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Synthesis of Mesostructured and Mesoporous Aluminum Organophosphonates Prepared by Using Diphosphonic Acids with Alkylene Groups

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Mesostructured and mesoporous aluminum organophosphonates (AOPs) with 2-D hexagonal structures (AOP-2) can be synthesized by using alkylene diphosphonic acids in the presence of alkyltrimethylammonium (C_n TMA) surfactants. In the aqueous system, mesostructured AOP-2 with short-range orderings was obtained by using methylene diphosphonic acid. Low-temperature calcination at 400 °C of the mesostructured AOP-2 led to the deformation of the mesostructures. In the ethanol–water system, highly ordered mesostructured AOP-2 can be prepared through the reaction of aluminum chloride and alkylene diphosphonic acids. The preparation of ordered mesoporous AOPs with methylene and ethylene groups was achieved by using the method to remove surfactant molecules by calcination at 400 °C. Mesoporous AOPs containing propylene groups cannot be obtained through a similar synthetic procedure containing the low-temperature calcination process. Thermal stabilities of the organic groups within the frameworks are significant for the formation of mesoporous phases. Also, the presence of the organic groups within the frameworks plays an important role in avoiding the deformation of the ordered mesostructures during calcination. The mesoporous AOP-2 having extremely hydrophilic surfaces is quite applicable for the removal of harmful organic compounds such as aldehydes.

Introduction

Chemically designed inorganic–organic hybrid materials have attracted much attention because of the combination of properties due to the inorganic and the organic components.¹ The hybrid materials would display full functions by making a large quantity of fine pores inside the materials. There have been many papers on the preparation of materials with uniform pores such as microporous zeolites and related materials.^{2–5} Recent development of ordered mesoporous materials^{6–9} and macroporous materials^{10–13} is outstanding for porous materials design. Each porous material can be

synthesized by using surfactant molecules or polymer beads (or silica spheres). Porous materials with high surface areas have been required for many engineering applications¹⁴ (catalysts, catalytic supports, adsorbents, gas storages, etc.) including potential applications (electric and optical devices, fuel cells, etc.). Almost all of the porous materials with uniform pores have been formed via cooperative organization in the presence of structure-directing agents such as hydrated organic molecules^{15–17} and surfactant assemblies.^{18–20} The formation of chemical bonds within inorganic frameworks is also important for maintaining the porous structures after the removal of the organic templates. In the cases of zeolites and related materials, all of the frameworks, except for defects, are bonded covalently through crystallization during hydrothermal treatments. All of the silicate species cannot be connected to each other within the frameworks of ordered mesoporous silicas because the interaction between silicate species and cationic surfactant molecules is required during the formation of mesostructures (cooperative organization). However, covalently bonded Si–O–Si networks are not few, and further condensation of the silicate frameworks occurs

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by calcination. Therefore, mesostructural deformation is suppressed during the removal of surfactant molecules, and then the preparation of ordered mesoporous silicas is possible.

The formation of covalent bonds between inorganic and organic species is severe when inorganic–organic hybrid materials are synthesized by mixing metal species and organic compounds. A new family of porous materials with metal–organic frameworks (MOFs) has been developed.^{4,21,22} These materials show the reversible sorption property for gases and organic vapors; for example, a favorable hydrogen storage property is greatly of interest.²¹ However, organic compounds act as ligands, and porous MOFs can only be obtained from materials with strong metal–oxygen–carbon bonds in the hybrid frameworks. Consequently, it is considered that the use of chemically designed inorganic–organic hybrid molecules is suitable for the preparation of inorganic–organic hybrid porous materials. Bridged silsesquioxanes ((RO)₃Si–R'–Si(OR)₃, R, R'; organic group) are good candidates useful as starting precursors with covalent metal–carbon bonds for the synthesis of inorganic–organic hybrid porous materials such as zeolitic²³ and ordered mesoporous materials.^{24–29} Periodic mesoporous organosilicas (PMOs) prepared by using bridged silsesquioxanes have attracted attention as novel chemically designed porous media. Innovative synthesis to yield PMOs with crystal-like walls was found recently,^{30–32} in accordance with the nature that bridged silsesquioxanes having rigid organic groups are self-organized.³³ Surfaces of molecularly arranged hybrid frameworks are useful for controlled inclusion of functional materials within ordered mesopores. Combining properties due to inorganic units and organic groups is also interesting, but not expected at present because the functions of silica are quite limited. Thus, the preparation of a wide variety of non-silica-based inorganic–organic hybrid materials is expected.^{34,35} Unfortunately, the preparation method of organically bridged metal alkoxides ((RO)₃Me–R'–Me(OR)₃, Me; metal) has not been developed so far.³⁶

One of the most famous hybrid materials is microporous zirconium phosphonates.^{37–45} Zirconium phosphate-like layers and organic pillars construct unique micropores which are formed through the controlled reactions of diphosphonic acids, phosphoric acid, and metal species. Organically bridged diphosphonic acids ((HO)₂OP–R–PO(OH)₂) containing covalent metal–organic bonds is one of the most attractive starting materials for designing frameworks of non-silica-based porous materials. Recently, the successful preparation of mesoporous aluminum organophosphonates (AOPs) by using methylene diphosphonic acid was reported as the first example of a surfactant-templated non-silica-based hybrid material.⁴⁶ This synthetic strategy is widely applicable for the compositional variation of both inorganic and organic components because a great deal of metals react with P–OH groups^{37–45,47–53} and because diphosphonic acids with a wide variety of organic groups can be obtained through modified Arbuzov reactions.⁵⁴

In the present paper, the synthesis of mesoporous AOPs by using methylene diphosphonic acid ((HO)₂OPCH₂PO(OH)₂) in the presence of alkyltrimethylammonium (C_nTMA) surfactants in the aqueous system is presented in detail. However, the 2-D hexagonal structure of the as-synthesized AOP was deteriorated during calcination. Therefore, new synthetic methods to prepare highly ordered mesoporous AOP-2 have been investigated in the presence of C_nTMA surfactants in the ethanol–water system. The synthesis was carried out by using alkylendiphosphonic acids ((HO)₂–OPC_nH_{2n}PO(OH)₂), and then effects of the organic groups within the hybrid frameworks have been determined.

