Preparation of New Silica Sol-Based Pillared Clays with High Surface Area and High Thermal Stability

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A new microporous sol-pillared clay was prepared by the ion-exchange of the interlayer Na^+ ions of montmorillonite with $SiO_2-Fe_2O_3$ mixed oxide sol particles. The mixed oxide sol solution was prepared by titrating an Fe^{3+} aqueous solution with NaOH in the presence of silica sol particles. Upon pillaring with the iron-modified silica sol particles, the basal spacing of the clay was expanded to a value as large as 63 Å and maintained at least up to 800 °C. More than 96% of the iron content was easily removed by acid washing, and the pillared clay was changed from brown to pale yellow in color, while the product retained the expanded basal spacing. On calcination at 400 °C, the $SiO_2-Fe_2O_3$ mixed oxide pillared clay had an extremely large BET surface area of 720 m^2/g. The acid-washed pillared clay had a larger surface area of 850 m^2/g, and a considerable surface area of about 550 m^2/g was retained even after calcination at 800 °C. Both pillared samples were characterized as microporous solids with weak acidic sites by an ammonia desorption measurement.

Introduction

There has been intense research activities on layer structured silicates pillared with inorganic or organic clusters, which are called pillared interlayer clays (PILCs).[1−3] Since these materials contain micropores larger than those of conventional zeolites and exhibit new properties depending on the nature of the pillars, they are of interest as new types of microporous solids that can serve as shape-selective catalysts, separating agents, supports, adsorbents, and so on.[1−3] In particular, clays pillared with metal oxides are of great importance because of their high thermal stability, high surface areas, and intrinsic catalytic activities.

These PILCs are usually prepared by ion-exchanging the cations in the interlayer region of clays with bulky alkylammonium cations, metal polyhydroxy cations, or positively charged colloidal particles. The intercalated species, as pillars, prevent the interlayer spaces from collapsing, thereby forming, an interlayer space, i.e., a two-dimensional porous network. On heating, the intercalated inorganic species are converted to metal oxide cluster, generating a stable microporous structure with a high surface area. So far, several metal oxide pillared clays have been prepared such as Al_2O_3,[4] ZrO_2,[5] Cr_2O_3,[6,7] TiO_2,[8,9] Fe_2O_3,[10,11] SiO_2,[12,13] Ga_2O_3,[14] V_2O_5,[15] and mixed oxide clusters.[16,17]

Permanent microporosity, large surface area, molecular sieving function, and thermal stability are the important physical characteristics of pillared clays needed for practical applications, especially for catalysts. However, the pillared clays so far obtained do not have sufficient stability. Most of the montmorillonites pillared with metal oxides begin to deteriorate at around 500 °C, with a loss of interlayer space, microporosity, and catalytic activity.

The use of oxide sol pillars has been considered as one way to overcome such a problem. In our previous study,[18] the negatively charged silica sol was modified to be positive by depositing TiO_2 sol particles, which could be intercalated successfully between negatively charged silicate layers to form SiO_2-TiO_2 sol pillared clays with high surface area and an improved thermal stability.

Silica is one of the oxides of interest to obtain thermally stable and catalytically active pillared clays. Some attempts to introduce silica pillars in clays have been reported: Endo et al.[12] and Lewis et al.[13] used organometallic pillaring agents like tris(acetylacetonato) silicon cations ($Si(acac)^{3+}$) and polyhedral oligosilsequioxane compounds as precursors. However, the resulting SiO_2 pillared clays showed relatively low surface areas and a small interlayer spacing, indicating the presence of only monolayer siloxane chains between the layers.

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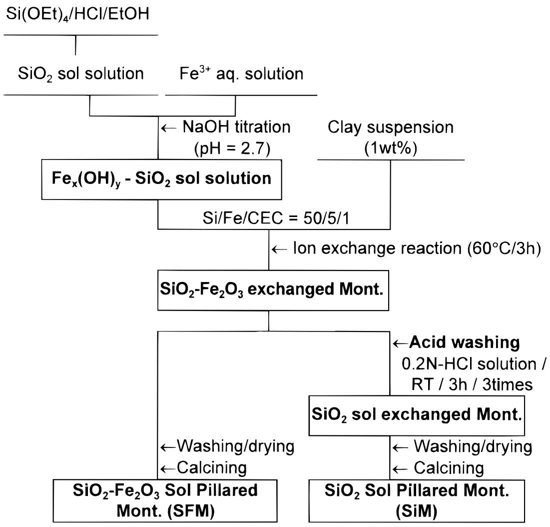

Figure 1. Schematic flow diagram for the preparation of $SiO_2-Fe_2O_3$ (SFM) and SiO_2 (SiM) sol pillared montmorillonites.

