Synthesis of Surfactant-assisted Microporous Layered Tin Phenylphosphonate

Nawal K. Mal, Masahiro Fujiwara,* Yusuke Yamada, and Masahiko Matsukata[†]
National Institute of Advanced Industrial Science and Technology, Kansai, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577
[†]*Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555*

Microporous layered tin phenylphosphonate has been prepared using sodium dodecylsulfate (SDS) as surfactant, it possesses high surface area ($255\,m^2\cdot g^{-1}$).

The chemistry of layered materials was greatly extended after the observation that metal (IV) phenylphosphonate, $[M^{IV}(O_3P\text{-}C_6H_5)_2]^{1-9}$ can be obtained in crystalline form with a layered structure similar to that of α-zirconium (IV) phosphate, $[Zr^{IV}(O_3P\text{–}OH)_2\cdot H_2O]^{10}$ or $[M^{IV}(O_3P\text{–}R)_2\cdot solvent]$ (where R = alkyl, aryl, alcoholic, amino, carboxylic, sulfonic, etc, and solvent is an intercalated molecules, when present).[6] Some of these were investigated as Brønsted and Lewis acids, hosts in intercalation compounds, protonic conductors, ion exchanger, photochemical reacants, molecular recognition materials and catalysts, absorbents for gas separations, and components for electrochemical devices such as solid state gas sensors.[2,8,11,12]

Layered Zr and components for Ti organophosphonates $[M^{IV}(O_3P\text{-}C_6H_5)_2]$ give solids with mesoporosity in character and hysteresis.[4–6,9] Organic surfactants (templates) are known by the formation of micelle to produce mesoporous MCM-41 with uniform narrow pore size distribution.[14]

Here, we report, for the first time, synthesis of microporous layered tin phenylphosphonate, $Sn^{IV}(O_3PC_6H_5)_2$ using SDS as surfactant in aqueous media. In a typical method, 0.02 mol of phenylphosphonic acid (3.33 g, 95%, Wako Chem.) in 40 g of H_2O was added to 0.01 mol of $SnCl_4\cdot5H_2O$ (3.58 g, 98%, Wako Chem.) in 30 g of H_2O under vigorous stirring. 5 mmol of SDS (1.52 g, 95%, Wako Chem.) was then added and stirred for 30 min. The gel was transferred to a Teflon lined stainless steel autoclave and heated at 423 K for 2 days. The final product was filtered, washed with distilled water, dried at 393 K for 1 day. The surfactant was removed by stirring mixture of 1 g of tin phenylphosphonate with 50 g of dry ethanol and 3 ml of HCl (1 M) at 333 K for 2 h. Finally, tin phenylphosphonate was filtered, washed with ethanol and dried at 393 K for 1 day and this product referred as to Sample 1. Sample 2 was prepared under the similar method without the addition of surfactant. For comparison, Sample 3 was prepared according to the procedure described for the synthesis of layered zirconium phenylphosphonate except that tin source was used instead of $ZrOCl_2\cdot8H_2O$.[1,2] 0.01 mol of $SnCl_4\cdot5H_2O$ was dissolved in 10 g of distilled water and 0.05 mol of concd HF (2.09 g, 48%, Wako Chem.) added. The mixture was held in a plastic bottle and kept at 353 K while adding 0.0205 mol of phenylphosphonic acid dissolved in 90 g of H_2O. Heating was carried out over a three days period, during which time a fine precipitated formed. The product was filtered, washed and dried at 393 K for 1 day. The phenyl group was readily sulfonated.[2] The sulfonation reaction was carried out by adding 2 g of Sample 1 (4.64 mmol) to 0.016 mol of fuming sulfuric acid (14.28 g, 20%, Aldrich Chem.). The mixture was kept at 348 K for 1 h. Water was added dropwise to convert the excess SO_3 to H_2SO_4 followed by the addition of 100 ml of methanol and centrifugation. Elemental analyses of the samples were carried out using ICP (Shimadzu ICPV-1017). Characterization of the samples was made using XRD (Cu-Kα radiation, $\alpha = 0.15406\,nm$), N_2 sorption at 77 K, TG-DTA, UV–vIS and FT-IR using KBr pellet.

