Preparation of Porous Silica-Pillared Montmorillonite: Simultaneous Intercalation of Amine-Tetraethylorthosilicate into H-Montmorillonite and Intra-Gallery Amine-Catalyzed Hydrolysis of Tetraethylorthosilicate

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Porous silica-pillared montmorillonites were prepared by simultaneous intercalation of dodecylamine-TEOS [tetraethylorthosilicate, $Si(OC_2H_5)_4$] into the H-montmorillonite and intragallery amine-catalyzed hydrolysis of TEOS. Mixtures of the H-montmorillonite, dodecylamine and TEOS at molar ratios of 1 : 2 : 15-30 and 1 : 2-6 : 20 resulted to swollen and viscous gel once at room temperature, allowing intercalation compounds which dodecylamine and TEOS were simultaneously intercalated into interlayer of H-montmorillonite. The hydrolysis of the gallery TEOS was conducted in water solution for 40 min at room temperature, affording siloxane-pillared H-montmorillonite. Calcination of samples at 500 °C in air resulted in silica-pillared montmorillonite with large specific surface areas between 403 and 577 m^2/g, depending on the reaction stoichiometry. The reaction at H-montmorillonite : dodecylamine : TEOS reaction stoichiometries of 1 : 2 : 15 and 1 : 4 : 20 resulted in high specific surface areas and mesopores with a narrow pore size distribution. Result indicates that the intragallery-amine catalyze the hydrolysis of gallery-TEOS and simultaneously have a role of gallery-templated micellar assemblies.

Keywords : H-montmorillonite, Silica-pillared montmorillonite, Intercalation.

Introduction

The study for the silica pillaring through layered phase has been reported by a few researchers.[1-10] 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 non-quantitative experimental process, time consuming, and uses expensive reagent such as TEOS and long chain amines. Recently, Kwon *et al.*[12] reported that the simultaneous intercalation of TEOS and amine into H^+-magadiite and successive interlamellar hydrolysis of TEOS in water resulted in mesoporous silica-pillared magadiites. Where, pillar precursor TEOS, during immersion of H-magadiite to amine-TEOS solution, can be intercalated into the interlayer with dodecylamine molecules. TEOS is capable of introducing directly into 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 expander 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.

The pillaring for the montmorillonite has been conducted by the ion exchange of interlayer cations for larger oligomeric cations, for example the Keggin ion or zirconyl cation and subsequent calcination at elevated temperatures. Pore size distributions of materials prepared in this way show that the majority of pores are in the microporous range, as may be expected due to the rather small pillars. Therefore, mesoporous pillared montmorillonite can be prepared by introducing gallery templates, such as quaternary ammonium cation and long chain amine. Montmorillonite ion exchanged with quaternary ammonium cation allows only increase of ~10 Å in gallery, because their cation exchanges capacity are limited. However, H-montmorillonite immersed in dodecylamine-hexane solution allows a dramatic increase in gallery to ~26 Å after drying.[13] It is attributed to the introduction of larger amount of amine into interlayer resulted in additional solvation of hydrogen bonded amine by free amine. The more gallery height increases and the more pillar precursor introduces into interlayer. Although this process can apply to the preparation of mesoporous silica pillared montmorillonite, related study has not been conducted yet. In this paper, we report that dodecylamine and TEOS can be simultaneously intercalated into H-montmorillonite in dodecylamine-TEOS solution, and successive interlamellar hydrolysis of TEOS in water results in mesoporous silica-pillared montmorillonites (SPB). Our method is quite different from previous methods[1,2,11] which introduced pillar precursor TEOS into 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. 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 pre-intercalation by amine or quaternary ammonium cation.

Experimental Section

Syntheses of H-montmorillonite. Materials used were HCl, ethanol, TEOS and dodecylamine of special grade. The montmorillonite was purchased from YAGURI (Japan). The commercial montmorillonite was purified using a sedimentation method. A 2 wt% montmorillonite slurry was stirred overnight at room temperature, then allowed to settle for 2 h. The sediment was removed by decantation. The purified montmorillonite was then recovered by centrifuging the decanted upper slurry, washed and oven dried for 5 h at 100 °C.

