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Thermal investigation of two FePO materials prepared in the presence of 1,2-diaminoethane

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Abstract

Two porous iron phosphates were synthesized hydrothermaly from a reaction mixture of $FeCl_3$:H_3PO_4:1,2-diaminoethane:H_2O in the molar ratio 1:3:5:70. The chemical formulas indicate difference only in water content; however, the crystal structures and thermal behaviour of the iron phosphates are completely different. After the removal of 1,2-diaminoethane and water, both products exhibit structural transformation. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The widespread use of aluminosilicates (zeolites) in absorption, catalysis and ion exchange processes directs synthetic efforts towards the development of novel inorganic porous materials. Generally, in the synthesis of open-framework materials organic templates (structure-directing agents) have been used for the generation of porous texture. This fact is of special interest since it enables not only pore size control but also the design of microporous solids with specifically tailored physico-chemical properties. Thus, during the last fifteen years many open-framework metallophosphates (MPOs) (M=Al, V, Co, Ga, Zn, Sn, In, Ni) have been discovered [1–8].

A large diversity of iron phosphates with open-frameworks have been recently synthesized under hydrothermal conditions [9–19]. These solids exhibit not only interesting structural features but also unique magnetic properties. Thus, mixed-valence iron fluorophosphates, ULM-10 and ULM-15, exhibit a magnetic ordering corresponding to different Fe^{2+}–Fe^{3+} or Fe^{3+}–Fe^{3+} interactions [13,14]. An iron phosphate that possesses unusually large elliptical voids of 24 (Fe, P) atoms exhibits a gradual low- to high-spin transformation [19]. Furthermore, iron phosphates have been known as effective catalysts [20]. However, data on thermal behaviour of iron phosphates with open-frameworks have still been very scarce.

In the present paper, we report thermal investigation of two iron phosphates synthesized in the presence of 1,2-diamnoethane (*en*).

2. Experimental

The synthesis was carried out in poly(tetrafluoroethylene)-lined stainless-steel containers under auto-

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geneous pressure. The reaction of $FeCl_3 \cdot 6H_2O$ (12.5 mmol), H_2O (870 mmol), H_3PO_4 (37.5 mmol), and *en* (62.5 mmol) at 190°C for 24 h yielded products containing two well distinct crystalline phases: a fine yellow crystalline solid and large black crystals. The phases could easily be separated: the black phase settled rapidly, whereas the yellow phase remained suspended in water long enough so as to be separated from the black phase by decanting. The products were washed with distilled water and dried at 80°C.

3. Instrumentation

The crystalline products were characterized by X-ray powder diffraction analysis (Simens D5000 diffractometer using CuKα radiation). Scanning electron microscopy (SEM) (JEOL JSM 5800) was used for the determination of crystal morphologies and dimensions.

Elemental composition of the products (Fe, P) was determined by using JEOL 5800 SEM with an energy dispersive X-ray analyser attachment (EDX). Carbon, hydrogen and nitrogen were determined with a standard C–H–N analyser.

Thermal analyses were performed using TG 951 and DSC 910 modules (TA Instruments, USA). Samples were heated in a 50 ml/min flow of helium in the temperature range from 20 to 800°C at a heating rate of 10°C/min.

4. Results and discussion

The synthesis of iron phosphate using 1,2-diaminoethane as the structure-directing agent yields two crystalline phases. In an attempt to obtain single phase product, we examined various molar ratios of reactants under various crystallization conditions (time and temperature). The reaction mixture composition reported here seems to be an optimal one. It has also been found that the crystallization at 190°C for 24 h results in a high yield (~90%) and gives the yellow phase, whereas a longer treatment (168 h) at the same temperature yields the black phase as a main one.

Crystal habits of the products are shown in Fig. 1. Black phase exhibits large truncated-edge cube-like crystals (>100 μm) while the yellow phase consists of plate-like crystals (~10–30 μm) mutually combined into aggregates. Elemental analysis when considering TGA and C–H–N-analysis results gives the following overall chemical formulas:

