Synthesis of Cubic $Pm\bar{3}n$ Mesostructured Titanium Oxophosphate

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A mesostructured titanium oxophosphate (designated as TOP) possessing a periodic three dimensional (3D) cubic $Pm\bar{3}n$ symmetry has been synthesized for the first time, via using divalent cationic surfactants in a post-synthesis strategy. And it was further found that 3D cubic $Pm\bar{3}n$ mesostructured TOP was more thermally stable than 2D hexagonal *P6mm* mesostructured counterpart.

Metal phosphate mesostructured molecular sieves have initiated considerable attractions for their potential applications in catalysis, adsorption, and separations. Recently, it was reported that iron-,[1] tin-,[2] nickel-,[3] titanium-,[4] and zirconium[5]-based mesostructured phosphates have been synthesized. Owing to mesostructured materials with 3D pore systems exhibit more advantages in mass transportation compared with those containing 1D channels because of percolation pathways, great efforts have been performed towards the synthesis of mesostructured materials with 3D mesostructures.[5] For instance, by means of a tri-headgroup quaternary ammonium surfactant, Shen et al.[5b] firstly obtained a highly ordered cubic mesostructured zirconium oxophosphate with $Pm\bar{3}n$ symmetry.

Here, we explored the fabrication of a highly ordered mesostructured TOP with cubic $Pm\bar{3}n$ symmetry templated by gemini cationic surfactants by a post-synthetic method.

In a typical synthesis, 0.001 mol of surfactant, 40.5 mL of sulfuric acid solution (1.0 M) were mixed to obtain a homogeneous solution, which was allowed to react at room temperature prior to the addition of 2.69 g of titanium *n*-butoxide ($Ti(OBu^n)_4$ 98%). The corresponding titanium oxophosphate sample was further obtained[4a,4b] with a post-synthetic strategy by adding the intermediate titanium oxide sulfate products to an aqueous solution of 50 mL of H_3PO_4 (0.5 M), and stirred for 5 h at room temperature. Template free products were obtained via direct calcination at 250 °C for 1 h and 400 °C for 3 h. To study the thermal stability, the samples were calcined at 250 °C for 1 h and x °C for another 3 h ($x = 450$, 550, 650, and 750). The structures were analyzed by powder X-ray diffraction (XRD) (Rigaku D/MAX-2200/PC) and transmission electron microscopy (TEM) (JEOL-3010, 300 kV).

Figure 1 shows XRD patterns of as-synthesized and calcined mesostructured TOP prepared by using alkyl divalent quaternary ammonium $C_nH_{2n+1}N(CH_3)_2(CH_2)_3N(CH_3)_3Br_2$ ($C_{n\text{-}3\text{-}1}$, $n =$ 14, 16, and 18) as structure-directing agents. The mesostructured TOP samples prepared using $C_{14\text{-}3\text{-}1}$ and $C_{16\text{-}3\text{-}1}$ show the XRD patterns with three well-resolved peaks in the region of $2\theta =$ 1.3–3.0° (Figures 1a and 1b), which are indexed to the 200, 210, and 211 reflections on the basis of the cubic system. Additional weak peaks in the range of 3.5–6° corresponding to the 321, 400, and 421 reflections indicate that the as-synthesized TOP has a high degree of cubic $Pm\bar{3}n$ mesoscopic organization. The XRD patterns of these two TOP samples after calcined retained three clear peaks 200, 210, and 211 characteristic of cubic ordered structure. Mesostructured TOP templated by $C_{18\text{-}3\text{-}1}$ exhibited unresolved XRD reflections (Figure 1c), whereas the structure was confirmed to be an ordered cubic $Pm\bar{3}n$ mesophase by its following TEM image. As shown in Figure 1, the unit cell parameter a of these three samples increases with the chain length growing of the surfactants in the order of $C_{14\text{-}3\text{-}1} < C_{16\text{-}3\text{-}1} < C_{18\text{-}3\text{-}1}$. The main reflection shifts slightly to the higher angle after calcinations indicating that calcination led to a slight shrinkage of pore size owing to the condensation of the terminal Ti–OH.[4]

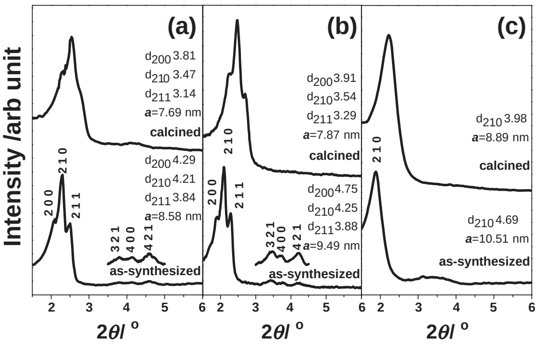

Figure 1. XRD patterns of as-synthesized and calcined mesoporous TOP templated by (a) $C_{14\text{-}3\text{-}1}$, (b) $C_{16\text{-}3\text{-}1}$, and (c) $C_{18\text{-}3\text{-}1}$.

