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Synthesis of Highly Ordered Thermally Stable Cubic Mesostructured Zirconium Oxophosphate Templated by Tri-Headgroup Quaternary Ammonium Surfactants

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Highly ordered cubic mesostructured zirconium oxophosphate with *Pm*3*n* symmetry analogous to SBA-1 silica is first obtained by using tri-headgroup quaternary ammonium surfactant $CH_3(CH_2)_{16}CH_2N(CH_3)_2CH_2CH_2N(CH_3)_2CH_2CH_2CH_2N(CH_3)_3Br_3$ ($C_{18-2-3-1}$) as a structure-directing agent and zirconium sulfate as an inorganic precursor under hydrothermal condition. X-ray diffraction (XRD), transmission electron microscopy (TEM), and ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) have been used to characterize these mesostructured zirconium-based composites. The cubic mesostructured zirconium oxophosphates are thermally stable up to 500 °C. In addition, a phase transition from *Pm*3*n* through mixed mesophase to *p*6*m* symmetry is observed through finely tuning the spacer methylene chain length among the hydrophilic headgroups in the multi-charged amphiphile (from $C_{18-2-3-1}$ through $C_{18-3-3-1}$ to $C_{18-3-4-1}$). ^{31}P MAS NMR spectra show that phosphorus has four types of chemical environments in the cubic mesostructured zirconium oxophosphate framework and three types of chemical environments in mixed or hexagonal zirconium oxophosphate mesophases.

Introduction

Non-siliceous materials with well-ordered and controllable structural features in mesoscale are greatly attractive because of their potential applications in the fields of catalysis, optics, electrics, and magnetism.[1,2] Since the discovery of M41S in 1992,[3,4] many great efforts have been performed to extend the surfactant templating strategy to the synthesis of mesostructured non-siliceous materials.[5−17] So far, several synthesis routes[6,7,9,11,14−22] have been developed, including designed inorganic−organic interplay via electrostatic, covalent bonding, hydrogen bonding, and tunable inorganic−inorganic interplay via "acid−base pairs".[23] As far as zirconium-based composites are concerned, templating[10,22] and scaffolding[24−26] mechanisms have been described, and several types of surfactants have been used to prepare zirconium-based mesostructured composites. For example, Yang et al.[9,12] synthesized the mesoporous zirconia with hexagonal and cubic structure from block copolymers under nonaqueous solution via templating mechanism. Using amphoteric cocamidopropyl betain as a template is another pathway to obtain a hexagonal mesophase zirconium compound.[22] Long chain primary alkyamines can lead to the formation of

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(1) Sayari, A. *Chem. Mater.* **1996**, *8*, 1840.

(2) Schüth, F. *Chem. Mater.* **2001**, *13*, 3184.

(3) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(4) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(5) Sayari, A.; Liu, P. *Micro. Mater.* **1997**, *12*, 179.

(6) Antonelli, D. M.; Ying, J. Y. *Angew. Chem, Int. Ed. Engl.* **1995**, *34*, 2014.

(7) Blanchard, J.; Trens, P.; Hudson, M.; Schüth, F. *Microporous Mesoporous Mater.* **2000**, *39*, 163.

(8) Bhaumik, A.; Inagaki, S. *J. Am. Chem. Soc.* **2001**, *123*, 691.

(9) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2813.

(10) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 426.

(11) Antonelli, D. M.; Ying, J. Y. *Chem. Mater.* **1996**, *8*, 874.

(12) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152.

(13) Ciesla, U.; Schacht, S.; Stucky, G. D.; Unger, K.; Schüth, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 541.

(14) Antonelli, D. M.; Nakahira, A.; Ying, J. Y. *Inorg. Chem.* **1996**, *35*, 3126.

(15) Wong, M. S.; Ying, J. Y. *Chem. Mater.* **1998**, *10*, 2067.

(16) Mizuno, N.; Hatayama, H.; Uchida, S.; Taguchi, A. *Chem. Mater.* **2001**, *13*, 179−184.

(17) Serre, C.; Hervieu, M.; Magnier, C.; Taulelle, F.; Ferey, G. *Chem. Mater.* **2002**, *14*, 180−188.

(18) Ciesla, U.; Demuth, D.; Leon, R.; Petroff, P.; Stucky, G.; Unger, K.; Schüth, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1387.

(19) Huo, Q.; Margolese, D.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *317*, *368*.

(20) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *108*, 1180.

(21) Jimenez-Jimenez, J.; Maireles-Torres, P.; Olivera-Pastor, P.; Rodriguez-Castellon, E.; Jimenez- Lopez, A.; Jones, D. J.; Roziere, J. *Adv. Mater.* **1998**, *10*, 812.

(22) Kim, A.; Bruinsma, P.; Chen, Y.; Wang, L.-Q.; Liu, J. *Chem. Commun.* **1997**, 161.

(23) Tian, B.; Liu, X.; Tu, B.; Yu, C.; Fan, J.; Wang, L.; Xie, S.; Stucky, G. D.; Zhao, D. *Nature Mater.* **2003**, *2*, 159.

