

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231680931>

# Organic modification of FSM-type mesoporous silicas derived from kanemite by silylation

ARTICLE *in* LANGMUIR · MARCH 1999

Impact Factor: 4.46 · DOI: 10.1021/la9815042

---

CITATIONS

76

---

READS

26

4 AUTHORS, INCLUDING:



Tatsuo Kimura

National Institute of Advanced Industrial Sci...

82 PUBLICATIONS 1,808 CITATIONS

SEE PROFILE



Yoshiyuki Sugahara

Waseda University

164 PUBLICATIONS 2,885 CITATIONS

SEE PROFILE

# Organic Modification of FSM-Type Mesoporous Silicas Derived from Kanemite by Silylation

Tatsuo Kimura,<sup>†</sup> Shuya Saeki,<sup>†</sup> Yoshiyuki Sugahara,<sup>†</sup> and Kazuyuki Kuroda<sup>\*,†,‡</sup>

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 October 26, 1998. In Final Form: February 2, 1999

Two kinds of FSM-type mesoporous silicas with different OH densities were prepared by calcination and acid treatment and modified with various silylating agents. The density of silanol groups in acid-treated FSM was about 1.5 times as large as that in calcined FSM (2.4 OH groups nm<sup>-2</sup>), determined by thermogravimetry and <sup>29</sup>Si MAS NMR. When calcined FSM was trimethylsilylated, 73% of the surface was covered with trimethylsilyl (TMS) groups. With the increase in the alkyl chain length of chloroalkyldimethylsilanes, the pore diameter of silylated FSM-type mesoporous silicas decreased. The silylated FSM-type mesoporous silicas possessed extremely hydrophobic pores. The hydrophobicity of the surfaces was also changed by using aminopropylethoxysilanes. In contrast, when the acid-treated FSM was silylated with chlorotrimethylsilane, TMS groups came into contact with one another (surface coverage ca. 100%) because of the presence of a larger amount of silanol groups. Moreover, the sensitive control of the pore size by silylation reaction was achieved by varying a grafted number of octyldimethylsilyl (ODMS) groups. ODMS groups were located near the inner surfaces in the mesoporous silica silylated in a lesser degree, and the groups were directed toward the center of mesopores in the fully silylated mesoporous silica.

## Introduction

Mesoporous silicas have some attractive characters such as high surface area, uniform mesopores, high adsorption capacities, and so on.<sup>1,2</sup> Therefore, these materials have drawn much attention for various applications to catalysts, catalyst supports, and adsorbents in which large molecules can be accessed.<sup>3</sup> Mesoporous silicas derived from a layered polysilicate kanemite (called FSM later)<sup>1</sup> and MCM-41<sup>2</sup> are original examples. One of the characteristics of such materials is the presence of silanol (Si–OH) groups on the surface of mesopores. The Si–OH groups can be modified by esterification<sup>4,5</sup> and silylation reactions.<sup>2b,6–16</sup> The first example of trimethylsilylation of ordered me-

soporous silicas was reported by us, and the silylation reactions were directly carried out without removal of alkyltrimethylammonium (ATMA) ions.<sup>6</sup> The pore diameters of the calcined products decreased, providing mesoporous silicas with various tuned pore diameters. Mobil researchers also reported trimethylsilylated MCM-41 after removal of ATMA ions.<sup>2b</sup> The trimethylsilylated material had smaller pore diameters than unmodified MCM-41 because of the modification on the inner surfaces.

There have been further reports on organic modification of mesoporous silicas and their applications. Mn(III) Schiff-base complex<sup>9</sup> or Co-complex<sup>10</sup> was functionalized into ordered mesopores by using MCM-41 premodified with amino groups. Tatsumi et al. reported that trimethylsilylated Ti-containing mesoporous silicas exhibited a remarkable catalytic activity for oxidation of alkenes and alkanes.<sup>12</sup> Moreover, two research groups simultaneously reported that mesoporous silicas grafted with (3-mercaptopropyl)silane (≡SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH) were extremely efficient in removing toxic metal ions.<sup>13,14</sup> However, there has been little information on the distribution and coverage of the silyl groups although several schematic models have been proposed. Information on the method to control both the density of silyl groups and the resulting orientation of the alkylsilyl groups in the pores is very important for the estimation of organically modified mesoporous materials as adsorbents.

<sup>†</sup> Department of Applied Chemistry.

<sup>‡</sup> Kagami Memorial Laboratory for Materials Science and Technology.

