Preparation of Silica-Pillared Fluorohectorite by Cointercalation of Polysiloxane and Polyvinyl Alcohol

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ポリシロキサンとポリビニルアルコールの同時インターカレーションによるシリカ架橋フッ素ヘクトライトの合成

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Silica-pillared clays with mesopores were prepared from fluorohectorite, aminopropyltriethoxysilane (APS) and tetraethoxysilane (TEOS) affected using polyvinyl alcohol (PVA). The presence of PVA was important in this synthesis and was effective on the porosity of the obtained silica-pillared clays. Based on the X-ray diffraction measurements, the basal spacings of the silica-pillared clays increased from 1.7 to 5.6 nm with an increase in the PVA concentration. As with the basal spacings, the peaks of the pore size distribution and the average pore diameter shifted up to approximately 3 nm. The pore volumes corresponded to the basal spacings expanded by cointercalation of PVA and polysiloxane. The pore properties and structures of the pillared clays were investigated and the results indicated the relation between the layer structure and pore structure.

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1. Introduction

The successful intercalations of pillaring species into the interlayer space of clay minerals have led to many attempts to prepare new classes of porous materials, which exhibit interesting properties for adsorption, separation and catalysis. Pillared clays are attracting interest with regard to their use under severe conditions since inorganic materials have better thermal and chemical stabilities than organic materials. Various sizes of inorganic polyhydroxocations have been intercalated as pillaring precursors to control the pore size.^{1)–3)} Silica is one of the oxides of interest for obtaining thermally stable and catalytically active pillared clays. Silica pillared clays have been prepared from a titania-silica or iron oxide-silica complex sol because silica precursors are silicate anions, which cannot enter between the clay sheets.^{4)–6)} In spite of the large interlayer distance of the sol pillared clay, the obtained pores were mainly micropores due to the multilayer stacking of the nanosize sol particles between the silicate layers. The mesoporous sol pillared clays have been synthesized using quaternary ammonium surfactants as templating agents.^{5),7)–10)} On the other hand, a silica pillared montmorillonite has been synthesized using ion exchangeable aminopropyltriethoxysilane (APS) to intercalate the clay sheets in aqueous solution instead of inorganic polyhydroxocations. The polycondensation by APS hydrolysis between the silicate layers was expected to form larger pores.¹¹⁾ However, there was no significant increase in the basal spacing even though the silica content significantly increased with the APS. The pore properties were not increased by the addition of an excess APS for the ion exchange capacity. The pre-intercalation of the alkylammonium ions between the clay layers and the controlled addition of water to the reaction achieved a significant enhancement in the surface area and pore volume. Polysiloxane, which are polycondensation of APS molecules, has been incorporated into

the clay layers.¹²⁾ The polysiloxane pillared clay provided micropores below 1 nm. The method that improves the pore properties can employ the cointercalation of nonionic templates, which are water-soluble polymer^{13)–16)} or are nonionic surfactants,^{9),17),18)} other than the cationic surfactants. We have prepared silica-pillared clays with larger surface areas and pore volumes using polysiloxane and polyvinyl alcohol (PVA)¹⁹⁾ as with the alumina-pillared clay or zirconia-pillared clay by the PVA method.^{13)–16)} The presence of PVA in the interlayer space left the distance between the silicate layers expanded. PVA was incorporated into the interlayer region of expandable clays without interfering with the ion exchange process.

We have recently reported the production of pillared clays with long basal spacings, large surface areas and pore volumes using APS and tetraethoxysilane (TEOS) with the PVA method.²⁰⁾ The pore sizes enlarged up to the meso region by changing the molar ratio of TEOS to APS. The gallery heights of the pillared clays shifted up to approximately 3 nm.

In this paper, we report the preparation of the silica-pillared fluorohectorite by the co-intercalation of the PVA and cationic polysiloxane, which consist of APS and TEOS. The influence of the PVA concentration on the obtained structure and pore properties of the porous materials is investigated.

