Synthesis of Interlamellar Silylated Derivatives of Magadiite and the Adsorption Behavior for Aliphatic Alcohols

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Interlayer silanol groups of a layered polysilicate magadiite ($Na_2H_2Si_{14}O_{30}\cdot nH_2O$) were silylated with octyltrichlorosilane via dodecyltrimethylammonium magadiite as the intermediate. Three organic derivatives with different degrees of silylation were prepared by varying the amount of the silylating reagent. Aliphatic alcohols with different alkyl chain lengths ($n = 8$, 12, and 16) were adsorbed into these derivatives at room temperature, and the adsorption behavior was examined. The basal spacings of the derivatized silicates were expanded after the adsorption, and larger spacings were observed when the derivatives with lower degrees of silylation and the alcohols with longer chain lengths were used. Because intercalated alcohols and alcohols taken up in the intercrystal spaces were desorbed by drying, the amounts of intercalated alcohols were estimated by surveying the relationship between the variation in the basal spacing and the amounts of alcohols in the samples treated under various drying conditions. Larger amounts of alcohols were adsorbed onto the derivatives with lower degree of silylation, indicating a possible control of the interlayer nanospace by varying the amount of grafting alkylsilyl groups.

Introduction

Intercalation compounds of inorganic layered materials with organic guest species provide very diverse nanocomposite materials, based on the combination of vast varieties of inorganic and organic substances. One of the organic modification methods of inorganic layered materials is grafting of organic groups. Although the kind of layered materials suitable for such derivatization is limited, organic derivatives of inorganic layered materials are superior to simple organic intercalation compounds because of the possible molecular design at a nanometer level. One of the properties of these derivatives is the capability of further accommodation of organic molecules because of the organophilicity of the interlayer surfaces, and various developments are expected in the fields of catalysts, adsorbents, photo- and electro-functional materials, and so on.[1] By choosing the bulkiness and the amount of modifying organic groups, unique properties, such as selective and specific introduction of guest species, have emerged.[2−5] Accordingly, various applications are proposed such as catalysis,[6,7] removal of toxic substances from aquatic environments,[8−13] sensing for specific molecules,[14] etc. Extensive research on the molecular design by choosing appropriate hosts and grafting groups is required to achieve better adsorption properties.

The interlayer spaces of the smectite group of clay minerals, such as montmorillonite and saponite, are normally modified by organoammonium cations, and the modified clay minerals have been studied from the viewpoints of the influences of the kind of organoammonium ions[15] and the layer charge densities on the adsorption properties. By changing the amount of alkylammonium ions introduced and by utilizing various smectites with different layer charge densities, the adsorption behavior for guest species is controlled.[16]

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(1) Ogawa, M.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2593.
(2) Johnson, J. W.; Jacobson, A. J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowsky, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 381.
(3) Cao G.; Mallouk, T. E. *Inorg. Chem.* **1991**, *30*, 1434.
(4) Fogg, A. M.; Dunn, J. S.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 351.
(5) Ogawa, M.; Okutomo, S.; Kuroda, K. *J. Am. Chem. Soc.* **1998**, *120*, 7361.
(6) Breen, C.; Watson, R. *Appl. Clay Sci.* **1998**, *12*, 479.
(7) Breen, C.; Moronta, A. *J. Phys. Chem. B* **1999**, *103*, 5675.
(8) Mortland, M. M.; Shaobai, S.; Boyd, S. A. *Clays Clay Miner.* **1986**, *34*, 581.
(9) Boyd, S. A.; Lee, J. F.; Mortland, M. M. *Nature* **1988**, *333*, 345.
(10) Lee, J. F.; Mortland, M. M.; Boyd, S. A. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2953.
(11) Kukkadapu, R. K.; Boyd, S. A. *Clays Clay Miner.* **1995**, *43*, 318.
(12) Mizutani, T.; Takano, T.; Ogoshi, H. *Langmuir* **1995**, *11*, 880.
(13) Sheng, G.; Boyd, S. A. *Clays Clay Miner.* **1998**, *46*, 10.
(14) Yan, Y.; Bein, T. *Chem. Mater.* **1993**, *5*, 905.
(15) Jaynes, W. F.; Vance, G. F. *Clays Clay Miner.* **1999**, *47*, 358.

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Layered zirconium phosphates also form various types of organic derivatives.[17] For example, interlayer phosphate groups react with ethylene oxide to form ester linkage.[18] By introducing phosphate ester groups into the interlayer surfaces, derivatized zirconium phosphates exhibit a guest binding property like that of crown-ether.[19] Octyl alcohol was adsorbed into decylamine intercalated zirconium phosphate by van der Waals interactions among the alkyl chains.[20] Adsorption and desorption of amines in zirconium phosphates pillared with poly(ethylene glycol) were also reported by changing the conformation of the polyethylene chains.[21]

Magadiite ($Na_2H_2Si_{14}O_{30}{\cdot}nH_2O$), a layered sodium polysilicate,[22] was used as a host for the organic derivatization in this study. The structure of the polysilicate is composed of SiO_4 tetrahedra. Magadiite has surface silanol groups, and the groups can be organically modified by silylation with various organosilanes. Organofunctional groups are grafted onto the surface by covalent bonding, which affords types of intercalation compounds different from those derived by ion exchange and ester formation. Magadiite was trimethylsilylated by the use of an intermediate which preintercalated dimethyl sulfoxide (DMSO) or *N*-methylformamide (NMF), as reported by Ruiz-Hitzky et al.[23] Dodecyltrimethylammonium (DTMA) exchanged magadiite was utilized as a more versatile intermediate for silylation reactions with various reagents containing various silyl groups, such as long chain alkylsilyl, perfluoroalkylsilyl, and γ-methacryloxypropylsilyl groups.[24−28]

