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Efficient Way to Attach Organosilyl Groups in the Interlayer Space of Layered Solids

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An efficient method to immobilize silane-coupling reagents on the interlayer space of a layered silicate, magadiite ($Na_2Si_{14}O_{29}\cdot nH_2O$), is reported. The silylation was conducted by concentrating a mixture containing the pre-synthesized dodecyltrimethylammonium-exchanged magadiite and a stoichiometric amount (molar ratio of silane-coupling reagent/$Si_{14}O_{29}$ unit of magadiite = 2.0) of (3-mercaptopropyl)trimethoxysilane. The resulting silylated derivative possessed basal spacing and had a composition comparable to those of the silylated derivative, prepared by using a previous silylation method, which involves dodecyltrimethylammonium-exchanged form with a much larger amount (molar ratio of silane-coupling reagent/$Si_{14}O_{29}$ unit of magadiite = 57) of the silane-coupling reagent. When the present method was employed, the surface coverage with (3-mercaptopropyl)silyl groups on the layer surface directly correlated to the amount of the silane-coupling reagent.

Surface modification of inorganic solids with organic molecular species is a way to prepare inorganic–organic hybrids.[1,2] Among the reported modification techniques, grafting of an organic molecular species, such as the silylation of surface hydroxy groups with silane-coupling reagents, has the potential for practical applications, because of the chemical and thermal stabilities of the resulting hybrids. Accordingly, the design of materials through the silylation of inorganic solids, such as mesoporous silicas,[3] layered silicates,[4,5] and layered titanates,[6] has been reported.

Grafting of organic functionalities into the interlayer space of layered solids has also been investigated.[4,7,8] The silylation of layered solids has resulted in the formation of hybrid materials with useful functions, such as adsorption selectivity,[9–13] swelling in organic solvents,[6,14–16] and thermoresponsive change of basal spacing.[16] The preparation of fillers for organic polymers,[17–19] novel crystalline silicas,[20–22] an organically pillared silicate,[23] and matrices for dyes[24,25] has also been investigated.

As a first example of the silylation of layered solids, Ruiz-Hitzky and his co-workers have reported the silylation of layered alkali silicates by reacting polar organic molecule-intercalated forms of the silicates with an excess amount of a silane-coupling reagent by refluxing.[4,5] Yanagisawa et al. have developed an alternative silylation method using the alkyltrimethylammonium-exchanged forms as intermediates, instead of the polar organic molecule-intercalated forms.[26] This method made the preparation of silylated derivatives with bulky silane-coupling reagents possible.[13,14,17,20–22] Note that these reported synthetic procedures required extremely large amounts of silane-coupling reagents.

In this paper, we report an alternative and efficient silylation method, in which only a stoichiometric amount of a silane-coupling reagent is required: a concentrated mixture of a dodecyltrimethylammonium-exchanged silicate and a silane-coupling reagent was used. The silylation of magadiite ($Na_2Si_{14}O_{29}\cdot nH_2O$)[27] with (3-mercaikeptopropyl)trimethoxysilane by using a "solvent evaporation method" was investigated, and the results were compared to those by using the conventional reflux method with a much larger amount of the silane-coupling reagent.

The controllability of the surface coverage with the silyl group on the silicate sheet by our solvent evaporation method was also examined. We report that the variation of the surface coverage with organosilyl groups led to products with controlled functions, such as adsorption selectivity and capability[9–12] and swelling ability in organic solvents.[15,16]

Experimental

Materials. Magadiite was synthesized by the reported method.[28] High-purity sodium silicate (SiO_2, 21.1 mass %; Na_2O, 6.57 mass %, Nihon Chemical Ind. Co.), silica gel (special grade, Wako Chemicals), NaOH, and distilled water were mixed at the molar ratio of SiO_2:NaOH:H_2O = 1:0.23:18.5. The mixture was sealed in a Teflon-lined stainless bottle and treated hydrothermally at 150 °C for 2 days. The product was separated by centrifugation (3500 rpm, 10 min), washed with a dilute aqueous solution of NaOH (pH 9.0) and dried at 40 °C for 2 days. Dodecyltrimethylammonium chloride (abbreviated as C_{12}TMACl, special grade) was purchased from Tokyo Chemical Industry Co., Ltd. (3-Mercaptopropyl)trimethoxysilane (MPS, 95%), was purchased from Aldrich and used as received.