H-montmorillonite was prepared by an ion exchange of exchangeable cations for H^+ in a 0.1 N HCl solution. The suspension composed of purified montmorillonite (40 g) and deionized water (500 ml) was slowly titrated with a 0.1 N HCl solution to a final pH of 1.8 and then maintained at the same value for an additional 24 h. The sample was recovered by filtering, washed with deionized water until Cl-free, and then dried in air for 5 h at 100 °C. The replacement of exchangeable cations by H^+ in the layered silicate produces organophilic properties in the interlayer surfaces, because the silanol groups produce hydrogen-bonding sites.

Silica-pillared H-montmorillonite derivatives. Mixtures of H-montmorillonite, dodecylamine and TEOS at molar ratios in the range 1 : 2-6 : 20 and 1 : 10 : 15-30 were allowed to react for 5 h at room temperature. Under this condition, the intercalation of dodecylamine and solvation of interlayer dodecylamine by TEOS expand the gallery, resulting in dodecylamine/TEOS co-intercalated H-montmorillonite 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-montmorillonite pastes (contained 0.5 g H-montmorillonite) 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 500 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 CuKα 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,[14] and the pore size distribution of SPB derivatives was determined by the method of Horvath and Kawazoe equation.[15] The scanning electron micrographs (SEM) were obtained from a JEOL JSM-840A scanning electron microscope.

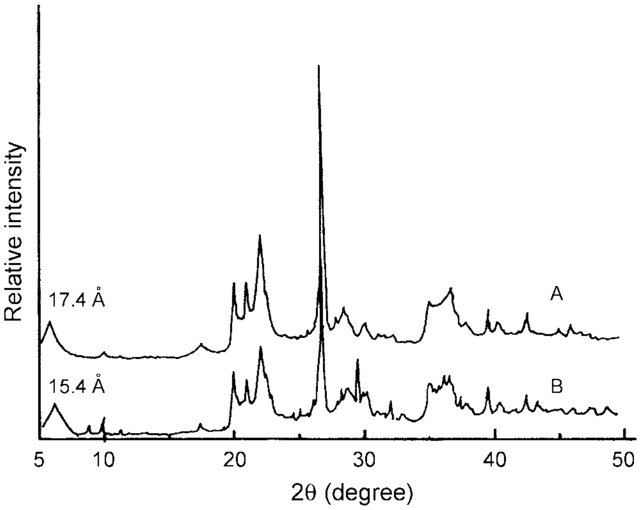

Figure 1. X-Ray diffraction patterns of purified montmorillonite (A) and H-montmorillonite (B).

Results and Discussion

Synthesis of H-montmorillonite. Figure 1(A) and 1(B) exhibit X-ray diffraction patterns of purified montmorillonite and H-montmorillonite, respectively. The basal spacing of the commercial montmorillonite was exhibited 12.3 Å, whereas that of the purified montmorillonite, as shown in Figure 1(A), was 17.4 Å. Since the basal spacing of the purified montmorillonite was higher compared with that of the commercial montmorillonite, this implies that the interlayer ions, such as Na^+, K^+, and Ca^{2+}, were partially solvated by water molecules. Gillery[16] reported that the basal spacing of clay minerals is closely related to the relative humidity. The slow titration of purified montmorillonite with 0.1 HCl resulted in the exchange of exchangeable cations for H^+ in the interlayer. The X-ray powder diffraction of the dried H-montmorillonite, as shown in Figure 1(B), exhibited 00 *l* reflections corresponding to basal spacing of 15.4 Å. This decrease in the basal spacing indicates a loss of the interlayer H_2O upon the replacement of Na^+ for H^+. In particular, although the X-ray peak of the montmorillonite did not change substantially before or after the acid treatment, there was a decrease in the basal spacing. This implies that the original structure was well preserves after the acid treatment.

Gallery amine-catalyzed hydrolysis of TEOS. Mixtures of the H-montmorillonite, dodecylamine and TEOS at molar ratios in the range 1 : 2 : 15-30 and 1 : 2-6 : 20 resulted in swollen and viscous gel, allowing intercalation compounds which dodecylamine and TEOS were simultaneously intercalated into interlayer of H-montmorillonite. Kwon *et al.*[9] showed that the gallery height of octylamine-intercarated 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 with the solvation of interlayer amine by solvent molecules.