TEM images and the corresponding Fourier diffractograms of the calcined mesostructured TOP templated by $C_{16\text{-}3\text{-}1}$, and $C_{18\text{-}3\text{-}1}$ are shown in Figure 2. All indices observed in FDs and powder XRD patterns are consistent with the extinction conditions for the cubic $Pm\bar{3}n$. The image exhibits a typical [100] projection of a well-ordered cubic $Pm\bar{3}n$ mesostructure analogous to the mesostructured silica SBA-1.[6,7]

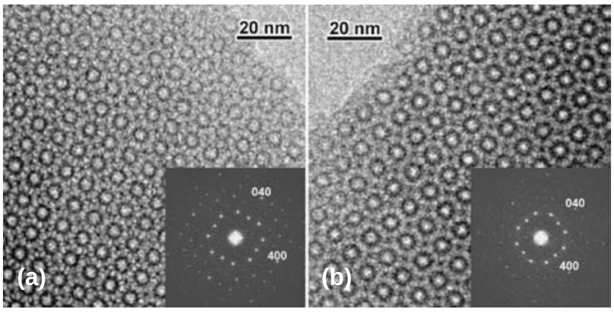

Figure 2. Typical TEM images and corresponding Fourier diffractogram patterns along [100] for TOP samples after calcined at 350 °C templated by (a) $C_{16\text{-}3\text{-}1}$, (b) $C_{18\text{-}3\text{-}1}$.

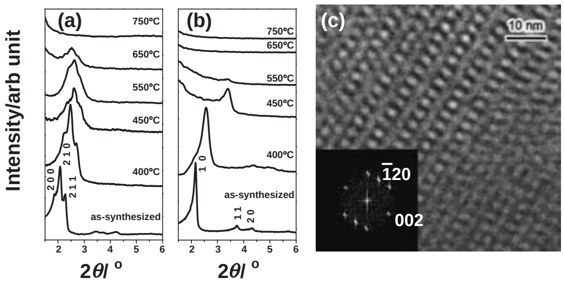

Figure 3. XRD patterns of TOP samples calcined at different temperatures templated by (A) $C_{16\text{-}3\text{-}1}$ and (B) CTMABr, and (C) TEM image along [110] and its Fourier diffractogram pattern for TOP sample templated by $C_{16\text{-}3\text{-}1}$ after calcined at 650 °C.

The XRD patterns of TOP templated by $C_{16\text{-}3\text{-}1}$ calcined at different temperatures are shown in Figure 3a. It is found that the cubic $Pm\bar{3}n$ mesostructures was retained even after calcined at 650 °C, which is further confirmed by the TEM image (Figure 3c). For comparison, 2D-hexagonal mesostructured TOP was prepared by use of cetyltrimethylammonium bromide (CTAB) according to literatures[4] and its XRD patterns are shown in Figure 3b. The obserued patterns indicate that the framework of 2D-hexagonal TOP collapsed at 450 °C. It is well known that the curvature of cubic $Pm\bar{3}n$ lyotropic liquid crystal mesophases is larger than that of 2D-hexagonal $P6mm$. Obviously, it is concluded that cubic $Pm\bar{3}n$ mesostructured TOP having a higher organic–inorganic interface curvature is more thermally stable than its 2D-hexagonal counterpart with a lower curvature. Wide-angle XRD patterns (see Supporting Information Figure S1) reveal that the samples with ordered pore structure calcined at below 750 °C are all amorphous. When the temperature reached 750 °C, the mesostructures of both TOP were destroyed and the composite were crystallized which was concluded from the resolved peaks in its wide-angle XRD patterns.[8]

Mesostructured titanium oxophosphate frameworks has been characterized by ^{31}P MAS NMR. 3D cubic mesostructured TOP templated by $C_{16\text{-}3\text{-}1}$ shows four resonance peaks centered at −4.6, −13.5, −21.5, and −31.0 ppm (See Surporting Information Figure S2), which can be attributed to tetrahedral phosphorus atoms connected to one, two, three, and four titanium atoms (corresponding to surface $(HO)_3PO\text{–}Ti$, $(HO)_2P(O\text{–}Ti)_2$, $HOP(O\text{–}Ti)_3$, and $P(O\text{–}Ti)_4$ groups).[5c,5d] The P/Ti molar ratio[5b] for the mesostructured TOP calcined at 450 °C was evaluated to be 0.97 by EDX (energy dispersive X-ray) analysis and the P/Ti molar ratio for the sample calcined 650 °C was around 0.89. The decrease of the molar ratio further indicated the destroyment of the mesostructures.