(24) Hudson, M. J.; Knowles, J. A. *J. Chem. Soc., Chem. Commun.* **1995**, 2083.

(25) Hudson, M. J.; Knowles, J. A. *J. Mater. Chem.* **1996**, *6*, 89.

(26) Fripiat, J. J.; Pacheco, G. *J. Phys. Chem. B* **2000**, *104*, 11906.

10.1021/cm0342389 CCC: $25.00

a lamellar phase.[27] Anionic surfactants[28,29] have also been used to synthesize the mesoporous zirconium via scaffold mechanism, but a disordered product was obtained. In addition, the cationic surfactant, alkyltrimethylammonium bromide[13,20,32,33] is the most popular in the synthesis of mesostructured zirconium oxide sulfate and zirconium oxophosphate. On the basis of a postsynthetic treatment with phosphoric acid to replace the sulfate groups with more thermally stable phosphate groups within the framework,[13] Schüth et al. have synthesized the zirconium oxide sulfate and thermally stable zirconium oxophosphate with two-dimensional (2D) hexagonal symmetry using alkyltri-methylammonium bromide.[32,13] However, most previous reports were focused on 2D hexagonal and disordered mesophase,[9] and up to now, only one stable cubic mesostructure ($Ia3d$) has been reported by Schüth *and* co-workers.[33,34] Such cubic mesostructured materials with interconnected pores may have more advantages for potential applications than 2D hexagonal mesophases.[35−38]

The difficulties to obtain the cubic mesophase zirconium-based composites are mainly attributed to the lack of suitable surfactants that have a proper interaction with inorganic precursor species.[2] Recently, Schüth and co-workers[39] reported the mesoporous zirconium oxophosphate with a cubic $Ia3d$ symmetry analogous to MCM-48 silica using a specific surfactant (benzyldimethystearl-ammonium chloride) via $Zr^{+}X-S-$ pathway (where $X-$is SO_4^{2-} and $S-$ is cationic surfactant), suggesting that the careful design of surfactants and increase of the interaction are essential to the synthesis of stable cubic mesostructued zirconium-based composites. The tri-headgroup quaternary ammonium surfactants ($C_{18}H_{37}N(CH_3)_2\text{-}(CH_2)_s\text{-}N(CH_3)_2\text{-}(CH_2)_mN(CH_3)_3$, denoted $C_{18-s-m-1}$) are a type of multi-charged cationic amphiphiles closely related to Gemini surfactant.[40−43] The spacer methylene chain length can strongly effect the curvature of the surfactant layers, and thus the micelle shape and the properties of the solution.[44−47] Furthermore, higher charge in the tri-headgroup amphiphile may make it more favorable to interact with the inorganic precursor species, which may lead to the successful synthesis of a new mesophase material.

Here, we report the synthesis of a new cubic mesostructured zirconium oxide sulfate and zirconium oxophosphate materials by using tri-headgroup quaternary ammonium surfactant $(CH_3(CH_2)_{16}CH_2N(CH_3)_2CH_2\text{-}CH_2N(CH_3)_2CH_2CH_2CH_2N\,(CH_3)_3\cdot Br_3$ ($C_{18-2-3-1}$) under the hydrothermal condition. The products exhibit well-ordered cubic mesostructure with $Pm3n$ symmetry analogous to SBA-1 mesoporous silica. In addition, a phase transition from $Pm3n$ through mixed mesophase to $p6m$ symmetry structure is observed by tuning the spacer methylene chain length among the hydrophilic headgroup.

Experimental Section

Chemicals. 1-Bromooctadecane, *N*,*N*,*N*′,*N*′-tetramethyl-1-2-ethyldiamine, and *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine were purchased from Acros. (3-Bromopropyl)trimethylammonium bromide was obtained from Aldrich. (4-Bromobutyl)trimethylammonium bromide was synthesized according to the gerneral procedure.[48] $Zr(SO_4)_2\cdot 4H_2O$ and orthophosphoric acid were obtained from China Chemical Reagent Corporation. All chemicals were used as received.

Surfactant Preparation. Tri-headgroup quarternary ammonium surfactants were prepared through two steps by the reaction of 1-bromooctadecane with corresponding *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine or *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine in acetone under refluxing condition, followed by reaction with (3-bromopropyl)trimethylammonium bromide or (4-bromobutyl) trimethylammonium bromide in propanol under refluxing condition. The resulting products were purified by re-crystallization from ethanol/acetone mixture. Detailed synthesis procedure was as follows: 50 mL of an acetone solution containing 10.5 g (31.5 mmol) of 1-bromooctadecane was added slowly to 150 mL of acetone containing 183 g (157.6 mmol) of *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine. The mixture was stirred for 24 h under refluxing conditions. The white intermediate product was cooled to room temperature, filtered, then washed with dry ether.A 4.49-g portion (10 mmol) of the intermediate product was further dissolved in propanol, and 2.61 g (10 mmol) of (3-bromopropyl)-trimethylammonium bromide was added to this solution. The resulted mixture was heated while stirred at 90 °C for 5 days under refluxing condition. The solvent was evaporated until a white viscous liquid was obtained, using a rotary evaporator at 40 °C. The white viscous liquid turned to solid upon cooling to room temperature. The product was obtained by re-crystallization from ethanol/acetone mixture for several times and was identified as $C_{18-2-3-1}$ by ^1H NMR spectrum after dissolution in D_2O.

