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Preparation and Properties of Clays Pillared with SiO_2-TiO_2 Sol Particles

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The silicate layers of montmorillonite clay were pillared with SiO_2–TiO_2 sol particles. Although only the SiO_2 sols were negatively charged, the SiO_2–TiO_2 mixed oxide sols were positively charged and could be ion-exchanged with the interlayer cations of montmorillonite. The resulting pillared clays had a basal spacing expanded to more than 40 Å; the spacing was maintained during calcination up to 773 K. The adsorption properties of the calcined samples were studied for nitrogen as well as organic vapors. A structural model for the arrangement of the intercalated sol particles is proposed in which small SiO_2–TiO_2 sol particles are packed between the silicate layers. Micropores with a slit width of 10—12 Å are formed in the interstices between the sol particles and the silicate layers.

Pillared clays are a growing new family of microporous materials in which the silicate layers of smectite clays are pillared with metal oxide particles to form zeolitic micropores between the silicate layers. Various kinds of metal oxides such as Al_2O_3,[1)] ZrO_2,[2)] Cr_2O_3,[3,4)] Fe_2O_3,[5–7)] TiO_2,[8,9)] ZrO_2–Al_2O_3,[10)] Al_2O_3–SiO_2,[11)] and Al_2O_3–Ga_2O_3[12,13)] have been introduced to make porous structures; their thermal stabilities, adsorption properties and catalytic activities have been extensively studied. Comprehensive reviews concerning recent developments in this field are available.[14–23)]

The first, and important, step in pillaring clay is an ion-exchange of the interlayer cations of clays with oligomeric hydroxy-metal cations as pillar precursors, which are converted into oxide pillars between the silicate layers by calcination. Although silica is also an interesting oxide for pillars, the precursory oligomeric ions available are in the form of silicate anions which cannot be used for cation exchange reactions. In order to avoid this problem, Endo et al.[24,25)] used tris(acetylacetonato)silicon(IV) complex cations, $[Si(acac)_3]^+$, for the precursor cations or neutral silicon compound, $SiCl_4$, which can be hydrolyzed in the interlayer spaces by in situ reactions. The silica pillared clays, thus obtained, showed relatively low surface area of 40—190 $m^2\,g^{-1}$ and a maximum basal spacing of 12.6 Å. This spacing implies the existence of pillars of one oxygen layer thickness. Lewis et al.[26)] introduced silica pillars by using polyhedral oligo-silsesquioxane compounds of the general formula $(ZSiO_{1.5})_n$, where n is an even number ($n \geq 4$) and Z is an organic moiety containing an atom(s) possessing cationic and/or coordinating characteristics, such as pyridine. The silsesquioxane intercalates into the interlayer spaces by the affinity of the organic groups with clays. Calcination of the products at 443—973 K yielded silica pillared products with basal spacings of 16.2—19.2 Å and surface areas of 140—400 $m^2\,g^{-1}$. Recently, Moini and Pinnavaia[27)] attempted direct intercalations of both commercial and hydrolyzed silica sol into montmorillonite. They found that relatively large surface-area solids of 250—460 $m^2\,g^{-1}$ were formed, though they could not obtain a regular intercalation phase. In the present study silica sol prepared by the hydrolysis of silicon tetraethoxide has been successfully intercalated into montmorillonite by modifying the sol with titania sol.

Experimental

Materials. Clay: A sodium montmorillonite (Kunipia G) was supplied by Kunimine Industrial Company, Japan. Its structural formula was determined to be $Na_{0.35}K_{0.01}Ca_{0.02}(Si_{3.89}Al_{0.11})(Al_{1.60}Mg_{0.32}Fe_{0.08})O_{10}(OH)_2 \cdot nH_2O$ and the cation exchange capacity (CEC) was measured to be 100 mequiv/100 g of clay. About a 1% aqueous suspension of the montmorillonite was used for the reaction with sol solutions.

Sol Solutions: A silica sol solution was prepared by mixing silicon tetraethoxide $Si(OC_2H_5)_4$, 2 M (1 M=1 mol dm^{-3}) HCl and ethanol in a ratio of 41.6 g/10 ml/12 ml at room temperature, according to Sakka et al.[28)] Titanium tetraisopropoxide $Ti(OC_3H_7)_4$ was hydrolyzed by adding it to a 1 M HCl solution in such a way that the molar ratio of $HCl/Ti(OC_3H_7)_4$ was about 4. The resulting slurry was peptized to a clear sol solution by continuous stirring for 3 h at room temperature.

