

# Synthesis of organic–inorganic hybrid mesoporous tin oxophosphate in the presence of anionic surfactant†

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Synthesis of novel mesoporous hybrid tin oxophosphate is reported from phenylphosphonic acid as the only precursor of phosphorus in the presence of anionic surfactant (SDS), which possesses a wormhole mesoporous structure and is stable even after calcination at 550 °C.

A few years after the invention of ordered mesoporous silica in 1992,<sup>1</sup> syntheses of organic–inorganic hybrid mesoporous silica were reported with the organic group present as terminal<sup>2</sup> or directly integrated<sup>3</sup> to the framework silica. Because of their large surface areas and well defined pore properties, these materials, especially hybrid ones, have great potential in environmental and industrial process.<sup>2c</sup> Later on, various mesoporous oxides other than silica, sulfides, phosphate and metals were prepared. Although varieties of pure and binary mesoporous metal phosphates such as Ti,<sup>4a,b</sup> Al,<sup>4c</sup> Zr,<sup>4d</sup> Nb,<sup>4e</sup> Sn<sup>4f,g</sup> etc. have been reported,<sup>5a</sup> only AlPO based hybrid materials<sup>5b,c</sup> have been claimed. Although framework-modified hybrid materials such as periodic mesoporous organosilicas (PMO) are synthesized from a single precursor,<sup>3</sup> terminally (surface) modified organic–inorganic hybrid metal oxide is generally prepared from a mixture of two precursors such as tetra-alkoxysilane and alkyl-trialkoxysilane for fabricating inorganic framework or inducing the organic part, respectively. As a milestone of our research on mesoporous materials,<sup>4e,f</sup> in this paper we report, for the first time, the synthesis of mesoporous hybrid tin oxophosphate from phenylphosphonic acid as the only precursor of phosphorus in the presence of anionic surfactant (SDS). The wormhole mesoporous structure<sup>6</sup> was extraordinarily stable and was maintained even after calcination.

In the general procedure, mesoporous hybrid tin oxophosphate was synthesized using the following molar composition; 1 SnO<sub>2</sub> : (0.25–1) C<sub>6</sub>H<sub>5</sub>PO(OH)<sub>2</sub> : (0.20–1) NaOH : (0.1–1.0) SDS : (60–300) H<sub>2</sub>O : (2.0–6.0) NH<sub>4</sub>OH. In a typical procedure, 4.16 g of phenylphosphonic acid (25 mmol, 95%, Wako Chem.) and 7.59 g of SDS (25 mmol, 95%, Wako Chem.) was dissolved in 30 g of H<sub>2</sub>O at 40 °C with stirring for 5 min. This clear solution was then added to 17.89 g of SnCl<sub>4</sub>·5H<sub>2</sub>O (50 mmol, 98%, Wako Chem.) in 15 g of H<sub>2</sub>O at room temperature with stirring for 10 min. Finally,

1 g of NaOH in 15 g of H<sub>2</sub>O and 14.0 g of aqueous NH<sub>4</sub>OH (30%) was added and stirred for 50 min. The resulting milky colored homogeneous gel was transferred to a Teflon lined stainless steel autoclave and heated at 180 °C for 16 h. After cooling (pH = 8.90), the solid product was filtered, washed with distilled water and dried at 100 °C for 1 d. 1 g of the as-synthesized material was treated with 100 ml of ethanol and 4 ml of HCl (2 M) at 80 °C for 4 h, filtered and dried at 100 °C for 1 d. This procedure was repeated to ensure complete removal of surfactant.

Calcination of this hybrid tin oxophenylphosphate was carried out at 550 °C for 2 h in air to obtain pure mesoporous tin oxophosphate. The cation exchange capacities of the mesoporous hybrid and calcined tin oxophosphate were measured by treatment of 1 g samples (dried at 120 °C under vacuum) with 500 ml of aqueous NH<sub>4</sub>NO<sub>3</sub> solution (1 M) at 80 °C for 12 h, then filtered and washed. The filtrate was collected in a measuring flask. This step was repeated and the collected solutions were analyzed using ICP (Shimadzu ICPV-1017) to measure the amount of sodium ions.

