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Synthesis and Characterization of A Novel Layered Aluminophosphate of Kanemite-like Structure

Soofin Cheng,* Jeng-Ning Tzeng, and Bo-Ya Hsu

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, R.O.C.

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The synthesis and structural characterization of a novel layered aluminophosphate (named AlPO-ntu) with a structure mimicking to that of the naturally occurring silicate mineral kanemite are described. This new compound was synthesized using the hydrothermal method and *n*-alkylamines as templates. On the basis of the results of thermal and elemental analysis, the chemical formulas were determined to be $AlPO_3(OH)_2[NH_2(CH_2)_xCH_3]$ ($x = 3$, 5, and 7) for templates of butyl-, hexyl-, and octylamines, respectively. Solid-state ^{27}Al and ^{31}P MAS NMR spectra showed that both elements were in tetrahedral coordination. FT-IR spectra and ion-exchange studies revealed that three of the tetrahedra oxygen are bridging between Al and P atoms. The fourth oxygen, pointing away from the aluminophosphate sheet, bears either a proton when adhering to aluminum or an alkylammonium ion when adhering to phosphorus. The alkylammonium ions are ready for ion-exchange, while the protons attached to the Al−O terminals are not exchangeable with alkaline ions. Similar to kanemite of single-layered structure, the aluminophosphate layers are able to reorganize and condense to form porous materials when the interlayer alkylammonium ions are exchanged by surfactant cations.

Introduction

The discovery of a series of microporous aluminophosphates by Wilson et al.[1,2] in 1982 opened up the new possibility in designing new materials for sorption and catalysis. By varying the templates and the synthesis conditions, aluminophophates of profoundly different porous structures have been prepared. Some of them are structurally the same as naturally occurring or synthetic aluminosilicate zeolites, e.g., AlPO-17 is an isostructural analogue to erionite, AlPO-20 to sodalite, and AlPO-34 to chabazite; however, many are new structures. Typically, the structure of these AlPO-based molecular sieves can be related to three-dimensional networks in which alternating AlO_4 and PO_4 tetrahedra are interconnected via oxygen atoms. The empirical formulas of these aluminophosphate compounds without considering the neutral template species trapped in the pores are $AlPO_4$, which is isoelectronic to SiO_2. The frameworks of aluminophosphate molecular sieves therefore are electroneutral and the compounds basically have no ion-exchange capacity. In the context of catalysis, negative charges have been introduced into the network by replacing a portion of phosphorus or aluminum in the framework by silicon or other cations of lower oxidation states.[3−5] As a result, the possibility of ion exchange is created and the positive counterions present in the extraframework which balance the charges can provide acid−base functions.

Although the three-dimensional framework aluminophosphates have received most of the attention, in recent years several structures of one- and two-dimensionally extended aluminophosphate solids have also been reported.[6−17] Different from the three-dimensional framework aluminophosphates, which have essentially atomic P/Al ratios of 1, most of the one- and two-dimensionally extended aluminophosphates reported up to date have the atomic P/Al ratios greater than 1. Although the variation of the sheet structures in layered aluminophosphates is as vivid as that in three-dimensional framework, to the best of our knowledge, none of them is isostructural to naturally occurring or synthetic layered silicates. The present paper is concerned with a novel layered aluminophosphate, named AlPO-ntu, in which both aluminum and phosphorus are tetrahedrally coordinated with the atomic P/Al ratio of 1 and the sheet structure mimicked to

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* Corresponding author.

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naturally occurring kenamite mineral. Kanemite has an idealized formula of $NaHSi_2O_5 \cdot 3H_2O$. The discovery of this alkali silicate mineral at Kanem, Lake Chad, was described by Johan and Maglione.[18] Later, various methods for the synthesis of kanemite were described by Beneke and Lagaly.[19] They also showed that kanemite has a layered structure, and the interlayer cations can be exchanged with a variety of organic cations. In the past few years, increasing attention has been received by kenamite because this layered silicate can either be used as starting material for preparing microporous materials through pillaring with silica[20] or transform to ordered mesoporous three-dimensional framework in the presence of alkyltrimethylammonium ions.[21−24] The novel layered aluminophosphate prepared in this paper has the sheet structure and ion-exchange properties very similar to kanemite. Its synthesis and chemical properties were examined.

Experimental Section

Synthesis of Layered Aluminophosphates. The mentioned compounds were synthesized based on the substrate composition of Al_2O_3:P_2O_5:(1.7−2.0)*n*-alkylamine:(25−70)H_2O. To an aqueous suspension of pseudoboehmite powder (Vista, Catapal A, 73.5% Al_2O_3), orthophosphoric acid (Janssen, 85%) and water were added dropwise, followed by vigorous stirring for 2 h. After the addition of *n*-alkylamine, either *n*-butyl, *n*-hexyl-, or *n*-octylamines (Janssen, reagent grade), the mixture was stirred for another 2 h or longer before it was loaded into Teflon-lined stainless steel autoclaves and heated at 180−200 °C for 48−72 h. The resultant crystallites were washed with deionized water thoroughly and dried at 50 °C.

Characterization Techniques. The Al and P compositions of the resultant samples were analyzed with ICP-AES (Allied Analytical System, Jarrell-Ash, Model IC AP 9000) using HCl-dissolved solutions. The C, H, and N compositions were analyzed with a Perkin-Elmer 2500 elemental analysis system. TGA was performed in N_2 environment on a duPont 951 thermogravimetric analyzer. The powder XRD patterns were recorded with a Philips PW 1840 automated powder diffractometer, using Ni-filtered Cu Kα radiation. The SEM photographs were taken using a Hitachi S-2400 scanning electron microscopy. Both transmission and diffuse reflectance FT-IR spectra were taken with a Bomem MB 100 FTIR spectrometer. Solid-state ^{27}Al MAS NMR spectra were taken with a Bruker MSL-500 spectrometer at a frequency of 130.32 MHz, rotation speed of 5 kHz, pulse length of 3.0 ms, recycling delay time of 1 s, and a 1 M $AlCl_3$ solution was used as external reference. Solid-state ^{31}P MAS NMR spectra were taken with a DMX-300 spectrometer at a frequency of 121.49 MHz, rotation speed of 5 kHz, pulse length of 7.0 ms, recycling delay time of 30 s, and a 85% H_3PO_4 solution was used as external reference.