(1) (a) Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988. (b) Inagaki, S.; Fukushima, Y.; Kuroda, K. *J. Chem. Soc., Chem. Commun.* **1993**, 680. (c) Inagaki, S.; Koiwai, A.; Suzuki, N.; Fukushima, Y.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1449.

(2) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.

(4) Ishikawa, T.; Matsuda, M.; Yasukawa, A.; Kondori, K.; Inagaki, S.; Fukushima, T.; Kondo, S. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1985.

(5) Kimura, T.; Kuroda, K.; Sugahara, Y.; Kuroda, K. *J. Porous Mater.* **1998**, *5*, 127.

(6) Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1535.

(7) Chen, J.; Li, Q.; Fu, R.; Xiao, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2694.

(8) (a) Zhao, X. S.; Lu, G. Q.; Whittaker, A. K.; Millar, G. J.; Zhu, H. Y. *J. Phys. Chem.* **1997**, *101*, 6525. (b) Zhao, X. S.; Lu, G. Q. *J. Phys. Chem.* **1998**, *102*, 1556.

(9) Sutra, P.; Brunel, D. *Chem. Commun.* **1996**, 2485.

(10) (a) Díaz, J. F.; Bedioui, F.; Briot, E.; Devynck, J.; Balkus, K. J., Jr. *MRS Symp. Proc.* **1996**, *431*, 89. (b) Díaz, J. F.; Balkus, K. J., Jr.; Bedioui, F.; Kurshev, V.; Kevan, L. *Chem. Mater.* **1997**, *9*, 61.

(11) Cauvel, A.; Renard, G.; Brunel, D. *J. Org. Chem.* **1997**, *62*, 749.

(12) Tatsumi, T.; Koyano, K. A.; Igarashi, N. *Chem. Commun.* **1998**, 325.

(13) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500.

(14) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923.

(15) (a) Anwender, R.; Roesky, R. *J. Chem. Soc., Dalton Trans.* **1997**, 137. (b) Anwender, R.; Palm, C.; Gerstberger, G.; Groeger, O.; Engelhardt, G. *Chem. Commun.* **1998**, 1811. (c) Anwender, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1998**, 847.

(16) Rhijn, W. M. V.; Vos, D. E. D.; Sels, B. F.; Bossart, W. D.; Jacobs, P. A. *Chem. Commun.* **1998**, 317.

On the basis of  $^{29}\text{Si}$  MAS NMR data,<sup>2,17</sup> MCM-type mesoporous silicas have been known to possess two kinds of Si—OH groups, which are  $\equiv\text{Si—OH}$  ( $\text{Q}^3$  environment) and  $=\text{Si}(\text{OH})_2$  ( $\text{Q}^2$  environment). The former  $\equiv\text{Si—OH}$  groups can be grouped into isolated and hydrogen-bonded ones on the basis of IR results. Chen et al. have estimated Si—OH groups as isolated and three types of hydrogen-bonded ones by silylation of MCM-41.<sup>7</sup> Zhao et al. also showed the presence of isolated  $\equiv\text{Si—OH}$  ( $\text{Q}^3$ ), hydrogen-bonded  $\equiv\text{Si—OH}$  ( $\text{Q}^3$ ), and geminal  $=\text{Si}(\text{OH})_2$  ( $\text{Q}^2$ ) in MCM-41.<sup>8a</sup> The presence of  $=\text{Si}(\text{OH})_2$  groups therefore leads to the tendency that all of the Si—OH groups in MCM-type mesoporous silicas cannot be modified.<sup>7–16</sup>

In contrast, there are few  $=\text{Si}(\text{OH})_2$  groups in FSM-type mesoporous silicas because  $^{29}\text{Si}$  MAS NMR signals due to the  $\text{Q}^2$  environment are hardly observed in FSM, owing to the original structure of kanemite composed of only a  $\text{SiO}_4$  unit with the  $\text{Q}^3$  environment.<sup>1</sup> Therefore, unreacted Si—OH groups after silylations can simply be monitored by  $^{29}\text{Si}$  MAS NMR. In our report on esterification of FSM-type mesoporous silicas, almost all of the Si—OH groups react with ethanol.<sup>5</sup> Consequently, FSM-type mesoporous silicas are suitable for both estimation of organically modified materials and formation of highly modified mesoporous silicas.

In this paper, organic modification of FSM-type mesoporous silicas was carried out by silylation under the presence of pyridine as an agent to trap hydrogen chloride generated during the reaction. For alkyltrimethylsilylated materials, two types of FSM-type mesoporous silicas prepared by calcination and extraction of ATMA ions were used to investigate the control of the pore sizes and the density of silyl groups. In addition, two kinds of amino-propylethoxysilane were used in order to control the hydrophobicity of FSM-type mesoporous silicas.

