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Preparation of Porous Silica-Pillared Layered Phase: Simultaneous Intercalation of Amine-Tetraethylorthosilicate into the H^+-Magadiite and Intragallery Amine-Catalyzed Hydrolysis of Tetraethylorthosilicate

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Porous silica-pillared H^+-magadiites were prepared by intragallery amine-catalyzed hydrolysis of TEOS [tetraethylorthosilicate, $Si(OC_2H_5)_4$]. Mixtures of the H^+-magadiite, dodecylamine, and TEOS at molar ratios of 1:2:15−30 and 1:2−10:20 resulted in swollen and viscous gel once at room temperature, allowing intercalation compounds in which dodecylamine and TEOS were simultaneously intercalated into interlayers of H^+-magadiite. The hydrolysis of the gallery TEOS was conducted in water solution for 40 min at room temperature, affording siloxane-pillared H^+-magadiites with a gallery height of between 30.2 and 39.2 Å. Calcination of samples at 538 °C in air resulted in silica-pillared magadiites with large specific surface areas between 607 and 830 m^2/g, depending on the reaction stoichiometry. The reaction at H^+-magadiite:dodecylamine:TEOS reaction stoichiometries of 1:2:15 and 1:6:20 resulted in optimum specific surface areas and mesopores with a narrow pore size distribution. Result indicates that the intragallery amine catalyzes the hydrolysis of gallery TEOS and simultaneously has a role of gallery-templated micellar assemblies.

Introduction

A few researchers[1−10] have reported that layered materials such as magadiite, kenyaite, and clay minerals could be transformed into pillared porous derivatives. In the recent years, Landis et al.[1] and Pinnavaia et al.[2,11] found that the pillaring could be facilitated by utilizing a preswelling step in which the interlayer is exposed to quaternary ammonium ion or long-chain amines. Although preswelling procedure is very effective route for the preparation of silica-pillared porous derivatives, it is of no practical use because it is a nonquantitative experimental process, is time-consuming, and uses expensive reagent such as TEOS (tetraethylorthosilicate) and long-chain amines. Recently, Kwon et al.[9] reported that the intercalation of octylamine into H^+-magadiite in organic solvents resulted in additional increase in gallery height than that in only octylamine. They indicated that the solvation of interlayer amine by the solvent molecules resulted in co-intercalation of the solvent molecules.

If pillar precursor TEOS is uses as a solvent, during intercalation of amine into the H^+-layered silicate in amine−TEOS solution, the TEOS can be intercalated into the interlayer with amine molecules. This is capable of introducing pillar precursor TEOS directly into the interlayer of layered phase without preswelling process by amine or quaternary ammonium ions, allowing simultaneous intercalation of amine and pillar precursor TEOS into the interlayer. The solid amines with the different chain length also can be conveniently used as gallery height expanders because of their good solubility in TEOS. This process allows treating quantitatively with the relationship among layered phase, gallery expander amine and pillar precursor TEOS in pillaring process. Although this appears to be a promising route in the preparation of pillared porous derivatives, the related study has not been conducted yet. In this paper, synthetic strategy was focused on the simultaneous intercalation of TEOS and dodecylamine into the H^+-magadiite without the preswelling step, and the catalytic function of dodecylamine as gallery template during the hydrolysis of gallery TEOS. We report that the intercalation of dodecylamine and TEOS into the H^+-magadiite can happen simultaneousiy in dodecylamine-TEOS solution, and successive interlamellar

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hydrolysis of TEOS in water results in porous silica-pillared H^+-magadiites (SPM). Our method is quite different from previous methods[1,2,11] which introduced pillar precursor TEOS into the interlayer by the partial exchange of interlayer amine by excess TEOS, after initial expansion of gallery height by the preintercalation of amine or quaternary ammoniun cation. Results indicate that the interlayer amine acts as the gallery height expander as well as the base catalyst and the intragallery template during interlamellar hydrolysis of TEOS. This method has the advantage of allowing silica-pillared derivatives from the layered phase for a short time by quantitative procedure with small amount of reagent without preintercalation by amine or quaternery ammonium cation.

Experimental Section

Synthesis of Na-Magadiite and H^+-Magadiite. Materials used were silica gel (Wakogel, Q-63), analytical reagent grade of NaOH, Na_2CO_3, ammonia water, and HCl. Tetraethylorthosilicate and dodecylamine were special grade (Aldrich, Milwaukee, WI).