2. Experimental

2.1 Syntheses and characterization of pillaring precursor

APS (2.32 g, Shin-Etsu Chemical Co., Ltd.) was neutralized by 5 mol/dm³ HCl solution (2.10 cm³). TEOS (2.19 g, Colcoat Co., Ltd.) was added dropwise to the reacting solution mixture under vigorous stirring (pH 2–4). The obtained solution was clear and was stored for one week at room temperature to form a gel. The gel was aged at 353 K for 24 h and the solvent was removed. The product gel was dissolved in

distilled water (10 cm^3) at 373 K.

The infrared spectra of the APS monomer and the silica precursor before dissolution were recorded on a JASCO FTIR-480Plus spectrometer after mixing with KBr. A sodium oleate aqueous solution (0.2 mol/dm^3 , 55 cm^3) was added to the silica-pillaring precursor solution in order to derive the siloxane with an ammonium group. The insoluble product was obtained by filtration using a membrane filter ($0.47 \mu\text{m}$, Millipore), washing the water-soluble siloxane and excess surfactant, then air drying. The water-insoluble product was calcined at 1073 K, and then the weight of the calcine was measured.

2.2 Reaction with clay

Fluorohectorite ($\text{Na}_{0.33}\text{Mg}_{2.67}\text{Li}_{0.33}\text{Si}_4\text{O}_{10}\text{F}_2$, Topy Industries, Ltd.) that was synthesized by a melting method was used as the host material. The cation exchange capacity (CEC) of the fluorohectorite is 0.70 meq/g . One gram of the clay was added to the aqueous PVA (degree of polymerization: 1000) (14 mass%; 20 g). Different amounts of distilled water were added to the suspension followed by stirring for 2 h. Silica-pillaring precursor solutions, which contained the ammonium group of 15-fold molar vs. the CEC of the host clay, were then added to the resultant mixtures. They followed by more stirring for 2 h. The determined PVA concentrations of the solutions were 0.0, 2.0, 4.0, 6.0, and 8.0 mass%. The pastes were separated by centrifugation. No further washing was carried out to investigate the effect of the PVA concentration, because PVA, which was water-soluble, would exude into the water. The pastes were dried at 353 K for 24 h. Next, the silica-intercalated clay was calcined at 873 K for 3 h in order to remove the organic components.

2.3 Characterization of pillared fluorohectorite

The X-ray diffraction measurements (XRD) were carried out using a Rigaku RINT 2200 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The specific surface area and total pore volume of the pillared clays were determined from the nitrogen adsorption-desorption isotherms at 77 K. These were recorded on a Quantachrome Autosorb1-AG. The samples were degassed at 423 K for over 4 h under vacuum before analysis. The pore size distributions were estimated by the BJH method²¹⁾ from the adsorption isotherms. The specific surface areas were estimated using the BET equation and the external areas were estimated by the t -plot method.²²⁾ Elemental analysis of the silica content of the sintered samples was carried out by X-ray fluorescence spectroscopy (XRF) using a Rigaku System 3270. Amorphous silica was used for the calibration of the intensity. The original fluorohectorite sample for comparison was calcined at 873 K for 3 h.

3. Results and discussion

The infrared spectra of APS monomer and the silica precursor before dissolution are respectively shown in Fig. 1. The spectrum of APS monomer (a) in Fig. 1 exhibited characteristic bands of the alkyl chain at 2960, 2931 and 2872 cm^{-1} ; characteristic bands of the primary amine at 3385, 1615 and 1485 cm^{-1} ; a characteristic band of C-N at 1146 cm^{-1} ; and a characteristic band of Si-O-C at 1100 cm^{-1} . The spectrum of the silica precursor (b) in Fig. 2 exhibited characteristic bands of the primary ammonium ion at 3000–2800, 2018, 1605 and 1486 cm^{-1} ; a characteristic band of the silanol group at 3500 cm^{-1} ; a characteristic band of C-N at 1132 cm^{-1} ; and a characteristic band of Si-O-Si at 1080 cm^{-1} . Based on these results, it was found that the neutralization and hydrolysis of APS and TEOS by hydrochloric acid solution produced the protonated ammonium ions and siloxane linkages. We cannot

Fig. 1. FTIR spectra of (a) APS monomer and (b) the polysiloxane consisting of APS and TEOS.

