Interlamellar Esterification of H-Magadiite with Aliphatic Alcohols

Yoshimichi Mitamura,[†] Yoshihiko Komori,[‡] Shigenobu Hayashi,[‡]
Yoshiyuki Sugahara,[†] and Kazuyuki Kuroda*,[†,§]

*Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku,
Tokyo 169-8555, Japan, National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan, Kagami Memorial Laboratory for Materials Science and
Technology, Waseda University, Nishiwaseda-2, Shinjuku-ku, Tokyo 169-0051, Japan*

Magadiite, a layered sodium polysilicate, was organically modified by esterification of interlayer silanol groups with various aliphatic alcohols. Methanol was directly reacted with H-magadiite (acid-treated magadiite) by refluxing. The methanol-treated product showed an increase in the basal spacing and the ^{13}C NMR signals due to methyl groups. The ^{2}H NMR spectrum of CD_3OD-treated H-magadiite showed Pake doublet patterns of quadrupole coupling constants of 43 and 48 kHz and asymmetry factors of 0, indicating the fixation of the C−O axis. When aliphatic alcohols with the carbon chain length longer than 4 were used, an H-magadiite/N-methylformamide (NMF) intercalation compound was used as an intermediate for esterification. The basal spacing of butanol-treated H-magadiite was 1.40 nm, the value of which was smaller than that of H-magadiite/NMF (1.63 nm) and larger than that of H-magadiite (1.15 nm). ^{13}C spin−lattice relaxation times (T_1) of butyl groups showed a low mobility of the α carbon. Other alcohols ($C_nH_{2n+1}OH$ ($n = 2−16$) and $(CH_3)_3$-COH) were also reacted with the silanol groups. The differential thermal analysis (DTA) curves of the products showed exothermic peaks. The alkyl chains are apparently lying parallel to the inner surface because almost constant basal spacings were observed despite the variation in the alkyl chain length. The butanol-treated H-magadiite was dispersed in toluene and cast, resulting in the formation of a transparent nanocomposite film.

Introduction

A wide variety of inorganic layered materials have been utilized to form intercalation compounds by incorporating organic substances in their interlayer spaces with the aim of preparing inorganic−organic supramolecular systems for possible applications in various fields.[1−3] Magadiite ($Na_2H_2Si_{14}O_{30}·xH_2O$) is one of the crystalline layered polysilicates whose layered structures are composed of SiO_4 tetrahedra.[4−7] These layered polysilicates and their acid-treated layered polysilicic acids have silanol groups in the interlayer region, and the silanol groups are reactive for further modification by organic substances, which yields silicate−organic nanocomposites.

The preparative methods of layered polysilicate−organic intercalation compounds are categorized into three types: (1) ion exchange of interlayer Na ions with organic cations, (2) interlayer adsorption of polar organic molecules, and (3) organic derivatization. Lagaly et al. reported the intercalation of organoammonium ions into magadiite by ion exchange of Na ions with organoammonium ions for the first time.[8,9] Polar organic molecules such as NMF are also intercalated into H-magadiite.[10] Ruiz-Hitzky et al. reported the first synthesis of the silylated derivative of magadiite by reaction with chlorotrimethylsilane.[11,12] We found that bulkier organic groups such as the diphenylmethylsilyl group are also incorporated into the interlayer region by using alkyltrimethylammonium-exchanged magadiite as an intermediate.[13,14] Organically derivatized layered polysilicates are expected to exhibit unique properties based on the specific arrangements of organic groups grafted

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onto the regularly distributed silanol groups in the interlayer spaces. We reported the synthesis of novel organic derivatives of magadiite by silylation with perfluoroalkylsilanes[15] and with monochlorodimethyl- and trichloro-octylsilanes and their characteristic adsorption properties.[16]

Esterification of silanol groups by alcohols is another way of modifying the surface properties of silica-based materials. Interactions between amorphous silica and alcohols have been studied extensively.[17,18] Esterified silica particles exhibit various properties due to functional groups, showing adsorption, ion exchange, and organophilicity.[19] The SiOC linkage is vulnerable to hydrolysis and alcoholysis in contrast to SiOSi bondings derived by silylation, which means that esterified derivatives can be utilized further as intermediates for transesterification. Organic molecules available for esterification are diverse, suggesting the formation of a variety of silicate–organic and –polymer nanocomposites.