Synthetic Na-magadiite was prepared by the reaction of $NaOH/Na_2CO_3-SiO_2$ system under hydrothermal conditions using a method analogous to those described by Fletcher and Bibby.[12] The experiment was carried out in a stainless steel autoclave without stirring for 60 h at 150 °C under autogenous pressure, using molar ratios of $SiO_2:NaOH:Na_2CO_3:H_2O = 15:1:2:300$. The product was filtered and washed with deionized water to remove excess NaOH or Na_2CO_3, and dried at 40 °C. H^+-magadiite was prepared by the ion exchange of Na-magadiite for H^+ in 0.1 N HCl solution using the method of Beneke and Lagaly.[13] The suspension, composed of Na-magadiite (40 g) and deionized water (500 mL), was titrated slowly with 0.1 N HCl solution to a final pH 1.8 and then maintained at the same value for an additional 24 h. H^+-magadiite was recovered by filtering, washed with deionized water until Cl-free, and then dried in air at 40 °C.

Silica-Pillared H^+-Magadiite Derivatives. Mixtures of H^+-magadiite, dodecylamine and TEOS at molar ratios in the range 1:2−10:20 and 1:10:15−30 were allowed to react for 5 h at room temperature. Under these condition, the galleries were expanded by the intercalation of dodecylamine and solvation of interlayer dodecylamine by TEOS, resulting in dodecylamine/TEOS co-intercalated H^+-magadiite gel. The gel was recovered by decanting unreacted solution after centrifugal separation.

Interlamellar hydrolysis of intercalated-TEOS was conducted in pure water solution. The reaction was conducted by dispersing dodecylamine/TEOS co-intercalated H^+-magadiite pastes in 10 mL of deionized water with stirring for 30 min at room temperature. Viscous gray gels changed into white solid after 5 min. The sample was filtered, washed three times with ethanol, and oven dried at 90 °C. Dried powders were calcined at 538 °C for 4 h in air to remove water, intragallery template dodecylamine and organic byproducts from TEOS hydrolysis.

X-ray diffraction data were recorded using a Rigaku diffractometer with Cu Kα radiation. Nitrogen adsorption/desorption isotherms were determined by Micromeritics ASAP 2000 at 77 K. All samples were outgassed at 300 °C under a vacuum for 4 h. Specific surface area was determined by the BET equation, and the pore size distribution of SPM derivatives was determined by the method of Horvath and Kawazoe equation.[14] The scanning electron micrographs (SEM) were obtained from a JEOL JSM-840A scanning electron microscope. Thermogravimetric analysis (TGA) was performed in air by using a Dupont 9900 thermogravimetric analyzer. All samples were heated to 900 °C at a heating rate of 10 °C/min. ^{29}Si MAS NMR was performed on a Bruker AM 300 solid NMR spectrophotometer.

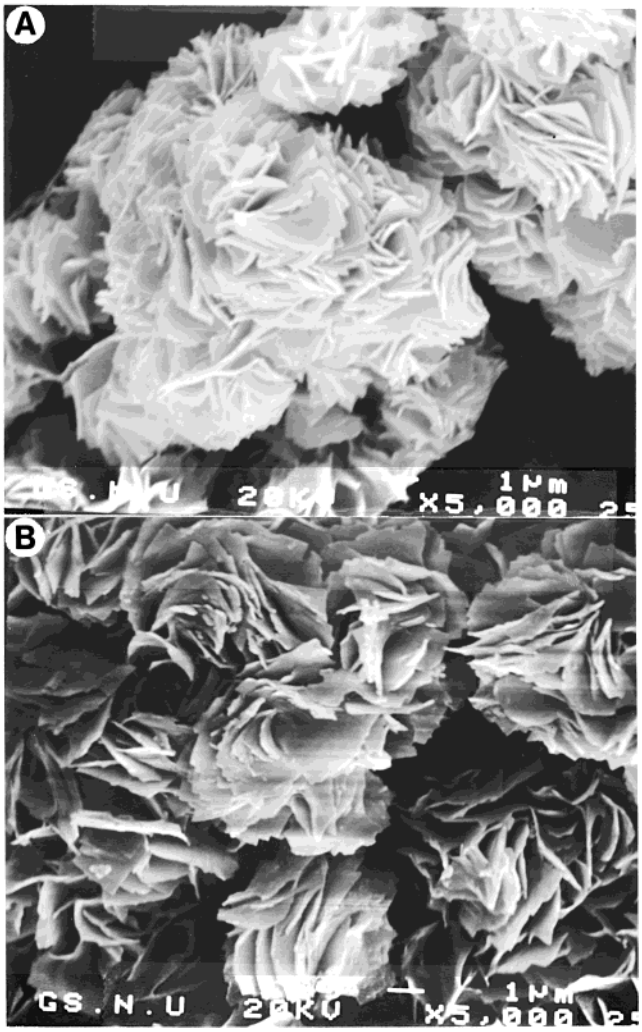

Figure 1. Scanning electron micrographs of Na-magadiite (A) and H^+-magadiite (B).