Experimental Section

Materials. Methylene, ethylene, and propylene diphosphonic acids ((HO)₂OPC_nH_{2n}PO(OH)₂, *n* = 1, 2, and 3) can be purchased from AZmax Co. Ltd. All of the diphosphonic acids were used without further purification. Alkyltrimethylammonium chlorides

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(C_n TMACl) with different alkyl chains ($n = 12-18$) were obtained from Tokyo Kasei Kogyo Co. An aqueous solution of 25 mass % tetramethylammonium hydroxide (TMAOH) and aluminum isopropoxide ($Al(O^iC_3H_7)_3$) were also obtained from Tokyo Kasei Kogyo Co. Aluminum chloride ($AlCl_3$) and ethanol were purchased from Wako Chemical Co.

Synthesis of Mesostructured Aluminum Organophosphonates (AOPs) in the Aqueous System. Mesostructured AOPs with 2-D hexagonal structures (named as AOP-2) were synthesized by using methylenediphosphonic acids $(HO)_2OPCH_2PO(OH)_2$ in the presence of C_n TMA surfactants. In a typical synthesis, 4.74 g of hexadecyltrimethylammonium chloride (C_{16} TMACl) was dissolved in an aqueous solution of TMAOH that was prepared by mixing 10.79 g of 25 mass % TMAOH and 8.75 mL of distilled water. Next, 5.36 g of $(HO)_2OPCH_2PO(OH)_2$ was added to the aqueous solution of C_{16} TMACl and allowed to be dissolved completely. After that, 6.14 g of $Al(O^iC_3H_7)_3$ was added to the clear solution under stirring, and the stirring was kept for 24 h. The resultant solution ($Al:P:C_{16}TMACl:TMAOH:H_2O = 1:2:1:2:65$, pH = 6.7) was dispersed in distilled water, and then a white solid was formed. The solid product was washed with distilled water repeatedly and dried at 50 °C.

Synthesis of Mesostructured AOP-2 in the Ethanol–Water System. Highly ordered mesostructured AOPs with 2-D hexagonal structures (called ordered AOP-2 here) can be synthesized by using $(HO)_2OPC_nH_{2n}PO(OH)_2$ in the presence of C_n TMACl surfactants. The typical synthetic procedure is described below. C_{16} TMACl (4.74 g) was dissolved in ethanol/water (30 mL/10 mL). After $(HO)_2OPCH_2PO(OH)_2$ (3.89 g) was added to the surfactant solution and dissolved completely, $AlCl_3$ (3.93 g) was added to the solution very slowly under vigorous stirring and the stirring was maintained for 30 min ($Al:2P:C_{16}TMACl:H_2O:C_2H_5OH = 2:1.5:1:37:44$). A clear solution was obtained and emptied into a dish to volatilize the solvents at room temperature. After complete drying at 50 °C, the solid product was powdered for analyses.

Synthetic conditions such as Al/2P ratio, which means the molar ratio of aluminum source to diphosphonic acid in the starting mixtures, were changed to investigate the optimal synthetic conditions. Mesostructured AOP-2 was also prepared by using $(HO)_2OPC_nH_{2n}PO(OH)_2$ ($n = 2$ and 3) under similar synthetic conditions. A mesostructured aluminophosphate (AIPO) with a 2-D hexagonal structure was prepared in the presence of C_{16} TMACl for further discussion about the effects of the presence of organic groups within the frameworks.

Removal of Surfactant Molecules. Extraction of only C_n TMA molecules by acid treatment has not been achieved yet because as-synthesized AOP-2 dissolved in acidic ethanol solutions useful for the removal of C_n TMA surfactants from PMOs.^{24–32} Especially, as-synthesized AOP-2 prepared in the ethanol–water system was completely dissolved in distilled water and partly dissolved in alcohols such as methanol and ethanol. Therefore, the removal of surfactant molecules was conducted by low-temperature calcination. The powder samples were heated at 400 °C for 1 h in flowing N_2 , followed by calcination at this temperature for 6 h in flowing O_2 .

Characterization. Powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku RINT 2100 diffractometer with monochromated Fe $K\alpha$ radiation. Transmission electron microscopic (TEM) images were taken by a JEOL JEM 2010, operated at 200 kV. Solid-state ^{27}Al and ^{31}P MAS NMR measurements were performed on a JEOL JNM CMX-400 spectrometer at spinning rates of 3 and 9 kHz and resonance frequencies of 104.17 and 161.84 MHz with 45° pulse lengths of 4.0 and 4.0 μ s and recycle times of 5 and 30 s, respectively. Solid-state ^{13}C CP/MAS NMR measurements were performed at 100.54 MHz using 5 s intervals

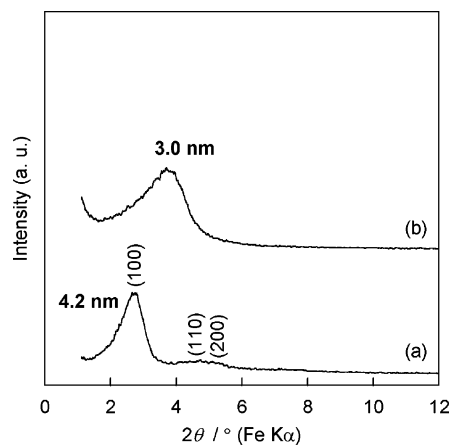


Figure 1. XRD patterns of (a) as-synthesized and (b) calcined AOPs prepared by using $(HO)_2OPCH_2PO(OH)_2$ in the presence of C_{16} TMACl in the aqueous system.