Here, we report esterification of interlayer silanol groups of H-magadiite with alcohols. Although Mercier et al. have already reported H-magadiite modified by ethylene glycol,[20] there remain many issues to be resolved for the general esterification of layered polysilicic acids. We used *n*-alcohols because (1) the esterification reactions are simpler than those of diols, which makes the characterization of the esterified products easier, and (2) they have lower boiling points, which allow for milder reaction conditions. In the present study, we characterized methanol- and butanol-treated H-magadiites by NMR and X-ray diffraction (XRD), infrared (IR), CHN elemental analysis, scanning electron microscopy (SEM), and thermal analysis. Esterified products derived from various alcohols are also presented.

Experimental Section

Na-Magadiite and H-Magadiite. Na-magadiite was prepared by the method of Kosuge et al.[21] The silica source was colloidal silica (Nissan Chemical Co., SiO_2: 20.6 wt %; Na_2O: 0.29 wt %). A suspension composed of $SiO_2:NaOH:H_2O = 1:0.23:18.5$ was treated at 420 K for 48 h in a sealed Teflon vessel. The white product was washed with an aqueous NaOH solution (pH = 9.0–9.5), centrifuged, and dried at 310 K for 48 h. After the purity of Na-magadiite was checked by XRD, ^{29}Si NMR, and chemical analysis, it was treated with hydrochloric acid (0.2 N), centrifuged, and dried at 310 K for 48 h to form H-magadiite. The powder XRD pattern of H-magadiite showed a basal spacing of 1.15 nm and the other peaks at higher angles were consistent with those reported previously.[21] The IR spectrum showed bands at 3640–3590 cm^{-1} due to ν(OH) of weakly hydrogen-bonded silanol groups and a broad band centered at 3450 cm^{-1} due to ν(OH) of strongly hydrogen-

bonded silanol groups and water.[22,23] The ^{29}Si cross-polarization (CP)/magic-angle-spinning (MAS) NMR spectrum exhibited signals at −101 ppm (Q^3) and −108, −110, −112, and −114 ppm (Q^4),[24] where Q^n means SiO_4 tetrahedra with n bridged oxygen atoms.

Intercalation of NMF into H-Magadiite (H-Magadiite/NMF). According to the method reported by Lagaly et al.,[10] H-magadiite was stirred in NMF at room temperature for 110 h, centrifuged, and dried in air. The XRD peak due to the basal spacing of H-magadiite disappeared, and a new peak at $2\theta = 5.4°$ ($d = 1.63$ nm) appeared.[10] An IR band due to ν(OH) appeared at 3620–3580 cm^{-1} along with a broad band centered at 3425 cm^{-1}. These bands had lower wavenumbers than those of H-magadiite, proving the interactions between the silanol groups and NMF.[12,25] The IR peaks at 2960, 2932, and 2852 cm^{-1} were assigned as ν(CH) of NMF. The peaks at 1668, 1544, 1416, and 1383 cm^{-1} were assigned as amide I, amide II, δ_s(CH$_3$), and δ(CH) of NMF, respectively.[25] The ^{13}C MAS NMR spectrum showed signals at 25.1 and 164 ppm assignable to −CH$_3$ and −C=O groups of NMF, respectively.[26] The ^{29}Si CP/MAS NMR spectrum exhibited signals at −101 ppm (Q^3) and −110, −112, and −114 ppm (Q^4). The thermogravimetric (TG)-DTA showed a mass loss of about 28% with an endothermic peak due to desorption of NMF. The amount of NMF was 1.6 mol of NMF per structural unit ($Si_{14}O_{30}$), being estimated by CHN and TG analyses. All these results confirmed the formation of H-magadiite/NMF.

Esterification. When methanol, deuterated methanol, and ethanol were used, H-magadiite was used for the esterification. The reaction mixtures were refluxed at the boiling points of the alcohols for 48 h. The products were centrifuged and dried at 390 K under reduced pressures. When butanol, pentanol, hexanol, octanol, nonanol, and 2-methyl-2-propanol (*tert*-butyl alcohol) were used, H-magadiite/NMF was refluxed in those alcohols at their boiling points for 48 h. The resultant powders were centrifuged and washed twice with hexane for 30 min. After the solution was dried in vacuo at 390 K, the esterified derivatives were obtained. When tetradecanol and hexadecanol were used, those alcohols were dissolved in benzene and the reaction mixtures with H-magadiite/NMF were refluxed for 48 h.

