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Synthesis, Crystal Structure, and Characterization of Layered Aluminum Methylphosphonate

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The first aluminum methylphosphonate with a layered structure, designated AlMepO-ζ, giving an ideal composition of $Al(OH)(O_3PCH_3)\cdot H_2O$ was synthesized with a hydrothermal procedure. AlMepO-ζ is monoclinic, space group $P2_1/c$, with $a = 7.8676(7)$, $b = 7.0744(13)$, $c = 9.4789(7)$, $\beta = 106.599(6)^\circ$. The framework in a sheet containing unidimensional [–Al–(OH)–Al–] chain is topologically the same as $VO(O_3PC_6H_5)\cdot H_2O$. Methyl groups protrude into the interlamellar space. TG-DTA and MAS-NMR results revealed the decomposition mechanism.

Layered oxide combined with organic functional groups has become of much interest as a molecularly engineered layered structure in recent years.[1)] In material engineering, organic compounds are advantageous in terms of flexible and molecularly tailored structure, while inorganic compounds are advantageous in the points of tailored and firm solid structure and thermal stability. Organophosphonate is one of the most useful and versatile sources to build layered organic-inorganic composites,[2)] because of its structural diversity and relatively simple synthesis procedure. Most of the known organophosphonates including mainly divalent,[1—8)] trivalent,[5,9)] and tetravalent[10—13)] metals have layered types of structure. They are potent in intercalation host material, catalyst, and ion exchanger etc. Nevertheless, no layered aluminum phosphonate has been reported except a patent claim[14)] without any sufficient characterization. Recently, we reported two aluminum methylphosphonates, designated AlMepO-α[15)] and -β,[16,17)] with unidimensional channel structures. Both compounds have neutral frameworks with an ideal composition of $Al_2(O_3PCH_3)_3$. They were synthesized from a mixture of pseudo-boehmite and methylphosphonic acid (P/Al = 1.5) under hydrothermal conditions. They are the first well-characterized aluminum organophosphonates. In the course of the study we found out that neutral or acidic compounds added to the starting mixture fundamentally gave AlMepO-β, while basic ones gave a new aluminum methylphosphonate compound of P/Al = 1 designated AlMepO-ζ.[18)] In this article we report synthesis, characterization, and crystal structure of AlMepO-ζ.

Experimental

Materials. Pseudo-boehmite was obtained from Condea Chemie (PURAL SCF, 74.4 wt% Al_2O_3, 25.6 wt% water). Methylphosphonic acid (98%) was obtained from Aldrich. Other organic reagents were obtained from Tokyo Kasei. All reagents were used without purification.

Synthesis. AlMepO-ζ was typically prepared as follows: The mixture of 0.685 g (10 mmol) of pseudo-boehmite powder, 1.467 g (15 mmol) of methylphosphonic acid, 2.5 ml of 2.0 M aqueous ammonia (5 mmol) and 4.22 g of water (400 mmol as total amount) was stirred for 1 h (1 M = 1 mol dm^{-3}). The mixture was hydrothermally treated at 160 °C for 48 h under an autogenous pressure in a stainless steel autoclave under static conditions. Polycrystalline AlMepO-ζ was filtered, washed with water, and air-dried. The total yield was 1.52 g (97%). Anal. Found: C, 7.1; H, 4.0; Al, 17.3; P, 20.1%. Calcd for $Al(OH)(O_3PCH_3)\cdot H_2O$: C, 7.7; H, 3.9; Al, 17.3; P, 19.9%.

Single crystals of AlMepO-ζ were obtained in a different preparation procedure. In a 20 ml Teflon® vessel, 1.467 g (15 mmol) of methylphosphonic acid was laid on the bottom of the vessel. Next, 0.685 g (10 mmol) of pseudo-boehmite powder was put over the methylphosphonic acid. Water was poured gently so as not to agitate the boehmite surface. After the mixture was left standing without stirring for 1 h the vessel was set in an autoclave, hydrothermally treated at 160 °C for 72 h under an autogenous pressure. The product was mainly AlMepO-β containing small amounts of plates of AlMepO-ζ. From the filtered and dried product, single crystals suitable for X-ray diffraction measurements were selected.