Results and Discussion

Structure Characterization. Figure 1 shows the X-ray powder diffraction patterns of the as-synthesized AlPO-ntu using *n*-alkylamines of different carbon chain lengths as templates. All three patterns predominantly consist of a series of peaks which have *d* spacings of the type d_{00l}/l, where l is an integer, and that is a strong indication of the occurrence of lamellar structures. The *d* spacings of the diffraction peaks at lowest 2θ vary from 19, 23, to 27 Å with the carbon chain length increasing from butyl-, hexyl-, to octylamine, respectively. When plotting these *d* spacings versus number of carbon atoms in *n*-alkylamines, a straight line with a gradient of 2.1 Å/carbon atom was obtained. Since alkyl chains grow by ca. 1.27 Å per added carbon, the gradient suggests that the *n*-alkylamines form bilayers between the aluminophosphate sheets.

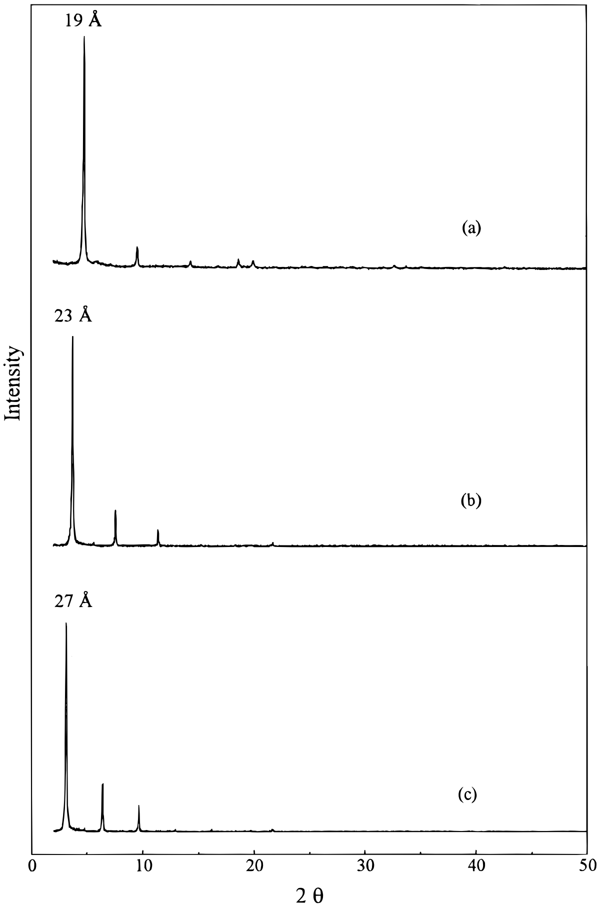

Figure 1. XRD patterns of as-synthesized AlPO-ntu with (a) *n*-butylamine, (b) *n*-hexylamine, and (c) octylamine as template.

The crystallites of as-synthesized AlPO-ntu have the shape of an oval platelet and their sizes ranged from ca. 0.5 to 10 μm, as observed by SEM. The platelet shapes are commonly observed on compounds of layered structures. That also explains the preferred orientation of (00*l*) planes in the XRD patterns.

Figure 2A,B show the ^{27}Al and ^{31}P MAS NMR spectra, respectively, of the as-synthesized AlPO-ntu. The spectra of the samples prepared with different *n*-alkylamines are all very similar and simple. Only one peak appears at 40 ppm in ^{27}Al MAS NMR spectra, and only one at −3.8 ppm in ^{31}P MAS NMR spectra. The chemical shift of ^{27}Al MAS NMR spectra is close to those of three-dimensional network aluminophosphates, in which tetrahedral coordinated Al appears at ca. 32−36 ppm.[25,26] Hence, the single peak at 40 ppm indicates that all Al atoms in the as-synthesized AlPO-ntu

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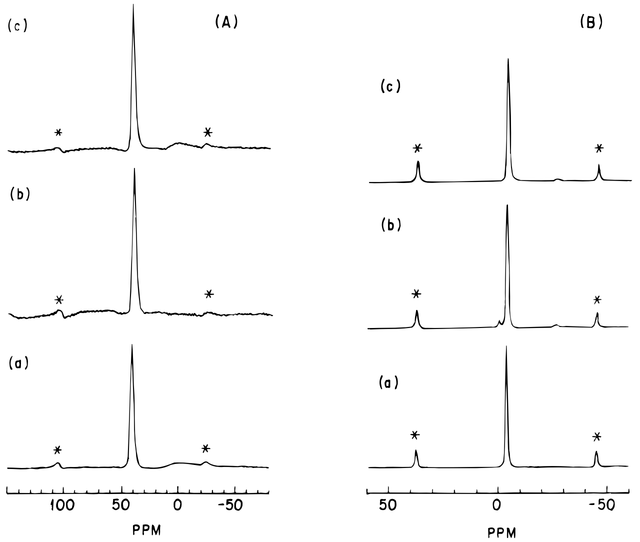

Figure 2. Solid-state (A) ^{27}Al and (B) ^{31}P MAS NMR spectra of as-synthesized AlPO-ntu with (a) *n*-butylamine, (b) *n*-hexylamine, and (c) octylamine as template. The peaks with asterisks are spin sidebands.

samples are in the same tetrahedral coordination environment. But, the chemical shift of -3.8 ppm in ^{31}P MAS NMR spectra is very different from those observed on three-dimensional network aluminophosphates, where P usually appears at -15 to -33 ppm.[25,26] Nevertheless, the single peak also implies that all P atoms in the as-synthesized samples are in the same coordination environment.

The AlPO-ntu samples prepared with different *n*-alkylamines also show very similar infrared spectra (Figure 3A). Absorptions below 1400 cm^{-1} are attributed to the lattice vibration of aluminophosphates, and an enlargement of this portion is shown in Figure 3B. Peaks at 950−1250 and 600−900 cm^{-1} regions correspond to the asymmetric and symmetric stretching vibrations, respectively, of TO_4 ($T = Al$ or P) tetrahedra. Peaks at 400−500 cm^{-1} are due to O−T−O bending, and the peak at ca. 735 cm^{-1} is a combination of Al−O and P−O vibrations.[27,28] However, it is noticeable that two strong absorptions appeared at 880 and 907 cm^{-1} for the layered AlPO-ntu were not observed in the spectra of aluminophosphates of three-dimensional framework.[28,29] The alkyl groups of amines give strong absorptions in the regions 2850−3000 and 1400−1600 cm^{-1}, which correspond to C−H stretching and bending vibrations, respectively. Nevertheless, the appearance of the broad ammonium band overlapping over νCH band at ca. 3100 cm^{-1} [30] implies that the *n*-alkylamines are present in the interlayer as alkylammonium ions instead of neutral molecules. On the other hand, a strong sharp absorption at 3580 cm^{-1} is apparently attributed to free O−H groups, which were not reported on aluminophosphates of three-dimensional framework either. The AlO−H stretching absorptions were reported to appear in the range ca. 3374−3620 cm^{-1}, depending on the coordination environment around Al,[31,32] but free PO−H stretching usually appears at ca. 3675 cm^{-1}.[28,29] Hence, the sharp peak at 3580 cm^{-1} is assigned to terminal AlO−H stretching.