Analyses. Powder X-ray diffraction patterns were obtained on a Mac Science MXP^3 using monochromated Cu Kα radiation with a scanning speed of 2° min^{-1}. ^{29}Si CP/MAS NMR spectra were recorded at 79.30 MHz using a JEOL NM-GSX-400 spectrometer with a MAS rate of 5 kHz. A delay time of 5 s was used. ^{13}C MAS spectra were recorded at 100.61 MHz on Bruker MSL400 and ASX400 spectrometers with a MAS rate of 5 kHz. The pulse sequences used were CP and the single-pulse sequence with high-power ^1H decoupling (HD). In the CP experiment, the contact time was set at 1 ms and the delay time was 6 s. In the HD spectra, the pulse flip angle was $\pi/4$ and the delay time was 10 s. We confirmed that the signal was not saturated in this condition. The temperature dependence of ^{13}C T_1 relaxation time was measured by the MSL400 spectrometer. Torcha's method was applied in the temperature range from 295 to 345 K. ^1H MAS NMR spectra were recorded at 400.13 MHz by the MSL400 pulsed spectrometer with a MAS rate of 8 kHz. The single-pulse sequence was used with the pulse flip angle of $\pi/4$ and the recycle delay of 5 s. The ^2H NMR spectrum was recorded for a static sample by the MSL400 spectrometer with Larmor frequency of 61.42 MHz. The quadrupole echo pulse sequence was used with the $\pi/2$ pulse width of 3.8 μs and the recycle delay of 5 s. TG-DTA curves were measured by a Mac Science 2000S at a heating

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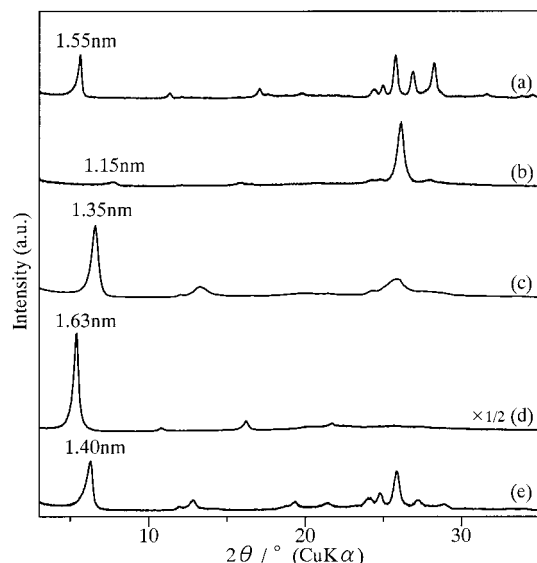
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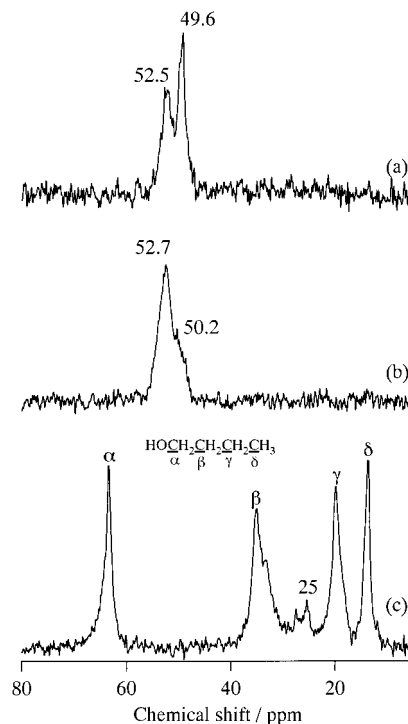(26) Komori, Y.; Sugahara, Y.; Kuroda, K. *J. Mater. Res.* **1998**, *13*, 930.

Figure 1. XRD patterns of (a) Na-magadiite, (b) H-magadiite, (c) methanol-treated H-magadiite, (d) H-magadiite/NMF, and (e) butanol-treated H-magadiite.

rate of 10 K/min under a dry air flow. TG-mass spectrometric (MS) analysis was performed with a combined Shimadzu TGA-50 and GCMS-QP1100EX under a He atmosphere at a heating rate of 10 K/min. IR spectra were recorded on a Perkin-Elmer FTIR-1640 using a KBr pellet technique. CHN analyses were conducted using a Perkin-Elmer PE-2400II apparatus. SEM images were observed by a Hitachi S-2500 microscope under 25 kV.