The use of hydroxy−SiAl oligocations was also reported to prepare Al_2O_3/SiO_2-pillared clays.[17] A direct intercalation of metal oxide sols (DIMOS) was attempted by Moini and Pinnavaia.[19] They mixed commercial hydrolyzed silica sol with montmorillonite directly and found that relatively large surface area solids of 250−460 m^2/g were obtained, though those were not a regular intercalation phase.

We have recently found that silica sols can also be modified with iron hydroxide, and incorporated between the silicate layers as pillars to form $SiO_2-Fe_2O_3$ pillared clays. Moreover, since the iron hydroxide deposited on the silica sol surface is highly soluble in an acidic aqueous solution, it may provide a simple way to prepare SiO_2 sol pillared clay by leaching out the iron species with acidic aqueous solution. In the present study, therefore, our primary attention is paid to the preparation of $SiO_2-Fe_2O_3$ pillared montmorillonite (SFM), which is then changed into SiO_2 sol pillared montmorillonite (SiM). Their thermal stability, adsorption behavior, and acidic properties wil be discussed in detail.

Experimental Section

Materials. The clay used was sodium montmorillonite (Kunipia G from Kunimine Industry) with a structural formula of $Na_{0.35}K_{0.01}Ca_{0.02}(Si_{3.89}Al_{0.11})(Al_{1.60}Mg_{0.32}Fe_{0.08})O_{10}(OH)_2\cdot nH_2O$ and the cation-exchange capacity (CEC) of 100 mequiv/100 g. An aqueous suspension (about 1 w/w%) of the montmorillonite was prepared and kept for 1 day before pillaring by ion exchange.

Synthesis of Sol Pillared Clays. The overall preparation sequence for $SiO_2-Fe_2O_3-$ and SiO_2-sol pillared montmorillonites is shown in Figure 1. A silica sol solution was prepared as previously reported[18] by mixing silicon tetraethoxide (TEOS), 2 N HCl, and ethanol in a ratio of 41.6 g/10 mL/12 mL and aging at room temperature for 2 h. The solution was mixed with a 0.25 mol L^{-1} $Fe(NO_3)_3\cdot 9H_2O$ solution in a molar ratio of Si/Fe = 10/1 and subsequently titrated with 0.2 mol L^{-1} NaOH solution to keep the pH of the mixed solution at around 2.7. During the titration, Fe^{3+} ions were partially hydrolyzed and deposited onto the silica sol surface. The mixed sol solution, thus prepared, was then mixed with a clay suspension in a molar ratio of Si/Fe/CEC = 50/5/1. Then the mixture was allowed to stand for 3 h at 60 °C to facilitate the exchange of the interlayer Na^+ ions with the mixed oxide sol particles. The exchanged product was separated by centrifugation, washed with a mixed solution of ethanol and water (1:1 of volume ratio) 5 times to remove excess sol solution, and then dried in a stream of air dry at room temperature. Finally, the dried samples were calcined in a temperature range 200−900 °C for 2 h (heating rate of 200 °C/h) to obtain $SiO_2-Fe_2O_3$ pillared samples.

Before drying, a part of the wet $SiO_2-Fe_2O_3$ exchanged montmorillonite was separated and dispersed in a 0.2 N HCl solution for 3 h at room temperature to leach out the iron species from the mixed sol particles, followed by separation by centrifugation. This procedure was repeated three times to remove soluble Fe species as much as possible from the product. During this treatment, the color of the sample changed from dark brown to pale yellow. Finally the sample was washed several times with distilled water, dried under a stream of dry air, and calcined in the temperature range 200−900 °C for 2 h (heating rate of 200 °C/h).