We reported that long chain alkyl alcohols are able to be adsorbed into the organic derivatives of magadiite treated with octyltrichlorosilane and a mixture of acetone/water subsequently, but that the derivatives modified with trialkylmonochlorosilane did not show the adsorption of alcohols to a large extent.[5] Unhydrolyzed −SiCl groups, which were incorporated onto the interlayer surface of magadiite, are changed to −Si−OH groups by washing the products with a mixture of acetone and water. Therefore, in addition to the hydrophobic interactions among those alkyl groups, the interactions between the generated SiOH groups and introduced organic alcohols are responsible for the adsorption of alcohols. This idea of using both of the interactions is different from those using organically modified smectites and layered zirconium phosphates.

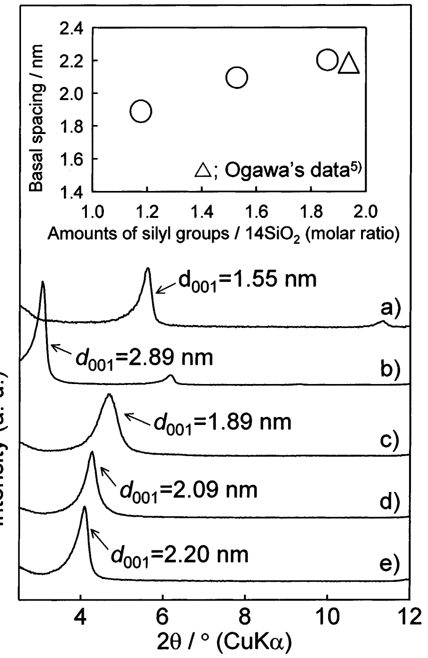

Figure 1. XRD patterns of (a) Na-Magadiite, (b) DTMA-Magadiite, (c) $C_8Si(1.18)$-Mag, (d) $C_8Si(1.53)$-Mag, and (e) C_8-Si(1.86)-Mag. Inset: variation of the basal spacing as a function of the amount of silyl groups.

However, there have been no detailed studies on the amounts of adsorbed alcohols and the interlayer environments of magadiite. To design the interlayer environments suitable for and specific to target molecules, for selective adsorbents and molecular sensors, it is very important to control the adsorption capacity and to investigate the interlayer environments in detail. In the present study, therefore, the interlayer structures of silylated derivatives of magadiite after alcohol adsorption were investigated in detail and the adsorption of alcohols was estimated. By changing the amounts of modifying agents, organic derivatives of magadiites with different adsorption capacities were prepared and the differences in their adsorption behavior were examined.

Experimental Section

Na-Magadiite and DTMA-Magadiite. Na-magadiite was prepared by a method reported previously.[29] High purity sodium silicate (SiO_2 21.1 mass % and Na_2O 6.57 mass %; Nihon Chemical Ind. Co.), SiO_2 (special grade, Wako Chemicals Co.), and distilled water were mixed at the ratio of $SiO_2/NaOH/H_2O = 1{:}0.23{:}18.5$. The mixture was sealed in a Teflon-lined autoclave (Taiatsu Glass Co., TAF-SR-100) and treated hydrothermally at 150 °C for 2 d. The product was washed with a dilute aqueous solution of NaOH (pH = 9.0∼9.5) and dried at 40 °C for 2 d. Na-magadiite was characterized by XRD and ^{29}Si CP/MAS NMR. As shown in Figure 1a, the basal spacing was 1.55 nm and the pattern coincided with that of a previous report.[22] Peaks due to impurities were not detected. The ^{29}Si MAS NMR spectrum showed the signals due to the characteristic Q^3 and Q^4 environments of Si atoms and was very similar to that reported previously. [24]

Dodecyltrimethylammonium chloride (DTMACl, special grade, Tokyo Kasei Co.) was used for the preparation of an intermediate. The procedure for the preparation was followed

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(16) Lee, J. F.; Mortland, M. M.; Chiou, C. T.; Kile, D. E.; Boyd, S. A. *Clays Clay Miner.* **1990**, *38*, 113.

(17) Alberti, G.; Casciola, M.; Costantino, U.; Vivani, R. *Adv. Mater.* **1996**, *8*, 291.

(18) Yamanaka, S.; Maeda, H.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1187.

(19) Yamanaka, S.; Yamagawa, K.; Hattori, M. *J. Inclusion Phenom.* **1984**, *2*, 297.

(20) Alberti, G.; Marmottini, F.; Cavalaglio, S.; Severi, D. *Langmuir* **2000**, *16*, 4165.

(21) Alberti, G.; Brunet, E.; Dionigi, C.; Juanes, O.; Mata, M. J.; Rodríguez-Ubis, J. C.; Vivani, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 22.

(22) Eugster, H. P. *Science* **1967**, *157*, 1177.

(23) Ruiz-Hitzky, E.; Rojo, J. M. *Nature* **1980**, *287*, 28.

(24) Yanagisawa, T.; Kuroda, K.; Kato, C. *React. Solids* **1988**, *5*, 167.

(25) Yanagisawa, T.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3743.

(26) Okutomo, S.; Kuroda, K.; Ogawa, M. *Appl. Clay Sci.* **1999**, *15*, 253.

(27) Ogawa, M.; Miyoshi, M.; Kuroda, K. *Chem. Mater.* **1998**, *10*, 3787.

