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Thermoanalytical investigation of nanocrystalline iron (II) phosphate obtained by spontaneous precipitation from aqueous solutions

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Abstract

$Fe_3(PO_4)_2{\cdot}8H_2O$ has been precipitated under supersaturation conditions from deaerated $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and K_2HPO_4 aqueous, ethanol–water and iso-propanol–water solutions at pH = 6.5 and ambient temperature. The precipitates have been characterised by TG/DTG/DTA and DSC techniques, chemical analysis, BET, and X-ray powder diffraction. The presence of ethanol and iso-propanol in the spontaneous precipitation process of ferrous phosphate leads to highly crystalline powder. Thermal treatment at 500 °C yields a poorly crystalline dehydrated iron phosphate.

Keywords: $Fe_3(PO_4)_2{\cdot}8H_2O$; Thermal analysis; Nano-sized particles; X-ray powder diffraction

1. Introduction

Soft solution processing is gaining interest for the preparation of inorganic materials because it allows for the preparation of powders at low temperatures using aqueous solution systems (AS) in environmentally benign conditions. It includes, precipitation methods, sol–gel process, hydrothermal techniques, which provide intimate mixing of the component elements in the solution allowing finer particles and high-purity materials to be produced by rapid homogeneous nucleation.

Recently, in the field of lithium ion batteries cathode materials are beginning to be prepared by solution-based methods [1]. $LiFePO_4$ is a candidate material for rechargeable lithium ion batteries, owing to its good electrochemical performances. In addition iron is environmentally friendly and cheap. However its preparation by the generally “high temperature” methods induces the sintering and aggregation of particles, which are deleterious for its electrochemical performance [2]. Nano-sized powders are desirable as starting precursors because it is expected that the final powders will reflect the homogeneity of the precursors. $Fe_3(PO_4)_2$ has been employed as the source of iron in the synthesis of $LiFePO_4$ [3].

Iron (II) phosphate is usually synthesised by precipitation following the addition of a solution sodium phosphate to a solution of iron (II) sulphate at 60–80 °C. Several acid phosphate are also known, e.g. $FeHPO_4{\cdot}H_2O$, $FeHPO_4{\cdot}2H_2O$ and $Fe(H_2PO_4)_2{\cdot}2H_2O$ [4].

In the present paper we report on the synthesis of $Fe_3(PO_4)_2{\cdot}8H_2O$ by spontaneous precipitation from deaerated $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and K_2HPO_4 aqueous, ethanol–water and iso-propanol–water solutions at pH = 6.5 and ambient temperature. The

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precipitates have been characterised by thermoanalytical techniques, chemical analysis, BET, and X-ray powder diffraction.

2. Experimental

2.1. Instrumentation

A TG–DTA apparatus SDT 2960 (TA Instruments, Dorking, England) was used. Samples between 5 and 10 mg were heated over the temperature range from ambient to 800 °C at a heating rate of 10 °C min^{-1} in N_2 at a flow rate of 100 ml min^{-1}. α-Al_2O_3 was used as reference material. Samples were run in open platinum pans. The MDSC 2920 (TA Instruments) was used for the DSC experiments. Samples were analysed in aluminium pans with lids, in an atmosphere of dry nitrogen flowing at 120 ml min^{-1}. Samples were equilibrated at −20 °C for 5 min and then ramped at 10 °C min^{-1} to 600 °C.

pH was measured with a SA520 pH-meter (Orion, Beverly, MA, USA), using a C2005-8 red rod combined pH electrode (Radiometer, Copenhagen, Denmark). For calibration, standard buffer solutions from Aldrich were used.

The elemental composition of the precipitates (Fe, P) was determined by flame and graphite atomic absorption spectrometry (Varian 220 FS, Melgrave, Vic., Australia), after dissolution of the powders in dilute hydrochloric acid. The amount of iron (II) in the samples was determined by automated potentiometric titration using 0.1 N $K_2Cr_2O_7$ standard solution.