Characterization of the Pillared Clays. Before air-drying, a small portion of wet product was spread on a quartz glass slide in order to achieve the preferred orientation of the samples. X-ray powder diffraction (XRD) patterns were measured on the orientated samples by using a diffractometer (SRA-M18XHF, MAC Science Co.) with graphite monochromatized Cu Kα radiation. Thermogravimetric (TG) analysis was performed at a heating rate of 5 °C/min under a stream of oxygen and nitrogen gas mixture (1:1). Infrared spectra (IR) were measured by a KBr disk method. Elemental analysis of the pillared products was carried out by an inductively coupled plasma (ICP) spectrometer (Perkin-Elmer Optima 3000) on the samples fused with lithium metaborate and dissolved in a 3% HNO_3 solution.

Adsorption−desorption isotherms of nitrogen were measured volumetrically at the liquid nitrogen temperature by using a computer-controlled volumetric system. The samples were degassed at 200 °C for 3 h under vacuum. Adsorption−desorption isotherms for some selected solvent vapors having different molecular sizes were measured gravimetrically at 25 °C by using a Cahn 1000 balance. The samples were also pretreated at 200 °C for 3 h under vacuum.

Temperature-programmed desorption (TPD) spectra of ammonia were recorded on SFM and SiM samples calcined at 600 °C by using a TCD detector. About 200 mg of each sample was reheated in a stream of helium for 1 h at 400 °C and cooled down to room temperature. Then, the sample was exposed to a flow of ammonia for 30 min; excess ammonia was purged by a flow of helium at room temperature for about 5 h. The measurement was carried out up to 550 °C for a heating rate of 5 °C/min and a helium flow rate of 100 mL/min.

Results

X-ray Diffraction Analysis. Figure 2a shows a series of XRD patterns of SFM calcined at different temperatures. Upon pillaring with $SiO_2-Fe_2O_3$ sol particles, the basal spacing of the clay was expanded to a value as large as 63 Å; higher order basal reflections (at least second) were observed clearly, suggesting that the sol-pillared layers were stacked in an ordered manner. This may be caused by a regular packing of the sol particles between the layers. Though the spacing was slightly decreased on heating, a distinct (001) reflection could be seen at least up to 800 °C, indicating that the pillared structure is well retained up to this high temperature. It is interesting to note that the intensity of the reflection appears to increase with calcination temperature.

On washing with a hydrochloric acid solution, the color of the product was turned into pale yellow from brown, but a well-ordered XRD pattern with a basal spacing very similar to that of SFM was observed as

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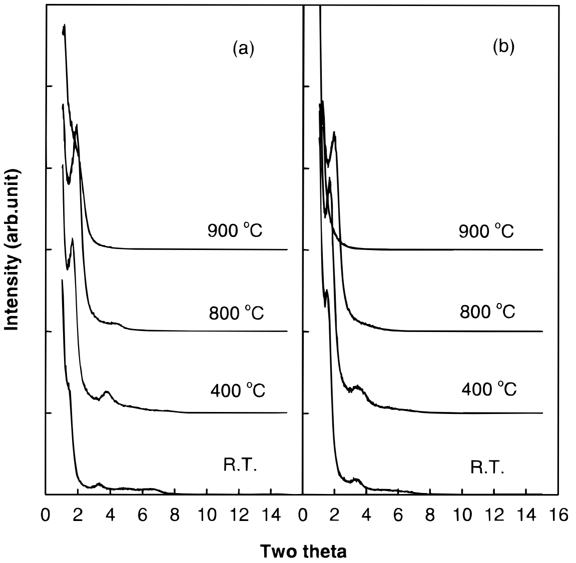

Figure 2. X-ray diffraction patterns of (a) $SiO_2-Fe_2O_3$ (SFM) and (b) SiO_2 (SiM) sol pillared montmorillonites calcined at different temperatures.

Table 1. Chemical Analysis Data of the $SiO_2-Fe_2O_3$ (SFM) and SiO_2 (SiM) Sol Pillared Clays

pillared sample	found, mol %			pillar compositions,[a] mol	
	SiO_2	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3
SFM	76.0	11.2	10.8	8.19	0.90
SiM	84.3	1.04	12.4	7.77	0.03

[a] The pillar compositions are given in moles on the basis of $[(SiO_2)_x(Fe_2O_3)_y][(Si_{3.89}Al_{0.11})(Al_{1.60}Mg_{0.32}Fe_{0.08})]O_{10}(OH)_2$ silicate layer.