(28) Isoda, K.; Kuroda, K.; Ogawa, M. *Chem. Mater.* **2000**, *12*, 1702.

(29) Kosuge, K.; Yamazaki, A.; Tsunashima, A.; Otsuka, R. *J. Ceram. Soc. Jpn.* **1992**, *100*, 326.

Table 1. Amounts of Octylsilyl Groups in the Derivatives

	amount of silylating reagent (per $14SiO_2$)	C (mass %)	H (mass %)	SiO_2 (mass %)	amount of silyl groups (per $14SiO_2$)
C_8Si(1.18)-Mag	0.77	10.7	2.22	85.2	1.18
C_8Si(1.53)-Mag	1.28	13.2	2.19	83.5	1.53
C_8Si(1.86)-Mag	1.95	15.7	2.68	83.8	1.86

by a method reported previously by us.[24] Na-magadiite (6.0 g) was dispersed in an aqueous solution of DTMACl (0.1 mol/L, 200 mL), and the mixture was stirred at room temperature for 5 d, and the reaction was repeated. Then, the product was washed with acetone two times and air-dried at room temperature. The basal spacing of DTMA-magadiite (DTMA-Mag) was 2.8 nm, indicating the ion exchange of Na^+ for $DTMA^+$. The IR spectrum of the product showed the peaks due to C−H stretchings and the TG-DTA curve showed weight losses accompanied by exothermic peaks, supporting the introduction of the organic groups between the layers. On ther basis of the CHN analysis and TG of the product (C, 2.45 mass %; H, 4.67 mass %; N, 1.71 mass %; and SiO_2, 63.0 mass %), the amount of DTMA was estimated to be 1.49 mol DTMA/14 SiO_2.

Silylation of the Intermediate. Octyltrichlorosilane (C_8SiCl_3, Tokyo Kasei Co., extra pure grade) was used as the silylating reagent. Distilled dry toluene was used as a solvent. Magadiite was silylated by a method reported by Ogawa et al.[5] DTMA-magadiite was dried at 100 °C for 2 h under a reduced pressure, and was mixed with toluene and a fixed amount of octyltrichlorosilane. Three samples with different degrees of modification were synthesized by changing the amount of the silylating reagent. Each reaction mixture was refluxed at 110 °C for 2 d in an N_2 atmosphere. The centrifuged precipitates were washed stepwise with toluene twice, a mixed solution of HCl (0.1 N) and acetone (1:1 in volume) three times, H_2O and acetone (1:1 in volume) until Cl^- free, and acetone twice. The products were dried at 40 °C for 2 d to yield the silylated derivatives (C_8Si-Mag).

Adsorption of Alcohols by Silylated Magadiites. Alcohols used for the adsorption measurements were butyl alcohol (abbreviated as C4OH, Kokusan Chemical Co.), hexyl alcohol (C6OH, Junsei Chemical Co.), octyl alcohol (C8OH, Kanto Chemical Co.), dodecyl alcohol (C12OH, Tokyo Kasei Co.), and hexadecyl alcohol (C16OH, Tokyo Kasei Co.), and all were special grade chemicals. C_8Si-Mag (0.1 g) was stirred in each alcohol at room temperature for 2 d, and the product was centrifuged. The supernatant was removed, and the solid product was analyzed. Liquid alcohols (C4OH−C8OH) were used in amounts of 40 mL, and solid alcohols (C12OH and C16OH; about 2 g) were dissolved in decane (40 mL, Kanto Chemical Co., special grade). The molar ratios of the alcohols over the $14SiO_2$ unit were 40 times higher than the unity.

Estimation of Alcohols in the Interlayer of Derivatized Magadiites. It was difficult to determine quantitatively the amounts of intercalated alcohol because the adsorption procedure was conducted in neat liquid alcohols or decane solutions and the amounts of alcohols taken up in the intercrystal spaces could not be neglected. In addition, because intercalated alcohols and alcohols taken up in the intercrystal spaces were desorbed by washing and drying, it was very difficult to determine quantitatively the amounts of intercalated alcohols. Therefore, after adsorption, the samples were dried gradually, and the variations in both the basal spacing and the amounts of the alcohols remaining in the samples (intercalted and taken up in the intercrystal spaces) were examined. The samples, after the adsorption, were dried on filter papers under ambient conditions or under a reduced pressure. Those samples dried under various conditions were subjected to XRD and TG analyses. By analyzing the desorption behavior, the amounts of intercalated alcohols were estimated (see below).

Characterization. X-ray powder diffraction patterns were obtained by a Mac Science MXP[3] diffractometer (monochromatic Cu Kα) for the characterization of the products, and a Mac Science M03XHF[22] diffractometer (Mn filtered Fe Kα) for the measurement of low diffraction angles. IR spectra were recorded on a Perkin-Elmer Fourier transform Spectrum One spectrometer using a KBr disk technique. TG and DTA curves were measured by a Mac Science 2000S instrument with a heating rate of 10 °C/min under a dry air flow. CHN analysis was conducted with a Perkin-Elmer PE2400II instrument. Solid state ^{29}Si MAS NMR spectra were recorded on a JEOL JNM-CMX400 spectrometer at a resonance frequency of 79.42 MHz with a 45° pulse and a recycle delay of 300 s. The spinning speed of samples was 6 kHz. Solid state ^{13}C CP/MAS NMR spectra were recorded on a JEOL GSX-400 spectrometer at a resonance frequency of 100.54 MHz and a recycle delay of 5 s with a sample rotation of 5 kHz and a 90° pulse. The ^{29}Si and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm.