The specific surface area of precipitates was measured using the BET method by nitrogen absorption at liquid nitrogen temperature (Nova 2000, QuantaChrome, FL, USA). Repetitive adsorption–desorption was employed to clean up the surface [5]. The estimated equivalent spherical diameter R_{BET} (nm) was calculated from surface area data obtained by a single-point analysis, S_s (m^2/g), and the sample density ρ_t (g/cm^3) using the following relationship:

$$R_{\text{BET}} = \frac{6000}{\rho_t S_s}$$

X-ray powder diffraction analysis was conducted with Philips PW 3710 diffractometer using Cu Kα radiation.

2.2. Reagents and standard solutions

Ultra-high-purity water (18 MΩ cm) obtained from a Milli-Q water production system (Millipore, Bedford, MA) and filtered through a 0.22 μm membrane filter was used to prepare all solutions and dilutions. $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ and K_2HPO_4 (Reagent Grade, Carlo Erba, Italy) crystalline solids were dissolved in deionized water to prepare iron and phosphate stock solutions and standardised by atomic absorption spectrometry. Stock solutions were always prepared just before each experiment. Stock standard solutions of iron and phosphorus (Aldrich) at 1000 ppm were used for the preparation of the working standard solutions for the iron and phosphorus AAS determination. All acids used were of analytical Reagent Grade. Ammonium hydroxide 32% weight (Electronic Grade, Rudi Pont) was used. Methanol and iso-propanol were used (Reagent Grade, Carlo Erba).

2.3. Preparation

A deaerated 0.1 M $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ solution (having an initial pH of 4.9) was added at ambient temperature to a constantly stirred solution of 0.067 M K_2HPO_4, previously dissolved in deionized water, ethanol–water, and iso-propanol–water solutions and neutralised to pH = 6.5 using concentrated ammonium hydroxide, in a 1:1 volume proportion. A white-blue precipitate started to form immediately.

The precipitates were kept in contact with the mother liquor for 7 days without stirring. The solution pH was monitored daily and adjusted to pH = 6.5. Aliquots of the supernatant were periodically withdrawn; filtered through membrane filter (0.8 μm) and the filtrates were analysed for the total iron and phosphorus content. The precipitates collected on membrane filter (0.8 μm) were washed several times with deionized water to make the powder free from undesired water-soluble impurity species. The recovered precipitates were dried in air in a dry-room (RH < 0.2%) for several days.

3. Results and discussion

The X-ray powder diffraction patterns of the AS-prepared materials obtained by spontaneous

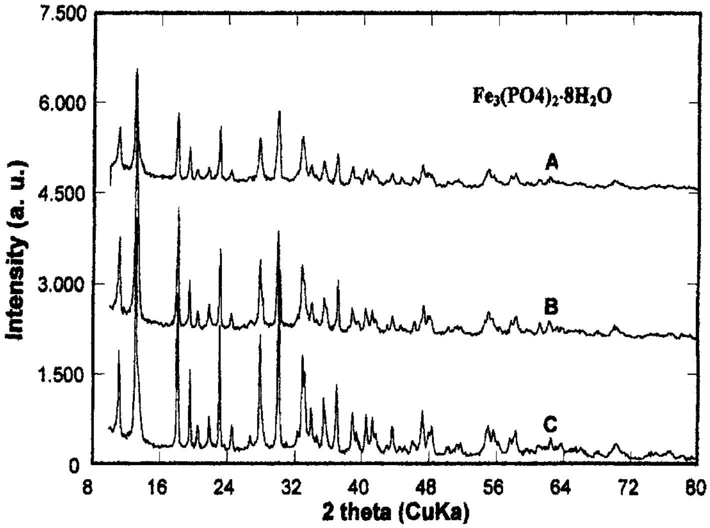

Fig. 1. XRD patterns of the AS-prepared iron (II) phosphate powders obtained in: (A) water; (B) water–methanol; (C) water–iso-propanol solutions.

precipitation from deaerated iron (II) and dipotassium phosphate aqueous, water–methanol, and water–iso-propanol solutions at pH = 6.5 and ambient temperature are shown in Fig. 1. All the characteristic peaks belong to the pure crystalline phase of $Fe_3(PO_4)_2{\cdot}8H_2O$ [6].

