

Synthesis of Novel Mesoporous Aluminum Organophosphonate by Using Organically Bridged Diphosphonic Acid

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Recent findings of periodic mesoporous organosilicas (PMOs) prepared by using bridged silsesquioxanes ($(RO)_3Si-R'-Si(OR)_3$, R, R'; organic group) show the possibility to control mesostructures of various inorganic–organic hybrid materials by surfactant-templating strategy.^{1–3} However, almost all of the corresponding research studies have focused on the synthesis of PMOs with a variety of functional organic groups.⁴ Inorganic components of the hybrid frameworks are limited to only silica because the preparation method of organically bridged metal alkoxides ($(RO)_3Me-R'-Me(OR)_3$, Me; metal) has not been developed so far.^{5,6} Then, non-silica-based inorganic–organic hybrid porous materials have been developed by using alkylene and arylidiphosphonates,^{7–9} leading to the formation of porous zirconium diphosphonates composed of zirconium phosphate-like layers cross-linked by the bridged organic groups. However, the covalently bonded organic groups are present between the sheets but not within the inorganic frameworks. Here, surfactant-templated hexagonal mesostructured and mesoporous non-silica-based materials containing homogeneously distributed and covalently bonded organic groups within the frameworks can be successfully prepared by using organically bridged

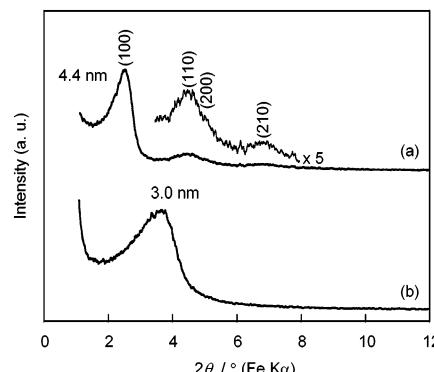


Figure 1. XRD patterns of (a) as-synthesized and (b) calcined AOP-2.

diphosphonic acids. However, the formation of P–O–P bonds between the diphosphonates is difficult in aqueous solution and thus hexagonal mesostructured aluminum organophosphonate was synthesized by utilizing the formation of Al–O–P linkages. The synthetic strategy to provide non-silica-based hybrid frameworks is widely applicable for the compositional variation of both inorganic and organic components because a large number of metals react with P–OH groups and phosphonate groups can be connected by a wide variety of organic groups.^{7–10}

A mesoporous aluminum organophosphonate (named AOP-2) was synthesized by using methylene diphosphonic acid ($(HO)_2OPCH_2PO(OH)_2$, AZmax Co. Ltd.) in the presence of octadecyltrimethylammonium ($C_{18}TMA$) surfactant. In a typical synthesis, 5.16 g of $C_{18}TMA$, 10.79 g of 25 mass % tetramethylammonium hydroxide (TMAOH), 5.36 g of $(HO)_2OPCH_2PO(OH)_2$, and 8.75 mL of distilled water were mixed until a clear solution was obtained. After the addition of 6.14 g of $Al(O'C_3H_7)_3$ to the clear solution under stirring, the stirring was maintained for 24 h. The resultant solution ($Al:P:C_{18}TMA:OH:H_2O = 1:2:1:2:65$, pH = 6.8) was dispersed in distilled water, leading to the formation of a white solid. The solid was washed with distilled water repeatedly and dried at 50 °C. The product was heated at 400 °C for 1 h in flowing N_2 , followed by calcination at the temperature for 6 h in flowing O_2 . Extraction of only a $C_{18}TMA$ molecule by acid treatment has not been achieved yet because as-synthesized AOP-2 was dissolved in acidic ethanol solution useful for the removal of surfactants from PMOs.¹

The XRD patterns of as-synthesized and calcined AOP-2 are shown in Figure 1. In the as-synthesized product, four peaks assignable to a 2-D hexagonal phase were observed at low scattering angles and the d_{100} value of the main peak was 4.4 nm though the peaks were ill-resolved. The TEM image of the as-synthesized

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(1) (a) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611. (b) Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660. (c) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304.

(2) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.

(3) (a) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539. (b) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867. (c) Asefa, T.; MacLachlan, M. J.; Grondy, H.; Coombs, N.; Ozin, G. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1808.

(4) Sayari, A.; Hamoudi, S. *Chem. Mater.* **2001**, *13*, 3168 and references therein.

(5) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*, Academic Press Inc.: London, 1978.

(6) Sanchez, C.; Soler-Illia, G. J. de A. A.; Ribot, F.; Lalot, T.; Mayer C. R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061.

