Synthesis of mesoporous aluminophosphates using surfactants with long alkyl chain lengths and triisopropylbenzene as a solubilizing agent

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Mesostructured organo-aluminophosphates were prepared by using surfactants with long alkyl chain lengths (C_{16} and C_{22}) and by utilizing solubilization of triisopropylbenzene; calcination of the mesostructured materials yielded thermally stable mesoporous aluminophosphates with surface areas >700 m^2 g^{-1} and with pore diameters in the range 1.8–3.9 nm.

Mesoporous silicas, denoted FSM[1] and M41S,[2] are very attractive materials for catalysts, catalyst supports and adsorbents for larger molecules than those treated in microporous crystals. Since microporous $AlPO_4$-*n* materials are known,[3] it is expected that mesostructured organo-aluminophosphates are useful for the formation of mesoporous aluminophosphates to enlarge the variety and possible applications of mesoporous materials. We have already reported the successful formation of a hexagonal mesostructured aluminophosphate (AlPO) by using hexadecyltrimethylammonium chloride.[4] Feng *et al.* also reported a hexagonal mesostructured material prepared in the presence of F^- ions, however, the porous structure collapsed upon calcination.[5] Recently a mesoporous aluminophosphate with large surface area (790 m^2 g^{-1}) was reported by Zhao *et al.*[6] Although the pore diameter of the product was reported to be *ca.* 4.0 nm, this value is somewhat questionable because it is too large judging from the values observed for ordered mesoporous silicas.[1,2] On the other hand, Holland *et al.*[7] and Cheng *et al.*[8] reported mesoporous aluminophosphate-based materials *via* layered intermediates; the porous materials, prepared by solvent extraction, are thermally unstable.

The hexagonal mesostructured AlPO reported by us had a less condensed framework, so that a microporous material formed after calcination in air.[4] Based on this result, it is expected that mesoporous AlPOs can be obtained by utilizing mesostructured AlPOs with larger hexagonal arrays. Here, we report the successful synthesis of thermally stable mesoporous AlPOs, based on this strategy.

Hexagonal mesostructured AlPOs were prepared by using $C_{16}H_{33}NMe_3Cl$ (C_{16}TMACl) and $C_{22}H_{45}NMe_3Cl$ (C_{22}TMACl), denoted as C_{16}-AlPO and C_{22}-AlPO, respectively. C_{16}-AlPO was prepared according to our previous paper.[4] C_{22}-AlPO was prepared as follows: C_{22}TMACl (containing a small amount of shorter alkyl chains), tetramethylammonium hydroxide (TMAOH, 25 mass% in water), 85% H_3PO_4, and water were mixed for several hours. Aluminium triisopropoxide was added to this mixture under vigorous stirring, and the stirring was continued for 1 day. The composition of the starting mixture was $Al_2O_3 : P_2O_5 : C_{22}$-TMACl : 2.0 TMAOH : 65.0 H_2O. The starting mixture was dispersed in distilled water at 70 °C, with formation of a white solid. This solid was washed with distilled water heated at 70 °C repeatedly, and dried at 80 °C. Solubilization of 1,3,5-triisopropylbenzene (TIPBz) into surfactant assemblage was also carried out for C_{22}TMACl; TIPBz has already been known to act as a solubilizing agent.[9] The synthesis procedure was the same as described above and TIPBz was added before the addition of aluminium triisopropoxide. The molar ratio of TIPBz/C_{22}TMACl in the starting mixture was 1, and this product was denoted as TIPBz/C_{22}-AlPO; the molar ratio of TIPBz/C_{22}TMACl in the TIPBz/C_{22}-AlPO was *ca.* 0.67 based on the CHN analysis, indicating that not all the TIPBz was solubilized in the surfactants. All the products were heated at 600 °C for 1 h in flowing N_2, followed by calcination at 600 °C for 1 h in flowing air. The calcined products were analyzed by XRD, N_2 adsorption, and ^{27}Al and ^{31}P MAS NMR spectroscopy performed on a JEOL GSX-400 with a spinning rate of 5 kHz (for ^{27}Al: frequency: 104.05 MHz; pulse angle: 45°; recycle time: 5 s, for ^{31}P: 161.70 MHz; 60°; 20 s, respectively).