Pillaring. The silica and titania sol solutions, thus prepared, were mixed in various ratios and then stirred for 30 min at room temperature; they were then added to the clay suspension. The mixed ratios are hereafter designated as 30/3/1, for example, where the first and second numbers refer to the molar ratios of silica and titania to the CEC equivalent (the third number) of the clay, respectively. The reaction temperature as well as the mixing ratio were variously changed. After stirring for different reaction times, the products were separated by centrifugation, washed with water several times, and dried in a stream of dry air at room temperature.

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Analyses. Before air-drying, a small portion of wet product was spread on a glass slide in order to achieve the preferred orientation of the sample. X-ray powder diffraction (XRD) patterns were measured on the oriented sample by using a diffractometer with graphite monochromatized Cu *Kα* radiation. Elemental analyses of the products were perfomed by an atomic absorption method on a sample fused with lithium metaborate at 1273 K and dissolved in a 3% HNO_3 solution.[29] Adsorption–desorption isotherms for nitrogen were measured volumetrically at the liquid nitrogen temperature by using a computer-controlled measurement system; the samples were precalcined at temperatures ranging from 373 to 773 K and degassed by evacuation at 473 K for 3 h prior to the measurement. Adsorption–desorption isotherms for various solvent vapors having different molecular sizes were measured gravimetrically at 298 K by using a quartz spring balance. The vapor pressures were measured by an electric pressure transducer, MKS Baratron (Model 315 BH).

Results

Pillaring. When only the silica sol solution was subjected to a reaction with montmorillonite, no swelling of the montmorillonite was observed, and the sol solution was clearly separated from the montmorillonite by centrifugation. However, the addition of even 1 part of the titania sol to 40 parts of the silica sol in mole is effective to increase the basal spacing to about 40 Å. Figure 1 shows a series of typical XRD patterns of the product obtained from a reaction mixture of 30/3/1 at 323 K, and thermally treated at room temperature (air-drying), 573 and 773 K. The basal spacing expanded to a value as large as 38 Å; higher order reflections (2nd and 3rd) were observed, suggesting the formation of a regularly intercalated compound. Though the spacing was slightly reduced upon heating, the structure appeared to be maintained at least up to 773 K. In order to observe the effect of the reaction temperature on the basal spacing, three mixtures (10/1/1, 30/3/1, and 50/5/1) were continuously stirred for 3 h at 298, 323, and 353 K. Figure 2 shows the basal spacing of the resulting products. Apparently, if larger amounts of sol solution and higher reaction temperatures are used, products with larger basal spacings are obtained. In order to avoid precipitation of the silica sol outside the clay at higher temperatures, most of the reactions were performed at 323 K, unless otherwise specified. Three different mixtures (100/10/1, 30/3/1, and 10/1/1) were used, and the change in the basal spacing was recorded as a function of the reaction time (Fig. 3). The spacing increased rapidly soon after the clay was mixed with the sol solutions, and then attained constant values after about 6 h, though a gradual increase was still observed after that. As can be seen from the figure,the amount of silica sol (10 times the equivalent of the CEC) seems not to be sufficient; an amount of 30—50 times the equivalent of the CEC would be required to obtain fully expanded products.

Nitrogen Adsorption. Figure 4 shows the nitrogen adsorption–desorption isotherm of a typical pillared

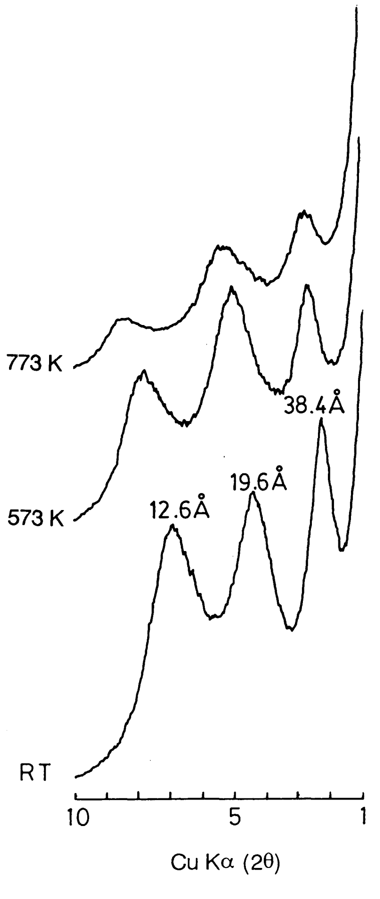

Fig. 1. X-Ray power diffraction patterns of a typical reaction product (30/3/1) air-dried at room temperature (RT) and calcined at 573 and 773 K.