Results and Discussion

Methanol-Treated H-Magadiite. The basal spacing of the product modified with methanol increased to 1.35 nm from that of H-magadiite (1.15 nm) (Figure 1). The ^{13}C HD/MAS NMR spectrum (Figure 2a) shows two signals at 52.5 and 49.6 ppm, which are assignable to the carbon atoms of methoxy groups.[27-30] The relative intensities of the two signals were 55 and 45%, respectively, which were quantitative under the present measuring conditions. In the CP spectrum, the relative intensities of the two signals were changed (Figure 2b). The signal was simulated by two signals at 52.7 ppm (73%) and 50.2 ppm (27%), which corresponded to 52.5 and 49.6 ppm in the HD spectrum, respectively. Because the methoxy groups of the signal at 53 ppm have better CP efficiency than those of 50 ppm, it is concluded that the former groups have lower mobility. In addition, the ^{13}C chemical shift reflects the interaction between hosts and guests. Judging from the reports that suggested that methyl groups, which have a stronger interaction with hosts, give a signal at higher frequency,[30,31] the methoxy groups, which show the signal at 53 ppm, have the stronger interaction with the host lattice. Two kinds of methoxy groups may arise from the interlamellar structure of magadiite and the stronger interaction with the host may induce the lower mobility of the methoxy

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Figure 2. ^{13}C MAS NMR spectra of (a, b) methanol-treated H-magadiite and (c) butanol-treated H-magadiite. The spectrum of (a) was measured with HD and the baseline was corrected to remove a very broad background signal. The spectra of (b) and (c) were measured with CP. In the spectrum (c), the peak at 25 ppm is due to the remaining NMF, as assigned from an H-magadiite/NMF spectrum (not shown).
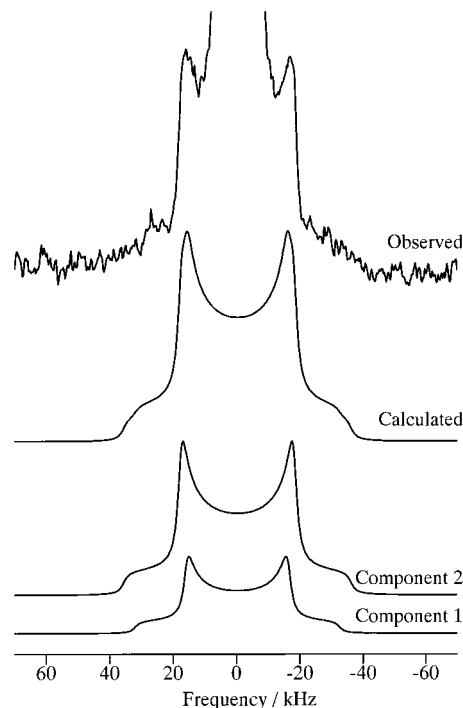
Figure 3. ^{2}H NMR spectra of methanol (CD₃OD)-treated H-magadiite. The broad central component in the observed spectrum is truncated. The calculated spectrum was obtained assuming the presence of two Pake doublet components.

group for 53 ppm, though the precise structure has not been determined yet.

H-magadiite treated with CD₃OD was characterized by ^{2}H NMR. The ^{2}H spectrum shown in Figure 3 is

composed of a central broad signal and a Pake doublet pattern. The central broad signal means the presence of species whose motions are isotropic. Because the product was dried at 390 K under reduced pressures, deuterated methanol should not be present. Therefore, this signal should come from D_2O and HDO, which were formed by the H−D exchange reactions among CD_3OD, SiOH, and H_2O. The protons in SiOH groups are exchanged with deuterium of CD_3OD to form SiOD and these SiOD groups are then re-exchanged with H of water re-adsorbed after drying. The Pake doublet pattern indicates anisotropic motion and the magnitude of the splitting demonstrates that the C−O axis in the CD_3O groups is fixed onto the interlamellar surface of H-magadiite. Additionally, this doublet pattern fits nicely to a simulation assuming the presence of two components (components 1 and 2 in Figure 3), which is consistent with the results of the ^{13}C MAS NMR spectra. The quadrupole coupling constants, asymmetry factors, and the intensities of the components 1 and 2 are 43 kHz, 0, and 40% and 48 kHz, 0, and 60%, respectively. The coupling constants show that the degree of the wobbling motion of the C−O axis of component 1 is larger than that of component 2. Component 1 of larger mobility and component 2 of lower mobility correspond to the ^{13}C MAS NMR signals at 50 and 53 ppm, respectively. The intensity ratio of component 1 to component 2 was also consistent with the result of ^{13}C MAS NMR spectra.

The DTA curve of the product showed a very small exothermic peak near 520 K (data not shown) assigned to the combustion of methoxyl groups. The CHN (C, 0.47%; H, 0.10%; N, 0%) and TG data showed that the grafted amount of methoxy groups is 0.34 mol/$Si_{14}O_{30}$ unit, which is consistent with the very small peak on the DTA curve. The reason for the low degree of grafting of methoxy groups is discussed later. All these findings confirm the interlamellar esterification of H-magadiite. Two different environments of the methoxy groups are also proved.

