doi:10.1246/cl.2010.496

Preparation of Hybrid Ordered Inorganic–Organic Mesostructures from an Asymmetrically Bridged Organic Precursor Containing Both Silanolate and Phosphonate

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Novel hybrid inorganic–organic mesostructures were hydrothermally prepared from pseudo-boehmite and an organic precursor containing both silanolate and phosphonate groups in the presence of cationic surfactants. The solid-state NMR revealed that aluminum species are mainly connected with phosphonate groups in the formed 2D hexagonal mesostructures.

Ordered mesoporous materials have aroused considerable interest because of well-defined pores with narrow size distributions as well as their high surface areas, stability, and a variety of textures.[1] Recently, introduction of organic groups in mesoporous silica frameworks attracted much attention.[2–5] It is expected that novel materials with both functionality/flexibility of organic groups and robustness of inorganic frameworks can be designed. Mesostructured organosilicas obtained from bridged organodisilanolate precursors $(R'O)_3Si–R–Si(OR')_3$ are typical ones known as "bridge type." The organic moieties are incorporated in the silica matrix and generally distributed in the pore walls. A number of bridged polysilanolate precursors have been successfully used as the sources of ordered mesostructures.[4] Especially, mesoporous phenylene–silica materials reported by Inagaki et al. have a 2D hexagonal array of mesopores as well as crystal-like pore walls, within which a short range regularity was confirmed.[5] While hybrid mesoporous materials including organic groups in the frameworks are mainly silica-based, hybrid mesoporous non-silica-based inorganic–organic materials have also been developed in metal organophosphonates.[6–8] They were prepared from metal sources, which readily react with phosphonate species, and monophosphonic acids $[R–PO(OH)_2]$ or diphosphonic acids $[(HO)_2OP–R–PO(OH)_2]$ as organophosphonate sources. Several mesoporous aluminum organophosphonates were successfully prepared by using cationic surfactants and triblock copolymers.[6,7] Although the structural stability of mesoporous aluminum organophosphonates proved to be lower than mesoporous organosilicas, it was reported that mild calcination or use of weak acids or organic solvents were effective in the template removal without destroying the structure. Apart from the aluminum compounds, a mesoporous tin phosphonate was also reported.[8] Thus, various metals can be potentially incorporated in ordered mesostructures by using organophosphonate linkers.

Although there were many reports on hybrid mesostructured inorganic–organic materials as described above, they were prepared solely from organic precursors including single linking functional groups, e.g., disilanolates and diphosphonates. In general, organosilanolate groups tend to condense each other forming a variety of stable mesostructures. Organophosphonate groups are known to link with various metal species and a variety of open-framework metal organophosphonates have been reported.[9] In this study we report on formation of hybrid ordered inorganic–organic mesostructures from a single organic precursor containing two different functional groups, silanolate $(–SiO_3{}^{3-})$ and phosphonate $(–PO_3{}^{2-})$. Such an asymmetrically bridged organic precursor was used for the first time as the source of mesostructures as far as we know and should be useful to construct ordered metal-containing organosilica frameworks.

The precursor diethylphosphatophenyltriethoxysilane (PPS) was prepared from 4-bromophenyltriethoxysilane[10] by the Arbuzov reaction using $NiBr_2$ as the catalyst. The high-boiling PPS containing nickel was hydrolyzed by refluxing in concentrated hydrochloric acid to obtain $[H_2O_3P–C_6H_4–SiO_{1.5}]$ (PPS-H).[11] The mesostructures were hydrothermally prepared from PPS-H, pseudo-boehmite, cationic surfactants $[C_nH_{2n+1}N(CH_3)_3\text{-}Br]$ (C_nTAB, $n = 14$, 16, and 18), and tetramethylammonium hydroxide (TMAOH). The product obtained from starting composition $1.0PPS\text{-}H \cdot 0.5Al_2O_3 \cdot 0.5TMA_2O \cdot 1.0C_nTAB \cdot 600H_2O$ at m °C ($m = 100$, 120, and 140) is denoted as C_nAPS-m.[11]

Powder X-ray diffraction (XRD) patterns of the products prepared at different temperatures using C_{16}TAB are shown in Figures 1a–1c. All the products give diffraction peaks at a small-angle region, indicating formation of ordered mesostructures. Especially, C_{16}APS-140 showed three distinct diffraction peaks assigned to (10), (11), and (20) reflections ($d = 3.5$, 2.0, and 1.8 nm, respectively) of a 2D-hexagonal lattice with $a = 4.0$ nm. When a surfactant with a longer alkyl chain is used, the diffraction peaks shift to lower angles and thus larger periodicity is obtained (Figures 1d–1f). In a wide-angle area, only amorphous halo was observed and periodicity in a molecular scale was not observed at any preparation conditions.

In transmission electron microscopy (TEM) images of the C_{16}APS-140, ordered hexagonal arrays of mesoporous channels

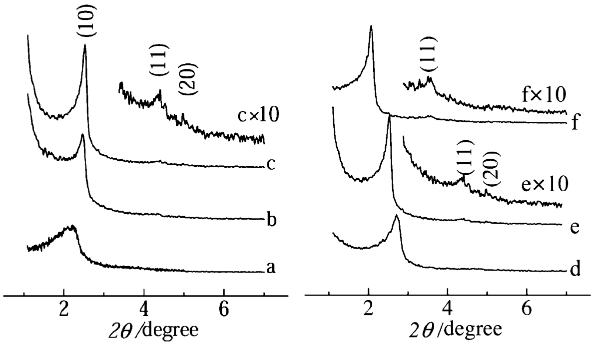

Figure 1. XRD patterns of C_{16}APS-m [a) $m = 100$, b) $m = 120$, and c) $m = 140$], and C_nAPS-140 [d) $n = 14$, e) $n = 16$, and f) $n = 18$].