## Experimental Section

**1. Synthesis of FSM-type Mesoporous Silicas.** An octadecyltrimethylammonium ( $\text{C}_{18}\text{TMA}$ ) silicate mesophase was prepared from kanemite according to the previous paper.<sup>1b</sup> The mesophase was calcined at  $700^\circ\text{C}$  in air to remove organic fractions. This calcined FSM-type mesoporous silica was denoted as FSM(C). In this calcination stage, the  $\text{SiO}_4$  units with the  $\text{Q}^3$  environment decreased as described below. Another FSM-type mesoporous silica was prepared by extraction of surfactants in order to avoid condensation of Si—OH groups by calcination. The extraction method was as follows: 1 g of the  $\text{C}_{18}\text{TMA}$  silicate mesophase was dispersed in a mixture of 100 mL of a 5 mM acetic acid aqueous solution and 400 mL of ethanol. This dispersion was stirred at room temperature for 24 h. These procedures were carried out twice, and the resultant product was air-dried. This acid-treated FSM-type mesoporous silica was denoted as FSM(A).

**2. Silylation of FSM(C) and FSM(A).** In a typical silylation procedure, FSM(C) was preheated at  $150^\circ\text{C}$  for 3 h under vacuum. After 1 g of FSM(C) was dispersed in 50 mL of toluene, 10 mL of a silylating agent was added to this suspension. The suspension was refluxed for 24 h in the presence of 10 mL of pyridine. This procedure was performed under a  $\text{N}_2$  atmosphere. The product was washed with chloroform and toluene and air-dried. Silylated FSM(A) materials were obtained as well. Chlorotrimethylsilane ( $\text{TMS—Cl}$ ), chlorobutyltrimethylsilane ( $\text{BDMS—Cl}$ ), and chlorooctyltrimethylsilane ( $\text{ODMS—Cl}$ ) were used without further purification. (3-Aminopropyl)dimethylethoxysilane ( $\text{APDMS—OEt}$ ) and (3-aminopropyl)triethoxysilane ( $\text{APS—OEt}_3$ ) were also used in order to investigate the degree of the hydrophobicity of modified FSM-type materials. In this case, pyridine was not added to the suspension. All of the silylating agents were obtained from

Chisso Chemical Co. Such a silylated FSM-type material was, for example, denoted as  $\text{TMS—FSM(C)}$ .

**3. Characterization.** Powder X-ray diffraction (XRD) patterns were obtained by using a Mac Science MXP<sup>3</sup> diffractometer with monochromated  $\text{Cu K}\alpha$  radiation. IR spectra were recorded on a Perkin-Elmer FTIR-1640 spectrometer by a Nujol technique after samples were dehydrated at  $120^\circ\text{C}$ . Most of the Si—OH groups after silylation should be isolated, so that the amount of Si—OH groups which might be involved in condensation during the treatment at  $120^\circ\text{C}$  should be very small. Thermogravimetric differential thermal analysis (TG-DTA) curves were obtained by a Mac Science 2000S apparatus. The density of Si—OH groups was calculated on the basis of the mass loss in the range higher than  $150^\circ\text{C}$  in order to eliminate the amount of adsorbed water. Solid-state  $^{29}\text{Si}$  MAS NMR measurement was performed on a JEOL GSX-400 spectrometer at a spinning rate of 5 kHz and a resonance frequency of 79.30 MHz with a  $45^\circ$  pulse length of 4.1  $\mu\text{s}$  and a recycle time of 60 s.  $^{29}\text{Si}$  MAS NMR spectra were deconvoluted with a standard MacFID software.<sup>18</sup> Solid-state  $^{13}\text{C}$  CP/MAS NMR was performed at a spinning rate of 5 kHz and a resonance frequency of 100.40 MHz with a pulse length of 5.1  $\mu\text{s}$  and a recycle time of 5 s. The chemical shifts were expressed with respect to tetramethylsilane. The amounts of organic fractions in the silylated products were determined by CHN analysis (Perkin-Elmer PE-2400II). Nitrogen adsorption isotherms were obtained by using a BELSORP 28 (Bel Japan, Inc.) at 77 K. Corresponding pore size distributions were calculated by the Horváth-Kawazoe method.<sup>19</sup> Water adsorption isotherms were obtained by using a BELSORP 18 (Bel Japan, Inc.) at 298 K, and the equilibrium was kept for 500 s after the change of pressure at each measurement point was below 4.0 Pa ( $3 \times 10^{-2}$  Torr). Samples were heated at  $120^\circ\text{C}$  for 3 h to a residual pressure of 1.3 Pa ( $10^{-2}$  Torr) prior to these adsorption measurements.