Fig. 2. X-ray diffraction pattern of (a) the original fluorohectorite, and the silica-pillared fluorohectorites prepared in (b) 0.0%, (c) 2.0%, (d) 4.0%, (e) 6.0% and (f) 8.0% PVA concentration after calcination at 873 K for 3 h.

clarify the degree of polymerization and the molecular weight of the silica precursors. The calcined water-insoluble silica precursor, which was organized by oreate, weighed 1.22 g. It

Table 1. Pillaring Silica Components of the Pillared Fluorohectorite Prepared in Different PVA Concentrations

PVA concentration /mass%	Component mixed ⁽¹⁾		Uptake silica found ^{(1),(2)} SiO ₂
	APS	TEOS	
0.0	15.0	15.0	15.6
2.0	15.0	15.0	27.4
4.0	15.0	15.0	25.5
6.0	15.0	15.0	25.8
8.0	15.0	15.0	22.8

1) Components are given in molar ratios to one equivalent of CEC of fluorohectorite.

2) Uptake silica component estimated from the original fluorohectorite (silica 62.4 mass%) and the synthesized pillared clays by XRF measurement

corresponded to 97% of the silica loading (APS and TEOS). This result indicates that the hydrolyzed APS combines with almost all the TEOS. As a result, a polysiloxane with a Si–O–Si framework is obtained when the hydrolysis of APS and TEOS is performed in a strongly acidic aqueous solution, such as a hydrochloric acid solution. Furthermore, the silica precursor gel can be dispersed in the water due to introducing water molecules into the hydrophilic spaces between the polysiloxanes which have ammonium groups and Cl[−].²³⁾

The integration between this silica precursor and fluorohectorite has been investigated for various concentrations of PVA, which are the important parameters influencing the pillaring process. It is postulated that this precursor involves an anion exchange as with polyaminopropylsiloxane hydrochloride,^{12),(23),(24)} which provides the reactivity with clay. **Table 1** shows the uptake of the silica contents in the silica-pillared fluorohectorite based on the XRF measurements and the source material contents of the loaded silica-precursors, which correspond to the molar ratios of the host clay CEC. The silica uptakes were calculated from the silica content of the original fluorohectorite, which was 62.4 mass%, and the silica contents of pillared fluorohectorite. We cannot deduce whether the adsorption of the silica precursor occurs at the internal or external surface of the clay. The silica uptake of the clay synthesized in dilute PVA solution corresponded very well with the silica molar content of the loaded precursor, as shown in Table 1. This is consistent with the above result which suggests that some silanol groups combine to form a siloxane linkage between APS and TEOS, because the silica-sol cannot be inserted alone in the interlayer space due to the negative charge of the sol particle.⁴⁾ It is probable that the silica precursor is a cationic polysiloxane like polyaminopropylsiloxane hydrochloride.²³⁾ The silica uptake slightly decreased with the change in the PVA concentration in the intercalation process. However, for the pillared fluorohectorite without PVA method, it held only half as much of the loaded silica precursor. It seems that a portion of the silica precursor remains in the supernatant liquid. An appropriate amount of PVA could be incorporated into the interlayer region of the expandable clays without interfering with the ion exchange process. In spite of addition of the silica-pillaring precursors containing an excess amount of the ammonium group on basis of the CEC of the host clay, many of the pillaring precursors were reacted with the fluorohectorites. We presume that the reason for the adsorption of the silica-pillaring precursor containing an excess amount of the ammonium group is as follows. The

ammonium groups of the polysiloxanes prepared from APS and TEOS and host clay sheets charged negatively interact with each other. It is probably that some of ammonium group of polysiloxane are exchanged with the cations of the host clays and the other ammonium groups of the polysiloxane do not contribute to the electrostatic attraction in the solution. It seems that the other excess ammonium groups incorporate Cl[−] as counter anions in the clay compensate the positive charge on polysiloxane when water is evaporated. Hence the polysiloxane linkage would permit the adsorption of polysiloxane containing more ammonium groups than the CEC of the clay.