(spinning rate; 5 kHz). The compositions of the products were measured by ICP (Jarrell Ash ICAP 1000S) and CHN (Thermo Finnigan Flash EA 1112) analyses. Nitrogen adsorption–desorption isotherms were measured by using a Quantachrome Autosorb-1 at 77 K. Specific surface areas and average pore diameters were calculated by the BET method⁵⁵ and the H–K method⁵⁶ using adsorption data, respectively. Water adsorption–desorption isotherms were measured by using a BELSORP 18 (Bel Japan Inc.) at 25 °C. Adsorption measurements of acetaldehyde were also conducted by using a Quantachrome Autosorb-1 at 25 °C. All of the samples were heated at 110 °C for 6 h under vacuum before all of the adsorption measurements.

Results and Discussion

Synthesis of Mesoporous Aluminum Methylenediphosphonates. Mesostructured AOPs were prepared by using $(HO)_2OPCH_2PO(OH)_2$ in the aqueous system. The XRD patterns of as-synthesized and calcined materials are shown in Figure 1. Although broad peaks were observed in the XRD pattern of the as-synthesized material, the peaks are possibly assignable to reflections due to a 2-D hexagonal phase ($p6mm$) according to the peak positions. By using a surfactant with a longer alkyl chain (C_{18} TMACl), XRD peaks became sharp and the short-range orderings of hexagonal arrangements can be taken by TEM, as reported previously.⁴⁶ In contrast, less ordered mesostructured AOPs were obtained by using surfactants with shorter alkyl chains (C_{14} TMACl and C_{12} TMACl). Those XRD peaks were broadened further after calcination. The N_2 adsorption–desorption isotherm of the calcined material prepared in the presence of C_{16} TMACl was almost type I. The BET surface area, the pore volume, and the pore diameter were 578 $m^2 g^{-1}$, 0.27 $cm^3 g^{-1}$, and 1.7 nm, respectively.

The compositions due to inorganic and organic components were investigated by ICP and CHN analyses, respectively. The Al/P (Al/2P) molar ratio in the hybrid framework was 0.73 (1.46). The carbon, hydrogen, and nitrogen contents in the as-synthesized material were 37.6, 8.8, and 2.2 mass %, respectively. According to the elemental analyses, the

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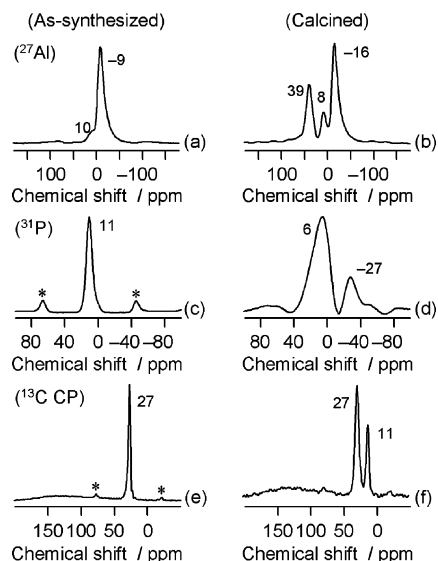


Figure 2. ^{27}Al MAS NMR spectra of (a) as-synthesized and (b) calcined AOPs prepared in the presence of $\text{C}_{16}\text{TMACl}$ in the aqueous system, ^{31}P MAS NMR spectra of (c) as-synthesized and (d) calcined AOPs, and ^{13}C CP/MAS NMR spectra of (e) $(\text{HO})_2\text{OPCH}_2\text{PO}(\text{OH})_2$ and (f) calcined AOP. Spinning sidebands are marked with asterisks.

formula of the as-synthesized material can be described as $\text{Al}_6(\text{O}_3\text{PCH}_2\text{PO}_3)_4 \cdot 3.7\text{C}_{16}\text{TMA} \cdot 21.8\text{H}_2\text{O}$, but negatively charged OH^- species such as terminal $\text{Al}-\text{OH}$ groups would be required in this formula because of the charge balance. The ^{27}Al MAS, ^{31}P MAS, and ^{13}C CP/MAS NMR spectra of as-synthesized and calcined materials are shown in Figure 2. The ^{27}Al MAS NMR spectrum of the as-synthesized material showed an asymmetric peak (at around -10 ppm) assignable to Al atoms in six-coordinated species. On the basis of the asymmetric profile, the Al atoms could be six-coordinated due to bonding to the PO_3 groups as well as to retained OH and H_2O .^{57–60} When samples are degassed at 550°C , the presence of $\text{Al}-\text{OH}$ and $\text{P}-\text{OH}$ groups can be detected by FT-IR.⁶¹ However, methylene groups in the hybrid framework were decomposed during calcination above 450°C (Supporting Information, Figure S1) and the meso-structural ordering was also lost simultaneously. Therefore, the presence of $\text{Al}-\text{OH}$ groups in the as-synthesized material could not be shown by FT-IR (Supporting Information, Figure S2). The AlO_6 species were partly converted to four-coordinated species (38 ppm) such as $\text{Al}(\text{OP})_4$ and/or $\text{Al}(\text{OP})_{4-x}(\text{OH})_x$ by calcination through dehydration.^{57–60} However, a large number of the six-coordinated Al species (-16 ppm) were maintained even after calcination at 400°C , meaning that a large amount of water molecules stayed in the calcined material. Nitrogen atoms were not detected in the calcined material by CHN analysis. This result reveals that all of the C_{16}TMA molecules can be removed by calcination at 400°C . Nevertheless, the calcined material contained 3.7 mass % of carbon atoms. The ^{13}C CP/MAS NMR spectrum showed that the remaining carbon atoms in