## Results and Discussion

**1. Characterization of FSM(C) and FSM(A).** The XRD patterns of both FSM(C) and FSM(A) showed four peaks in low  $2\theta$  angle assignable to a hexagonal structure; both of the  $d_{100}$  values were 4.2 nm. The  $\text{N}_2$  isotherms of FSM(C) and FSM(A) showed type IV behavior characteristic of mesoporous materials.<sup>1,2</sup> The BET surface areas, the pore volumes, and the average pore diameters are shown in Table 1. From these XRD and  $\text{N}_2$  adsorption results, there are no particular differences in the porosities between FSM(C) and FSM(A) obtained by calcination and acid treatment, respectively.

The  $^{29}\text{Si}$  MAS NMR spectra of the  $\text{C}_{18}\text{TMA}$  silicate mesophase, FSM(C), and FSM(A) are shown in Figure 1. In the  $^{29}\text{Si}$  MAS NMR spectrum of the  $\text{C}_{18}\text{TMA}$  silicate mesophase, the broad peaks due to the  $\text{Q}^3$  and  $\text{Q}^4$  environments were observed at around  $-100$  and  $-109$  ppm, respectively. The  $\text{Q}^3/\text{Q}^4$  ratio of the  $\text{C}_{18}\text{TMA}$  silicate mesophase was ca. 1.1. The spectrum of FSM(C) exhibited a large peak due to the  $\text{Q}^4$  environment with a shoulder peak due to the  $\text{Q}^3$  environment; the  $\text{Q}^3/\text{Q}^4$  ratio was ca. 0.3. This  $\text{Q}^3$  peak implies the presence of  $\equiv\text{Si—OH}$  groups. These results indicate that condensation of  $\equiv\text{Si—OH}$  groups occurred during calcination up to  $700^\circ\text{C}$  and that a relatively small amount of  $\equiv\text{Si—OH}$  groups is present in FSM(C). In the  $^{29}\text{Si}$  MAS NMR spectrum of FSM(A), both  $\text{Q}^3$  and  $\text{Q}^4$  peaks were distinctly observed at  $-101$  and  $-110$  ppm, respectively. The  $\text{Q}^3/\text{Q}^4$  ratio of FSM(A) (ca. 0.5) suggests that a larger number of  $\equiv\text{Si—OH}$  groups is present after extraction of surfactants.  $^{13}\text{C}$  CP/MAS NMR and TG-DTA analyses of FSM(A) showed the presence of a slight amount of  $\text{C}_{18}\text{TMA}$  ions (ca. 5 wt %). A small amount of ethoxy groups which were probably

(17) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2317.

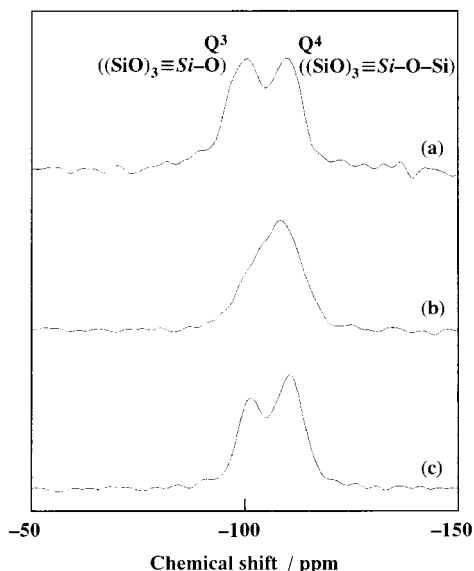
(18) The software is an NMR data processing software which has been programmed to read data files from almost any commercial spectrometers. The errors inherent in the process are roughly on the order of 10%. The user's manual can be obtained from Tecmag, Inc.

(19) Horváth, G.; Kawazoe, K. *J. Chem. Eng. Jpn.* **1983**, *16*, 470.