The XRD patterns of the pillared clays after calcination at 873 K are shown in Fig. 2. The pillared clay without PVA (b) shows 001 basal spacing of about 1.7 nm. It is apparent that the distance becomes larger than the raw material hectorite (a) of 1.2 nm. The XRD pattern profiles of the pillared clay with PVA and without PVA become broad. This indicates that the pillaring results in more irregular structures of the clay and the increase of heterogeneity provide the weakening of reflection intensity. Pillared clays give XRD patterns typical of layer structure in which ordering along c axis only is visible because of the intensive orientation owing to plate form. The 001 peaks of the pillared clay with PVA 2% (c), 4% (d), 6% (e), and 8% (f) were observed at $2\theta = 1.91^\circ$ ($d = 4.62$ nm), $2\theta = 1.71^\circ$ ($d = 5.16$ nm), $2\theta = 1.64^\circ$ ($d = 5.38$ nm), and $2\theta = 1.53^\circ$ ($d = 5.77$ nm), respectively. We assigned the peaks of $d(001)$ of approximately 1/2 and 1/3 to the high order reflections 00 l as with other pillared clays with PVA method,^{13)–16)} although the peaks at around 3.5 nm and 5.5 nm were not distinct due to the broad pattern. The peaks at a low diffraction angle correspond to the basal spacings enlarged by the simultaneous intercalation of the polysiloxane and PVA between the clay layers. The pillared clays exhibited the 001 reflection at a lower diffraction angle with an increase in the PVA concentration, indicating an expansion of the distance between the silicate layers. The gallery height of the sample synthesized in 8.0 mass% PVA is estimated to be 4.8 nm by subtracting the 0.96 nm thickness of the silicate layer⁴⁾ from the basal spacing value of 5.8 nm. As above description, the gallery heights of the sample synthesized at PVA 2.0, 4.0 and 6.0 mass% are estimated to be 3.4, 4.2 and 4.4 nm. On the other hand, pillared clays without the PVA method had a broad peak at a basal spacing of around 1.7 nm. This result agrees with the intercalation of APS¹¹⁾ or of the polyaminopropylsiloxane hydrochloride^{12),(19)} without the template method. The rearrangement of the polysiloxane, such as polyaminopropylsiloxane, may provide the gallery height of approximately 0.7 nm between the clay layers in any polymerization or configuration. The presence of PVA during pillaring is necessary for the expansion of the distance between the silicate layers as with the intercalation of the polyhydroxoaluminium or polyhydroxozirconium.¹³⁾

The detailed information of the pore structure in these pillared clays must be derived from the nitrogen adsorption-desorption data. The nitrogen adsorption-desorption isotherms at 77 K of the pillared fluorohectorite in PVA 0.0, 2.0, and 8.0 mass% are shown in Fig. 3. A higher adsorption capacity is seen in the pillared fluorohectorite with the PVA treatment than that without the PVA treatment. The isotherm for 0.0% (a) of PVA indicated a typical figure generally observed for microporous substance. Adsorption below a relative pressure of 0.4 occupied most of the overall amount adsorbed, indicating the existence of a large number of micropores. In contrast, the adsorptions of sample of PVA 2.0%

Fig. 3. Nitrogen adsorption-desorption isotherms at 77 K for the silica-pillared fluorohectorite prepared in (a) 0.0%, (b) 2.0% and (c) 8.0% of PVA concentration.