Results and Discussion

Synthesis of Na-Magadiite and H^+-Magadiite: Hydrothermal reaction of silica gel for 60 h at 150 °C produced well-crystallized Na-magadiite. The X-ray powder diffraction pattern of an air-dried product exhibits several 00*l* reflections corresponding to a basal spacing of 15.7 Å. The peak positions for this synthetic product agree closely with the values reported previously.[13] The slow titration of Na-magadiite with 0.1 N HCl resulted in the exchange of Na^+ for H^+ in the layer structure. The X-ray powder diffraction pattern of air-dried H^+-magadiite exhibits 00*l* reflections corresponding to a basal spacing of 11.8 Å, in agreement with earlier work.[13] The decrease in basal spacing indicates a loss of interlayer H_2O upon replacement of Na^+ by H^+.

The scanning electron micrographs of Na-magadiite and H^+-magadiite are shown in Figure 1. Na-magadiite in Figure 1A shows a particle morphology composed of silicate layers intergrown to form spherical nodules resembling rosettes. H^+-magadiite in Figure 1B also exhibits the particle morphology characteristic of Na-

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Table 1. Composition of Synthetic Na-Magadiite and H^+-Magadiite

	weight percent				atomic ratio		
samples	Na_2O^a	$SiO_2{}^a$	H_2O	total	Na^a	Si^a	H_2O
Na-magadiite	6.1	80.2	13.5	99.8	2.06	14	7.9
H^+-magadiite	–	96.1	3.9	100	–	14	2.5

[a] EDS data.

magadiite. The chemical compositions of Na-magadiite and H^+-magadiite were obtained by combining the results of thermogravimetric analysis and EDS analysis (the content of silica and sodium). The thermogravimetric curve was shown that air-dried Na-magadiite lost 12% of its total weight as water below 300 °C. An additional 1.5 wt % is lost between 300 °C and 900 °C. The weight loss above 300 °C is assigned to the dehydration of silanol groups. The chemical compositions of Na-magadiite and H^+-magadiite are listed in Table 1. By combining the Na_2O (6.1 wt %), SiO_2 (80.2 wt %), and weight loss, we obtained an empirical composition for synthetic Na-magadiite of $Na_2Si_{14}O_{29}\cdot 8H_2O$, which compares well with the earlier work of Lagaly et al.,[15] Grace et al.[16] and McAtee et al.[17] (The degree of hydration can be different due to sample treatments.) Thermal analysis of H^+-magadiite indicated an initial weight loss of 1.2% below 300 °C due to the desorption of H_2O. The 2.7% weight loss above 300 °C is attributed to the elimination of OH groups from the structure. From the water loss together with the absence of sodium, we obtained an empirical unit cell composition of $H_{2.0}Si_{14}O_{29}\cdot H_2O$ for H^+-magadiite.

Interlamellar Hydrolysis of TEOS. Mixtures of the H^+-magadiite, dodecylamine and TEOS at molar ratios in the range 1:2:15–30 and 1:2–10:20 resulted in a swollen and viscous gel, allowing intercalation compounds in which dodecylamine and TEOS were simultaneously intercalated into the interlayers of H^+-magadiite. Kwon et al.[9] showed that the gallery height of octylamine-intercalated H^+-magadiite could be greatly affected by a type of solvent molecules introduced. They also indicated that the additional increase in gallery height was attributed to the steric effect such as an arrangement and size of solvated molecules accompanied by the solvation of interlayer amine by solvent molecules.