Synthesis of the Dodecyltrimethylammonium-Exchanged Form. The silylation was conducted using the dodecyltrimethylammonium-exchanged form of magadiite (C_{12}TMA–magadiite) as the intermediate. A reported procedure for the preparation of C_{12}TMA–magadiite was used.[26] Magadiite (6.0 g) was dispersed in an aqueous solution of C_{12}TMACl (0.1 M, 200 mL), and the mixture was stirred at room temperature for 5 days. The reaction

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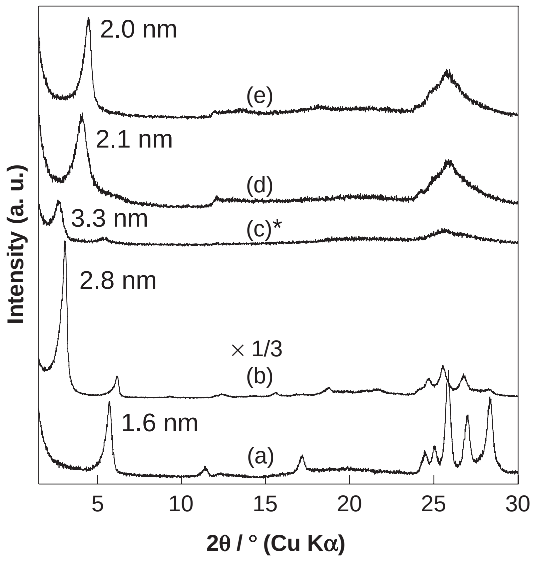

Fig. 1. XRD patterns of (a) magadiite, (b) C_{12}TMA–magadiite, and (c) unwashed and (d) washed MPS–magadiite(eva) with HCl–ethanol solution, and (e) MPS–magadiite(ref). Asterisk indicates that the powder was measured using a smaller sample holder.

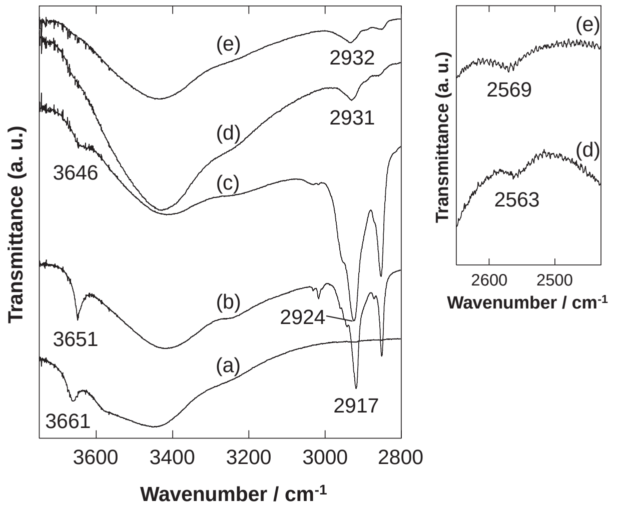

Fig. 2. FT-IR spectra of (a) magadiite, (b) C_{12}TMA–magadiite, and (c) unwashed and (d) washed MPS–magadiite(eva) with HCl–ethanol solution, and (e) MPS–magadiite(ref). Inset: expansion of a frequency region at 2650–2400 cm^{-1}.

was then repeated. The product was separated by centrifugation (4000 rpm, 20 min) and washed with acetone. A basal spacing of 2.8 nm (Fig. 1b) and the IR spectrum (Fig. 2b) were identical to those reported previously,[26] indicating the formation of C_{12}TMA–magadiite. On the basis of the CHN elemental analysis and the thermogravimetric (TG) curve (C, 24.2 mass %; H, 4.3 mass %; N, 1.6 mass %; and SiO_2, 63.0 mass %), the amount of the adsorbed C_{12}TMA was estimated to be 1.5 groups per $Si_{14}O_{29}$.