(7) (a) Alberti, G.; Murcia-Mascarós, S.; Vivani, R. *Mater. Chem. Phys.* **1993**, *35*, 187. (b) Alberti, G.; Costantino, U.; Vivani, R.; Zappelli, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1357. (c) Alberti, G.; Marmottini, F.; Murcia-Mascarós, S.; Vivani, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1594. (d) Alberti, G.; Murcia-Mascarós, S.; Vivani, R. *J. Am. Chem. Soc.* **1998**, *120*, 9291.

(8) Yang, H. C.; Aoki, K.; Hong, H. G.; Sackett, D. D.; Arrendt, M. F.; Yau, S. L.; Bell, C. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1993**, *115*, 11855.

(9) (a) Clearfield, A. *Chem. Mater.* **1998**, *10*, 2801. (b) Clearfield, A.; Wang, Z. *J. Chem. Soc., Dalton Trans.* **2002**, 2937. (c) Clearfield, A.; Wang, Z.; Bellinghausen, P. *J. Solid State Chem.* **2002**, *167*, 2937. (d) Wang, Z.; Heising, J. M.; Clearfield, A. *J. Am. Chem. Soc.* **2003**, *125*, 10375.

(10) (a) Gao, Q.; Guillou, N.; Nogues, M.; Cheetham, A. K.; Ferey, G. *Chem. Mater.* **1999**, *11*, 2937. (b) Claessens, R. A. M. J.; Kolar, Z. I. *Langmuir* **2000**, *16*, 1360. (c) Finn, R. C.; Lam, R.; Greedan, J. E.; Zubietta, J. *Inorg. Chem.* **2001**, *40*, 3745. (d) Serre, C.; Ferey, G. *Inorg. Chem.* **2001**, *40*, 5350. (e) Zheng, L.-M.; Gao, S.; Song, H.-H.; Decurtins, S.; Jacobson, A. J.; Xin, X.-Q. *Chem. Mater.* **2002**, *14*, 3143. (f) Costantino, U.; Nocchetti, M.; Vivani, R. *J. Am. Chem. Soc.* **2002**, *124*, 8428. (g) Mao, J.-G.; Wang, Z.; Clearfield, A. *Inorg. Chem.* **2002**, *41*, 2334.

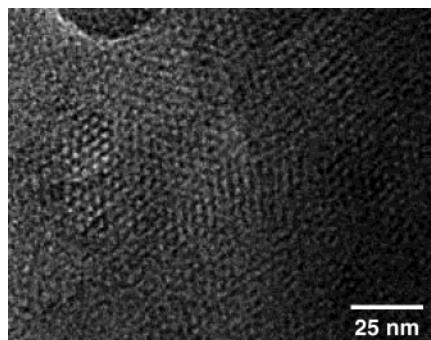


Figure 2. TEM image of as-synthesized AOP-2.

product is shown in Figure 2, indicating the presence of ordered hexagonal arrangements in the as-synthesized AOP-2. However, the orderings are in short range, being in agreement with the ill-resolved XRD peaks. In addition, striped patterns were also observed, meaning that the as-synthesized product has one-dimensional arrangements originating from the 2-D hexagonal structure. The XRD peaks were broadened upon calcination ($d = 3.0$ nm), revealing that the periodicity of pores deteriorates. The N_2 adsorption isotherm of the calcined product showed behavior between types I and IV (Supporting Figure S1, see Supporting Information). The BET surface area, the pore volume, and the average pore diameter (λ) were $738\text{ m}^2\text{ g}^{-1}$, $0.32\text{ cm}^3\text{ g}^{-1}$, and 1.8 nm , respectively.