**Table 1. Characteristics of FSM-Type Mesoporous Silicas and the Silylated FSMs and Grafted Numbers of the Organic Groups in the Silylated FSMs**

	BET surface area/ (m <sup>2</sup> g <sup>-1</sup> )	pore volume/ (mL g <sup>-1</sup> )	pore size/ nm	carbon content/ (wt %)	no. of grafted groups <sup>a</sup> /nm <sup>-2</sup>
FSM(C)	850	0.63	3.6		
TMS-	570	0.40	2.9	7.3	1.7
BDMS-	560	0.38	2.6	10.4	1.3
ODMS-	360	0.23	2.3	16.4	1.3
APDMS-	410	0.38	2.8	9.8	1.1
APS-	410	0.20	2.2	10.6	1.7
FSM(A)	890	0.70	3.6		
TMS-	430	0.37	3.1	10.0	2.4
ODMS-	280	0.21	2.2	16.0	1.2

<sup>a</sup> The grafted numbers for all of the silylated materials were calculated by the carbon contents of the silylated products and the BET surface areas of FSM(A) and FSM(C).

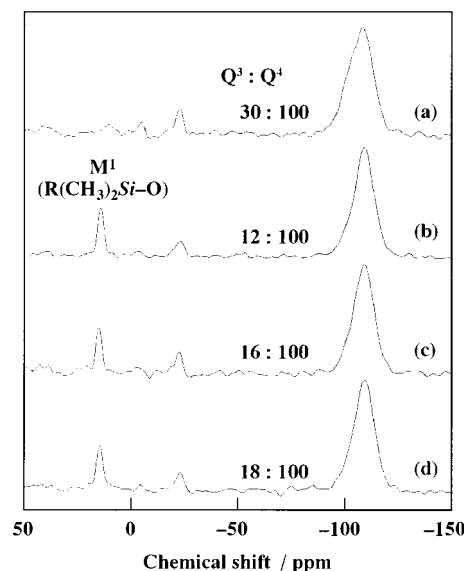
**Figure 1.** <sup>29</sup>Si MAS NMR spectra of (a) C<sub>18</sub>TMA silicate mesophase, (b) FSM(C), and (c) FSM(A).

formed in the stage of extraction was also detected (ca. 3 wt %). The residual C<sub>18</sub>TMA ions were eliminated during silylation reactions, which was confirmed by CHN analysis, indicating the absence of nitrogen atoms in all of the silylated FSM(A) materials.

The density of ≡Si-OH groups in FSM(C) was estimated to be 2.4 groups nm<sup>-2</sup> based on the mass loss in the range of 150–1100 °C. However, an accurate estimation of ≡Si-OH groups in FSM(A) by TG was impossible because it contained small amounts of both C<sub>18</sub>TMA ions and ethoxy groups. The density of ≡Si-OH groups in FSM(A) was estimated to be 3.6 groups nm<sup>-2</sup>, being calculated by the comparison of the Q<sup>3</sup>/Q<sup>4</sup> ratios of FSM(C) and FSM(A) monitored by <sup>29</sup>Si MAS NMR. The nature of surface ≡Si-OH groups was investigated by IR. The IR spectra of FSM(C) and FSM(A) showed that the bands due to ν<sub>OH</sub> of ≡Si-OH groups were observed at 3692 and 3672 cm<sup>-1</sup>, respectively. The difference of the wavenumbers suggests that the ≡Si-OH groups in FSM(A) are in a stronger hydrogen-bonded state than those in FSM(C).

**2. Silylation with Chloroalkyldimethylsilanes.** The XRD patterns of all of the silylated FSM(C) showed that their hexagonal structures are retained with the same *d*<sub>100</sub> values (4.2 nm) as that observed for parent FSM(C), indicating the successful silylation without collapse of the original hexagonal structure.

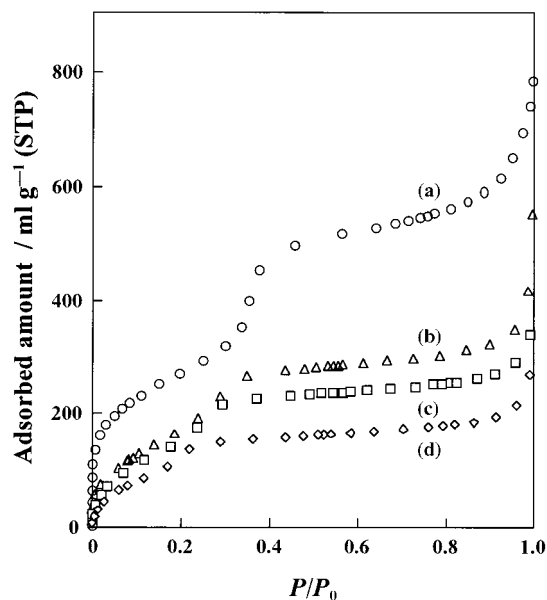
The <sup>29</sup>Si MAS NMR spectrum of TMS-FSM(C) and the ratio of Q<sup>3</sup>/Q<sup>4</sup> are shown in Figure 2. The spectrum of TMS-FSM(C) indicated that an intense Q<sup>4</sup> peak with a