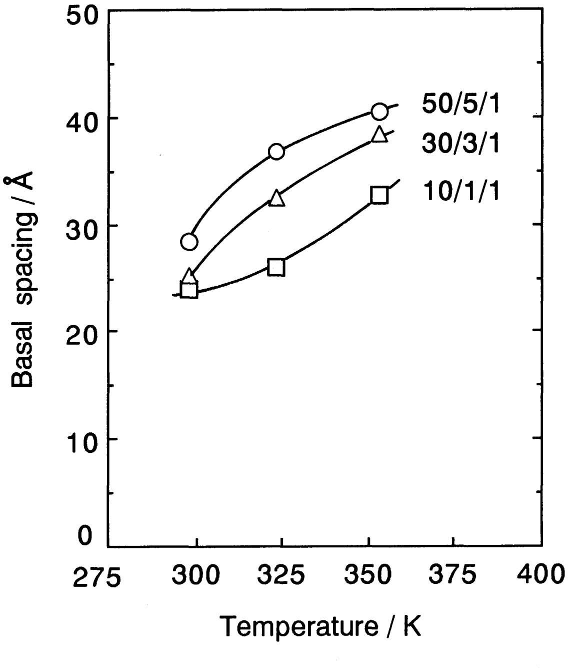

Fig. 2. Basal spacings of the products obtained from three different mixtures of SiO_2–TiO_2 sols and clay as a function of the reaction temperature.

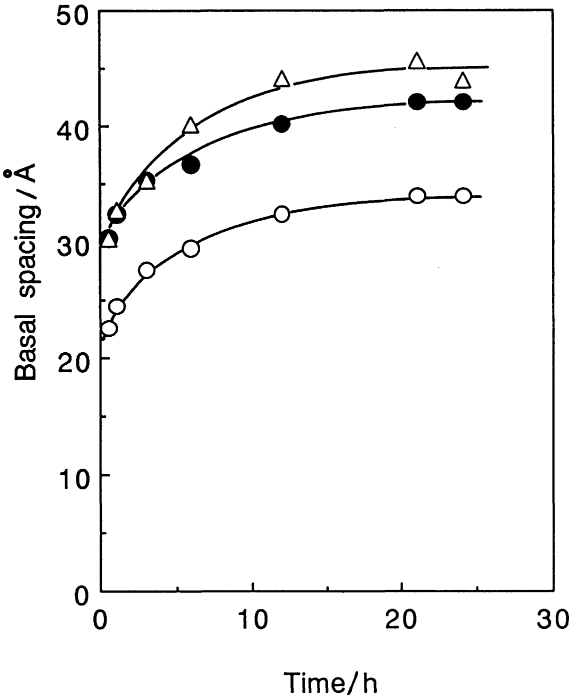

Fig. 3. Basal spacings of the products as a function of the reaction time at 323 K. Three different mixtures were examined: ○, 10/1/1; ●, 30/3/1; △, 100/10/1.

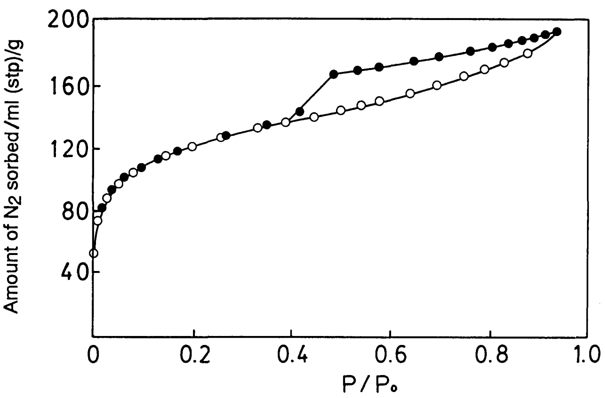

Fig. 4. Adsorption–desorption isotherm of nitrogen for a typical reaction product (50/5/1) calcined at 773 K; ○, adsorption and ●, desorption.

