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Synthesis, structure and phase transformation of layered iron phenyl phosphate

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ABSTRACT

Iron phenyl phosphate (FePP) was synthesized from a mixture of $FeCl_3$ and phenyl phosphate ($C_6H_5PO_4H_2$) in aqueous media. X-ray diffraction (XRD) pattern of the FePP exhibited a peak at $2\theta = 5.6^\circ$ and a broad hump at $2\theta = 15–35^\circ$. The FePP was plate-like particles and gave rise to the lattice patterns having uniform alternating spacings of ca. 1.5 nm and ca. 1.2 nm. The chemical formula of FePP could be shown as $Fe(OH)(C_6H_5PO_4H)_{1.6}(H_2PO_4)_{0.4}\cdot5.1H_2O$. These facts allow us to infer that the FePP was composed of a multilayer alternating bilayer of phenyl groups and amorphous iron phosphate phases. The synthetic FePP particle was aged at pH 6.0 and 85 °C for different periods of 0–120 h in aqueous media. Aging for 96 h disappeared the FePP and formed monoclinic $FePO_4\cdot2H_2O$. Further, the monoclinic $FePO_4\cdot2H_2O$ transformed in orthorhombic $FePO_4\cdot2H_2O$ by aging for 120 h. The orthorhombic $FePO_4\cdot2H_2O$ was rod-shaped particles with the size of ca. 18 nm in width and ca. 45 nm in length and its specific surface area was 25 $m^2\,g^{-1}$. From these results, it can be presumed that the FePP is dissolved, hydrolyzed and reprecipitated to crystalline $FePO_4\cdot2H_2O$.

1. Introduction

Iron(III) phosphate ($FePO_4$) and iron(III) phosphate hydrate ($FePO_4\cdot2H_2O$) are used in steel and glass industries [1,2] and are developed as catalyst [3–6] and removal of heavy metals [7]. Recently, these materials are focused on application for cathodes in lithium secondary batteries [8–18]. There are many studies for preparation of $FePO_4$ and $FePO_4\cdot2H_2O$. Generally, $FePO_4\cdot nH_2O$ is obtained by mixing aqueous Fe^{3+} and $PO_4{}^{3-}$ solutions and the material adopts a berlinite structure related to α-quartz form at normal pressure [19]. While, synthesis of monoclinic and orthorombic $FePO_4\cdot nH_2O$ is able to be prepared by extracting Li in lithium iron phosphate $LiFePO_4$ [18].

On the other hand, organically templated framework iron phosphates with one-dimensional and two-dimensional structures have been developed because of their potential uses in catalysis, selective sorption and other applications [20–23]. Mandal et al. have reported the preparation and structure of one-dimensional iron fluro-phosphate, $[NH_2CH_2CH_2CH(NH_3)CH_2CH_3]^{2+1}{}_\infty[FeF(HPO_4)_2]^{2-}$ and quasi-one-dimensional three-legged iron phosphate ladder, $[H_3N(CH_2)_3NH_2(CH_3)_3NH_3][Fe_3F_6(HPO_4)_2(PO_4)]\cdot3H_2O$ [20,21]. Two-dimensional fluorinated iron phosphate, $Fe_2F_2(2,2'\text{-bpy})(HPO_4)_2(H_2O)$ (bpy = 2,2′-bipyridine) was synthesized by Chang et al. [22]. Also, Meng et al. prepared the organic amine-coordinated iron phosphate compound, $[Fe(phen)(HPO_4)(H_2PO_4)_{0.5}H_2O]$ (phen = 1,10-phenanthroline), by hydrothermal method [23].

Previously, we reported the synthesis of layered metal (Ca, Al or Ti) organic (alkyl or phenyl) phosphates with two-dimensional structure by a mixture of organic phosphate ions and metal ions in aqueous media [24–27]. These materials are composed of a multilayer alternating bilayer of alkyl or phenyl groups of the phosphates and amorphous metal phosphate phases. Furthermore, it is indicated that the calcium phenyl phosphate is transformed in inorganic calcium phosphate of calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) by hydrolysis at pH ≥ 6.0 in aqueous media [27]. Provided iron phenyl phosphate (FePP) is prepared, inorganic iron(III) phosphate can be obtained from FePP by hydrolysis as well as the case of calcium phenyl phosphate.

The aim of this study was to synthesize the layered iron phenyl phosphate and to elucidate the structure and phase transformation of the material by hydrolysis. So, we prepared FePP by the reaction of Fe^{3+} and phenyl phosphate ions and the resultant was aged at pH 6.0 and 85 °C in aqueous media. The product thus formed was characterized by various means. Based on the results obtained, a phase transformation mechanism of FePP in inorganic iron phosphate was discussed.