Results

Silylation of Magadiite. Table 1 lists the amounts of octyltrichlorosilane used and octylsilyl groups after the grafting onto magadiite on the basis of the data by CHN and TG analyses. The nitrogen contents were almost zero, confirming the almost complete removal of DTMA ions by the washing procedure. These silylated magadiites listed in Table 1 are designated as C_8Si(1.18)-Mag, C_8Si(1.53)-Mag, and C_8Si(1.86)-Mag.

The XRD patterns of the silylated products are shown in Figure 1. The basal spacings of the products are different from those of Na-magadiite and the intermediate, suggesting the intercalation of octylsilyl groups. The basal spacings increased with the amount of grafted silyl groups (C_8Si(1.18)-Mag, 1.89 nm; C_8Si(1.53)-Mag, 2.09 nm; and C_8Si(1.86)-Mag, 2.20 nm), as shown in Figure 1 inset.

The IR spectra of the silylated products, shown in Figure 2c−e), exhibited the bands (△) due to C−H stretching at around 2900 cm^{-1}. The single and sharp band due to the weakly hydrogen-bonded OH stretching was observed at 3650∼3660 cm^{-1} for the spectra of Na-magadiite and DTMA-magadiite. After silylation, the band became broad or was split to a couple of bands at around 3660∼3700 cm^{-1}. The broad bands (▲) at 3500∼3400 cm^{-1}, assignable to hydrogen-bonded hydroxyl groups, were decreased after silylation.

Figure 3 shows the ^{29}Si NMR spectra of the products. The spectra of Na-magadiite (Figure 3a) and DTMA-magadiite only showed the signals due to the Q^3 ($-O\mathbf{Si}(OSi)_3$) and Q^4 ($\mathbf{Si}(OSi)_4$) environments of Si at around −98 ppm and −110 ppm, respectively. New signals at −54 ppm, assigned to T^2 ($R\mathbf{Si}(OSi)_2O-$) environments, were observed for the silylated samples (Figure 3b−d). The intensity of the signal was increased and the ratio of Q^3/Q^4 was decreased with the degree of silylation.

The ^{13}C CP/MAS NMR spectra are shown in Figure 4. All the signals were assigned to the carbons in the octylsilyl groups, which confirms the retention of the carbon chains of the silylating reagent after both refluxing and washing.

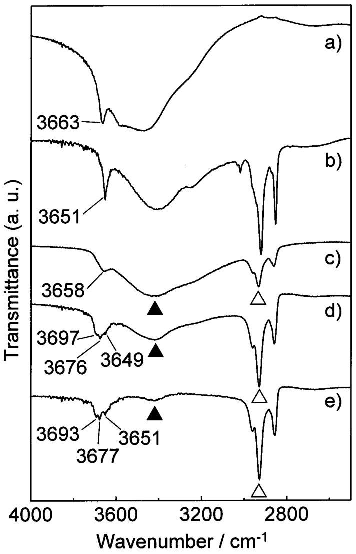

Figure 2. IR spectra of (a) Na-Magadiite, (b) DTMA-Magadiite, (c) $C_8Si(1.18)$-Mag, (d) $C_8Si(1.53)$-Mag, and (e) $C_8Si(1.86)$-Mag.

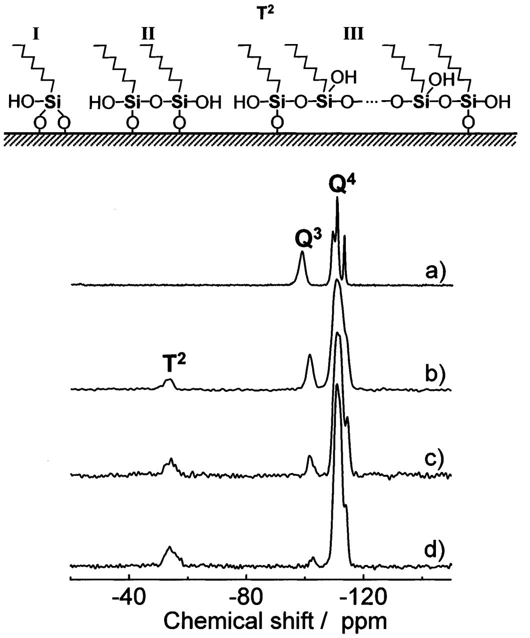

Figure 3. ^{29}Si NMR spectra of (a) Na-Magadiite, (b) $C_8Si(1.18)$-Mag, (c) $C_8Si(1.53)$-Mag, and (d) $C_8Si(1.86)$-Mag. Inset: schematic model of octylsilyl groups (**I**) immobilized on the silicate sheet by bridging two SiO_4 tetrahedra, (**II**) bonded with the silicate sheet and with one Si−OH group linked to another octylsilyl group, and (**III**) bonded partly with the silicate sheet forming polyoctylsiloxane.

Adsorption of Alcohols into C_8Si-Mag. C8OH, C12OH, and C16OH were adsorbed into $C_8Si(1.18)$-Mag, $C_8Si(1.53)$-Mag, and $C_8Si(1.86)$-Mag. For $C_8Si(1.18)$-Mag and $C_8Si(1.86)$-Mag, the alcohols with shorter chains (C4OH and C6OH) were also adsorbed. The XRD patterns of the products after adsorption are displayed in Figure 5 parts I−III. The basal spacing increased after the adsorption of alcohols and with the increase in the length of the alkyl groups.