**Figure 2.** <sup>29</sup>Si MAS NMR spectra of (a) FSM(C), (b) TMS-FSM(C), (c) BDMS-FSM(C), and (d) ODMS-FSM(C).

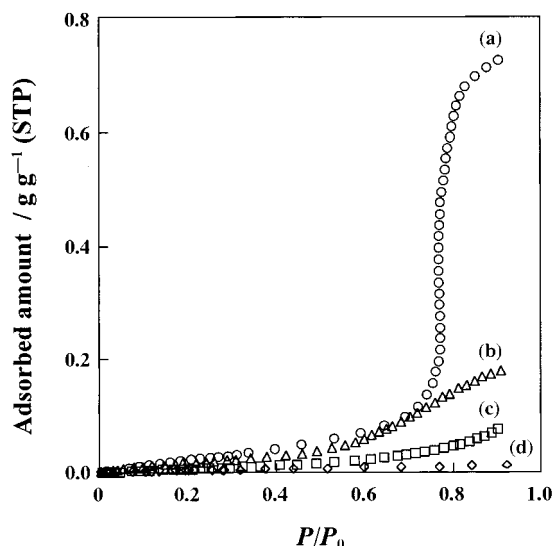
very small Q<sup>3</sup> peak was observed and that a M<sup>1</sup> peak, which is assignable to fixed silyl groups, appeared. This result exhibits that a very large number of the ≡Si-OH groups reacted with TMS-Cl. The grafted number of TMS groups was 1.7 groups nm<sup>-2</sup>. The projected surface area of the TMS groups as a cylinder is estimated to be about 0.43 nm<sup>2</sup>.<sup>20</sup> Accordingly, the surface coverage with TMS groups is calculated at ca. 73%. The highest surface coverage of TMS groups in MCM-41 is 85% only when parent MCM-41 was preheated over 450 °C.<sup>8b</sup> When MCM-41 is treated at below 300 °C under vacuum, the coverage is 30–44%.<sup>8b</sup> In our system, FSM(C) was pretreated at 150 °C for 3 h under vacuum; nevertheless, TMS-FSM(C) showed a higher degree of surface modification. This result may partly be caused by the presence of pyridine as a trapping agent of hydrogen chloride.

The <sup>29</sup>Si MAS NMR spectra of BDMS- and ODMS-FSM(C) are shown in Figure 2. Both of the spectra showed the Q<sup>4</sup> and M<sup>1</sup> peaks with a small Q<sup>3</sup> peak. This result also indicates that a large number of ≡Si-OH groups reacted with BDMS-Cl or ODMS-Cl. The N<sub>2</sub> adsorption isotherms of unmodified and silylated FSM(C) are shown in Figure 3. The adsorbed amount and the relative pressure of capillary condensation decreased with an increase in the alkyl chain length of the alkyldimethylsilyl groups. The BET surface areas, the pore volumes, and the average pore diameters are listed in Table 1. All of the values decreased as the length of the alkyl chains increased. The





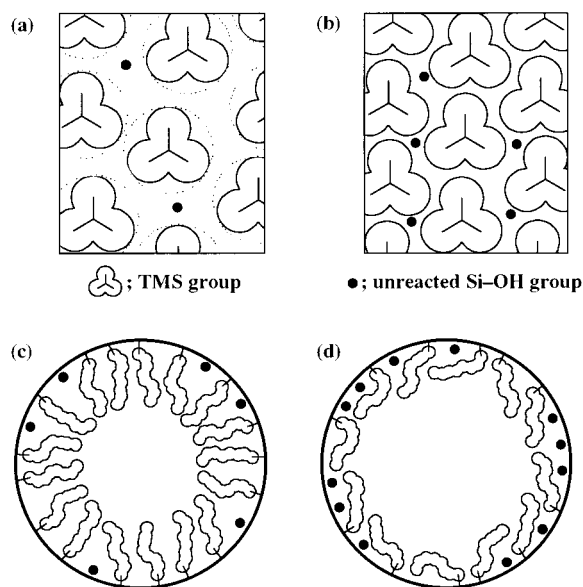
**Figure 3.** Nitrogen adsorption isotherms of (a) FSM(C), (b) TMS-FSM(C), (c) BDMS-FSM(C), and (d) ODMS-FSM(C).



