 3 M HCl solution (entry 10) yields a less crystalline material ($S_{\mathrm{BET}} = 62\ \mathrm{m^2\ g^{-1}}$). In absence of acid (entry 11) the same material **5** was isolated in quantitative yield and characterised by IR, microanalysis and XRD powder pattern. However, BET analysis (203.4 $\mathrm{m^2\ g^{-1}}$) indicated a poorly crystalline material. Despite the pH of the solution in this experiment being clearly acidic (pH = 1) owing to zirconyl chloride, the concentration of HCl was low (0.3 M) compared to experiments carried out in 9 M HCl. The synthesis of hybrid materials using a very low concentration of HCl could be useful when precursors are sensitive to strong acidic solutions such as when ether or cyano functions are used.

Fig. 1 shows some powder X-ray diffractograms for materials **5**, which corroborate the results obtained by BET measurement.

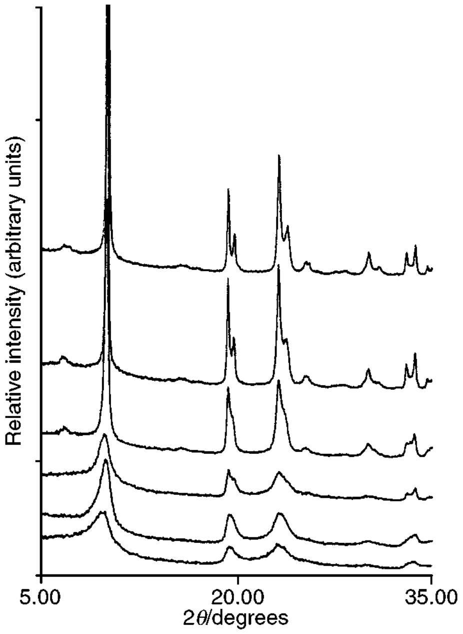
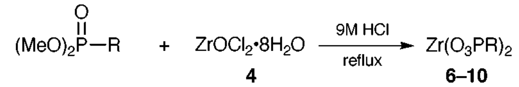


Fig. 1 Powder X-Ray diffractograms for material **5** corresponding to experiments detailed in Table 1: (a) entry 5, (b) entry 13, (c) entry 6, (d) entry 7, (e) entry 11, (f) entry 8. Corresponding BET surface areas ($\mathrm{m^2\ g^{-1}}$: (a) 249.2, (b) 203.4, (c) 86.0, (d) 38.4, (e) 28.8, (f) 26.0.

This new method is compatible with the use of other phosphonates. Materials **6** and **7** (Table 2) prepared by this method are identical to those prepared previously by other synthetic routes. In the case of compound **7**, a pillared structure was obtained. In addition, novel materials **8–10**, have been synthesised by using this method and were fully characterised.

Table 2 Synthesis of layered zirconium phosphonates **6–10**



$$(\mathrm{MeO})_2\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{-R} + \underset{\mathbf{4}}{\mathrm{ZrOCl_2\cdot 8H_2O}} \xrightarrow[\text{reflux}]{\text{9M HCl}} \underset{\mathbf{6\text{–}10}}{\mathrm{Zr(O_3PR)_2}}$$

Entry	R	Product	Interlayer distance/Å
1	CH_2CO_2H[a]	**6**[a]	11.1 (Lit.[12] 11.1)
2[c]	$CH_2C_6H_4CH_2$	**7**[d]	10.9 (Lit.[13] 10.8)
3	CH_2Ph	**8**[b]	15.8
4	Et	**9**[b]	10.8
5	CCl_3	**10**[b]	11.5

[a] Ethyl dimethylphosphonoacetate was used as substrate but hydrolysis of the ester function leads to carboxylic functionalities in the interlayer space. [b] $n = 2$. [c] Dimethyl α,α′-*p*-xylenediphosphonate was used and a pillared structure was obtained. [d] $n = 1$.

The access to new zirconium phosphonate materials shows the advantage of using a phosphonate directly rather than a phosphonic acid. Thus the number of steps to produce the necessary organic substrate is reduced and its purification can be more easily accomplished. Furthermore, very slight differences, in terms of crystallinity, have been observed between this new method and that using phosphonic acid. It has also been demonstrated that this new method is suitable for the use of different phosphonates and diphosphonates to give either layered or pillared structures.

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Notes and references

† *Example of preparation of compound* **5** (*entry 9, Table 1*): a solution of dimethyl methylphosphonate (3.72 g, 30 mmol) and zirconyl chloride (5.80 g, 18 mmol) in aqueous 9 M HCl solution (120 ml) was refluxed for 112 h. The solid was recovered by filtration, washed with distilled water (200 ml) and acetone (50 ml), dried at 40 °C for 18 h and at 200 °C for 24 h.

‡ *Selected microanalyses for compound* **5**: Anal. calc. for $Zr(O_3PCH_3)_2$: C, 8.60; H, 2.17; P, 22.18. Found (entry 3, Table 1) : C, 8.32; H, 2.27; P, 20.15; Found (entry 1, Table 1): C, 8.37; H, 2.54; P, 22.03%.

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