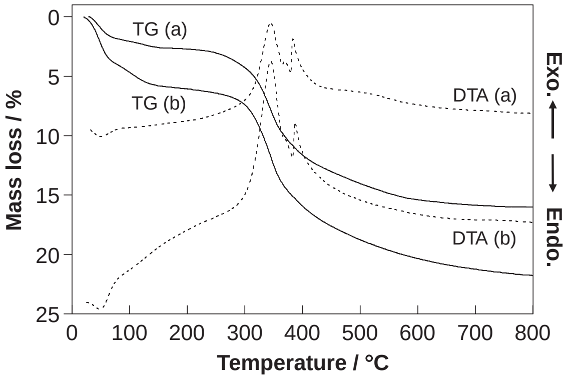

Fig. 3. TG (solid line)-DTA (dashed line) curves of (a) MPS–magadiite(ref) and (b) MPS–magadiite(eva).

Silylation by Solvent Evaporation Method. C_{12}TMA–magadiite (0.50 g) was dispersed in toluene (30 mL) solution of MPS (0.16, 0.12, or 0.080 mL, which corresponds to MPS/$Si_{14}O_{29}$ molar ratio of 2.0, 1.5, or 1.0), and the mixture was concentrated for 1–2 h at 90 hPa and 60 °C to evaporate completely the solvent using rotary evaporator (Büchi Rotavapor R200/205). For silylation with a smaller MPS/$Si_{14}O_{29}$ ratio (1.5 or 1.0), the method was slightly modified: the mixture of C_{12}TMA–magadiite (0.20 g) and MPS (47 or 31 μL) in a toluene (20 mL) solution was aged at 60 °C for 2 or 3 days before evaporating the solvent. The products were washed with a mixture of aqueous 0.1 M HCl and ethanol (1:1 in volume). The silylated derivatives thus obtained are abbreviated as MPS–magadiite(eva).

Silylation by Reflux Method. C_{12}TMA–magadiite (2.5 g) was dispersed in MPS (25 g) acetonitrile (250 mL) solution, and the mixture was stirred at 60 °C for 2 days under a flow of nitrogen. The product was separated by centrifugation (4000 rpm, 20 min) and washed with acetonitrile to remove excess MPS and then with a mixture of aqueous 0.1 M HCl and ethanol (1:1 in volume) to remove any remaining C_{12}TMA. The silylated derivatives thus obtained are abbreviated as MPS–magadiite(ref).

Characterization. X-ray diffraction (XRD) patterns of products were recorded on a Rigaku RAD IB powder diffractometer equipped with monochromatic Cu Kα radiation operated at 20 mA and 40 kV. Infrared (IR) spectra of KBr disks were recorded on a Shimadzu FT-8200 Fourier-transform infrared spectrophotometer at a resolution of 1.0 cm^{-1}. TG and differential thermal analysis (DTA) curves were recorded on a Rigaku TG8120 at a heating rate of 10 °C min^{-1} under air using α-Al_2O_3 as a standard material. Scanning electron microscopy (SEM) was performed on a Hitachi S-2380N.

