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Synthesis of a novel mesoporous tin phosphate, $SnPO_4$

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Novel mesoporous tin phosphates have been synthesized using alkyltrimethylammonium bromide (alkyl = C_8–C_{18}) as surfactant; the structure of the materials is stable at 500 °C. UV–VIS spectra show tetrahedral coordination of tin.

Following the discovery of M41S, silica mesoporous molecular sieves[1] have attracted considerable attention because of their large internal surface area and narrow pore size distribution, and potential application of these materials to use as absorbents, catalysts and catalyst supports.[2] This methodology has been extended to prepare a variety of mesoporous aluminophosphates[3,4] and metal oxides[5] by supermolecular assembly pathways. Recently, the syntheses of a few other metal (Zr, Ti, V and Fe) phosphate mesoporous molecular sieves have been reported.[6–9]

Pillared tin phosphates are used as sorbents, catalysts and electrical conductors (Li^+ ion exchanged).[10,11] Mesoporous tin phosphate may be very useful for catalysis. However, the synthesis of mesoporous tin phosphate has not been reported until now.

Here, we report, for the first time, the synthesis of mesoporous tin phosphate using cationic surfactant, $CH_3(CH_2)_nN(CH_3)_3Br$ (n = 7, 11, 15 or 17). In a typical synthesis, 3.46 g of H_3PO_4 (85%, Wako Chem.) was added to 5.26 g of $SnCl_4$ (99%, Wako Chem.) in 100 g of water and stirred for 30 min. To this clear solution, aqueous ammonia was added until the pH became 2.70 which led to a precipitate which was filtered off and washed with distilled water several times to remove chloride ions. The P/Sn molar ratio of this material was 1.26 (by elemental analysis). 20 g of water and 25 g of tetramethylammonium hydroxide (25% aqueous, Aldrich) were added to the filtered (solid) materials and stirred for 30 min to obtain a clear solution. 7.59 g of hexadecyltrimethylammonium bromide (96%, Wako Chem.) (Sn/surfactant = 1.0, molar ratio) was then added and stirred for 2 h. Finally, after the required amount of H_3PO_4 (5.2 g) was added, the clear solution led to a to precipitate, with the pH being maintained at 3.75. The synthesis gel was then transferred to a propylene bottle and statically heated at 65 °C under autogenous pressure for 2 days. The resultant product was filtered off, washed with deionized water and dried in vacuum at 200 °C for 12 h. The structure was analyzed by XRD (Shimadzu XRD-6000) and TEM (Hitachi H-9000NA, 300 kV). XRD showed the *d* spacing of the 100 layer in the layered material was 3.81 nm as shown in Fig. 1(a). TEM confirmed the presence of the layered structure [Fig. 2(a)] the structure of which collapsed above 350 °C.

2.0 g of the surfactant containing layered material was suspended in 100 g of water and statically heated at 175 °C for 2 days. After decanting and washing, the solid material was dried at 100 °C for 1 day and then calcined at 500 °C for 2 h to remove the surfactant. The resultant solid material is referred to as $SnPO_4$. For comparison, mesoporous SnO_2 was synthesized according to a procedure described elsewhere[12] and calcined at 500 °C for 2 h.

The P/Sn molar ratio of the layered material and $SnPO_4$ were the same (1.21). This value indicates that excess $H_2PO_4^-$ and HPO_4^{2-} ions were present to balance the unit positive charge on the framework of $SnPO_4$. The XRD pattern of the surfactant–$SnPO_4$ and calcined $SnPO_4$ are shown in Fig. 1(b) and (c), respectively. The *d* spacing of the 100 plane in surfactant–$SnPO_4$ is 3.87 nm, whereas after calcination it was reduced to 3.50 nm. The calcined $SnPO_4$ shows a very broad diffraction peak at low angle, which is characteristic of mesostructure formation. TEM images of the surfactant–$SnPO_4$ confirms the hexagonal structure as shown in Fig. 2(b). TG (Seiko, SSC/5200) analysis shows that wt% loss between 150 and 500 °C due to removal of surfactant and condensation of hydroxy groups are 50.4 and 37.6% for the layered structure and hexagonal $SnPO_4$, respectively. This indicates that dissociation and rearrangement of bonds occur between surfactant and metal ions during hydrothermal heating at 175 °C. A possible explanation for the formation of the hexagonal structure is that surfactant remaining in the layer forms micelles in water at 175 °C and forces the layers to bend.[8,13] Fig. 3 shows the N_2 sorption isotherm of calcined $SnPO_4$ measured at −196 °C using a Bellsorp-28 instrument; the isotherm is of type IV.[1] The

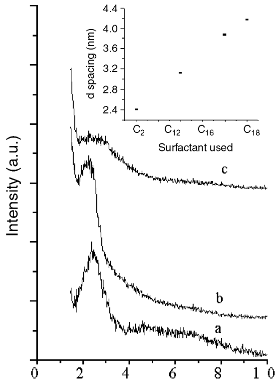

Fig. 1 XRD profiles of (a) surfactant-layered tin phosphate, (b) surfactant–$SnPO_4$ (hexagonal) and (c) $SnPO_4$ after calcination at 500 °C for 2 h. Inset: Change in *d* spacing of surfactant–$SnPO_4$ as a function of alkyl length of surfactant.