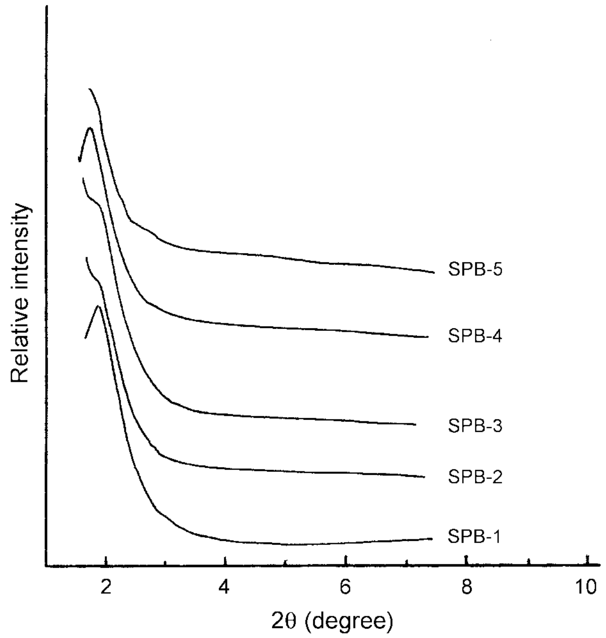

Figure 2. X-Ray diffraction patterns for the calcined silica-pillared montmorillonite prepared at H-montmorillonite : dodecylamine : TEOS reaction stoichiometry of 1 : 2 : 15 (SPB-1), 1 : 2 : 20 (SPB-2), 1 : 2 : 30 (SPB-3), 1 : 4 : 20 (SPB-4) and 1 : 6 : 20 (SPB-5).

Addition of water for the gels resulted in intra-gallery 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 montmorillonite. The powder X-ray diffraction patterns for siloxane-pillared samples were exhibited broad and diffuse peak near ~2 degrees. However, Figure 2 shows that the calcination of samples yielded silica-pillared montmorillonite with well-ordered basal spacing. The basal spacing for the samples prepared at H-montmorillonite : dodecylamine : TEOS reaction stoichiometries of 1 : 2 : 15 and 1 : 4 : 20 were 47.0 and 50.2 Å. Since the layer thickness of H-montmorillonite is 15.4 Å, the corresponding gallery heights of SPB-1 and SPB-4 are 31.6 and 34.8 Å, respectively. The increase in peak intensity and sharpness by calcination indicates 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.*[17] reported that the intensity of X-ray peaks depends on the existence or not of pore-filling materials. If the dodecylamine molecules form micelle template in the gallery, the thickness of dodecylamine molecular assembly should be ~28 Å. Gallery height (31.6 and 34.8 Å) in silica-pillared montmorillonites are above this value. This proves that dodecylamine act as micelle template during interlamellar hydrolysis of TEOS. These gallery heights for silica pillared montmorillonites are similar to that of silica pillared H-magadiite reported in our previous study.[12] This shows that the simultaneous intercalation of pillar precursor TEOS and amine into H-layered phase and interlamellar hydrolysis of TEOS can be conventional route leading to the silica pillaring through layered phase. Here, interlayer amine acts as the gallery height expander as well as the base catalyst and the intragallery template during interlamellar hydrolysis of TEOS. Table 1 summarizes gallery heights for calcined SPB products. SPB-1 and 4 products exhibit well-ordered basal spacing, proving that the elimination of gallery amine by calcination does not bring about collapse of expended gallery. No peaks exhibited in X-ray powder diffraction for SPB-2 and SPB-3, but leave traces of the peak of shoulder type, allowing only a partial pillaring. A broad and diffuse peak near 2 degrees appeared in the uncalcined SPB-5 disappeared after calcination, implying that the elimination of gallery amine leads to severe destruction in layered structure. This implies that the molar ratio of dodecylamine and TEOS in the gallery can be an important factor in successful silica pillaring into layered phase. If the ratio of amine compared with TEOS is too low, amine can not intercalate into H-montmorillonite enough to have a role as gallery template. Kwon *et al.*[12] indicated that amine concentration have an important role in the intercalation of amine through the layered phase and gallery expansion. They showed that the intercalation compound with well ordered basal spacing did not formed in amine solution of lower concentration. However, 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-catalysed 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. Figure 3(A) and 3(C) exhibit typical SEM image for the siloxane-pillared samples prepared at H-montmorillonite : dodecylamine : TEOS reaction stoichiometries of 1 : 2 : 15 (SPB-1) and 1 : 6 : 20 (SPB-5), respectively. It shows that the expansion caused by dodecylamine intercalation and polycondensation of gallery TEOS result in swollen particle morphology. This phenomenon appears clearly in SPB-5 with a larger molar ratio of dodecylamine. Figure 3(B) and 3(D) exhibit SEM image for the calcined SPB-1 and SPB-5, respectively. They show that calcination of samples result in contracted particle