Butanol-Treated H-Magadiite. Because butanol molecules were not directly intercalated into H-magadiite, H-magadiite/NMF was used as the intermediate. The basal spacing of butanol-treated H-magadiite (Figure 1e) is 1.40 nm, the value of which is larger than that of H-magadiite (1.15 nm; Figure 1b) and smaller than that of H-magadiite/NMF (1.63 nm; Figure 1d). The sample heated at 510 K for 60 min showed a basal spacing of 1.38 nm whereas the spacing of H-magadiite/NMF heated under the same conditions was 1.14 nm. Consequently, the spacing of 1.40 nm results from the expansion due to the intercalation of butanol. The profile at around at $2\theta = 20°−30°$ is also different from that of H-magadiite.

Three exothermic peaks in the DTA curve of butanol-treated H-magadiite (Figure 4b) were observed at about 510, 610, and 650 K while those of H-magadiite (data not shown) and H-magadiite/NMF showed no exothermic peaks. The TG curve had two steps of mass losses, which were 2.1 and 8.4%, respectively. The TG-MS results showed that no fragments due to free butanol
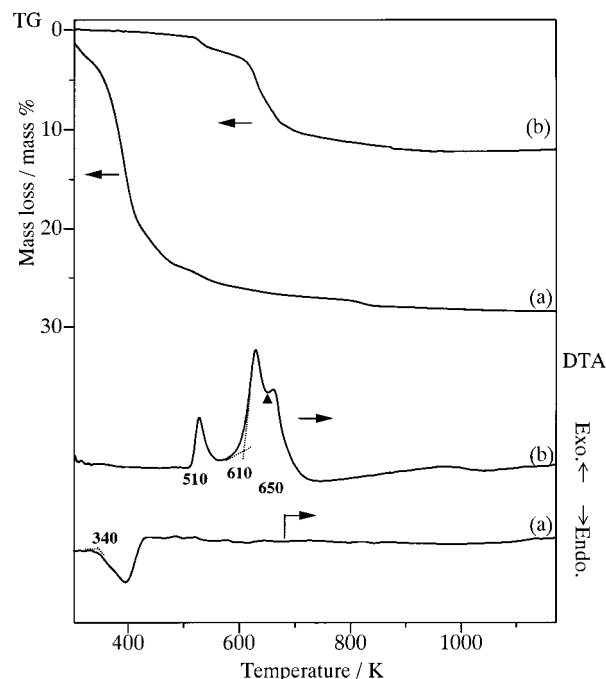
Figure 4. TG-DTA curves of (a) H-magadiite/NMF and (b) butanol-treated H-magadiite.

Table 1. ^{13}C Spin−Lattice Relaxation Results of Butanol-Treated Magadiite Measured by Torcha's Method

temperature/K	T_1/s			
	α	β	γ	δ
295	1.1	2.0	2.4	2.7
315	1.8	2.6	2.7	3.3
335	2.0	3.2	3.8	4.2
345	2.6	4.0	4.8	5.2

(m/e 31, 41, 43, 56, and 61) were observed, which also supports the esterification.[33]

Figure 2c shows the ^{13}C MAS NMR spectrum of butanol-treated H-magadiite. The signals were observed at 64 ppm, 35 ppm (with a shoulder at 33 ppm), 20 ppm, and 14 ppm, which are due to the carbon atoms at the nearest position to O atoms (α), the second (β), the third (γ), and the fourth (δ), respectively. These values are shifted to higher frequencies by 1.5−0.5 ppm than those found in free butanol. This result shows a tendency similar to the relation between tetrabutoxysilane and butanol,[34] indicating the presence of butoxy groups.

^{13}C spin−lattice relaxation times (T_1) of the butoxy groups were measured to differentiate mobile and attached species. The T_1 values are listed in Table 1. The relaxation curves were exponential and fitted by one component. The T_1 value of the α carbon was 1.1 s at 295 K and the T_1 value increased monotonically from the α carbon to the δ carbon. All the T_1 values increased as the temperature of the system increased. ^{13}C spins in the butoxy group relax through fluctuation of dipolar interaction with nearby ^1H spins. The $1/T_1$ values are