Addition of water for the gels resulted in intragallery amine-catalyzed hydrolysis of TEOS. The hydrolysis of TEOS in the existence of gallery amine happens within 5 min in pure water, allowing siloxane-pillared H^+-magadiites with well-ordered basal spacings. Figure 2 exhibits powder X-ray diffraction patterns for siloxane-pillared samples prepared at H^+-magadiite:dodecylamine:TEOS reaction stoichiometries of 1:2:15 (SPM-1), 1:2:20 (SPM-2), 1:2:30 (SPM-3), 1:6:20 (SPM-4), and 1:10:20 (SPM-5). These products exhibit refractions corresponding to basal spacings of 44.1, 48.3, 51.4, 42.2, and 32.8 Å, respectively. Since the layer thickness of H^+-magadiite is 11.8 Å, the corresponding gallery heights are 32.3, 36.5, 39.6, 30.4, and 21.0 Å, respectively. These gallery heights for siloxane intercalates are ~9–23 Å larger than that obtained from the octylamine preswelling process and subsequent interlamellar hydrolysis of TEOS in ethanol.[2] The difference of chain length between octylamine (chain length, 11.5 Å) and dodecylamine (chain length, 16.5 Å) allows an increase of ~5 Å in gallery height. This large increase in gallery height is caused by the outflow control of TEOS according to rapid interlamellar hydrolysis of TEOS in pure water. The gallery height increases as the molar ratio of TEOS increases (SPM-1, SPM-2, and SPM-3), but decreases as the ratio of dodecylamine increases (SPM-2, SPM-4, and SPM-5). This implies that the pillar size and strength formed by hydrolytic polycondensation depends on the quantity of gallery TEOS.

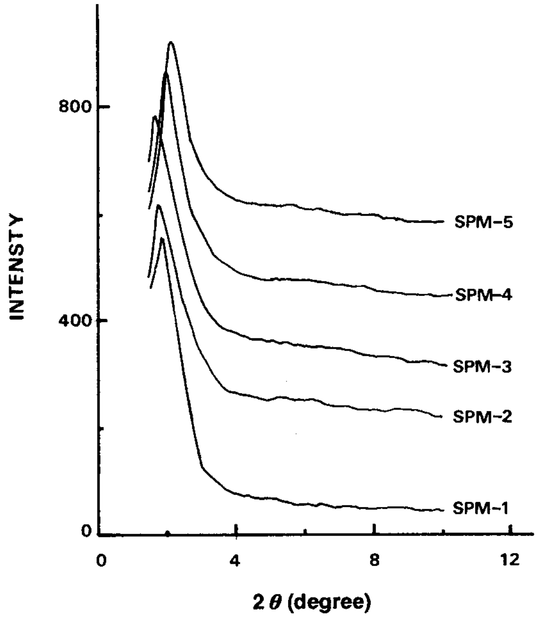

Figure 2. X-ray diffraction patterns for the uncalcined silica-pillared H^+-magadiite prepared at H^+-magadiite:dodecylamine: TEOS reaction stoichiometry of 1:2:15 (SPM-1), 1:2:20 (SPM-2), 1:2:30 (SPM-3), 1:6:20 (SPM-4), and 1:10:20 (SPM-5).

Calcination of samples yielded silica-pillared H^+-magadiites with basal spacing only 2–3 Å smaller than the siloxane-pillared samples (Figure 3). Especially, calcined samples brought out a substantial increase of the scattering intensity. This suggests that the calcination process can increase the scattering contrast between the wall and the pores due to the elimination of the pore-filling material. Marler et al.[19] reported that the intensity of X-ray peaks depends on the existence or not of pore-filling materials. Table 2 summerizes gallery heights for the uncalcined and calcined SPM products. SPM-1, -2, -3, and -4 products exhibit well-ordered basal spacings, proving that the elimination of gallery amine by calcination does not bring about collapse of expended gallery. Figure 4A and 4B exhibit typical SEM image for the samples with well-ordered basal spacing. The platelets are well preserved without a severe destruction except for a little swelling compared with H^+-magadiite. X-ray peak for SPM-5 disappears

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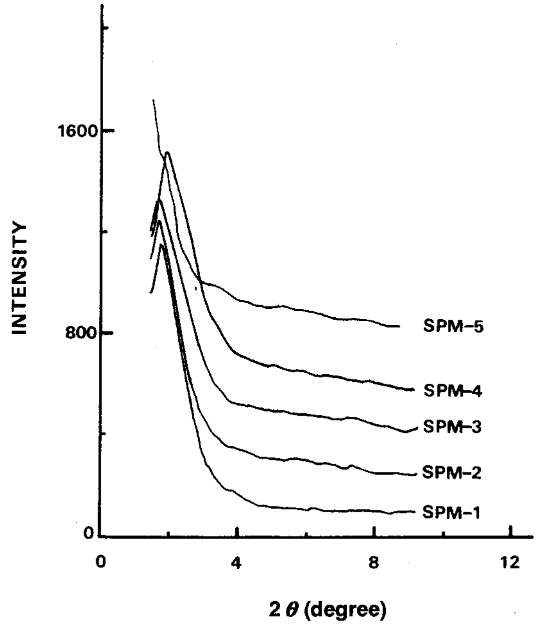