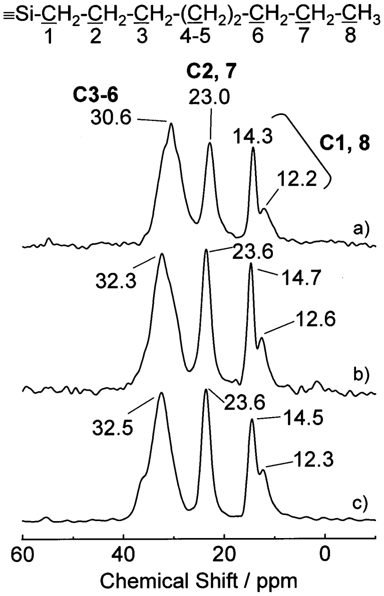

Figure 4. ^{13}C CP/MAS NMR spectra of (a) $C_8Si(1.18)$-Mag, (b) $C_8Si(1.53)$-Mag, and (c) $C_8Si(1.86)$-Mag.

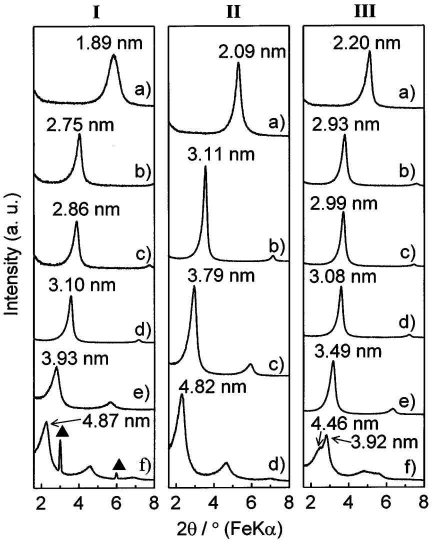

Figure 5. XRD patterns of samples after alcohol adsorption of **I**: (a) $C_8Si(1.18)$-Mag, (b) $C_8Si(1.18)$-Mag/C4OH, (c) $C_8Si(1.18)$-Mag/C6OH, (d) $C_8Si(1.18)$-Mag/C8OH, (e) $C_8Si(1.18)$-Mag/C12OH, and (f) $C_8Si(1.18)$-Mag/C16OH; **II**: (a) $C_8Si(1.53)$-Mag, (b) $C_8Si(1.53)$-Mag/C8OH, (c) $C_8Si(1.53)$-Mag/C12OH, and (d) $C_8Si(1.53)$-Mag/C16OH; **III**: (a) $C_8Si(1.86)$-Mag, (b) $C_8Si(1.86)$-Mag/C4OH, (c) $C_8Si(1.86)$-Mag/C6OH, (d) $C_8Si(1.86)$-Mag/C8OH, (e) $C_8Si(1.86)$-Mag/C12OH, and (f) $C_8Si(1.86)$-Mag/C16OH (▲, C16OH).

Figure 6 shows the relationship between the alkyl chain length of the alcohols and the interlayer spacing (Δd) of the products after adsorption which was calculated by the subtraction of the basal spacing of H-magadiite (1.15 nm)[23] from the basal spacing of the products. When C12OH and C16OH were adsorbed, larger interlayer spacings were observed for the derivatives with lower degree of organic modification. When C8OH was adsorbed, the derivatives with different degrees of modification showed almost the same interlayer spacings. In the adsorption of C8OH to C16OH, the interlayer spacings increased linearly with the alkyl chain length. The variation in the interlayer spacings of the products with the alkyl chain length after the adsorption of C4OH and C6OH was not remarkable and apparent differences were not found for the derivatives.

Estimation of the Amounts of Intercalated Alcohols. C12OH was adsorbed onto $C_8Si(1.18)$-Mag and

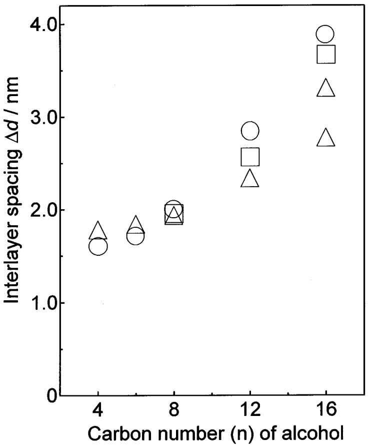

Figure 6. Δd vs n (○, $C_8Si(1.18)$-Mag; □, $C_8Si(1.53)$-Mag; △, $C_8Si(1.86)$-Mag).

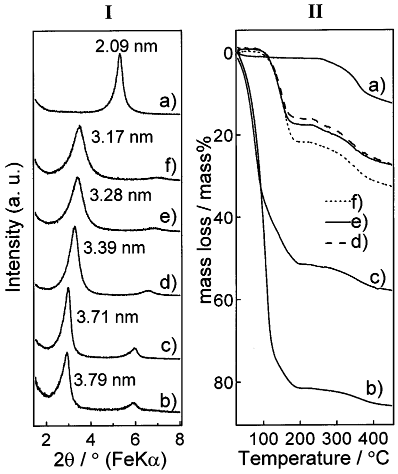

Figure 7. XRD patterns (**I**) and TG curves (**II**) of (a) C_8Si-(1.53)-Mag and (b–f) C8Si(1.53)-Mag/C12OH: (b) after centrifugation, (c) developed on a filter paper, (d) air-dried on a filter paper for 1 d, (e) vacuum-dried for 3 h after (d), and (f) vacuum-dried for further 5 h after (e).