Results and Discussion

The XRD pattern of MPS–magadiite(eva) is shown in Fig. 1d together with those of magadiite and C_{12}TMA–magadiite. The basal spacing of C_{12}TMA–magadiite (2.8 nm) degreased to 2.1 nm upon silylation and washing. In the IR spectrum of MPS–magadiite(eva), the absorption band due to SiO–H stretching vibration at 3651 cm^{-1} disappeared, and the intensity of the absorption bands due to C–H stretching vibration at around 2900 cm^{-1} was weaker, whereas the absorption band due to S–H stretching vibration at around 2563 cm^{-1} appeared upon the reactions (Fig. 2d). These results indicate that the (3-mercaptopropyl)silyl groups attach to the silicate layers through Si–O–Si bonds. From the TG curve (Fig. 3b), the amount of the attached MPS was determined to be 2.1 groups

Table 1. Composition, Basal Spacing, and Surface Coverage of the Silylated Derivatives

Amount of used MPS /mol per $Si_{14}O_{29}$	Method of silylation	Amount of attached silyl groups/mol per $Si_{14}O_{29}$[a)]	Basal spacing /nm	Distance between adjacent silyl groups/nm	Aging of reaction mixture before solvent evaporation
57	Reflux	1.7	2.0	0.56	—
2.0	Concentration	2.1	2.1	0.50	×
1.5		1.5	2.3, 1.4	—	×
1.0		1.0	2.1, 1.3	—	×
1.5		1.5	1.7	0.59	○
1.0		1.0	1.4	0.73	○

a) Calculated from the mass loss due to the oxidative decomposition of the attached MPS in the temperature range of 280–800 °C and the residual mass at 800 °C. The decomposed MPS was supposed to be $SH(CH_2)_3$– and all the residual mass at 800 °C was assumed to be the SiO_2 content of magadiite.

per $Si_{14}O_{29}$ (Table 1). The absence of the adsorption band due to C–N stretching vibration at 1468 cm^{-1} indicates that all of the C_{12}TMA is deintercalated during the reactions.

Figure 1e depicts the XRD pattern of MPS–magadiite(ref). The basal spacing was 2.0 nm, which was less than that (2.8 nm) of C_{12}TMA–magadiite. In the IR spectrum of the MPS–magadiite(ref), the absorption band due to the interlayer SiO–H stretching vibration at 3651 cm^{-1} was absent, the intensity of the absorption bands due to C–H stretching vibration at around 2900 cm^{-1} was weaker, and an absorption band due to S–H stretching vibration appeared at 2569 cm^{-1} upon the reaction (Fig. 2e). Similar results were obtained for MPS–magadiite(eva), indicating the silylation of magadiite with MPS by refluxing. The amount of the attached MPS was calculated to be 1.7 groups per $Si_{14}O_{29}$, which was smaller than that (2.1) of MPS–magadiite(eva), although a much larger amount of MPS was employed for the reflux method (Table 1). It should be noted here that the solvent evaporation method requires only a stoichiometric amount of MPS to obtain the silylated derivative with basal spacing and a composition comparable to those of the silylated derivative prepared by the reflux method (Table 1). The preparation of silylated derivatives by using the reflux method requires excess amounts of silane-coupling reagent.[4–6,12,14–17,20–23]

A SEM image of MPS–magadiite(ref) is shown in Fig. 4a. Magadiite forms spherical nodules that resemble rosettes. Although the rosette morphology was lost, the morphology of each plate was preserved after the silylation with MPS, which has been reported for the silylation of magadiite with alkylchlorosilanes[29] and (γ-methacryloxypropyl)trimethoxysilane.[17] A SEM image of MPS–magadiite(eva) showed that the platy morphology was preserved when the silylation was conducted by the solvent evaporation method (Fig. 4b).

The surface coverage with silyl groups on oxide sheets, which correlates to the distance between the adjacent silyl groups, is calculated from the composition of the silylated derivatives (groups per unit cell) and the surface area per unit cell of the parent layered solids.[12,15,16] Because the crystal structure of magadiite has not yet been determined, the surface area of magadiite was calculated on the basis of the report by Brindley using the following parameters: $a = b = 0.73$ nm, $c = 1.57$ nm, and $\beta = 96.8°$.[30] The surface area per unit cell was estimated to be $0.73 \times 0.73 = 0.53\ nm^2$. The distance between the adjacent (3-mercaptopropyl)silyl groups for MPS–magadiite(eva) and MPS–magadiite(ref) were thus calculated to be 0.50 nm ($=(0.53/2.1)^{1/2}$) and 0.56 ($=(0.53/1.7)^{1/2}$), respectively (Table 1). Judging from the observed basal spacing (ca. 2.0 nm) and the length of MPS (1.0 nm as $SH(CH_2)_3$-$Si(OH)_2$–O), the attached MPS is thought to form an inter-