the calcined material are due to methylene groups bonded to P atoms ($\equiv\text{P}-\text{CH}_2-\text{P}\equiv$) observed at 27 ppm. The peak at 11 ppm is assignable to carbon atoms in methyl groups bonded to P atoms⁶² ($\equiv\text{P}-\text{CH}_3$) that are formed through the decomposition of diphosphonate groups. The result is also confirmed in the ^{31}P MAS NMR spectra of the calcined material. The ^{31}P MAS NMR spectrum of the as-synthesized material showed a broad signal centered at 11 ppm, indicating that all of the P atoms can be assignable to P atoms in phosphonate groups ($\equiv\text{P}-\text{CH}_2-\text{P}\equiv$). It is considered that the formation of $\text{Al}-\text{O}-\text{P}$ bonds occurs in the framework because the peak is observed at higher magnetic fields than that observed for $(\text{HO})_2\text{OPCH}_2\text{PO}(\text{OH})_2$ (27 ppm). AlPO domains and methylene groups are arranged alternatively in the hybrid framework. Even after calcination, a broad peak due to phosphonate groups was mainly observed centered at around 6 ppm ($\equiv\text{P}-\text{CH}_2-\text{P}\equiv$ and $\equiv\text{P}-\text{CH}_3$), but the presence of a small amount of phosphate groups was found at around -27 ppm (PO_4). Thus, the synthesis of surfactant-templated mesoporous materials composed of non-silica-based hybrid frameworks was achieved. According to the DTA analysis (Supporting Information, Figure S1), the organic groups within the hybrid framework were thermally stable up to 450°C .

On the basis of the formula of the as-synthesized material, the carbon content of the calcined material is calculated to be 5.6 mass % if the complete removal of C_{16}TMA and water molecules without decomposition of the methylene groups ($\text{Al}_6(\text{O}_3\text{PCH}_2\text{PO}_3)_4$) took place. Twelve mass % of water molecules was physically adsorbed on the calcined material (Supporting Information, Figure S1), and then 5.0 mass % of carbon atoms should be present in the calcined material. Accordingly, 26 mass % of carbon atoms is lost during the calcination process. However, the amount of water molecules coordinated to Al atoms is not taken into account in the above calculation. If all of the water molecules remain in the calcined material ($\text{Al}_6(\text{O}_3\text{PCH}_2\text{PO}_3)_4 \cdot 21.8\text{H}_2\text{O}$), the calcined material will contain 3.9 mass % of carbon atoms, close to the CHN analysis data. Actually, a part of the coordinated water molecules were eliminated during calcination (see Figure 2). More carbon atoms (>3.9 mass %) should be present in the calcined material if all of the methylene groups are maintained in the hybrid framework. Consequently, it is certain that the methylene groups are partly lost during calcination.

Synthesis of Ordered Mesoporous AOP-2 in the Ethanol–Water System. The synthesis of non-silica-based hybrid mesoporous materials was achieved, but the periodicity was lowered by calcination. Therefore, another synthetic method to obtain highly ordered mesoporous AOPs was investigated. This synthetic method was originally reported by Tian et al., who have mainly studied the synthesis of various metal phosphates including aluminophosphates (AlPOs) through various “acid–base pair routes” by using nonaqueous solutions of block copolymers.^{63,64} In the present study, highly

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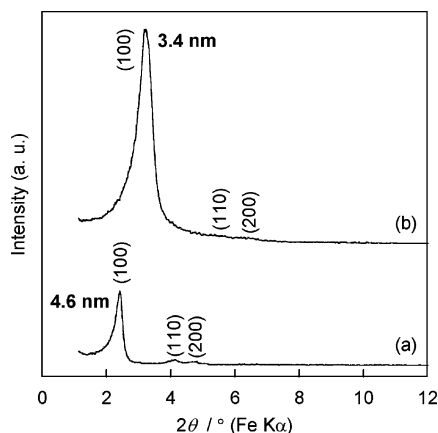


Figure 3. XRD patterns of (a) as-synthesized and (b) calcined aluminum methylenediphosphonates prepared in the presence of C_{16} TMACI in the ethanol–water system.

ordered AOP-2 can be successfully synthesized by modifying the “acid–base pair route” concept in the presence of C_n -TMA surfactants.

The XRD patterns of as-synthesized and calcined materials are shown in Figure 3. The XRD pattern of the as-synthesized material exhibits four well-resolved reflections assignable to a 2-D hexagonal structure with a unit cell parameter of 5.3 nm ($d_{100} = 4.6$ nm). After calcination at 400 °C, an intensity of the main peak ($d_{100} = 3.4$ nm) was increased remarkably, and the higher order reflections were observed. Similar XRD results have often been found in many papers on highly ordered mesoporous silicas,^{6–9} being related to the successful removal of surfactant molecules without deformation of the periodic 2-D hexagonal mesostructure. The result was confirmed further by TEM; the TEM images of as-synthesized and calcined materials are shown in Figure 4. In the as-synthesized material, well-ordered hexagonal arrays of one-dimensional mesopores were observed. One-dimensional ordered mesopores were maintained after calcination. The N_2 adsorption–desorption isotherm of the calcined material is shown in Figure 5. A type IV isotherm characteristic of ordered mesoporous materials was observed, and the pore size distribution centered at 2.2 nm was sharp. Also, both the BET surface area ($788 \text{ m}^2 \text{ g}^{-1}$) and the pore volume ($0.44 \text{ cm}^3 \text{ g}^{-1}$) were very high.