Analytical values of Sample 1 are, 27.59% Sn, 33.41% C, 2.35% H and 14.39% P. These values are consistent with possible empirical formula, $Sn(O_3PC_6H_5)_2$; 27.56% Sn, 33.43% C, 2.32% H and 14.40% P. This result well agrees with TG analysis as discussed later. Formula of the Sample 1 after sulfonation was $Sn(O_3PC_6H_4SO_3H)_{1.1}(O_3PC_6H_5)_{0.7}(O_3POH)_{0.2}\cdot3.2H_2O$. X-ray powder patterns of Samples 1, 2 and 3 are shown in Figure 1. They are isomorphous[1–3] and have structure similar[10] to zirconium phenylphosphonate. Interplanar spacing, d_{001} of Sample 1 is 1.45 nm, which is little smaller than zirconium phenylphosphonate ($d_{001} = 1.47\,nm$)[1] due to smaller ionic radii of Sn^{4+} (0.083 nm, oh) compare to Zr^{4+} (0.086 nm, oh). N_2 adsorption-desorption isotherm and pore size distribution of Samples 1, 2, and 3 are shown in Figure 2. Sample 1 shows type I isotherm to confirm microporous in nature, where as Samples 2 and 3 show Type IV isotherm due to mesoporous character. However, Sample 1 after calcinations at 873 K is mesoporous (Type IV isotherm) because of burning of organic moiety (Figure 2d). It is worth to note that plots b, c and d in Figure 2A are offset by 50, 100 and 150, respectively, for clarity. These three mesoporous samples have very small microporosity as evident from the small extent of adsorption at $P/P_0 < 0.05$ as discussed below. Pore size distributions show the interesting results, Sample 2, which is prepared in the absence of surfactant shows peak pore diameter (pore size maxima) at 3.3 nm measured from pore size distribution curve, whereas Sample 3 shows broad pore size distribution with peak pore diameter at 15.7 nm. Sample 1 after calcination at 873 K exhibits relatively narrower pore size distribution with peak pore diameter at ca. 7 nm compare to Sample 3. Pore size distributions were calculated from adsorption branches of the isotherm using BJH (Barrett–Joyner–Halenda) method.[15] BET specific surface areas of Samples 1, 2 and 3 are 255, 197 and 135 $m^2\cdot g^{-1}$, respectively, and corresponding total pore volumes are 0.06, 0.16 and 0.33 $cm^3\cdot g^{-1}$, respectively.
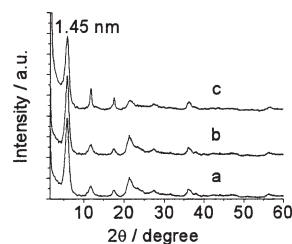

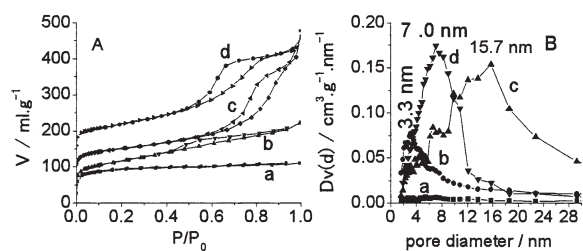**Figure 1.** XRD profiles: (a) Sample 1, (b) Sample 2 and (c) Sample 3.

Figure 2. N_2 adsorption-desorption isotherms (A) and pore size distributions curve (B): (a) Sample 1, (b) Sample 2, (c) Sample 3 and (d) Sample 1 after cacination at 873 K for 2 h. (Isotherms: b, c and d offset by 50, 100 and 150, respectively, for clarity.)

Micropore volumes calculated using MP method in Samples 1, 2 and 3 are 0.059, 0.023, 0.014 $cm^3 \cdot g^{-1}$, respectively, which are 98.3, 14.4 and 4.2%, with respect to total pore volume, respectively. Microporosity in Sample 1 is 2.6 to 4.2 times more than Samples 2 and 3. It clearly shows that SDS is essential to prepare the microporous sample without any mesoporosity. BET specific surface area and pore volume of Sample 1 after calcination at 873 K are 203 $m^2 \cdot g^{-1}$ and 0.29 $cm^3 \cdot g^{-1}$, respectively. Surface area of tin phenylphosphonate is much higher than titanium phenylphosphonate (62 to 145 $m^2 \cdot g^{-1}$).[5] FT-IR spectra of Samples 1 and 3 are similar in nature (Figure 3). Absence of bands at 2945 and 2850 cm^{-1} in Sample 1 confirms the removal of surfactant. H_2O and OH groups are absent as no band is existing at ca. 3400 cm^{-1}. Presence of bands at 693, 729, 749 and 1438 cm^{-1} is identification of phenyl group.[2] TG analyses of Sample 1 before and after surfactant removal, and Sample 3 are shown in Figure 4. Sample 1 before surfactant removal shows three distinct weight loss at 481, 553 and 658 K, first two slope is due to decomposition and desorption of surfactant, respectively, and later (last) one due to loss of phenyl groups. Sample 1 (after surfactant removal) and Sample 3 show one distinct weight loss at 658 K corresponding to 28.6%, which fairly matches with content of phenyl group.
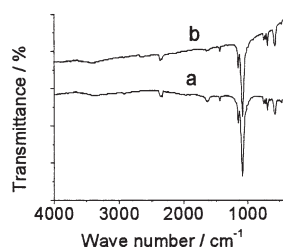

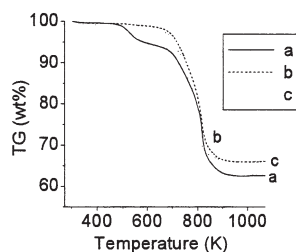**Figure 3.** FT-IR spectra: (a) Sample 1 and (b) Sample 3.