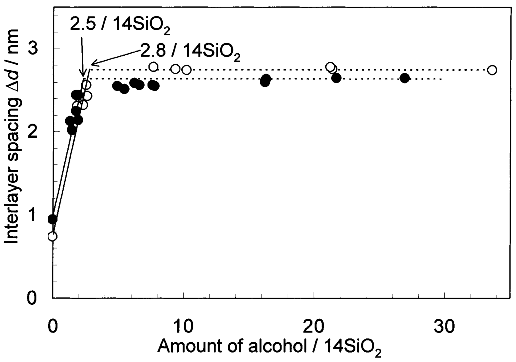

Figure 8. Δd vs amount of alcohol (○, $C_8Si(1.18)$-Mag/C12OH; ●, $C_8Si(1.53)$-Mag/C12OH).

$C_8Si(1.53)$-Mag and the samples [$C_8Si(1.18)$-Mag/C12OH and $C_8Si(1.53)$-Mag/C12OH] after drying under various conditions were subjected to XRD and TG analyses. Figure 7 I shows the variation in the XRD patterns of $C_8Si(1.53)$-Mag/C12OH in the various drying stages. The interlayer spacing decreased with the process of the drying (from b to f). The TG curve after the adsorption of alcohol (Figure 7 II) showed an additional weight loss up to 200 °C. The weight losses in this region became smaller as the drying proceeded (from b to f). These weight losses can be ascribed to desorption of alcohols intercalated into the interlayers and alcohols taken up in the intercrystal spaces as well as a solvent.

Two weight losses up to 200 °C were observed for the samples in the initial stages of drying (Figure 7 II, b and c); the first loss occurred before 100 °C and the second one occurred between 100 °C and 200 °C, suggesting that alcohols with two different adsorbed states are present in the samples. The former one up to 100 °C was decreased and disappeared with drying from b, c to d and only the latter one at around 100–200 °C was observed. Consequently, the former weight loss up to 100 °C is ascribed to evaporation of *n*-dacane and alcohols which were not intercalated into the interlayer space. The latter weight loss in the range between 100 °C and 200 °C is ascribable to desorption of intercalated alcohols. Accordingly, for the sample of the drying stage of d, the solvent and alcohols adsorbed taken up in the intercrystal spaces can be neglected.

In the present study, the weight loss observed up to 200 °C was assumed to be due to the desorption of C12OH because the amount of the solvent should be very small due to its nonpolar nature, and the molar ratios of alcohols/$14SiO_2$ unit were calculated. Figure 8 shows the relationship between Δd and the amount of alcohols of the $C_8Si(1.18)$ and $C_8Si(1.53)$-Mag/C12OH systems in various drying stages. In the initial stage of drying (the ratio of alcohol/$14SiO_2$ was about 4 or higher), the interlayer spacings were almost similar irrespective of the amounts of the alcohols. In the latter stage of drying (the ratio of alcohol/$14SiO_2$ was about 4 or lower), a decrease in the basal spacing was observed with desorption of alcohols. When the range of the ratio of alcohol/$14SiO_2$ was about 4 or higher, alcohols taken up in the intercrystal spaces were desorbed and, on further drying, intercalated alcohols start to be deintercalated. By defining the interlayer spacing of the silylated derivative before the adsorption as the interlayer spacing at zero in the amount of alcohols, and by inserting the interlayer spacing of the silylated derivative in the plot, the relation between the spacings in the latter drying stages (y axis) and the amount of alcohols (x axis) is linearly approximated. Thus, the amount of intercalated alcohols was determined as a value in the x-axis at the crossing point of the two lines which are the line described above and that derived from the extrapolation of the basal spacings of the products just after the centrifugation. The amounts of alcohols intercalated in the samples were calculated to be 2.8/$14SiO_2$ for C8Si(1.18)-Mag/C12OH and 2.3/SiO_2 for $C_8Si(1.53)$-Mag/C12OH. The effect of decane was excluded by the fact that decane was not intercalated, as evidenced by XRD, and was not present under highly dried conditions, as evidenced by TG.

Discussion

Silylation of Magadiite. The relationship between the basal spacing and the amount of grafted silyl groups is shown in the inset of Figure 1. The basal spacing increased linearly with the amount of the groups and the previous result (plotted as △,[5] is also plotted on the line obtained in this study. The peak profiles due to (001) of the silylated products are not broadened, suggesting that octylsilyl groups were intercalated and

Table 2. Observed Peak Area of the ^{29}Si MAS NMR Signals and the Calculated Values Based on the Bonding Model Depicted in the Inset of Figure 3

	% T^2	% Q^3	% Q^4	Q^4/Q^3	$(Q^4 - T^2 \times 2)/(Q^3 + T^2 \times 2)$ (I)	$(Q^4 - T^2)/(Q^3 + T^2)$ (II)
Na-Mag	–	26	74	2.81	–	–
C_8Si(1.18)-Mag	6.0	14	78	5.70	2.60	3.68
C_8Si(1.53)-Mag	8.7	5.5	86	15.5	2.97	5.40
C_8Si(1.86)-Mag	11	2.3	86	36.9	2.56	5.50

grafted into the interlayer space without segregation. Because the increase in the basal spacing is monotonic, the amount of grafted silyl groups can be controlled and it is possible to synthesize the organic derivatives with the interlayer space grafted homogeneously. We have proposed a model that interlayer octylsilyl groups take an interdigitated monolayer in the interlayer space, based on the size of the silyl groups and the interlayer spacing.[5] The present results, showing the continuous increase in the basal spacing with the amount of grafted silyl groups, strongly support the model.