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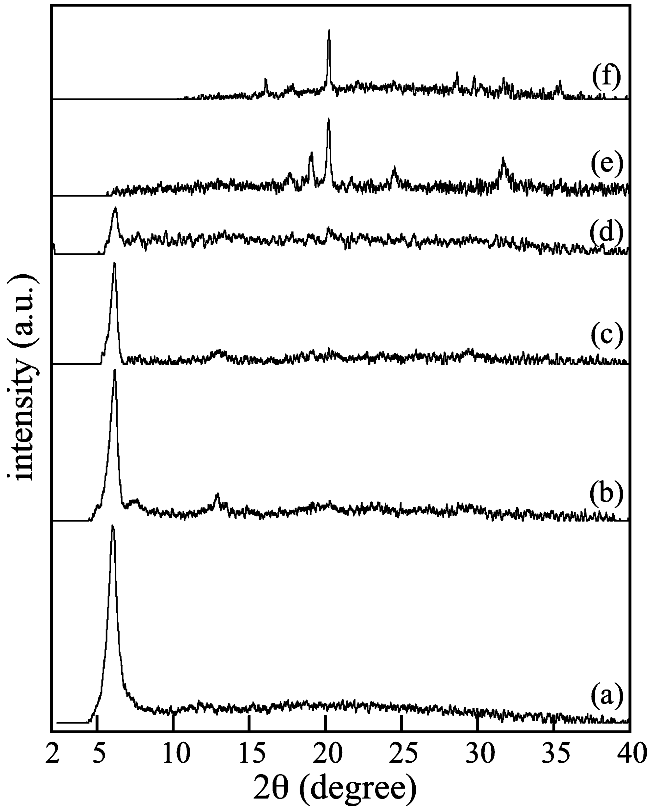

Fig. 1. XRD patterns of (a) FePP and ((b)–(f)) FePP aged for different t_a. t_a (h): (b) 24, (c) 48, (d) 72, (e) 96, (f) 120.

2. Experimental

2.1. Preparation of FePP

FePP was prepared by a following wet method. 6.10 mmol of phenyl phosphate ($C_6H_5OPO_3H_2$: PP) were dissolved into 50.0 ml of distilled-deionized water free from CO_2 in a sealed polypropylene vessel by stirring for 1 h at room temperature. After stirring, 5.0 ml of 310.0 mmol dm^{-3} $FeCl_3$ were added dropwise to the aqueous PP solution. The suspension formed was aged for 1 h under stirring condition at room temperature. The solution pH after preparing the FePP was 1.38. The resultant was filtered off, washed with distilled-deionized water and finally dried at 50 °C in a vacuum oven for 1 day.

2.2. Phase transformation of FePP in $FePO_4 \cdot 2H_2O$

The synthetic FePP particles (500.0 mg) and distilled-deionized water (50.0 ml) were added in a sealed polypropylene vessel. Then, pH of the solution suspending FePP was adjusted to 6.0 by adding 0.01 mol dm^{-3} NH_3 solutions and the suspension was aged at 85 °C for 0–120 h. The resultant was treated and dried as the same procedure employed for FePP as described above.

All the chemicals supplied from Kanto Chemical Co. were reagent grade and were used without further purification.

2.3. Characterization

The products thus obtained were characterized by a variety of conventional techniques. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered CuKα radiation (30 kV, 16 mA). Particle morphology was observed by a JEOL transmission electron microscope (TEM). Carbon content

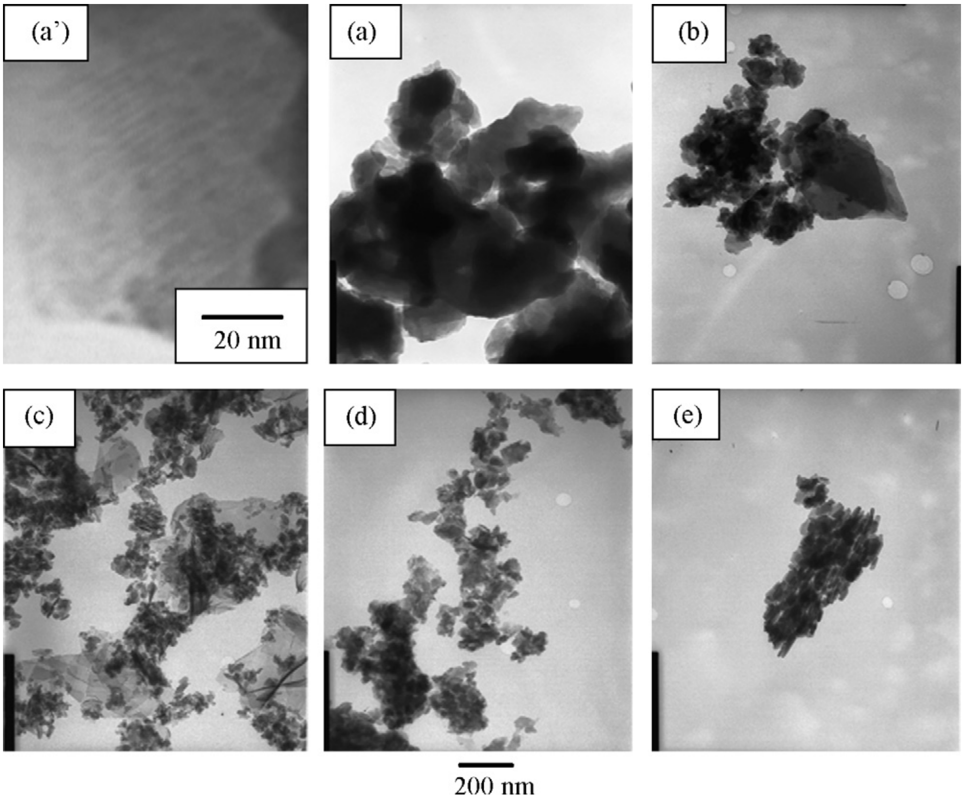

Fig. 2. TEM pictures of (a) FePP and ((b)–(e)) FePP aged for different t_a. t_a (h): (b) 24, (c) 72, (d) 96, (e) 120. (a′): Expanded region of (a).