clay (50/5/1). The adsorption isotherm gives a good fit on the Langmuir (Type I) as well as the BET (infinite number of adsorption layers) equation, the regression coefficients being 0.9978 and 0.9989, respectively. A much better fit was obtained using the BET equation for a limited number of nitrogen adsorption layers.[30] The number of the layers was estimated to be 2—3. Figure 5 shows the basal spacings and the surface areas of the sample (50/5/1) as a function of the calcination temperature. The basal spacing and the high specific surface area were maintained at least up to 773 K. For convenience, two kinds of specific surface areas determined by applying the BET (infinite adsorption)

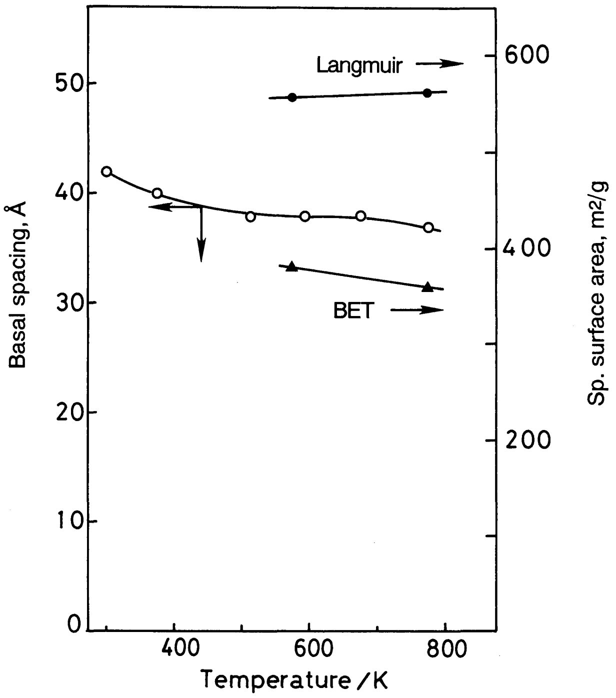

Fig. 5. Basal spacings and the specific surface areas of the sample as a function of the heat-treatment temperature. Two-kinds of surface areas (BET and Langmuir) were compared.

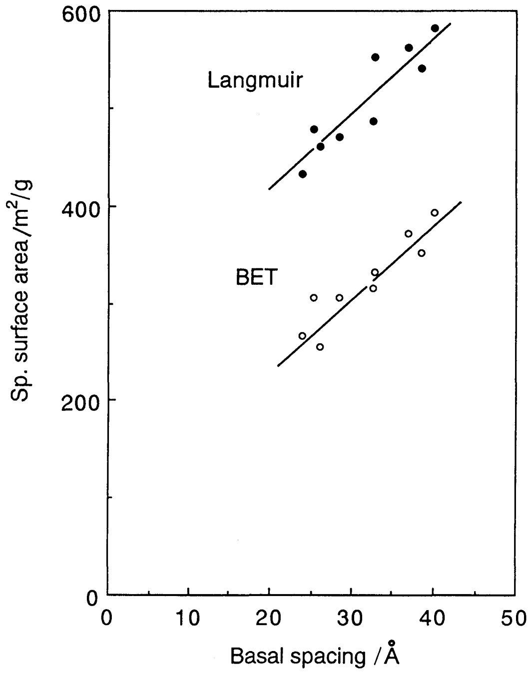

Fig. 6. Specific surface areas as a function of the basal spacing of the samples shown in Fig. 2. Two kinds of surface areas (BET and Langmuir) were compared.

and Langmuir equations are shown together in the figure. The former surface area is related to the amount of nitrogen required for mono-molecular coverage of the pores; the latter one is related to the pore filling capacity by liquid nitrogen (1 ml of gaseous nitrogen (stp) corresponds to 1.547×10^{-3} ml of liquid nitrogen). Figure 6 shows the relationship between the basal spacing and the surface areas for the samples shown in Fig. 2. The surface areas increased almost linearly with the spacing, suggesting that the porosity of the interlayer spaces is almost constant, irrespective of the basal spacing.

Effect of the Sol Composition. Sol solutions with a variety of SiO_2/TiO_2 molar ratios were prepared and mixed with the montmorillonite suspension. The pillared products were separated and analyzed concerning the SiO_2, TiO_2, and Al_2O_3 contents by atomic absorption method. Both the reaction conditions and the analytical results are listed in Table 1. The composition of the silicate layers of the clay was assumed to be unchanged.