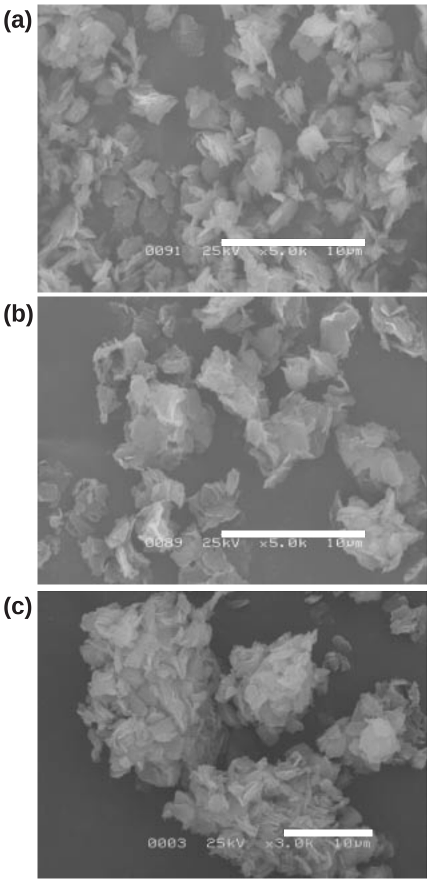

Fig. 4. SEM images of (a) MPS–magadiite(ref) and MPS–magadiite(eva) ($MPS_{1.5}$–magadiite as an example) after (b) and before (c) washing with HCl–ethanol solution. Scale bars: 10 µm.

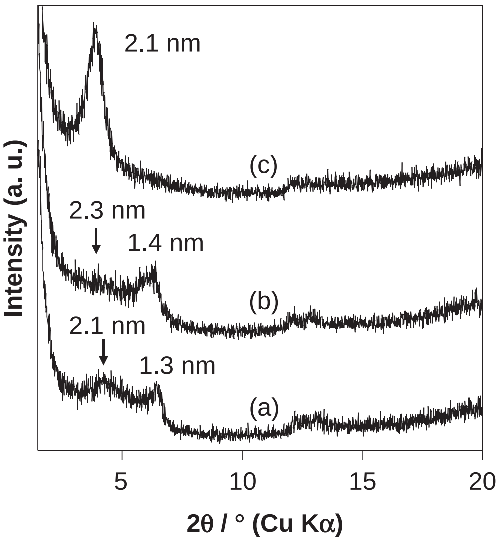

Fig. 5. XRD patterns of silylated derivatives prepared by the concentration of the mixture containing different amounts of MPS: (a) 1.0, (b) 1.5, and (c) 2.0 groups per $Si_{14}O_{29}$.

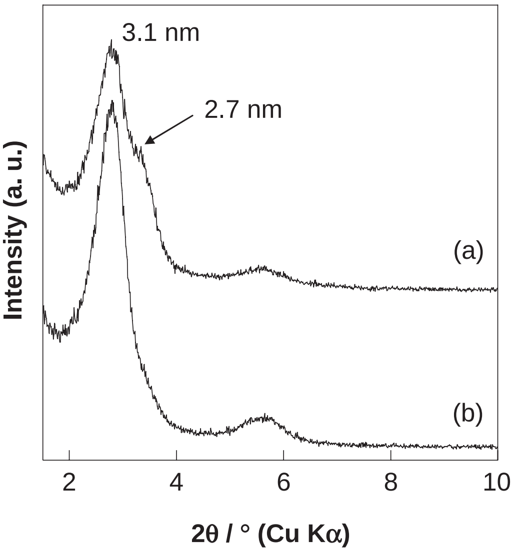

Fig. 6. XRD patterns of products accumulated at (a) earlier and (b) later stage of the concentration.

digitated monolayer arrangement in the silylated derivatives. Taking the lateral size of (3-mercaptopropyl)silyl group (0.5 nm × 0.5 nm as $SH(CH_2)_3Si(OH)_2$–O) into consideration, (3-mercaptopropyl)silyl groups densely covered the interlayer space in the two silylated derivatives.