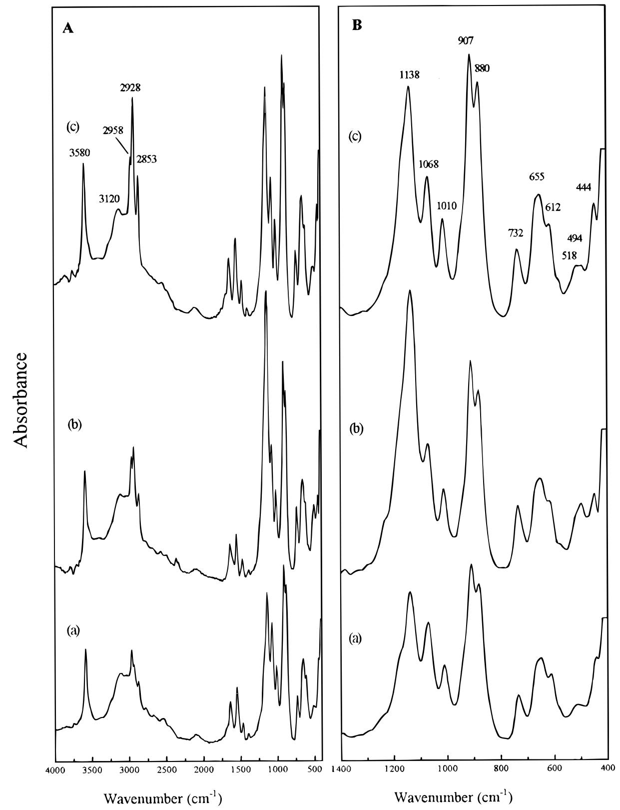

Figure 3. FT-IR spectra of as-synthesized AlPO-ntu with (a) *n*-butylamine, (b) *n*-hexylamine, and (c) octylamine as template.

The TGA profiles of the as-synthesized AlPO-ntu compounds show obvious weight losses started at ca. 200 °C (Figure 4). The weight losses as a function of temperature are tabulated in Table 1. Because the amount of weight losses around 200−300 °C is proportional to the carbon chain length of alkylamines, it is attributed mainly to the decomposition of interlayer alkylammonium ions. Consistently, the XRD study on the quenched samples showed that the structure of as-synthesized AlPO-ntu was retained after heating the samples at 200 °C, and it became amorphous after heating above 300 °C. The slight weight losses at temperatures lower than 120 °C are considered due to the release of physically adsorbed water molecules since the amount is proportional to the hydrophilicity of the alkylamines. On the other hand, the extending weight losses at temperatures higher than 320 °C are probably a result of slow desorption of decomposed carbon residues.

Figure 5 is the ^{27}Al and ^{31}P solid-state NMR spectra of AlPO-ntu, prepared with butylamine as template, after heating the sample at various temperatures. Only one peak centered at 40 ppm was seen in the ^{27}Al NMR spectra, and the peak became broader after the samples were calcined at higher temperatures. Little informa-

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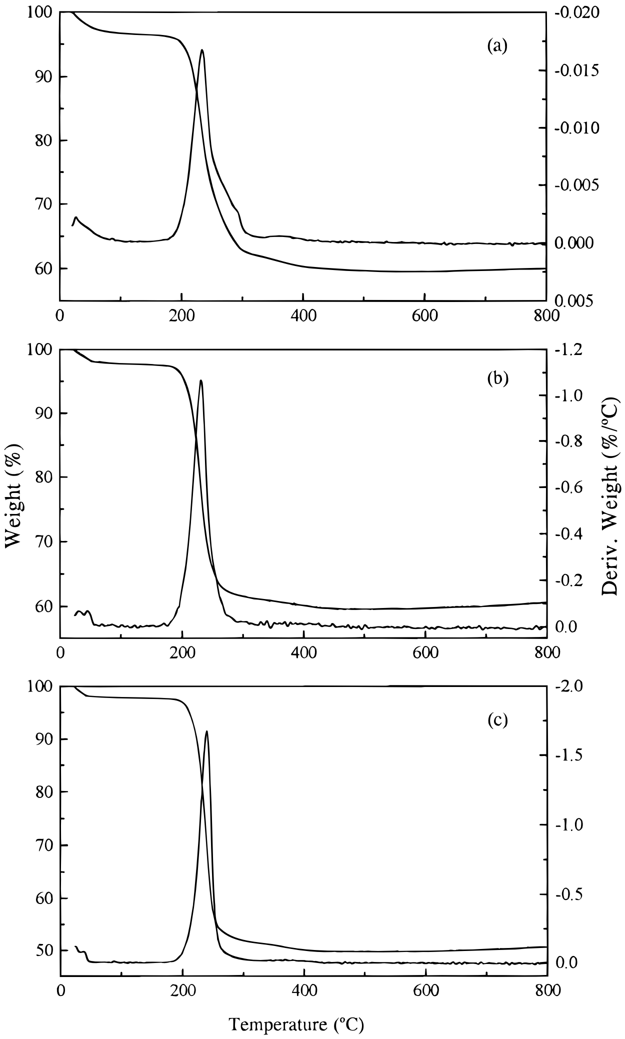

Figure 4. TGA profiles of as-synthesized AlPO-ntu with (a) *n*-butylamine, (b) *n*-hexylamine, and (c) octylamine as template.

Table 1. TGA Data of Layered Aluminophosphates under Nitrogen Atmosphere

sample	temp range (°C)	wt loss (%)	total wt loss (%)
AlPO-ntu-4[a]	25−128	2.4	37.7
	194−318	33.0	
	318−800	2.3	
AlPO-ntu-6	25−124	2.2	41.4
	206−323	37.2	
	323−800	2.0	
AlPO-ntu-8	25−105	1.2	50.7
	214−337	46.3	
	337−800	3.2	

[a] The carbon numbers of *n*-alkylamines used as template.

tion can be drawn from the spectra due to the strong quadrupolar interaction between ^{27}Al nuclei of $I = {}^{5}/_{2}$, except confirming that the Al atoms remain in tetrahedral coordination. In contrast, there is an obvious shift from −3.6 to −26.4 ppm and broadening of the peak in the ^{31}P NMR spectra after AlPO-ntu was heated at temperatures above 300 °C. Since the ^{31}P NMR signals of aluminophosphate of three-dimensional framework usually appear at −19 to −30 ppm,[26] these results indicate that the layered structure of AlPO-ntu is destroyed and the compound transforms to a three-dimensional network after interlayer amine species have been removed through heating. The resultant compound was found to be X-ray amorphous, which was also reflected by the broadness of the peaks in the NMR spectra. Hence, the crystal nature of this condensed phase could not be resolved. Nevertheless, the shift of the ^{31}P NMR peak from −3.6 to −26.4 ppm, which is where aluminophosphates of three-dimensional framework usually appear, implies that the condensation is probably through the formation of Al−O−P linkage between the sheets. Another remark about the ^{31}P NMR is that the −3.6 ppm peak observed on the layered structures may be assigned to the "Q_3" phosphorus or the $^{-}OP(OAl)_3$ unit with a terminal P−O group, in contrast to that at −26.4 ppm for the "Q_4" phosphorus or the $P(OAl)_4$ unit.