Other tri-headgroup quaternary ammonium surfactants, i.e., $C_{18-3-4-1}$ and $C_{18-3-3-1}$ were also synthesized by the reaction of 1-bromooctadecane with *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine, followed with (4-bromobutyl)trimethyl-ammonium bromide or (3-bromopropyl)trimethylammonium bromide.

Synthesis. Mesostructured zirconium-based composites were obtained by adding the surfactant ($C_{18-3-4-1}$, $C_{18-3-3-1}$, or $C_{18-2-3-1}$) solution to the zirconium sulfate solution under stirring, followed by hydrothermal reaction and posttreatment with aqueous solution of phosphate acid. A typical synthesis was as follows: 4.0 g (11.2 mmol) of zirconium sulfate was dissolved in 50 g of distilled water at room temperature. To this solution, 3.0 g (4.2 mmol) of $C_{18-2-3-1}$ dissolved in 80 g of H_2O was added. The mixture was vigorously stirred at 18 °C

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(27) Reddy, J. S.; Sayari, A. *Catal. Lett.* **1996**, *38*, 219.

(28) Pacheco, G.; Zhao, E.; Garcia, A.; Sklyarov, A.; Fripiat, J. J. *Chem. Commun.* **1997**, 491.

(29) Pacheco, G.; Zhao, E.; Garcia, A.; Sklyarov, A.; Fripiat, J. J. *J. Mater. Chem.* **1998**, *8*, 219.

(30) Parvulescu, V. P.; Endruschat, U.; Lehmann, C. W.; Grange, P.; Poncelet, G.; Bonnemann, H. *Microporous Mesoporous Mater.* **2001**, *44*−*45*, 221.

(31) Romannikov, V. N.; Fenelonov, V. B.; Paukshtis, E. A.; Drevyankon. A. Y.; Zaikovskii, V. I. *Microporous Mesoporous Mater.* **1998**, *21*, 411.

(32) Ciesla, U.; Fröba, M.; Stucky, G. D.; Schüth, F. *Chem. Mater.* **1999**, *11*, 227.

(33) Schüth, F.; Ciesla, U.; Schacht, S.; Thieme, M.; Huo, Q.; Stucky, G. D. *Mater. Res. Bull.* **1999**, *34*, 483.

(34) Schüth, F. *Stud. Surf. Sci. Catal.* **2001**, *135*, 1.

(35) Ryoo, R.; Jun, S.; Kim J. M.; Kim, M. J. *J. Chem. Soc., Chem. Commun.* **1997**, 2225.

(36) Walker, J. V.; Morey, M.; Carlsson, A.; Davidson, A.; Stucky, G. D.; Butler, A. *J. Am. Chem. Soc.* **1997**, *119*, 6921.

(37) Morey, M. S.; Davidson, A.; Stucky, G. D. *J. Porous Mater.* **1998**, *5*, 195.

(38) Neeray, S.; Rao, C. N. R. *J. Mater. Chem.* **1998**, *8*, 1631.

(39) Kleitz, F.; Thomson, S. J.; Liu, Z.; Terasaki, O.; Schüth, F. *Chem. Mater.* **2002**, *14*, 4134.

(40) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(41) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.

(42) Alami, E.; Levy, H.; Zana, R. *Langmuir* **1993**, *9*, 940.

(43) Zana, R.; Talmon, Y. *Nature* **1993**, *362*, 229.

(44) Danino, D.; Talmon, Y.; Zana, R. *Langmuir* **1995**, *11*, 1448.

(45) Rosen, M. J. *Chem. Technol.* **1993**, *23*, 30.

(46) Zana, R. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 566.

(47) Zana, R.; Talmon, Y. *Nature (London)* **1993**, *362*, 228.

(48) Thanei-wyss, P.; Waser, P. G. *Helv. Chim. Acta* **1983**, *66*, 217.