Method of sulfonation: 1.20 g of ammonium exchanged hybrid Sn oxophenylphosphate dried at 120 °C under vacuum was placed in a 10 mL two necked flask at 40 °C under nitrogen. 4 g of fuming sulfuric acid (28%) was added and stirred for 6 h. After cooling to room temperature, 50 mL of diethyl ether was added and filtered. Finally, the solid washed with distilled water several times to remove all unreacted fuming sulfuric acid and decomposed sulfuric acid. Then solid was dried at 80 °C for 12 h under vacuum.

To evaluate the amount of acid sites (SO<sub>3</sub>H) in the sulfonated sample, 20 mg of dried sample was mixed with 50 g of H<sub>2</sub>O and stirred for 18 h at room temperature. Finally, it was titrated against 0.01 M NaOH using an Automatic Potentiometric Titrator AT-510.

Proton conductivity measurements: The sample for proton conductivity measurement was a pellet of 4 mm diameter and 0.3 mm thickness formed using the cold-pressing technique at a pressure of 100 MPa for 2 min. Silver paste was applied on both sides of the pellet as ionic blocking electrodes. Conductivity was determined by the ac impedance method using a PC controlled SI 1260 impedance/gain-phase analyzer (Solarton) at 298 K. The IS (Impedance Spectroscopy) measurements were performed over the frequency range 1 Hz–10 MHz at an oscillator amplitude of 10 mV. Proton conductivity was measured between 0 to 90 % relative humidity.

XRD (Cu-K $\alpha$  radiation) profiles of hybrid and calcined mesoporous tin oxophosphates are shown in Fig. 1. Interplanar spaces of as-synthesized, surfactant extracted and calcined materials are 3.37, 3.77 and 3.80 nm, respectively. Crystallinity and interplanar

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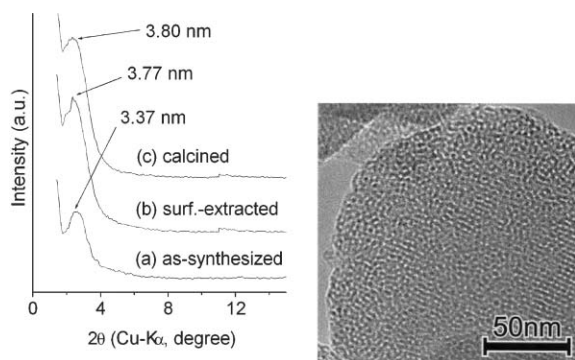
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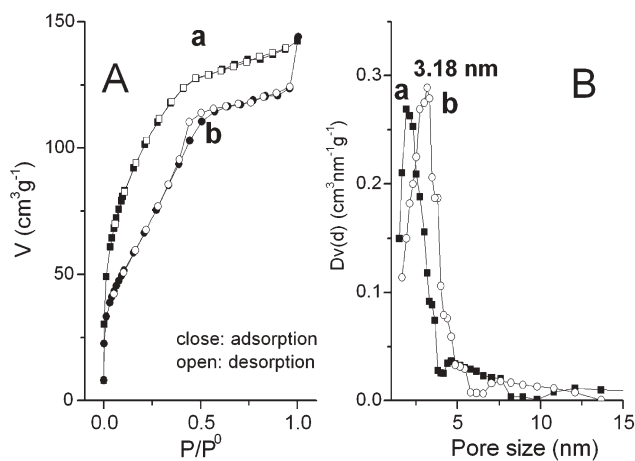


**Fig. 1** XRD profiles of hybrid mesoporous tin oxophenylphosphates, (a) as-synthesized, (b) surfactant extracted and (c) after calcination at 823 K (left). A TEM image of mesoporous hybrid tin oxophenylphosphate (right).

spacing of the hybrid material increased after surfactant extraction and calcination due to removal of surfactant and condensation of Sn–OH and C<sub>6</sub>H<sub>5</sub>P–OH groups in the case of calcination. Hybrid mesoporous tin oxophenylphosphate retained its structure even after calcination at 550 °C. A transmission electron microscope (TEM: 300 kV) image shows a disordered arrangement of pores suggesting a wormhole-like structure (Fig. 1).<sup>2e</sup> The TEM image of calcined sample is also similar in nature to this hybrid sample.

