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Synthesis of a novel mesoporous iron phosphate

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A novel mesoporous iron phosphate, possessing a specific surface area of 254 m^2 g^{-1} and average pore diameter of 2.6 nm, is synthesized using a fluoride route.

Since the discovery of M41s silica molecular sieves in 1992,[1] mesoporous materials, possessing remarkably large internal surface areas and narrow pore size distributions, have attracted considerable attention for their great potential application as catalysts, absorbents, and host materials. Several supermolecular assembly pathways have also been developed and extended to synthesize a variety of mesoporous metal oxides[2] and aluminophosphates.[3–6] Compared to those successes, however, only a few preparative approaches have been reported for the preparation of mesoporous transition metal phosphates.[7–10]

Iron phosphate has been reported as a good catalyst for selective oxidation reactions, *e.g.* oxidative dehydrogenation of isobutyric acid to methacrylic acid, a versatile raw material for various polymers,[11] and partial oxidation of methane or ethane to oxygenates.[12] Iron phosphates with novel mesostructure would be interesting in terms of structure and catalytic performance. Huang *et al.*[13] have reported microporous iron phosphate with an open framework and a cell volume of 2957.5 Å^3 and expected it to be a novel catalyst. The preparation of mesoporous iron phosphate, however, has not been reported so far, although the preparation of mesoporous aluminium phosphate has been reported. Considering the similarity between iron and aluminium in their chemical properties, the preparation of mesoporous iron phosphate should be feasible. Unfortunately, despite substantial effort we failed to synthesize mesoporous iron phosphate using similar methods reported for the preparation of mesoporous aluminium phosphate.

Using a series of surfactants and different experimental conditions, we have finally prepared some mesostructural lamellar and porous iron phosphates. Here we report our successful synthesis and characterization of ordered mesoporous iron phosphate with an average pore size of 2.6 nm.

In a typical sample preparation route, 8.08 g $Fe(NO_3)_3$ was dissolved in 80 g distilled water and 7.16 g Na_2HPO_4, dissolved in 80 g distilled water, was added with stirring. The resulting $FePO_4$ precipitate was recovered by centrifugation and washed by distilled water. The precipitate was suspended in 20 g distilled water, followed by dropping 1.32 g HF (40 wt%) into the suspension with vigorous stirring. When a transparent solution was obtained, 2.88 g sodium dodecyl sulfate (surfactant), dissolved in 10 g water, was added to the solution with stirring at room temperature for 30 min. The resultant mixture was heated to 60 °C and held for 2.5 h. After cooling to room temperature, a light yellow precipitate was observed in the solution which was recovered by centrifugation, followed by repeated washing with water and acetone. The resultant solid was dried at room temperature.

Removal of the surfactant species from the as-synthesized solid was carried out by anion exchange in a manner similar to that reported by Holland *et al.*[14] for the preparation of mesoporous aluminophosphate. The as-synthesized solid (0.7 g) was mixed with a 0.05 M ethanol solution of sodium acetate (50 ml) with stirring at room temperature for 40 min. The solid was then recovered by centrifugation, washed thoroughly using ethanol and dried at room temperature. XRD (Rigaku D/Max-RA diffractometer), TEM (JEOL-200CX; 160 kV), FTIR (Nicolet 170SX FTIR spectrometer) and nitrogen sorption (Micromeritics ASAP 2000 sorption analyzer) were used to characterize the resultants.

A strong absorption peak at *ca.* 1252 cm^{-1}, characteristic of $(ROSO_3)^-$, was observed in the FTIR spectra of the surfactant containing sample which vanished after acetate-treatment, indicating no residual dodecyl sulfate species in the acetate-treated sample. This appears to suggest the complete removal of the surfactant in the sample. X-Ray diffraction patterns of as-synthesized sample and acetate-treated sample are shown in Fig. 1. Both patterns show a sharp diffraction peak (100) at low angle ($2\theta \approx 2.4$ and 2.3°, for the surfactant containing and acetate-treated samples, respectively). The low-angle diffraction peaks suggest a mesoporous structure of the obtained iron phosphate samples. The slight shift to higher angle for the acetate-treated sample reveals slight contraction of mesostructure of iron phosphate upon surfactant removal. A TEM photograph, (Fig. 2) confirms the mesoporous structure of the acetate-treated samples. The isothermal N_2 sorption data of the

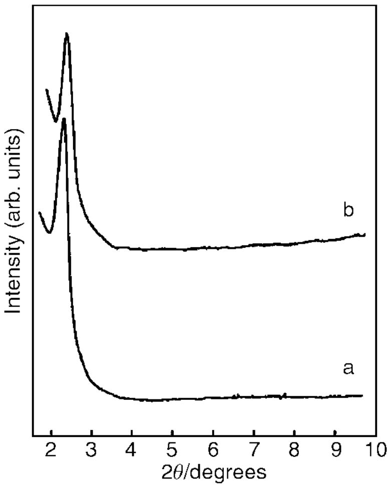

Fig. 1 XRD patterns of the as-synthesized sample (a) and acetate-treated sample (b).