Figure 3. X-ray diffraction patterns for the calcined silica-pillared H^+-magadiite prepared at H^+-magadiite:dodecylamine:TEOS reaction stoichiometry of 1:2:15 (SPM-1), 1:2:20 (SPM-2), 1:2:30 (SPM-3), 1:6:20 (SPM-4), and 1:10:20 (SPM-5).

Table 2. Physical Properties of SPM Products Prepared by Interlamellar Dodecylamine-Catalyzed Hydrolysis of TEOS into the H^+-Magadiite[a]

	molar ratios of reactant mixtures			gallery height (Å)	
sample	MG	DDA	TEOS	uncalcined	calcined
SPM-1	1	2	15	32.2	29.3
SPM-2	1	2	20	36.5	33.0
SPM-3	1	2	30	39.6	36.5
SPM-4	1	6	20	30.4	28.4
SPM-5	1	10	20	21.0	–

[a] MG = H^+-magadiite; TEOS = tetraethylorthosilicate; DDA = dodecylamine; SPM = silica-pillared H^+-magadiite; Gallery height = basal spacing − 11.8 Å (thickness of H^+-magadiite).

after calcination, implying that the elimination of gallery amine leads to severe destruction in layered structure. SEM image shown in Figure 4C exhibits well a severe destruction in platelets as expecting from X-ray diffraction pattern. This implies that the molar ratio of amine and TEOS in the gallery can be an important factor in successful silica pillaring. If the ratio of amine compared with TEOS in the gallery is too high, the quantity of TEOS needed in the formation of pillar is not enough. The strength of siloxane pillar formed by amine-catalyzed hydrolysis of TEOS may be too weak to prop layered structure and gallery nearly maintained by template amine. The elimination of gallery amine by calcination can bring about a disordered collapse of gallery. In this process, TEOS will not flow out from interlayer during hydrolysis because of their water insolubility property and rapid hydrolysis in the existence of gallery amine. Therefore, this process can minimize the extragallery silica, allowing easily siloxane-pillared H^+-magadiites.

