Synthesis of Novel Lamellar Iron Phosphate

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Meso-structured lamellar iron phosphates with varied *d*-spacings have been synthesized from ferric acetylacetonate and *n*-alkylammonium dihydrogenphosphates, which serve as both template and reactant.

Since the discovery of M41S silica molecular sieves in 1992,[1] several supramolecular assembly pathways have been reported and extended to synthesis of a variety of meso-structured metal oxides[2] and aluminophosphates.[3–6] Compared to a pile of work on synthesis of silica related meso-structured compounds, however, the preparation and characterization of metal phosphates with meso-structure have been less reported, albeit some metal phosphates are also viewed as refractory compounds. Recently, meso-structured V–P–O compounds with either lamellar or hexagonal structure have been prepared.[7–9] Fe–P–O compound is also particularly interesting because it is a useful catalyst for selective oxidation reactions such as oxidative dehydrogenation of isobutyric acid to methacrylic acid, which is a versatile raw material for various polymers.[10] The interest in iron phosphates and related solids having low dimensional, i.e., 1D or 2D structures is currently increasing also due to more applications, such as magnetic application, emerge.[11] Up to date, iron phosphates with interesting microporous structure have been known,[12,13] but no meso-structured Fe–P–O have been reported.

In the present work we report successful synthesis of a set of iron phosphates possessing meso-structure, of which *d*-spacing depends on the size of surfactant molecules used. Alkylammonium dihydrogenphosphates were used as P source and prepared in a manner similar with that reported by Oliver.[14] Ferric acetylacetonate ($Fe(acac)_3$, 2.21 g), used as Fe source, was added to aqueous solution of sodium hydroxide (0.4 g sodium hydroxide dissolved in 10 g distilled water) under vigorous stirring. After stirring the Fe containing solution for 5 h, 0.01 mol alkylammonium dihydrogenphosphate dissolved in the mixture of ethanol and water was added in. The resulted mixture, with composition of 0.67 $Fe(acac)_3$: 1.0 H_3PO_4 : 1.0 $C_nH_{2n+1}NH_2$: 1.0 NaOH : 8.7 EtOH : 200 H_2O, was vigorously stirred for another 1 h followed by heating at 393 K in an autoclave for one week. Then the precipitation, recovered by centrifugation when the autoclave cooled down, was washed thoroughly with water and followed with acetone. At last by drying the solid at room temperature the meso-structured lamellar Fe–P–O compounds was obtained. Powder X-ray diffraction (XRD) measurements were carried out using a Shimadzu XD-3A diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) images were obtained using a JEM-200CX transmission electron microscope with applied voltage of 200 kV. Infrared Spectra (IR) were registered using a Nicolet 170SX FT-IR spectrometer on the sample containing dry KBr pellets. Fe and P contents were determined with a Jarrell-Ash 1100 inductively couple plasma (ICP) spectrometer. Thermal gravimetry (TG) and differential thermal analysis (DTA) curves were recorded on a TA Instrument 2100 at a heating rate of 5 K min^{-1} in N_2 streams. C, H, and N elements were assayed by a Perkin–Elmer CHN elemental analyzer.

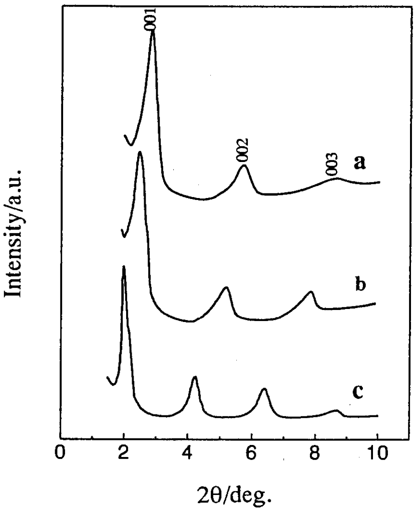

Figure 1. XRD patterns of (a) as-synthesized FePO-$C_{10}NH_2$ samples (b) as-synthesized FePO-$C_{12}NH_2$ samples (c) as-synthesized FePO-$C_{16}NH_2$ samples.