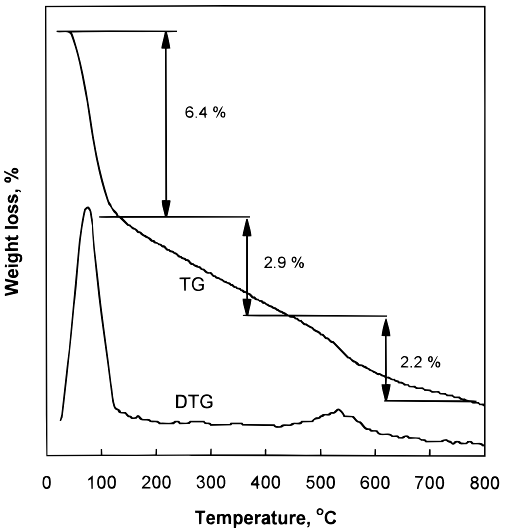

Figure 3. TG-DTG curves of SiO_2 sol pillared montmorillonite (SiM).

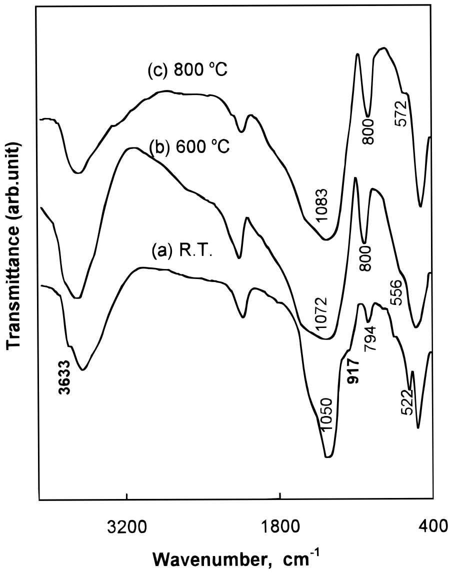

Figure 4. FT-IR spectra of SiO_2 sol pillared montmorillonites thermally treated at different temperatures.

shown in Figure 1b. This indicates that the iron species is successfully removed from the $SiO_2-Fe_2O_3$ sol pillars without destroying the interlayer arrangement of sol particles. The basal spacing larger than 50 Å can also be maintained even after calcination at 800 °C; the acid-washed sample (SiM) was as thermally stable as SFM.

Chemical Analysis. The compositions of the pillared products were determined on the samples before and after the acid washing and are listed in Table 1. It was assumed that the composition of the silicate layer of montmorillonite was unchanged during the reaction. It was reported that the composition of the clay was maintained even in a more acidic condition such as in zirconyl chloride solutions in the preparation of zirconia pillared clays.[5] The amounts of SiO_2 and Fe_2O_3 coming from the silicate layer were estimated from the Al_2O_3 content and subtracted from the total SiO_2 and Fe_2O_3 contents, respectively. As can be seen from Table 1, more than 9 mol equiv of $SiO_2 + Fe_2O_3$ is taken up by the clay in SFM. This amount is much larger than that of SiO_2-TiO_2 sol pillared clay (~7 mol equiv) with a basal spacing of about 40 Å, which was prepared in a previous study.[18] The larger amount of pillar content can be the reason for the larger interlayer separation of SFM. On acid washing, the Fe_2O_3 content in the pillared clay (SiM) was reduced from 9.90 to 0.38%, i.e., more than 96% of iron was removed from the pillar by acid washing. The residual iron may be strongly bound to the negative charge of the silicate layers or occluded in the sol particles.