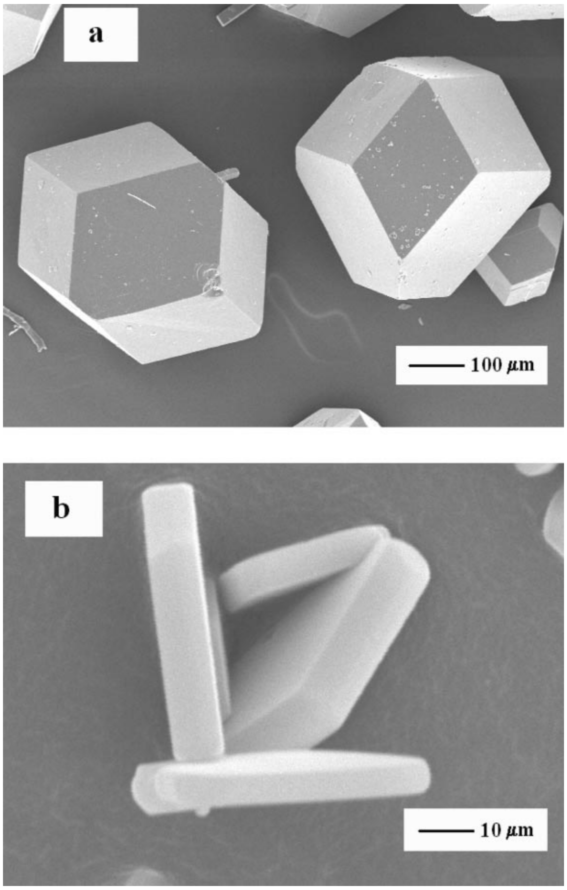

Fig. 1. Crystal morphologies of black (a) and yellow (b) products.

Black phase : $FePO_4 \times 0.5en \times 0.25H_2O$

Yellow phase : $FePO_4 \times 0.5en \times H_2O$

The XRD patterns of the products are given in Fig. 2. Although the chemical formulas are similar, indicating a difference only in water content, the diffractograms show completely different crystal phases. The first phase is consistent with a three-dimensional (3-D) open-framework, mixed valence (Fe^{3+}/Fe^{2+}) iron phosphate [9]. Until now it has been known that crystals of this solid appear as a co-product in very low yield (~1%) obtained from a fluoride medium in the presence of 1,2-diaminoethane as template. The

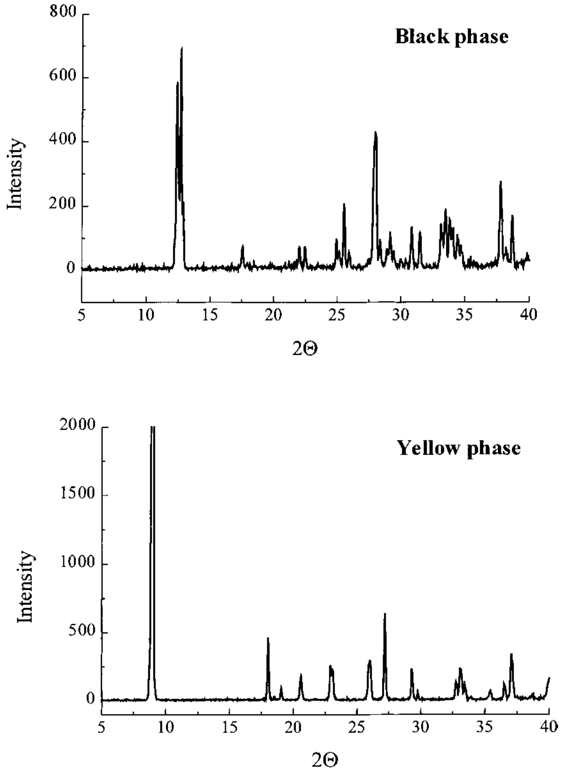

Fig. 2. XRD patterns of the products.

diffractogram of the second, yellow phase corresponds to that of the layered two-dimensional (2-D) iron phosphate [11].

The organic (*en*) species are occluded within both the framework structures. The 3-D framework contains protonated *en* species ($en\mathrm{H_2}^+$) strongly H-bonded to the oxygen atoms of the framework [9]. The structure of the 2-D iron phosphate consists of Fe–O–P chains linked into the sheets that are separated by $en\mathrm{H_2}^+$ ions. The $en\mathrm{H_2}^+$ species connect adjacent layers via a complicated hydrogen bonded network [11].[1]

Fig. 3 shows TGA and DSC curves of the products. Up to ~400°C, both TGA and DTG profiles are not significantly different for both the products. It is evident that there is no weight loss up to 200°C. For the black phase, that indicates that water molecules (which together with *en* occupy the framework tunnels) are strongly bounded to the framework. Accordingly, over the 200–400°C range, the black phase displays two DTG maxima at 354 and 370°C, respectively. The yellow phase exhibits one sharp DTG maximum at 314°C. Finally, for both the solids, it can be seen that the removal of hydroxyl groups (i.e. water molecules) and *en* proceeds simultaneously. However, it is evident that the major difference between the phases appears in the weight loss that occurs at higher temperatures. For the black phase the weight loss up to 400°C is the major one. Namely, a 15.1% weight loss is observed up to 400°C, the overall weight loss (up to 800°C) being 20.1%. For the yellow phase, there are two approximately equal weight losses. The first loss (12.6%) takes place within the same temperature range as for the black phase, while the second one (11.7%) is over the range from 500 to 650°C. Accordingly, the high-temperature weight loss for the yellow phase is higher than that for the black one. This seems unexpected, since it has been known that a low-degradation temperature of organic mole-

