

## Perfluoroalkylsilylation of the Interlayer Silanol Groups of a Layered Silicate, Magadiite

Makoto Ogawa,<sup>\*,†</sup> Masanori Miyoshi,<sup>‡</sup> and Kazuyuki Kuroda<sup>‡,§</sup>

*Presto, Japan Science and Technology Corporation, and Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan, Department of Applied Chemistry, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169-8555, Japan, and Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda 2-8-26, Shinjuku-ku, Tokyo 169-0051, Japan*

Received September 22, 1998

Revised Manuscript Received October 26, 1998

Intercalation of organic guest species into layered inorganic solids is a way of constructing an ordered inorganic–organic assembly with unique microstructures controlled by host–guest and guest–guest interactions.<sup>1</sup> Besides the basic scientific studies on intercalation, the applications of the intercalation compounds as adsorbates,<sup>2</sup> membranes,<sup>3</sup> supports for catalysts,<sup>4</sup> and photoactive species<sup>5</sup> have extensively been investigated. The family of crystalline alkali metal polysilicates includes kanemite, makatite, octosilicate, magadiite, and kenyaite is a class of layered silicates with guest-accommodating capability.<sup>6</sup> The structure of these layered silicates is build up of one or multiple sheets of SiO<sub>4</sub> tetrahedra with hydroxylated interlayer surface. The reaction between organochlorosilanes and hydroxylated surfaces leads a creation of organically modified surfaces where organic moieties are covalently attached.<sup>7</sup> This chemistry has been applied to the modification of the interlayer space of the crystalline layered silicic acids.<sup>8,9</sup> The organosilyl derivatives are expected to have higher stability if compared with the organoammonium-exchanged silicates,<sup>10</sup> because the organic groups are attached by covalent bonds. The preparations of alkylsilylated derivatives of octosilicate,

magadiite, and kenyaite have been reported so far;<sup>8,9,11–13</sup> however, their properties and possible applications have not been well established. Very recently, we have reported the preparation of organosilylated magadiites with controlled microstructures and properties toward adsorbents with selectivity.<sup>14</sup> Further studies on the construction of unique microstructures in the interlayer space of layered silicates are worth performing.

In this paper, we report the preparation of fluoroalkylsilylated magadiite as a new type of chemically modified materials. Fluoroalkyl-containing silanes comprise a class of silylating agent due to the low surface energy associated with the fluorinated alkyl chains that, in turn, impart unique properties to the layered silicic acids. The coating of hydroxylated surface with fluoroalkylsilyl groups has been investigated to modify the surface properties of solids.<sup>15</sup> Biocompatible and water and oil repellent surfaces which are not available by the alkylsilylation have been obtained so far.

Dodecyltrimethylammonium (abbreviated as C<sub>12</sub>-TMA) exchanged silicates were used as the intermediates for the silylation. We have succeeded in the interlayer silylation with bulky organosilyl group by utilizing the C<sub>12</sub>TMA-exchanged silicates as the intermediates for the silylation.<sup>11–13</sup> The expanded hydrophobic interlayer space made it possible to introduce bulky organic groups. The C<sub>12</sub>TMA-magadiite was prepared by an ion exchange reaction between Na-magadiite, which was prepared by the method described by Kosuge et al.,<sup>16</sup> and an aqueous C<sub>12</sub>TMA chloride solution. The basal spacing of the C<sub>12</sub>TMA-magadiite was 2.81 nm (Figure 1b), which shows an expansion of the interlayer space of ca. 1.7 nm. The XRD, infrared spectrum, and the elemental (C, H, N) analysis (Table 1) were consistent with those reported previously,<sup>8,9,14,17</sup> indicating the formation of the C<sub>12</sub>TMA-magadiite with the composition of  $\{[(C_{12}TMA)_{1.8}H_{0.2}]Si_{14}O_{29}nH_2O\}$ .

The dried C<sub>12</sub>TMA-magadiite was suspended in a mixture of an organochlorosilane, [2-(perfluorohexyl)ethyl]dimethylchlorosilane (C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>SiCl; abbreviated as FHES, supplied from Chisso Co.), and toluene under nitrogen flow for 48 h, and the product was separated by centrifugation and washed with toluene and acetone. The X-ray diffraction pattern of the silylated derivative is shown in Figure 1c. Although the basal spacing (2.83 nm of the FHES-magadiite) was

\* To whom correspondence should be addressed.

<sup>†</sup> Japan Science and Technology Corp. and Department of Earth Sciences, Waseda University.

<sup>‡</sup> Department of Applied Chemistry, Waseda University.