Measurement. Analyses for carbon and hydrogen content were performed on an organic elemental analyzer (Carlo Erba, EA1108). Phosphorus and aluminum analysis was done on an ICP spectrometer (Thermo Jarrell Ash, IRIS/AP) after the samples were dissolved in aqua regia on heating. X-Ray powder diffraction patterns (XRD) were measured at 303 K on a MAC Science MXP-18 diffractometer with Cu $K\alpha$ radiation.

All of the solid-state NMR measurements were performed using 4 mm zirconia rotors on a Bruker AMX-500 spectrometer equipped with magic angle spinning (MAS) unit. The ^{13}C CP/MAS-NMR spectra were recorded at 125.76 MHz referenced to an external glycine standard (176.46 ppm) with a contact time of 1 ms, a delay time of 10 s and a spinning rate of 4 kHz. The ^{27}Al MAS-NMR spectra were recorded at 130.32 MHz referenced to a 1 M aqueous solution of aluminum nitrate (0 ppm) with a spinning rate of 4—5 kHz, ca. 5° pulse and a recycle delay of 1 s. The ^{31}P MAS-NMR spectra were recorded at 202.46 MHz referenced to 85% phosphoric acid (0 ppm) with a spinning rate of 4—5 kHz, 20° pulse and a recycle delay of 60 s.

Thermogravimetry-differential thermal analysis (TG-DTA) was performed on a MAC Science TG-DTA 2000 instrument both under a flow of dry air or of nitrogen at 100 ml min^{-1}. The samples were well pulverized prior to the measurement.

Crystal Structure Determination. The crystal data and experimental details are summarized in Table 1. X-Ray measurements were performed on a Rigaku AFC-7 diffractometer using the ω–2θ technique for the range of $4.49 \leq 2\theta \leq 89.85°$. Cell parameters determined on 25 randomly taken reflections in the range of $66.73 \leq 2\theta \leq 69.75°$ corresponded to a monoclinic cell. On the basis of the systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) the space group was determined to be $P2_1/c$ to lead to a successful solution and refinement. An empirical absorption correction based on the ψ scan measurement was applied. The structure was solved by the direct method using SHELXS-86[19] and refined based on F^2 by the full-matrix least-squares method using SHELXL-93.[20] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the methyl group were placed geometrically and the other hydrogen atoms were located from the ΔF map. All hydrogen atoms were refined isotropically. The $F_o - F_c$ table was deposited as Document No. 70002 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Crystallographic Information for AlMepO-ζ

Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a/Å	7.8676(7)
b/Å	7.0744(13)
c/Å	9.4789(7)
β/°	106.599(6)
V/Å^3	505.59(11)
Empirical formula	CH_6AlO_5P
Formular weight	156.01
D_x/g cm^{-3}	2.050
Radiation	Mo $K\alpha$
λ/Å	0.71069
Monochrometer	Graphite
Crystal dimension /mm^3	$0.30 \times 0.25 \times 0.08$
Scan mode	ω–2θ
Absorption correction	Empirical via ψ scan
Transmission factor	0.922—1.000
2θ range	89.85
$h\,k\,l$ range	$h = 0$—15
	$k = 0$—14
	$l = -18$—18
Number of standard reflections	3
Temperature /°C	27
Total reflections	4144
Independent reflections	4144
Observed reflections	2736
Parameters	74
$R(F_o)^{a)}(I > 2\sigma(I))$	0.0342
$R_W(F_o{}^2)^{b)}$ (all data)	0.1083
S	0.929
$\Delta\rho_{max}$/eÅ^{-3}	0.62
$\Delta\rho_{min}$/eÅ^{-3}	−0.44

a) $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
b) $R_w(F_o{}^2) = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma w F_o{}^4\}^{1/2}$.
$w^{-1} = \sigma^2(F_o{}^2) + (0.0593P)^2 + 0.0886P$; $P = (F_o{}^2 + 2F_c{}^2)/3$.

