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# Synthesis of silica pillared clay by cointercalation of polysiloxane and polyvinyl alcohol

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# CHAPTER 1

# GENERAL INTRODUCTION

## 1.1 Backgrounds to the development and application of the pillared clays

Pillaring is commonly used procedure to transform a layered crystalline inorganic compound into a material with microporosity and mesoporosity. The kind of 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. The early report concerning pillared clay originate in the work of Brindley and Semples[1]. Then, the proposed calcination process made the preservation of clay mineral structure and of a pillar structure possible. 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. The resulting materials have an increased interlamellar distance, an increase pore volume, and are accessible by molecules in specific size range, i.e. they exhibit interesting properties for adsorption, separation, catalysis and molecular sieving properties.

The one of the major trend of the research interest on the pillared clays is how to control pore sizes [2,3]. The selection of the kind of the precursor is followed as pore size control procedure. Many research results are listed in Table 1-1 [2,4]. There are respectively the peculiar layer structures in relation to the cation species, the extensions of basal spacing are below 1 nm in most cases. The basal spacings of the silica sol pillared clay attain a considerable distance, because the condensed silica sols are

relative large particles. The silica sol pillared clays have large basal spacings, however it should be recognized that the basal spacings are not equal to the pore size in these results [3]. Moreover, the pillaring silica sols except containing ammonium group must involve other metal oxide, because silica sol cannot be inserted alone between aluminosilicate layers, which charge negatively, owing to the negative charge of the particle.

Table 1-1 Precursor cation used in pillaring clay and the resulting basal spacings [2,4]

| Pillar oxide | Precursor | Basal spacing(nm) |
|---|---|---|
| $Al_2O_3$ | $[Al1_3O_4(OH)_{24}]^{7+}$ | 1.7-1.9 |
| $ZrO_2$ | $[Zr_4(OH)_{14}]^{2+}$ | 1.7-2 |
| $Fe_2O_3$ | $[Fe_3O(OCOCH_3)_6]^{+}$ | 1.7 |
| $Cr_2O_3$ | $[Cr_n(OH)_m]^{(3n-m)+}$ | 1.7-2.1 |
| $Bi_2O_3$ | $[Bi_6(OH)_{12}]^{6+}$ | 1.6 |
| $Al_2O_3$-$SiO_2$ | $[Al_{13}O_4(OH)_{24-n}]$-$[OSi(OH)_3]_n^{7+}$ | 1.7-1.9 |
| $TiO_2$ | Sol solution | 2.4-2.7 |
| $SiO_2$ | Aminopropyltriethoxysilane | 1.7-1.9 |
| $SiO_2$-$TiO_2$ | Sol solution | 4-5 |
| $SiO_2$-$Fe_2O_3$ | Sol solution | 4-10 |

Next, it followed simultaneous intercalation of pillaring inorganic agent and organic compound as pore size control procedure. The capable organic compound penetrating clay sheets is restricted to be nonionic polar compound or be cationic molecule such as alkylammonium ion because of charged clay sheets. It becomes a large void space because the organic compound is excluded at calcination there, and the pore characteristic can be improved as a result.

At present point, valuable inorganic porous materials and the pore size are shown in Fig1-1 [2]. Zeolite have been known the only microporous crystal, in which micropores are as small as molecular scale (< 2nm). Xerogels and porous glass are controllable over a wide range. However, those are in region of mesopores and macropores. On the other hand, the syntheses of mesoporous silica have been tried in porous materials field with a great deal of success, and then those research works have been progressing [5-11]. The high regularity mesoporous silica is called FSM-16, MCM-41. Their intermediates consist of silicate anions and organic templates. The silicate anions and organic templates form liquid crystalline because of the self-organization of the organic templates and the interaction of molecules. The mesoporous silica has more advantage and superiority than the pillared clays. It seems that the superior parts are the homogeneity, ingenuity and crystalline of the pore size. If only the simple molecule species are adsorbed or are involved, mesoporous silica might be the most excellent. However, the material with the micropore and mesopore characteristic of the width of distribution is also necessary such functional material as the impurities removal substance of the indeterminate compound by adsorption. Pillared clays have the micropore and mesopore with a wide distribution at the expense of the

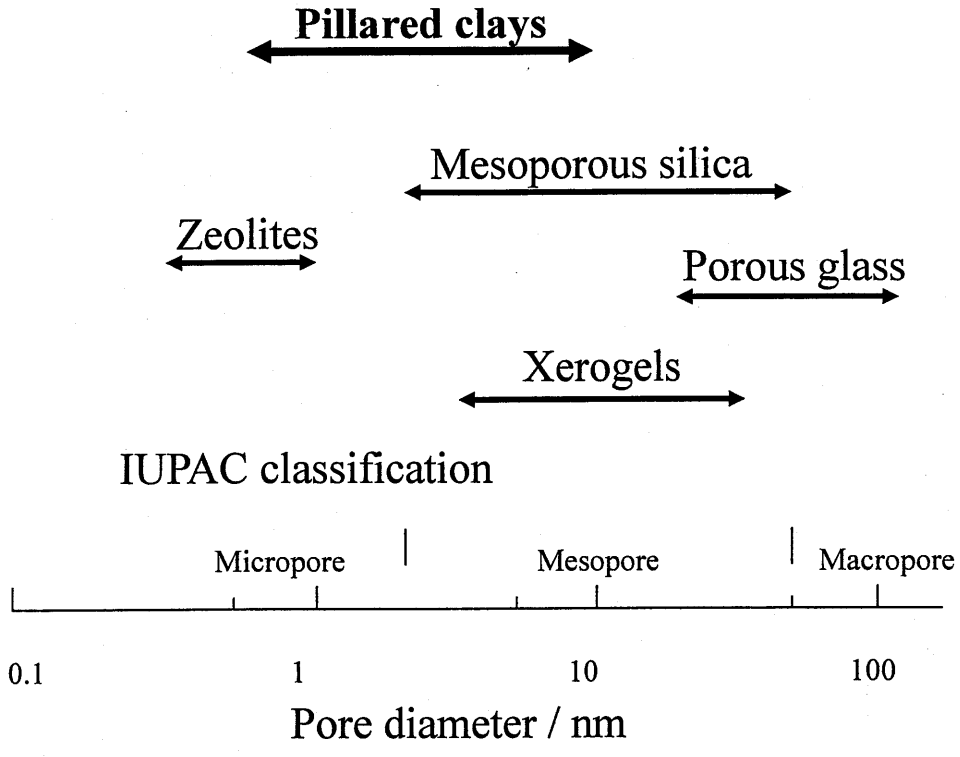


Fig1-1. Inorganic porous material and their approximate pore diameter with reference to the IUPAC classification[2]

elaborateness. In addition, it is economical, because the expensive organic template used in synthesizing the most of mesoporous silica is not used. It is consequentially suitable for a large amount of synthesis, because pillared clays can be synthesized in a high concentration solution though the most of mesoporous silica can be synthesized only from the dilute solution. It therefore appears that the pillared clays are the promising material with the microporosity and mesoporosity in terms of industry.

Recently, the following fields are paid to attention as an applicable field of the microporous and mesoporous material that can be supplied in large quantities. The high humidity becomes a problem in the housing condition, because they are for causes of allergy and dew drop. As the humidity measure, it dehumidifies with an air compressor. The result is that the energy expenditure keeps increasing. The material that can put steam in and out to keep appropriate humidity is profitable for the solution of energy and environmental problems. The porous material is brought to attention as the functional material [12]. There are some effective sizes in the water vapor adsorption because it is based on the theory of the capillary condensation. The relationship between vapor pressure and the capillary condensation of pores with Kelvin radius $r_K$ upon desorption is given by the equation

$$\ln ( P/P_0 ) = -2\gamma s V_m / r_K RT$$

where $\gamma s$ and $V_m$ are surface tension and molar volume of condensable gas, respectively, R is the gas constant, and temperature [13]. The relationships between the pore radius and humidity are calculated using above equation, and are listed in Table 1-2. It is

appropriate to being able to keep between humidity from 40 to 70 %, and to have a capability of vapor adsorption and desorption. It is considered that the effectual radius for humidity control is from 3 to 5 nm from the numerical value in Table 1-2.

Next, the food engineering is enumerated as other applicable field. The support material for the bioreactor and the removal material of the waste component from a liquid product are them. The molecular weight of the enzymes is several tens of thousands, and its size is from several nanometers to ten nanometers. The dissolved low-molecular -weight protein and peptide in fermented food production liquids to remove have molecular weights above 5000 [14]. The correlation diagram between molecular weight and molecular size, what is base on assumption that the peptide is spherical shape, is shown in Fig1-2. It is found from Fig1-2 that the pore radius of the several nanometers is suitable to absorb various kinds of the peptide molecules.

Table 1-2 Relation between relative humidity and Pore diameter

| Relative humidity / % | Pore diameter / nm |
|---|---|
| 13 | 1.1 |
| 33 | 2.0 |
| 42 | 2.6 |
| 52 | 3.4 |
| 74 | 7.4 |
| 85 | 13.8 |
| 93 | 30.8 |
| 97 | 73.2 |

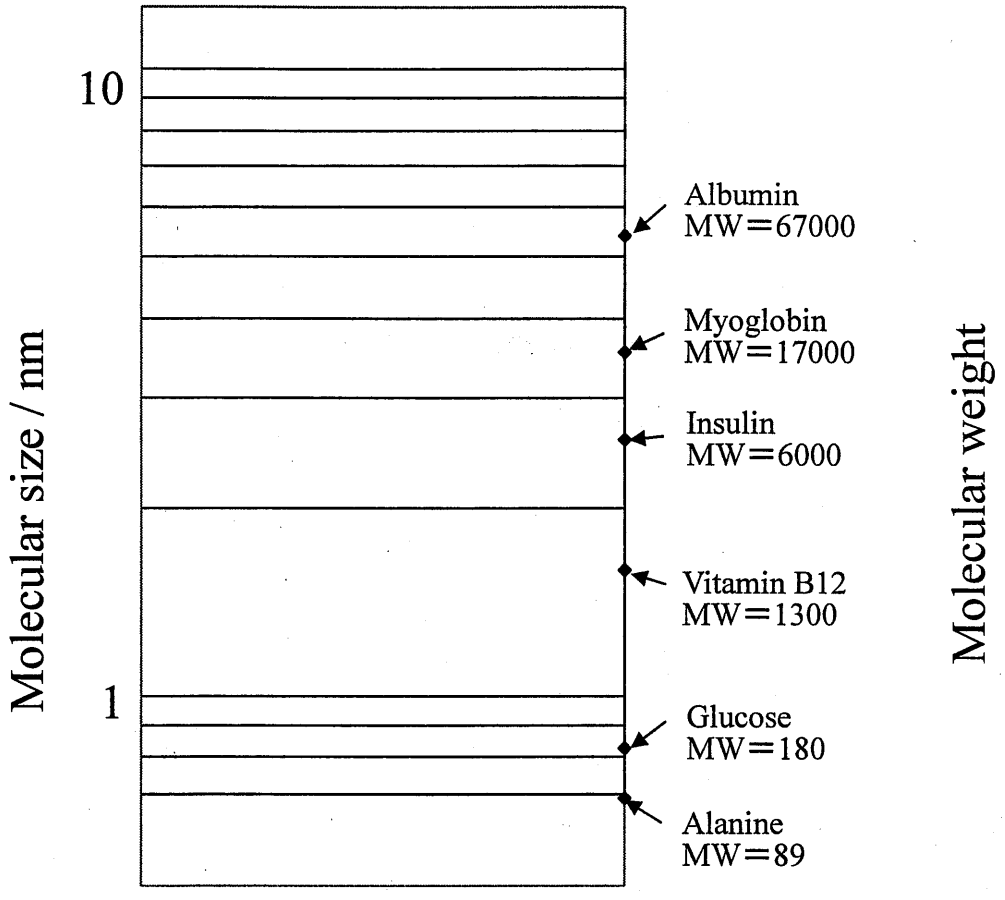


Fig1-2. Relation between the molecular size and weight of organic compound molecule.