Figure 4. TG analyses of Sample 1, (a) before and (b) after surfactant removal, and (c) Sample 3.

Presence of band at ca. 270 nm in Samples 1, 2 and 3 confirm the octahedral coordination of tin.

The micropore in Sample 1 is due to interlayer space as expected. Whereas in Samples 2 and 3 mesopores may originate from end-side particle interactions, a part of which could be internal pores formed by cutting layers owing to hydrolysis and loss of phosphonates arising from their more hydrolyzable nature.[9] Sn is covalently bonded to six oxygens of six different phosphonate groups. Phosphonate group is tetrahedrally coordinated to three oxygens and one phenyl group, having positive charge on phosphorous ion, which may hydrolyze in acidic solution. When surfactant sodium dodecylsulfate was used, the negatively charged dodecylsulfate ions stabilize the positively charged phosphorous cations. Another role of surfactant is to form the micelle[17] and interact with inorganic species to form uniform mesoporous inorganic materials. It may possible that in the presence of surfactant layered tin phenylphosphonate forms within the mesopore, parallel to the cylindrical pore (with average pore diameter ca. 7 nm). Because Sample 1 is micropore and after calcination at 873 K the layered structure was collapsed (amorphous in nature from XRD), producing mesopore with peak pore diameter at 7 nm. Microporous tin phenylphosphonate would be very useful as selective ion exchanger. Sulphonated $Sn(O_3PC_6H_4SO_3H)_{1.1}(O_3PC_6H_5)_{0.7}(O_3POH)_{0.2}$ would be very effective catalyst with strong Brønsted acidity (greater than that of ZeY and ZSM-5),[13] proton conductor[2] and active for number of organic reactions including conversion of oximes, semicarbazones and tosylhydrazones to their respective carbonyl compounds, like sulfonated zirconium phenylphosphonate.[13,16]

References
1 G. Alberti, U. Costantino, S. Allulli, and N. Tomassini, *J. Inorg. Nucl. Chem.*, **40**, 1113 (1978).
2 E. W. Stein, Sr., A. Clearfield, and M. A. Subramanian, *Solid State Ionics*, **83**, 113 (1996).
3 C. Y. Yang and A. Clearfield, *React. Polym.*, **5**, 13 (1987).
4 M. B. Dines and P. M. Digaicomo, *Inorg. Chem.*, **20**, 92 (1981).
5 M. A. Villa-Garcia, E. Jaimez, A. Bortun, J. R. Garcia, and J. Rodriguez, *J. Porous Mater.*, **2**, 85 (1995).
6 E. Jaimez, A. Bortun, G. B. Hix, J. R. Garcia, J. Rodriguez, and R. C. T. Slade, *J. Chem. Soc., Dalton Trans.*, **1996**, 2285; and references cited therein.
7 R. J. P. Corriu, D. Leclercq, P. H. Mutin, L. Sarlin, and A. Vioux, *J. Mater. Chem.*, **8**, 1827 (1998).
8 A. Clearfield, in "Progress in Inorganic Chemistry," ed. by K. D. Karlin, John Wiley, New York (1998), pp 371-510.
9 P. O. Pastor, P. M. Torres, E. R. Castellon, and A. J. Lopez, *Chem. Mater.*, **8**, 1758 (1996).
10 M. D. Poojary, H.-L. Hu, F. L. Campbell, III, and A. Clearfield, *Acta Crystallogr., Sect. B*, **49**, 996 (1993).
11 M. Ogawa and K. Kuroda, *Chem. Rev.*, **95**, 399 (1995).
12 A. Clearfield, in "Surface Organometallic Chemistry: Molecular Apploaches to Surface Catalysis," ed. by J. M. Basset, Kluwer Academic Publishers, Norwell, MA (1998), pp 269-371.
13 A. Clearfield and Z. Wang, *J. Chem. Soc., Dalton Trans.*, **2002**, 2937.
14 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
15 E. P. Barrett, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
16 M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, and U. Costantino, *Tetrahedron Lett.*, **39**, 8159 (1998).