Results and Discussion

Synthesis. As already reported, AlMepO-β is the main product in most cases when neutral or acidic organic compounds were added to the starting mixture (pseudo-boehmite/methylphosphonic acid/additive = 1 : 1.5 : 0.5).[18] AlMepO-ζ giving an ideal formula of $Al(OH)(O_3PCH_3) \cdot H_2O$ was obtained always when basic additives such as ammonia, R_4NOH ($R = CH_3$, C_2H_5, C_3H_7, and C_4H_9), or NaOH were added. These additives were not detected in the product by the elemental analysis. Use of $NaAlO_2$ as an aluminum source with no additive was also favorable for formation of AlMepO-ζ. In the synthesis of $AlPO_4$ molecular sieve, use of quaternary ammonium hydroxide or alkyl amine as structure-directing agents generally leads to formation of different microporous phases.[21] Also it was reported that use of similar organic structure-directing agents in oxovanadium organophosphonate system causes them to form layered-based open-framework structures.[22] Our result revealed, however, that quaternary ammonium hydroxide doesn't work as a structure-directing agent in aluminum methylphosphonate system but only works as a base to neutralize excessive methylphosphonic acid.

Crystal Structure. Atomic coordinates and thermal parameters for the atoms of AlMepO-ζ are given in Table 2; bond lengths and angles are listed in Table 3. The crystal packing is shown in Figs. 1 and 2. Aluminum atom has an octahedral coordination. The six vertex oxygen atoms are three phosphonate oxygens (O1, O4, and O5), two hydroxo oxygens (O2 and O2′ related to O2 by $2-x$, $y+1/2$, $5/2-z$), and one coordinated water oxygen (O3). Al–O3 (2.073 Å) is longer than the other Al–O bonds (1.861—1.881 Å). The three oxygens of the phosphonate group (O1, O4, and O5) are all connected with aluminum atoms. The $[AlO_6]$ octahedra forms a unidimensional [–Al–(OH)–Al–] chain by sharing vertex hydroxo oxygens (O2) in the direction of the b axis, as is shown in the view of the bc plane (Fig. 1). The methylphosphonate group bridges neighboring aluminum atoms in the chain via O4 and O5 to form a serpentine [–Al–O5–P–O4–Al]

Table 2. Fractional Atomic Coordinates and Equivalent Isotopic Displacement Parameters ($U_{eq} \times 10^3$/Å^2)

Atom	x	y	z	U_{eq}
P	0.76641(3)	0.12972(4)	0.90441(3)	8.45(5)
Al	0.98621(4)	0.11835(4)	1.23874(3)	9.07(6)
O1	0.7951(1)	0.1375(1)	1.00700(8)	13.3(1)
O2	0.9331(1)	−0.1339(1)	1.26701(9)	11.6(1)
O3	1.1840(1)	0.1012(1)	1.4371(1)	18.1(2)
O4	0.8448(1)	−0.0495(1)	0.8578(1)	13.6(1)
O5	0.8388(1)	0.3110(1)	0.85457(9)	13.8(1)
C	0.5319(2)	0.1258(2)	0.8202(2)	20.7(2)
HCA	0.5080(2)	0.129(2)	0.7151(2)	31.0
HCB	0.4788(3)	0.234(1)	0.852(1)	31.0
HCC	0.4829(3)	0.0125(9)	0.848(1)	31.0
H2A	0.828(3)	−0.139(2)	1.257(2)	17.4
H3A	1.183(3)	0.189(3)	1.488(3)	27.1
H3B	1.180(3)	0.023(3)	1.475(3)	27.1

Table 3. Bond Lengths (Å) and Angles (°)