In the IR spectra (Figure 2), the intensity of the CH stretching band observed at 2900 cm^{-1} (△) was increased with the grafting, corresponding to the increase in the amount of silyl groups. The band due to weakly hydrogen-bonded OH groups, found at 3650−3700 cm^{-1}, varied before and after the silylation, indicating the presence of hydroxyl groups interacting with the surroundings different from those of Na- and DTMA-magadiites. These results strongly suggest that silanol groups (═Si(R)−O−H) were newly formed from the silyl groups bonded to the interlamellar surfaces. The intensity of the broad band at 3400−3500 cm^{-1}, being ascribable to hydrogen-bonded OH groups, was reduced with the grafting possibly because of the reduction of the hydrogen bonds between adjacent surface silanol groups.

The ^{29}Si MAS NMR spectra of the silylated products (Figure 3) exhibited the signals ascribable to the T^2 environments of Si at −54 ppm. With the grafting the intensity of the T^2 peaks increased and the ratio of Q^4/Q^3 was also increased, confirming the progress of silylation (Table 2). The fact that the signal due to the T^2 region was observed means two possible bonding states, as depicted in the inset of Figure 3. The state I exhibits one silylating reagent reacting with two OH groups on the surface and the state II shows that one reagent reacts with one silanol site and the further bonding occurs between remaining silanol groups of the adjacent grafting groups. In the case of state I two Q^3 sites are consumed for one reagent, and one Q^3 site is utilized for one reagent in the state II. The Si environments in the derivatives were quantitatively estimated based on the peak areas of the signals due to T^2, Q^3, and Q^4 environments. When the state I is assumed, new Q^4 sites should form from the Q^3 sites capped by the silylating reagent, and the original ratio of Q^4/Q^3 can be calculated by $(Q^4 - 2T^2)/(Q^3 + 2T^2)$. If the state II is assumed, the original ratio can be calculated by $(Q^4 - T^2)/(Q^3 + T^2)$. The calculated values are listed in Table 2. If we assume polymerization of the silylating reagent in the interlayer space (state III, Figure 3), the ratio should be calculated from the formula of $(Q^4 - T^2 \times 2/n)/(Q^3 + T^2 \times 2/n)$, and the values should become larger than those of states I and II, being exceedingly deviated from the original ratio. Because the original ratio of Q^4/Q^3 of Na-magadiite is 2.81, the values based on the state I are closest to the original ratio, indicating that model I is the main feature of the bondings in the interlayer space. Accordingly, polymerization of the silylating reagent in the interlayer space is very unlikely.

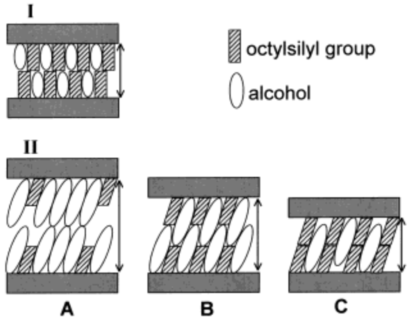

Figure 9. Schematic for the possible orientation of silyl groups and alcohols: **I**, after adsorption of C8OH; **II**: **A**, alcohols-alcohols bilayer, **B**, silyl groups-alcohols bilayer, and **C**, silyl groups-silyl groups bilayer.

The amounts of grafted octylsilyl groups, calculated from CHN data and TG analysis, increased with the amounts of the silylating reagent used, as Table 1 shows. All the results confirm the formation of the organic derivatives modified quantitatively, though a small part of magadiite was possibly dissolved during the washing and silylation processes, which is suggested by the tendency of higher ratio of grafted silyl groups over the silicate unit than the nominal values.

Arrangements of Intercalated Alcohols in the Interlayer Space. As evidenced by XRD and TG, the silylated derivatives can accommodate alcohols by expanding the interlayer space. The relationship between the interlayer spacing and the number of carbon atoms (n) in the alcohols is shown in Figure 6. The interlayer spacing increased linearly, and, when n is smaller than 8, the slope is different from that for $n \geq 8$. This behavior results from the fact that the carbon number of the silyl groups is eight and that the alcohols with shorter alkyl chain lengths do not interact with the octylsilyl groups in a paraffin-like manner.

When $n = 8$. After the adsorption of octyl alcohol (C8OH), the basal spacings of all the silylated derivatives with different degrees of silylation were ca. 2 nm. Because the length of the octyl group is ca. 1 nm, both octylsilyl groups and octyl groups of the alcohol are thought to take bilayer arrangements with their molecular axes perpendicular to the silicate layers, as shown in Figure 9 I.

When $n > 8$. As Figure 6 shows, after the adsorption of alcohols, the interlayer spacing of the silylated products with higher degree of silylation was smaller than that of the product with lower degree of silylation. The amounts of intercalated alcohols depend on the density of octylsilyl groups. The product with smaller amounts of silyl groups can accommodate larger amounts of alcohols than that with larger amounts of silyl groups.

The possible arrangements of the alcohols and the silyl groups are schematically shown in Figure 9 II. The case A displays that the basal spacing is determined by a bilayer arrangement of alcohols, and the case B shows that the spacing is governed by the combination of the sizes of alcohols and octylsilyl groups. The case C displays the spacing induced by a bilayer arrangement of octylsilyl groups in which alcohols are present among the silyl groups. Because the spacing varies substantially with the alkyl chain length of alcohols used, alcohols and octylsilyl groups can take an arrangement represented in case A or B.

For the derivatives of $C_8Si(1.18)$-Mag and $C_8Si(1.53)$-Mag, the model structure A explains the arrangement most reasonably because the observed basal spacing cannot be realized by the arrangements of the alkyl groups represented by the model B.