Considering the synthetic process, the Al/P molar ratio of the framework was identical to that of the starting mixture (Al/2P = 4/3), checked by ICP (Al/P = 0.67). The calcined material contained 2.8 mass % of carbon atoms (CHN). The ^{27}Al MAS, ^{31}P MAS, and ^{13}C CP/MAS NMR spectra of as-synthesized and calcined materials are shown in Figure 6. All of the NMR spectra are similar to those observed for the aluminum methylenediphosphonates prepared in the aqueous system described above (see Figure 2). In the ^{13}C CP/MAS NMR spectrum of the calcined material, two peaks were observed at 11 and 28 ppm, assignable to carbon atoms in methyl ($\equiv\text{P}-\text{CH}_3$) and methylene groups ($\equiv\text{P}-\text{CH}_2-\text{P}\equiv$), respectively. The ^{31}P MAS NMR spectrum exhibited two broad peaks centered at 6 ppm ($\equiv\text{P}-\text{CH}_2-\text{P}\equiv$ and

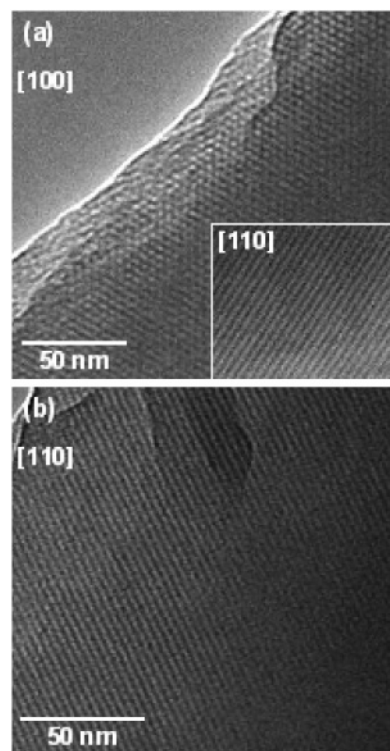


Figure 4. TEM images of (a) as-synthesized and (b) calcined aluminum methylenediphosphonates prepared in the presence of C_{16} TMACI in the ethanol–water system.

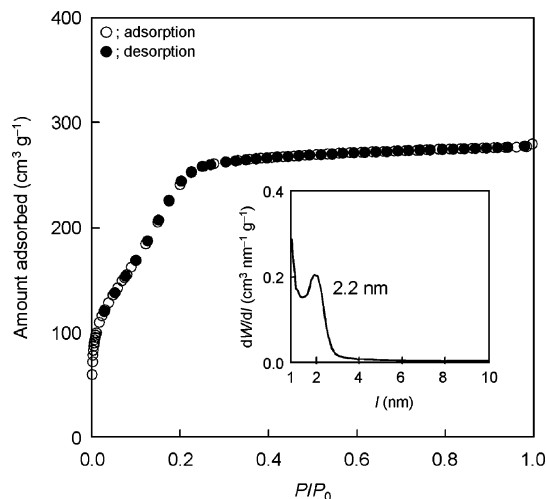


Figure 5. N_2 adsorption–desorption isotherm and the corresponding pore size distribution of calcined AOP-2 prepared in the presence of C_{16} TMACI in the ethanol–water system.

$\equiv\text{P}-\text{CH}_3$) and -26 ppm (PO_4). Both methylene and methyl groups are present within the framework.

Investigation of the Optimal Synthetic Conditions of Mesostructured and Mesoporous AOP-2 with Methylene Groups. Optimal synthetic conditions of the ordered AOP-2 in the ethanol–water system have been determined on the basis of the following experiment. The XRD patterns of as-synthesized and calcined aluminum methylenediphosphonates with different Al/2P molar ratios are shown in Figure 7. Highly ordered mesostructured materials can be obtained by using the same synthetic procedure without regard to the Al/2P molar ratios in the starting mixtures. However, the periodic mesostructures were maintained after calcination where the Al/2P molar ratios were higher than 6/4 (1.50),

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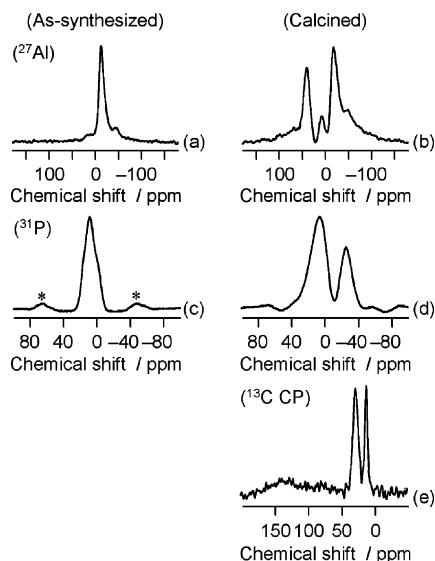


Figure 6. ^{27}Al MAS NMR spectra of (a) as-synthesized and (b) calcined AOP-2 prepared in the presence of $\text{C}_{16}\text{TMACl}$ in the ethanol–water system, ^{31}P MAS NMR spectra of (c) as-synthesized and (d) calcined AOP-2, and ^{13}C CP/MAS NMR spectra of (e) calcined AOP-2. Spinning sidebands are marked with asterisks.

