# Lamellar Mesostructured Aluminum Organophosphonate with Unique Crystalline Framework

Tatsuo Kimura,*[1] Daisuke Nakashima,[2] and Nobuyoshi Miyamoto[2]
[1]*Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Shimoshidami, Moriyama-ku, Nagoya 463-8560*
[2]*Department of Life, Environment and Materials Science, Fukuoka Institute of Technology, Wajiro-Higashi, Higashi-ku, Fukuoka 811-0295*

(Received July 6, 2009; CL-090633; E-mail: t-kimura@aist.go.jp)

Lamellar mesostructured aluminum organophosphonate (AOP-1) with unique inorganic–organic hybrid framework can be prepared from the reactions of aluminium triisopropoxide with methylene diphosphonic acid in the presence of alkyltrimethylammonium surfactants, which is the first example of the preparation of layered aluminum organophosphonate with pure hybrid framework mainly composed of Al, P, and organic group.

Inorganic–organic hybrid materials have attracted much attention because of the combined properties of inorganic units and organic moieties.[1] Hybrid frameworks are integrated by chemical reactions such as condensation of organometal alkoxides and related materials. Consequently, the structural design of starting organometal compounds at the molecular level is the most important factor for obtaining fascinating hybrid materials with managed surfaces and functions. A number of porous inorganic–organic hybrid materials have been reported to date,[2–9] because porous structures promise to deliver unique properties due to hybrid frameworks.

Organically bridged diphosphonic acids are one of the most interesting precursors for preparing non-silica-based hybrid materials such as metal phosphonates.[5] But they have often acted as linkers between inorganic layers. They can also be used for synthesizing non-silica-based hybrid mesoporous materials (HMMs) using amphiphilic organic molecules.[10,11] Morphological controls (film, spherical particles) of ordered mesoporous aluminum organophosphonate (AOP) have been achieved for extensive applications.[12] Here, inorganic–organic hybrid mesostructured materials were synthesized from methylene diphosphonic acid ($(HO)_2OPCH_2PO(OH)_2$) in the presence of alkyltrimethylammonium ($C_nTMA$) surfactants. Surfactant-templated mesoporous AOPs have normally been obtained as amorphous phases,[10–12] while lamellar mesostructured AOP (named as AOP-1) obtained here is the first example of non-silica-based mesostructured material with a crystalline hybrid framework. It is well known that crystalinity of the frameworks is quite important for improving properties due to inorganic units.

Periodic mesoporous organosilica (PMO) is interesting as a new family of HMMs.[2–4] Almost all corresponding research has focused on the variation of organic groups in the hybrid frameworks to expand functions. Incorporation of inorganic heteroatoms into the inorganic part of the hybrid frameworks has been studied for the design of mesoporous catalysts with strongly hydrophobic surfaces. In some cases, periodic molecular structures of organic groups were found in pore walls.[4] A periodicity in the framework was also reported in the case of Al containing PMO.[13] Only one paper on that of a lamellar phase with a crystal-like hybrid framework was published.[14] Therefore, insight into successful preparation of crystalline non-silica-based hybrid mesostructured material is very important for the compositional variation of both inorganic units and organic groups in hybrid frameworks of mesostructured and mesoporous materials.

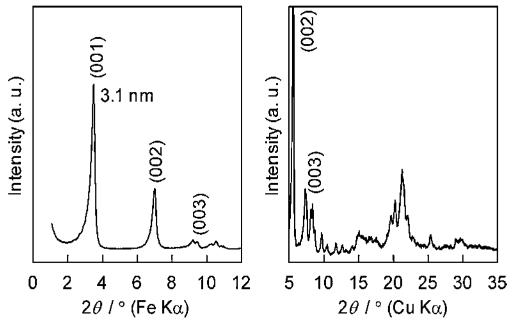


**Figure 1.** Low- and high-angle XRD patterns of lamellar mesostructured AOP-1.

Experimental details including analyses are described in Supporting Information.[15] The composition of lamellar AOP-1 analyzed by ICP and CHN was $Al_4(O_3PCH_2PO_3)_3 \cdot 9C_{16}TMA \cdot 24H_2O$. The low- and high-angle XRD patterns of AOP-1 are shown in Figure 1. A peak at a $d$-spacing of 3.1 nm and higher order diffractions were observed in low diffraction angles. In addition to those peaks, some peaks due to a periodicity in the hybrid framework were recorded. However, crystal structure of the hybrid framework has not been defined yet because of the ill-resolved peaks. The TEM image of AOP-1 is shown in Figure 2, showing clear striped patterns with the repeated distance of ca. 3.3 nm.