Thermal Analysis. Figure 3 shows the results of thermogravimetric (TG) analysis of the SiM. A differential thermogravimetric (DTG) analysis curve is also overlapped in the figure. The first weight loss at around 100 °C is attributed to the loss of adsorbed water. The second one, corresponding to the dehydration of pillars, occurs gradually in the temperature range 150−450 °C, and finally an additional weight loss due to the dehydroxylation of silicate layers of the clay appears near 550 °C. This temperature is lower than that of the dehydroxylation of silicate layers without pillars by 100 °C. The lowering of the dehydroxylation temperature can be attributed to the condensation between the silicate layer and pillars.[20,21]

FT-IR Spectroscopy. The FT-IR spectra of SiM samples thermally treated at different temperatures are compared in Figure 4. In the spectra, the absorption bands at about 920 and 3630 cm^{-1} are assigned to the librational and the stretching vibration modes of the dioctahedral OH groups, respectively. The intense

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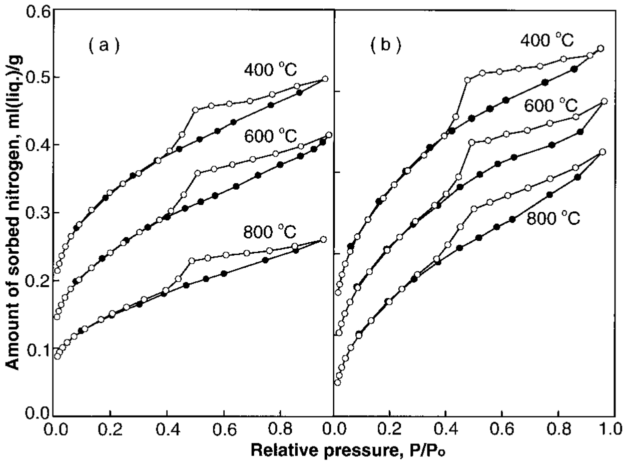

Figure 5. Nitrogen adsorption−desorption isotherms of (a) $SiO_2-Fe_2O_3$ (SFM) and (b) SiO_2 (SiM) sol pillared montmorillonites calcined at different temperatures.

absorption band at about 1050 cm^{-1} is due to the vibration of Si−O−Si in the tetrahedral layer, and the absorption at 795 cm^{-1} is due to the Si−O−Si symmetrical stretching of free silica.[20,21] On heating to 600 °C, the librational band at 920 cm^{-1} and stretching vibrational one at 3630 cm^{-1} nearly disappeared, which indicates the dehydroxylation of the octahedral layer.[20,21]

Nitrogen Adsorption Studies. The nitrogen adsorption−desorption isotherms of SFM and SiM samples calcined at different temperatures are shown in Figure 5a,b respectively. The adsorption isotherms give a good fit on the Langmuir (type I) as well as the BET equations; a much better fit is obtained on the BET equation for a limited number of nitrogen adsorption layers.[22] Even after calcining at 800 °C, overall isotherm shapes show no significant change, suggesting the interlayer pore structures formed in sol pillared clays are well retained at least up to this temperature. As can be seen from the figure, the adsorption isotherms of SiM exhibit a slightly larger nitrogen uptake compared to those of SFM at higher P/P_0. This might be due to the enlarged pore dimension by acid washing; as the iron species are removed from the pillar surface or interstices between the sol particles, the interlayer pore size becomes larger, which gives rise to the enhanced nitrogen uptake at higher P/P_0. In addition, the removal of iron species from the small interstices between sol particles and clay layers increases the microporosity in SiM samples.