Table 1. Physical Properties for Calcined SPB Products Prepared by Interlamellar Dodecylamine Catalyzed Hydrolysis of TEOS into the H-montmorillonite

Samples	Molar ratios of reactant mixtures			Gallery height (Å)	Specific surface area (m^2/g)	H-K pore size (Å)
	MG	DDA	TEOS			
SPB-1	1	2	15	31.6	577	25
SPB-2	1	2	20	–	412	Diffused
SPB-3	1	2	30	–	403	"
SPB-4	1	4	20	34.8	469	30
SPB-5	1	6	20	–	547	Diffused
HM	–	–	–	–	77	–

HM=H-montmorillonite; TEOS=tetraethylorthosilicate; DDA=dodecylamine; SPB=silica-pillared montmorillonite; Gallery height=basal spacing -15.4 Å (Thickness of H-montmorillonite); H-K pore size=Horvath and Kawazoe pore size.

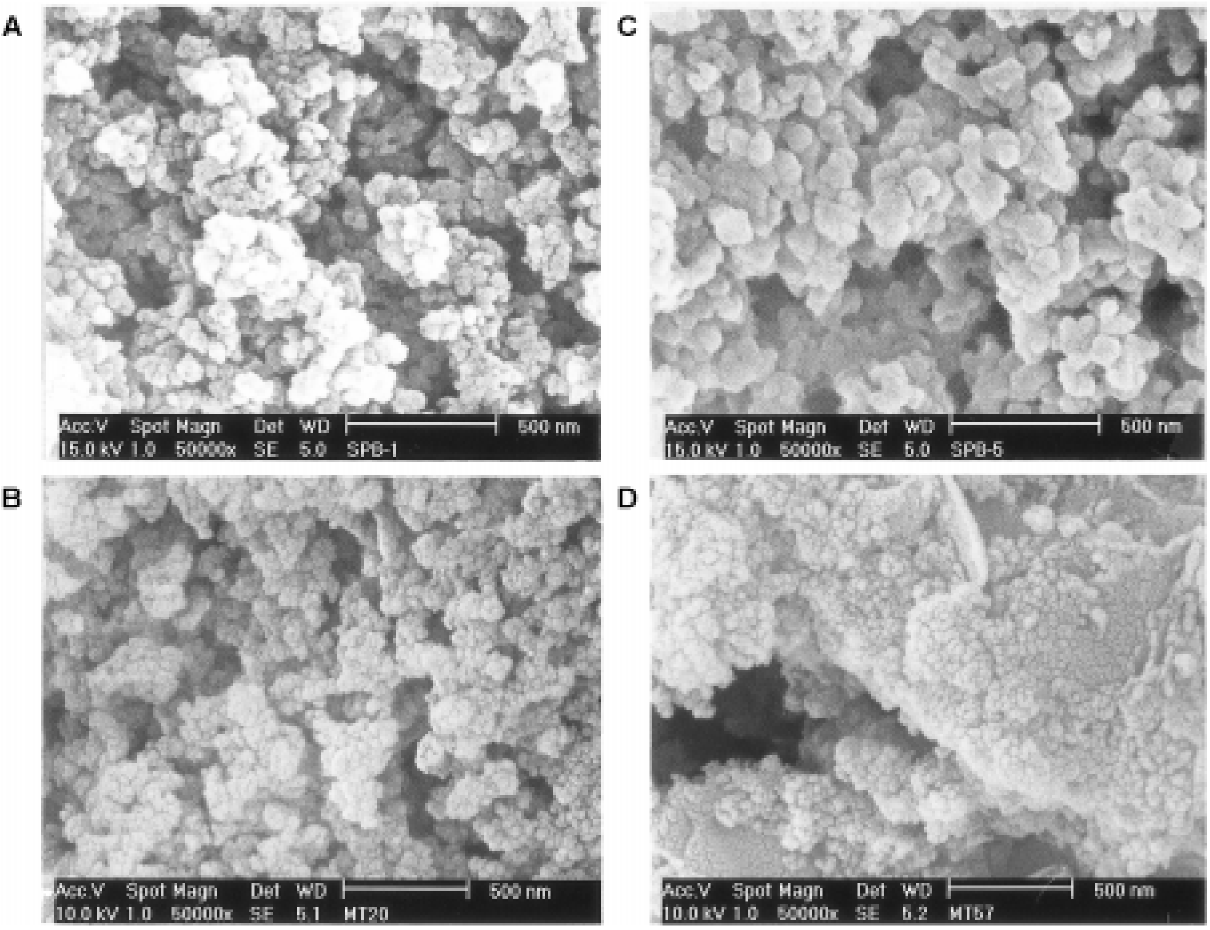

Figure 3. The scanning electron micrographs for the silica-pillared montmorillonite prepared at H-montmorillonite : dodecylamine : TEOS reaction stoichiometry of 1 : 2 : 15 (SPB-1) and 1 : 6 : 20 (SPB-5): (A) uncalcined SPB-1, (B) calcined SPB-1, (C) uncalcined SPB-5, (D) calcined SPB-5.

morphology. SPB-1 results in a little contraction without a change in particle morphology. However, SPB-5 appears a severe change with large contraction. This proves that the higher molar ratio of amine compared with TEOS collapses the gallery, weakening the strength of siloxane pillar in the gallery. In this process, TEOS will