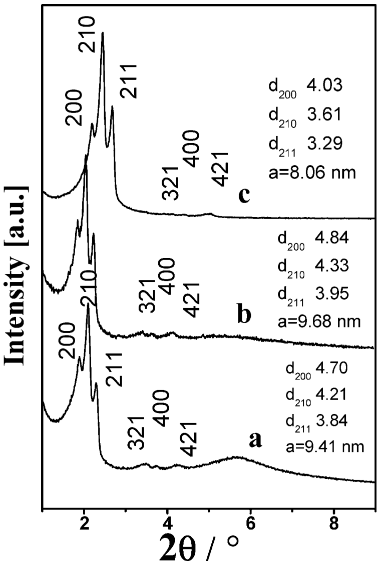

Figure 1. XRD patterns for the mesostructured zirconium-based composites: (a) as-synthesized zirconium oxide sulfate, (b) fresh zirconium oxophosphate, and (c) calcined zirconium oxophosphate.

for 2 h and then transferred to a Teflon bottle and stored for 4 days at 100 °C under static conditions. After cooling to room temperature, the zirconium oxide sulfate product was collected, filtered, and dried in air. The corresponding zirconium oxophosphate sample was further obtained[13,32,39] by adding the intermediate zirconium oxide sulfate products to an aqueous solution of 200 mL of H_3PO_4 (1.0 M), and stirred for 24 h at room temperature. The resultant products were filtered, washed with water, and dried in air. Template free products were obtained via calcination at 300 °C for 3 h, followed by 6 h at 500 °C (the heating rate was 1 °C/min) under oxygen condition (the ramp rate was 50 mL/min).

Characterization. Small-angle powder X-ray diffraction (XRD) patterns were recorded with a Bruker D4 powder X-ray diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) images were taken with a JEOL JEM2011 electron microscope operating at 200 kV. Solid-state ^{31}P magic angle spinning nuclear resonance (MAS NMR) sprectra were collected on a Bruker DMX 300 at 121.49 MHz. An 85% H_3PO_4 solution was used as the external reference.

Results and Discussion

Synthesis. Figure 1 shows typical XRD patterns for mesostructured zirconium oxide prepared by using $C_{18-2-3-1}$ as a structure-directing agent. The as-synthesized mesostructured zirconium oxide sulfate composite shows six resolved diffraction peaks with $d = 4.70$, 4.21, 3.84, 2.51, 2.35, and 2.05 nm; in addition, a broad peak in the region of $2\theta = 4.5-7.5$ can also be observed (Figure 1a). After the treatment with phosphoric acid, the diffraction peaks for the mesostructured zirconium oxophosphate are shifted to a little lower 2θ angles with $d = 4.84$, 4.33, 3.95, 2.59, 2.42, and 2.11 nm (Figure 1 b), and the broad peak disappears. Both sets of diffraction peaks can be indexed to the (200), (210), (211), (321), (400), and (421) reflections of 3D cubic mesostructures with $Pm3n$ space group.[49,50] The unit cell parameters of a are 9.41 and 9.68 nm for the untreated and treated samples, respectively. After calcinations at 500 °C for 6 h in air, three well-resolved diffraction peaks can be observed at $d = 4.03$, 3.61, and 3.29 nm (Figure 1c), which can be indexed to (200), (210), and (211), respectively, indicating that the mesostructured zirconium oxophosphate composites are thermally stable. The unit cell parameter (a) of the calcined product is 8.06 nm, suggesting structural shrinkage upon thermal treatment.

TEM images and corresponding Fourier diffractograms of calcined mesostructured zirconium oxophosphate composites are shown in Figure 2. The images exhibit typical [100], [110], and [210] projection planes of the cubic $Pm3n$ mesophase, clearly indicating that the mesostructured zirconium oxophosphates have well-ordered cubic mesostructure analogous to mesoporous silica SBA-1. To the best of our knowledge, the cubic mesostructured zirconium-based composites with $Pm3n$ symmetry have not been reported previously.

XRD measurements show that zirconium sulfate-based composites are thermally unstable, and collapse upon calcination at 350 °C. The stable mesostructured zirconium oxophosphates can be obtained after treatment with aqueous solution of H_3PO_4 (1.0 M). The S/Zr molar ratio for the zirconium oxide sulfate mesostructure is evaluated to be 0.28 by EDX (energy-dispersive X-ray) analysis. After the phosphatation, no sulfate can be detected and the P/Zr molar ratio for the calcined zirconium phosphate mesophase is around 0.99.

A thermogravimetric profile for as-synthesized cubic mesostructure zirconium oxophosphate is shown in Figure 3. A weight loss (6%) below 115 °C can be attributed to the removal of physisorbed water. A second weight loss of 53% occurs between 115 °C and 440 °C resulting mainly from the combustion of the surfactants. A slight weight loss (2%) after 440 °C may be attributed to the loss of carbonaceous species in the pore channels.[51] These results suggest that nearly all organic species can be burned after calcined at 500 °C

Although the calcined zirconium oxophosphates are thermally stable up to 500 °C, N_2 adsorption/desorption measurements show that the BET surface area is very low. One of the possible reasons may be that the cubic mesostructured zirconium oxophosphates with $Pm3n$ symmetry has a cage type structure whose pore window is quite small[49,50] and easy to be closed upon calcination induced shrinkage process, although the mesostructure is retained.

