Lamellar organominerals: intercalation of phenylphosphonate into the layers of bayerite

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The reaction of phenylphosphonic acid with the aluminium hydroxide bayerite affords a layered aluminium phosphonate compound of formula $Al_2(O_3PPh)_3 \cdot 4H_2O$.

The last few years have seen an increasing interest in the preparation of derivatives of transition-metal phosphonates. These compounds are generally characterized by a lamellar structure depending greatly upon the choice of the metal. It also varies with the experimental conditions and the nature of the substitution of the organic entities inserted between the layers. These layered materials can be modified to form a variety of intercalation compounds and pillared structures.[1]

Most of the studies performed so far have been based on tetravalent metals, $M(O_3PR)_2 \cdot xH_2O$, and, more particularly, on vanadium[2,3] and on zirconium.[4] A variety of phosphonates based on divalent metals $M^{II}(HO_3PR)_2$ (M = Mg, Mn, Co, Cu, Ni, Zn, *etc.*) have been described.[5]

Very few compounds based on trivalent metals have been reported. A family of trivalent metallic phosphonates was recently synthesized and characterized:[6] $LnH(O_3PR)_2$ (Ln = La, Sm, Ce). Some compounds, based on di-[7] and trivalent[8] iron were reported with structures similar to those observed for divalent metals. With the exception of copper, which assumes a square-pyramidal coordination,[9] the metal is in all cases octahedrally coordinated, forming lamellar structures.[10] Organic entities and water molecules can be intercalated in the interlamellar spaces.

Surprisingly, while bayerite, $Al(OH)_3$, has a layered structure, no phosphonate intercalation compounds have thus far been reported for this mineral. Maeda *et al.*[11] have recently synthesized a microporous material resulting from the reaction of methylphosphonic acid with pseudoboehmite.

The synthesis of the first intercalation compound of a phosphonate in the bayerite structure is reported here. The resulting compound was characterized by X-ray diffraction, X-ray fluorescence, thermal and chemical analysis, IR and ^{31}P and ^{13}C MAS NMR.

Bayerite was synthesized following the procedure described in the literature.[12] This aluminium hydroxide has a lamellar structure made of layers of aluminium coordinated octahedrally by hydroxy groups. The layers are stacked and linked together by a network of hydrogen bonds. Aluminium atoms occupy two-thirds of the octahedral sites formed by hydroxy groups.[13]

The aluminium phosphonate was prepared by suspending 1.0 g of bayerite in 100 ml of a 0.10 M aqueous solution of phenylphosphonic acid at pH 6.8. The resulting reaction mixture was heated at 75–80 °C for 14 h, followed by filtration of the product and vacuum drying at 80 °C.

Fig. 1 shows the XRD spectrum of the resulting product, which has preserved its lamellar structure, with an interlamellar spacing, d_{001}, of 14.35 Å. This value is comparable to reported data for similar compounds.[5,8,14] The d_{001} spacings suggest a perpendicular orientation of the phenyl groups to the layers. The presence of bands between 930 and 1200 cm^{-1} in the IR spectrum confirms the presence of phosphonate groups in this lamellar compound.[9,14,15] The following data were obtained from chemical analysis: C, 35.93; H, 3.48%. A P/Al ratio of 1.5(1) was obtained from X-ray fluorescence. A formula $Al_2(O_3PPh)_3 \cdot 4H_2O$ **1** is thus indicated, corresponding to the proposed structure shown in Fig. 2, in agreement with the X-ray data. This structure is analogous to a previously reported structure for lanthanum(III) phenylphosphonate.[16]

A thermogravimetric analysis of **1** (Fig. 3) shows three mass losses. The first, between 66 and 67 °C, corresponds to the desorption of surface water. The second, between 250 and 293 °C, is attributed to the loss of interlamellar water and the final mass loss between 600 and 680 °C results from the loss of

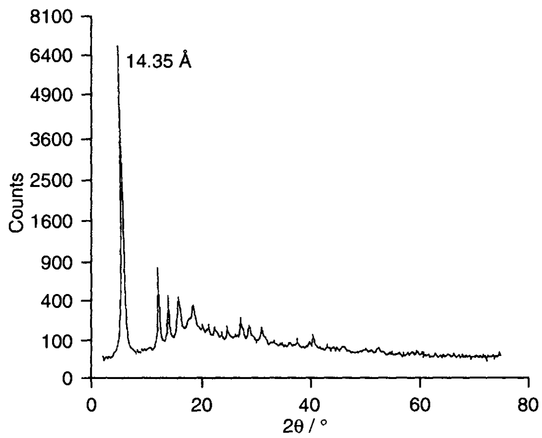

Fig. 1 XRD pattern of **1** (2θ = 2–75°)

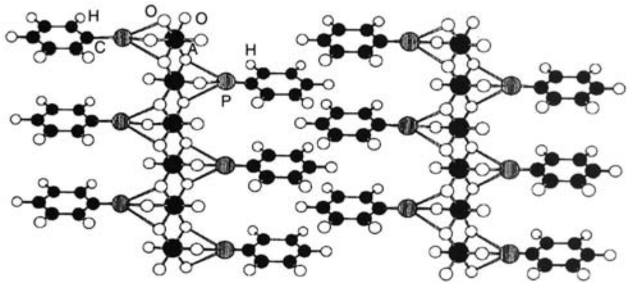

Fig. 2 Proposed structure for compound **1**

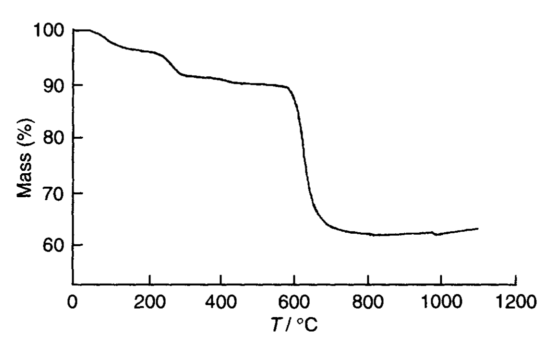

Fig. 3 TGA profile of **1**

organic material, showing the high thermal stability of the compound. Only 26% of the intercalated material was lost in the TGA experiment, compared to a calculated 39% on the basis of the elemental analysis and X-ray fluorescence data. The resulting powder was grey. This behaviour, common for this type of intercalation product, can be attributed to an incomplete combustion of the intercalated organic material. The solid-state ^{31}P MAS NMR spectrum shows only one resonance peak at δ *ca.* 0, indicating the presence of one predominant site for phosphorus atoms. The ^{27}Al MAS NMR spectrum indicates an octahedral coordination of the aluminium. This is in contrast with the results of Maeda *et al.*[11] which have shown, in the case of the reaction of methylphosphonic acid with pseudoboehmite, the appearance of tetrahedral aluminium sites. All the results of the X-ray, NMR and TGA analysis of this work are in agreement with the proposed structure of **1**. The material reported here illustrates the structural versatility of compounds made by the reaction of phosphonate derivatives with aluminium hydroxides.

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Footnote

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