The structure directing role of 1,3-diaminopropane in the hydrothermal synthesis of iron(III) phosphate

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Abstract: 1,3-Diaminopropane (DAP) was used as a structure-directing agent for the hydrothermal synthesis of an organically templated iron phosphate. During crystallization at 180 ºC, iron phosphate (FePO-DAP) with a layered structure was formed after one day. Longer crystallization yielded a mixture of FePO-DAP and leucophosphite, raising the question whether a transformation of FePO-DAP to leucophosphite occurs, or wheter DAP decomposes under hydrothermal conditions resulting in leucophosphite formation. Lattice energy and free energy calculations strongly support the supposition that a decomposition of DAP occurs prior to the formation of leucophosphite.

Keywords: FePO, iron phosphate, hydrothermal synthesis, GULP, open-framework.

INTRODUCTION

Aluminosilicate and aluminophosphate molecular sieves are important industrial materials, which have been widely used as ion-exchangers, adsorbents and catalysts. Recently, there has been considerable interest in the preparation of open-framework solids based on transition metal phosphates owing to their potential applications in the areas of catalysis, optics, electronics, and magnetics.[1–3] In this sense, organically templated iron phosphates (FePO) are of particular interest because of their rich structural chemistry.[4] FePOs can exhibit 1-D chain structures, 2-D sheet structures, and 3-D open-framework structures.[5] The main reason for the structural diversity of iron phosphates probably lies in the fact that iron possesses the ability to easily adopt different oxidation numbers (+2 and/or +3) as well as different coordination geometries.

Recently, we have begun an investigation of the hydrothermal synthesis of FePOs exploring different organic species as structure-directing agents (templates).[6,7] The obtained FePOs crystallized under rather mild conditions which

confirmed the enhanced structural diversity. In some cases, even water molecules (usually present in the voids of the structures) seemed to play a crucial structural role during crystallization. For example, two completely different FePO structures arise from a same reaction mixture exhibiting essentially the same chemical formula but differing only in the water content.[6]

In this paper we report the results of employing 1,3-diaminopropane (DAP) as a template in the crystallization of FePO. Until now, there have been two FePO structures reported with this diamine.[8,9] However, both were obtained under reaction conditions (temperature, mole ratio of the reactants, duration of the crystallization) different from the conditions reported here.

EXPERIMENTAL

The synthesis was carried out hydrothermally in poly(tetrafluoroethylene)-lined stainless-steel containers. The reactants were used in the following mole ratio: $FeCl_3 : 2H_3PO_4 : 5DAP : 100H_2O$, whereby a dark-red solution resulted. The solution was prepared by the successive addition of phosphoric acid and DAP to an aqueous solution of $FeCl_3$ under vigorous stirring (an Ultra-Turrax T 25; Janke and Kunkel GmbH was used). The initial pH was about 11 which was decreased to 10 by the end of the reaction. Crystallization was performed at 180 ºC for 1–8 days. The crystalline products were filtered and washed with distilled water, ultrasonically treated in order to remove amorphous impurities, and air-dried.

Instrumentation

The crystal morphology and elemental analysis (Fe and P) were determined using a JEOL 5800 SEM with an energy disperse X-ray analyzer attachment (EDX). Carbon, hydrogen and nitrogen were determined using a standard C-H-N analyzer.

The crystallinity of the product was controlled by X-ray powder diffraction (XRD) using a Phillips diffractometer PW 1710 (with CuKα radiation) in 0.04º 2θ steps from 5–50º 2θ with 1 s per step. Thermogravimetrical analyses and differential scanning calorimetry (TGA and DSC) were performed using a SDT 2960 simultaneous DSC/TGA instrument (TA Instruments) at a heating rate of 10 ºC min^{-1} under static air atmosphere.

The ^{57}Fe Mössbauer transition spectra were recorded on a constant acceleration spectrometer at 300 K with ^{57}Co in Rh matrix as the source. Isomer shifts hyperfine parameters were refined to Lorenzian lines using a least-squares fitting procedure.

Computational details

The lattice energy and free energy calculations for $[H_3N(CH_2)_3NH_3]Fe_2O(PO_4)_2$ (FePO-DAP) and $NH_4Fe_2(OH)(H_2O)(PO_4)_2 \cdot H_2O$ (leucophosphite) were carried out using the program GULP.[10] GULP (general utility lattice program) implements a lattice energy minimization technique.[11] The interactions between atoms are expressed by a Buckingham potential (consisting of a repulsive exponential and an attractive dispersion term between pairs of species) plus a coulombic potential. The polarizability of the highly polarizable oxygen ions is represented by a shell model,[12] which comprises rigid cores coupled to the shells by a harmonic spring. The shell model absorbs most of the effects that can arise through partial covalency of the system.[13] To represent covalency more realistically, a term describing bond bending is also included.[13] Such a use of the potentials together with formal ionic charges has in recent years been successfully applied in the investigation of microporous materials.[14-19]

The experimentally determined crystal structures of FePO-DAP[8] and leucophosphite[20] were used in the GULP calculations. Although Ref. 20 refers to an aluminum compound, the iron material has been found to be isomorphous.