## 1.2 Host materials used for the synthesis of pillared clay

The clay minerals what is called smectite is generally used as host materials for the synthesis of pillared clay. The host materials and the compositions are listed in Table 1-3. Montmorillonite, which is naturally occurring material, is the representative clay of expandable clay. It is most popular and useful ion exchangeable host structure for the intercalation. It has high reactivity and is used commonly for the synthesis of clay organic nanocomposite. The crystal structure of such a smectite clay sheet is shown in Fig1-3. The structure of montmorillonite is composed of stacked aluminosilicate layers with a thickness of nanometer level. The thickness of single aluminosilicate layer is 0.96 nm. The layer structured aluminosilicate is composed of two silica-tetrahedral sheets and one gibbsite $Al(OH)_3$ octahedral sheet coupled to form 2:1 silicate layers. The $Al^{3+}$ cation of the octahedral sheet are partially substituted by lower electrovalence cations such as $Mg^{2+}$ and $Fe^{2+}$, and the aluminosilicate layers are negatively charged. These net negative charges are balanced by the positive cations such as $Na^+$, $K^+$, and $Ca^{2+}$ occupying the interlayer spaces. The layered water molecules are configurated in alkali ions. The enlarged distance between aluminosilicate sheets is maintained by hydration sphere of alkali ions. In the case of synthetic hectorite, octahedral sheets consist of the magnesium hydrate $Mg(OH)_2$, The $Mg^{2+}$ cation of the octahedral sheet are partially substituted by lower electrovalence cations such as $Li^+$.

Table 1-3 Clay minerals and the compositions

| | |
|---|---|
| Montmorillonite | $Na_{1/3}[Al_{2-1/3}Mg_{1/3}][Si_4]O_{10}(OH)_2 \cdot nH_2O$ |
| Na hectorite | $Na_{1/3}[Mg_{3-1/3}Li_{1/3}][Si_4]O_{10}(OH,F)_2 \cdot nH_2O$ |
| Saponite | $Na_{1/3}[Mg][Si_{4-1/3}Al_{1/3}]O_{10}(OH,F)_2 \cdot nH_2O$ |
| Na tetrasilic mica | $Na[Mg_{2.5}][Si_4]O_{10}F_2 \cdot nH_2O$ |

$Na_{2/3}Si_8(Al_{10/3}Mg_{2/3})O_{20}(OH)_4$

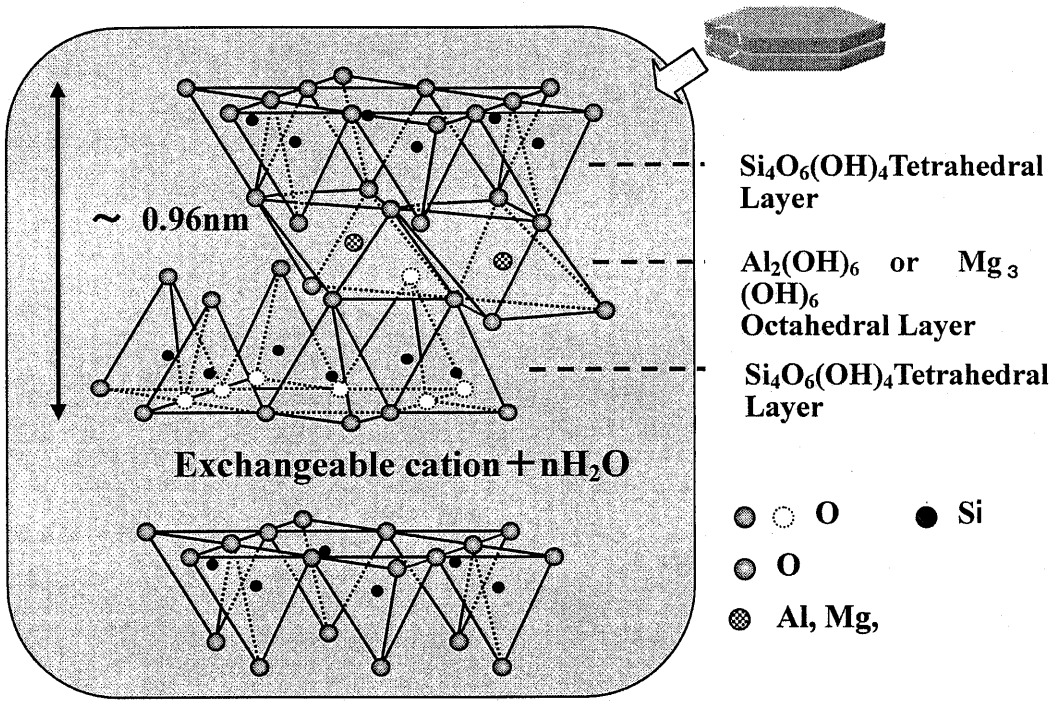


Fig1-3. Structure of montmorillonite

## 1.3 Mechanisms for intercalation and synthesis of pillared clay

Intercalation is insertion of guest species in the interlayer region of clay minerals such as montmorillonite, which is a typical ion exchangeable layered crystal. The interlayer cations can be exchanged with various kinds of guest cation, furthermore they can be exchanged with voluminous cations such as quarterly alkyl ammonium ions and metal hydroxyl ions. Neutral polar molecules are another guest compound. They can directly intercalate into interlayer spaces of clay sheets. The driving force for the intercalation is mainly due to dipole-cation interactions similar to the interactions involved in the solvation of cations in an electrolyte solution. On the contrary, nonpolar molecules cannot intercalate into the interlayer spaces regardless of their molecular sizes, because they can have only weak interaction with interlayer cations. Common scheme for the synthesis of pillared clays are illustrated in Fig1-4. The main reaction for the insertion of pillars is ion exchange. The hydrated interlayer cations between clay sheets are exchanged with cationic precursors such as polynuclear metal hydroxyl cations and polysiloxanes containing aminogroup. Next to the ion exchange procedure, the clay is separated by centrifugation and washed with water. The intercalated cationic precursors are then transformed into metal oxide pillars by calcination. This interlayer region, which is the space between adjacent layers of clay mineral, is called gallery height. The gallery height is a measure of approximate pore sizes formed between layers, although in some cases the pore size is smaller than the interlayer separation value [15-17].

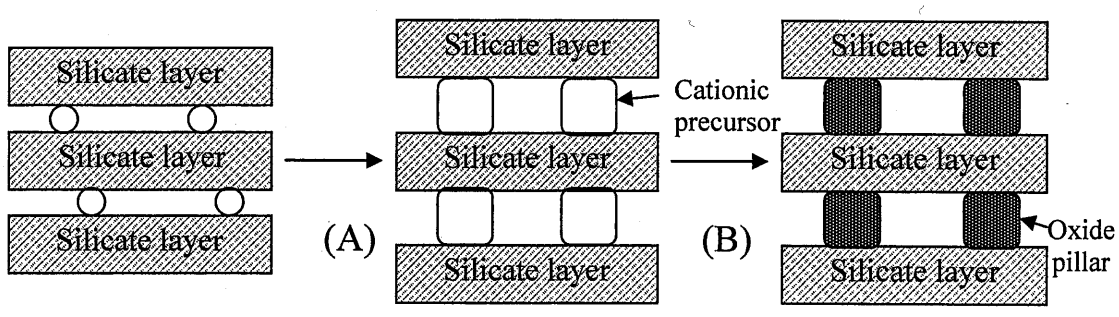


Fig1-4 Schematic illustration of the pillaring process in clay. (A)ion exchange with precursory cations and (B) conversion to oxide by calcination.

## 1.4 Pillaring agent

Pillaring is the process by which a layered compound is transformed into a thermally stable micro- and mesoporous material with retention of the layer structure. A pillaring agent is any compound, which can be intercalated between adjacent layers of a layered compound. It maintains the spacing between adjacent layers on removal of the solvent. The pillaring procedure originates from the work of Brindley and Semples[1] on clay minerals. They found that thermally stable inorganic oligomer, which is hydroxyl-aluminium could be intercalated between clay sheets. The reason was proposed to be an ion exchange reaction, followed by solvent removal. The latter work [18] is typically a calcination process with preservation of clay mineral structure and of a pillar structure. It has long been known that $Al^{3+}$ can be extensively hydrolyzed ($OH^-/Al^{3+}$=2.5), without precipitation, by addition of a base to or by dissolution of Al-metal in an Al-salt solution. The polynuclear cations exist in such solutions [19,20]. The mainly polynuclear cations are what is called the Keggin type Al oligomer, $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$. The resulting Al-pillared clays have an increased gallery height and increased pore volume in the micropore range. The pillared polyhydroxyaluminium clays have a sharp pore size distribution at 0.7 to 0.9 nm. Positively charged oxide sol particles can also be directly exchanged with interlayer cation of clay. $TiO_2$ sol which are prepared by hydrolysis of titanium tetraisopropoxide $Ti(OC_3H_7)_4$ can be inserted between clay sheets owing to the positive charge[21,22]. The titania pillared clays have a pore size distribution at 1.4 to 1.8 nm. The pillared structure is thermally stable above 773K, maintaining the pillar height as large as 1.4 nm and high surface area (300 $m^2/g$). The pillar heights are almost twice as large as

those of alumina pillared clays.

Silica sol is also one of the oxide sols of interest as pillars, because it promises not only to fill chemical stability of the substance and a peculiar catalyst attribute, but also to make it to the comparatively large particle by the condensations. However, silica sol alone cannot be incorporated with negatively charged clay aluminosilicate layers, because silica sol is negatively charged. It can be intercalated by the modification with positive ions on the surfaces [23,24]. Additions of $Ti^{4+}$ and $Fe^{3+}$ are sufficient to change the charge of the surface [15,16,21,22,25]. If the silica sols, which are obtained by hydrolysis of tetraethoxysilane (TEOS), are charged and intercalated, the gallery heights expand to more than 3 nm. Although the gallery heights are large, the nitrogen adsorption isotherms are Langmuir type, indicating that the pore size much smaller than the pillar height. Yamanaka proposed a structure model of arrangements silica-titania mixed sol particles [2]. It was confirmed that the sol particles were packed in the interlayer space in which micropores were formed in the interspace between the sol particles and the aluminosilicate layers. The direct intercalation of silica oxide sols has been tested as a route to pillared clay with high gallery [26]. Although the silica-clay products did not exhibit XRD evidence for long range order, complete segregation of clay and silica into separate phases was precluded by surface area values that were substantially larger than those from pure silica and clay components. The relationship between layer structure and pore was not indicated in the result.

Other methods are demonstrated as the synthesis methods of the silica pillared clays. It is considered that the pillar element is condensed between layers according to the method of the hydrolysis in situ between clay sheets. The methods provide the pillared

clay of silica whose sols are unsuitable for the intercalation because of its negatively surface charge. Silica has been intercalated in swelling clays by hydrolysis and oxidation of tri(acetylaceton)silicon(IV) cation, $Si(acac)_3^+$ in the interlayer regions of the minerals [27-29]. The $Si(acac)_3^+$ ions have been placed on the interlamellar surfaces by ion exchange and by in situ reaction. The hydrolysis reactions were observed and the silicic acids were formed in the interlayer. The basal spacings after calcinations at 773 K were observed at 1.26 nm of any products, indicating the presence of intercalated monolayer siloxane chains.

Other methods have been performed by Ahenach et al. [4,30-32]. Silica pillared clays has been synthesized using aminopropyltriethoxysilane (APS), the organic part of which is removed upon calcination. The XRD analysis results showed an increase in the basal spacing to a value of 1.7 nm probably due to the insertion of two layers of silica between clay sheets. In case of in situ hydrolysis of APS, however, a material with lower surface area and pore volume was obtained due to the clay interlayer space being completely occupied by silica pillars. It was demonstrated that a template synthesis method was applied in order to reduce the density of the pillars between clay sheets.

Silica pillared clay was prepared by ion exchange of alkali ions of swelling clay with cationic polysiloxane [33]. The cationic polysiloxane was prepared by sol-gel reaction of APS catalyzed by a strong acid such as hydrochloric acid. In the XRD profiles, this compound indicates the formation of a structural phase. The peak shifted due to a change in the humidity and the resulting product was completely dispersed in water [34]. In addition, the d-values of each peak of the anion-exchanged product shifted while depending on the bulk of the counter anion [34,35]. The transmission

electron microscopy images showed a stripe pattern, indicating that the polysiloxane parallel stacking. They, therefore, estimated that the product had the structure of a stacking of rodlike polymer with Si-O-Si framework at the core and ammonium groups extruding outside. The product material had a d-value of 1.8 nm, even though the positive polysiloxane reacted with the negative clay monolayer. Although the obtained material provided micropore in the interlayer space, it was significant that the polysiloxane which was much larger than molecule could be incorporated between clay sheets.