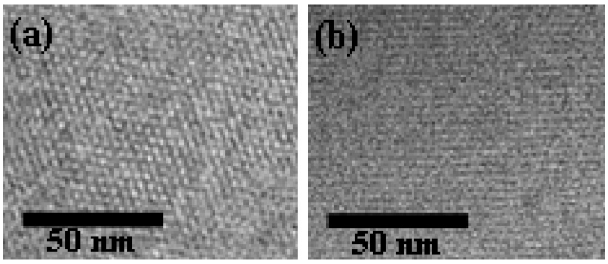

Figure 2. TEM images of C_{16}APS-140 mesostructure viewed (a) along and (b) across the channel direction.

(Figure 2a) as well as parallel channels (Figure 2b) are observed. These images are typical of 2D hexagonal mesoporous silicas. The basal spacing is estimated to be ca. 3.5 nm from the images. This is consistent with the XRD results, confirming the ordered 2D hexagonal structure.

According to the ICP-AES and CHN elemental analysis, the composition of the as-synthesized C_{16}APS-140 was represented in a formula of $0.52Al_2O_3\cdot1.0(O_2PC_6H_4SiO_{1.5})\cdot0.42C_{16}\text{-}TMA_2O\cdot2.3H_2O$. The molar ratio of Si:P:Al was 1.0:1.0:1.1, indicating that C_{16}APS-140 obtained as a precipitate from the liquid phase almost retained the Al/PPS ratio of the starting aqueous gel and that TMA was not incorporated.

The ^{29}Si MAS NMR of C_{16}APS-140 (Figure S2a[11]) exhibits a broad peak centered at −70 ppm, while that of PPS-H showed a peak at −75 ppm (Figure S1a[11]). These peaks are reasonably assigned to T^n species $[R\text{–}\mathit{Si}(OSi)_n(OH)_{3-n}]$, because the reported phenylene-bridged organosilicas gave resonances around −60 to −80 ppm.[5,12] According to the observed chemical shift, contribution of T^2 species $[R\text{–}\mathit{Si}(OSi)_2(OH)]$ should be largest accompanied with T^3 and T^1 species. Since no apparent peak is observed in the higher field (Q-site region), it is assumed that cleavage of Si–C bonds during the hydrothermal reaction is negligible.

The ^{27}Al MAS NMR of C_{16}APS-140 (Figure S2d[11]) gives two resonances at 40 and 7 ppm. According to literature resonances from four-coordinate Al species in aluminoorganosilanolates are observed at 50–60 ppm,[13] while they appear at 30–40 ppm in aluminoorganophosphonates.[6] The observed resonance at 40 ppm, therefore, indicates that the aluminum species are four-coordinate and mainly connected to phosphonate groups rather than silanolate groups. The resonance at 7 ppm is similarly assigned to five-coordinate Al species connected to phosphonate groups.

The ^{31}P MAS NMR of PPS-H gives a resonance at 16.9 ppm (Figure S1b[11]), and the observed shift is typical of free arylphosphonic acids. Meanwhile, C_{16}APS-140 gives a broad peak centered at 0.7 ppm (Figure S2b[11]). In cases of the reported mesoporous aluminophosphates, signals assigned at phosphate groups connected to aluminum species were observed around −25 ppm.[7] The reported mesoporous aluminum organophosphonates gave signals at 0–10 ppm.[6] In crystalline aluminum phenylphosphonates, resonances arising from hydrogen phenylphosphonate groups connected to aluminum species were observed in this range.[14] It is, therefore, confirmed that no cleavage of the P–C bonds occurs. The observed resonance is mainly assigned at $[HO_3\mathit{P}\text{–}C_6H_4\text{–}]$, where hydrogen phosphonate groups are bonded with aluminum species. Accordingly, all the MAS NMR results clearly support that PPS is pristinely incorporated in the framework. It is reasonable to conclude that the silanolate groups mainly condense each other and that the phosphonate groups condense with aluminum species, both contributing in mesostructure formation, though the condensation of the framework is insufficient (Figure S3[11]).

In our attempts to template removal, the occluded surfactants were not sufficiently extracted with acetic acid/EtOH solutions, which was reported to be effective in the case of mesoporous aluminum dimethylenediphosphonates.[7] Acid treatment using HCl/EtOH solutions, as well as calcination at 400 °C, led to removal of the surfactants, though the structural regularity was lost to show low N_2 adsorption capacities. This may be partly due to the insufficient condensation of the framework species.

In conclusion, novel hybrid inorganic–organic mesostructures were prepared by using an asymmetrically bridged organic precursor containing both silanolate and phosphonate groups. As far as we recognize, this is the first report on the mesostructured materials composed of different inorganic domains, i.e., silic-onate and metal phosphonate, segregated with an organic linker. Although the framework stability is not high, elaborate design of framework structures and compositions should contribute to novel mesoporous materials with tailored sorption and catalytic properties.

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 21550186) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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