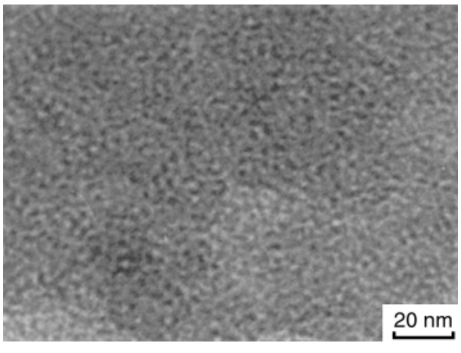

Fig. 2 TEM image of mesoporous iron phosphate after surfactant extraction.

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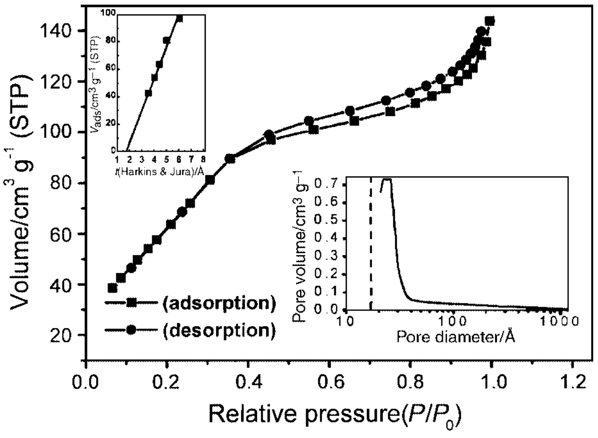
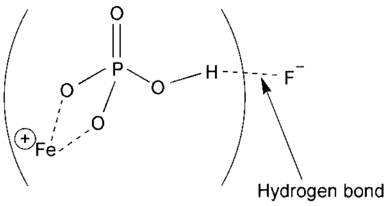


Fig. 3 Nitrogen adsorption–desorption isotherm of acetate-treated sample measured at 77 K, insets show pore diameter distribution of the sample (right) and *t*-plot (left).

acetate-treated sample at 77 K are shown in Fig. 3. The type-IV isotherm with a small hysteresis loop is similar to that of mesoporous zirconium phosphate reported in ref. 7. Quantitative calculation shows the acetate-treated mesoporous iron phosphate possesses a BET surface area of *ca.* 254 m^2 g^{-1} and a pore volume of 0.21 cm^3 g^{-1}, similar to documented non-silicate mesoporous solids, and narrow a distribution of pore diameter centered at 2.6 nm (Fig. 3, right inset). The linear *t*-plot suggests the sample possess uniform pores (Fig. 3, left inset). With the unit cell dimension ($a_0 = 2d_{100}/\sqrt{3}$) and the pore diameter, the wall thickness can be calculated as *ca.* 1.6 nm, much thicker than that of typical siliceous MCM41 (*ca.* 1.0 nm). The greater molecular weight and much thicker walls of the pores should be responsible for the lower BET specific surface area on comparing the mesoporous iron phosphate to M41s mesoporous silica.

We have attempted many routes other than *via* HF but all gave layer structures rather than an ordered mesoporous structure. Fluorides other than HF, *e.g.*, ammonium fluoride and sodium fluoride, were tested but failed to give mesoporous iron phosphate. It appears HF plays an important role in the mesoporous iron phosphate synthesis. Undissociated HF molecules (aqueous HF is a weak acid with pK_a ≈ 4) may react with iron phosphate to form ion pairs, as shown in Scheme 1. F ions bonding to $[Fe–P-O–H]^+$ *via* hydrogen bonding so adjusting the charge density of $[Fe–P-O–H]^+$ allow matching of the surface charge of the surfactant micelles, resulting in the formation of hexagonal mesoporous iron phosphate.



Scheme 1 The effect of fluoride on the charge density of Fe–P–O clusters.

In conclusion, a novel mesoporous iron phosphate has been synthesized for the first time using a fluoride route. After removal of surfactant by acetate-exchange, mesoporous iron phosphate with a surface area of 254 m^2 g^{-1} and average pore size of 2.6 nm was obtained.

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