Table 1. Chemical Analysis Data of Pillared Clays Prepared under Different Conditions

Sol compositions	Reaction conditions		Analytical results/%			Pillar compositions[a)]			
SiO_2/TiO_2/CEC	Temp/K	Time/h	SiO_2	TiO_2	Al_2O_3	$SiO_2(x)$	$TiO_2(y)$	$x+y$	x/y
24/6/1	323	10	64.6	15.0	12.7	3.49	1.29	4.78	2.70
15/15/1	323	10	50.8	31.8	9.43	4.15	3.82	7.97	1.08
6/24/1	323	10	31.9	51.7	8.29	1.74	6.97	8.71	0.25
10/1/1	323	3	73.0	5.70	12.4	4.66	0.50	5.16	9.32
30/3/1	323	3	73.0	8.15	10.9	5.83	0.82	6.65	7.11
50/5/1	323	3	70.5	10.35	10.2	6.15	1.11	7.26	5.54

a) The compositions (x and y) are given in moles for $O_{10}(OH)_2$ anion basis of the silicate layer.

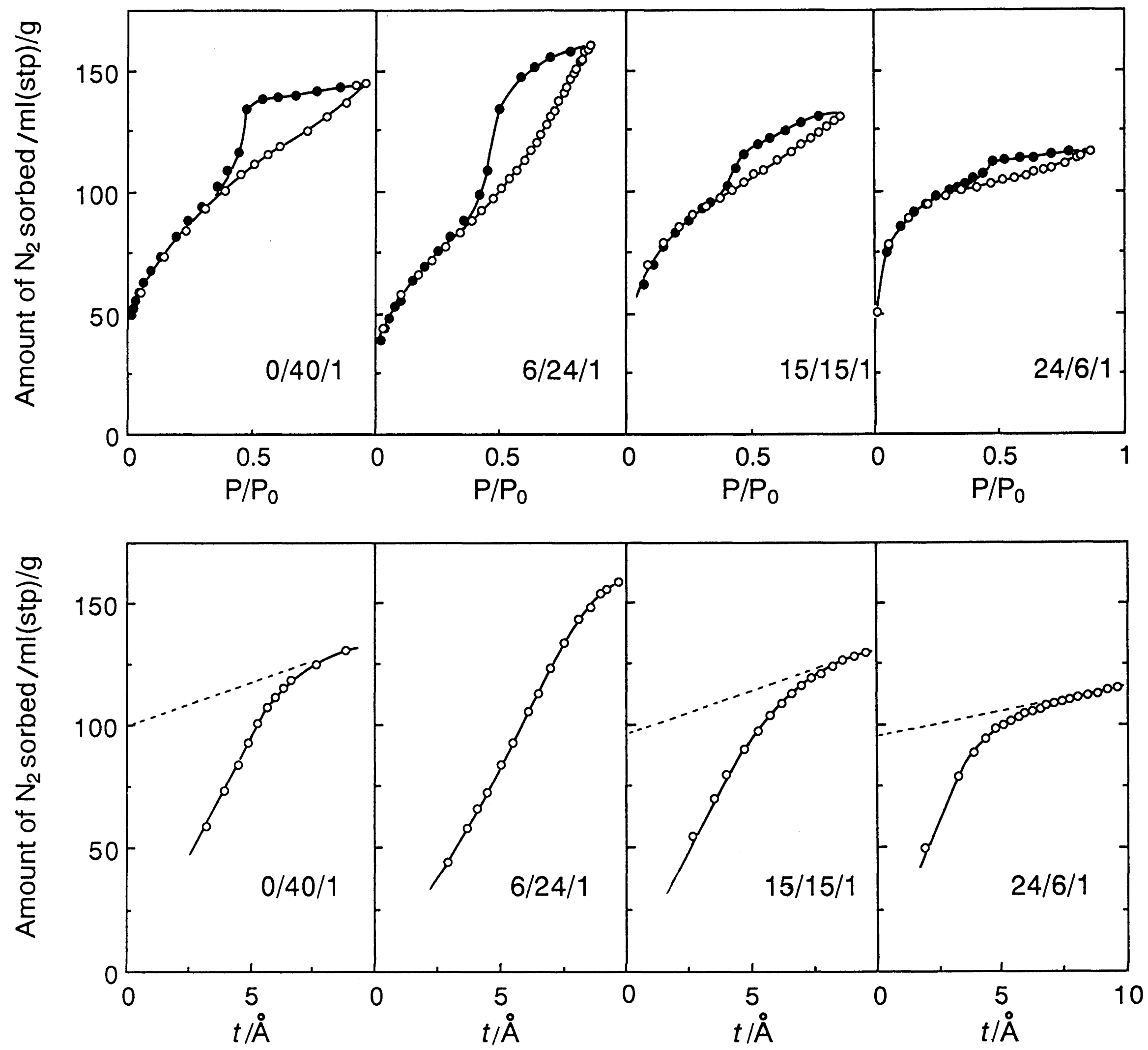

Fig. 7. Adsorption–desorption isotherms (upper), and the respective t-plots (lower), for pillared clays prepared by using the sol solutions with different SiO_2/TiO_2 ratios.

The amount of SiO_2 coming from the silicate layer was estimated from the Al_2O_3 content and subtracted from the total SiO_2 content. The resulting sol formula, $(SiO_2)_x(TiO_2)_y$, are shown on the $O_{10}(OH)_2$ anion basis of the clay. As can be seen from the table, more than 6—7 molar equivalents of SiO_2+TiO_2 are taken up by the clay, and the SiO_2/TiO_2 ratio of the interlayer sol composition is always higher than the corresponding ratio of the sol in the solution used. There is a tendency that the interlayer sol composition deviates to a larger extent from the composition of the solution when a larger amount of the sol to the CEC is used and the SiO_2/TiO_2 ratio is higher.