## 1.5 Cointercalation method of organic compound and aluminosilicate layer

Many attempts pillaring metal oxide resulted in the pillared clays with micropore. 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 particles between the aluminosilicate layers. It appeared that coexistence of the organic template with the inorganic pillaring agent is effective to form large pores [4,17,36-38]. The mesoporous silica pillared clays have been synthesized using quaternary ammonium surfactants as templating agents [17,36-38]. The silica pillared clays had the large gallery height expanded up to 4 nm. The complex method of TEOS and quaternary ammonium had significant in accomplishment to the synthesis of pillared clay with meso region pores. This method did not have an absolute advantage over something in terms of economical efficiency, because the expensive organic template used in synthesizing is used as with mesoporous silica.

For other organic compounds, polar polymers can be coexistent with pillaring agent.

Neutral molecule or polymer can incorporate in the layer structure as described in Section 1.3 if they have polarization. The possibility of cointercalating organic species together with the pillaring $Al_{13}$ ions, which is the Keggins type oligomer, has been proposed using nonionic surfactants [39-41]. Alkyl polyether surfactants containing hydrophobic and hydrophilic chain segments were used. The nonionic polyether surfactants could be incorporated with Al oligomers in clay sheets, and improved the hydrolytic stability of intercalated Al oligomers on the gallery surface. In contrast to the improvement of the surface areas and pore volumes, the usage of nonionic polyether surfactants caused an increase in basal spacing from 1.9 to 2.3 nm, which were from 1.0 to 1.3 nm in terms of the gallery height. The use of the alkyl polyether surfactants during synthesis facilitated clay platelet flocculation, although caused immediate layer flocculation during Al ions exchange and did not alter loading of Al oligomers in the galleries.

The basal spacings were expanded to approximately 3 nm by pillaring clays with polyhydroxocations in the presence of polyvinyl alcohol (PVA) unlike conventional pillaring method [42-45]. PVA can penetrate into the interlayer space because it is a polar polymer. Pillared fluorine micas, which had swelling property, were similarly prepared in the presence of PVA [46,47]. The amount of pillars increased with increasing concentration of pillaring agent, which supported the expansion of the distance between aluminosilicate layers. In contrast with the pillaring in the presence of PVA, the amount of pillars was almost the same irrespective of the concentration of pillaring agent without PVA. The basal spacing was also independent of the concentration. It was found that PVA was incorporated in the interlayer space of clay

without disturbing the ion exchange for pillaring process. PVA left the extended gallery space expanded and provided conditions for condensation of smaller Al oligomers into larger species. It seems that PVA cointercalation method shows the promise of the method for preparing pillared clays with control of the gallery height between aluminosilicate layers in a desired way, although the gallery height and pore diameter are extended up to only 2 nm because of the attempts of the intercalation of polyhydroxocations size below 1 nm.

## 1.6 Characterizations of pillared clay

A pillared clay has the following characteristics; ( i ) the aluminosilicate layers are propped apart vertically and do not collapse upon removal of the solvent and upon calcination; ( ii )the minimum increase in basal spacing is the diameter of $N_2$ molecule, commonly used to measure surface areas and pore volumes; (iii) the pillaring agent has molecular dimensions and laterally spaced in the interlayer space on a molecular length scale; (iv) the interlayer space is porous and at least accessible to molecules as large as $N_2$; there is no upper limit to the size of the pores. No order of pillars is required in interlayer region. The silicate layer of clay must be ordered as so to give an XRD pattern which allows the determination of the d001 spacing.

The representative characterization procedures for pillared clay are as follows [48]. A basal spacing is estimated from XRD pattern after removal of the solvent and after calcination. In general, the regularity of the product and information on the interlayer space between silicate sheets are obtained by observing a peculiar peak to the layer structure that appears on the low angle. The XRD pattern shows the d001 peak at a low

angle. A gallery height, which is an interlayer space distance between adjacent layers of clay mineral, of the pillared clay is derived to be a numerical value by subtracting the 0.96nm thickness of the silicate layer [2] from the basal spacing value.

Porosity in the mesoporous region is generally evaluated from $N_2$ adsorption -desorption at 77 K. The porous properties of the surface area and pore size, etc. are evaluated by using a suitable model for the expected pore size from the isotherms. The specific surface area is estimated using the BET equation from the $N_2$ adsorption data in a $P/P_0$(relative pressure) range of 0.05-0.3. Pore volume distribution with respect to pore radius is analyzed from $N_2$ adsorption isotherm on the assumption that equilibrium between gas phase and the adsorbed phase is determined by two mechanisms: physical adsorption on the pore wall and capillary condensation in inner volume [49]. In this work, the pore size distributions were estimated by the BJH method from the adsorption isotherms. The external areas, which are surface area outside micropores, are estimated by the t-plot method. The isotherm data of porous material can be plotted against t, and such a plot is known as the t-plot. The replacement of the relative pressure for a nonporous solid reference by the statistical thickness provides the t-plot [50]. If the multilayer adsorption mechanism is applicable over the entire range pressure, t-plot is a straight line passing through the origin and its slope is proportional to the surface area of the solid. However, in a porous solid with pore size distribution, smaller pores are completely filled with adsorbate molecules as the relative increase. Hence those pores are no longer available for further accommodating of adsorbate molecules. As a result, the slope of the t-plot decreases as the adsorption progresses further. The slope is proportional to the extra surface area, which is result of eliminating the influence of

micropores.

Commonly, it is proposed that the pillars prop the silicate sheets as the structural model for pillared clay. Though it is thought that there are correlations between the layer structure of clay and the pore structure, it is necessary to ensure that the observed porosity is result of pillaring and not simply a consequence of interparticle texture [2]. It was confirmed that the basal spacing increased rapidly soon after the clay mixed with sol solutions and then attained constant values at approximately 4 nm. However the nitrogen adsorption isotherm of sol pillared clay fitted on the BET plot for limited number of adsorption layers, suggesting that pore sizes were much smaller than the gallery height [3,17]. This result also suggests that the pore sizes are of the order of the molecular dimensions examined.

## 1.7 Subject of the present thesis

The present investigation is motivated from the review above mentioned. It is aimed at indicating the possibility that the processes provide the promise for the industrial production of microporous and mesoporous materials, because the pillaring method reduces the amount of solvent needed for the other methods and does not require the particular condition such as hydrothermal synthesis condition for the assembly. It is expected that the porous material is used for the industrial process and the adsorption material etc. of the mass processing when pore size can be enhanced to the mesoporous area without using the expensive organic template.

In this thesis, the results of process and the properties of the products on the synthesis of the silica pillared clay are discussed in the effect of the organic compound

coexistence and the form of pillaring agent. It has been understood that the coexistence of PVA is only effective in continuously expanding between layers as the above description. The other molecules such as alkyl ether surfactants or alkyl ammonium salt can burrow into the interlayer space and the complex with pillaring agent can only improve the surface area and the pore volume owing to the change of pillar filling. The gallery heights are confined to the size of inorganic pillaring compound. On the other hand, the cointercalation of PVA and pillaring agent can expand the interlayer space without depending on the size of pillaring agent. It is presumed possible to develop the synthesis of the pillared clay with larger pore than in the past. In addition, it seems likely that the large size agent such as polycondensation compound bring the expanded gallery height. The author therefore investigates the synthetic procedure and properties of the pillared clays, which are made from PVA and polysiloxane with cation exchangeable.

In Chapter 2, the effects of the coexistence of PVA are described, when the pillaring precursors consisting from APS are intercalated. The pillaring precursors are made from APS by sol-gel method and the amino groups are neutralized by hydrochloric acid solution. It is noticed that the precursor gels can be soluble in water, although they are condensation products. The PVA effects are discussed on comparing investigation of the presence of PVA or of the absence of PVA. It is demonstrated that the increase of the amount of the pillaring precursor give the influence of the porosity and structure of the pillared clays.

In Chapter 3, the intercalations of the precursor made from APS and TEOS are described. Although the simultaneous intercalation of the precondensation precursor and

PVA proved expectation in Chapter 2, it seemed that the gallery height was limited dilatation and the pore properties also showed micropore region. The complex of APS and TEOS was therefore synthesized to enlarge the pillaring precursor. Any composite precursor was able to incorporate at the presence of PVA. The intent to cause size change gave variety to the molar ratio of TEOS to APS in the synthesis of the precursor. It is noted that the molar ratio of TEOS to APS provide the results of the porosity and structure of the pillared clays.

In Chapter 4, the influence of PVA concentration is described. It was noted in Chapter 3 that the composite precursor could expand the gallery height and that the pore properties also showed mesopore region. Then it investigated whether the amount of PVA between aluminosilicate layers bring the porosity of pillared clay. The porosities such as a pore diameter or pore volume can be compared with the structure caused by PVA concentration owing to the constancy of the amount of pillaring agent. The consistent correlate of the pore diameters and pore volumes for the gallery heights is shown.

In Chapter 5, the synthesis by cointercalation of polysiloxane and PVA using synthetic hectorite is described. In some industrial fields, it is necessary to prepare the porous material which transition metal is free, because the transition metals of the kind cause unexpected alteration to chemical production. The hectorite which is synthetic clay does not include iron oxide which is included approximately 3 wt% in montmorillonite. It was confirmed that the pillared clay using hectorite could be prepared in the same manner as that of montmorillonite. The behavior of pillared clay using hectorite in syntheses was similar to it of the pillared clay in case of using

montmorillonite. The porosities of products are described and the certain difference on the exfoliation of clay with that using montmorillonite is discussed.

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# CHAPTER 2

# EFFECT OF POLYVINYL ALCOHOL ON THE SYNTHESIS OF SILICA PILLARED CLAY BY USING 3-AMINOPROPYLTRIETHOXYSILANE


## Abstract of Chapter 2

Silica pillared clays with large interlayer distance were synthesized by the simultaneous intercalation of 3-aminopropyltriethoxysilane (APS) and PVA. Characterization of the synthetic silica pillared clay was done by X-ray diffraction measurement, nitrogen adsorption-desorption measurement and X-ray fluorescence analysis. The gallery height of the synthesized pillared clay was 1.3 nm in the presence of PVA, and it was found that the gallery height was twice as large as that of the pillared clay synthesized without using PVA. The specific surface area and pore volume of the pillared clay obtained with PVA were larger than those obtained without PVA. It was confirmed that the interlayer distance was enlarged with increase in the amount of pillaring precursors only by using PVA.

## 2.1. Introduction

As above description in Chapter 1.4, various sizes of inorganic polyhydroxocations have been intercalated into the layer compound as pillaring precursors [1-3]. Silica is one of the oxides of interest to obtain thermally stable and catalytically active pillared clays. Silica pillared clays have been synthesized from a titania-silica or iron oxide-silica complex sol, because silica precursors are silicate anions which cannot enter between the negatively charged clay sheets [4-6]. The intercalation of silica sol resulted in the large interlayer distance of the sol pillared clay. In spite of the gallery height of the pillared clay, the pores were mainly micropores due to the multilayer stacking of the nanosized sol particles between the aluminosilicate layers. On the other hand, a silica pillared montmorillonite has been synthesized using ion exchangeable APS instead of inorganic precursors. The intercalation of APS was expected to expand the interlayer distance due to the polycondensation by hydrolysis[7]. However, there was no significant increase in the basal spacing even though the silica content significantly increased with the APS. The porosities were not increased by the addition of an excess APS for ion exchange capacity. Kaneko et al. have synthesized the polysiloxane made from APS and investigated the structure and the properties [8]. The polysiloxane was prepared by sol gel reaction. The product was the rodlike polysiloxane assembly. The polysiloxane which had parallel stacking were dispersed in water. The intercalation of these large compounds would be expected to expand the interlayer distance, as with the intercalation of sol particles. It was clarified that the PVA presence in the interlayer space retained the distance between the silicate layers expanded [9-12]. PVA was incorporated into the interlayer region of expandable clays without interfering

with the ion exchange process.

In this chapter, the author describes the effect of PVA addition on the synthesis of the silica pillared clay by using the polysiloxane from APS. The PVA treatment was effective in exfoliating the claysheets and in improving the pore properties.