P–O1	1.522(1)	O1–P–O4	112.02(5)	O2–Al–O4^{ii}	92.33(4)
P–O4	1.530(1)	O1–P–O5	109.22(5)	O2–Al–O5^{iii}	88.26(4)
P–O5	1.532(1)	O1–P–C	106.91(6)	O2^{i}–Al–O3	84.74(4)
P–C	1.789(1)	O4–P–O5	112.90(5)	O2^{i}–Al–O4^{ii}	86.30(4)
Al–O1	1.861(1)	O4–P–C	107.91(6)	O2^{i}–Al–O5^{iii}	92.24(4)
Al–O2	1.869(1)	O5–P–C	107.60(6)	O3–Al–O4^{ii}	88.51(4)
Al–O2^{i}	1.870(1)	O1–Al–O2	91.95(4)	O3–Al–O5^{iii}	85.09(4)
Al–O3	2.073(1)	O1–Al–O2^{i}	95.99(4)	O4^{ii}–Al–O5^{iii}	173.54(5)
Al–O4^{ii}	1.881(1)	O1–Al–O3	175.11(4)	P–O1–Al	136.83(5)
Al–O5^{iii}	1.878(1)	O1–Al–O4^{ii}	96.36(4)	Al–O2–Al^{iv}	143.03(4)
		O1–Al–O5^{iii}	90.05(4)	P–O4–Al^{ii}	138.98(5)
		O2–Al–O2^{i}	172.05(2)	P–O5–Al^{v}	138.51(5)
		O2–Al–O3	87.40(4)		

Hydrogen Bond Parameters

	O···O	H···O	<O–H···O
O3–H3A···O4^{i}	3.192(1)	2.41(2)	175(2)
O3–H3B···O5^{iv}	2.889(1)	2.24(2)	166(2)

i: $\bar{x}$+2, *y*+1/2, $\bar{z}$+5/2, *ii*: $\bar{x}$+2, $\bar{y}$, $\bar{z}$+2, *iii*: *x*, $\bar{y}$+1/2, *z*+1/2, *iv*: $\bar{x}$+2, *y*-1/2, $\bar{z}$+5/2, *v*: *x*, $\bar{y}$+1/2, *z*-1/2.

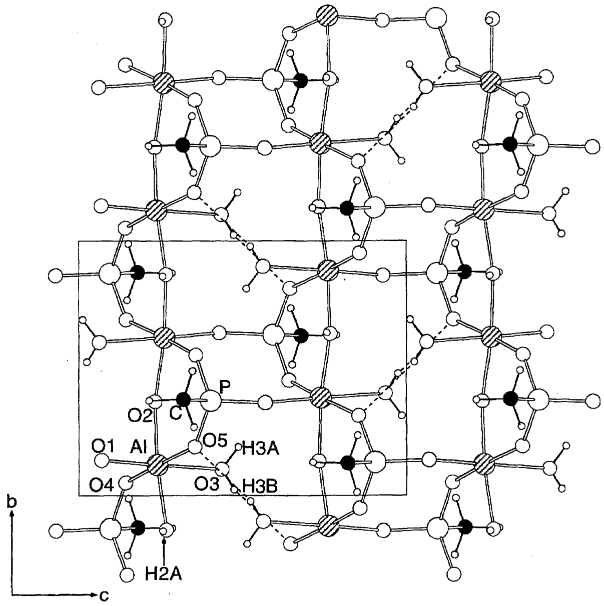

Fig. 1. View of the *bc* plane of AlMepO-ζ. The framework represents the unit cell in the plane.

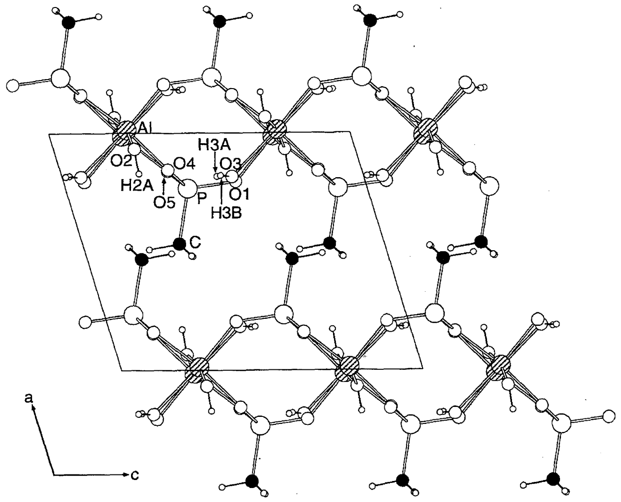

Fig. 2. View of the *ac* plane AlMepO-ζ. The framework represents the unit cell in the plane.