The results of the chemical analysis of the precipitates give rise to a molar ratio $Fe_{total}{:}P_{total} = 3{:}2$. The results of the potentiometric determination gives a 30 wt.% Fe^{2+} in all compounds. The onset of the precipitation resulted in a drop in the solution pH according to the following equation:

$$3Fe^{2+}\,(l) + 2HPO_4{}^{2-}\,(l) + 8H_2O\,(l) \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O\,(s) + 2H^+\,(l) \qquad (1)$$

In Table 1 the concentrations of iron and phosphate in the mother liquor and the solution pH values are reported as a function of the number of days of storage. As it can be seen the high stability of the pH in the solution indicates that the precipitation process has completely stopped in few minutes. The yields were within 1%, relative standard deviation.

Specific surface area of the AS-prepared iron (II) phosphate powders ranged between 20 and 25 m^2/g (±2 m^2/g), which corresponds to an estimated equivalent diameter (d_{BET}) of 21–20 nm. Typically particles with average diameters between 80 and 200 nm were reproducibly obtained.

Table 1
Concentration of iron and phosphate in the mother liquor and the solution pH values as a function of days of storage

Time days	[Fe]/10^{-4} M	[P]/10^{-4} M	pH
3	1.1	0.71	6.50
4	1.1	0.71	6.49
5	1.1	0.70	6.48
6	1.0	0.70	6.50
7	1.0	0.70	6.50

The TG/DTG/DTA curves of the AS-prepared precipitate obtained from aqueous solution is shown in Fig. 2a. The TG curve shows a weight loss between 50 and 500 °C, which is related to elimination of crystallisation water. It can be divided in two areas: 50–200 and 200–500 °C. The respective weight losses are 18.6 and 6.9% by mass, which correspond to 6 and 2 mol of water. The total mass loss is 25.5% ($8H_2O$). In the DTG curve are observed the corresponding peaks at 133, 195 and 283 °C. Five endothermic effects over the temperature region are shown in the DTA curve, namely at 88, 108, 133, 195, and 283 °C. At higher temperatures two width exothermic peaks are displayed in the DTA curves, namely, at 544 and 588 °C, which are not accompanied by appreciable weight loss in the TG curve.

The TG/DTG/DTA curves of the AS-prepared precipitate obtained from water–ethanol medium aqueous solution is shown in Fig. 2b. The TG curve shows that the elimination of crystallisation water occurs between 50 and 500 °C in three overlapping stages: 50–161, 161–202, and 202–500 °C. The respective