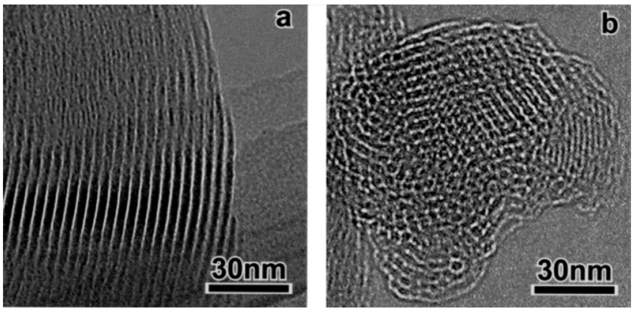

Fig. 2 TEM spectra of (a) surfactant-layered tin phosphate and (b) surfactant–$SnPO_4$.

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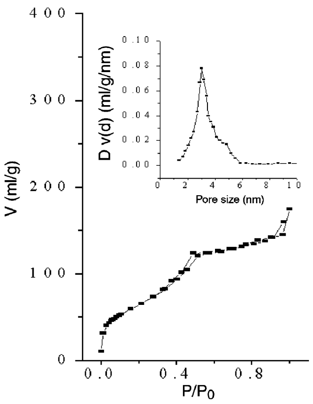

Fig. 3 N_2 adsorption–desorption isotherms of $SnPO_4$ after calcination at 500 °C for 2 h. Inset: Pore size distribution of $SnPO_4$.

pore size distribution curve (Fig. 3, inset) shows that $SnPO_4$ has a broad pore size distribution with an average pore diameter (APD) of 2.96 nm, calculated from the adsorption branch of the isotherm using the BJH method (APD = $4V_P/S_{BJH}$, where V_P = mesopore volume, S_{BJH} = BJH specific surface area).[14] The BET surface area and pore volume of the sample are 230 $m^2\ g^{-1}$ and 0.21 $cm^3\ g^{-1}$, respectively, which is lower than for MCM-41 mesoporous silica but lying in the range of surface areas of other non-siliceous mesoporous solids.[6,9,15] The FT-IR (JASCO FT/IR-230) spectrum of calcined $SnPO_4$ shows the presence of a band at 1050 cm^{-1}, which is absent in mesoporous SnO_2, suggesting a formation of Sn–O–P networks in mesoporous $SnPO_4$ (Fig. 4). Extraction of calcined $SnPO_4$ samples with dilute HCl did not remove any tin from the samples, confirming the absence of Sn^{2+} ions and presence of Sn^{4+} ions in samples. UV–VIS (JASCO V-560) spectra of calcined forms of $SnPO_4$ and SnO_2 are shown in Fig. 5. $SnPO_4$ calcined at 500 or 800 °C showed a band at 220 nm arising from tetrahedral coordination of Sn^{4+} ions, whereas mesoporous SnO_2 showed a band at 303 nm due to octahedral coordination of Sn species. For Sn–Sil–1 (MFI structure) tetra-coordinated Sn species are evidenced by a band at 208 nm.[16] The environment with four –O–P attached to Sn in mesoporous $SnPO_4$ instead of four –O–Si in Sn–Sil–1 may be responsible for this shift. A similar shift in the UV–VIS band of mesoporous titanium phosphate was observed to higher wavelength compared with TS-1 (MFI structure).[7] The absence of a UV–VIS band at *ca.* 303 nm in $SnPO_4$ after calcination at 800 °C, leading to an amorphous material (confirmed by XRD), and the absence of an exotherm due to crystallization and segregation was observed in TG–TDA, confirmed that no SnO_2 phase was present in our samples. Detailed characterization including ^{119}Sn MAS NMR and catalytic activity are in progress.

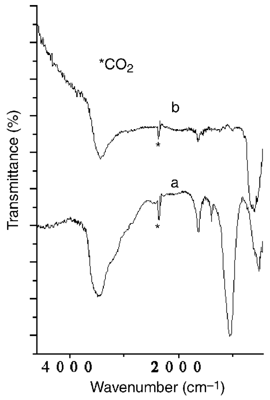

Fig. 4 FT-IR spectra of calcined mesoporous (a) $SnPO_4$ and (b) SnO_2.

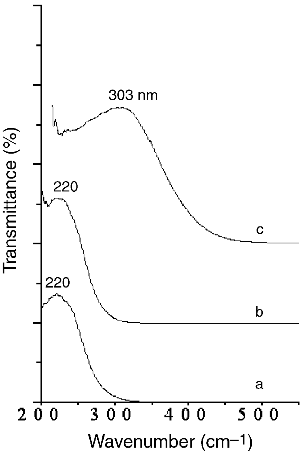

Fig. 5 UV–VIS spectra of mesoporous $SnPO_4$ after calcination at 500 °C (a) and 800 °C (b), and SnO_2 after calcination at 500 °C (c).

In conclusion, mesoporous $SnPO_4$ has been synthesized, for the first time, using cationic surfactants, it possesses a BET specific surface area of 230 $m^2\ g^{-1}$, a pore volume of 0.21 $cm^3\ g^{-1}$ and an average pore diameter of 2.96 nm.

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