## 2.2. Experimental Section

The synthetic procedures are the followings; APS (2.54 g, Shinetsu Chemi. Co.) was neutralized by 5 mol/dm$^3$ HCl solution (2.30 cm$^3$) to protonate amino group. The resultant solution was clear and left for one week at room temperature to form a gel. The gel was aged at 353 K for 24 hours and the solvent was removed. The product was abbreviated as APSHC. Some of the hydroxyl groups may be condensed to form a polymerized siloxane material. APSHC was dissolved in distill water (10 cm$^3$). One gram of montmorillonite (Kunipia F; Kunimine Kogyo Co.) with cation exchange capacity (CEC) of 1.15meq/g was suspended in 50 cm$^3$ and kept for 24 hours. The PVA (degree of polymerization:500; Wako pure chem. Co.) solution (10 wt%, 10g.) was added to the suspension followed by stirring. Silica pillaring precursor solution ranging from 0 to 30-fold molar of APSHC for the CEC was then added to the resultant mixture, followed by additional stirring. The paste was separated by centrifugation. It was re-suspended in water. The suspension was poured on a glass plate in order to orientate the clay sheets and dried in 353 K for 24 hours to remove solvent, and then that was calcined at 873 K for 3 hours in order to remove the organic components.

The X-ray diffraction measurements were carried out by Rigaku RINT 2200 X-ray diffractometer with Cu-K$\alpha$ radiation. The specific surface area and total pore

volume of the pillared clays were obtained from $N_2$ adsorption-desorption isotherms at 77 K. These were recorded on Quantachrome Autosorb-AG1. The samples were degassed at 423 K over 4hour under vacuum before analysis. The specific surface areas were estimated by using BET equation and the external surface areas were estimated by the t-plot method [13]. The pore size distributions were estimated by BJH method [14]. Elemental analysis of the silica content of the calcined samples was carried out by Rigaku System 3270 X-ray fluorescence spectroscopy (XRF). The qualitative elemental analysis of $Cl^-$ of the APSHC-clay complex before calcination was carried out by XRF. The infrared spectra were recorded on a JASCO FTIR-480Plus spectrometer after mixing the samples with KBr.

## 2.3. Results and discussion

The infrared spectra of APS and APSHC are shown in Fig. 2-1. The spectrum of APS 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 $cm^{-1}$; a characteristic band of Si-O-C at 1100 $cm^{-1}$. The spectrum of APSHC exhibited characteristic bands of the primary ammonium ion at 3000-2800, 2034, 1610 and 1486 $cm^{-1}$; a characteristic band of silanol group at 3500 $cm^{-1}$; a characteristic band of Si-O-Si at 1040 $cm^{-1}$. From the results, it was found that the neutralization and hydrolysis of APS by hydrochloric acid solution resulted in the protonated ammonium ions and siloxane linkages. The author cannot clarify the degree of polymerization and the molecular weight of APSHC. However, a polysiloxane with Si-O-Si framework is obtained when the hydrolysis of APS are performed in a strongly

acidic aqueous solution such as hydrochloric acid solution until the solvent is distilled off [8,15]. Furthermore, APSHC is dispersed in the water owing to the introduction of water molecules into hydrophilic space between the polysiloxanes, since these have ammonium groups and $Cl^-$ as counter anions[8].

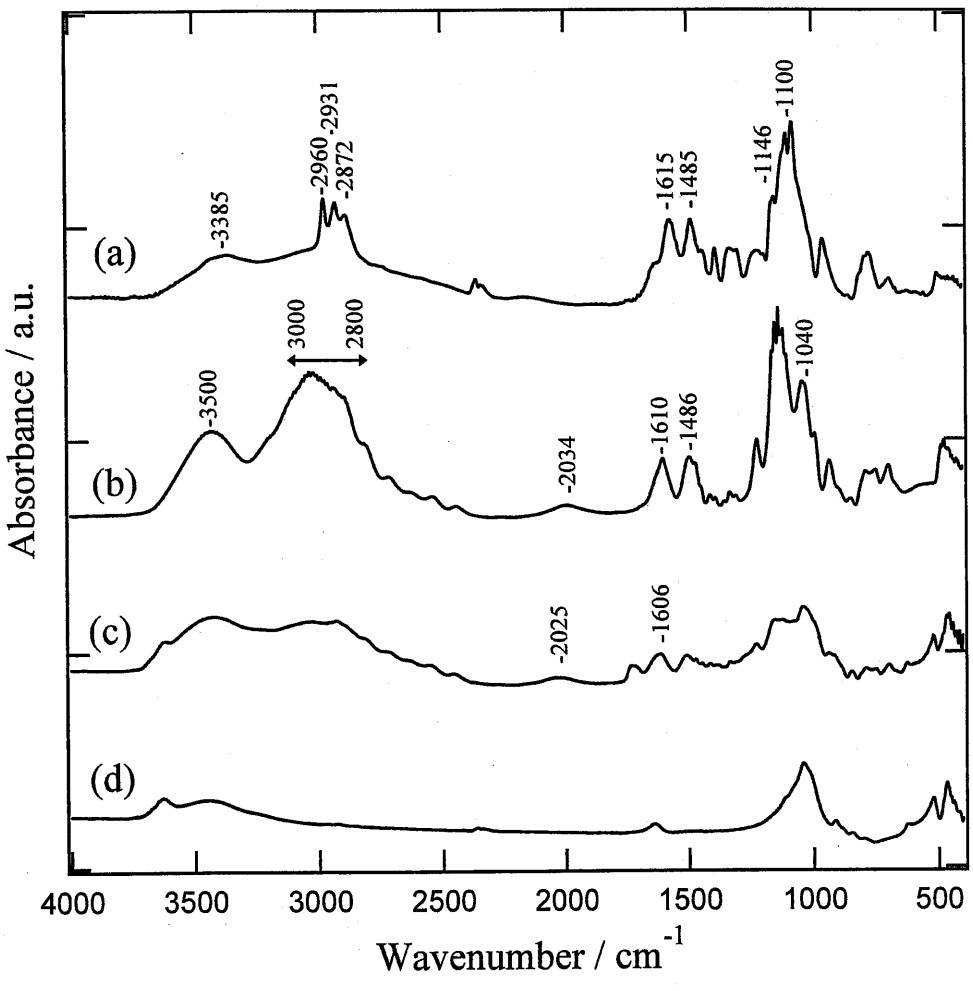


Fig. 2-1 FTIR spectra for APS monomer (a), APSHC (b), Montmorillonite -APSHC complex (APSHC/CEC=10) with PVA before calcination (c), and Montmorillonite (d).

Table 2-1 shows the silica contents based on XRF measurements of calcined samples and silica contents up to which those of the original montmorillonite and the loaded silica precursors were added. In case of APSHC solutions containing ammonium group of a 10-fold molar for the CEC of the host clay, the silica content by XRF agreed with silica content calculated from original clay and that of APSHC, whether PVA treatment carried out or not. It seems that PVA can be incorporated into the interlayer region of expandable clays without interfering with the ion exchange process as with alumina-pillared clays[9]. However, a portion of APSHC remained in the supernatant liquid, when APSHC solutions containing a 30-fold amount of ammonium group on the basis of the CEC of the host clay was loaded with the clay suspension. The sample with PVA held more APSHC than that without PVA even in that case.

Table 2-1. Silica contents of pillared clays

| APSHC/CEC of Clay | $SiO_2$ contents calculated[1)] / wt% | $SiO_2$ contents found[2)] / wt% |
|---|---|---|
| 10(without PVA) | 79.1 | 78.1 |
| 10(with PVA) | 79.1 | 78.5 |
| 30(without PVA) | 88.5 | 80.4 |
| 30(with PVA) | 88.5 | 84.6 |

1) Silica content calculated from the original montmorillonite (silica 64.7 wt%) and silica component of APSHC

2) Silica content of pillared clay by XRF measurement

As shown in Fig. 2-1, the infrared spectra of the clay and APSHC-clay complex before calcination indicate the existence of ammonium groups. The spectrum of APSHC-clay complex exhibited characteristic bands of the primary ammonium ion at 3000-2800, 2025 and 1606 $cm^{-1}$. These bands were absent in the spectrum of Montmorillonite. A considerable amount of chlorine was found in the APSHC-clay complex before calcination by the qualitative elemental analysis. XRD patterns of samples without PVA method and samples with PVA method before calcination are shown in Figs. 2-2(A) and 2-2(B). The d values of (001) peaks in XRD patterns without PVA method exhibited a slightly increase with the amounts of APSHC. On the other hand, the d-spacings with PVA method were found to become larger in proportion to the amount of APSHC and these were expanded to more than 5.9 nm ($2\theta$ =1.5°). The small peaks at 6.5° (d = 1.36 nm) in both patterns indicated the external adsorption of APSHC [8]. These results suggested the intercalation of the significant proportion to the addition of APSHC in the presence of PVA. Figure 2-3(A) shows the XRD patterns of calcined samples consisting of montmorillonite and APSHC without PVA. The d values of (001) peaks in XRD patterns were constantly 1.7 nm irrespective of the increase of the amounts of APSHC. The gallery height is estimated to be 0.7 nm by subtracting the thickness of the aluminosilicate layer of 0.96 nm[3] from the basal spacing value of 1.7 nm. The XRD patterns of the synthesized sample with PVA are shown in Fig. 2-3(B). The peaks were shifted to a lower angle with the increase of the amount of APSHC. The gallery height varied successively from 0.7 to 2 nm. In the case of the ion exchange reaction with APSHC prior to PVA addition, the XRD pattern was nearly the same as that of the sample without PVA and the gallery height was 0.7 nm.

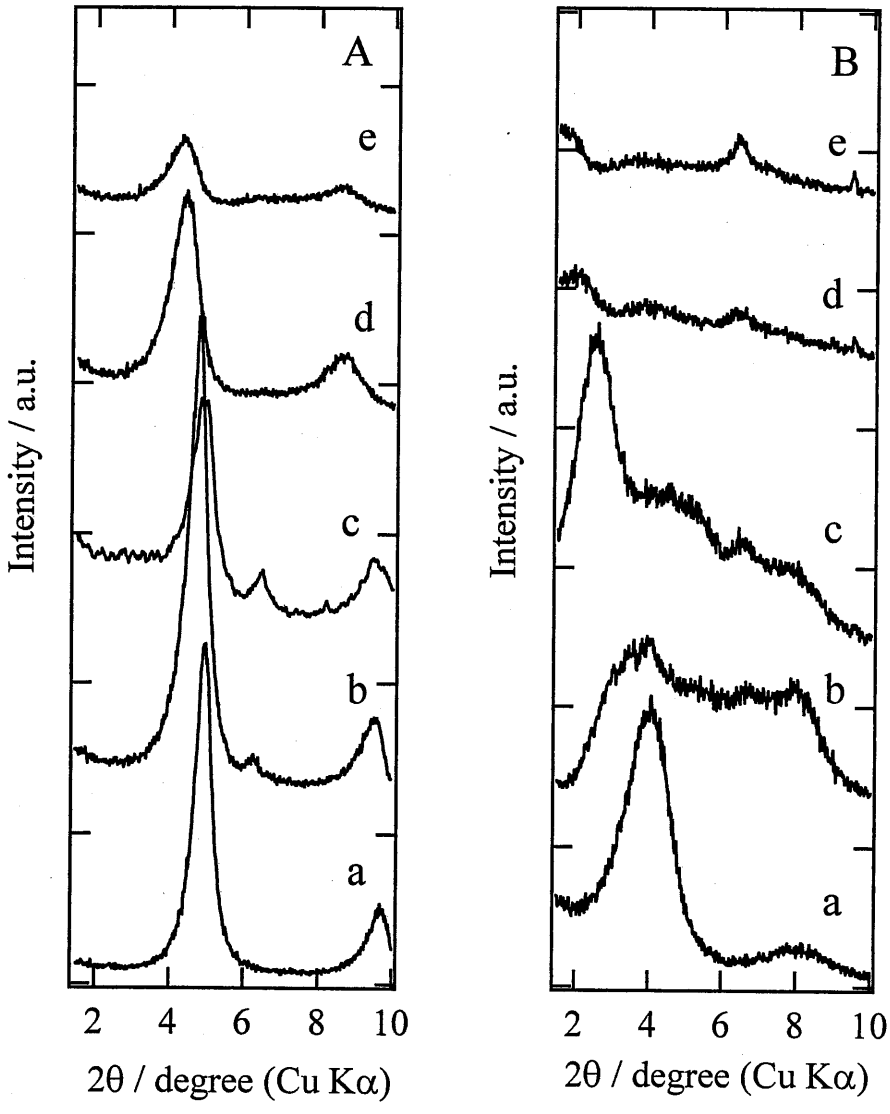


Fig. 2-2 X-ray diffraction patterns of silica-pillared clays prepared in the absence of PVA(A) and in the presence of PVA(B) before calcination. The molar ratio of APSHC/CEC of clay is 2(a), 5(b), 10(c), 20(d), and 30(e).