<sup>§</sup> Kagami Memorial Laboratory for Materials Science and Technology, Waseda University.

(1) Alberti, G.; Bein, T. (Eds.) *Comprehensive supramolecular chemistry*; Pergamon: Oxford, 1996; Vol. 7.

(2) Barrer, B. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: London, 1978. Boyd, S. A.; Lee, J. A.; Mortland, M. M. *Nature* **1988**, *333*, 345–347. Boyd, S. A.; Shaobai, S.; Lee, J. F.; Mortland, M. M. *Clays Clay Miner.* **1988**, *36*, 125–130.

(3) Okahata, Y.; Shimizu, A. *Langmuir* **1989**, *5*, 954–959.

(4) Hu, N.; Rusling, J. F. *Anal. Chem.* **1991**, *63*, 2163–2168.

(5) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995**, *95*, 399–438.

(6) Lagaly, G. *Adv. Colloid Interface Sci.* **1979**, *11*, 105–148.

(7) (a) Wirth, M. J.; Fairbank, R. W. P.; Fatunmbi, H. O. *Science* **1997**, *275*, 44–47. (b) Ulman, A. *An Introduction of Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly*; Academic Press: San Diego, 1991.

(8) Ruiz-Hitzky, E.; Rojo, M. *Nature* **1980**, *287*, 28–30.

(9) Ruiz-Hitzky, E.; Rojo, M.; Lagaly, G. *Colloid Polym. Sci.* **1985**, *263*, 1025–1030.

(10) Ogawa, M.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2593–2618.

(11) Yanagisawa, T.; Kuroda, K.; Kato, C. *React. Solids* **1988**, *5*, 167–175.

(12) Yanagisawa, T.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3743–3745.

(13) Endo, K.; Sugahara, Y.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3352–3355.

(14) Ogawa, M.; Okutomo, S.; Kuroda, K. *J. Am. Chem. Soc.* **1998**, *120*, 7361–7362.

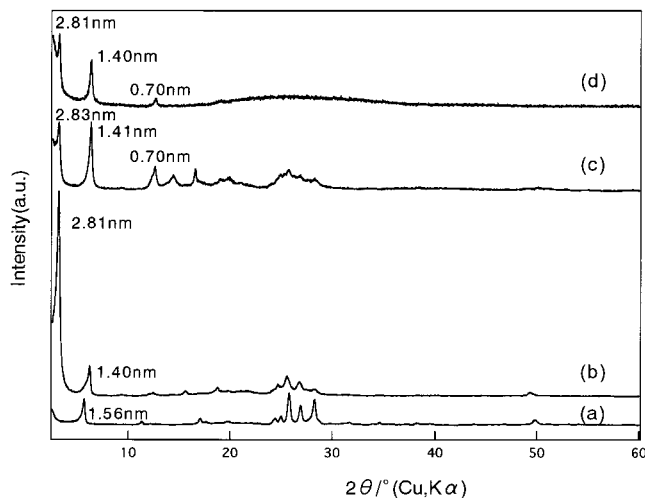
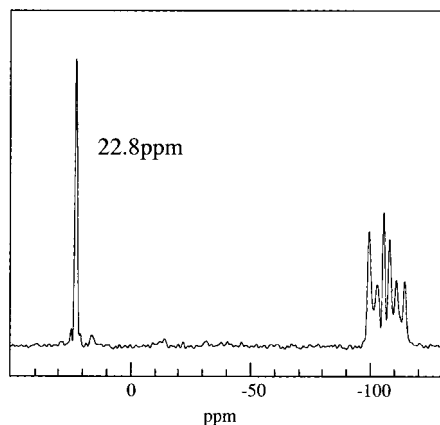
(15) (a) Tripp, C. P.; Veregin, R. P. N.; Hair, M. L. *Langmuir* **1993**, *9*, 3518–3522. (b) Tada, H.; Nagayama, H. *Langmuir* **1995**, *11*, 136–142. (c) Yoshino, N.; Yamamoto, Y.; Hamano, K.; Kawase, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1754–1758. (d) Xindu, G.; Carr, P. W. *J. Chromatogr.* **1983**, *269*, 96–102. (e) Ge, S.; Takahara, A.; Kajiyama, T. *J. Vac. Sci. Technol. A* **1994**, *12*, 2530–2536. (f) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1011–1012.

(16) Kosuge, K.; Yamazaki, A.; Tsunashima, A.; Otsuka, R. *J. Ceram. Soc. Jpn.* **1992**, *100*, 326–331.

(17) Ogawa, M.; Maeda, N. *Clay Miner.* In press.