The preliminary indexed XRD patterns of the as-synthesized compounds are presented in Figure 1. The patterns of iron phosphates assembled with alkylammonium clearly demonstrate the lamellar structure with distances between layers from 4.40 to 3.28 nm deduced from values of 001 reflections. The *d* (001) values of the as-synthesized compounds varied with carbon number of alkylammonium main chain. The plots of *d*-spaces against the number of CH_2 units in main chain of the used alkylammonium, shown in Figure 2, gave a straight line with a slope of ~0.2 nm/CH_2, in close agreement with twice the increase of 1.27 Å/CH_2 for an extended alkyl chain. This is similar to that observed in aluminum-base systems.[15] The inorganic layer thickness of 1.4 nm could be deduced from the figure by extrapolation. The angle of alkyl chains of ~40° towards inorganic layer could also be obtained accordingly. The lamellar phase obtained for current meso-structured iron phosphate was further confirmed by TEM images. Figure 3 shows a typical TEM image obtained on a sample with dodecylamine used as template, it reveals an interlayer spacing of ca 3.7 nm. In addition, electron diffraction patterns recorded at the same area indicated that the inorganic layer (Fe–P–O) may have an ordered crystal structure to some extent, deduced from diffuse electron diffraction spots visible in Figure 3 inset. In fact, when

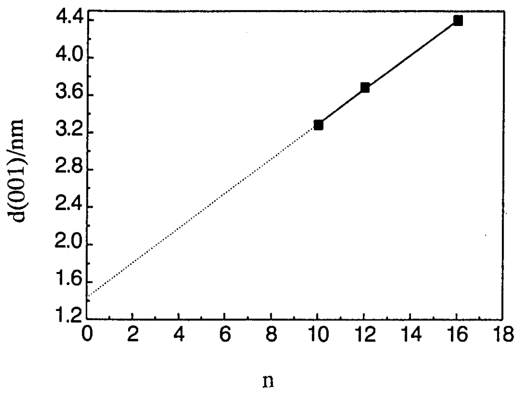

Figure 2. Relationship between the interlayer spacing d(001) of as-synthesized compounds and the carbon number of alkylammonium.

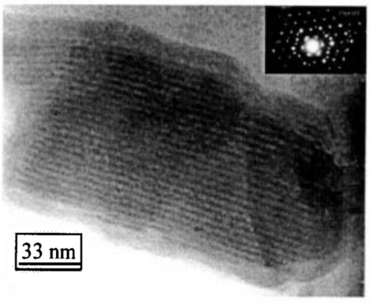

Figure 3. TEM image of as-synthesized FePO-$C_{12}NH_2$ sample and selected-area electron diffraction patterns (the inset).

the alkylammonium templates in the as-synthesized compounds were extracted, the resulted powders showed some characteristic peaks of $FePO_4$ in XRD patterns. It is interesting that the inorganic layer of as-synthesized meso-structured compound has a crystalline structure, which is seldom reported in other meso-structured materials. Yang et al. have reported that walls of meso-porous TiO_2 and WO_3, fabricated by slow hydrolysis of chloride precursors at 313 K, are made up of nanocrystalline oxides, characterized by diffuse electron diffraction rings.[16] Meso-structured crystalline heteropoly compounds with surfactants have also been reported by Iwamoto et al.[17,18]

The absorption peaks around 1571 cm^{-1} and 1523 cm^{-1}, characteristic of $Fe(acac)_3$, totally vanished in FT-IR spectra of as-synthesized sample, indicative of no residue $Fe(acac)_3$ existing in the synthesized samples. The composition of the synthesized samples is $(C_nH_{2n+1}NH_2)_{0.8}Fe(PO_4)_{1.0-1.2}\cdot 0.8H_2O$ (n = 10, 12, 16) deduced from the results of ICP, TG–DTA and elemental analysis. Obviously, part of P source lost during the synthesis, which was also reported in the synthesis of meso-structured zirconium phosphate.[19] In current strategy of synthesis, the alkylammonium phosphate played dual roles, i.e., P supplier as well as template at the same time; and the key to success is ferric acetylacetonate was used as Fe source to get better control on reaction and condensation between Fe and P sources. Moreover, before mixing with P containing solution $Fe(acac)_3$ was partly pre-hydrolyzed in NaOH solution, which would be helpful to shorten crystallization time.

To the best of our knowledge, this is the first report showing the formation of a meso-structured lamellar and crystalline Fe–P–O compound. The as-synthesized compound could be a proper precursor to transform to mesoporous materials, and could be used as a catalyst precursor, or catalyst support, etc. Further research work is under way.

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