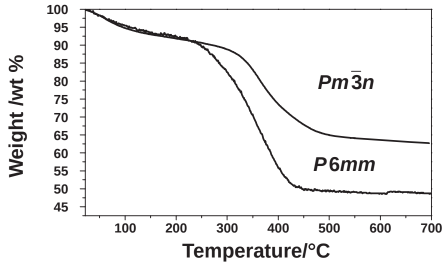

Figure 4. TGAs of as-synthesized mesostructured cubic and 2D-hexagonal titanium oxophosphate templated by $C_{16\text{-}3\text{-}1}$ and CTMABr, respectively.

It is interesting to note that the total weight loss is ca. 51 and ca. 35 wt % for 2D-hexagonal and cubic mesostructured TOP, respectively, as shown in thermogravimetric profile (Figure 4), which implies a higher ratio of organic contents to titanium oxophosphate walls in 2D-hexagonal TOP than that of cubic $Pm\bar{3}n$.[8] The ratio of inorganic wall to surfactant may be an important factor that affects the framework restructuring during calcination.

The surface area of the calcined $Pm\bar{3}n$ mesostructured TOP was very low as is similar to the $Pm\bar{3}n$ mesostructured zirconium oxophosphate reported previously (see Supporting Information Figure S3).[5] It is speculated that for the cage-type mesostructured materials the windows pores connecting the neighboring cavities are easily contracted after the removal of surfactants.

In conclusion, well-ordered 3D-mesostructured TOP with cubic $Pm\bar{3}n$ symmetry have been synthesized by gemini surfactants in a post-synthesis strategy. The ability to prepare well-defined 3D cubic structure with high thermal stability would open up new perspectives for both fundamental studies and their applications in catalysis, adsorption and separation.

This work was supported by the National Natural Science Foundation of China (Grant No. 20425102), OT thanks Swedish Science Research Council (VR) and Japan Science and Technology Agency (JST) for financial support.

References

1 X. Guo, W. Ding, X. Wang, Q. Yan, *Chem. Commun.* **2001**, 709.
2 N. K. Mal, S. Ichikawa, M. Fujiwara, *Chem. Commun.* **2002**, 112.
3 S. H. Jhung, J. Chang, S. Park, P. M. Forster, G. Férey, A. K. Cheetham, *Chem. Mater.* **2004**, *16*, 1394.
4 a) M. Thieme, F. Schüth, *Microporous Mesostructured Mater.* **1999**, *27*, 193. b) J. Blanchard, F. Schüth, P. Trens, M. Hudson, *Microporous Mesostructured Mater.* **2000**, *39*, 163. c) T. Czuryszkiewicz, F. Kleitz, F. Schuth, M. Linden, *Chem. Mater.* **2003**, *15*, 3704. d) T. Czuryszkiewicz, F. Kleitz, F. Schüth, M. Lindén, *Chem. Mater.* **2003**, *15*, 3704. e) B. Tian, X. Liu, B. Tu, C. Yu, J. Fan, L. Wang, S. Xie, G. D. Stucky, D. Zhao, *Nat. Mater.* **2003**, *2*, 159. f) A. Bhaumik, S. Inagaki, *J. Am. Chem. Soc.* **2001**, *123*, 691.
5 a) F. Kleitz, S. J. Thomson, Z. Liu, O. Terasaki, F. Schüth, *Chem. Mater.* **2002**, *14*, 4134. b) S. Shen, B. Tian, C. Yu, S. Xie, Z. Zhang, B. Tu, D. Zhao, *Chem. Mater.* **2003**, *15*, 4046. c) J. Fan, C. Yu, F. Gao, J. Lei, B. Tian, L. Wang, Q. Luo, B. Tu, W. Zhou, D. Zhao, *Angew. Chem.* **2003**, *115*, 3254. d) H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, M. Danjyoc, M. Tsuhakoc, *J. Am. Chem. Soc.* **1997**, *7*, 1063.
6 Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, *8*, 1147.
7 S. Che, Y. Sakamoto, O. Terasaki, T. Tatsumi, *Chem. Mater.* **2001**, *13*, 2237.
8 a) F. Kleitz, W. Schmidt, F. Schüth, *Microporous Mesostructured Mater.* **2001**, *44–45*, 95. b) S. Shen, B. Tian, C. Yu, S. Xie, Z. Zhang, B. Tu, D. Zhao, *Chem. Mater.* **2003**, *15*, 4046.

Published on the web (Advance View) March 18, 2006; DOI 10.1246/cl.2006.400