Synthesis of Mesoporous Iron Phosphate Using PAMAM Dendrimer as a Single Molecular Template

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A successful demonstration of the formation of mesostructural pores in iron phosphate has been reported by using generation 4.0 poly(amido amine) dendrimer as a single molecular template.

The study on mesoporous materials has been an active research field owing to their great potential applications as absorbents, catalysts, and catalyst supports.[1,2] Up to now, a series of papers have been published on the preparation of mesoporous metal (Al, Zr, Ti, V, and Sn) phosphate[3] and metal oxides[4] by supramolecular assembly pathways. It has been known that iron phosphate is a good catalyst for selective oxidation reactions,[5,6] and its catalytic performance has a close relation to its structure.[7] Using a fluoride route with surfactants as templates, Guo et al.[8] have prepared mesostructural porous iron phosphates. To date, most of mesoporous materials are derived with supramolecular assemblies of surfactants, which template the inorganic components during synthesis. However, it is difficult to prepare mesoporous iron phosphate by a simple surfactant template method. Therefore, the study of developing new templates for mesoporous materials will enrich the field of preparation of this kind of materials.

It has been known that high generation poly(amido amine) (PAMAM) dendrimers are oligomeric molecules with quasi-spherical morphology.[9] The special structure of dendrimers should render them useful unimolecular templates for the preparation of mesoporous materials. Larsen et al.[10] and Mitra et al.[11] reported on the preparation of dendrimer-templated cavities in amorphous silica. Recently, Huang et al.[12] presented the formation of nanopores in titania ultrathin film using generation 4.0 OH–terminated PAMAM dendrimer monolayer as template. In this communication, we report on a successful demonstration of the formation of ordered mesostructural pores in iron phosphate by using generation 4.0 NH_2–terminated PAMAM dendrimer (G4-NH_2) as a single molecular template.

The typical sample preparation route was as follows: 0.2 g of commercial (Aldrich) G4-NH_2 and 0.6 g of Na_2HPO_4 were dissolved in 15 g of distilled water and stirred for 15 min. In the mixed solution (pH 7.8), 0.7 g of $FeCl_3$, dissolved in 10 g of distilled water, was added under vigorous stirring. The mixture was stirred at room temperature for 4 h. The resulting yellow precipitate was collected by filtration, washed with distilled water and dried in vacuum at 120 °C for 12 h. Removal of the dendrimer species from the as-synthesized solid was carried out by calcination at 500 °C for 2 h, condition of which is the same as that reported by Mal et al.[3] for the preparation of mesoporous tin phosphate by removing surfactant. Removing the template was not progressive by using solvent (e.g. methanol, ethanol, or chloroform) extraction method. FTIR absorption spectrometer, transmission electron microscope (TEM) and X-ray diffractometer were used to characterize the obtained solid.

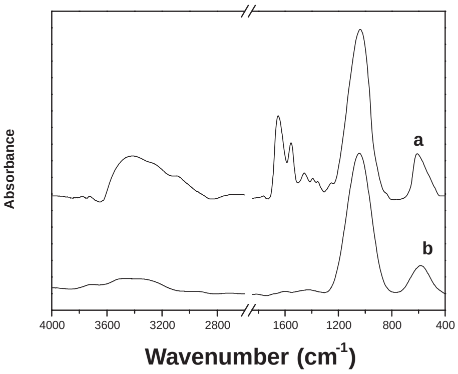


Figure 1. IR spectra of the as-synthesized solid (a) and calcined sample (b).

Figure 1 shows IR spectra of the as-synthesized and calcined solids. In Figure 1a, the strong absorption bands at 1650 and 1550 cm^{-1} are assigned to amide I and II of dendrimer, respectively.[13] The strong and broad band at 1035 cm^{-1} is ascribed to the asymmetric stretching mode (ν_{as}(P–O)) of PO_4^{3-} and the medium band at 606 cm^{-1} is due to the asymmetric deformation mode (ν_{as}(O–P–O)) of PO_4^{3-}.[14] These results prove that the obtained solid is a hybrid material of $FePO_4$ and dendrimer. After calcination, the strong bands at 1650 and 1550 cm^{-1} vanished (Figure 2b), implying no residual dendrimer species in the calcined sample. This indicates that, using calcination method, the dendrimer templates in $FePO_4$ solid can be removed completely.