The $^{27}Al$ and $^{31}P$ MAS NMR spectra of the lamellar AOP-1 are shown in Figure 3. The $^{31}P$ MAS NMR spectrum showed that sharp peaks were observed in the range from 9 to 15 ppm, being related to the XRD result that the hybrid framework is crystalline. The difference in the chemical shifts between AOP-1 and $(HO)_2OPCH_2PO(OH)_2$ (27 ppm) is associated with the formation of Al–O–P bonds. Judging from the chemical shifts (close to those observed for 2-D hexagonal products composed of amorphous AOP frameworks[10]), the framework is not condensed adequately. The half of P atoms is possibly bonded to Al atoms through oxygen and residual P–O units may be interacted with $C_{16}TMA$ cations. The $^{27}Al$ MAS NMR spectrum of AOP-1 showed that a peak observed at $-14$ ppm was assignable to $Al(OP)_{6-x}(H_2O)_x$.[16] On the basis of the NMR data, it is believed that P atoms in methylene diphosphonate ($\equiv PCH_2P \equiv$) groups are bonded to $AlO_6$ species that are partly ligated by water molecules.

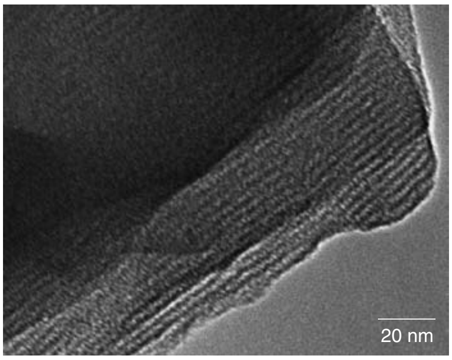


**Figure 2.** Typical TEM image of lamellar mesostructured AOP-1.

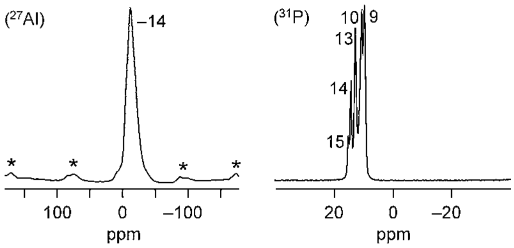


**Figure 3.** (a) $^{27}$Al and (b) $^{31}$P MAS NMR spectra of lamellar mesostructured AOP-1.

The use of $(HO)_2OP–R–PO(OH)_2$ (R; organic group) to produce inorganic–organic hybrid materials has been directed to the formation of a variety of layered metal phosphonates.[5,6] Frameworks of the layered materials are analogous to those of metal phosphates, but not to integrated inorganic units and organic groups. The organic groups covalently bonded to P atoms are present as pillars between the inorganic sheets. Several AOPs with zeolitic and layered structures have also been prepared from (mono)phosphonic acids.[17–19] Although the organic groups are attached to the surfaces of inorganic frameworks, Harvey et al. have synthesized a layered AOP with alternating inorganic units and organic groups from ethylenediphosphonic acid ($(HO)_2OPC_2H_4PO(OH)_2$).[20] The ethylene groups are embedded in the hybrid framework, but the framework is not constructed from Al, P, and the organic group only. P atoms are bonded to $AlO_6$ units, which is a common structure for the reported crystalline AOPs. The six-coordinated Al atoms are surrounded by four oxygen atoms (two Al–O–P bonds and two water ligands) and two F atoms, meaning that the framework is not pure.

In the present study, methylene groups can be embedded in the sheets (integrated hybrid frameworks) of the lamellar AOP-1 by a surfactant-assisted strategy. Al atoms are six-coordinated, connected to oxygen atoms only, and bonded to P atoms through oxygen atoms and water molecules are ligated to the Al atoms. Lamellar AOP-1 prepared using $C_n$TMA ($n = 14–18$) is the first example of the preparation of layered (lamellar) AOP with pure inorganic–organic hybrid frameworks.[15] Synthesis by using $(HO)_2OPC_2H_4PO(OH)_2$ was also conducted under similar conditions in the presence of $C_{16}$TMACl. The XRD patterns of products obtained at room temperature and 150 °C (Figure S5) give us the following insights.[15] A main peak at a $d$-spacing of 4.5 nm was observed with the high order diffractions, revealing the formation of a lamellar phase at room temperature. However, there were no peaks arising from crystalline framework in higher diffraction angles. In the product obtained at 150 °C, in addition to a peak shift of the main peak to 5.1 nm, several humps, which were possibly related to crystallinity of the hybrid framework, appeared. Further crystallization by extension of the reaction time led to collapse of the mesostructure.

