

Understanding the building-up process of three dimensional open-framework metal phosphates: Acid degradation of the 3D structures to lower dimensional structures†

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Acid degradation of 3D zinc phosphates primarily yields a one-dimensional ladder compound, an observation that is significant considering that the latter forms 3D structures on heating in water.

A large variety of open-framework inorganic materials with fascinating architectures has been synthesized and characterized in recent years. These include aluminosilicates,¹ phosphates,² carboxylates,³ selenites⁴ and sulfates.⁵ One of the intriguing aspects of these materials is concerned with their mode of formation.⁶ It is not clear as to how such complex three-dimensional (3D) structures are formed and whether the formation of such structures involves a building-up process starting from distinct secondary building units (SBUs). It is important to unravel these mechanistic issues to be able to rationally design these materials. The possible role of SBUs in the building-up process has been recognised by Férey.⁷ In the case of open-framework metal phosphates, it has been shown that low-dimensional structures do indeed transform to 3D structures.^{6,8} Thus, zero-,^{8a} one-,^{8b} and two-dimensional^{8c} zinc phosphates transform to 3D structures under relatively simple reaction conditions, specially in the presence of amines. A linear chain gallium phosphate has been found to transform to a 3D structure as well.⁹ A relevant question in this connection pertains to the reversibility of such transformations. Does a 3D open-framework structure undergo degradative transformations to lower dimensional structures? If so, can one isolate 1D or 2D structures on acid treatment of 3D metal phosphates? In order to answer this important question, we have carried out a systematic study of the acid-induced degradation of 3D zinc phosphates. The study has revealed that the 3D structures do indeed transform to the 1D ladder structure under acidic conditions, thereby demonstrating the reversibility of the 1D–3D transformation.

Acid-induced degradation studies were carried out† on the 3D zinc phosphate, $[C_6N_4H_{22}]_{0.5}[Zn_2(PO_4)_2]$,¹⁰ **I**, analogous to gismondine,¹ built up of a double-crankshaft chain and possessing an 8-membered ring channel in all three crystallographic directions (Fig. 1a). On treatment with H_3PO_4 under hydrothermal conditions at 150 °C for 24 h, **I** transforms to another 3D structure of composition $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$,¹⁰ **II**, even at relatively low acid concentrations (molar ratio of **I**: H_3PO_4 = 1:0.25–0.5). **II**, with a 16-membered channel along the *a*-axis (Fig. 1b), is a slightly lower density structure (2.62 g cm⁻³ compared to 2.63 g cm⁻³ of **I**). As the acid concentration is increased, however, a one-dimensional ladder structure, $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$,¹⁰ **III** (Fig. 1c), and a two-dimensional layer structure, $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$,¹⁰ **IV** (Fig. 1d), are obtained along with **II**, the proportion of **IV** increasing with the acid concentration and becoming 100% when the **I**: H_3PO_4 ratio is 1:1.25 or greater. The evolution of the

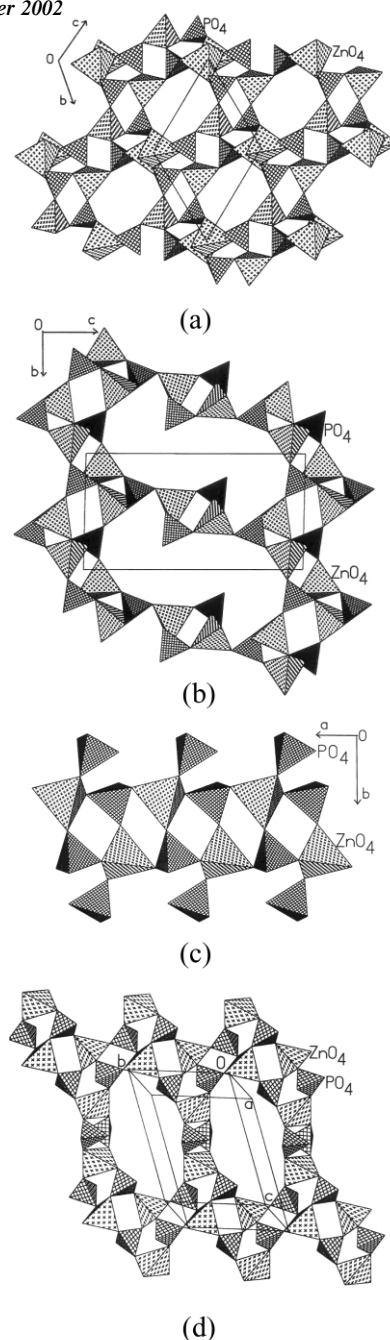


Fig. 1 (a) Polyhedral view of **I** along the *a*-axis showing the 8-membered channel. Amine molecules are omitted for clarity. (b) Polyhedral view of **II** along the *a*-axis showing the 16-membered channel. Amine molecules are omitted for clarity. (c) Structure of **III** showing the 4-membered ladder like chain propagating along the *a*-axis. (d) The layered structure of **IV**, with the protonated amine molecule sitting in the 12-membered aperture. (Compounds **I**, **II**, **III** and **IV** in this communication correspond to the compounds **III**, **IV**, **I** and **II** respectively in ref. 10).