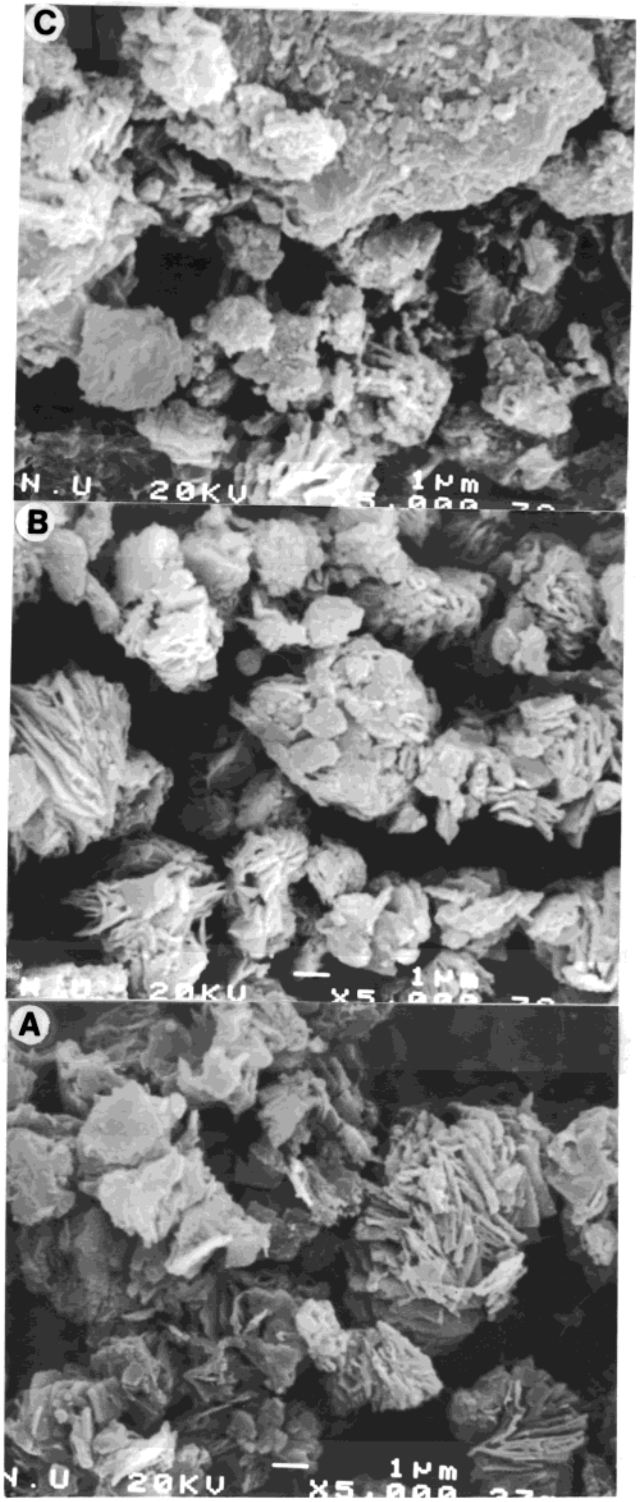

Figure 4. The scanning electron micrographs for the calcined silica-pillared H^+-magadiites prepared at H^+-magadiite:dodecylamine:TEOS reaction stoichiometry of 1:6:20 (A), 1:2:30 (B), and 1:10:20 (C).

The nitrogen adsorption/desorption isotherms shown in Figure 5 were obtained for calcined (538 °C) samples. Surface areas were obtained by fitting the adsorption data below $P/P_0 = 0.1$ to the BET equation.[20] The BET surface areas and the microporous and nonmicroporous surface areas for SPM products are listed in Table 32. The specific surface area of H^+-magadiite is on more than 50 m^2/g. The silica-pillared magadiites, however, exhibit dramatically larger surface areas, between 607 and 830 m^2/g, depending on the molar ratio of dodecylamine and TEOS used in the reaction. Figure 6 exhibits

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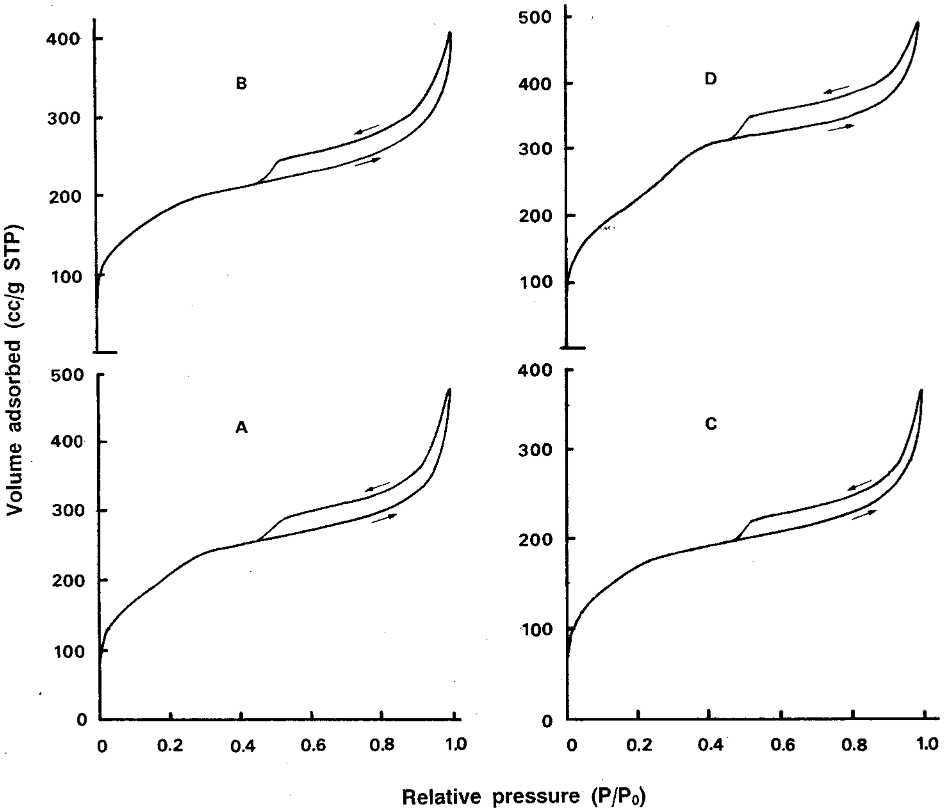

Figure 5. Nitrogen adsorption isotherms for the calcined silica-pillared H^+-magadiites prepared at H^+-magadiite:dodecylamine: TEOS reaction stoichiometry of 1:2:15 (A), 1:2:20 (B), 1:2:30 (C), and 1:6:20 (D). Up-curve: adsorption. Down-curve: desorption.