**Figure 4.** Water adsorption isotherms of (a) FSM(C), (b) APS-FSM(C), (c) APDMS-FSM(C), and (d) BDMS-FSM(C).

decrease in the pore volume is related to the successful modification of inner surfaces of FSM(C); the  $^{13}\text{C}$  CP/MAS NMR spectra of all of the silylated FSM(C) showed typical signals due to carbon atoms of TMS, BDMS, and ODMS groups.<sup>21</sup> Recently, Jaroniec et al. have reported a similar tendency for silylation of MCM-41 with a large pore of 5.0 nm.<sup>22</sup>

**3. Hydrophobicity of Silylated FSM(C).** The hydrophobic nature of the silylated FSM(C) was examined by water adsorption measurement. The water adsorption isotherms of unmodified FSM(C) and BDMS-, APDMS-, and APS-FSM(C) are shown in Figure 4. The isotherms of TMS- and ODMS-FSM(C) (not shown in Figure 4 for clarity) are the same as that of BDMS-FSM(C). The isotherm of the unmodified FSM(C) showed type V behavior, indicating weak interaction between the surface of FSM(C) and water molecules. The increase in the



**Figure 5.** Proposed distributions of TMS groups in (a) TMS-FSM(C) and (b) TMS-FSM(A) and those of ODMS groups with (c) large and (d) small grafted numbers.

adsorbed amount was observed at a relative pressure of ca. 0.7. The adsorbed amount of water for BDMS-FSM(C) was much lower than those observed for TMS-MCM-41<sup>8b</sup> and phenyl-modified MCM-41.<sup>23</sup>

The isotherms of APS-, APDMS-, and BDMS-FSM(C) showed that adsorbed amounts of water intensely decreased (0.18 g g<sup>-1</sup> for APS-FSM(C), 0.08 g g<sup>-1</sup> for APDMS-FSM(C), and 0.01 g g<sup>-1</sup> for BDMS-FSM(C)) as compared with that observed for the unmodified FSM(C) (0.72 g g<sup>-1</sup>). This result indicates that the degree of hydrophobicity is variable according to the functional groups of the silylating agents. The difference in the hydrophobic nature of the silylated products is caused by the presence of alkyl or aminopropyl groups. Although both APS- and APDMS-FSM(C) have aminopropyl groups, the hydrophobicities are different. The grafted numbers of aminopropyl groups were 1.7 and 1.1 groups nm<sup>-2</sup>, respectively. The difference is due to the number of reactive groups in the silylating agents.

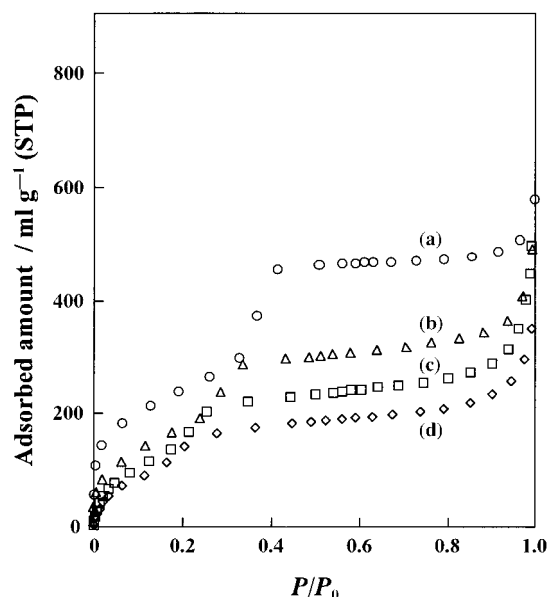
**4. Variation in the Density of Alkyldimethylsilyl Groups.** On the basis of the surface coverage of TMS groups (73%) on the surface of TMS-FSM(C), the distribution of TMS groups is shown in Figure 5a. Although a large number of the Si-OH groups in FSM(C) reacted with TMS-Cl, FSM(A) with a higher OH density was used to achieve higher surface coverage by TMS groups. The grafted number of TMS groups was 2.4 groups nm<sup>-2</sup> in TMS-FSM(A), and the surface coverage of TMS groups is calculated to be slightly higher than 100% (103%) if the TMS group is assumed as a cylinder.<sup>20</sup> Consequently, the modified shape (a "clover" type) of the TMS group is employed, and the distribution is shown in Figure 5b. In comparison with the TMS groups in TMS-FSM(C), those in TMS-FSM(A) are highly packed. Therefore, the silylation reaction fully proceeds, and no further silylation reactions occur for TMS-FSM(A).