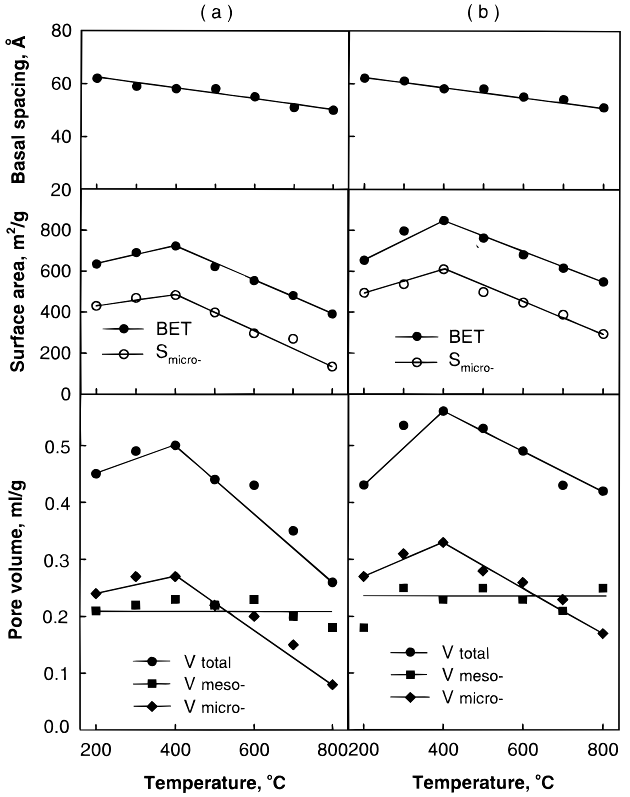

Figure 6. Basal spacings and total-, micro-, and mesoporosities of (a) $SiO_2-Fe_2O_3$ (SFM) and (b) SiO_2 (SiM) sol pillared montmorillonites as a function of calcination temperature.

The specific surface areas (BET) and pore volumes were estimated from the nitrogen adsorption isotherms and the corresponding *t*-plots[22] and are summarized in Figure 6 together with the basal spacings determined by XRD as a function of the calcination temperature. In the case of SFM, high surface area of 720 m^2/g and the total pore volume of 0.50 mL/g are obtained for the sample calcined at 400 °C. A significant amount of the surface area of 390 m^2/g is retained even after heating at 800 °C, implying that the pores formed by pillaring of the oxide sol particles are quite stable. Remarkably high BET specific surface area of 850 m^2/g is obtained for SiM sample calcined at 400 °C and the significant portion of surface area of 550 m^2/g (about 65% of the maximum value) is retained even after the calcination at 800 °C. This is one of the most thermally stable pillared clays ever prepared.

The micropore volumes of SFM and SiM increase slowly up to 400 °C and then decrease linearly, while the mesopore volumes are nearly constant in the whole temperature range. The increase of microporosity in the lower temperature range can be attributed to the dehydration of hydrous sol particles upon heating. Then, the micropore volumes gradually decrease due to the sintering of sol particles. From this analysis, it can be concluded that the high surface areas and porosities of sol pillared clays originate mainly from the micropores developed between the sol particles.

Solvent Adsorption. Adsorption−desorption isotherms for various solvent vapors with different molecular sizes were measured at 25 °C on SFM and SiM samples calcined at 400 °C as shown in Figure 7a,b, respectively. The adsorption isotherms for large molecules such as toluene and mesitylene fit the Langmuir plot, whereas those for smaller molecules such as water and methanol fit the BET plot. This finding suggests that the pore sizes are of the order of the largest molecular sizes examined (7.6 Å for mesitylene). This is also in good agreement with the finding that the nitrogen adsorption isotherms fit the BET plot for a limited number of adsorption layers.

As can be seen from Figure 7, the adsorption of water on sol pillared clays is slightly suppressed in the lower P/P_0, which can be attributed to the hydrophobic nature of oxide pillar surfaces.[23,24] The adsorption of methanol

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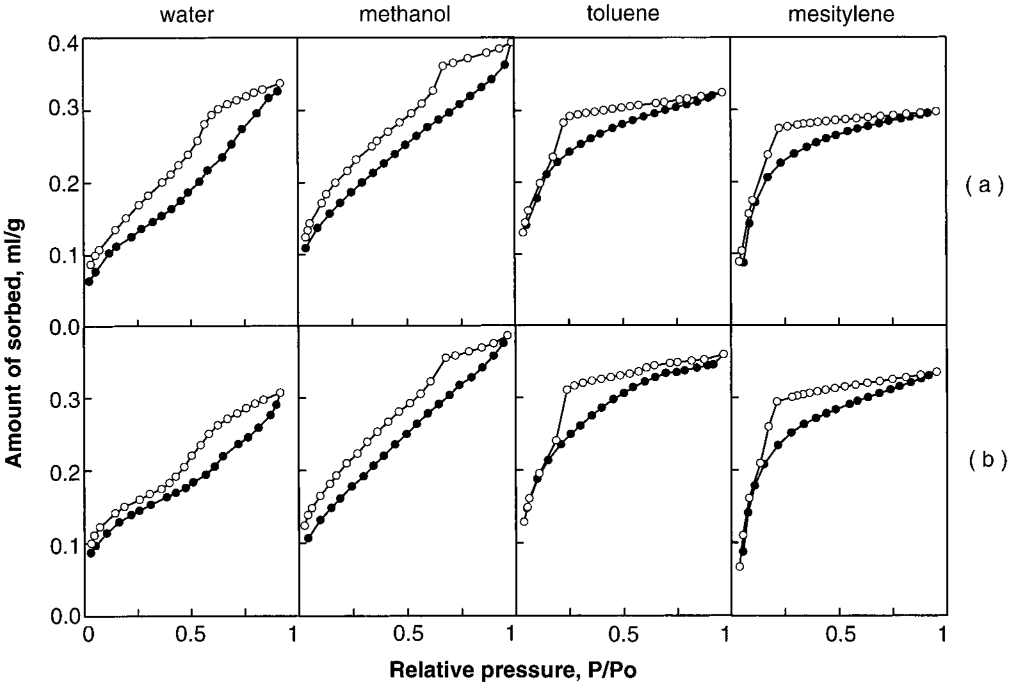