RESULTS AND DISCUSSION

Red-orange plate crystals were obtained from the reaction mixture heated for 1 day (Fig. 1a). According to the XRD pattern given in Fig. 2, these crystals belong to only one crystalline phase. A suitable crystal was also taken to determine its unit cell dimensions. The crystal data together with elemental analysis results lead to the conclusion that the obtained FePO-DAP, $[H_3N(CH_2)_3NH_3]Fe_2O(PO_4)_2$, possesses identical structural parameters as that obtained in Ref. 8. The structure contains 2-D sheets constructed from FeO_5 units, which share corners with the phosphate tetrahedra. Diprotonated DAP species are located between the layers.
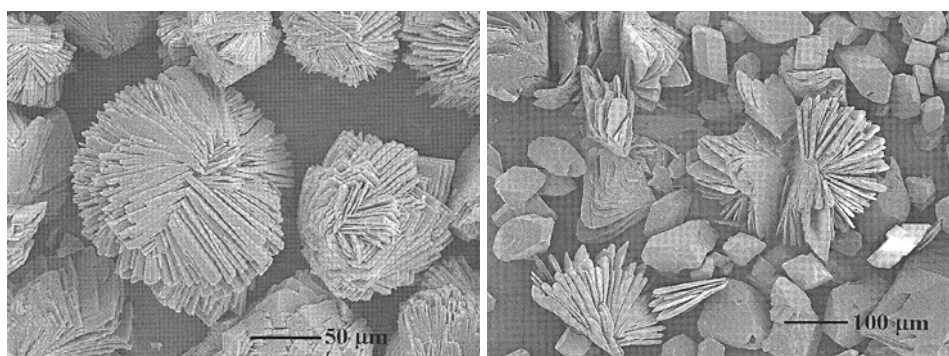

Fig. 1. SEM microphotograph of FePO-DAP (a), and of the mixture of FePO-DAP and leucophosphite (b).

Since Mössbauer spectra of organically templated FePOs are scarce in the literature, a room-temperature Mössbauer spectrum of FePO-DAP was recorded
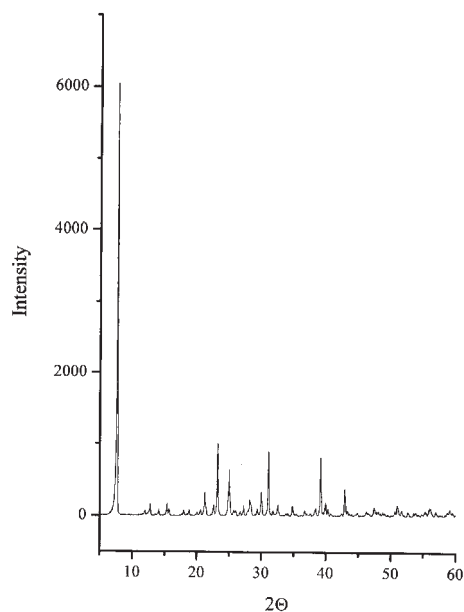

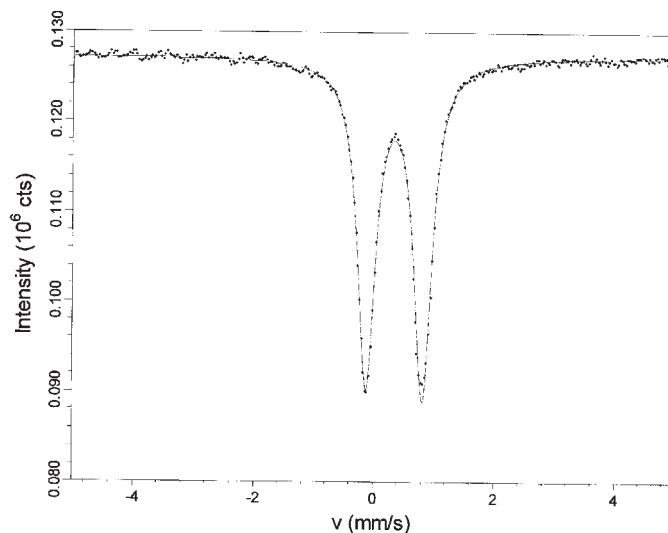Fig. 2. X-ray powder diffractogram of FePO-DAP.

Fig. 3. Room temperature Mössbauer spectrum of FePO-DAP.