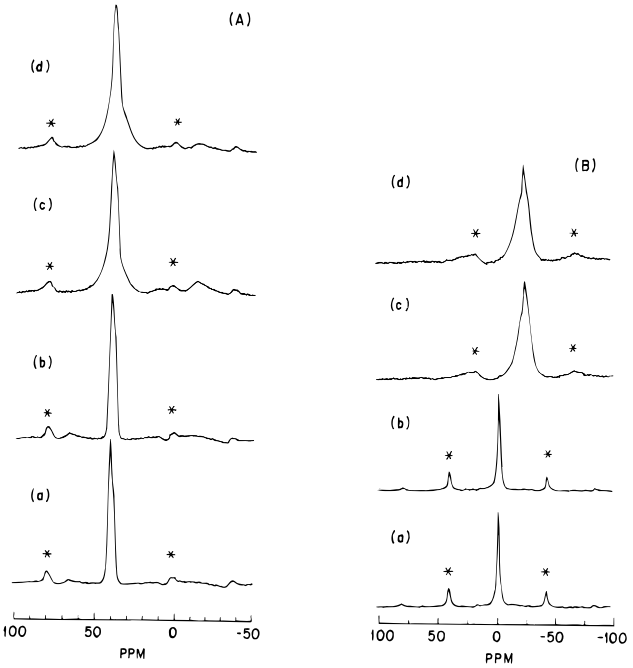

Figure 5. Solid-state (A) ^{27}Al and (B) ^{31}P MAS NMR spectra of AlPO-ntu-4 (a) as-synthesized, and after calcination at (b) 200, (c) 400, and (d) 600 °C. The peaks with asterisks are spin sidebands.

The chemical compositions of the as-synthesized AlPO-ntu were determined with ICP-AES and C, H, N analyzer. On the basis of the analytical data (Table 2), the empirical formulas are in the form $AlPO_3(OH)_2[NH_2(CH_2)_nCH_3]$, where $n = 3$, 5 or 7 for butyl-, hexyl-, and octylamines, respectively. It is noticeable that the atomic ratios of Al:P:N are all around 1:1:1. Since NMR spectra show that both Al and P are in tetrahedral coordination and the IR study indicates the presence of alkylammonium ions as well as free AlO−H groups, the chemical formulas are better stated as $Al(OH)P[O^{-}\ {}^{+}NH_3(CH_2)_nCH_3]O_3$. In other words, the interlayer alkylamines are forming alkylammonium ions and attached to the terminal P−O groups. This is reasonable in considering that the protons in P−OH groups are more acidic than those in Al−OH. As a result, the P−OH groups were not seen. Instead, the neutralized product of alkylammonium ions are formed and attached to the P−O^{-} terminals through electrostatic interaction.

Ion-Exchange Properties. The interlayer alkylammonium ions were further confirmed by ion-exchange with alkali ions. A 0.3 g portion of the AlPO-ntu compounds was stirred with 50 mL of 1 M NaCl or KCl solution for 3 days, followed by washing with 95%

Table 2. Elemental Analysis Results of As-Synthesized Layer Aluminophosphates

sample		P	Al	C	H	N	O	assigned formula
AlPO-ntu-4	wt ratio	1.51	1.26	2.19	0.57	0.62	4.34	
	molar ratio	1.09	1.05	4.11	12.9	1	5.10	$AlPO_3(OH)_2(NH_2C_4H_9)$
AlPO-ntu-6	wt ratio	1.02	0.98	2.36	0.54	0.45	3.83	
	molar ratio	1.03	1.03	6.15	16.9	1	5.50	$AlPO_3(OH)_2(NH_2C_6H_{13})$
AlPO-ntu-8	wt ratio	1.21	1.06	3.29	0.73	0.47	3.35	
	molar ratio	1.16	1.17	8.16	21.6	1	5.22	$AlPO_3(OH)_2(NH_2C_8H_{17})$

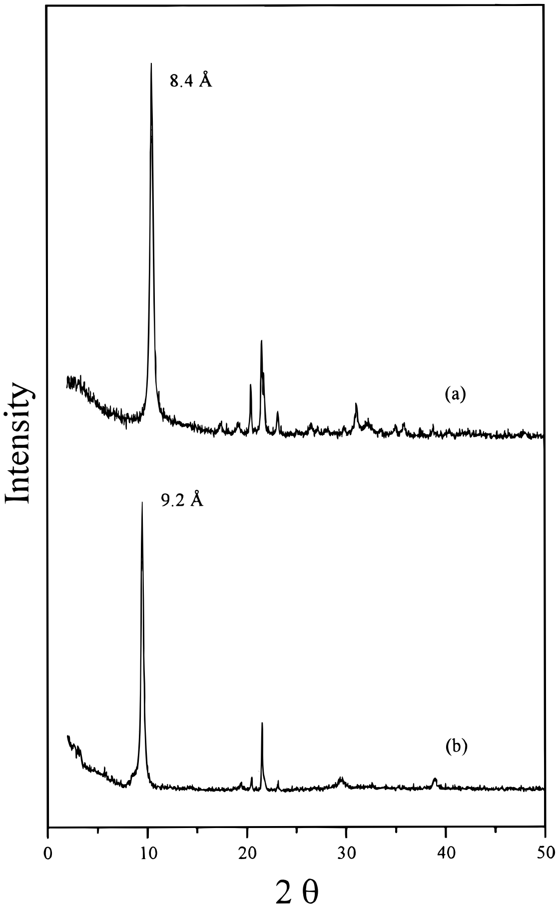

Figure 6. XRD patterns of (a) Na^+- and (b) K^+-exchanged AlPO-ntu.

alcohol and drying at 50 °C. Figure 6 shows that the *d* spacings shrink to 8.4 and 9.2 Å, respectively, for Na^+- and K^+-exchanged products, and these changes are independent of the amines originally incorporated in AlPO-ntu. By subtracting the diameters of Na^+ and K^+ ions (2.0 and 2.7 Å, respectively) from the *d* spacings, a layer thickness of ca. 6.4 Å is obtained. The strongest lines of the X-ray powder pattern of Na–AlPO-ntu are 8.4 (10), 4.36 (3), 4.14 (4), 3.86 (2), and 3.00 (1) Å. Again, the preferred orientation of the (00*l*) planes, which likely correspond to peaks at 8.4 and 4.14 Å, was observed on the pattern. The interlayer distance of 8.4 Å is smaller than 10.3 Å reported for kanemite with 2–3 hydrated waters per formula. However, that of the dehydrated kanemite can shrink to 7.73–6.35 Å.[18] Hence, the interlayer distances obtained for Na^+- and K^+-exchanged AlPO-ntu are in the reasonable range as those for monophyllosilicates made of single tetrahedra layer.