Table 3. Surface Area Analyses (m^2/g) for Calcined SPM Products Prepared by Interlamellar Dodecylamine-Catalyzed Hydrolysis of TEOS into the H^+-Magadiite[a]

	molar ratios of reactant mixtures						
sample	MG	DDA	TEOS	S_{BET}	S_{mic}	S	H−K pore size (Å)
SPM-1	1	2	15	761.2	615.5	145.7	24
SPM-2	1	2	20	680.7	536.0	144.7	diffused
SPM-3	1	2	30	606.5	490.5	116.0	diffused
SPM-4	1	6	20	829.4	702.9	126.4	26
SPM-5	1	10	20				
MG				50.0			

[a] S_{BET} is the N_2 BET surface area; S_{mic} and S are the microporous and nonmicroporous surface areas, respectively, obtained from t-plots of the nitrogen adsorption data. H−K pore size = Horvath and Kawazoe pore size.

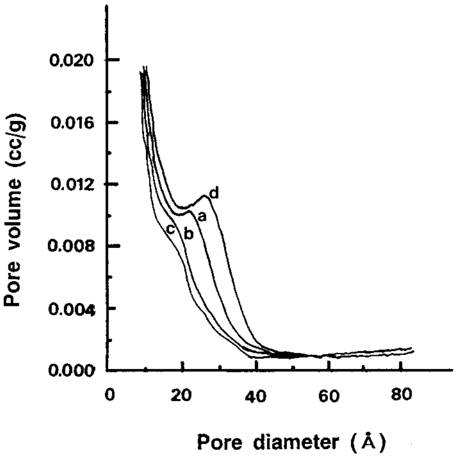

Figure 6. The pore size distributions for the calcined silica-pillared H^+-magadiites prepared at H^+-magadiite:dodecylamine:TEOS reaction stoichiometry of 1:2:15 (a), 1:2:20 (b), 1:2:30 (c), and 1:6:20 (d).

various pore size distributions of SPM products. SPM-1 and SPM-4, as shown in Figure 6, show a narrow pore size distribution in the range 20−30 Å similar to the MCM-41 related materials. This indicates that the pore size distribution relies on the molar ratio of dodecylamine/TEOS within the gallery and also implies that the gallery dodecylamine can act as micelle template.

Tanev and Pinnavaia[21] recently demonstrated that the assembly of hexagonal mesoporous metal oxides also could be achieved by hydrogen bonding between neutral amine and TEOS. Pinnavaia et al.[11] also reported that the neutral amines had an important role in the formation of gallery micellar assemblies, during the hydrolysis of TEOS in the gallery of layered phase ion-exchanged with quaternary ammonium cations. Our results also show that the gallery-templated synthesis can be conducted by dodecylamine only without pre-intercalated quaternary ammonium cations. An intermediate value in the molar ratio of dodecylamine/TEOS in the gallery can afford an ideal condition for the formation of micellar neutral amine assemblies. This reaction condition will lead to the gallery-templated hydrolysis of TEOS by dodecylamine. The dependence of dodecylamine/TEOS molar ratio on the formation of mesoporous SPM products (a and d curves in Figure 6) reflects on this explanation. The difference in mesopore size shown in SPM-1 and SPM-4 is attributed to the change in the shape of dodecylamine assemblies caused by the difference of dodecylamine/TEOS molar ratio in the gallery.