The nitrogen adsorption–desorption isotherms and the *t*-plot for the samples prepared by using sol solutions having different SiO_2/TiO_2 ratios are shown in Fig. 7. The TiO_2 pillared clay had an adsorption isotherm of Type IV according to the classification of Brunauer, Deming, Deming, and Teller,[31] as reported in a previous paper.[8] With an increase in the SiO_2/TiO_2 ratio of the sol solution used, the isotherm became more Type-I-like, suggesting that the pores formed in the interlayer spaces must be smaller than ca. 15 Å in diameter. A *t*-plot is given for the adsorption isotherm of each sample in the figure. The pillared clays prepared from the sol solutions with higher SiO_2/TiO_2 ratios showed a downward deviation in the *t*-plot at the high-pressure region. The line extrapolated from the high-pressure branch to the adsorption axis gives a large intercept which is equivalent to the microporous volume.[30] The nitrogen adsorption isotherm for a pillared clay with a low SiO_2/TiO_2 ratio of 6/24 showed a slight upward deviation. This deviation suggests the existence of a small fraction volume of mesopores. The slit width of the pores can be estimated from the *t* value, where the *t*-plot shows a downward deviation; a value twice this *t* value is assigned to an approximate slit width of the pores. The slit width of the pores, thus obtained, is shown in Table 2, together with other adsorption data calculated from the isotherms and the *t*-plots shown in

Table 2. Adsorption Data for Pillared Clays Prepared under the Sol Solutions with Different Compositions

Sol compositions $SiO_2/TiO_2/CEC$	Sp. surface area/m^2 g^{-1}		Micropore volume	Slit width $2t$
	BET	Langmuir	ml g^{-1}	Å
0/40/1	284		0.147	14
6/24/1	249			
15/15/1	280	473	0.142	12
24/6/1	286	463	0.142	10