It should be noted that careful control of the crystallization temperature is essential for obtaining the 3D cubic ($Pm3n$) mesostructured zirconium oxide sulfates. The synthetic temperature should be altered in the range of 10−25 °C; the increase of the temperature will lead to the less ordered cubic mesophase. The optimum temperature for the synthesis of the cubic mesostructured zirconium oxide sulfates is 18 °C, probably because this low temperature facilitates the formation of the $Pm3n$ globular mesophase. In addition, increasing the hydrothermal temperature (from 100 to 130 °C) can shorten the synthesis time from 4 to 2 days.

Phase Transition. More interestingly, a phase transfer is observed by finely tuning the spacer methylene

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(49) Sakamoto, Y.; Kaneda, M.; Terasaki, O.; Zhao, D.; Kim, J.; Stucky, G. D.; Shin, H. J.; Ryoo, R. *Nature* **2000**, *408*, 449.

(50) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(51) Kleitz, F.; Schmidt, W.; Schüth F. *Microporous Mesoporous Mater.* **2001**, *44−45*, 95.

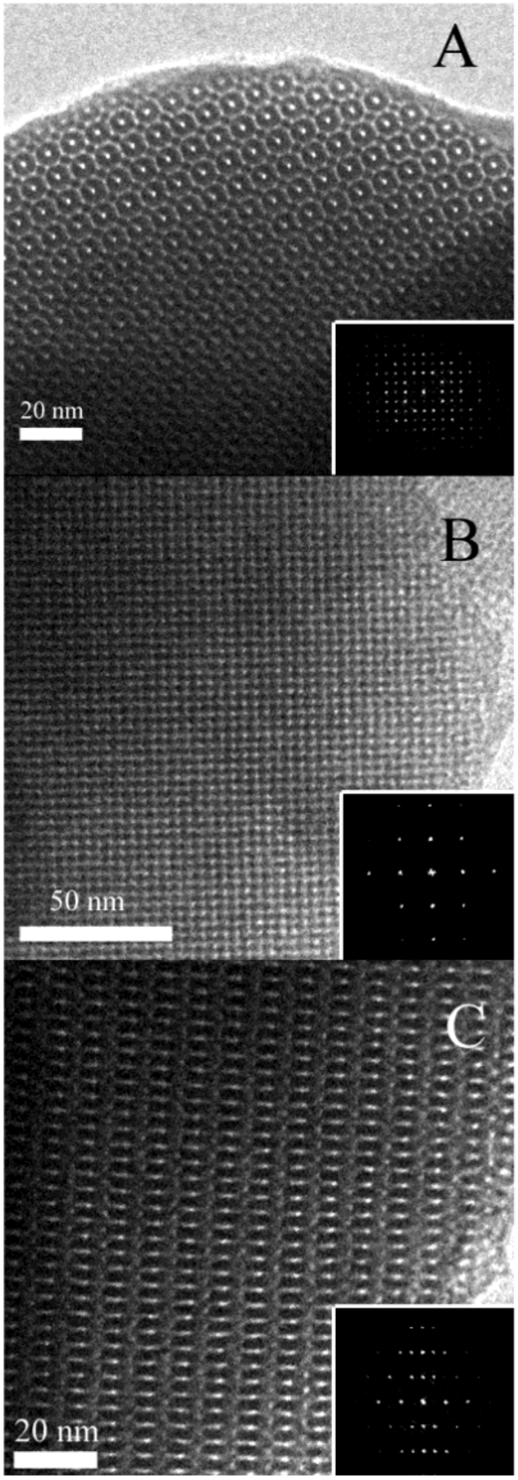

Figure 2. TEM images and Fourier diffractogram patterns for the calcined mesostructured zirconium oxophosphates along (A) [100], (B) [110], and (C) [210].

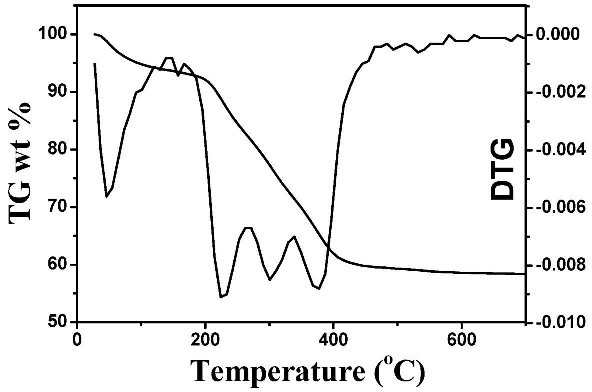

Figure 3. TG/DTG curves of as-synthesized cubic mesostructured zirconium oxophosphate prepared from tri-headgroup surfactant $C_{18-2-3-1}$.