In summary, a crystalline lamellar mesostructured AOP (AOP-1) can be synthesized by using $(HO)_2OPCH_2PO(OH)_2$ in the presence of $C_n$TMA ($n \geq 14$) surfactants. The insight strongly suggests the possibility for obtaining mesostructured materials with integrated hybrid frameworks constructed by various inorganic units such as transition-metal phosphate-like units and organic groups originating from diphosphonic acids.

### References and Notes

1 C. Sanchez, G. J. de A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, V. Cabuil, *Chem. Mater.* **2001**, *13*, 3061; C. Sanchez, C. Boissiére, D. Grosso, C. Laberty, L. Nicole, *Chem. Mater.* **2008**, *20*, 682; M. Llusar, C. Sanchez, *Chem. Mater.* **2008**, *20*, 782.
2 F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem., Int. Ed.* **2006**, *45*, 3216.
3 M. P. Kapoor, S. Inagaki, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1463.
4 S. Fujita, S. Inagaki, *Chem. Mater.* **2008**, *20*, 891.
5 A. Clearfield, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268; A. Clearfield, in *Progress in Inorganic Chemistry*, ed. by K. D. Karlin, Wiley, New York, **1998**, pp. 371–510.
6 K. Maeda, *Microporous Mesoporous Mater.* **2004**, *73*, 47.
7 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705.
8 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217.
9 D. Tanaka, S. Kitagawa, *Chem. Mater.* **2008**, *20*, 922.
10 T. Kimura, *Chem. Mater.* **2003**, *15*, 3742; T. Kimura, *Chem. Mater.* **2005**, *17*, 337; T. Kimura, *Chem. Mater.* **2005**, *17*, 5521; T. Kimura, K. Kato, *J. Mater. Chem.* **2007**, *17*, 559; T. Kimura, K. Kato, *Microporous Mesoporous Mater.* **2007**, *101*, 207.
11 J. E. Haskouri, C. Guillem, J. Latorre, A. Beltrán, D. Beltrán, P. Amorós, *Eur. J. Inorg. Chem.* **2004**, 1804; J. E. Haskouri, C. Guillem, J. Latorre, A. Beltrán, D. Beltrán, P. Amorós, *Chem. Mater.* **2004**, *16*, 4359.
12 T. Kimura, K. Kato, *New J. Chem.* **2007**, *31*, 1488; T. Kimura, K. Kato, Y. Yamauchi, *Chem. Commun.* **2009**, 4938.
13 Y. Xia, W. Wang, R. Mokaya, *J. Am. Chem. Soc.* **2005**, *127*, 790.
14 K. Okamoto, M. P. Kapoor, S. Inagaki, *Chem. Commun.* **2005**, 1423.
15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
16 T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Lett.* **1997**, 983; T. Kimura, Y. Sugahara, K. Kuroda, *Microporous Mesoporous Mater.* **1998**, *22*, 115; T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Commun.* **1998**, 559; T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Mater.* **1999**, *11*, 508. T. Kimura, *Chem. Lett.* **2002**, 770; T. Kimura, *J. Mater. Chem.* **2003**, *13*, 3072; T. Kimura, *Microporous Mesoporous Mater.* **2005**, *77*, 97.
17 G. B. Hix, V. J. Carter, D. S. Wragg, R. E. Morris, P. A. Wright, *J. Mater. Chem.* **1999**, *9*, 179; G. B. Hix, D. S. Wragg, I. Bull, R. E. Morris, P. A. Wright, *Chem. Commun.* **1999**, 2421; M. Edgar, V. J. Carter, P. Grewal, L.-J. Sawers, E. Sastre, D. P. Tunstall, P. A. Cox, P. Lightfoot, P. A. Wright, *Chem. Mater.* **2002**, *14*, 3432.
18 A. Cabeza, M. A. G. Aranda, S. Bruque, D. M. Poojary, A. Clearfield, J. Sanz, *Inorg. Chem.* **1998**, *37*, 4168.
19 G. B. Hix, D. S. Wragg, P. A. Wright, R. E. Morris, *J. Chem. Soc., Dalton Trans.* **1998**, 3359.
20 H. G. Harvey, S. J. Teat, M. P. Attfield, *J. Mater. Chem.* **2000**, *10*, 2632.

Published on the web (Advance View) August 22, 2009; doi:10.1246/cl.2009.916