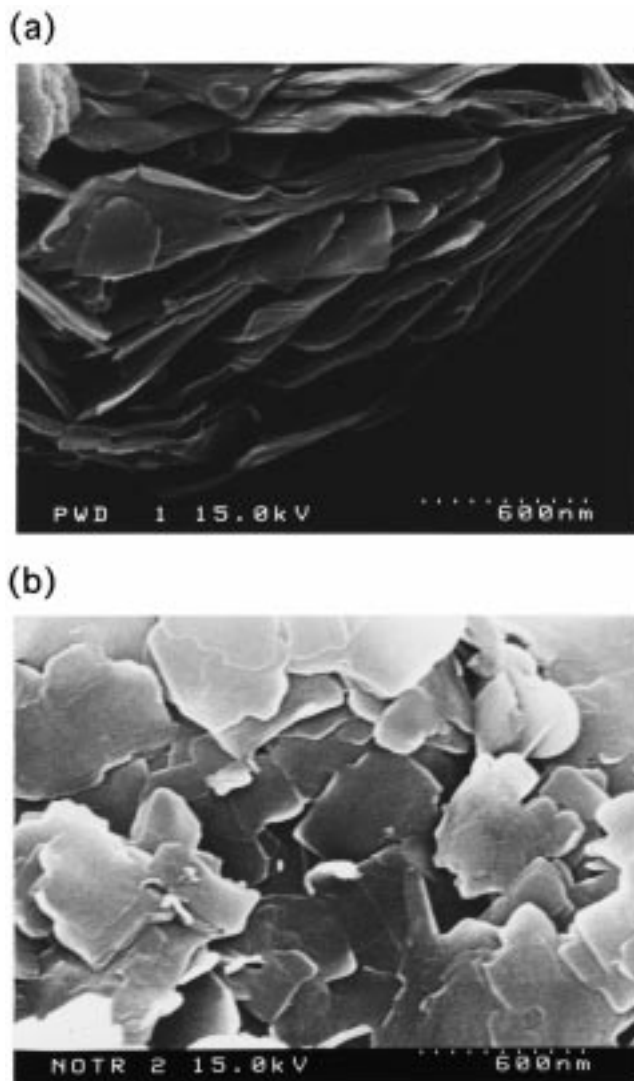
**Table 1.** the Elemental Analysis of the C<sub>12</sub>TMA-Magadiite and the FHES-Magadiite

sample	C/mass %	H/mass %	N/mass %
C <sub>12</sub> TMA-magadiite	21.2	4.48	1.62
FHES-magadiite	13.6	0.96	0.05

**Figure 1.** X-ray diffraction patterns of (a) Na-magadiite, (b) the C<sub>12</sub>TMA-magadiite, (c) the FHES-magadiite, and (d) the cast films of the FHES-magadiite.**Figure 2.** <sup>29</sup>Si MAS NMR spectrum of the FHES-magadiite.

similar to that of the C<sub>12</sub>TMA-magadiite, the introduction of the FHES groups in the interlayer space of magadiite was evidenced by IR, NMR, and elemental analysis. The infrared spectrum of the FHES-magadiite showed the decrease in the bands at 2918 and 2952 cm<sup>-1</sup> due to C–H stretching vibration of C<sub>12</sub>TMA ions and the appearance of a band ascribable to the Si–C stretching vibration of FHES group at 854 cm<sup>-1</sup>. In the <sup>29</sup>Si MAS NMR spectrum of the silylated product (Figure 2), a signal due to the M<sup>1</sup> environment of silicon (Si–O–Si–R<sub>3</sub>) appeared at 22.8 ppm, indicating that the organochlorosilane reacted with the silanol groups present in the interlayer surface to form siloxane bonds.

The deintercalation of C<sub>12</sub>TMA during the silylation was confirmed by the absence of N in the elemental analysis (Table 1) of the silylated product. From the analysis, the amount of the attached FHES group was determined to be 1.60 mol per Si<sub>14</sub>O<sub>29</sub> unit of magadiite. All these observations indicate the formation of FHES-magadiite with the formula {[FHES]<sub>1.6</sub>H<sub>0.4</sub>}[Si<sub>14</sub>O<sub>29</sub>]. The expanded interlayer space of the C<sub>12</sub>TMA-magadiite

**Figure 3.** Scanning electron micrographs of (a) the FHES-magadiite and (b) the surface of the cast film of the FHES-magadiite.

made it possible to introduce bulky FHES group in the interlayer space of magadiite.