Fig. 4. Pore size distribution curves of silica-pillared fluorohectorites prepared (a) without PVA, (b) in 2.0% PVA, and (c) in 8.0% PVA.

(b) and 8.0% (c) increased in the high relative pressure region. PVA treatment results in a significant increase in the porosity and the adsorption capacity of clay. The obvious hysteresis in the isotherms of (b) and (c) in Fig. 3 is attributed to the existence of mesopores. Figure 4 shows the pore size distributions derived from the nitrogen adsorption isotherms of the pillared fluorohectorites by intercalation of the polysiloxane at different PVA concentrations. These curves were obtained by the BJH method.²¹⁾ Based on the nitrogen adsorption-desorption measurements, the pore size of the silica-pillared clays increased with the increase in the PVA concentration. They gave the pore size distribution of the mesopores and

Fig. 5. BET surface area of the silica-pillared fluorohectorites plotted against PVA concentration.

micropores, which had the peaks at 2.3, 3.1 nm and below 1.0 nm, respectively. This result presented the same tendency as the increase in the gallery heights determined from the XRD measurements, which had a difference by about a nanometer in the estimated data. It appears that the pore size depends on the layer structure, because the *d*-spacing increase approximately corresponds to the peak shift amount of the pore distribution. On the contrary, the amount of intercalated silica pillars estimated by the XRF measurement is decreased with an increase in the PVA concentration. The clay sheets were swollen by the simultaneous intercalation of the pillaring precursors and PVA. The clay sheets were expanded as the PVA concentration increased. The silica pillar formation and PVA decomposition by calcination would form pores composed of the silica pillars and clay sheets. The pore size was greater than that of the other silica pillared clay using polysiloxanes.¹²⁾

The other pore properties of the silica-pillared fluorohectorites are shown in Figs. 5–8. As shown in Fig. 5, these pillared clays had BET surface areas from 160 to 270 m²/g of which were half that of the other pillared montmorillonite.^{6),11),13)} This result also conformed to that of fluorine mica.^{15),16)} This contraction might be due to the insufficiency of the clay delamination. The increase in PVA reduced the BET surface areas contrary to the extension of the gallery height. These reductions may be due to the decreasing micropores in the silica pillar penetrated by the PVA molecules rather than the structural change in the clay sheets, because it is assumed that a simple change in the gallery height produces not a change in surface area but an increase in the pore volume.

On the other hand, the external surface areas increased (Fig. 6), which were estimated by the *t*-plot method. The external surface areas, which are comprised of mesopore areas, were obtained from the slope of linear portion of the *t*-plot at a higher *t*-value. The *t*-plots of pillared clays revealed two linear sections. The curves suggested the presence of micropores and mesopores. More mesopores were developed by the PVA treatment, as indicated by the upward deviation of the adsorption isotherm at a higher relative pressure in Fig. 3. The synthesized sample in 8.0 mass% PVA gave an external sur-

Fig. 6. Effect of PVA concentration on the external surface area estimated by *t*-method of the silica-pillared fluorohectorites.

Fig. 8. Effects of PVA concentration on the basal spacing from XRD data and average pore diameter of the silica-pillared fluorohectorite.

Fig. 7. Effects of PVA concentration on the basal spacing from XRD data and pore volume of the silica-pillared fluorohectorite.