(Fig. 3). The spectrum shows the presence of a symmetrical doublet with $CS = 0.35$ mm/s (chemical shift), $QS = 0.94$ mm/s (quadruple splitting), and $FWHM = 0.36$ mm/s (full width at half-maximum). The CS value characterizes high spin Fe^{3+} in a bipyramidal environment.[21]

If the reaction mixture is hydrothermally treated for a longer time period, FePO-DAP is no longer the sole crystalline product. Thus, the SEM picture of the product obtained after an 8 day long crystallization shows a mixture of two crystalline phases (Fig. 1b). Beside the orange-colored FePO-DAP plates, a new phase
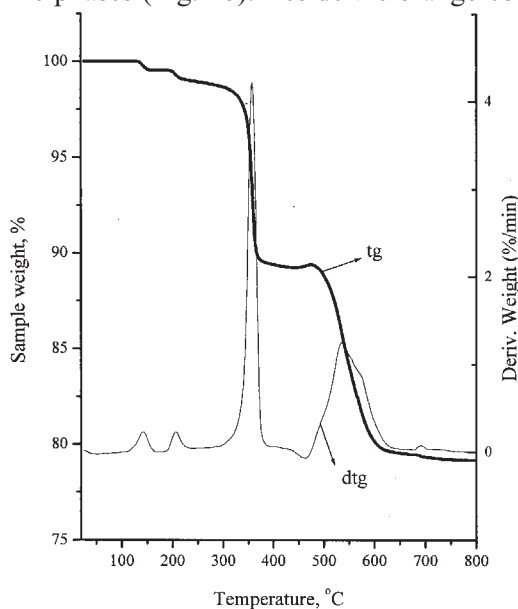

Fig. 4. TG/DTG curves of FePO-DAP.

featuring truncated polyhedral-shaped dark red crystals is also present; the latter can be separated manually from the FePO-DAP crystals. The XRD pattern of this phase shows that it belongs to leucophosphite, hydrated ammonium iron(III) phosphate – $NH_4Fe_2(OH)(H_2O)(PO_4)_2 \cdot H_2O$. This means that during prolonged hydrothermal crystallization, either the initially formed FePO-DAP partly transforms to leucophosphite, or a decomposition of DAP occurs in the reaction mixture yielding NH_4^+ ions which then template the formation of leucophosphite. It is known that some templates can undergo decomposition in the course of the crystallization process, and that the species formed by such decomposition can themselves act as templates.[22,23] It is also known that under hydrothermal conditions, a transformation of one open-framework metallophosphate crystalline phase into another crystalline phase can take place.[24]

TABLE I. Lattice energies (E) and lattice free energies (G) of $[H_3N(CH_2)_3NH_3]Fe_2O(PO_4)_2$ (FePO-DAP) and $NH_4Fe_2(OH)(H_2O)(PO_4)_2 \cdot H_2O$ (leucophosphite) obtained by the GULP calculations (in kJ per mole Fe).

	E	G
FePO-DAP	–26470	–26430
leucophosphite	–24850	–24740

In order to explain the formation of leucophosphite together with FePO-DAP on prolonged crystallization, the lattice energies and free energies of FePO-DAP and of leucophosphite were calculated to estimate the relative stabilities of the two solids. The energies were calculated using the program GULP[11] and the results are listed in Table I. It is evident that FePO-DAP has a more negative lattice energy (1620 kJ per mole Fe lower) as well as a more negative lattice free energy (1690 kJ per mole Fe lower) than leucophosphite. This strongly suggests that it is unlikely that FePO-DAP simply transforms to leucophosphite under hydrothermal conditions. Instead, it is more probable that, during the above-mentioned prolonged crystallization process, a decomposition of DAP in the reaction system occurs leading to the formation of ammonium ions which template the formation of leucophosphite.

It is interesting that the DAP species inside the FePO structure decomposes in such manner that in the first step the mass loss of about 10.5 % corresponds to the release of C_3H_4. The product left after this stage contains ammonium cations (according to the C,N analysis) and is crystallographically amorphous. It is thermally stable over the 370–480 ºC range (Fig. 4). The ammonium cations are released from the system in the second step, which is completed up to 640 ºC.

И З В О Д

СТРУКТУРНО-УСМЕРАВАЈУЋА УЛОГА 1,3-ДИАМИНОПРОПАНА У ХИДРОТЕРМАЛНОЈ СИНТЕЗИ ГВОЖЂЕ(III)-ФОСФАТА

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1,3-Диаминопропан (DAP) је употребљен као структурни агенс у синтези гвожђе-фосфата. Током једнодневне кристализације на 180 ºC долази до настајања гвожђе-фосфата са слојевитом структуром (FePO-DAP). У току продужене кристализације настаје смеша FePO-DAP и леукофосфита што отвара питање да ли долази до трансформације FePO-DAP у леукофосфит, или се DAP разлаже у условима хидротермалне кристализације уз даљи настанак леукофосфита. Прорачун енергије решетке и слободне енергије доказује да разградња DAP претходи настанку леукофосфита.

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