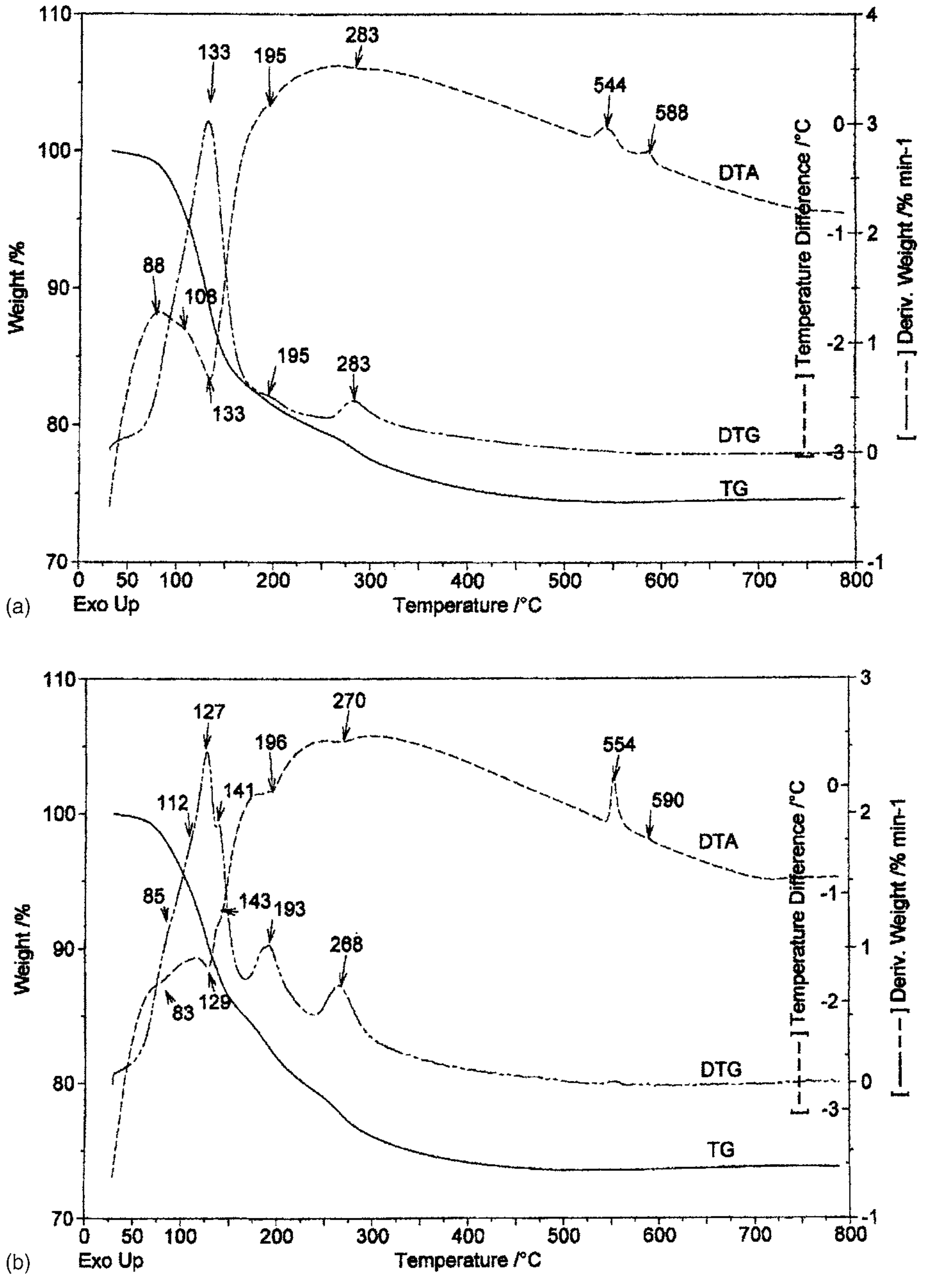

Fig. 2. TG/DTG/DTA curves of the AS-prepared precipitates obtained from: (a) water; (b) water–ethanol; (c) water–iso-propanol solutions. Heating rate of 10 °C min^{-1} in N_2 at flow rate of 100 ml min^{-1}.