not flow out from interlayer during hydrolysis because of their water insoluble property and rapid hydrolysis in the existence of gallery amine. Therefore, this process can minimize the extra-gallery silica, allowing easily siloxane-pillared montmorillonite. Large increase in gallery height for SPB-1 and SPB-4 is caused by the outflow control of TEOS according to rapid interlamellar hydrolysis of TEOS in pure water.

The nitrogen adsorption/desorption isotherms shown in Figure 4 were obtained for calcined (500 °C) samples. A step, in SPB-1 and SPB-4, occurs in the adsorption curve at a partial pressure from 0.2 to 0.4, which is indicative of the filling of framework-confined mesopores with an average H-K pore size of 25 Å and 30 Å, respectively. Surface areas were obtained by fitting the adsorption data below $P/P_0=0.1$ to the BET equation.[14] Surface areas for SPB products are listed in Table 1. The specific surface area of H-montmorillonite is no more than 77 m^2/g. The silica-pillared mont-

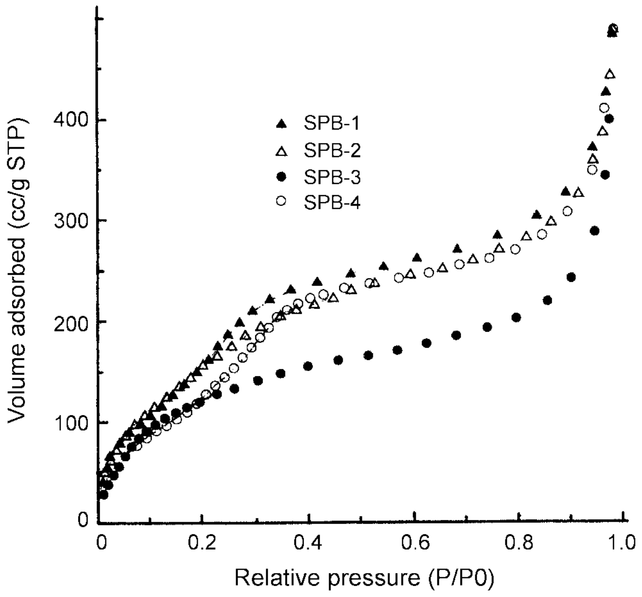

Figure 4. Nitrogen adsorption isotherms for the calcined silica-pillared montmorillonite prepared at H-montmorillonite : dodecylamine : TEOS reaction stoichiometry of 1 : 2 : 15 (SPB-1), 1 : 2 : 20 (SPB-2), 1 : 2 : 30 (SPB-3) and 1 : 4 : 20 (SPB-4).