† Electronic supplementary information (ESI) available: typical experimental parameters. See <http://www.rsc.org/suppdata/cc/b2/b210037c/>

Table 1 Conditions for the degradation of compound **I** on treatment with 1M H₃PO₄

Compositions	Conditions				Product(s)
	T/°C	t/h	pH	end pH	
I: 1M H ₃ PO ₄ :H ₂ O					
1:0.25:200	150	24	<2	<2	II
1:0.5:200	150	24	<2	<2	II
1:0.75:200	150	24	<2	<2	II, III, IV
1:1:200	150	24	<2	<2	II, III, IV
1:1.25:200	150	24	<2	<2	IV
1:1.5:200	150	24	<2	<2	IV
1:2–5:200	150	24	<2	<2	IV
1:>5:200	150	24	<2	<2	Dissolution

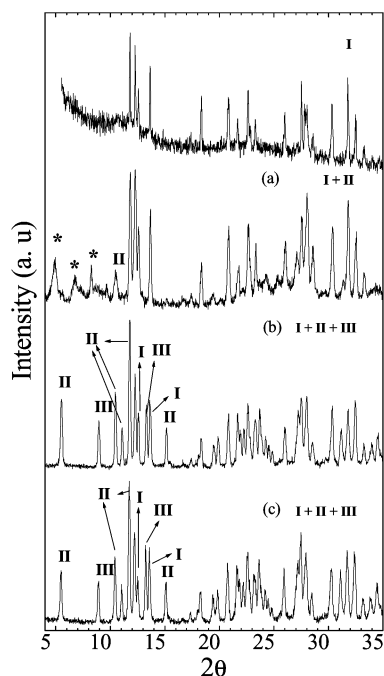


Fig. 2 Time dependent changes observed in the reaction of **I** with 1M H₃PO₄ under hydrothermal conditions (**I**:H₃PO₄ = 1:0.25). The powder XRD patterns show the evolution of the various phases as a function of reaction time. (a) 10 min, (b) 25 min and (c) 50 min. Asterisk denotes an unidentified phase.

different phases with the increasing acid concentration is summarised in Table 1. Using H₂SO₄ or HCl in place of H₃PO₄ also transforms **I** to **II** at low acid concentrations, and to **IV** at high acid concentrations.

In order to understand the evolution of different phases in the acid degradation of **I**, we carried out a time-dependent study, keeping the **I**:H₃PO₄ ratio fixed at 1:0.25. Some of the results are shown in Fig. 2 in the form of XRD data. Within 10 min of the reaction, **I** transforms to **II**, admixed with an unidentified phase with low angle lines at $d = 17.5, 12.1$ and 10.2 Å. After 25 min, however, the ladder phase, **III**, is formed along with **II**, but the unidentified phase is no longer present. A mixture of **II** and **III** along with the unreacted **I** is obtained after 30, 40 and 50 min of the reaction. A mixture of **II** and **III** (without any **I**) is found after 12 h. In order to examine whether **I** transforms to **II** or **III** under nonhydrothermal conditions, we reacted **I** with a H₃PO₄ solution in an open beaker. While no transformation occurred at 25 °C, **I** transformed to **II** or **III** at 100 °C, depending on the **I**:H₃PO₄ ratio.

Since the 3D zinc phosphate **II** is the initial product of the acid treatment of **I**, we have examined the transformation of **II** in acid media under hydrothermal conditions: **II** transforms to

III at low acid concentrations (**II**:H₃PO₄ = 1:0.25–0.75) and to the layered structure, **IV**, at higher acid concentrations, hopeite being the other product.

The present study clearly shows that the 3D zinc phosphate, **I**, transforms in a facile manner to the lower dimensional ladder (**III**) and/or layer (**IV**) structure through a lower density 3D structure, **II**.

The primary degradation of the 3D structures is the 1D ladder compound **III**, which undergoes a transformation to the layered compound **IV** on acid treatment at 150 °C.‡

It is known that the ladder compound **III** transforms to **II** on heating with water and to **I** on heating with water in the presence of an amine.^{6,8b} The present finding that the 3D zinc phosphates, **I** and **II**, transform primarily to the 1D ladder compound, **III**, under acidic conditions demonstrates the reversibility of the 3D–1D transformation.

Notes and references

‡ *Synthesis*: The syntheses of **I–IV** (formed in the presence of triethylenetetramine, TETA) are reported in the literature.¹⁰ In order to obtain a good yield of pure materials, we had to modify the synthetic conditions in some cases. The detailed synthetic conditions are listed in Table S1 and supplied as supplementary information.† All the four starting materials were characterized using powder XRD. The powder XRD patterns were in good agreement with their simulated patterns generated from known single crystal data.

In order to study the behavior of **I** under acidic conditions, **I** was hydrothermally treated in the presence of, 1M H₃PO₄, 1M H₂SO₄ or 1M HCl, with varying **I**:acid ratios. The acid concentration was progressively increased till the reactants dissolved fully to give a clear solution and no solid product resulted after hydrothermal treatment. Typically, 0.100 g of **I** was taken in a 7 ml PTFE-lined acid digestion bomb and treated under hydrothermal conditions at 150 °C for a period of 24 h. Similar studies were carried out in which hydrothermal treatment of the relevant composition of reactants was carried out for different periods, and the final products analyzed by powder XRD. The resulting products were generally single crystalline, although mixtures of polycrystalline and single crystalline phases were obtained in certain cases. Typical experimental parameters along with the products obtained in the acid-degradation reactions of **I** are listed in Tables 1 and S2 (electronic supplementary information).

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