N<sub>2</sub> adsorption–desorption isotherms and pore size distributions of mesoporous hybrid and pure tin oxophosphate are shown in Fig. 2 and their results were summarized in Table 1. Both samples showed a type of *IV* isotherm characteristic of mesoporous materials. They possessed narrow pore size distributions with peak pore diameters shifted to a higher value from 1.92 to 3.18 nm after calcination. BET specific surface areas of the hybrid sample decreased after calcination from 371 to 247 m<sup>2</sup> g<sup>−1</sup> and pore volume (*V<sub>p</sub>*) increased after calcination from 0.187 to 0.229 cm<sup>3</sup> g<sup>−1</sup>, respectively.

<sup>13</sup>C and <sup>31</sup>P MAS NMR (JEOL CMX-400) spectra of the hybrid tin oxophenylphosphate and calcined samples are shown in Fig. 3. The hybrid sample exhibited two resonances at 131.6 and



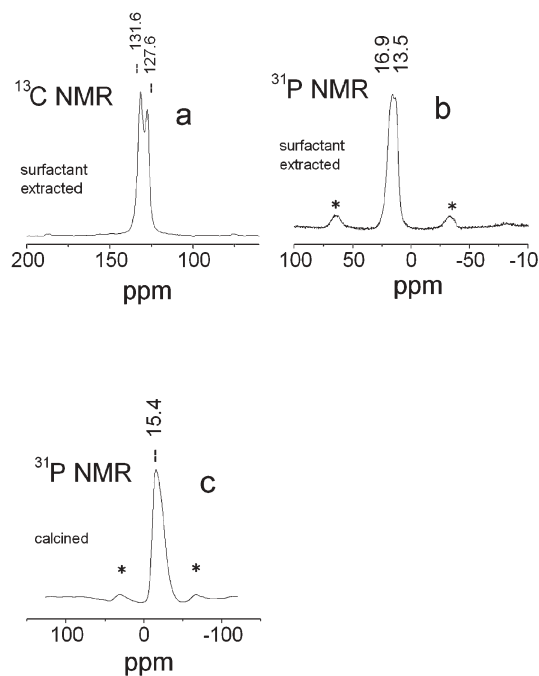
**Fig. 2** N<sub>2</sub> adsorption–desorption isotherms (A) and pore size distributions from the adsorption branch of isotherms using BJH method (B) of surfactant extracted mesoporous hybrid tin oxophenylphosphate (a) and calcined tin oxophosphate (b).

**Table 1** Physico-chemical properties of hybrid tin oxophenylphosphate and calcined tin oxophosphate

Status	<i>d</i> /nm	<i>S</i> <sub>BET</sub> /m <sup>2</sup> g <sup>−1</sup>	<i>V<sub>p</sub></i> /cm <sup>3</sup> g <sup>−1</sup>	PPD <sup>a</sup> /nm	Na <sup>+</sup> ex. cap <sup>b</sup> /mmol g <sup>−1</sup>
Hybrid	3.77	371	0.187	1.92	5.00
Calcined	3.80	247	0.229	3.18	5.79

<sup>a</sup> Peak pore diameter from adsorption branch of isotherms. <sup>b</sup> Na ion exchange capacity.

127.6 ppm in the <sup>13</sup>C MAS NMR spectrum due to the phenyl group.<sup>7</sup> Peaks at 16.9 [C<sub>6</sub>H<sub>5</sub>P(OH)O<sub>2</sub>] and 13.5 ppm [C<sub>6</sub>H<sub>5</sub>PO<sub>3</sub>] in the <sup>31</sup>P NMR spectrum further confirmed the presence of the phenyl group and the tetrahedral coordination of phosphorus.<sup>7</sup> The absence of a peak at 30 ppm in <sup>1</sup>H–<sup>13</sup>C CP/MAS NMR indicates that all the surfactant was removed during extraction. The absence of any other bands in this spectrum revealed that all the phosphorus atoms are attached to the phenyl groups in the hybrid material. After calcination, a single resonance at −15.4 ppm indicated the formation of tetrahedrally coordinated phosphate (PO<sub>4</sub>) species in organic free mesoporous tin oxophosphate. FT-IR spectra of the mesoporous hybrid and the calcined tin oxophosphate further confirmed the presence of phenyl and the Sn–O–P bond (see ESI†). UV-Vis spectrum of the hybrid mesoporous tin oxophenylphosphate shows two bands at 278 and 298 nm assigned to an octahedral coordination of Sn as Sn–O–PC<sub>6</sub>H<sub>5</sub> and Sn–O–Sn, respectively (see ESI†). No band is present at 220 nm confirming the absence of tetrahedrally coordinated tin species.<sup>4f</sup> In the cases of mesoporous tin phosphate and tin oxide, the tetra-coordinated Sn–O–P band is reported to be present at 220 nm and the octahedral coordinated Sn–O–Sn band is present at 303 nm.<sup>4f</sup> In the case of microporous tin silicate with octahedral tin species shows a band at 285 to 300 nm.<sup>8</sup>