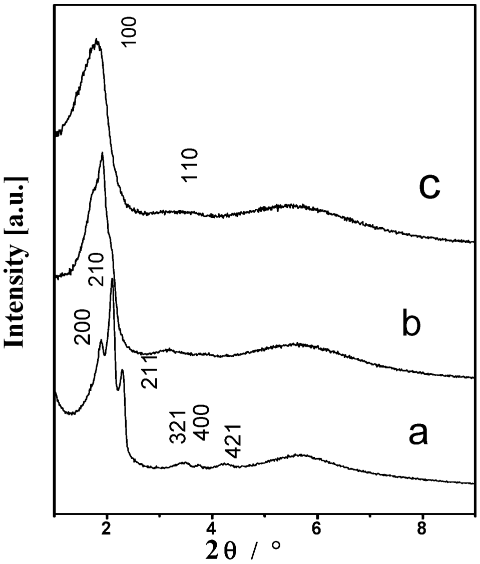

Figure 4. XRD patterns for as-synthesized mesostructured zirconium oxide sulfate composites templated from tri-headgroup surfactants (a) $C_{18-2-3-1}$, (b) $C_{18-3-3-1}$, and (c) $C_{18-3-4-1}$.

chain length among the hydrophilic headgroups of the templates. Figure 4 shows XRD patterns for as-synthesized zirconium oxide sulfate prepared by using three kinds of tri-headgroup quaternary ammonium surfactants ($C_{18-2-3-1}$, $C_{18-3-3-1}$, and $C_{18-3-4-1}$) as structure directing agents. It is clear that upon increasing the spacer chain length among the hydrophilic headgroup (from $s = 2$, $m = 3$ to $s = 3$, $m = 3$, and $s = 3$, $m = 4$), cubic ($Pm3n$ symmetry), mixed and a 2D hexagonal mesophase ($p6m$ symmetry) zirconium oxide sulfates can be obtained, respectively, implying that from $C_{18-2-3-1}$ through $C_{18-3-3-1}$ to $C_{18-3-4-1}$, a phase transfer occurs. XRD patterns for mesostructued zirconium oxophosphates treated with aqueous solution of H_3PO_4 and their calcined analogues with 2D hexagonal or mixed mesophase structure are also shown in Figure 5.

TEM images further reveal that the mesophase transfer can be achieved by finely tuning the spacer methylene chain length among the hydrophilic headgroups of the multi-charged cationic surfactants. Figure 6 shows a 2D hexagonally mesostructured zirconium oxophosphate with $p6m$ symmetry prepared by using $C_{18-3-4-1}$ as a structure-directing agent, recorded along the [001] and [100] directions. By using $C_{18-3-3-1}$ as a template, a mixed mesophase of hexagonal ($p6m$) and cubic ($Pm3n$) symmetries can be observed in one domain (Figure 7), further indicating the mixed mesophase is formed.

^{31}P MAS NMR. Changes in the mesostructured zirconium oxophosphate frameworks caused by the phase transition can be further characterized by ^{31}P MAS NMR (Figure 8 and Table 1). 3D cubic mesostructured zirconium oxophosphate (ZrPO-1) shows four resonance peaks centered at −7.6, −14.9, −20.9, and

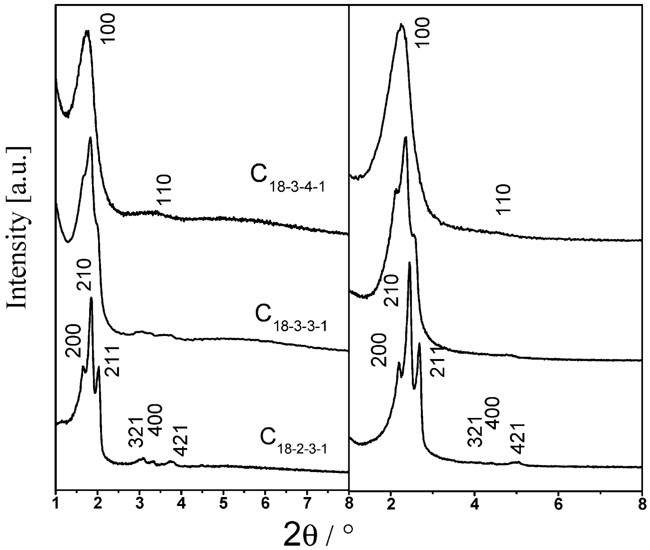

Figure 5. XRD patterns for the fresh (left) and calcined (right) mesostructured zirconium oxophosphate composites prepared by using different tri-headgroup surfactant as the templates.