When $C_8Si(1.86)$-Mag was used for the adsorption, the model B is also applicable to explain the following two systems of $C_8Si(1.86)$-Mag/C12OH and C16OH. In the case of $C_8Si(1.86)$-Mag/C16OH, the peaks due to the basal spacing was split into two values. The spacing of $\Delta d = 3.31$ nm cannot be explained by the model B, meaning the probable arrangement depicted in model A. As shown in Figure 6, the plot designated as △ of $\Delta d = 3.31$ nm is out of the straight line of the interlayer spacing and *n* (alkyl chain length). Consequently, when alcohols were adsorbed onto $C_8Si(1.86)$-Mag, the interlayer structures can mainly be expressed by the model B, though a part of phase ($\Delta d = 3.31$ nm) can be represented by the model A.

When n < 8. Figure 6 shows that the degree of the variation of Δd with the alkyl chain length of alcohols (*n*) is different from and smaller than those found for the samples of $n \geq 8$. The influence of the alkyl chain length of alcohols on the variation in the basal spacing in a lesser degree is explained by the fact that alkyl chain length of alcohols is shorter than that of the silyl groups and that the alkyl chains in the interlayer space do not tend to take all trans conformation. Large differences in Δd were not found and only slightly smaller values of Δd values were obtained in the derivative with the lowest degree of modification when the same alcohols were adsorbed onto the derivatives. This may be explained by the assumption that the shorter chain lengths of the alcohols cannot contribute to the basal spacing, and, consequently, the influence of the size of silyl groups surpasses that of alcohols.

Packing of Intercalated Alcohols and Octylsilyl Groups in the Gallery of Magadiite. The amounts of intercalated alcohols were $2.8/14SiO_2$ for $C_8Si(1.18)$-Mag/C12OH and $2.3/14SiO_2$ for $C_8Si(1.53)$-Mag/C12OH, indicating that larger amounts of alcohols were intercalated into the derivative with the lower degree of modification. This finding supports that the interlayer space provides the adsorption sites. The values of the amounts of intercalated alcohols (2.3 and $2.8/14SiO_2$) also indicate that the weights of intercalated alcohols are about 0.4 to 0.5 times larger than those of the derivative before adsorption, which means a substantial uptake of alcohols into the organic derivatives.

On the basis of the amounts of intercalated alcohols and the grafted amount of silyl groups, the packing states of those organics can be discussed. Because the crystal structure of magadiite has not been determined yet, the interlamellar suface area of magadiite cannot be calculated in a precise manner. On the basis of the report by Brindley,[30] the parameters of $a = b = 0.73$ nm, $c = 1.57$ nm, and $\beta = 96.8°$ were used in this study, and the surface area in the interlayer space was estimated to be ca. 0.53 nm^2 ($a \times b$). On the basis of these values, the interlayer volume was calculated by the following equation.

$$\text{interlayer volume } (\mathrm{nm^3/14SiO_2}) = \text{interlayer spacing } \Delta d \text{ (nm)} \times \text{interlayer surface area } (\mathrm{nm^2/14SiO}\mathbf{2})$$

In the next step, the size of C12OH was calculated on the assumption that the molecule is a rectangular parallelepiped. The volume was multiplied with the amounts of silyl groups/$14SiO_2$ and alcohols/$14SiO_2$ and the volume of all the molecules and groups present in the interlayer space ($nm^3/14SiO_2$).

From these calculations, the packing degrees are ca. 115% for $C_8Si(1.18)$-Mag/C12OH and ca. 113% for $C_8Si(1.53)$-Mag/C12OH, meaning that alcohols and the silyl groups are closely packed in the interlayer space. Such high values may be ascribed partly to the alcohols interacted with silyl groups grafted onto outer surfaces in a manner similar to that found in the interlayer spaces, though such a contribution should be low based on the relatively large particle size of magadiite. In any case, the interlayer space after silylation is effectively utilized for the adsorption of alcohols. The amounts of alcohols intercalated varied with the degree of silylation, and this indicates that the adsorbing capacity can be controlled by the interlamellar modification. It may be interesting to know the interactions between octyl groups and alkyl chains of alcohol in the interlayer space by ^{13}C NMR. However, the samples were wet after the adsorption of alcohols and the alcohols taken up in the intercrystal spaces may affect the ^{13}C NMR spectra. Therefore, ^{13}C NMR results for these samples are not so useful for the discussion. As described in the above section, the amounts of alcohols accommodated in the interlayer space are quite large. These findings are very useful for the design of interlayer space of layered materials toward selective adsorption of organic substances by using their specific characteristics such as steric hindrance and functional groups. Well-designed interlayer space can be effectively expanded to accommodate specific organic substances, proving the efficacy of the material systems.

Conclusions

Successful modification of the interlayer surface of magadiite is realized by the reaction of dodecyltrimethylammonium magadiite with octyltrichlorosilane. The degree of homogeneous octylsilylation is controlled by simply changing the amount of silylating reagent. After the adsorption of alcohols onto the derivatives with different degrees of silylation, the samples with lower

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[30] Brindley, G. W. *Am. Miner.* **1969**, *54*, 1583.

degree of silylation exhibit larger basal spacings and adsorb larger amounts of alcohols than do the samples with higher degree of silylation. Intercalated alcohols and grafted silyl groups are packed densely in the gallery. The control of the pore volume used for the adsorption is also feasible. Selective adsorption of organic substances by changing the pore volume, the polarity of grafted groups, and the surroundings in the interlayer space should be further studied to utilize layered materials for future potential applications.

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