chain along the [–Al–(OH)–Al–] chain. The remaining phosphonate oxygen O1 is bound to an aluminum atom in the adjacent row. Such two-dimensional sheets on the *bc* plane include 12-membered rings (4Al and 2P) and 8-membered rings (2Al and 2P) between the [–Al–O5–P–O4–Al–] chains.

The sheets are situated at the angle equal to *β* to the *a*-axis with an interlayer distance of 7.540 Å, as shown in Fig. 2. The methyl groups protrude into the interlayer space above and below the inorganic sheets. The P–C bond of methylphosphonate is inclined at an angle of 81° to the layer plane. Also, water molecules coordinated to aluminum atoms stick out of the sheets. One hydrogen (H3B) of the water molecule forms a hydrogen bond with O5, as depicted with a dotted line in Fig. 1. There are two hydrogen bonds above and below the sheet across a 12-membered ring as shown in Fig. 2. Although the other hydrogen (H3A) is toward O4 (Table 3), the O3–O4 distance is too long for a hydrogen bond. Every hydroxo group in a [–Al–(OH)–Al–] chain protrudes above and below the plane alternately. The hydroxo groups [O2–H2A, 0.80(2) Å] form no hydrogen bond, as shown in Fig. 2.

The framework structure in a sheet of layered metal phosphonate fundamentally depends on the charge of the metal.[2)] Phosphonates of tetravalent metals $M^{IV}(O_3PR)_2$ [M = Zr and Sn][10—12)] take structures similar to α-Zr-$(HOPO_3)_2 \cdot H_2O$. Most phosphonates of divalent metals give a formula $M^{II}(O_3PR) \cdot H_2O$ [M = Ca, Cd, Cu, Fe, Mg, Mn, and Zn].[3—9)] Trivalent metal gives $HM^{III}(O_3PR)_2$ [M = Fe][9)] and $M^{III}(HO_3PR)(O_3PR)$ [M = Ln][2)] with a structure similar to $M^{IV}(O_3PR)_2$.[22)] In these typical structures, a metal atom is

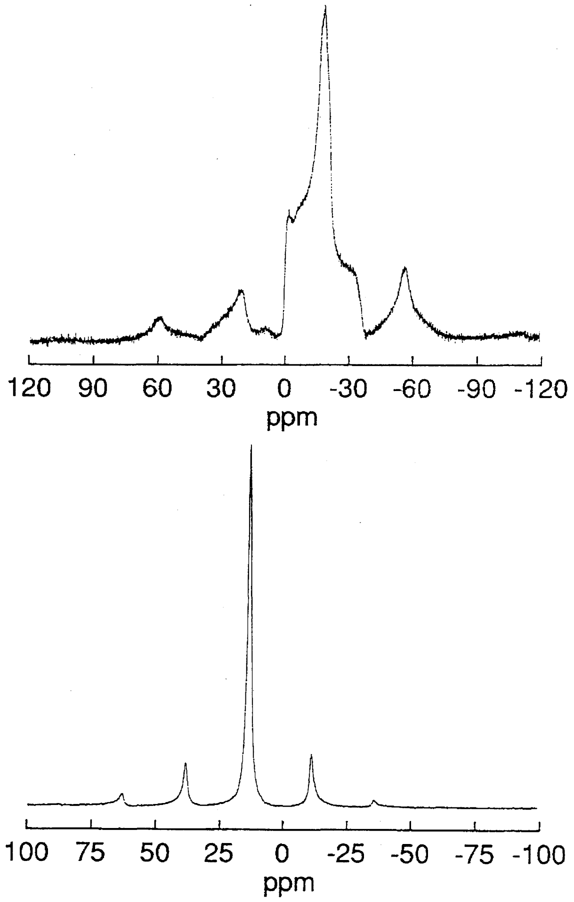

Fig. 3. ^{27}Al (top) and ^{31}P (bottom) MAS-NMR of as-synthesized AlMepO-ζ.