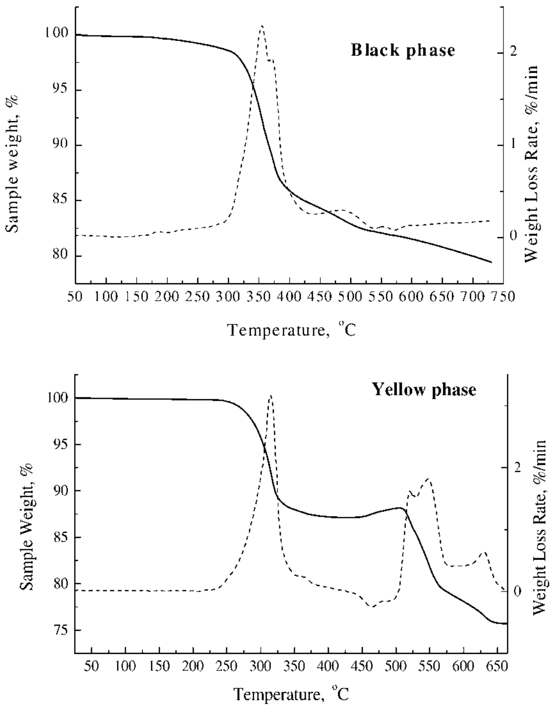

Fig. 3. TGA and DTA curves of the products.

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[1] Fe(III) ions are coordinated not only by four oxygen atoms from $\mathrm{PO_4}$ tetrahedra but also by bridging OH groups. The resulting negative charge of the framework is compensated for by the interlayer $en\mathrm{H_2}^+$ cations.

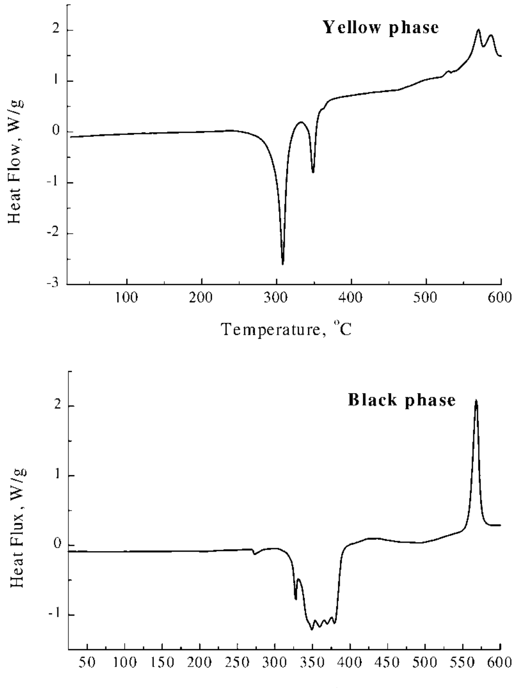

Fig. 4. DSC profiles of the products.

cules is characteristic of a layered structure [21]. This could suggest stronger '*en*-FePO' interactions in the yellow product than in the black one.

DSC profiles of the solids are given in Fig. 4. The DSC curve of yellow product shows two sharp endotherms centred at 308 and 348°C, and two exotherms at 569 and 585°C. The endotherms are attributed to hydroxyl removal and organic decomposition, respectively, while appearance of the exotherms indicates a two-step structural transformation of the FePO framework. Black product displays significantly different DSC profile. Although it also exhibits two endotherms, the second endotherm consists of four well distinct peaks. Thus, the first endotherm in DSC curve of black phase is centered at 328°C, while the others are at 350, 360, 369 and 389°C. It seems likely that the first one is due to the water removal, while the others indicate the decomposition of *en*. Several-step decomposition of the organics may have at least two origins: (1) all *en* species are not crystalographically equivalent or/and (2) '*en*-FePO' interactions differ. The sharp exotherm at 568°C indicates that the process of the loss of water and en causes a structural transformation of the FePO framework.

The thermal decomposition of the products has also been studied by high-temperature X-ray diffraction.

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