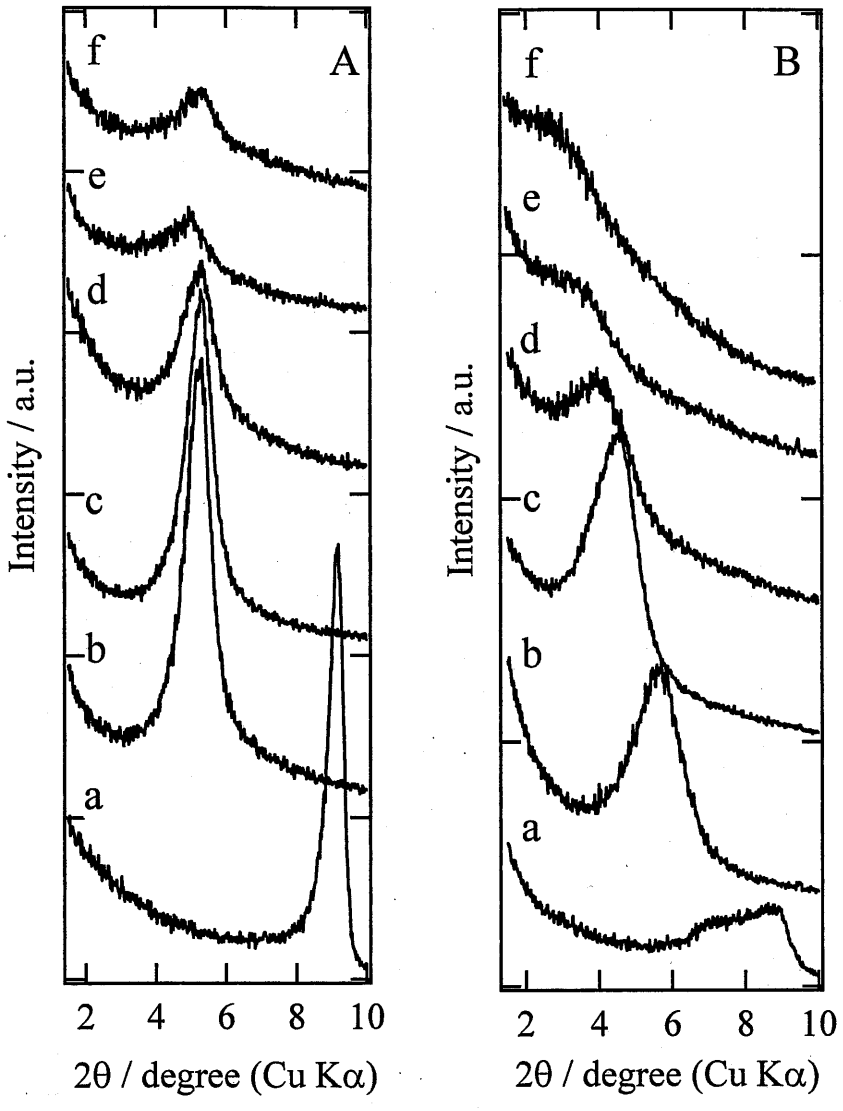


Fig. 2-3 X-ray powder diffraction patterns of silica-pillared clays prepared in the absence of PVA(A) and in the presence of PVA(B) calcined at 873 K for 3h. The molar ratio of APSHC/CEC of clay is 0(a), 2(b), 5(c), 10(d), 20(e), and 30(f).

The gallery height of the sample with PVA treatment was twice as large as that of the pillared clay synthesized from a 10-fold amount of APSHC for CEC without using PVA. As a result, it is suggested that PVA plays an important role in the incorporation of larger amount of APSHC between clay sheets and in the expansion of the gallery height. It is inferred that the previously intercalated PVA enhances swelling of clay and incorporating APSHC without the interruption of ion exchange reactions. On the other hand, the APSHC may be excluded from interlayer space in the absence of PVA. The author cannot exactly prove the proportion of the internal adsorption of APSHC from the results of XRD and XRF measurements. However, it was elucidated that the simultaneously intercalation of PVA and APSHC produced larger basal spacing and larger silica uptake than the intercalation without PVA. It is assumed that the hydrophilic properties of APSHC and PVA result in co-intercalation into claysheets. APSHC intercalated in the presence of PVA were changed into silica pillar by firing and the interlayer distance was expandable successively in proportion to the addition of APSHC.

The author presumes the reason for the adsorption of the excess amount of APSHC from the structure of APSHC[8] and above results as follows. The ammonium groups of the polysiloxane APSHC and host clay sheets charged negatively interact with each other. It is possible that the cations of the host clay are exchanged with some of the ammonium group of the polysiloxane APSHC 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 to compensate the positive charge on polysiloxane when water evaporates. Hence the

polysiloxane linkage would permit more adsorption of APSHC than CEC of the clay. On the other hand, the saturation of such chemical adsorptions on the internal and external surface of clay might cause the difference between silica content found and silica loaded, which contained a 30-fold amount of ammonium group for the CEC. PVA treatment would stimulate the internal adsorption of APSHC as seen from XRD and XRF. Absolutely, it is sure that a certain amount of APSHC can be adsorbed to the external surface of clay owing to the insufficiency of wash with water, which avoids removing PVA.

The $N_2$ adsorption-desorption isotherms of the pillared clays calcined at 873K is shown in Fig. 2-4. The adsorption isotherm of pillared clay with PVA method exhibited larger nitrogen adsorption at higher relative pressure than that without PVA method. As shown in Fig. 2-5, the pore size distribution curves of the samples with and without PVA method indicated the difference in the pore property. These gave the size distribution of micropore. The pore distribution curve of pillared-clay with PVA method indicated larger adsorbed volume at mesopore region (>2 nm) than that of pillared-clay without PVA method. The results of pore structures are shown in Table 2-2.

Table 2-2. Results of porous properties of pillared clay samples

| APSHC /CEC of Clay | Surface area /$m^2g^{-1}$ | External surface area / $m^2g^{-1}$ | Total pore volume /$cm^3g^{-1}$ |
|---|---|---|---|
| 10 (without PVA) | 522 | 50 | 0.26 |
| 10(with PVA) | 561 | 92 | 0.34 |
| 30(with PVA) | 530 | 82 | 0.28 |

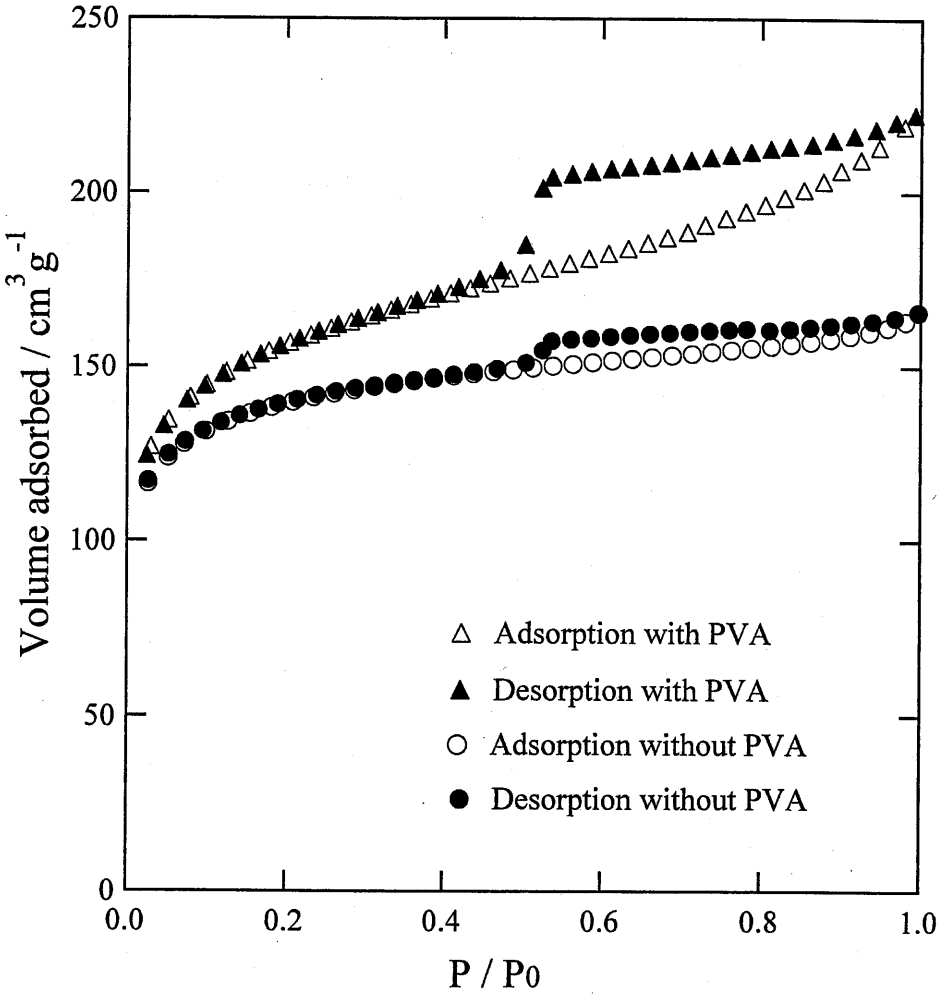


Fig.2-4 Nitrogen adsorption-desorption isotherms at 77K for silica-pillared clay prepared by using a 10-fold molar of APSHC for the CEC with PVA and without PVA.

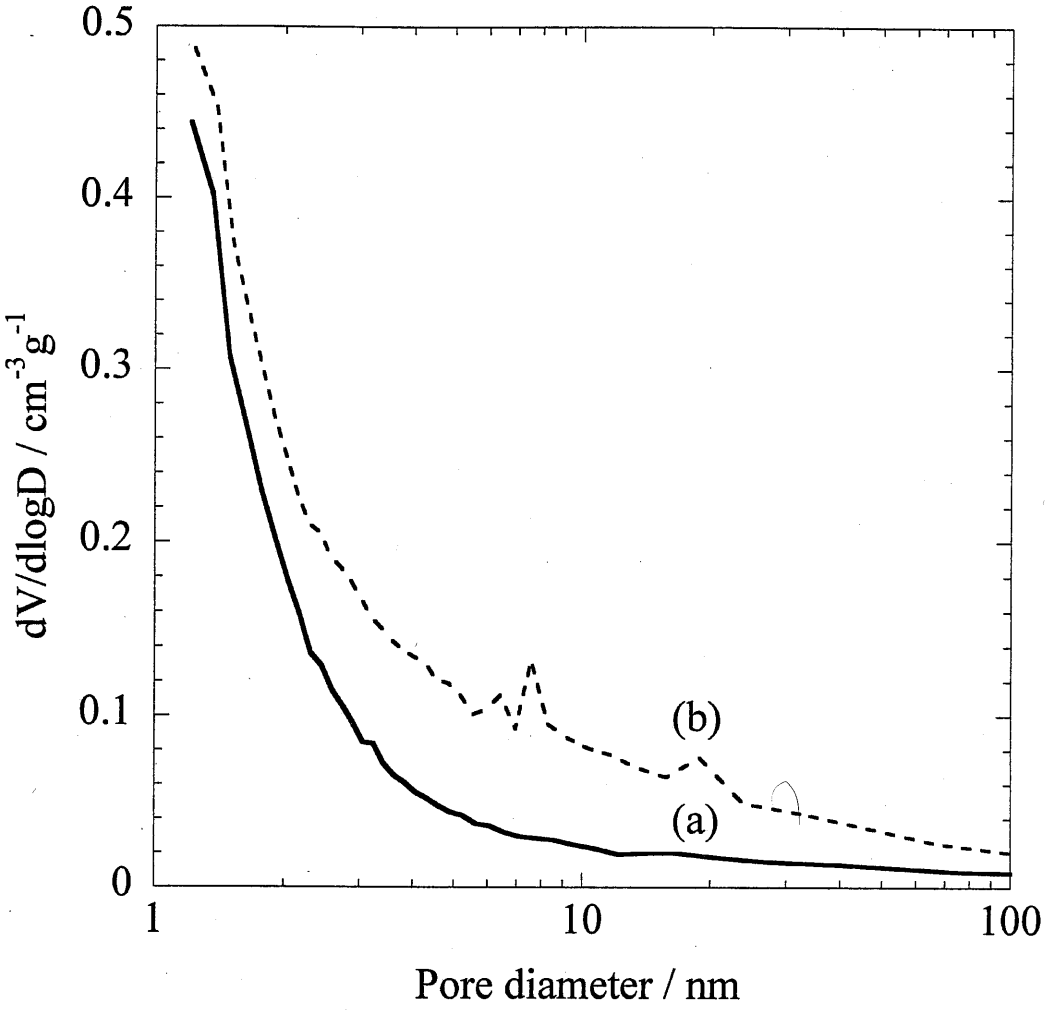


Fig. 2-5 Pore size distribution curves of silica-pillared clays (APSHC/CEC=10) without PVA(a), and with PVA(b).