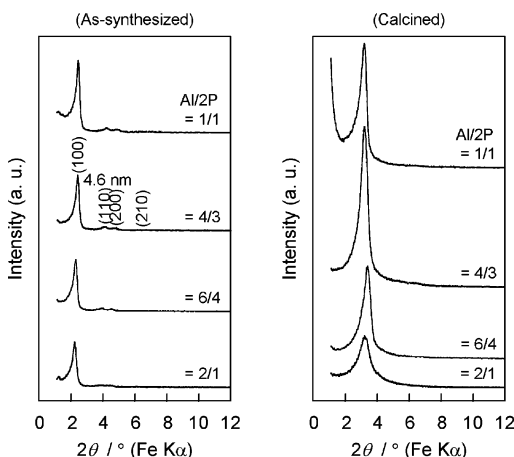


Figure 7. XRD patterns of as-synthesized and calcined aluminum methylenediphosphonates with different Al/2P molar ratios prepared in the presence of $\text{C}_{16}\text{TMACl}$ in the ethanol–water system.

Table 1. Porous Structures of Calcined Aluminum Methylenediphosphonates with Different Al/2P Molar Ratios Prepared in the Presence of $\text{C}_{16}\text{TMACl}$ in the Ethanol–Water System

Al/2P molar ratio	BET surface area / $\text{m}^2 \text{g}^{-1}$	pore volume / $\text{cm}^3 \text{g}^{-1}$	average pore diameter /nm
Methylene			
1/1	654	0.36	2.1
4/3	788	0.44	2.2
6/4	738	0.37	1.9
2/1	793	0.38	2.1
Ethylene			
6/4	708	0.32	1.9
Propylene			
6/4	71	0.04	

especially at around 4/3 (1.33). The porosities of the calcined materials are listed in Table 1. According to the BET surface areas, the pore volumes, and the pore size distributions, it is concluded that the Al/2P molar ratios at around 4/3 are quite suitable synthetic conditions for the synthesis of highly ordered mesoporous aluminum methylenediphosphonates.

The formation mechanism of 2-D hexagonal mesostructured AOP-2 under highly acidic conditions (in the ethanol–water system) can be explained as follows. It is well known that P–OH groups in phosphates are protonated (P–OH_2^+) and Al species are present as $\text{Al}(\text{H}_2\text{O})_6^{3+}$ under highly acidic conditions.⁶⁵ In the present system, it is rational to consider that cationic P–OH₂⁺ groups and cationic $\text{Al}(\text{H}_2\text{O})_6^{3+}$ species, which respectively originated from $(\text{HO})_2\text{OPCH}_2\text{–PO}(\text{OH})_2$ and AlCl_3 , are present in highly acidic starting mixtures. Because these cationic inorganic species are repulsed, the formation of Al–O–P bonds would be suppressed during the formation of mesostructured materials. Therefore, almost all of the Al species in the as-synthesized AOP-2 are six-coordinated (see Figure 6), revealing that the frameworks are less condensed. In addition, the condensation of orthophosphoric species would lead to pyrophosphates ($2\text{PO}(\text{OH})_3 \rightarrow (\text{HO})_2\text{OP–O–PO}(\text{OH})_2 + \text{H}_2\text{O}$).⁶⁵ However, this reaction does not occur in aqueous solutions at room temperature. Synthetic conditions that P–OH₂⁺ groups are likely to draw near should be avoided, and then aluminum and phosphonate species can be mixed in the starting mixtures homogeneously. Therefore, the presence of anionic Cl^- species is required for interacting between cationic $\text{C}_n\text{–TMA}^+$ molecules and cationic inorganic species such as P–OH₂⁺. Indeed, the presence of chlorine atoms (5.6 mass %) was detected in the as-synthesized material by ion chromatography. In addition, excess $\text{C}_{16}\text{TMACl}$ molecules have never been recovered as a mixed phase in the as-synthesized material (checked by XRD). TG-DTA curves of the as-synthesized material are quite different from those observed for $\text{C}_{16}\text{TMACl}$. The results indicate that all of the $\text{C}_{16}\text{TMACl}$ molecules are present in the ordered AOP-2. Accordingly, the mesostructured material is formed through the $\text{S}^+\text{X}^-\text{I}^+$ pathway because the Cl^- anions are present during the formation process of the mesostructured material. Thus, syntheses under conditions with the Al/2P molar ratios at around 4/3 are preferable to obtain highly ordered mesostructured precursors because interactive points such as P–OH₂⁺ groups can be ensured and the groups are detached from each other by the presence of a moderate amount of Al species under the synthetic conditions.

Synthesis of Mesostructured and Mesoporous AOPs with Alkylene Groups. Mesostructured AOPs with alkylene groups were prepared by using $(\text{HO})_2\text{OPCH}_n\text{PO}(\text{OH})_2$ ($n = 1, 2$, and 3) in the ethanol–water system (Al/2P = 1/1). The XRD patterns of as-synthesized AOPs with alkylene groups are shown in Figure 8. All of the XRD patterns of the as-synthesized materials show well-resolved reflections assignable to 2-D hexagonal structures. For example, a typical TEM image of the mesostructured AOP with ethylene groups is shown in Figure 9. A clear TEM image along the [100] direction of the 2-D hexagonal structure was observed. However, the periodic mesostructure was almost lost after calcination at 400 °C.