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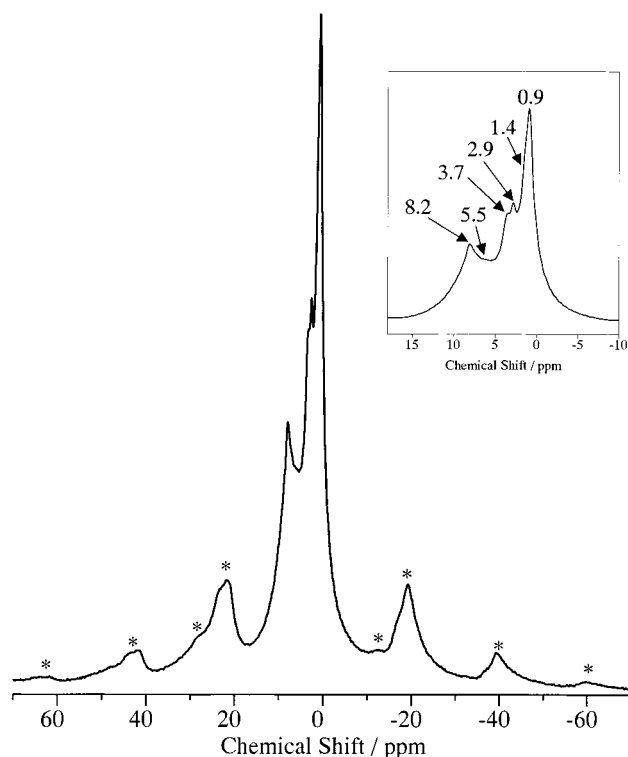
Figure 5. ^{1}H MAS NMR spectrum of butanol-treated H-magadiite. Asterisks indicate spinning sidebands. The inset shows an expanded profile of the isotropic signals.

approximately proportional to $\omega_C \tau_c / (1 + \omega_C{}^2 \tau_c{}^2)$, where ω_C is the [13]C Larmor frequency in angular frequency unit and τ_c is the correlation time of the motion. τ_c obeys Arrhenius relation usually: $\tau_c = \tau_c{}^0 \exp(E_a / kT)$, where $\tau_c{}^0$ is the inverse of the frequency factor, E_a is the activation energy, k is Boltzmann's constant, and T is temperature. The above equations indicate that the T_1 value takes its minimum when $\omega_C \tau_c$ is about 1. The temperature dependence obtained for the butoxy group leads to the conclusion that the correlation time is much shorter than $1/\omega_C$, that is, 1 ns. In this high-temperature region, the higher mobility (i.e., the shorter correlation time) corresponds to the longer T_1 value. The T_1 values of the carbon atoms are in the following order: $\alpha < \beta < \gamma < \delta$, and this order corresponds to the order of mobility. In conclusion, this finding also proves the esterification of H-magadiite with butanol.

The CHN data (C, 5.75%; H, 1.03%; N, 0.53%) indicate that butanol-treated H-magadiite has a composition of $(C_4H_9)_{1.0}H_3Si_{14}O_{30}\cdot 0.31NMF$. The presence of residual NMF molecules is confirmed by the ^{13}C NMR spectrum, which shows C=O (164 ppm) and CH_3 signals (25 ppm). The amount of remaining NMF molecules was remarkably decreased to ca. $^1/_5$ times the amount in the H-magadiite/NMF intermediate.

The ^{29}Si CP/MAS NMR spectrum of butanol-treated H-magadiite exhibits the signals at -101 ppm due to a Q^3 environment and at -110, -112, and -114 ppm due to Q^4 environments of the SiO_4 tetrahedra (data not shown). The spectrum is consistent with that of H-magadiite/NMF, which indicates the retention of the silicate structure of magadiite.

Figure 5 shows the ^{1}H NMR spectrum of the butanol-treated H-magadiite. On the basis of the spectrum deconvolution, the signals at 0.9, 1.4, and 2.9 ppm are
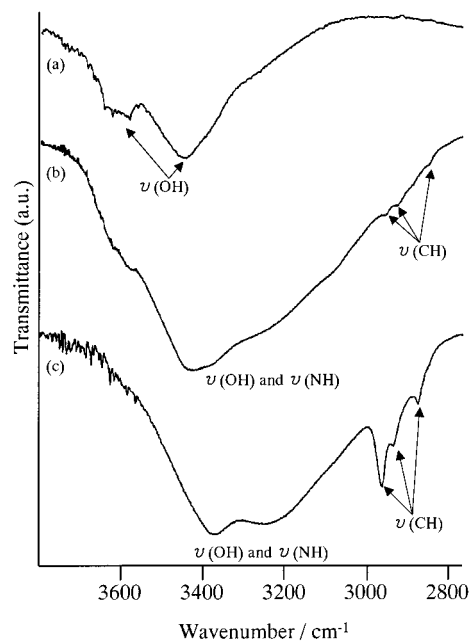

Figure 6. IR spectra of (a) H-magadiite, (b) H-magadiite/NMF, and (c) butanol-treated H-magadiite.

assigned to the H atoms in the organic groups (CH_3, 0.9 ppm; $CH_3-CH_2CH_2-$, 1.4 ppm; $-CH_2-O$, 2.9 ppm).[34] In addition, the appearance of spinning sidebands corresponding to the above isotropic signals shows the residual dipole−dipole interaction due to the anisotropy in the molecular motions, which is consistent with the results showing immobilization of alcohols. Signals at 3.7, 5.5, and 8.2 ppm were also observed and are ascribed to protons of silanol groups of H-magadiite. The signal at 8.2 ppm occurs at a higher frequency than those found for silanol groups in H-magadiite (3.8, 5.7 ppm).[35] These particular interlamellar silanol groups display a particularly strong hydrogen bonding.