Figure 7. Adsorption−desorption isotherms of (a) $SiO_2-Fe_2O_3$ (SFM) and (b) SiO_2 (SiM) sol pillared montmorillonites calcined at 400 °C for different solvents.

increases linearly with vapor pressure, and the desorption branch does not meet the adsorption branch even at very low relative pressure. According to the literature,[25,26] methanol can undergo a surface condensation reaction by which methanol reacts with surface silanol to give $-OCH_3$ groups firmly attached to the surface. This unique chemical affinity between the silica surface and methanol may increase the methanol adsorption in the sol pillared clays. Moreover, the strong interaction leads to chemical adsorption of methanol (fixation of $-OCH_3$ groups) on pillar surfaces, resulting in irreversible adsorption−desorption isotherms. The Langmuir type adsorption behavior of toluene and mesitylene molecules on both samples reflects that the multilayer adsorption of such molecules is restricted due to the limited pore sizes, which is consistent with the result of nitrogen adsorption analysis. All the isotherms exhibit hysteresis extending to very low P/P_0. It is difficult to put forward a single explanation for this, but irreversible adsorption of water and methanol (possibly chemical reaction) on pillar surfaces and the activated entry of large adsorbate molecules (toluene and mesitylene) through small pores might be responsible for the hysteresis in the low-pressure region.

Acidic Property. The TPD spectra for SFM and SiM heated at 600 °C are compared in Figure 8. The spectra consist of two peaks: (i) a strong peak at 80−100 °C and (ii) a weak one in the temperature range 200−300 °C. Peak (i) can be attributed to the desorption of ammonia weakly bound to acidic sites; the desorption peak at 80 °C for SFM is slightly shifted to higher temperature for SiM. Peak (ii), which is due to the ammonia desorption from higher acidic sites, is also shifted from 270 °C for SFM to 300 °C for SiM. These shifts can be interpreted in terms of the removal of weakly acidic Fe_2O_3 covering the surfaces of silica sols and silicate layers by acid washing. The relatively low desorption temperatures indicate that SiM and SFM are characterized as weak acidic solids.

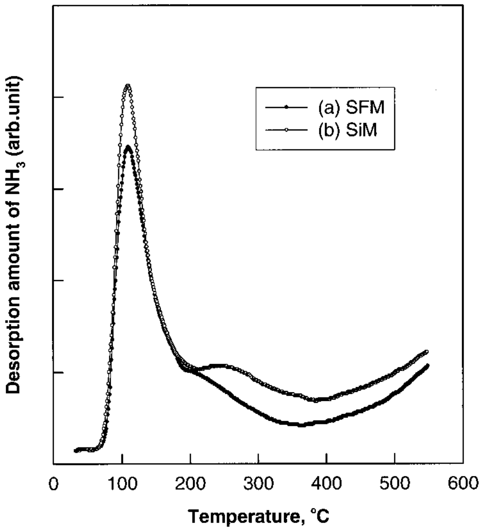

Figure 8. Temperature-programmed desorption (TPD) spectra of ammonia for the (a) SiO_2-Fe_2O_3 (SFM) and (b) SiO_2 (SiM) sol pillared montmorillonites calcined at 600 °C.