face area of 53 m²/g that accounted for approximately one quarter of the surface area. It is possible that the decreases in the micropores are more than that of the total surface areas. The pore volumes and *d*-basal spacings versus the PVA concentrations are shown in Fig. 7. The pore volumes were found to correspond to the basal spacings based on the XRD measurements. The pore volumes of the pillared clays are enlarged by the PVA method, which supports the expansion of the distance between the silicate layers. The average pore diameters are shown in Fig. 8 as a function of the PVA concentration. The average pore diameters increased with the increasing concentration of PVA as with the mesopore area. The average pore diameters suggested the same tendency of the basal spacings. These results suggested a relation between the interlayer distance height and pore properties. The behavior of such pore properties on the pillared clay including the pore volume and average pore diameter is consistent with the change in the *d*-

basal spacing. The pore sizes of the porous clays were proportional not to the surface areas but to the pore volumes. These results were similar to the behavior of the porous clays synthesized using surfactants.^{8),9)} As the alkyl chain of the surfactants increased in length, the mean radius of the framework pores in the porous clays increased. It seems that the PVA concentration would similarly contribute to the pore size of the pillared clays using the PVA method. The significantly changes were brought on the pore volumes and basal spacings whether there is PVA treatment. It is assumed that the surface area become the nearly value even if pillar content is separated from clay, however the layer structural change by pillaring can influence the basal spacings and pore volumes. The result suggests the evidence that the presence of PVA would advance incorporating of pillaring precursor and the absence of PVA would interrupt more penetrating of pillaring precursor. Based on these results, it is clear that there is an important influence of PVA on the pillaring mechanism.

However, there are differences of approximately 2 nm between the above pore diameters estimated by the nitrogen adsorption and the gallery heights which are considered to subtract the thickness of a silicate layer from the *d*-basal spacings. We reported that there were few differences between the pore size estimated by the adsorption isotherm and the gallery height estimated by XRD in the silica-pillared montmorillonite.²⁰⁾ Furthermore, the BET surface area of the silica-pillared montmorillonite of the previous work was a double of the BET surface area of this study despite using nearly the same amount of the pillaring silica. Based on these results, it can be presumed that the fluorohectorite used in this study delaminates into the multilayer stack.

The SEM image of representative sample of synthesized pillared clay in 2% PVA is shown in Fig. 9. The structure of pillared clay with large basal spacing was a scale structure which had the clay sheet stacked. The plate dimension of pillared clay was the size of the order of micrometer as seen from the step structure in Fig. 9.

Fig. 9. SEM image of the surface of the silica pillared fluorohectorite prepared in 2 mass% PVA.

4. Conclusions

We synthesized silica-pillared fluorohectorites with a various mesopore sizes using a polysiloxane with different PVA concentrations. In spite of adding the silica-pillaring precursor containing a 15-fold ammonium group amount based on the CEC of the host clay, the pillaring precursor of more 70 mol% was intercalated into the fluorohectorites over the tested PVA concentration range. PVA could expand the clay sheets and stimulate the intercalation of large amounts of polysiloxane which might be attributed to the ion exchange of some of polysiloxane for sodium ions. It seems that the siloxane linkages between the silane molecules allow the incorporation of more of the silica precursor, which was prepared from APS and TEOS by the sol-gel method, in the low PVA concentration. Based on the XRD pattern, the *d*-basal spacing increased up to approximately 6 nm. The pillar height of the pillared clay was adjusted by varying the concentration of PVA. It was found that the peaks of the pore size distribution and the average pore diameters had a tendency similar to the XRD measurements, which had a certain degree of difference. The pore volumes corresponded to the basal spacings expanded by coin-tecalation of PVA and polysiloxane. PVA had an influence on the other pore properties of the pillared fluorohectorites. It was found that the increase in the PVA concentration caused an enlargement in the interlayer space and the decrease in micropores. The PVA concentration contributed to the pore size for which the pillaring height depended on the PVA concentration. On the other hand, the increase in the PVA concentration provided the opposite results for the BET surface areas. The high PVA concentration interfered with intercalation of the pillaring silica precursors, which would form a certain micropore and surface area in silica pillars. The reduction of the intricate micropores probably contributes to this result. The small BET surface areas in comparison with the silica-pillared montmorillonites²⁰⁾ and the difference between the interlayer space estimated from the XRD measurement

and the pore structures derived from the nitrogen-adsorption isotherms may be attributed to an insufficient exfoliation of the fluorohectorite.

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