The IR bands due to ν(CH) were observed at 2964, 2938, and 2878 cm^{-1} (Figure 6c). The intensities of these bands are stronger than those found in H-magadiite/NMF (Figure 6b), supporting the significant presence of butoxy groups. The bands at 3640−3590 cm^{-1} assignable to ν(OH) due to weakly hydrogen-bonded silanol groups[22] found in H-magadiite (Figure 6a) shifted to lower wavenumbers because of the change in the hydrogen bondings. The broad peaks at 3378 and 3244 cm^{-1} due to hydrogen-bonded ν(OH) and ν(NH) were also observed. These peaks suggest that there are silanol groups whose hydrogen bonding is stronger than those found in H-magadiite, which is in agreement with the results of ^{1}H NMR.

Butanol-treated H-magadiite disperses well in toluene, where H-magadiite does not. Figure 7 shows the dispersibility of 0.1 g of butanol-treated H-magadiite (Figure 7a) and H-magadiite (Figure 7b) in 20 mL of toluene. In contrast to the aggregation property of H-magadiites, the esterified H-magadiite shows a stable dispersibility in organic solvents such as toluene. The sample dispersed in toluene was allowed to stand for 2 days and the supernatant solution containing a well-exfoliated portion of butanol-treated H-magadiite was

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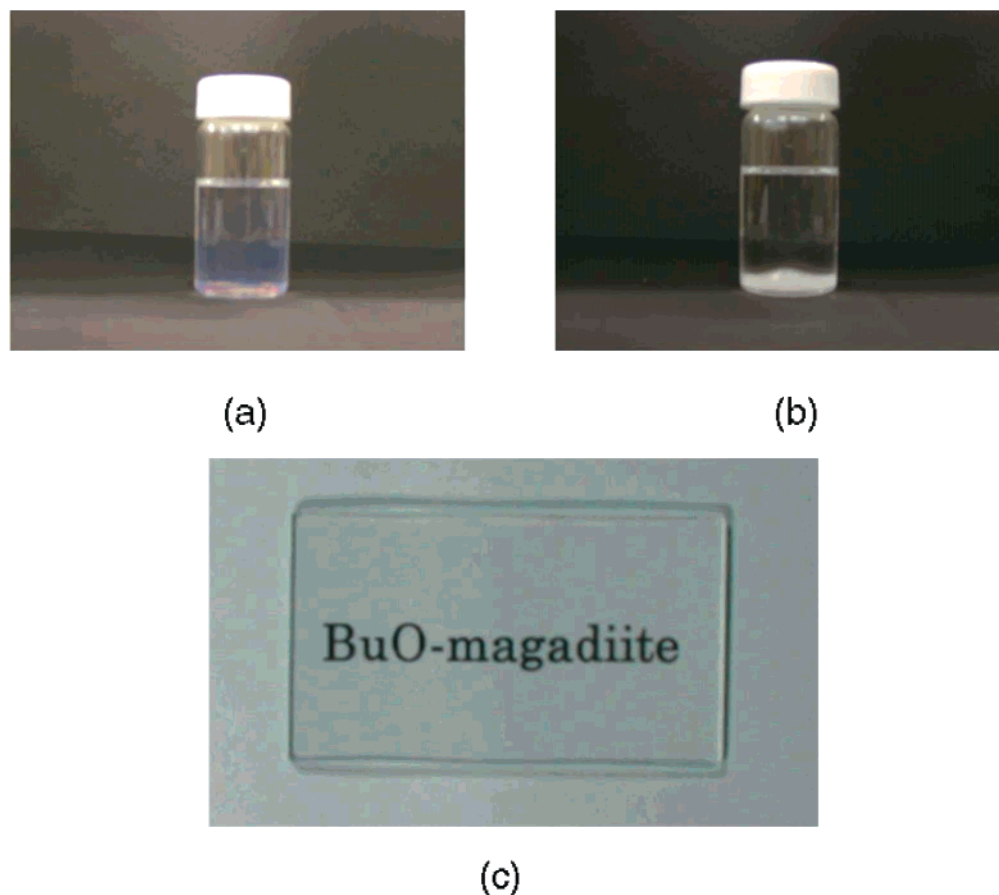
Figure 7. Photographs of (a) butanol-treated H-magadiite dispersed in toluene, (b) H-magadiite in toluene, and (c) a cast film.