Figure 1c depicts the XRD pattern of MPS–magadiite(eva) before washing with HCl–ethanol solution. The basal spacing was 3.3 nm, which was larger than that of C_{12}TMA–magadiite (2.8 nm), indicating the co-adsorption of C_{12}TMA and MPS in the interlayer space of the unwashed MPS–magadiite(eva). In the IR spectrum of the unwashed MPS–magadiite(eva), the intensity of the absorption band due to the interlayer silanol groups at 3641 cm^{-1} was weaker (Fig. 2c). These results show that MPS was intercalated and a part of the MPS was attached on the silicate sheet during the solvent evaporation. Upon the reaction between the intercalated MPS and the interlayer silanol groups, methanol or water is thought to be generated to make a part of the pre-intercalated C_{12}TMA, which interacted with the surface silanol group, deintercalate.[17] In the SEM image of the unwashed MPS–magadiite(eva), aggregated particles were observed, which is explained by the result that the deintercalated C_{12}TMA acts as a binder to adhere the silicate particles (Fig. 4c). After the washing, C_{12}TMA fully deintercalates and all the interlayer silanol groups react with MPS (Fig. 1d and Fig. 2d), so that the silylation becomes complete with the deintercalation of the remaining C_{12}TMA during the washing. HCl, ethanol, or by-products (methanol or water) are thought to make C_{12}TMA deintercalate.[17,26]

A silylated derivative with large surface coverage was successfully synthesized by the solvent evaporation method. We have reported that the control of the surface coverage of magadiite[10] or $K_2Ti_4O_9$[16] with octylsilyl or octadecylsilyl groups resulted in the formation of the silylated derivatives with controlled properties, such as adsorptive and swelling ones. Controlled surface coverage has been achieved by using the reflux method, in which it is difficult to tune the surface coverage directly by the amount of the added silane-coupling reagents.[10,16] The possibility controlling the surface coverage by using the solvent evaporation method was examined. Figure 5 shows XRD patterns of the silylated derivatives prepared with different amounts of MPS. When the amounts of the added MPS were small, the diffraction line due to the basal spacing splitted, indicating a heterogeneous distribution of the attached (3-mercaptopropyl)silyl groups. This phenomenon is explained as follows: the concentration of the mixture of C_{12}TMA–magadiite and MPS toluene solution proceeds the accumulation of solids on the side of a flask. When the concentration of MPS in the mixture is low, it is difficult for MPS to intercalate into C_{12}TMA–magadiite, and thus, solids with the smaller amount MPS accumulate during earlier stage of the solvent evaporation. Upon concentration of the mixture, MPS intercalates into the hydrophobic interlayer space of C_{12}TMA–magadiite to accumulate solids with a homogenous composition. Consequently, products with the heterogeneously distributed MPS are obtained. This hypothesis is supported by the result that the XRD pattern of the product, which accumulated at earlier stage of the solvent evaporation, shows the presence of a phase with the smaller basal spacing (Fig. 6).