The arrangement of ODMS groups was also discussed on the basis of the grafted numbers and the pore sizes of the silylated materials. Both ODMS-FSM(C) and ODMS-FSM(A) have almost the same grafted numbers (1.2–1.3 groups nm<sup>-2</sup>). This fact indicates that the grafted number

(21) Hays, G. R.; Clague, A. D. H.; Huis, R.; Velden, G. V. D. *Appl. Surf. Sci.* **1982**, *10*, 247.

(22) Jaroniec, C. P.; Kruk, M.; Jaroniec, M.; Sayari, A. *J. Phys. Chem.* **1998**, *102*, 5503.

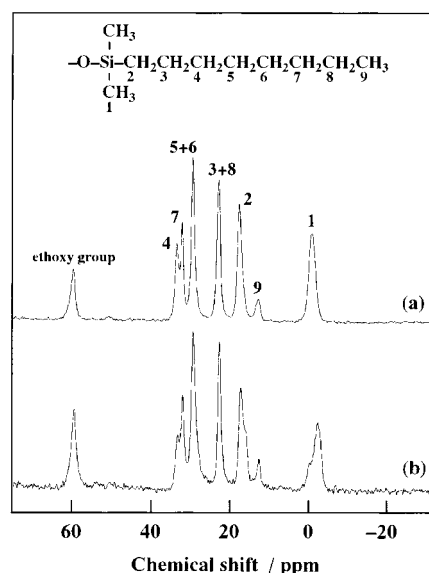
(23) Bambrugh, C. M.; Slade, R. C. T.; Williams, R. T.; Burkett, S. L.; Sims, S. D.; Mann, S. *J. Colloid Interface Sci.* **1998**, *201*, 220.



**Figure 6.** Nitrogen adsorption isotherms of (a) FSM(A) and ODMS-FSM(A) silylated with (b) 0.05, (c) 0.5, and (d) 1.0 mL of ODMS-Cl. The pore sizes of silylated FSM(A) were 3.0, 2.5, and 2.3 nm, respectively.

of ODMS groups is limited by their steric hindrance. If the octyl groups have all-trans conformation (length of the octyl group 0.51 nm), the size of ODMS group is calculated to be 0.74 nm; the pore size of the silylated materials decreases from 3.6 to 2.1 nm. Actually, the pore sizes decreased from 3.6 to 2.2–2.3 nm by the presence of ODMS groups. The proposed distribution of ODMS groups is shown in Figure 5c, showing that the octyl groups are directed to the center of mesopores.

In addition, we tried to prepare ODMS-FSM(A) with lower grafted numbers. The  $N_2$  adsorption isotherms of unmodified FSM(A) and ODMS-FSM(A) with various grafted numbers are shown in Figure 6. With an increase in the amount of ODMS groups, the adsorbed amount and the relative pressure of capillary condensation decreased as in the case of the products derived with the silylating agents with different alkyl chain lengths. ODMS-FSM(A) with the lowest grafted number has a pore size of 3.0 nm. This value is very similar to those of TMS-FSM(A) and TMS-FSM(C). Therefore, it is considered that the octyl groups are located near the surface (Figure 6d). Although the pore size can be controlled by using silylating agents with different alkyl chain lengths, the size is merely varied with the alkyl chain length. More sensitive control of the pore size by silylation reactions is possible by using the change in the grafted number of ODMS groups.



**Figure 7.** Kimura et al.

## Conclusions

FSM-type mesoporous silicas with different densities of silanol groups were silylated using chloroalkyldimethylsilanes and aminopropylethoxysilanes. When silylating agents are properly chosen, the pore size and the hydrophobicity can be controlled. On the basis of the relation between the grafted number of silyl groups and the change of pore sizes, the distribution and the arrangement of trimethylsilyl and octyldimethylsilyl groups have been presented. In this system, a large number of Si-OH groups in calcined FSM-type mesoporous silica can react with chlorotrimethylsilane. When acid-treated FSM-type mesoporous silica which has a larger amount of Si-OH groups was used, all of the surfaces were covered with trimethylsilyl groups. The reaction between octyldimethylsilane and Si-OH groups is suppressed to some extent because of their steric hindrance. Octyl groups in octyldimethylsilyl groups were directed to the center of mesopores or were located near the surface depending on the grafted numbers of octyldimethylsilyl groups. Further investigation is necessary for the mobility and conformation of fixed alkyl chains under practical conditions where the modified mesoporous materials are utilized as adsorbents and catalysts.

**Acknowledgment.** The financial assistance from a Grant-in-Aid for the Special Priority Area by the Ministry of Education, Science, and Culture of the Japanese Government is gratefully acknowledged.

LA9815042