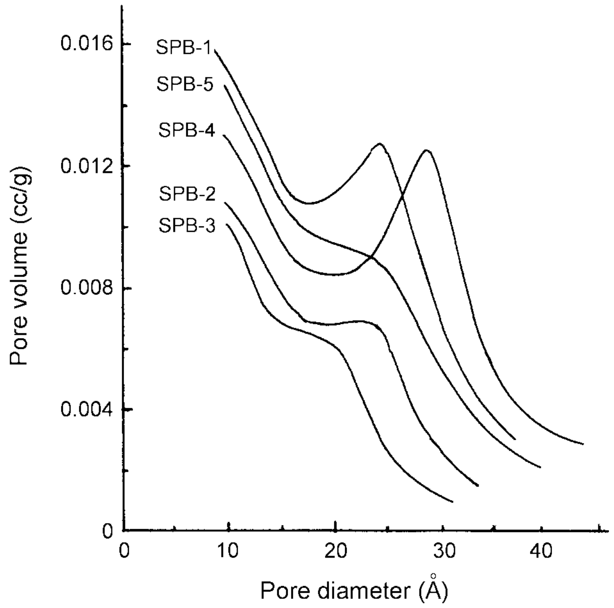

Figure 5. The pore size distributions for the calcined silica-pillared montmorillonite prepared at H-montmorillonite : dodecylamine : TEOS reaction stoichiometry of 1 : 2 : 15 (SPB-1), 1 : 2 : 20 (SPB-2), 1 : 2 : 30 (SPB-3), 1 : 4 : 20 (SPB-4), and 1 : 6 : 20 (SPB-5).

morillonite, however, exhibit dramatically larger surface areas, between 403 and 577 m^2/g, depending on the molar ratio of dodecylamine and TEOS used in the reaction. Figure 5 exhibits various pore size distributions of SPB products. SPB-1 and SPB-4 show a narrow pore size distribution in the range 25 Å and 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[18] 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 SPB products (SPB-1 and SPB-4) 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.

Most of total surface area, in SPB products, is due to the presence of micropore < 20 Å in diameter. In the porous materials formed by gallery template reaction, specific surface area consists of micropore by pore walls acted as pillars and mesopore by burn-off of templates. Therefore, the lateral spacing between pillars as conventional pillared layered materials does not solely contribute to the increase of microporosity. Porous layered phase formed by gallery-templated synthesis showed 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. (SPB-2 and SPB-3)

In particular, the physical properties of SPB products prepared by our method are very similar to those of the mesoporous MCM 41.[19,20] 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.

Mechanism. Figure 6 shows a proposed mechanism for the formation of SPB products by gallery-templated process. The ion exchange of montorillonite by H^+ will afford interaction sites accessible to dodecylamine by forming silanol groups (Figure 6b). The reaction between H-montmorillonite and dodecylamine-TEOS solution forms an intercalate with a lammellar bilayer of dodecylamine molecules. Here, solvation of interlayer dodecylamine by TEOS molecules allows an additional increase in gallery height compared with only dodecylamine-intercalated type (Figure 6c). The addition of pure water to this intercalated derivative introduces water molecules into the gallery, leading to the hydrolysis of gallery TEOS. In the water suspension, during hydrolysis of gallery TEOS, polar head group NH_2- of gallery dodecylamine will be arranged in the direction of water and hydrophobic alkyl chains focused on the core. This arrangement of the gallery dodecylamine molecules can afford a micellar assemblies similar to quaternary-ammonium surfactant. TEOS and water molecules will be crowded around the surface of micellar dodecylamine assemblies formed in the gallery. Polar NH_2- groups in the micelle surface will be catalyzed hydrolysis reaction between TEOS and water, resulting in hydrous silica templated around a monolayer of micellar dodecylamine assemblies (Figure 6d). The calcination step (Figure 6e) removes the template and completes the dehydroxylation and cross-linking of the gallery-assembled silica structure.