The XRD patterns of all the products before calcination are shown in Fig. 1. The XRD peaks of the C_{16}-AlPO can be assigned to (100), (110) and (200) of a hexagonal phase. The XRD peaks of both C_{22}-AlPO and TIPBz/C_{22}-AlPO can also be assigned to (100), (110), (200) and (210) of hexagonal phases. The lattice parameters (a_0) of the C_{16}-AlPO, C_{22}-AlPO and TIPBz/C_{22}-AlPO were 4.8, 5.8 and 7.2 nm, respectively. These XRD results indicate the formation of mesostructured AlPOs with large hexagonal arrays by utilizing C_{22}TMA and solubilization of TIPBz.

In the XRD patterns of the calcined products (Fig.1), the d_{100} peak shifted from 4.1 to 2.8 nm for C_{16}-AlPO after calcination, and the XRD patterns showed a shift from 5.1 to 3.7 nm for C_{22}-AlPO and a shift from 6.2 to 4.6 nm for TIPBz/C_{22}-AlPO. The lattice parameters (a_0: $2d_{100}/\sqrt{3}$) of the calcined C_{16}-AlPO, calcined C_{22}-AlPO and calcined TIPBz/C_{22}-AlPO were 3.2, 4.3 and 5.3 nm, respectively, if we assume that the calcined products retain the hexagonal structures. The shrinkages are

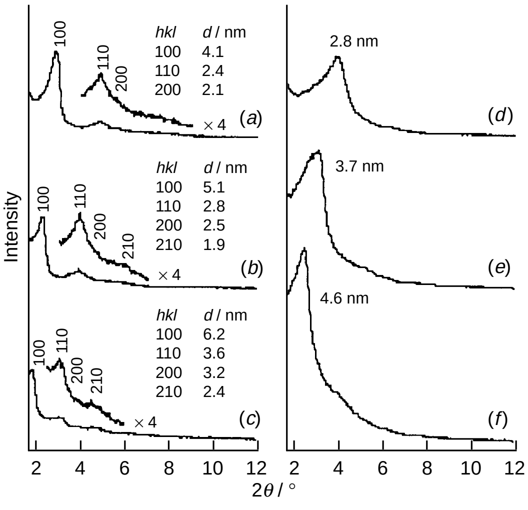

Fig. 1 XRD patterns of (*a*) C_{16}-AlPO, (*b*) C_{22}-AlPO and (*c*) TIPBz/C_{22}-AlPO, (*d*) calcined C_{16}-AlPO, (*e*) calcined C_{22}-AlPO and (*f*) calcined TIPBz/C_{22}-AlPO. These patterns were recorded on a Mac Science M03XHF^{22} diffractometer with monochromated Fe-Kα radiation.

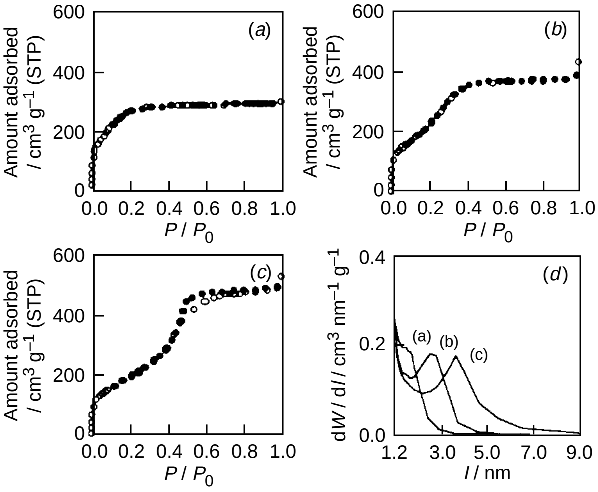

Fig. 2 N_2 adsorption isotherms of calcined (*a*) C_{16}-AlPO, (*b*) C_{22}-AlPO and (*c*) TIPBz/C_{22}-AlPO. Filled symbols denote desorption. Corresponding pore size distributions of the calcined products are shown in (*d*). These isotherms were obtained by a BELSORP 28 (Bel Japan, Inc.) at 77 K.

larger than those observed for silica-based mesoporous materials[2] because of less condensed frameworks as described below. In addition, the XRD peaks of all the products were broadened after calcination. These results suggest that the porous structures remained, although the sizes and the regularities of the hexagonal arrays decreased upon calcination.