Elemental analysis of the Na^+-exchanged AlPO-ntu shows the atomic ratio of Al:P:Na:N to be around 1.00: 0.91:0.89:0.05, confirming that most of the interlayer alkylammonium ions have been exchanged by Na^+ ions. The resultant compound has a chemical formula close to $NaHAlPO_5 \cdot xH_2O$, which is mimicked to that of kanemite, idealized $NaHSi_2O_5 \cdot 3H_2O$.

Structure of AlPO-ntu Layer. Although the crystal structure of kanemite has not been determined, results from ^{29}Si MAS NMR spectra and X-ray diffractographs indicate it to be a thin layered polysilicate.[33] Each layer of kanemite is made of a single sheet of SiO_4 tetrahedra and all the Si atoms are confirmed by the ^{29}Si NMR spectra to be in Q_3 $(Na,H)OSi(OSi)_3$ environment. Most of the silicates with layer structures are formed of six-membered rings of tetrahedra, and only in very rare examples are based on alternative four- and eight-membered rings of tetrahedra.[34] In the known structures of a potassium hydrogen silicate ($KHSi_2O_5$) and the silicic acid ($H_2Si_2O_5$), each silicon atom shares three oxygen atoms with other Si atoms to form six-Si-atom rings and extend indefinitely in two dimensions.[35] Different from the silicate structure in talc, which has unshared oxygens pointed in the same direction, the single-sheet silicate has them pointed toward both sides of sheet. There are two ways to arrange the Si atoms. When the six Si atoms in a ring are arranged in the chair form, the unshared oxygens are pointing alternatively up and down the sheet. When the rings are in boat form, the unshared oxygens are pointing toward different directions in pair. Because both $KHSi_2O_5$ and $H_2Si_2O_5$ have the latter structure, Apperley et al.[33] boldly proposed the structure of the kanemite sheet to be similar.

Because solid-state NMR results show both Al and P are in a single coordination environment, the lamellar structure of AlPO-ntu is likely similar to that of kanemite or $KHSi_2O_5$. Al and P shall arrange alternatively in the sheet formed of six-membered rings of tetrahedra, and each ring consists of three Al and three P atoms. The schematic representation of the proposed structure is shown in Figure 7. In which, the six-T-member rings are in boat form and the unshared oxygen atoms in pairs, bonded to adjacent Al and P, point toward different sides alternatively. If the rings are in chair form, the unshared oxygens bonded to Al will point toward one side and those bonded to P toward the other side. In such an arrangement, either the alkylammonium ions adhered to P–O terminals could no longer form bilayers in the as-synthesized AlPO-ntu, or the Al–OH terminals from adjacent two aluminophosphate sheets would face each other and result in a thick sheet more than twice the thickness of a single sheet. These are conflicted from what has been observed. Therefore, the lamellar structure of AlPO-ntu is most likely similar to that of kanemite or $KHSi_2O_5$. The other possibility that the AlPO-ntu sheet is formed of alternative four-

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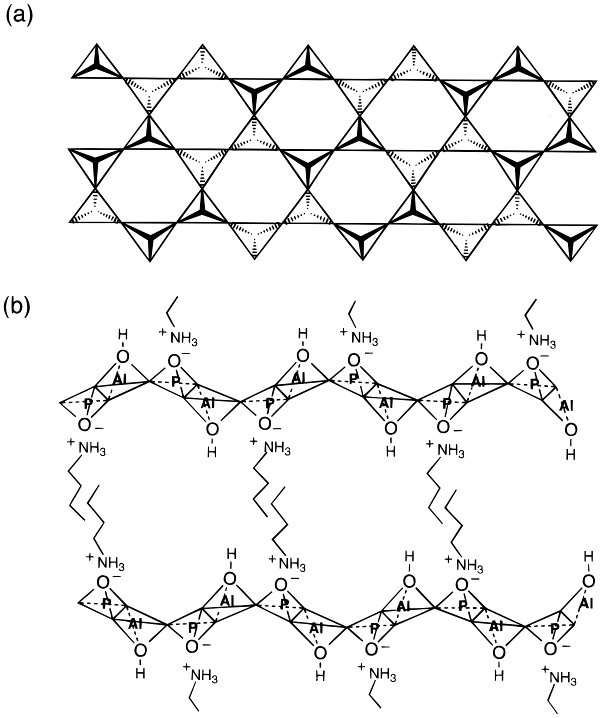

Figure 7. Schematic representation of (a) the layer projection of six-T-member ring and (b) the layer stacking in APO-ntu with butylamine in the interlayer.

and eight-membered rings of tetrahedra is also ruled out. In the known silicate examples, which are rare and the layers are held together by divalent cations, the vertexes of the tetrahedra in four-membered rings always point to the same side of the sheet.[34] To form bilayers of alkylammonium ions, the vertexes of the tetrahedra in alternate four-rings have to point to opposite sides of the layer. In such an arrangement, either the P−O terminals pointing in the same side of a sheet will distribute nonhomogeneously, and the resulting alkylammonium bilayer structure is not thermodynamically stable, or the eight-member rings have to fold into cubic shape and a thick layer of two fused tetrahedra thickness is resulted.