connected to another metal atom via phosphonates. On the contrary, an oxovanadium compound VO(O$_3$PC$_6$H$_5$)·H$_2$O has –V=O–V– chains in the sheet structure.[13] The sheet structure of AlMepO-ζ is topologically the same as this compound. However, a –V=O–V– chain in VO(O$_3$PC$_6$H$_5$)·H$_2$O contains a long V–O bond and a short V=O bond, while the length of a Al–O bond is the same in a –Al–(OH)–Al– chain of AlMepO-ζ. Furthermore, VO(O$_3$PC$_6$H$_5$)·H$_2$O crystallizes in a higher symmetry space group, $C2/c$, than $P2_1/c$ of AlMepO-ζ.

Characterization. Figure 3 shows ^{27}Al and ^{31}P MAS-NMR of the as-synthesized sample. The ^{27}Al MAS-NMR gives broad peak at $\delta = -18.5$ with an irregular and asymmetrical line shape owing to quadrupole effects. The peak position is reasonable for an octahedral aluminum compared with that of AlMepO-α ($\delta = -21.3$) and $-\beta$ ($\delta = -17.5$).[24] However, the octahedral aluminum sites of both AlMepO-α and -β give a symmetrical peak. The fact that Al–O3 bond is longer than the other Al–O bonds in AlMepO-ζ makes a distorted aluminate octahedron to cause an asymmetrical line shape. The ^{31}P MAS-NMR gives a signal at $\delta = 13.6$. For AlMepO-α and -β, the ^{31}P chemical shift ranges from $\delta = 0$ to 15.[24] Using this data, a rational assignment was made based on an assumed linear correlation between the ^{31}P chemical shifts and the mean Al–O–P angles.[24] According to the assignment, the phosphorus center with the smaller mean Al–O– P angle gives the ^{31}P signal at the lower magnetic field. The calculated mean Al–O–P angle for the phosphorus site of AlMepO-ζ [138.11(3)°] is as small as the smallest mean angles observed for AlMepO-β [min. 140.3(4)° and max. 151.3 (5)°]. The ^{13}C CP/MAS-NMR gave a doublet at $\delta = 13.8$ (^1J(C,P) = 160 Hz). Although AlMepO-α and -β gave complicated patterns around 12—16 ppm owing to influence from adjacent different phosphorus centers,[24] AlMepO-ζ gives a simple pattern because it contains only one independent phosphorus site. Compared with neat methylphosphonic acid ($\delta = 11.3$, ^1J(C,P) = 140 Hz) the peak position and the coupling constant are reasonable.

Figure 4 shows TG-DTA under dry air and nitrogen. Both DTA curves give two endothermic peaks at 326 and 393 °C accompanied by weight loss of ca. 13.2 and 3.7 %, respectively. From the comparison with the calculated weight loss on dehydration of the coordinated water (11.5%) and hydro-