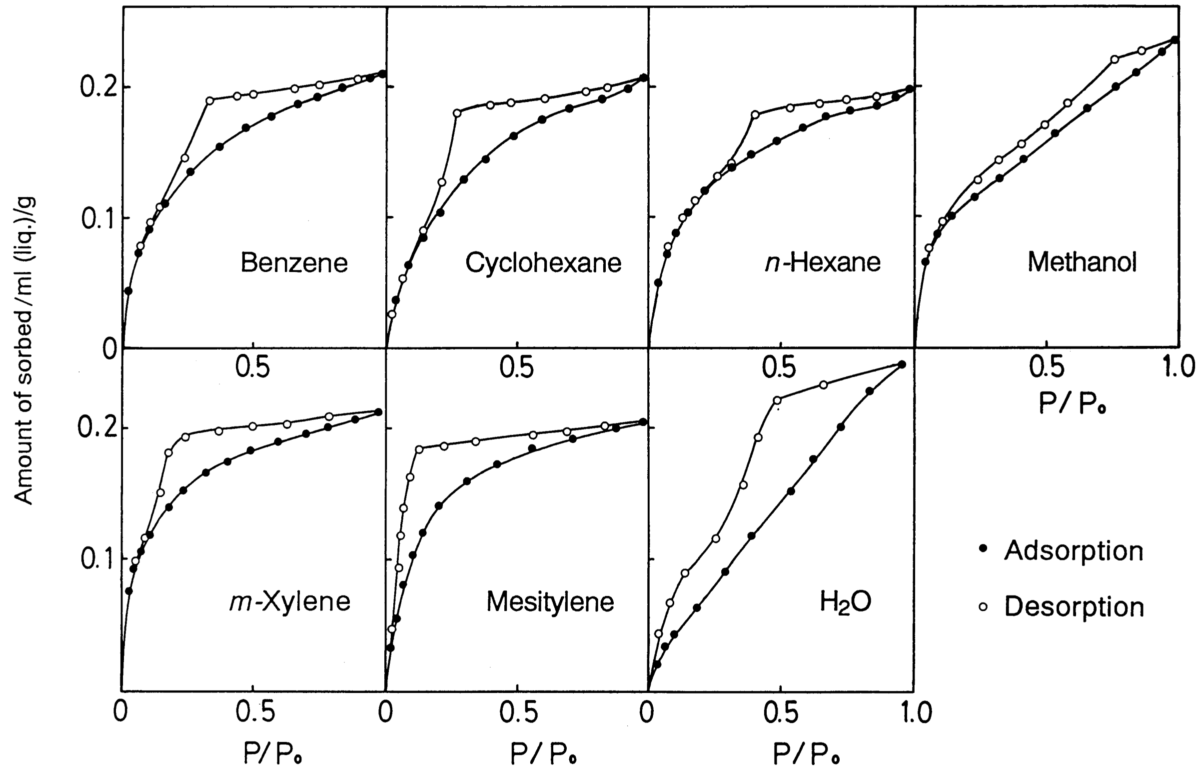

Fig. 8. Adsorption–desorption isotherms of sol pillared clay for different solvent vapors.

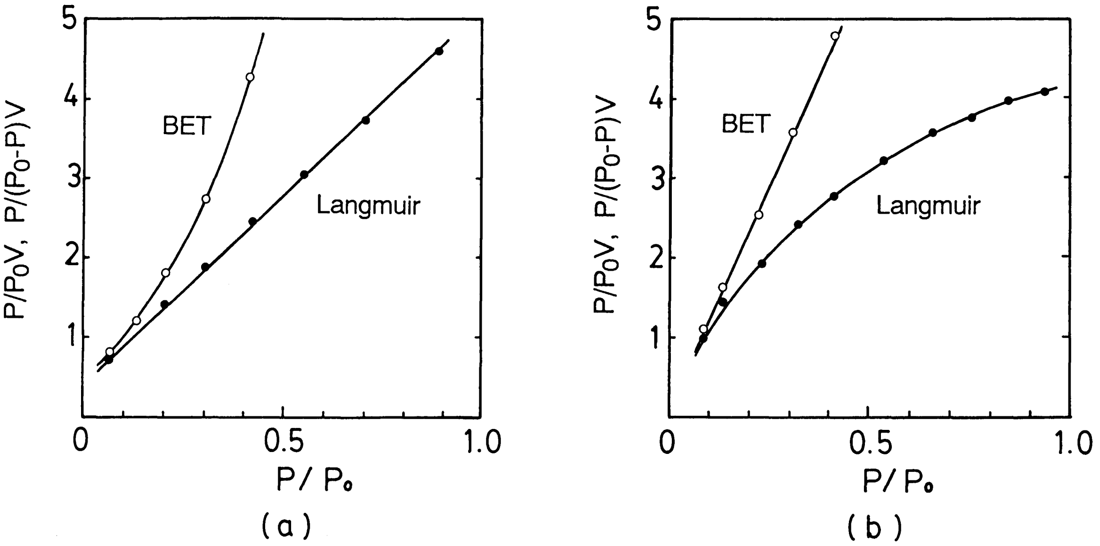

Fig. 9. Langmuir (P/P_0V vs. P/P_0) and BET ($P/(P_0-P)V$ vs. P/P_0) plots for the adsorption of mesitylene (a) and methanol (b).