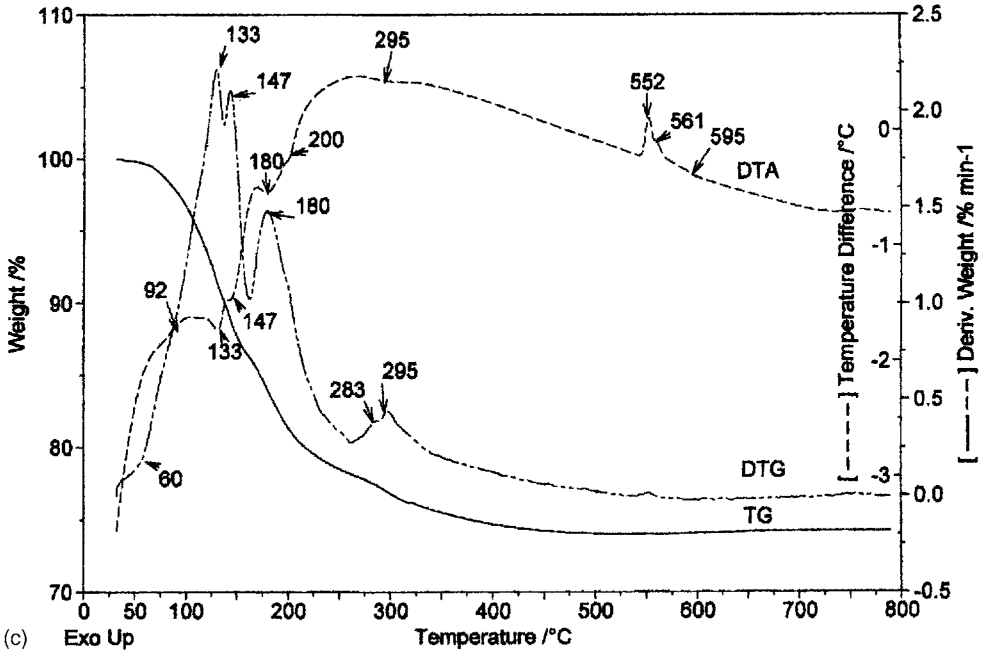

Fig. 2. (*Continued*).

weight losses are 14.4, 5.8 and 5.9% by mass, which correspond to 4, 2 and 2 mol of water. The total mass loss is 26.3% ($8H_2O$). In the DTG curve are observed the corresponding peaks at 85, 112, 127, 141, 193 and 268 °C. Five endothermic effects over the temperature region are shown in the DTA curve, namely at 83, 129, 143, 196, and 270 °C. At higher temperatures a large exothermic peak at 554 °C is displayed in the DTA curve, followed by a small exothermic effect at 590 °C, which are not accompanied by appreciable weight loss in the TG curve.

The TG/DTG/DTA curves of the AS-prepared precipitate obtained from water–iso-propanol medium is shown in Fig. 2c. The TG curve shows that the displacement of crystallisation water occurs between 50 and 500 °C in three overlapping steps: 50–157, 157–222, and 222–500 °C. The respective weight losses are 13.4, 8.1, and 4.3% by mass, which corresponds to 4, 3, and 1 mol of water. The total mass loss is then 25.4% ($8H_2O$). In the DTG curve are observed the corresponding peaks at 60, 133, 147, 180, 283 and 295 °C. Six endothermic effects over the temperature region are shown in the DTA curve, namely at 92, 133, 147, 180, 200 and 295 °C. At higher temperatures three exothermic effects are displayed in the DTA curves, namely, at 552, 561, and 595 °C, which are not accompanied by appreciable weight loss in the TG curve.

The DSC curves of all the precipitates show a single large endothermic peaks at 161, 157 and 150 °C, respectively (Fig. 3). The profiles of their peaks are quite similar.

In order to know the exact number of crystallisation water moles and the effect of its removal, thermal treatment was carried out in the DTA unit. When the temperature of 600 °C is reached with flowing nitrogen, the heating is stopped and the samples are cooled down to room temperature and subjected to X-ray analysis. XRD patterns of the final products show the formation of a poorly crystallised dehydrate $Fe_3(PO_4)_2$ phase. However, when the AS-prepared precipitates are submitted to heat at 500 °C in an oven in argon + 5% hydrogen atmosphere the samples obtained by precipitation from water and water–methanol systems undergoes to strong dehydration as identified by XRD (Fig. 4), whereas the sample obtained by precipitation from water–iso-propanol system does not show the formation of the crystalline anhydrous salt. However,