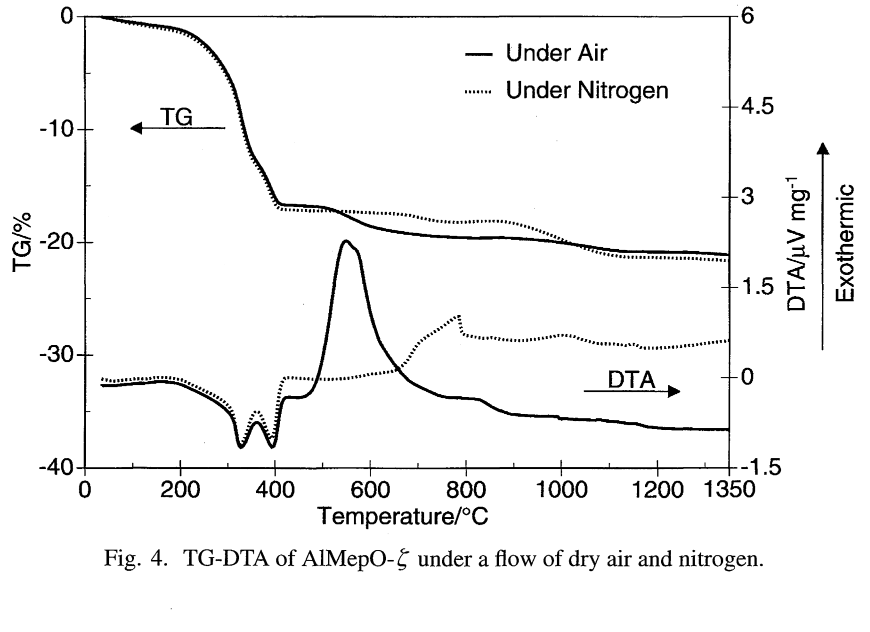

Fig. 4. TG-DTA of AlMepO-ζ under a flow of dry air and nitrogen.

xo group (5.8%), it is obvious that the coordinated water desorbs at 326 °C, followed by dehydration from the hydroxo groups at 393°C. The intense exothermic peak at 547 °C under air is attributed to the decomposition of the methyl parts and methylphosphonate is oxidized to phosphate ($AlPO_4$ tridymite) above the temperature. Under nitrogen the weight decreases gradually from 600 to 1100 °C and no clear DTA peaks appear because the methyl groups are not oxidized but carbonized. The product at 1350°C under nitrogen was also $AlPO_4$ tridymite of a poor crystallinity. This TG-DTA result suggests that the decomposition of AlMepO-ζ structure proceeds via an intermediate with 5-coordinate aluminum by elimination of the coordinated water molecule. A sample heated at 400 °C for 2 h in vacuo gave two broad peaks at $\delta = 16.0$ and 39.7 assigned to 5- and 4-coordinate aluminum in ^{27}Al MAS-NMR. A single peak at $\delta = 38.4$, which is attribute to 4-coordinate aluminum of $AlPO_4$, was observed for the sample treated at 600 °C. These results support the proposed decomposition mechanism.

The organophosphonate of many transition metals like Cd, Co, Cu, and Zn intercalates amine[6,8,25] and the oxovanadium compound intercalates alcohol.[13,26] For the isostructural $VO(O_3PC_6H_5)\cdot H_2O$ intercalation of hexanol under a reflux condition was reported.[13] These reactions proceed by coordination of guest molecules to the metal instead of the occupied water. We have tried intercalation of alcohol, amine, and hydrocarbon into AlMepO-ζ at ambient temperature and at elevated temperatures up to 200°C. Evacuation of the sample up to 400°C prior to the exposure to the guest species was also tried. So far no indication of intercalation have been observed by XRD under any conditions we tried. Such inability of intercalation in AlMepO-ζ is derived not from its structure but from the coordination property of aluminum. For AlMepO-ζ water–aluminum interaction is probably strong enough to prevent the substitution by the guest molecules.

Conclusions

The first layered phase of aluminum methylphosphonate, $Al(OH)(O_3PCH_3)\cdot H_2O$, [27] designated AlMepO-ζ, was obtained in a hydrothermal reaction. The crystal structure of the trivalent aluminum methylphosphonates proved to be different from the typical divalent or tetravalent metal compounds. The sheet structure contains unidimensional chains of aluminum via hydroxo bridges.

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27) During preparation of this article we were led to know that researchers at St. Andrews, UK were publishing the same crystal structure (V. J. Carter and P. A. Wright, personal communication, L.-J. Sawer, V. J. Carter, A. R. Armstrong, P. A. Wright, and B. E. Gore, *J. Chem. Soc., Dalton Trans.*, in press), which makes us urge the publication of the present results. Their preparation procedure is, however, different from ours and they solved the crystal structure by the Rietveld method using laboratory X-ray powder diffraction data because they obtained polycrystalline samples.