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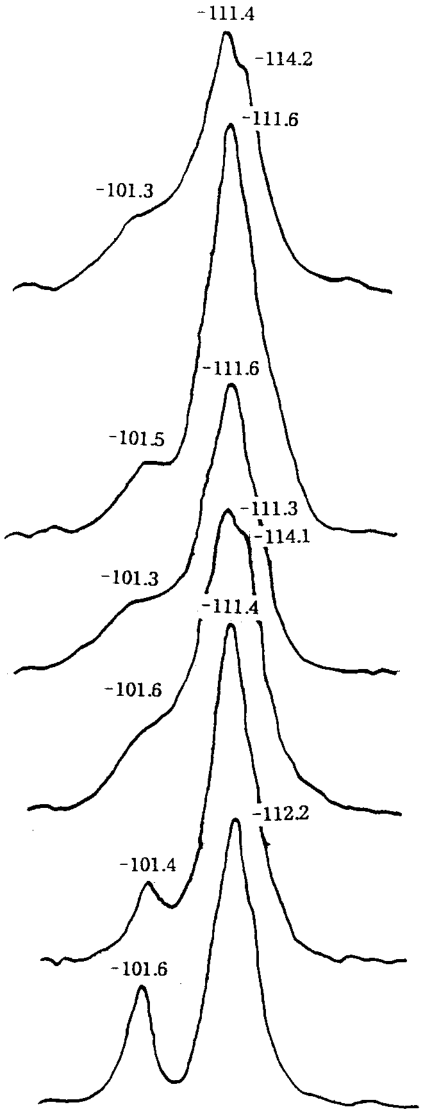

Figure 7. ^{29}Si MAS NMR spectra for the H$^+$-magadiite and calcined SPM products.

Most of total surface area is due to the presence of micropore < 20 Å in diameter. In the porous materials formed by gallery-templated reaction, specific surface area consists of micropore by pore walls acted as pillars and mesopore by burnoff of templates. Therefore, the lateral spacing between pillars as conventional pillared layered materials does not solely contribute to the increase of microporosity. The porous layered phase formed by gallery-templated synthesis showed an intrinsic increase in gallery height compared with conventional pillared layered materials. If the molar ratio of dodecylamine in the gallery is lower than an intermediate value compared with TEOS, gallery amine will not act as micelle template but as lateral spacing filler between pillars. In this condition, the increase of gallery TEOS will lead to the symmetrical increase in pillar size, resulting in microporosity without mesopore (SPM-2 and SPM-3).

Figure 7 exhibits the ^{29}Si MAS NMR spectra for the H$^+$-magadiite and calcined SPM products. All of these materials exhibit a Q^{3}HOSi(OSi)$_3$ resonance near −100 ppm and multiple Q^{4}Si(OSi)$_4$ lines in the range −110 to −114 ppm. The Q^{3}HOSi(OSi)$_3$ resonance line appears clearly in H$^+$-magadiite, but indistinctly in SPM product developing prominently a multiple Q^{4}Si(OSi)$_4$ lines. Resonance lines in SPM products are different from the previous reports,[2,3] in which Q^{3}HOSi(OSi)$_3$ resonance line appear clearly in all silica pillared sample. They are very similar to those of the MCM 41 related materials. The development of multiple Q^{4}Si(OSi)$_4$ lines implies that gallery TEOS transforms into the SiO$_4$ tetrahedra by gallery dodecylamine-catalyzed hydrolysis in water.

In particular, the physical properties of SPM products prepared by our method are very similar to those of the mesoporous MCM 41.[22,23] Although generally, mesoporous silica-pillared layered silicates are known to have a broad pore size distribution compared with MCM 41, because of their complementary chemical functionality and the stable pore size distribution in the micropore to small mesopore range (10−20 Å), silica-pillared layered silicates may offer new opportunities for the rational design of heterogeneous catalyst systems.

Conclusion

Simultaneous intercalation of amine-TEOS into the H$^+$-type layered phase and subsequent intragallery amine-catalyzed hydrolysis of TEOS have the promising route in the silica pillaring, because of their effective and quantitative process performed for a short time by a small amount of reagent without preswelling by amine or quaternary ammonium cation. SPM products prepared by this process exhibit microporous and mesoporous property with a large surface areas between 607 and 830 m^2/g, and narrow pore size distributions ~23−27 Å. Especially, the hydrolysis of gallery TEOS in water solution resulted in siloxane-pillared H$^+$-magadiites with supergallery between 21.0 and 39.6 Å. This large increase in gallery height indicates that TEOS does not flow out from interlayer during hydrolysis of TEOS because of their water insolubility properties and rapid hydrolysis in the existence of gallery amine. Resultingly, this process can minimize the extragallery silica, allowing easily siloxane-pillared H$^+$-magadiites. Results indicated that the gallery amine acted as gallery height expander as well as base catalyst and intragallery template during interlamellar hydrolysis of TEOS.

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