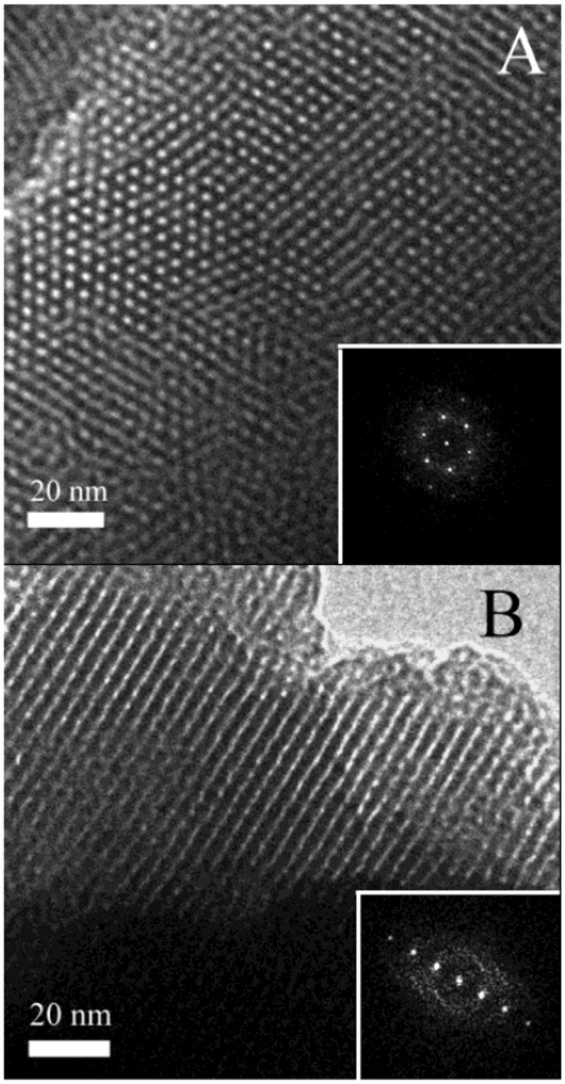

Figure 6. TEM images and Fourier diffractograms patterns for the calcined mesostructured (*p*6*m*) zirconium oxophosphate template with $C_{18-3-4-1}$ along (A) [001] and (B) [100].

−29.5 ppm, which can be assigned to tetrahedral phosphorus-connected one, two, three, and four zirconia

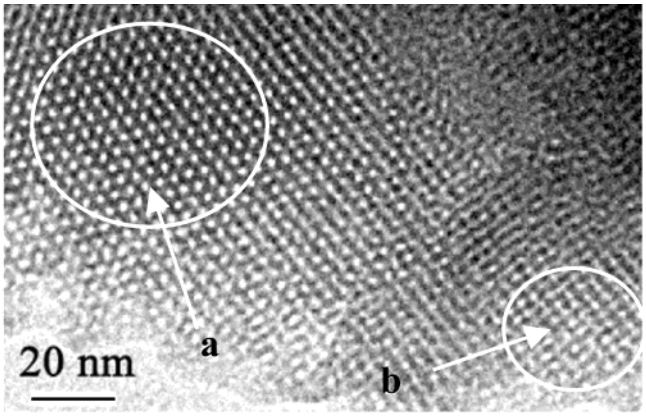

Figure 7. TEM images for the mixed mesophase of calcined zirconium oxophosphate templated by $C_{18-3-3-1}$: (a) is the hexagonal mesophase along [001] direction; (b) is the cubic mesophase along [110] direction.

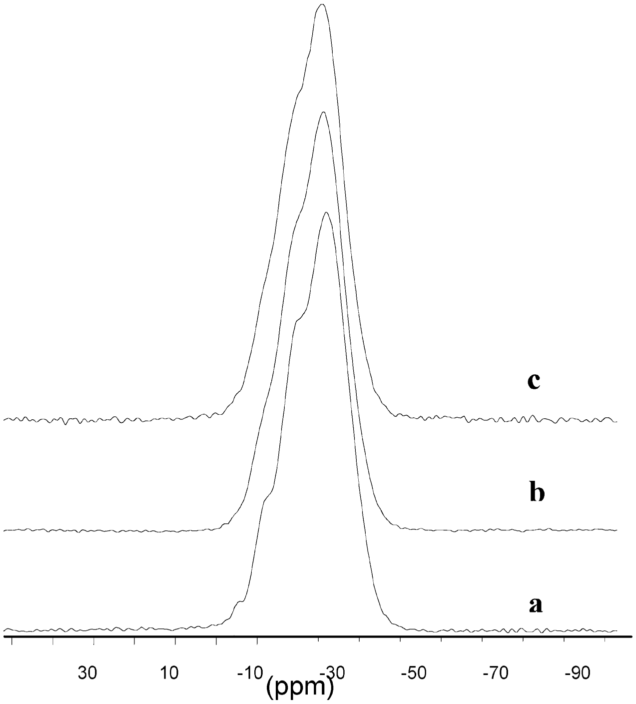

Figure 8. ^{31}P MAS NMR spectra of calcined zirconium oxophosphate templated by different tri-headgroup amphiphiles: (a) $C_{18-2-3-1}$, (b) $C_{18-3-3-1}$, and (c) $C_{18-3-4-1}$.

(corresponding to surface $(HO)_3PO{-}Zr$, $(HO)_2P(O{-}Zr)_2$, $HOP(O{-}Zr)_3$, and $P(O{-}Zr)_4$ groups),[52−56] whereas in the mixed mesophase (ZrPO-2), the resonance at −7.6 ppm disappears, and the other three resonance peaks correspond to $(HO)_2P(O{-}Zr)_2$, $HOP(O{-}Zr)_3$, and $P(O{-}Zr)_4$ species appear at −16.7, −21.3, and −28.8 ppm, respectively. Three resonance peaks corresponding to phosphorus environment in 2D hexagonal mesophase (ZrPO-3) are shifted to −16.2, −20.6 and −28.3 ppm. The changes may be related to the phase transfer and resultant from different curvature of the inorganic walls of the mesostructures.