Table 2. Basal Spacing and Amount of Alkoxyl Groups of Alcohol-Treated Magadiites

alcohols	basal spacing/nm	amount of alkoxyl groups (mol)/$Si_{14}O_{30}$
CH_3OH	1.35	0.30
CH_3CH_2OH	1.39	0.93
$CH_3(CH_2)_3OH$	1.40	0.96
$CH_3(CH_2)_4OH$	1.38	0.85
$CH_3(CH_2)_5OH$	1.37	0.40
$CH_3(CH_2)_7OH$	1.39	0.41
$CH_3(CH_2)_8OH$	1.37	0.27
$CH_3(CH_2)_{13}OH$	1.38	0.22
$CH_3(CH_2)_{15}OH$	1.38	0.20
$(CH_3)_3COH$	1.55	0.66

cast on a glass substrate to form a transparent film (Figure 7c). The formation of films is important for optical and photochemical device applications. The characterization of the films is under way.

Other Alcohols. The basal spacings and the organic contents are listed in Table 2. The basal spacings are larger than that of H-magadiite (1.15 nm) and smaller than that of H-magadiite/NMF (1.63 nm). The basal spacing does not vary with the chain length of the aliphatic alcohols used, suggesting the highly tilted arrangements of the alkyl chains in the interlayer region.

In the TG-DTA curves of the sample with ethanol, slight exothermic peaks were observed, which are possibly due to a small amount of the grafted organic groups. The samples modified with the other *n*-alcohols mainly exhibited two intense exothermic peaks, the lower peak begins in the range of 470−600 K and the higher one starts in the range of 560−650 K. The sample from 2-methyl-2-propanol showed two exothermic peaks at higher exothermic temperatures (around 570 and 720 K).

The CHN and TG data indicate that about one molecule per $Si_{14}O_{30}$ unit was reacted for the samples ethanol, butanol, and pentanol. When the alkyl chain length increased, the degree of incorporation decreased stepwise and the value reached ca. 0.2 for the samples modified by tetradecanol and hexadecanol. Because the alkyl chains are so tilted, virtually parallel to the layered silicate structure, the steric hindrance resulting from the increase in the alkyl chains length is notable in this direction. Thus, the alkoxy group/Si ratio was lowered in the higher alcohols. On the other hand, the amount of methanol-treated H-magadiite deviated from this tendency. The esterification is a dehydration reaction of acid and base. Silanol groups in magadiite correspond to solid acid,[36] while alcohols act as a base relatively. Acidity of methanol is stronger than that of water whereas those of other alcohols are weaker. Therefore, it is suggested that methoxy groups once formed tend to be hydrolyzed to form silanol groups again and that other alkoxy groups do not. The basal spacing of the esterified product with 2-methyl-2-propanol was 1.55 nm, and this large spacing is ascribable to the bulkier organic groups. Platy morphologies were observed in the SEM images of all the products, showing the retention of the basic layer structure of magadiite (data not shown).

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(36) Werner, V. H.-J.; Beneke, K.; Lagaly, G. *Z. Anorg. Allg. Chem.* **1980**, *470*, 118.

Conclusions

Organic esterification of interlayer silanol groups of H-magadiite with various aliphatic alcohols was performed. A Pake doublet pattern was observed in the ^{2}H NMR spectrum of CD$_3$OD-treated H-magadiite, indicating the fixation of the C−O bond. The ^{13}C spin−lattice relaxation times (T_1) of butyl groups indicated that the mobility of the carbon atoms at the α position was lower than those of the other carbon atoms. The DTA curves of the esterified products showed exothermic peaks in the expected organic decomposition range. All these findings demonstrate esterification of interlamellar silanol groups of H-magadiite with alcohols. The basal spacing of magadiite modified with normal alcohols showed almost constant values of ca. 1.4 nm. These basal spacings suggested that the alkyl chains lie in parallel within the layer. The butanol-treated H-magadiite was dispersed in toluene and the suspension was utilized to form a transparent magadiite−organic nanocomposite film, which would be useful for a future optical medium to immobilize various photoactive substances in its confined environment. The products are also very useful for incorporation of other organic groups by using transesterification.

Supporting Information Available: ^{29}Si CP/MAS NMR of H-magadiite, H-magadiite/NMF, and butanol-treated H-magadiite (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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