Conclusion

Simultaneous intercalation of dodecylamine-TEOS into the

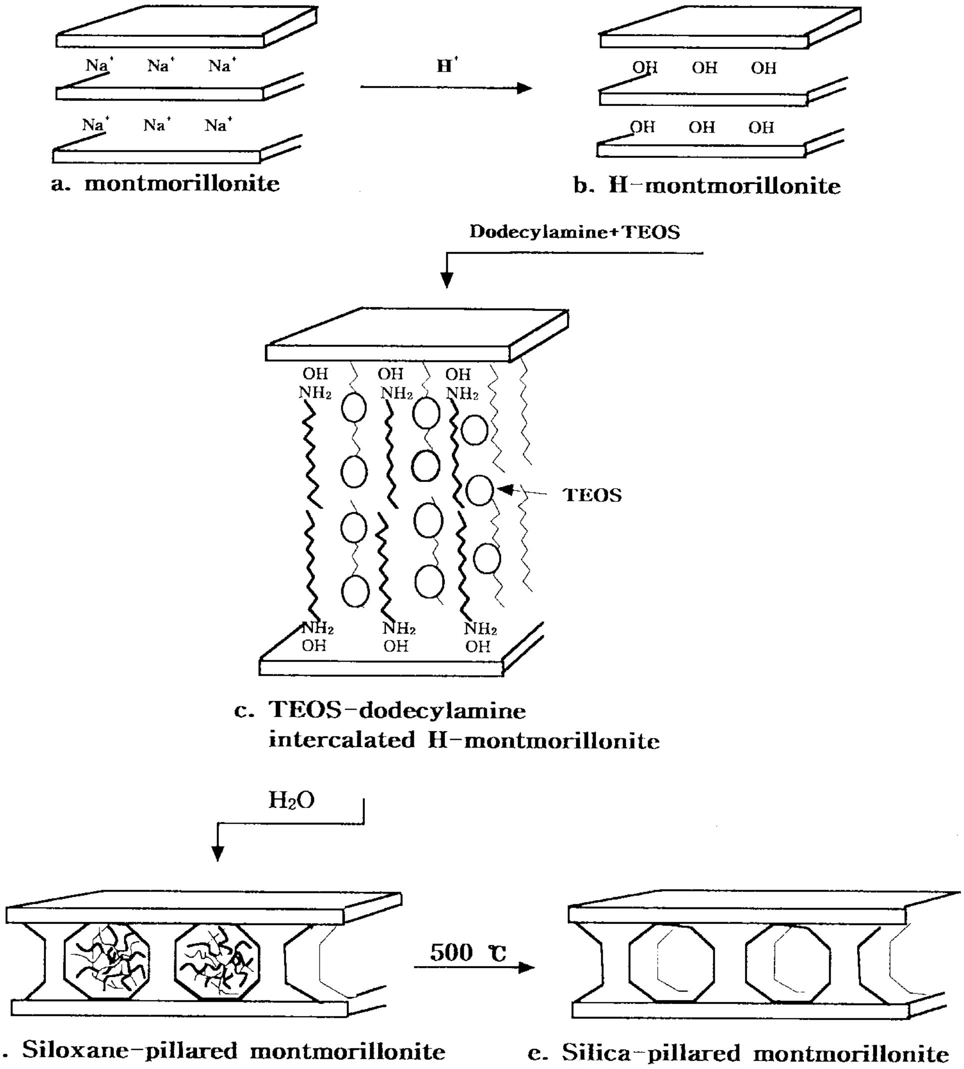

Figure 6. Hypothetical draws for the silica pillaring of H-montmorillonite by simultaneous intercalation of dodecylamine-TEOS and gallery-templated hydrolysis of TEOS.

H-montmorillonite and subsequent intra-gallery 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 pre-swelling by amine or quaternary ammonium cation. SPB products prepared by this process exhibit microporous and mesoporous property with a large surface areas between 403 and 577 m^2/g, and narrow pore size distributions ~25 - 30 Å. Especially, the hydrolysis of gallery TEOS in water solution resulted in silica-pillared montmorillonite with super-gallery ~31.6 - 34.8 Å. This large increase in gallery height indicates that TEOS does not flow out from interlayer during hydrolysis of TEOS because of their water insoluble property and rapid hydrolysis in the existence of gallery amine. Resultingly, this process can minimize the extra-gallery silica, allowing easily silica-pillared montmorillonite. Results indicated that the gallery amine acted as gallery height expander as well as base catalyst and intra-gallery template during interlamellar hydrolysis of TEOS.

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