The external surface areas, which comprised mesopore areas, were obtained from the slope of liner portion of the t-plot at a higher t-value. The t-plots of pillared-clay revealed two liner sections. The curves suggested the presence of the micropore and mesopore. Porosity appeared owing to APSHC intercalation whereas the original montmorillonite had a small porosity. Further, PVA treatment increased more surface area, more pore volume and more external surface area. This would be due to the enlarged pore dimension by PVA treatment, because PVA expanded the clay sheets and PVA was removed from interlayer by calcination. In contrast, it showed that the increment of APSHC reduced the clay porosity due to the increase of silica contents. It is possible that the pillaring silica is closely filled in the interlayer space, because the intercalation of a triple amount of APSHC increased the gallery height by only half.

## 2.4 Summary of Chapter 2

In summary of Chapter 2, this intercalation process with PVA achieved the synthesis of silica pillared clay with large basal spacing. It seems that these results are attributed to the hydrophilic property of PVA and APSHC. PVA played an important role in the incorporation of larger amount of APSHC between clay sheets and in the improving the pore structures. The amount of APSHC affected the significant change of the interlayer distance. It was expandable up to 3 nm by increase the amount of APSHC with PVA treatment. The simultaneous intercalation of APSHC and PVA produced larger porosity, the specific surface area was 561 $m^2/g$ and total pore volume was 0.34 $cm^3/g$. However, the increment of the amount of APSHC produced larger gallery height, while it decreased pore properties.

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# CHAPTER 3

# PREPARATION OF SILICA PILLARED CLAYS USING AMINOPROPYLTRIETHOXYSILANE AND TETRAETHOXYSILANE


## Abstract of Chapter 3

Silica pillared clays with micropores and mesopores were prepared from montmorillonite, APS and TEOS with PVA. The silica precursors were synthesized by the sol-gel method, of which the molar ratio of TEOS to APS was varied from 0 to 1.5. Most of the loaded silica precursors reacted with clay. The pore properties and structures of the pillared clays were investigated. Based on X-ray diffraction measurements, the basal spacings of the silica pillared clays increased from 2.1 to 4.3 nm with the increase silica amount in the loaded precursor. As with the basal spacings, the peaks of the pore size distribution shifted up to 2.6 nm. The specific surface areas and pore volumes tended to increase with an increase in the loaded silica contents.

## 3.1 Introduction

The methods of the hydrolysis of silane compound or the others in situ between clay sheets are expected to increase the gallery height of pillared clays. It is considered that the pillar element is condensed between layers according to the method of the hydrolysis in situ between clay sheets. The preparations of silica pillared clay from the silane compounds and clays have been carried out [1-6]. Silica pillared montmorillonite has been synthesized using ion exchangeable APS to intercalate the clay sheets[7]. However, there was no significant increase in the basal spacing even though the silica content significantly increased with the APS. Then silica has been intercalated in swelling clays by hydrolysis and oxidation of tri(acetylaceton)silicon(IV) cation, $Si(acac)_3^+$ in the interlayer regions of the minerals [1,8,9], while these gallery heights were below 1.6 nm and these pore sizes were micropore (< 2nm). The intercalations of titania-silica or iron oxide-silica complex sol prepared outside clay sheets were attempted [10-12]. 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 aluminosilicate layers.

In Chapter 2, the author described the production of pillared clays by cointercalation of PVA and the polysiloxane made from APS outside clay sheets [13]. It was evident that the presence of PVA in the interlayer space left the distance between the aluminosilicate layers expanded as with other pillared clays by PVA method [14-17]. It was found that PVA was incorporated into the interlayer region of expandable clays without interfering with the ion exchange process even if pillaring agent was the large compound such as the polysiloxane made from APS. However, the pore sizes of the

synthesized pillared clays were < 2 nm.

In this chapter, the author describes new preparation which varies the pore size up to the meso region by changing the mole ratio of TEOS to APS intercalated with PVA method. The linkage formed by reacting TEOS with APS would produce the condensed polysiloxane. The gallery heights consecutively up to meso region were changed by the intercalation of various polysiloxanes. The author confirmed the relationship between the interlayer distance and pore sizes.

## 3.2. Experimental Section

### 3.2.1 Syntheses of pillaring precursor

APS (2.54 g, Shinetsu Chem. Co) was neutralized by 5 mol/dm$^3$ HCl solution (2.30 cm$^3$, Wako Pure Chem. Ind. Ltd.). TEOS (Colcoat Co.,Ltd.) was added dropwise into the reacting solution mixture under vigorous stirring (pH 2-4). The molar ratio of TEOS to APS, hereafter denoted by n, was varied between 0 and 1.5. The obtained solutions were clear and they were left for one week at room temperature to form a gel. The gels were aged at 353 K for 24 hours. Some of the hydroxyl groups may be condensed to form a polymerized silica material. Each product gel was dissolved in distilled water (10 cm$^3$) at 373 K.

### 3.2.2 Reaction with clay

Montmorillonite (Kunipia F; Kunimine Kogyo Co.) was used as the host material. The CEC of montmorillonite is 1.15meq/g. Aqueous PVA (degree of polymerization:1000, reagent grade, Wako Pure Chem. Ind. Ltd.) (10 wt%;10g.) was added to each suspension (clay 1 g in 50 cm$^3$ of distilled water) followed by stirring.

Each silica-pillaring precursor solution, which contains the different silica content, was then added to the resultant mixture, followed by more stirring. The pastes were separated by centrifugations. Each paste was re-suspended in water (10 $cm^3$). The suspensions were poured on a glass plate in order to orientate the clay sheets and then dried in 353 K for 24 hours. Next, the silica-intercalated clays were calcined at 873 K for 3 hours in order to remove the organic components.

3.2.3 Characterization

The X-ray diffraction measurements were carried out on Rigaku RINT 2200 X-ray diffractometer with Cu-K$\alpha$ radiation. The specific surface area and total pore volume of the pillared clays were determined from $N_2$ adsorption-desorption isotherms at 77 K. These were recorded on Quantachrome Autosorb1-AG. The samples were degassed at 423 K over 4h under vacuum before analysis. The pore size distributions were estimated by the BJH method[18] from adsorption isotherms and the specific surface areas were estimated by fitting the adsorption data in a $p/p_0$ range of 0.03 - 0.1 to the BET equation. Elemental analysis of the silica content of the sintered samples was carried out using Rigaku System 3270 X-ray fluorescence spectroscopy. The carbon residue analyses were performed on HORIBA EMIA-110 the carbon analyzer of the infrared adsorption method after combustion.

## 3.3. Results and Discussion

Table 3-1 shows the theoretical silica and the actual silica contents based on the XRF measurements of the calcined samples. The theoretical silica fraction was the silica content in the original montmorillonite and loaded silica-precursor divided by the sum

of the weight of the clay plus that in the silica precursor. In spite of the silica pillaring precursor containing an ammonium group of 10-fold for the CEC of the host clay, the silica content by XRF corresponded very well with the theoretical silica content. Furthermore, the agreement of the measurement and calculation in Table 3-1 indicates that most of the loaded silica precursors reacted with the clay in the TEOS/APS ratio range of 0 to 1.5. The author presumes the reason for the above results as follows. The silica precursors are polysiloxanes in which some silanol groups combine to form a siloxane linkage [13,19]. The ammonium groups of the polysiloxane and host clay sheets charged negatively interact with each other. It is possible that some ammonium groups are exchanged with the cation of the host clay and the others do not contribute to the electrostatic attraction in the solution since they attract $Cl^-$ as counter anions. Hence the polysiloxane linkage would permit more incorporation of the silica component, which derives from APS and TEOS, than it expected from the CEC of the clay.

Table 3-1. Properties of silica pillared montmorillonite prepared with different TEOS/APS molar ratios

| TEOS/APS | $SiO_2$ content calculated[1)] / wt.% | $SiO_2$ content found[2)] / wt.% | BET specific surface area / $m^2g^{-1}$ | Total pore volume (p/po=0.99) / $cm^3g^{-1}$ |
|---|---|---|---|---|
| 0 | 79.1 | 78.5 | 561 | 0.34 |
| 0.5 | 82.7 | 81.7 | 687 | 0.41 |
| 1 | 85.2 | 85.5 | 675 | 0.42 |
| 1.5 | 87.1 | 87.4 | 690 | 0.53 |

1) Theoretical silica fraction calculated from the original montmorillonite (silica 64.7 wt%) and silica component of TEOS and APS.

2) Actual silica content of pillared clay by XRF measurement

It was clarified that the prior sol-gel condensation would provide siloxane linkages between APS and TEOS, because the silica sol cannot be inserted alone in the interlayer space owing to the negative charge of the sol particle [10]. The silica acquisition by the clay was efficient as compared with the sol silica pillared clays [12]. This seems to be due to a stronger ion exchange of an ammonium group than a metal oxide silica complex sol.

The 001 and 003 XRD reflections of the pillared clays before calcination are shown in Fig.3-1. The 001 and 003 peaks shifted to a lower diffraction angle with the increasing molar ratio of TEOS to APS. The peaks at low diffraction angles corresponded to basal spacings enlarged by the simultaneous intercalation of the pillaring precursors and PVA between the clay layers. The 001 reflection at n = 1.5 was assumed from the 003 reflection to be approximately 7nm. Figure 3-2 shows the XRD patterns of the pillared clays prepared with the different molar ratios of TEOS to APS treated at 873 K. The peaks shifted to higher diffraction angles upon heat treatment at 873 K due to the dehydration and thermal decomposition of PVA and the organic groups. There were no significant peaks above 15 degrees after the calcination (Fig.3-3). Pillared clays exhibited the 001 reflection at a lower diffraction angle with an increase in the ratio of TEOS to APS, indicating an expansion of the distance between the aluminosilicate layers. The pillar height of the sample at n = 1.5 is estimated to be 3.3 nm by subtracting it from the basal spacing value of 4.3 nm, the thickness of the aluminosilicate layer of 0.96nm. On the other hand, pillared clays without the PVA method had peaks at a basal spacing of around 1.7 nm, which were independent of the molar ratio of TEOS to APS, as in the Chapter 2 [13].

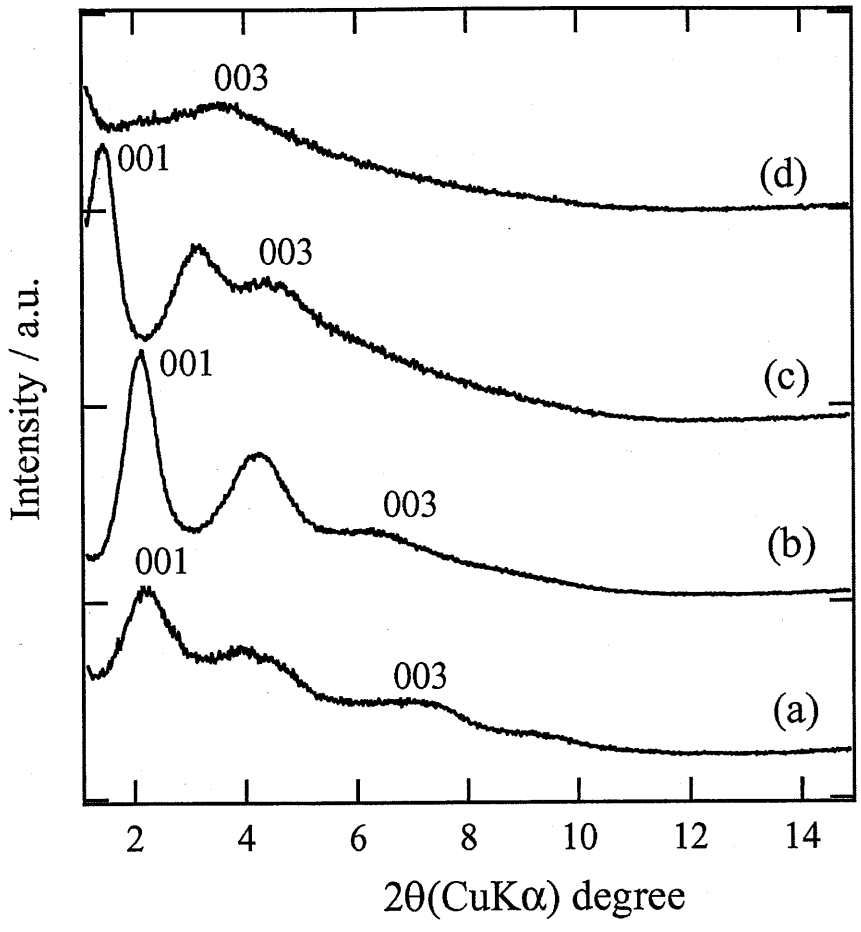


Fig.3-1. XRD patterns of silica-pillared clays prepared in the presence of PVA before calcination. The molar ratio of TEOS/APS is 0(a), 0.5(b), 1(c), and 1.5(d).