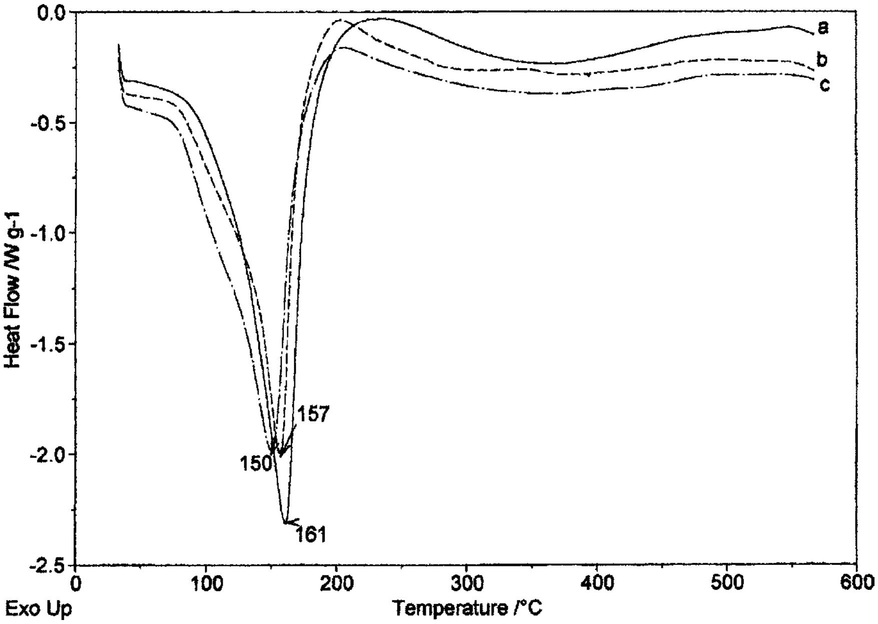

Fig. 3. DSC signals of the AS-prepared precipitates obtained from: (a) water; (b) water–ethanol; (c) water–iso-propanol solutions. Heating rate of 10 °C min^{-1} in flowing N_2.

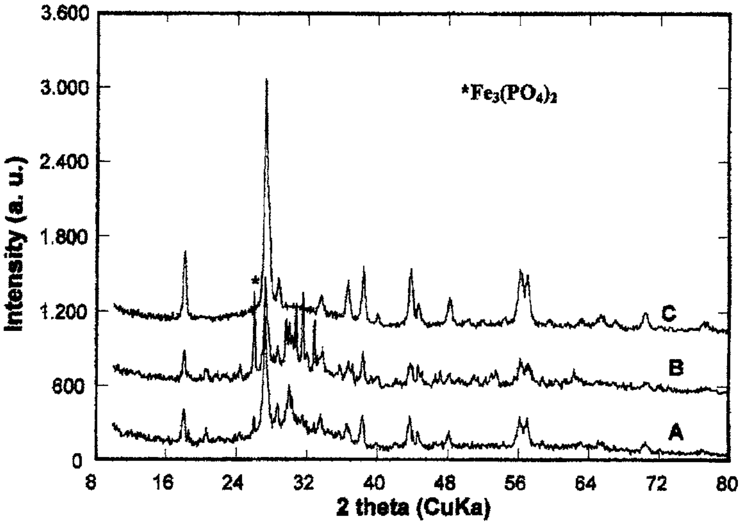

Fig. 4. XRD patterns of the precipitate powders obtained from: (A) water; (B) water–methanol; (C) water–iso-propanol solutions after thermal treatment at 500 °C in Ar + 5% H_2.

the single phase of the final product of the thermal heating of the precipitate from water–iso-propanol system has not been clearly identified by us.

4. Conclusions

$Fe_3(PO_4)_2 \cdot 8H_2O$ has been obtained by spontaneous precipitation from deaerated $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and K_2HPO_4 aqueous, ethanol–water and iso-propanol –water solutions at pH $=$ 6.5 and ambient temperature. The presence of ethanol and iso-propanol in the spontaneous precipitation process of ferrous phosphate leads to highly crystalline powder and this is reflected in a more evidence of their dehydration process during heating. The final dehydration product is $Fe_3(PO_4)_2$, which depends on the surrounding atmosphere during the thermal treatment.

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