Fig. 7. The slit width of the pores is in the range 10—12 Å, and decreases with an increase in the SiO_2/TiO_2 ratio of the sol solutions used.

Adsorption of Solvent Molecules. Adsorption–desorption isotherms for various kinds of solvent vapors were measured at 298 K on the sample (30/3/1), and are shown in Fig. 8. In Fig. 9 some of the adsorption data are plotted using Langmuir and BET isotherms. The adsorption isotherms for large molecules fit the Langmuir linear plot, whereas those for smaller molecules, such as water and methanol, fit the BET plot. This finding suggests that the pore sizes are in the order of the largest molecular sizes examined. This is also in good agreement with the finding that the nitrogen adsorption isotherm fitted the BET plot for a limited number of adsorption layers. In the figure the amount of adsorbed vapors is plotted in the liquidous volumes of the solvents. The amount of adsorption near the saturation vapor pressure for each solvent corresponds to the total pore volume to be filled with the liquid. The pore volumes (porosity), thus calculated, are listed in Table 3. The porosities for the solvents with relatively large sizes are in the range 0.20—0.21 ml g^{-1}; those for small sizes are about 0.25 ml g^{-1}. The difference in the porosity is attributed to the existence of ultramicropores which are accessible only by small molecules, such as water and methyl alcohol, but not by larger molecules.

Table 3. Pore Volumes of the Pillared Clays for Various Solvent Vapors and the Types of the Adsorption Isotherms

Solvents	Pore volumes ml g^{-1}	Isotherm
Benzene	0.21	Langmuir
Cyclohexane	0.20	Langmuir
n-Hexane	0.20	Langmuir
m-Xylene	0.21	Langmuir
Mesitylene	0.20	Langmuir
Methanol	0.24	BET
Water	0.25	BET

Discussion

The silica sol particles obtained by the hydrolysis of silicon tetraethoxide are negatively charged, and can be converted into positively charged sols by a modification with a small amount of titanium ions. The modified sol particles can be ion-exchanged with the interlayer cations of montmorillonite. The resulting clays have basal spacing values remarkably larger than those ever reported for clays pillared with ceramic oxides. As shown in a previous paper,[8] the clay pillared with TiO_2 sol particles had a basal spacing ranging from 24 to 27 Å. The nitrogen adsorption isotherm was of Type IV. The TiO_2 pillar height was estimated to be 15—18 Å. In SiO_2-TiO_2 pillared clays, although the basal spacing was much larger than those of the TiO_2 pillared clays, the nitrogen adsorption isotherm was of Type I-like, suggesting that the pore sizes were much smaller than the pillar heights. In addition, as shown in Fig. 6, the packing density of the interlayer sol particles seems to be uniform irrespective of the interlayer distance; the pore sizes are about 10—12 Å from the adsorption studies.

Taking these findings together, we propose a structural model for the SiO_2–TiO_2 sol pillared clays in Fig. 10; the average size of the SiO_2–TiO_2 sol particles must be much smaller than the interlayer spaces. Such small sol particles are packed uniformly so as to form small pores between the sols and silicate layers. The sols are modified by the TiO_2 on the surface and are positively charged. In the present study we used only one hydrolyzed condition in the preparation of the SiO_2 sol solution from silicon tetraethoxide. Different hydro-

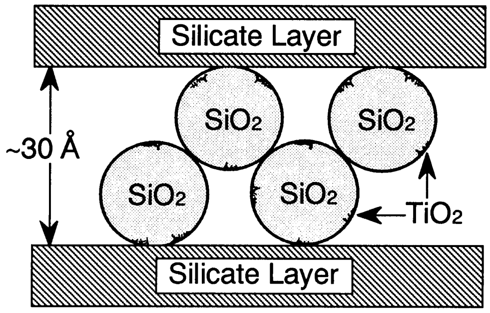

Fig. 10. Schematic structural model of the arrangement of the SiO_2–TiO_2 sol particles in the interlayer space of montmorillonite.

lysis conditions will provide SiO_2 sols with different sizes and distributions.

The strong acidic properties of the SiO_2–TiO_2 pillared clays has been reported elsewhere.[32] In a very recent study, the SiO_2–TiO_2 sol pillars were replaced in part with organic cations (octadecyltrimethylammonium). It was found that burning off the organic part left behind mesopores in the interlayer spaces.[33]

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