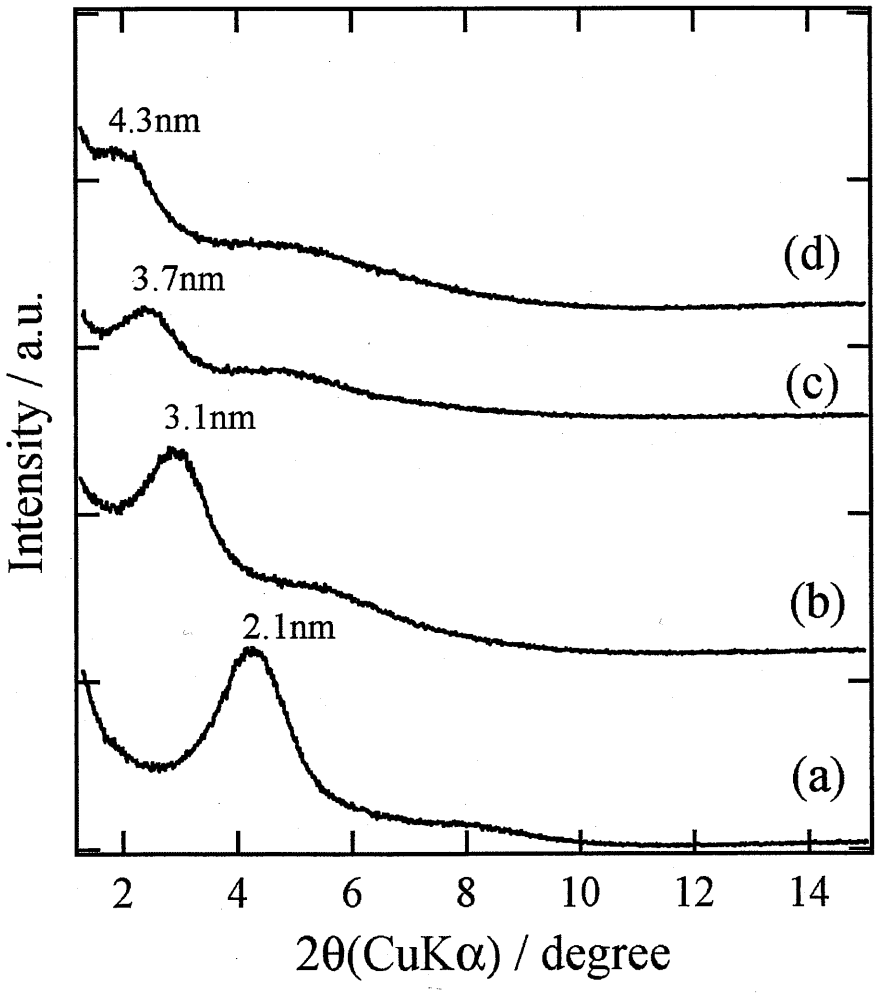


Fig.3-2. XRD patterns (1-15 degree) of silica-pillared clays prepared in the presence of PVA calcined at 873K for 3 hours. The molar ratio of TEOS/APS is 0(a), 0.5(b), 1(c), and 1.5(d).

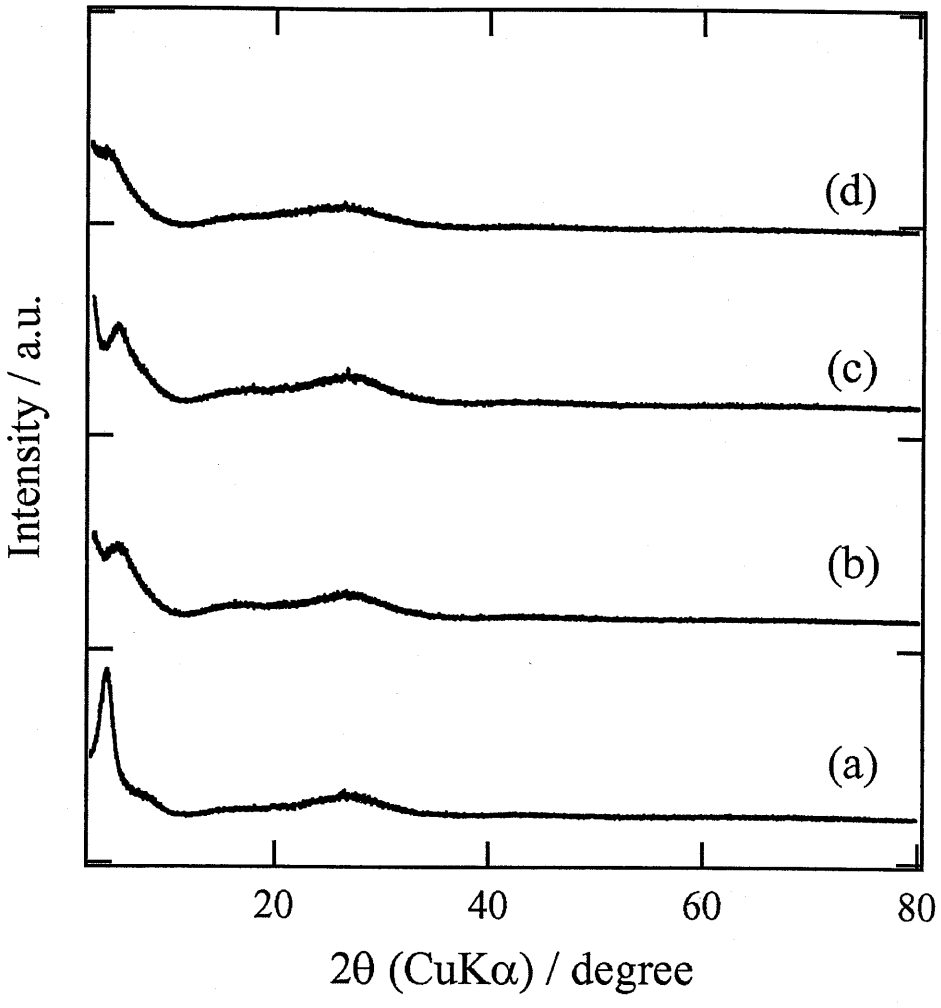


Fig.3-3. XRD patterns (3-80 degree) of silica-pillared clays prepared in the presence of PVA calcined at 873K for 3 hours. The molar ratio of TEOS/APS is 0(a), 0.5(b), 1(c), and 1.5(d).

The presence of PVA during pillaring is necessary for the expansion of the distance between the aluminosilicate layers as with the polyhydroxoaluminium or polyhydroxozirconium [14-17]. The PVA treatment would due to the enlarged pore dimension, because PVA expanded the clay sheets and PVA was removed from the interlayer by the calcination.

The nitrogen adsorption-desorption isotherms shown in Fig.3-4 were obtained for silica pillared clays (n=0, 1, 1.5). This suggests a dependence of porosity on the molar ratio of TEOS to APS and a presence of micropores. Figure 3-5 shows the pore distributions derived from the nitrogen adsorption isotherms of the pillared clays by intercalation of the silica precursors with different molar ratios of TEOS to APS. The distribution curves had the peaks at 1.5 (n = 0.5), 2.0 (n = 1.0), and 2.6 nm (n =1.5). The curves at n = 0 exhibited no peak due to microporosity. This result corresponded with the interlayer distance determined from the XRD measurements. The amount of intercalated silica pillar was dependent on the molar ratio of TEOS to APS. Therefore, the pore diameter depends on the amount of intercalated silica pillar. The clay sheets were swollen by the simultaneous intercalation of the pillaring precursors and PVA. The silica precursors were pillared and the PVA molecules were decomposed by calcination in the interlayer regions, consequently, pores were formed from the silica pillars and clay sheets.

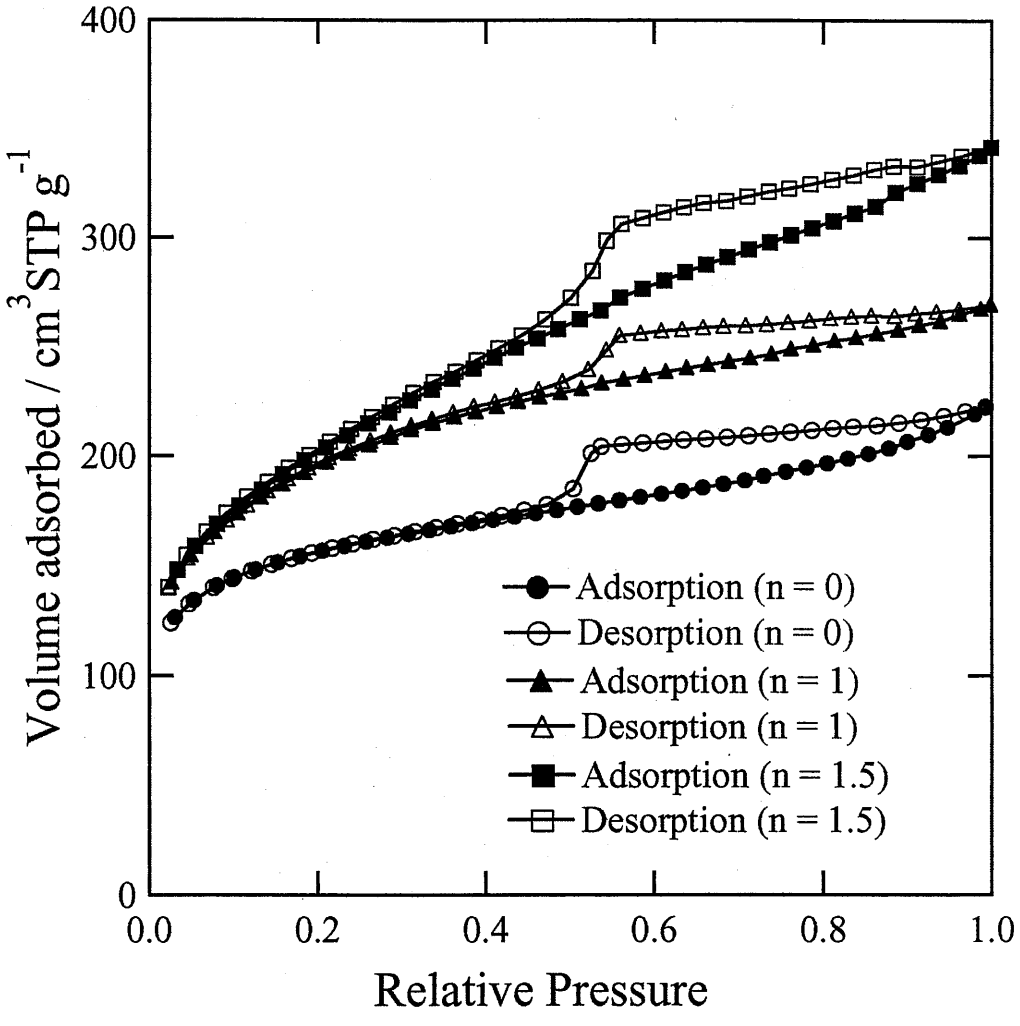


Fig.3-4. Nitrogen adsorption-desorption isotherms at 77 K for silica-pillared clays. The molar ratio of TEOS/APS is n = 0, n = 1, and n = 1.5.