**Fig. 3** <sup>13</sup>C MAS NMR spectrum of surfactant extracted mesoporous hybrid tin oxophenylphosphate (a), and <sup>31</sup>P MAS NMR spectra of hybrid tin oxophenylphosphate (b) and calcined tin oxophosphate (c).

The contents of Sn, P, S, Na, C, H and N in the hybrid and calcined samples were analyzed by ICP (Shimadzu ICPV-1017) and other methods. Na ion exchange capacity was also measured independently to confirm the presence of Na ions outside the framework as cations. Based on the elemental analysis results the molar composition of hybrid and calcined samples were derived as  $[(\text{SnO}_3)_{0.37} \text{Sn}_{0.21}(\text{O}_3\text{PC}_6\text{H}_5)_{0.42}] \cdot 0.74\text{Na}$  and  $[(\text{SnO}_3)_{0.30} \text{Sn}_{0.28}(\text{O}_4\text{P})_{0.42}] \cdot 0.74\text{Na}$ , respectively (see ESI†). In this formula, Sn is octahedrally coordinated to  $\text{SnO}_2$  and  $\text{C}_6\text{H}_5\text{PO}_3^{2-}$  (hybrid sample) or  $\text{PO}_4^{3-}$  (calcined sample), whereas phosphorus in  $\text{C}_6\text{H}_5\text{PO}_3^{2-}$  is tetrahedrally coordinated to three Sn in the hybrid sample and  $\text{PO}_4^{3-}$  is attached to four Sn in the calcined sample. The P/Sn molar ratio in the hybrid and calcined product was 0.724. The high thermal stability of mesoporous hybrid and calcined tin oxophosphate is probably due to a higher wall thickness. It is worth noting that the mesoporous structure was retained even after calcination at 550 °C, whereas in the cases of all the other reported mesoporous tin phosphates their structure collapsed above 500 °C.<sup>4f,g,5a</sup> Thermal gravimetric analysis (TGA) of hybrid tin phosphate and the sulfonated derivative shows that the phenyl group burned at 500 °C in both cases (hybrid and sulfonated derivatives), whereas the sulfonic acid group is decomposed at 200 °C.

The number of acid sites ( $\text{SO}_3\text{H}$ ) in sulfonated hybrid mesoporous tin oxophenylphosphate is 1.19 mmol acid  $\text{g}^{-1}$  sample. The titration curve is shown in the ESI†. On average each phenyl group was sulfonated by one  $\text{SO}_3\text{H}$  group. The proton conductivity of the sample is  $10^{-2} \text{ S cm}^{-1}$  at 90% relative humidity, which is nearly the same as observed for Nafion 117.<sup>9</sup> In the case of Nafion 117, the number of acid sites is 1 mmol  $\text{g}^{-1}$  sample.<sup>9</sup> In our hybrid sample the high proton conductivity is obviously due to the high number of acid sites. This sulfonated hybrid sample is a potential candidate for developing the membrane and for use as a support for cathode and anode materials in fuel-cell technology. Sulfonated hybrid tin oxophosphate is bi-functional and can be used as both electron and proton conductors, whereas the sulfonated silica derivative is a proton conductor only. The surface area and porosity of mesoporous hybrid tin phosphate material is smaller in comparison with mesoporous sulfonic acid containing silica material.

In conclusion, we have reported here a novel and general method for the preparation of mesoporous hybrid tin oxophenylphosphate

using phenylphosphonic acid as a single source of phosphorus in the presence of sodium dodecyl sulfate as surfactant. A stable hybrid tin oxophenylphosphate retained its structure even after calcination at 550 °C to produce pure mesoporous tin phosphate. Sulfonated hybrid tin oxophosphate has potential use as a membrane, a support for anode and cathode materials in fuel cell technology. In addition to this, their use in shape-selective acid–base catalysis is expected due to its high surface area and narrow pore size distributions.

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