The successful removal of $C_{18}\text{TMA}$ molecules by calcination without decomposition of the methylene groups is related to the difference of thermal stabilities between the methylene groups and the $C_{18}\text{TMA}$ molecules. For example, the TG-DTA analysis (in air) showed that the combustion of the $C_{18}\text{TMA}$ molecules in the as-synthesized product was started by heating at around $245\text{ }^\circ\text{C}$ (Supporting Figure S2, see Supporting Information). In the calcined product, mass loss except for desorption of adsorbed water ($\sim 150\text{ }^\circ\text{C}$) was not observed below $450\text{ }^\circ\text{C}$. The decomposition of methylene diphosphonates was started at around $470\text{ }^\circ\text{C}$ with exothermic reaction mainly due to the oxidation of P atoms and then the diphosphonates were decomposed up to $650\text{ }^\circ\text{C}$ completely. The decomposition of organic groups in mesoporous silica-based materials such as $\equiv\text{Si}-\text{CH}_3$ and $\equiv\text{Si}-\text{C}_2\text{H}_4-\text{Si}\equiv$ starts at around $470\text{ }^\circ\text{C}^{11}$ and $280\text{ }^\circ\text{C}^{12}$ (in air), respectively. Removal of surfactants at very low temperature ($250\text{ }^\circ\text{C}$ in N_2) is required to obtain PMOs without decomposition of the bridged organic groups.¹³ Similar organic groups in aluminum organophosphonates such as $\equiv\text{P}-\text{CH}_3$ and $\equiv\text{P}-\text{C}_2\text{H}_4-\text{P}\equiv$ are decomposed above $550\text{ }^\circ\text{C}^{14}$ and $380\text{ }^\circ\text{C}^{15}$ (in O_2), respectively. This comparison may reveal the improvement of the thermal stability of organic groups bonded to P atoms as phosphates are well-known as anti-

combustion agents. Thus, bridged methylene groups remain in the hybrid framework, even after calcination at $400\text{ }^\circ\text{C}$.

The carbon and nitrogen contents of the as-synthesized and calcined AOP-2 were investigated by the CHN analysis. The as-synthesized product contained 38.4 mass % of carbon atoms and 2.0 mass % of nitrogen atoms. The result means that 45.3 mass % of $C_{18}\text{TMA}$ molecules and 2.2 mass % of methylene groups are present in the as-synthesized product. Even after calcination, 3.8 mass % of carbon atoms remained in the product while nitrogen atoms were not detected by CHN. The ^{13}C CP/MAS NMR spectrum of the calcined product showed that two peaks are observed at 11 and 28 ppm (Supporting Figure S3, see Supporting Information). The presence of the peak at 28 ppm proves that the carbon atoms remained as in the methylene ($-\text{CH}_2-$) groups. The peak at 11 ppm is assignable to carbon atoms in methyl ($-\text{CH}_3$) groups¹⁶ that are formed through the degradation of diphosphonate groups ($\equiv\text{P}-\text{CH}_2-\text{P}\equiv\rightarrow\equiv\text{P}-\text{CH}_3+\text{O}-\text{P}\equiv$). The ^{31}P MAS NMR spectrum of the calcined AOP-2 also showed the presence of both phosphonate (centered at 6 ppm) and phosphate groups (centered at -18 ppm) (Supporting Figure S3, see Supporting Information). When 3.8 mass % of carbon atoms is derived from methylene and methyl groups, the density of the organic groups is calculated to be 2.6 per nm^2 . The number of the remaining methylene groups in the calcined AOP-2 is now under investigation.

The Al/P molar ratio (0.73) was checked by ICP. On the basis of the ICP and CHN analyses, the formula of the as-synthesized AOP-2 is represented as $\text{Al}_6(\text{O}_3\text{PCH}_2-\text{PO}_3)_4 \cdot 3.8\text{C}_{18}\text{TMA} \cdot 21.0\text{H}_2\text{O}$ but does not balance the charge. Negatively charged OH^- species such as terminal Al-OH groups would be required in this formula. The ^{27}Al and ^{31}P MAS NMR spectra of the as-synthesized and calcined AOP-2 are shown in Figure S2. The ^{27}Al MAS NMR spectrum of the as-synthesized product showed that a peak was observed at -11 ppm , indicating that Al atoms are six-coordinated $(\text{Al}(\text{OP})_{6-x-y}(\text{H}_2\text{O})_x(\text{OH})_y)$. The AlO_6 species were partly converted to four-coordinated species (38 ppm) by calcination and the four-coordinated species can be assigned to $\text{Al}(\text{OP})_4$ and/or $\text{Al}(\text{OP})_{4-x}(\text{OH})_x$ species on the basis of the chemical shift and the asymmetric profile.¹⁷ In the ^{31}P MAS NMR spectrum of the as-synthesized product, a broad signal was observed centered at 11 ppm , being assignable to phosphorus atoms in $\text{O}_3\text{P}-\text{C}$ species.^{18c} By the formation of Al-O-P bonds, the framework structure of AOP-2 is considered as being composed of alternative aluminophosphate-like domains and the bridged organic groups.

After the first preparation of aluminum methylphosphonates ($\text{AlMepO}-\alpha$ and $-\beta$),¹⁸ layered aluminum organophosphonates were synthesized by using methylphosphonate^{14,16,19} and ethylene diphosphonate.¹⁵ In the latter case, Al-F-Al chains are bridged by ethylene

(11) Shigeno, T.; Nagao, M.; Kimura, T.; Kuroda, K. *Langmuir* **2002**, *18*, 8102.