TEM image of the dendrimer–$FePO_4$ solid is shown in Figure 2. The image confirms the formation of hexagonal ordering of electron density-less, spherical spots in the specimen, as marked in Figure 2. The diameter of these spots is uniform (around 3.2 nm) with center-to-center distance (a_0, shown in Scheme 1) of 5.1 nm. The diameter of the spots is much smaller than the size of free generation 4.0 PAMAM dendrimer in solution (ca. 4.5 nm in radius[9]). Nevertheless, it can be indicated that the electron density-less, spherical spot observed in the specimen on TEM should be the space occupied by a single PAMAM dendrimer molecule. The difference between the diameter of the spots observed on TEM and size of free dendrimer may be due to the shrink of dendrimer and/or the penetration of $FePO_4$ into outer layers of dendrimer. In preparation of G4-NH_2–$FePO_4$ at pH 7.8, since protonated terminals are shielded from electrostatic repulsion by binding of PO_4^{3-}, periphery in G4-NH_2 may shrink as well as non-protonated interior. Thus G4-NH_2 can have a condensed structure. Using SANS technique, Imae et al.[15] demonstrated the penetration of water into

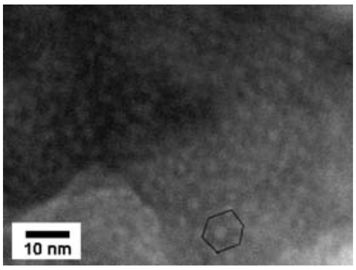


Figure 2. TEM image of the dendrimer–$FePO_4$ solid.

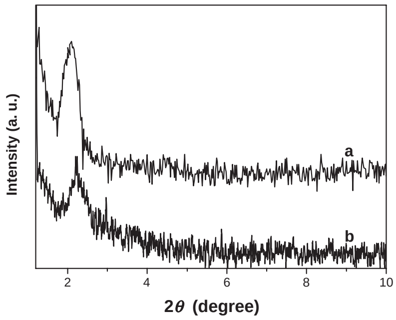
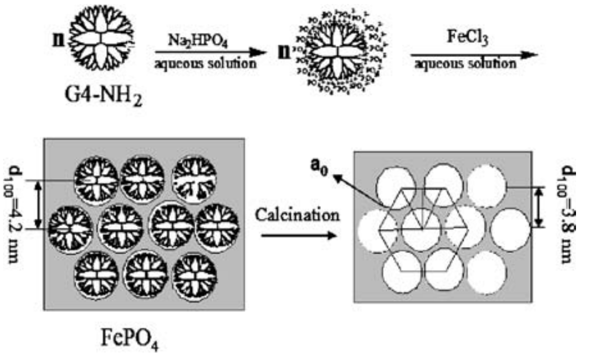


Figure 3. X-Ray diffraction patterns of the as-synthesized (a) and calcined (b) solids.

dendrimers in an aqueous solution. The penetration of $FePO_4$ into outer layer in dendrimer–$FePO_4$ preparation also can render smaller diameter of the spots observed on TEM.

The X-ray diffraction patterns of as-synthesized and calcined solids are shown in Figures 3a and 3b, respectively. It can be notified from Figure 2a that the pattern of dendrimer-containing solid displays a sharp hexagonal [100] diffraction peak at low angle ($2\theta = 2.1°$), indicating the ordered mesoporous structure of the obtained iron phosphate solid. The corresponding d spacing of the [100] plane is 4.2 nm. The calcined $FePO_4$ solid presented a relatively broad diffraction peak at 2.3°, which is characteristic of mesostructure conservation. Comparing to the dendrimer-containing solid, the corresponding d spacing of the [100] plane of calcined solid was reduced to 3.8 nm. The slight reduction of d space for the calcined solid reveals slight contraction of mesostructure of iron phosphate upon dendrimer removal. In preparation of mesoporous inorganic materials, the contraction phenomenon is commonly observed after removal of surfactant template.[8]

The proposed mechanism of the replication of PAMAM dendrimer molecules as nanopores in iron phosphate is shown in Scheme 1. In the Na_2HPO_4 solution, negatively charged phosphate groups surround the protonated primary amine terminal groups of G4 PAMAM dendrimer by electrostatic interaction. After addition of aqueous $FeCl_3$ solution, $FePO_4$ precipitates including PAMAM dendrimer and forms an organic–inorganic hybrid. Removing the PAMAM dendrimer in the hybrid by calcination, replication of PAMAM dendrimer molecules as nanopores in iron phosphate is achieved.



Scheme 1. Schematic representation of the formation process of nanoporous $FePO_4$.

In conclusion, a mesoporous iron phosphate has been synthesized by replicating PAMAM dendrimer. A single PAMAM dendrimer produced a nanopore in iron phosphate. It is expected that, using different generation of PAMAM dendrimer as a template, the pore size of mesoporous iron phosphate can be controlled.

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