The possibility if removing C_{16}TMA molecules by calcination has been explored further. The XRD patterns of as-synthesized and calcined AOPs with alkylene groups ob-

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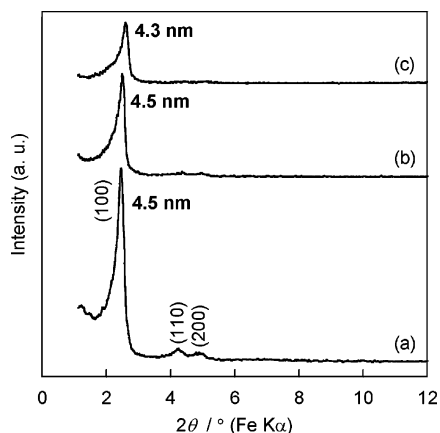


Figure 8. XRD patterns of as-synthesized AOPs with (a) methylene, (b) ethylene, and (c) propylene groups ($\text{Al}/2\text{P} = 1/1$) in the ethanol–water system.

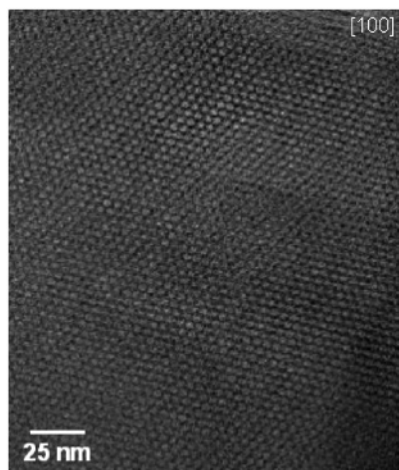


Figure 9. TEM image of the as-synthesized AOP with ethylene groups ($\text{Al}/2\text{P} = 1/1$) in the ethanol–water system.

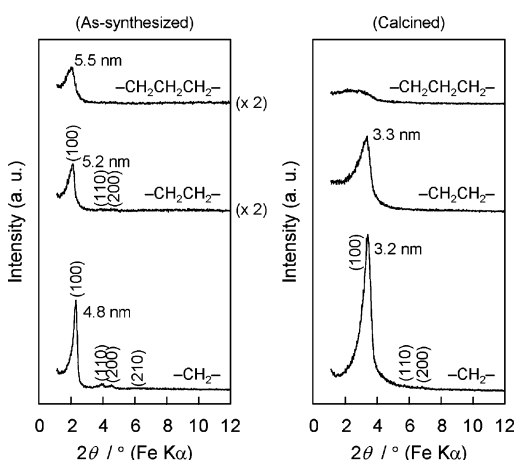


Figure 10. XRD patterns of as-synthesized and calcined AOPs with alkylene groups ($\text{Al}/2\text{P} = 6/4$) in the ethanol–water system.

tained under the condition with $\text{Al}/2\text{P} = 6/4$ are shown in Figure 10. As mentioned above, the mesostructured AOP with methylene groups can be converted to a mesoporous material with a high surface area (see Table 1). When all of the methylene groups were decomposed by calcination at higher temperatures above $550\text{ }^{\circ}\text{C}$, the 2-D hexagonal structure was lost completely. Mesoporous inorganic compounds such as AIPOs cannot be obtained from mesostructured AOPs. In the mesostructured AOP with ethylene

groups, an intense peak ($d_{100} = 3.3\text{ nm}$) was also observed even after calcination at $400\text{ }^{\circ}\text{C}$, affording a mesoporous AOP with ethylene groups. The BET surface area, the pore volume, and the pore diameter were $708\text{ m}^2\text{ g}^{-1}$, $0.32\text{ cm}^3\text{ g}^{-1}$, and 1.9 nm , respectively. Anyhow, mesoporous AOPs containing propylene groups cannot be obtained by using the method to remove surfactant molecules by calcination because the propylene groups are less thermally stable than methylene and ethylene groups.

Likewise, an ordered 2-D hexagonal mesostructured AIPO can be obtained by using AlCl_3 and H_3PO_4 in the presence of $\text{C}_{16}\text{TMACl}$ (Supporting Information, Figure S3). However, the removal of the $\text{C}_{16}\text{TMACl}$ molecules by calcination led to disordering of the 2-D hexagonal structure (Supporting Information, Figure S3). The pore size distribution of the calcined AIPO was very broad, although the N_2 adsorption–desorption isotherm showed a type IV behavior (Supporting Information, Figure S4). The result suggests that the presence of thermally stable alkylene groups such as methylene ones within the framework is very important for the formation of ordered mesoporous AOP-2. In addition, disordered mesoporous AOP-2 is obtained from 2-D hexagonal mesostructured precursor whose XRD peaks are ill-resolved, as mentioned above.⁴⁶ This means that the preparation of highly ordered mesostructured precursors is also needed for obtaining ordered mesoporous AOPs.

The mesostructural periodicities of periodic mesoporous organosilicas (PMOs) are higher than those of ordered mesoporous silicas, which would be improved by the presence of organic groups within the hybrid frameworks. The morphologies of the particles are often corresponded with the mesostructures distinctly.²⁵ Mesostructural distortion caused by condensation of inorganic species would be relieved by the presence of flexible organic groups within the hybrid frameworks. In the present system, the 2-D hexagonal mesostructure would be retained even after the substantial shrinkage during calcination because of the presence of thermally stable alkylene groups within the hybrid framework. Stabilities of mesostructured AIPOs can be also improved by modification with organosilanes, and the stabilities are concerned with thermal stabilities of the organic groups.^{66,67} Mesoporous AOP-2 with methylene and ethylene groups can be obtained by low-temperature calcination because these organic groups, especially methylene ones, are thermally stable. Additionally, it will be required immediately to expand methods to extract surfactant molecules as in the case of PMOs^{24–32} because the synthesis of ordered mesoporous AOPs with various functional organic groups is greatly of interest.