(12) Kruk, M.; Jaroniec, M.; Guan, S.; Inagaki, S. *J. Phys. Chem. B* **2001**, *105*, 681.

(13) Lu, Y.; Fan, H.; Doke, N.; Loy, D. A.; Assink, R. A.; LaVan, D. A.; Brinker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5258.

(14) (a) Hix, G. B.; Carter, V. J.; Wragg, D. S.; Morris, R. E.; Wright, P. A. *J. Mater. Chem.* **1999**, *9*, 179. (b) Hix, G. B.; Wragg, D. S.; Bull, I.; Morris, R. E.; Wright, P. A. *Chem. Commun.* **1999**, 2421.

(15) (a) Hervey, H. G.; Teat S. J.; Attfield, M. P. *J. Mater. Chem.* **2000**, *2632*. (b) Hervey, H. G.; Hu, J.; Attfield, M. P. *Chem. Mater.* **2003**, *15*, 179.

(16) Carter, V. J.; Wright, P. A.; Gale, J. D.; Moriss R. E.; Sastre, E.; Perez-Pariente, J. *J. Mater. Chem.* **1997**, *7*, 2287.

(17) (a) Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Lett.* **1997**, *983*. (b) Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Commun.* **1998**, *559*. (c) Kimura, T.; Sugahara, Y.; Kuroda, K. *Microporous Mesoporous Mater.* **1998**, *22*, 115. (d) Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Mater.* **1999**, *11*, 508.

diphosphonate groups. In the present system, methylene diphosphonate groups can be successfully incorporated within the framework of the mesostructured product. Although water adsorption isotherms of microporous AlMepO- α and - β show type II behavior due to hydrophobic surfaces,^{18c} the isotherm of calcined AOP-2 was type IV despite the presence of hydrophobic organic groups within the framework. This is an indication that the surfaces of AOP-2 are hydrophilic.

In the research fields of periodic mesoporous materials, hybrid frameworks have attracted much attention to their applications to novel reaction media.^{1–4} The use of bridged silsesquioxanes leads to the formation of alternative networks of inorganic units and organic groups within silica walls of periodic mesopores. Because the non-siliceous frameworks are useful for wide-ranging applications to electronics, optics, and so on, the preparation of non-siliceous mesoporous materials composed of inorganic–organic hybrid frameworks has been expected by surfactant templating. Recently, organically modified hexagonal mesostructured aluminophosphates have been successfully prepared by using alkyltrimethoxysilanes.²⁰ The organic groups are present at the surface of the frameworks but all the organic fractions are eliminated by calcination. The present

(18) (a) Maeda, K.; Akimoto, J.; Kiyozumi Y.; Mizukami, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1033. (b) Maeda, K.; Akimoto, J.; Kiyozumi Y.; Mizukami, F. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1199. (c) Maeda, K.; Kiyozumi Y.; Mizukami, F. *J. Phys. Chem. B* **1997**, 101, 4402.

(19) Maeda, K.; Hashiguchi, Y.; Kiyozumi Y.; Mizukami, F. *Bull. Chem. Soc. Jpn.* **1997**, 70, 345.

(20) Kimura, T. *Chem. Lett.* **2002**, 770.

system is the first example for the synthesis of surfactant-templated non-silica-based mesoporous materials with inorganic–organic hybrid frameworks.

In conclusion, surfactant-templated porous aluminum organophosphonate is synthesized by using organically bridged diphosphonates and the organic moieties are distributed within the framework of the material homogeneously. Despite the potential and interest applications of metal phosphonates (ion exchangers, catalysts, nonlinear optics),²¹ diphosphonates have been used as only linkers through the substitution of phosphates in layered compounds to date. In the present system, the use of organically bridged diphosphonic acids in the presence of surfactants is simply applicable for the synthesis of non-silica-based inorganic–organic hybrid mesoporous materials, showing the possibility of designing a wide variety of porous materials with various compositions and pore sizes in the range from micro- to meso- and macroporous regions.

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Supporting Information Available: Figures S1 (N₂ isotherm), S2 (TG-DTA), and S3 (²⁷Al, ³¹P, and ¹³C(CP) MAS NMR) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) (a) Clearfield, A. *Curr. Opin. Solid State Mater.* **1996**, 1, 268. (b) Clearfield, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1998; pp 371–510.