Properties of Na$^+$-Exchanged AlPO-ntu. Na$^+$-exchanged AlPO-ntu shows better thermal stability than the alkylammonium precursors. The X-ray diffractographs demonstrate that although the crystallinity decreases with calcination temperature, the layered structure is well retained up to 300 °C (Figure 8). At 400 °C, most of the characteristic peaks of Na−AlPO-ntu nearly disappears, and at 600 °C, the compound was transformed to another crystalline structure with characteristic diffraction pattern similar to that of $Na_4Al_5H_8(PO_4)_9 \cdot 10H_2O$.[36] The phase transformation as a function of temperature is also confirmed with in situ diffuse reflectance FT-IR spectroscopy. Figure 9 shows that the absorptions in aluminophosphate lattice vibration region have only little changes after the alkylammonium ions in AlPO-ntu were replaced by Na$^+$ ions. The splitting of the 1138 cm^{-1} peak into two at 1131 and 1191 cm^{-1} is probably a result of variation in Al−O−P angle.[37] The same reason shall account for the merging of the two peaks at 880 and 907 cm^{-1} into one broad peak at 903 cm^{-1}. These peaks became diffused and all merged into a broad band when the compound was calcined at 400 °C. At this temperature, an amorphous phase was observed with XRD. After calcination at 600

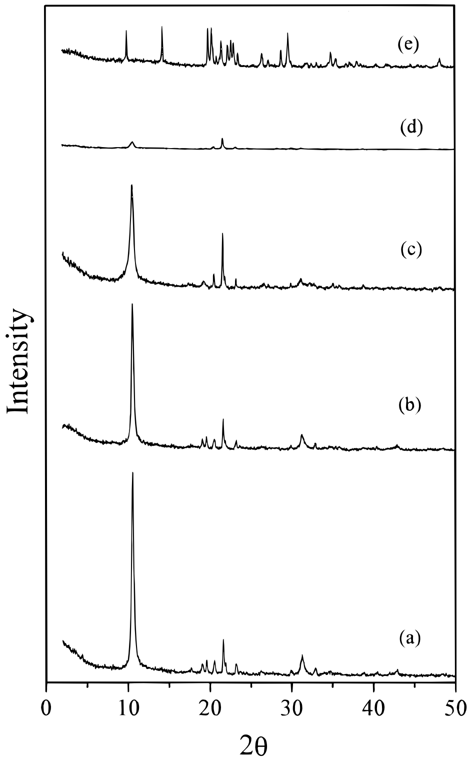

Figure 8. XRD patterns of Na$^+$-exchanged AlPO-ntu (a) at room temperature and after calcination at (b) 200, (c) 300, (d) 400, and (e) 600 °C.

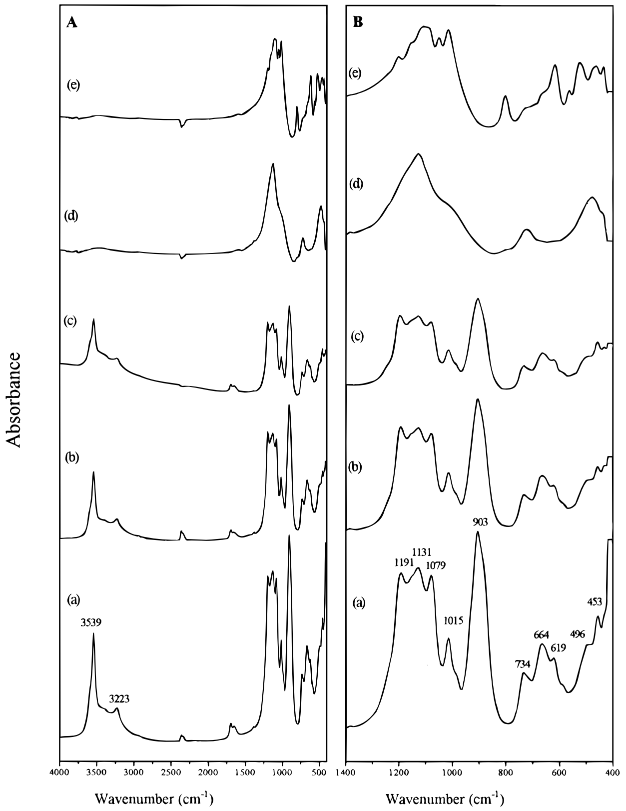

Figure 9. In situ diffused reflectance FT-IR spectra of Na$^+$-exchanged AlPO-ntu (a) at room temperature and after calcination at (b) 200, (c) 300, (d) 400, and (e) 600 °C.

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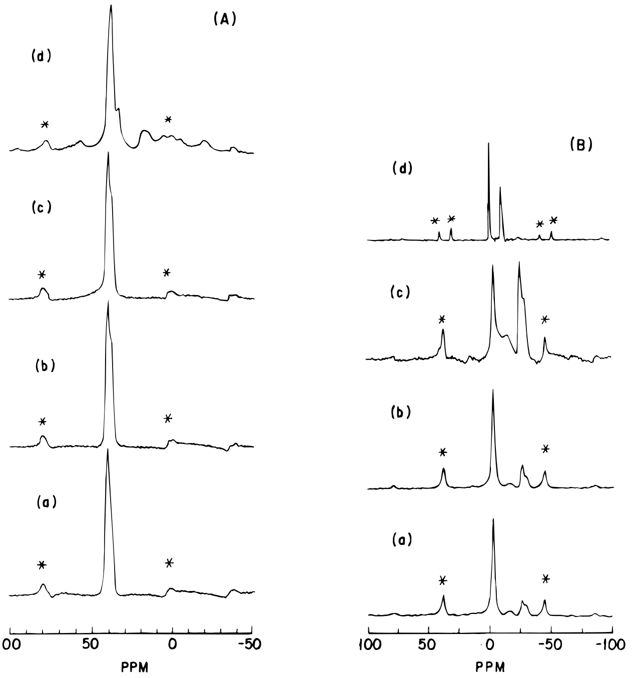

Figure 10. Solid-state (A) ^{27}Al and (B) ^{31}P MAS NMR spectra of Na$^+$-exchanged AlPO-ntu (a) at room temperature, and after calcination at (b) 200, (c) 400, and (d) 600 °C. The peaks with asterisks are spin sidebands.

°C, some sharp peaks appear again in the IR spectrum, as XRD confirms the formation of new crystalline phase. With the exchange of alkylammonium ions by Na$^+$ ions, the ammonium band at ca. 3100 cm^{-1} as well as the absorptions of C−H stretching and bending disappear. However, the strong sharp absorption of free AlO−H stretching still remains except a slight shift from 3580 to 3540 cm^{-1}, up to a calcination temperature of 400 °C. The shift is proposed due to that the AlO−H group may form hydrogen bond to adjacent alkylammonium ion through oxygen in the as-synthesized AlPO-ntu, while this H bond is no longer present when the alkylammonium ion is replaced by Na$^+$. These results along with that of elemental analysis imply that the protons adhered to Al−O terminals are not exchangeable with alkali ions. Besides, the IR studies also show that the dehydroxylation of these AlO−H groups in Na−AlPO-ntu is completed at around 400 °C.