Properties of Ordered AOP-2. Surface properties of the ordered AOP-2 have been investigated on the basis of water and acetaldehyde adsorption measurements. The water adsorption–desorption isotherm of the ordered AOP-2 (pore diameter; 2.2 nm) with methylene groups is shown in Figure 11. The water adsorption isotherm showing a type IV behavior revealed that the ordered AOP-2 possesses hydro-

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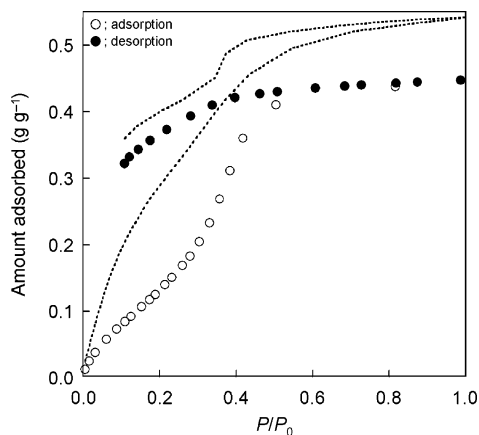


Figure 11. H₂O adsorption–desorption isotherm of calcined AOP-2 prepared in the presence of C₁₆TMACl in the ethanol–water system. The isotherm for the mesoporous AIPO prepared by using AlCl₃ and H₃PO₄ in the presence of C₁₆TMACl is shown as dotted lines for comparison.

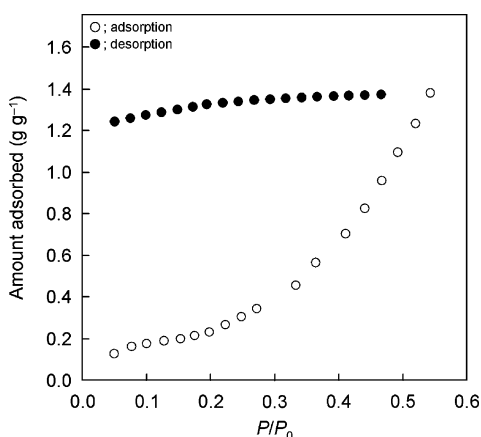


Figure 12. Acetaldehyde adsorption–desorption isotherm of calcined AOP-2 prepared in the presence of C₁₆TMACl in the ethanol–water system.

philic surfaces due to AIPO domains as in the case of mesoporous AIPO.⁵⁹ However, the hydrophilic property is weakened slightly according to the presence of hydrophobic methylene groups, on the basis of the comparison to the water adsorption–desorption isotherm observed for a mesoporous AIPO with the same pore diameter (2.1 nm) (dotted lines in Figure 11).

The adsorption and desorption behavior of acetaldehyde on the surfaces of the ordered AOP-2 is greatly of interest, as shown in Figure 12. Acetaldehyde molecules can be adsorbed on the surfaces of the ordered AOP-2 even at very low relative pressures ($P/P_0 < 0.1$ of the adsorption branch). Once acetaldehyde molecules are adsorbed on the surfaces of the ordered AOP-2, acetaldehyde molecules cannot be desorbed from the surface even under vacuum ($P/P_0 < 0.1$ of the desorption branch). The similar result can be obtained from the adsorption–desorption experiment of acetaldehyde

on the surfaces of mesoporous AIPO. It is considered that oxygen atoms in water and acetaldehyde molecules would interact with the surfaces of the ordered AOP-2 very strongly. Accordingly, AIPO domains within the frameworks of mesoporous materials are fairly useful adsorbents for harmful organic molecules such as aldehydes. Also, it is considered that mesoporous AOPs are possibly available for catching volatile organic compounds (VOCs) because benzene molecules can be adsorbed on the surface of mesoporous AIPO.⁵⁹

Conclusions

Surfactant-templated mesoporous aluminum organophosphonates (AOPs) with alkylene groups can be synthesized by using the corresponding diphosphonic acids in the aqueous and ethanol–water systems. In addition to the preparation of highly ordered mesostructured precursors, the presence of thermally stable organic groups within the hybrid framework is very important for the formation of ordered mesoporous AOPs. The mesoporous AOPs are useful as adsorbents for removing harmful organic compounds such as aldehydes. The use of triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymers such as Pluronic P123 (EO₂₀PO₇₀EO₂₀), Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆), and Pluronic F68 (EO₈₀PO₃₀EO₈₀) led to the formation of ordered mesoporous AOP-2 with large pores. Mesoporous AOPs with 2-D hexagonal phases can be also prepared by using alkyl poly(ethylene oxide) surfactants such as Brij 56 (C₁₆EO₁₀) and Brij 58 (C₁₆EO₂₀). With the successful synthesis of various ordered stable mesoporous metal phosphates through the reactions of inorganic acid–base pairs such as metal chlorides and phosphoric acid,⁶³ the use of organically bridged diphosphonic acids to produce non-silica-based inorganic–organic hybrid frameworks opens new routes for the synthesis of a huge number of non-silica-based hybrid mesoporous materials, which are potentially applicable in the various research fields.

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Supporting Information Available: Figures S1 (TG-DTA), S2 (FT-IR), S3 (XRD), and S4 (N₂ isotherm) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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