To obtain products with the homogeneously distributed (3-mercaptopropyl)silyl groups, the reaction mixtures were allowed to react at 60 °C for 2–3 days before solvent evaporation. The XRD patterns of the products thus obtained only showed a single phase (Fig. 7). It is thought that MPS intercalates into C_{12}TMA–magadiite homogeneously during the aging. Figure 8 shows the difference in the basal spacing of MPS–magadiites(eva) with different compositions. There was a linear relationship between the basal spacing and the composition, indicating that the distance between the adjacent (3-mercaptopropyl)silyl groups varies systematically.[10,16] Note that all of the added MPS was attached in the present solvent

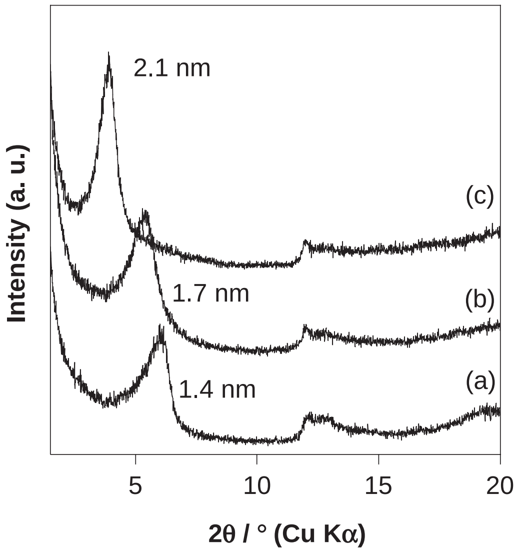

Fig. 7. XRD patterns of MPS–magadiites(eva) with different surface coverage: (a) 1.0, (b) 1.5, and (c) 2.1 groups per $Si_{14}O_{29}$.

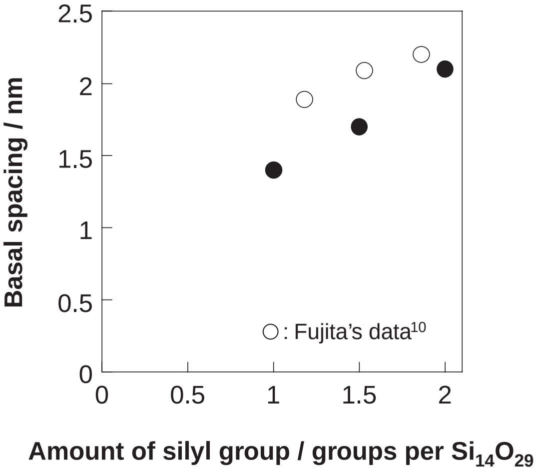

Fig. 8. Variation of the basal spacing of (●) MPS–magadiites(eva) and (○) the octyltrichlorosilane-silylated derivatives of magadiite[10] as a function of the surface coverage.

evaporation method. Precise control of the surface coverage with organosilyl group is possible by using the solvent evaporation method.

The linear relationship between the basal spacing and the amounts of the attached octylsilyl group for the silylated derivatives of magadiite with octyltrichlorosilane[10] is also shown in Fig. 8. The line was parallel to that for MPS–magadiites(eva), suggesting that the bond angle of Si–O–Si is constant regardless of the kinds of silanes and varies with the surface coverage. It is shown that the octyltrichlorosilane is attached to the interlayer surface of magadiite by bridging the two interlayer silanol groups without regard to the surface coverage.[10] Because the bond angle of Si–O–Si depends on the number of the surface silanol groups bonded to a silane coupling reagent, the parallel relationship between the two lines also suggests that (3-mercaptopropyl)trimethoxysilane is immobilized by reacting one methoxy group with the two interlayer silanol groups of the three MPS–magadiites(eva).

Conclusion

We reported the synthesis of the silylated derivative of magadiite by concentrating a mixture of the dodecyltrimethylammonium-exchanged form and a stoichiometric amount of MPS. The nanostructure and composition of the silylated derivative were comparable to those of the silylated derivative prepared by refluxing the dodecyltrimethylammonium-exchanged form with a much larger amount of the silane-coupling reagent. The surface coverage with (3-mercaptopropyl)silyl groups was controlled stoichiometrically by changing the amount of the added silane-coupling reagent. The present method should be applicable to the synthesis of the silylated derivatives of other layered solids with various silane-coupling reagents.

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