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(52) Benhamza, H.; Barboux, P.; Bouhaouss, A.; Josien, F. A.; Livage, J. *J. Mater. Chem.* **1991**, *1*, 681.

(53) Clayden, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1877.

(54) Maclachlan, D. J.; Morgan, K. R. *J. Phys. Chem.* **1990**, *94*, 7656.

(55) Bortun, A. I.; Bortun, L.; Clearfield, A.; Villa-Garcia, M. A.; Garcia, J. R.; Rodriguez, J. *J. Mater. Res.* **1996**, *11*, 2490.

(56) Mudrakovskii, I. L.; Shmachkova, V. P.; Kotsarendo, N. S.; Mastikhin, V. M. *J. Phys. Chem. Solids* **1986**, *47*, 335.

Table 1. ^{31}P NMR Chemical Shift (ppm) and P/Zr Ratio of Calcined Mesostructured Zirconium Oxophosphate

	$(HO)_3PO{-}Zr$	$(HO)_2P(O{-}Zr)_2$	$HOP(O{-}Zr)_3$	$P(O{-}Zr)_4$	P/Zr ratio
ZrPO-1	−7.6	−14.7	−20.9	−29.5	0.99
ZrPO-2		−16.7	−21.3	−28.8	0.98
ZrPO-3		−16.2	−20.6	−28.3	1.05

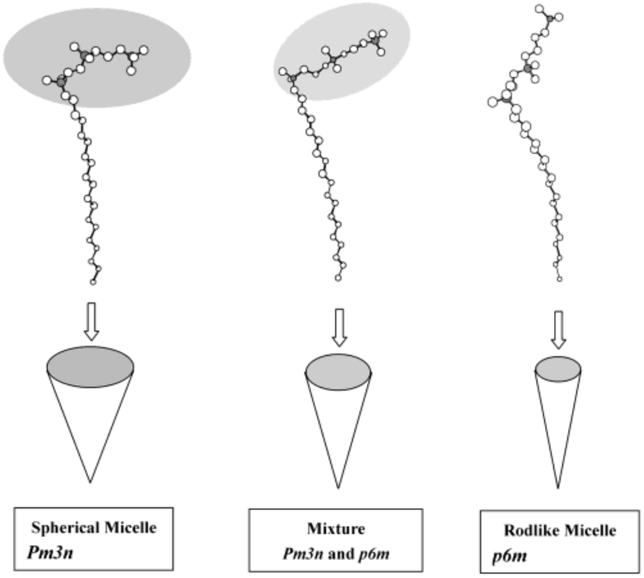

Figure 9. Representative schematic drawings of phase transformation of the tri-headgroup quaternary ammonium surfactants via finely tuning the spacer methylene chain length: (A) $C_{18-2-3-1}$; (B) $C_{18-3-3-1}$; (C) $C_{18-3-4-1}$.

We speculate that the phase transfer upon the tuning of spacers is related to surface charge density and the volume of the headgroup of the surfactants[57] (Figure 9). In the aqueous solution, the surfactant molecular $C_{18-2-3-1}$ is favorable to aggregate a spherical micelle, which leads to generate the caged cubic (*Pm*3*n*) mesostructured zirconium-based composite. In constrast, increasing the spacer methylene chain length among the hydrophilic headgroup (in the case of $C_{18-3-3-1}$ and $C_{18-3-4-1}$), will reduce the average surface charge density and the volume of the headgroup, namely lowering the effective interaction between the headgroups and the inorganic species and decreasing the surface curvature. Therefore, the mixed mesophase and the hexagonal mesophase with lower surface curvature are formed.

Conclusions

A new highly ordered thermally stable cubic mesostrucured zirconium oxophosphate with *Pm*3*n* symmetry has been synthesized by using tri-headgroup quaternary ammonium surfactant as a structure-directing agent. A phase transformation is occurred from *Pm*3*n* through mixed mesophase to *p*6*m* symmetry by finely tuning the spacer methylene chain length among the hydrophilic headgroup in the multi-charged amphiphile. The mesophase is much dependent on the average surface charge density and the volume of the headgroup of the surfactants. The phosphorus in the cubic mesostructured zirconium oxophosphate framework has four types of chemical environments and is different from that in the hexagonal zirconium oxophosphate mesophase, as the latter shows three types of chemical environments. Such cubic mesostructured zirconium based composites can be of great interest in terms of catalysis and other areas.

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Supporting Information Available: N_2 adsorption/desorption isotherms for the studied compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(57) Zana, R. *Adv. Colloid Inteface. Sci.* **2002**, *97*, 205 and references therein.

(58) Huo, Q.; Lein, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.