Discussion

Silica sol particles obtained by the acid hydrolysis of TEOS are negatively charged and are not suitable for use as pillar precursors. As a result of this study, it was proved that the surface charge of silica sol particles could be changed to positive with Fe^{3+} polyhydroxy cations and easily taken up by montmorillonite by ion-exchange. As a charge modifier, Fe^{3+} ion has the following advantages over the other elements. At first, polyhydroxy cations of iron can be obtained easily by hydrolysis of iron salts in an acidic pH range.[27,28] Since the surface of silica particle has negative charge in this pH range, the Fe^{3+} ions are deposited onto the silica

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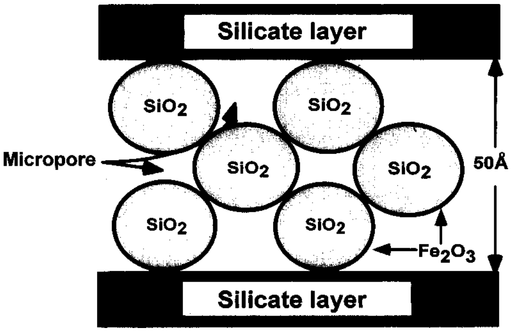

Figure 9. Schematic structural model of silica sol pillared montmorillonite.

surface, then grow to polycation species by a base titration. Second, the iron hydroxides or oxides are highly soluble in the acidic aqueous solution,[29] which enables us to remove iron species by washing with the acidic aqueous solution after the ion-exchanging reaction. In addition, aqueous Fe^{3+} ion species carry a unique color (brown), which makes it possible to monitor the degree of the removal of the iron by the naked eye.

The resulting $SiO_2-Fe_2O_3$ and SiO_2 sol pillared clays show basal spacings as large as ~60 Å with a regular stacking sequence as judged from the XRD data (Figure 2). However, the nitrogen adsorption isotherms are of type I (Figure 5), indicating that the pores are much smaller than the basal spacing. In our previous report,[18] we proposed a multilayer arrangement of sol particles for SiO_2-TiO_2 sol pillared clays, where micropores are formed in the interstices between the sol particles and the silicate layers of clay. A similar arrangement of sol particles would also be expected in silica sol pillared clays as shown in Figure 9.

As can be seen from Table 1, more than 9 mol equiv of $SiO_2-Fe_2O_3$ was taken up by the clay ($O_{10}(OH)_2$ anion basis). This amount is much larger than that of SiO_2-TiO_2 sol pillared clay (~7 mol equiv).[18] This large interlayered sol content may be the reason for the larger interlayer separation and higher specific surface areas of sol pillared clays.

Besides the high specific surface area, SFM and SiM exhibit high thermal stability. The thermal stability of pillared clay is determined by the stabilities of silicate lattices and pillar species. Although the decomposition of the structural OH groups of dioctahedral smectites occurs in the temperature range 600−650 °C, the framework of the silicate layer can be stabilized up to higher temperatures if the structural OH groups are converted to O^{2-} ions by condensation with oxides or hydroxides between the silicate layers.[20,21,30] The TG and IR studies clearly showed that such condensation occurred at temperatures below 600 °C in the silica sol-based pillared clays. The destruction of the pillared structures should be caused by the sintering of pillars and a total reaction between pillars and silicate layers. As discussed above (Table 1), a large amount of sol particles were intercalated between the silicate layers and close-packed in an ordered manner. It is very likely that the high thermal stability of SFM and SiM is due to the large pillar content and high sintering resistance of oxide sol particles.

Conclusions

$SiO_2-Fe_2O_3$ sol pillared montmorillonite can be obtained by intercalating positively charged $SiO_2-Fe_2O_3$ mixed oxide sol particles into the silicate layers of montmorillonite. By leaching out the iron species from the $SiO_2-Fe_2O_3$ sol pillars with an acidic solution, SiO_2 sol pillared montmorillonite was derived. It was found that the resulting sol pillared clays showed a large basal spacing up to 60 Å and the interlayered sol particles stacked in a quite ordered manner, generating micropores between sol particles and silicate layers. Remarkably high BET specific surface areas up to 720 m^2/g for SFM and 850 m^2/g for SiM, respectively, were observed. The obtained porous structure was retained at least up to 800 °C due to the larger pillar content and sintering resistance of the sol particles. Both SFM and SiM samples could be characterized as microporous solids with weak acidic sites.

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