The structural changes of AlPO-ntu after Na$^+$-ion exchange and through heat treatment are well revealed in the ^{31}P NMR spectra, while the ^{27}Al NMR spectra demonstrate that all Al atoms remain tetrahedrally coordinated (Figure 10). Na$^+$-exchanged AlPO-ntu gives mainly a strong signal at −4.5 ppm in the ^{31}P NMR spectra, in addition to two small peaks at −25.0 and −29.4 ppm. The main peak corresponds to phosphorus in Q_3 environment. The results confirm that the sheet structure is retained after Na$^+$-exchange. The slight upfield shift from −3.6 to −4.5 ppm is probably due to the stronger polarizability of Na$^+$ ion in comparison to that of alkylammonium ion. On the other hand, the two small peaks at −25.0 and −29.4 ppm shall correspond to phosphorus in Q_4 environments. The presence of these peaks implies that a small portion of the sheet structures probably forms cross-link during Na$^+$ ion-exchange reaction. The ease in interlayer linkage is common to thin-layer compounds, such as kanemite, due to the high flexibility of the sheet. These two Q_4 peaks grow strongly after the compound turns amorphous at 400 °C. At 600 °C, they diminish and another two sharp peaks appear at −3.0 and −11.8 ppm accompanied with the formation of a new crystalline phase.

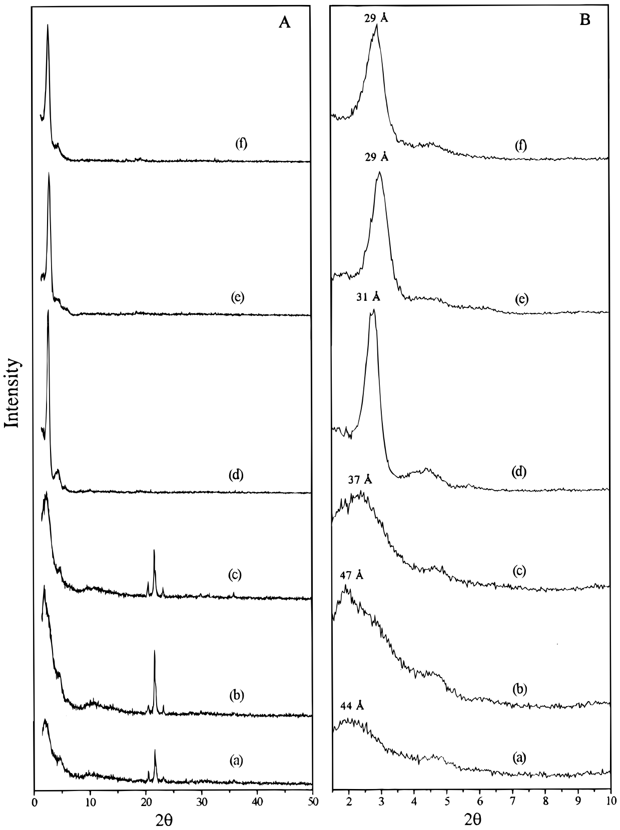

Figure 11. XRD patterns of AlPO-ntu after exchange with C_{16}TMA for various time periods: (a) 6, (b) 12, (c) 18, (d) 20, (e) 30, and (f) 40 h.

Condensation of AlPO-ntu Layers in Solution of Organic Surfactant. The condensation behavior of AlPO-ntu in hexadecyltrimethylammonium chloride (C_{16}TMACl) solution was compared to that of kanemite. A portion of *n*-BuNH$_3$−AlPO-ntu was added to a 0.1 M C_{16}TMACl solution in 1:150 weight ratio. The suspension was stirred at 80 °C for various periods of time. Figure 11 shows that the *d* spacing corresponding to the lowest diffraction angle expands to ca. 44 Å after 6 days. The distance increases further to 47 Å after 12 days, then shrinks with time until a constant value of 29 Å in 30 days. The variation of *d* spacings and results of elemental analysis of the materials are tabulated in Table 3. The 47 Å *d* spacing was also reported for organic-kanemite materials prepared with C_{16}TMA.[21,23] This peak is therefore assigned to AlPO-ntu containing C_{16}TMA cations in the interlayer, which form a bilayer structure. Table 3 shows that the P/Al molar ratios in the samples remain close to one through the exchange period, while the N/P molar ratio reaches a maximum after 12 days and then decreases with lengthening of the exchange time up to 30 days. Since the solution has a pH value of 7 and therefore the proton concentration is very low, the only explanation for the change of elemental analysis data and the shrinkage of *d* spacing after 12 days is that condensation of aluminophosphate layers occurs. Indeed, Figure 12 shows that the intensity ratio of characteristic lattice vibration of layered aluminophosphate around 900 cm^{-1} to that of bulk around 1100 cm^{-1} decreases slightly after AlPO-ntu was

Table 3. Elemental Analysis Results and *d* Spacings of AlPO-ntu-4 after Exchange with C_{16}TMA for Different Reaction Periods and Those after Posttreatment

samples	exchange time (day)	*d* spacing (Å)	molar composition N	P	Al
ML-6	6	44	0.353	1	1.07
ML-12	12	47	0.429	1	1.10
ML-18	18	37	0.324	1	1.04
ML-20	20	31	0.293	1	1.10
ML-30	30	29	0.218	1	1.12
ML-40	40	29	0.223	1	1.09
posttreatment					
540-ML-40[a]			0.015	1	1.12
Na-ML-40[b]	3	22	0.018	1	1.10
H-ML-40[c]	3	22	0.018	1	1.12

[a] ML-40 after calcination at 540 °C. [b] ML-40 after ion exchange with Na^+. [c] ML-40 after ion exchange with H^+.

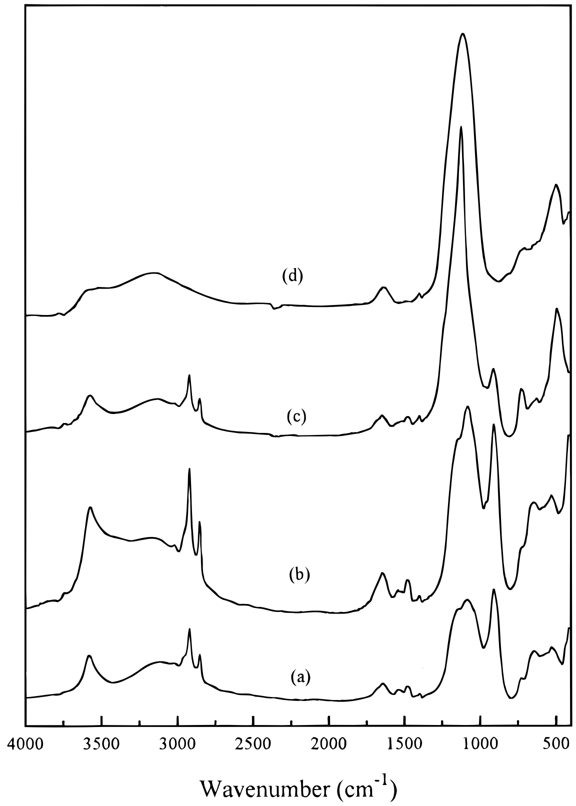

Figure 12. FT-IR spectra of AlPO-ntu exchanged with C_{16}-TMA for various time periods: (a) 6, (b) 18, (c) 40, and (d) sample ML-40 after calcination at 540 °C.