The FHES-magadiite thus obtained showed two unique characteristics, high thermal stability and film-forming ability, which have not been achieved for analogous octyldimethylsilylated-magadiite.<sup>18</sup> The TG (thermogravimetric analysis) curve of the FHES-magadiite showed a weight loss ascribable to the oxidative decomposition of the attached FHES groups starting at 400 °C, which is much higher if compared with that (230 °C) observed for the octyldimethylsilylated-magadiite. The improved thermal stability of the FHES-magadiite is worth noting as a merit of the present materials design for practical applications.

Another important characteristic of the FHES-magadiite is a film-forming capability. A thin film of the FHES-magadiite has been prepared with the following procedure: 10 mg of the FHES-magadiite was dispersed in 10 mL of 2-(perfluorohexyl)ethanol with sonication.

(18) The octyldimethylsilylated-magadiites were prepared by the reaction between the C<sub>12</sub>TMA-magadiite and octyldimethylchlorosilane. Their preparation and characterization have been described in a separate paper.<sup>14</sup>

After the nonswelling portion was separated by centrifugation, the supernatant was cast on a trimethylsilylated-glass substrate, so that a turbid thin film formed on the substrate. The X-ray diffraction pattern of the cast film is shown in Figure 1d. The basal spacing did not change during the film preparation, indicating that 2-(perfluorohexyl)ethanol is evaporated and the attached FHES groups are retained during the film preparation. The X-ray diffraction pattern as well as the scanning electron micrograph (Figure 3) of the film showed that the film is composed of oriented aggregates of the FHES-magadiite with their basal plane parallel to the substrate.

It has been well-known that the smectite group of clay minerals form oriented films by casting the aqueous suspension on solid substrate.<sup>19</sup> The exfoliation of layered transition metal oxides,<sup>20</sup> zirconium phosphate,<sup>21</sup> and transition metal dichalcogenides<sup>22</sup> is a current topic partly because of their applications as

photocatalysts and molecular devices. However, the preparation of thin films of the organically derivatized magadiite has not been reported previously. The ability to form the suspension as well as the cast film of the FHES-magadiite may open up new opportunities for the application of layered silicates.

In summary, we have reported the synthesis of the [2-(perfluorohexyl)ethyl]dimethylsilylated derivative of a layered silicate, magadiite. Organoammonium-magadiites have been used as adsorbents,<sup>23</sup> the starting materials for pillaring,<sup>24</sup> and polymer-silicate nanocomposites.<sup>25</sup> The layered silicate modified with a perfluoroalkylsilyl group prepared in the present study is a potential material alternative to the organoammonium-exchanged materials due to its improved stability and the film-forming ability. Surface dimension and the packing of the fluoroalkyl groups are shown to be controlling factors of the oil-repellent properties.<sup>15f</sup> Since layered polysilicates with different structure and morphology are known, the fluoroalkylsilylation of layered polysilicates are worth investigating for controlled surface properties.

CM980660R

(19) Van Olphen, H. *An Introduction to Clay Colloid Chemistry*, 2nd ed.; Wiley-Interscience: New York, 1977. Hotta, Y.; Inukai, K.; Taniguchi, M.; Nakata, M.; Yamagishi, A. *Langmuir* **1997**, *13*, 6697-6703.

(20) (a) Keller, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817-8812. (b) Sasaki, T.; Watanabe, M.; Hashizume, H.; Yamada, H.; Nakazawa, H. *J. Am. Chem. Soc.* **1996**, *118*, 8329-8335. (c) Sasaki, T.; Nakano, S.; Yamauchi, S.; Watanabe, M. *Chem. Mater.* **1997**, *9*, 602-608. (d) Abe, R.; Hara, M.; Kondo, J. N.; Domen, K.; Shinohara, K.; Tanaka, A. *Chem. Mater.* **1998**, *10*, 1647-1651.

(21) Alberti, G.; Casciola, M.; Constantino, U. *J. Colloid Interface Sci.* **1985**, *107*, 256-263.

(22) Yang, D.; Sandoval, S. J.; Divigalptiya, W. M. R.; Irwin, J. C.; Frindt, R. F. *Phys. Rev. B* **1991**, *43*, 12053-1256.

(23) Kim, C. S.; Yates, D. M.; Heaney, P. J. *Clays Clay Miner.* **1997**, *45*, 881-885.

(24) (a) Landis, M. E.; Aufdembrink, B. A.; Chu, P.; Johnson, I. D.; Kirker, G. W.; Rubin, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 3819-3190. (b) Dailey, J. S.; Pinnavaia, T. J. *Chem. Mater.* **1992**, *4*, 855-863.

(25) Wang, Z.; Lan, T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2200.