Hexagonal arrays with relatively ordered arrangements were observed in the TEM images of all the products before calcination. After calcination, disordered arrays were obtained, and the periodic distances of these arrays decreased. These TEM images are in agreement with the XRD results. No other phases were detected in any TEM images.

The N_2 adsorption isotherms and the pore size distributions of the calcined products, calculated by the Horváth–Kawazoe method,[10] are shown in Fig. 2. The N_2 adsorption isotherm of calcined C_{16}-AlPO showed almost type I behavior, indicating the presence of micropores; the pore diameter was *ca.* 1.8 nm. In contrast, the isotherms of the calcined C_{22}-AlPO and TIPBz/C_{22}-AlPO showed type IV behavior. The calcined C_{22}-AlPO had a BET surface area of 760 $m^2\ g^{-1}$, a pore volume of 0.56 $cm^3\ g^{-1}$ and an average pore diameter of 2.8 nm. For the calcined TIPBz/C_{22}-AlPO, the BET surface area and the pore volume were 720 $m^2\ g^{-1}$ and 0.72 $cm^3\ g^{-1}$, respectively. The pore diameter was *ca.* 3.9 nm.

The structural changes during calcination can be monitored by ^{27}Al and ^{31}P MAS NMR measurements before and after calcination. The ^{31}P MAS NMR spectra of the uncalcined products showed several peaks in the range δ 0 to -20, indicating the uncalcined products had less condensed frameworks.[4,11,12] A broad peak centered at $\delta\,-21$ was observed after calcination indicating condensation of the frameworks.[11,12] The ^{27}Al MAS NMR spectra of the uncalcined products showed that signals due to both four- (Al^{IV}) and six-coordinate Al (Al^{VI}) at δ *ca.* 43 and 1, respectively. Based on the Al^{IV}/Al^{VI} intensity ratios, varying from *ca.* 0.6 (C_{16}-AlPO) to *ca.* 0.3 (C_{22}-AlPO and TIPBz/C_{22}-AlPO), a large amount of Al^{VI} is present in the uncalcined products and they may be coordinated with not only PO_4 units but also water molecules,[4] being related to less condensed frameworks. Only a broad signal due to Al^{IV} was observed at *ca.* δ 39 for each calcined product; the chemical shift strongly suggesting that the $Al^{IV}O_4$ units are surrounded by mainly P.[11,13] Although the Al/P ratios (1.5), discussed below, might suggest the presence of Al–O–Al bonds, such bonds are unlikely, judging from very different chemical shifts expected for $[Al^{IV}O_4(nAl)]$ (n = 1–4).[13]

Both N_2 adsorption and NMR results indicate that the pore sizes can be controlled although shrinkage must be taken into consideration, so that the C_{22}-AlPO and TIPBz/C_{22}-AlPO changed to mesoporous materials after calcination owing to the larger hexagonal arrays.

The C_nTMA/(Al + P) ratios were 0.25 (C_{16}-AlPO), 0.19 (C_{22}-AlPO) and 0.16 (TIPBz/C_{22}-AlPO), and the Al/P ratios of all the products were *ca.* 1.5. This Al/P value is different from unity which would be expected for an ideal three-dimensional $AlPO_4$-*n*.[3] The Al/P ratios of mesostructured and/or mesoporous aluminophosphates reported by Feng *et al.*,[5] Zhao *et al.*,[6] Holland *et al.*,[7] and Cheng *et al.*[8] are 2.9, 0.64, 1.5, and 1.0, respectively. Although the Al/P ratios of mesoporous AlPOs reported here are similar to those reported by Holland *et al.*,[7] the coordination of Al atoms is six for their materials while it is mainly four for ours. For the other three materials, the Al/P ratios are clearly different. Nevertheless, the coordination of Al atoms in the material reported by Feng *et al.*[5] is similar to ours. However, because there is little information on the aluminophosphate frameworks in those reports, appropriate comparison with our materials is not possible at present.

In conclusion, thermally stable mesoporous AlPOs were obtained by calcination of hexagonal mesostructured AlPOs prepared by using both C_{22}TMA as a micelle aggregate and TIPBz as a solubilizer. This method can be applicable for the preparation of various mesoporous materials from less condensed inorganic units–surfactant mesostructured materials, which normally afford microporous materials owing to substantial shrinkage. A study on the surface structure of these mesoporous AlPO is now in progress.

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