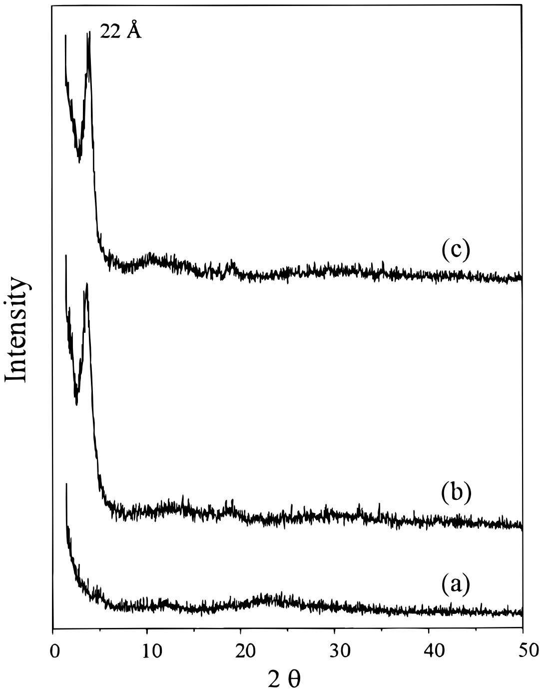

Figure 13. XRD patterns of ML-40 after (a) calcination at 540 °C, (b) Na^+ and (c) H^+ exchange.

stirred in C_{16}TMACl solution for 18 days. After longer exchange period, the former peak shrinks even markedly. These results along with the change of the XRD pattern demonstrate that the AlPO-ntu layers are reorganizing under the influence of the exchanged surfactant cations and transform to some kind of porous structure. Unfortunately, the resulting porous aluminophosphate compound is thermally unstable. Calcination at 540 °C to burn off the template molecules leads to collapse of the ordered structure and formation of a X-ray amorphous phase (Figure 13). Nevertheless, most of the template cations in ML-40 (AlPO-ntu after exchange with C_{16}TMA for 40 days) could be removed by ion-exchange with 0.4 M acetic acid in ethanol or with 3 M NaCl in H_2O/ethanol (1:1 volumetric ratio) solution. The N/P molar ratios of the resultant compounds were found to decrease from 0.223 to ca. 0.018 (Table 3). The *d* spacings of both H^+- and Na^+-exchanged ML-40 samples are similar and have values around 22 Å. The maintenance of the large *d* spacing through H^+- and Na^+-ion exchange is further evidence that sample ML-40 is probably a porous network instead of a dense phase or a layered compound. However, the shrinkage of the *d* spacing value from 29 to 22 Å indicates that further condensation of the framework occurs during the ion-exchange processes with ML-40. Unfortunately, the porous structures could not sustain thermal treatment at temperatures higher than 100 °C before surface area measurement, and no hexagonal arrangement of tunneling pores as that of MCM-41 was detected on transmission electron micrographs.

For the formation of mesoporous materials from kanemite in solution of quaternary ammonium surfactant, Chen et al.[23] proposed two mechanisms: one is the dissolution of silicate layers and the reconstruction of MCM-41 structure directed by the liquid-crystal template, the other is the reorganization of the kanemite layers driven by the structural change of exchanged surfactant cations from bilayer to cylindrical micelle and resulting in short-range hexagonal arrangement. Under our exchange condition, the solution has a pH of 7 and dissolution of aluminophosphate is considered to be negligible. Therefore, the second mechanism shall have greater possibility. However, the *d* spacing of 29 Å obtained at final stage of condensation is much smaller than that of 44−47 Å observed for mesoporous materials from kanemite. These results indicate that the condensation of aluminophosphate is not stopped at the stage of forming three-dimensional network around the cylindrical micelle. The less stability of aluminophosphate framework in comparison to that of silica is attributed to the higher polarity and less covalence of the Al−O and P−O bonds than Si−O bond. The ease in framework rearrangement and condensation is also observed on other aluminophosphate molecular sieves. It is well-known that the VPI-5 molecular sieve, which is the aluminophosphate molecular sieve possessed the largest unidimensional channels known up to date, tend to condense the 18 T-atom channel to 14 T-atom channel and transform to another crystalline phase $AlPO_4$-8 at temperatures higher than ca. 100 °C.[38]

Conclusions

By using *n*-alkylamines of four to eight carbon chain length as templates, a novel aluminophosphate (AlPO-ntu) of lamellar structure was synthesized under hydrothermal condition. The as-synthesized AlPO-ntu compounds have chemical compositions led to formula $AlPO_3(OH)_2[NH_2(CH_2)_nCH_3]$, where $n = 3$, 5, or 7 for butyl-, hexyl-, and octylamines, respectively. Solid-state ^{27}Al and ^{31}P NMR spectra demonstrate that both Al and P atoms are tetrahedrally coordinated and in single coordination environments. These results accompanied with those from X-ray diffraction, ion-exchange properties and FT-IR spectra strongly support that the sheet structure of AlPO-ntu is similar to that of kanemite. The AlO_4 and PO_4 tetrahedra lie alternatively and form sheets of interlocking six-T-member rings. Each tetrahedral TO_4 group ($T = Al$ or P) has three oxygen atoms bonded to three different T atoms, while the fourth unshared oxygen atom on AlO_4 bears a proton and that on PO_4 bears an alkylammonium ion. The alkylammonium ions are exchangeable with alkali ions, but the protons on Al−O terminals are not. The six-T-member rings in aluminophosphate layer shall arrange in boat form in order to explain the thin-sheet structure observed and the bilayer structure formed by the interlayer alkylammonium ions. The Na^+-exchanged AlPO-ntu has a chemical formula $NaHAlPO_5 \cdot xH_2O$, which is isoelectronic to naturally occurring silicate mineral, kanemite with a formula $NaHSi_2O_5 \cdot 3H_2O$. Moreover, the AlPO-ntu layers act similarly as the single-layered silicate in condensation and transforming to porous network under the influence of the polar headgroup of exchanged surfactant cations. Nevertheless, the resultant porous structure has no long-range arrangement of hexagonal pores and is thermally unstable.

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