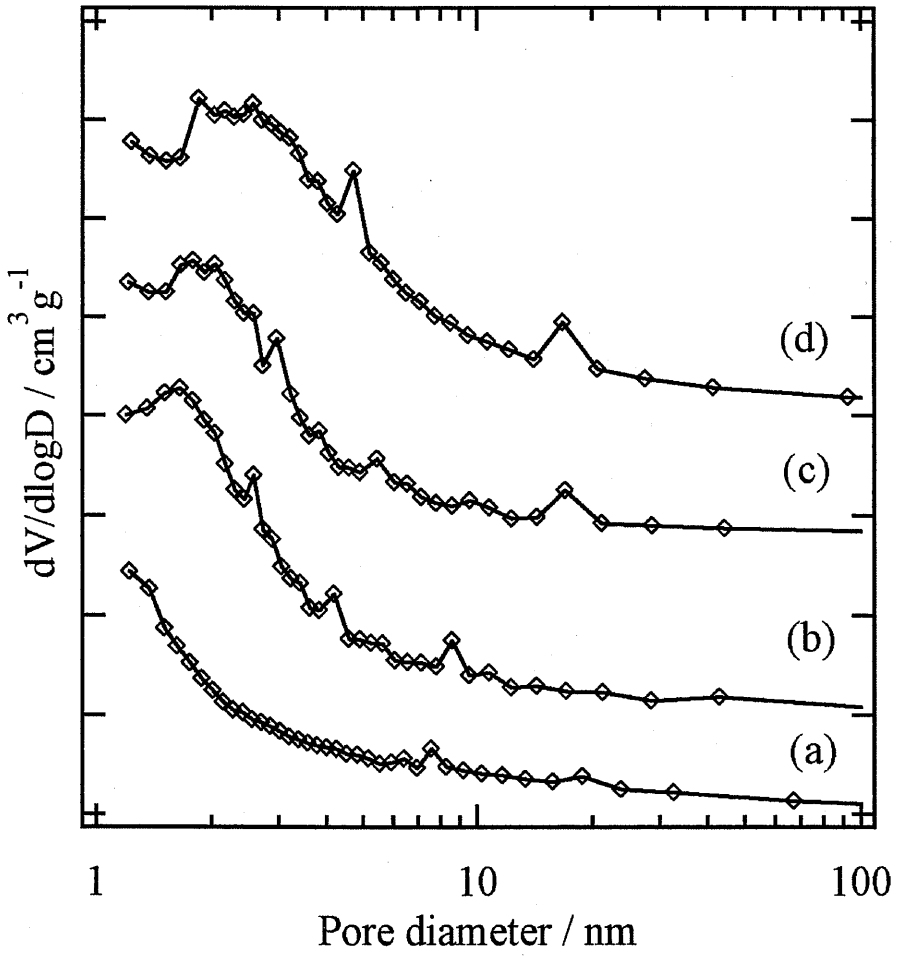


Fig.3-5. Pore size distribution curves of silica-pillared clays prepared in the presence of PVA calcined at 873K for 3 hours. The molar ratio of TEOS/APS is 0(a), 0.5(b), 1(c), and 1.5(d).

The specific surface areas and pore volumes of the silica pillared clays are shown in Table 3-1. The author could confirm few effects of the unremoved organic components since the carbon residue contents of all silica pillared clays were below 0.5 % from the carbon analysis results. It became clear that the increase in the TEOS/ APS molar ratio of the precursor trended to cause a change in the specific surface area and pore volume. This suggests that the total pore volume increased with the increasing pillaring silica, which supports the expansion of the distance between the aluminosilicate layers.

## 3.4. Summary of Chapter 3

The author synthesized silica pillared clays with a various micro and meso pores from montmorillonite, APS and TEOS with PVA. The pillar height of the pillared clay was adjusted by varying the molar ratio of TEOS to APS. Based on the pore size distribution and the XRD pattern, the pore size increased to approximately 3 nm. All of the silica-precursors prepared from APS and TEOS by the sol gel method reacted with montmorillonite. It seems that the siloxane linkages between the silane molecules enhance the incorporation of the silica precursor which contains a 10-fold amount of ammonium group for CEC and a large amount of silanol groups without interaction with the clay. For the sol gel reaction by hydrolysis, the polycondensation of TEOS and APS would lead to the larger precursors that could produce silica pillared clays with a long basal spacing.

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# CHAPTER 4

# INFLUENCE OF POLYVINYL ALCOHOL ON THE SYNTHESIS OF SILICA PILLARED CLAY BY INTERCALATION OF POLYSILOXANE


## Abstract of Chapter 4

In different concentrations of the PVA solution, silica pillared clays with mesopore were synthesized from montmorillonite, APS and TEOS. The concentration of PVA was important in this synthesis and effective on the porosity of the obtained silica pillared clays. The pore properties and structures of the pillared clays were investigated. Based on X-ray diffraction measurements, the basal spacings of the silica pillared clays increased from 3.5 to 5.3 nm with the increase PVA concentration. As with the basal spacings, the peaks of the pore size distribution and the average pore diameter shifted up to approximately 4 nm. As the concentration of PVA increased, the mesopore areas and pore volumes tended to increase, and the BET surface areas trended to decrease.

## 4.1. Introduction

One of the development directions of pillared clay is enlargement of the pore size. The principle methods for the purpose are the usage of organic template and the growth of pillaring agents [1]. In the intercalation method of grown sols, the pores were mainly micropores due to the multilayer stacking the nanosize particles between the aluminosilicate layers in spite of the large interlayer distance of the sol pillared clay [2]. Then the polycondensation by APS hydrolysis in situ between aluminosilicate layers has been expected to form larger pores [3]. The silica pillared montmorillonite was synthesized using ion exchangeable APS to intercalate the clay sheets in aqueous solution. However, there was no significant increase in the basal spacing even though the silica content significantly increased with the APS. Polysiloxane to which APS molecules are condensed outside aluminosilicate layers has been incorporated into the clay layers [4]. The pillared clay by incorporating the polysiloxane provided only micropores below 1 nm. The author already described in Chapter 2 that silica pillared clays with large surface areas and pore volumes have been prepared using the polysiloxane and PVA [5] as with the alumina-pillared clay or zirconia-pillared clay by the PVA method [6-9]. The presence of PVA in the interlayer space left the distance between the aluminosilicate layers expanded. PVA can be incorporated into the interlayer region of expandable clays without interfering with the ion exchange process. Furthermore, the author described the production of pillared clays with the long basal spacings, large surface areas and pore volumes using APS and TEOS with the PVA method in Chapter 3[10]. The pore sizes varied up to the meso region by changing the mole ratio of TEOS to APS.

This chapter describes the preparation which varies the pore size by of incorporating cationic polysiloxane in a broad range of PVA concentrations. The influence of PVA concentration is investigated on the pore property of the silica pillared clays obtained.

## 4.2. Experimental Section

### 4.2.1 Syntheses of pillaring precursor

APS (2.54 g) was neutralized by 5 mol/dm$^3$ HCl solution (2.30 cm$^3$). TEOS (2.39 g) was added dropwise into the reacting solution mixture under vigorous stirring (pH 2-4). The obtained solution was clear and left for one week at room temperature to form a gel. The gel was aged at 353 K for 24 hours. The product gel was dissolved in distilled water (10 cm$^3$) at 373 K.

### 2.2 Reaction with clay

Montmorillonite (Kunipia F; Kunimine Kogyo Co.) was used as the host material. The cation exchange capacity (CEC) of montmorillonite is 1.15meq/g. One gram of the clay was added to aqueous PVA (degree of polymerization:1000) (10 wt%;20g). Different appropriate amounts of distilled water were added to the suspension followed by stirring for 2 hours. A silica-pillaring precursor solution, which contained the ammonium group of 10-fold molar for CEC of the host clay, was then added to the resultant mixture, followed by more stirring for 2 hours. The determinate PVA concentrations of the solutions were respectively 0, 1.4, 2.0, 4.0, 6.0 wt%. The paste was separated by centrifugations. No further washing was carried out to investigate the effect of PVA concentration, because PVA which was water-soluble could seep into

water. The paste was dried in 353 K for 24 hours. Next, the silica-intercalated clay was calcined at 873 K for 3 hours in order to remove the organic components.

4.2.3 Characterization

The X-ray diffraction measurements were carried out on Rigaku RINT 2200 X-ray diffractometer with Cu-K$\alpha$ radiation. The specific surface area and total pore volume of the pillared clays were determined from nitrogen adsorption-desorption isotherms at 77 K. These were recorded on Quantachrome Autosorb1-AG. The samples were degassed at 423 K over 4h under vacuum before analysis. The pore size distributions were estimated by the BJH method [11] from adsorption isotherms. The specific surface areas were estimated using the BET equation and the mesopore areas were estimated by the t-plot method [12]. Elemental analysis of the silica content of the sintered samples was carried out using Rigaku System 3270 X-ray fluorescence spectroscopy. The original clay sample for comparison was calcined at 873 K for 3 hours. Amorphous silica was used on the calibration of intensity.

## 4.3. Results and Discussion

The integration between this silica precursor and clay has been investigated for various concentrations of PVA, which are the important parameters influencing the pillaring process. It is probably that this precursor involves anion exchange as with polyaminopropylsiloxane hydrochloride [4,13,14], which provides the reactivity with clay. Table 4-1 shows the uptake of the silica contents in the synthesized clay based on the XRF measurements and the source materials contents of silica-precursors loaded, which are corresponding to the molar ratios of the host clay CEC. The silica uptakes

were calculated from the original clay silica content, which was 64.7 wt%, and the pillared clay silica contents. The author 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 content molar of the precursor loaded, as shown in Table 4-1. The silica uptake slightly decreased with the increment of PVA concentration in the intercalation progress. A certain degree of PVA could be incorporated into the interlayer region of expandable clays without interfering with the ion exchange process. In spite of adding the silica-pillaring precursor containing ten equivalents of ammonium group on basis of the CEC of the host clay, the pillaring precursor of more 80 mol% was introduced into the pillared clays.

Table 4-1. Pillaring silica components of the pillared montmorillonite prepared with different PVA concentrations.

| PVA concentration | Component mixed [1)] | | Uptake silica found[1),2)] |
|---|---|---|---|
| /wt% | APS | TEOS | $SiO_2$ |
| 1.4 | 10 | 10 | 18.6 |
| 2 | 10 | 10 | 18.4 |
| 4 | 10 | 10 | 17.3 |
| 6 | 10 | 10 | 16.9 |

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

2) Uptake silica component estimated from the original montmorillonite (silica 64.7 wt%) and the synthesized pillared clays by XRF measurement

This suggests that most amounts of the silica precursor found in the clay may be due to an ion exchange of the interlayer sodium ions for parts of the ammonium group of the polysiloxane, in which some unreacted ammonium group remain. It is possibly 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 owing to the negative charge of the sol particle [1,15,16]. It was probably that the silica precursor was a cationic polysiloxane as with polyaminopropylsiloxane hydrochloride [14].

The XRD patterns of the pillared clays after calcination at 873K are shown in Fig.4-1. The broad diffraction peaks were observed at $2\theta = 2.52°$ (d=3.5nm), $2\theta = 2.31°$ (d=3.8nm), $2\theta = 2.01°$ (d=4.4nm) and $2\theta = 1.67°$ (d=5.3nm), indicating a layered structure. Pillared clays exhibited the 001 reflection at a lower diffraction angle with an increase in PVA concentration, indicating an expansion of the distance between the aluminosilicate layers. The peaks at low diffraction angles corresponded to basal spacings enlarged by the simultaneous intercalation of the pillaring precursors and PVA between the clay layers. The pillar height of the sample synthesized at PVA 6wt% is estimated to be 4.3 nm by subtracting it from the basal spacing value of 5.3 nm, the thickness of the aluminosilicate layer of 0.96nm[1]. As discussed previously, the pillar heights of the sample synthesized at PVA 1.4, 2.0 and 4.0wt% are estimated to be 2.5, 2.8 and 3.4 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 gives agreement with the intercalation of APS [3] or polyaminopropylsiloxane hydrochloride [5] without template method. The rearrangement of the polysiloxane such as polyaminopropylsiloxane may provide the gallery height of approximately 0.7 nm between clay layers in any

polymerization or configuration. The presence of PVA during pillaring is necessary for the expansion of the distance between the aluminosilicate layers as with the intercalation of the polyhydroxoaluminium or polyhydroxozirconium [6].

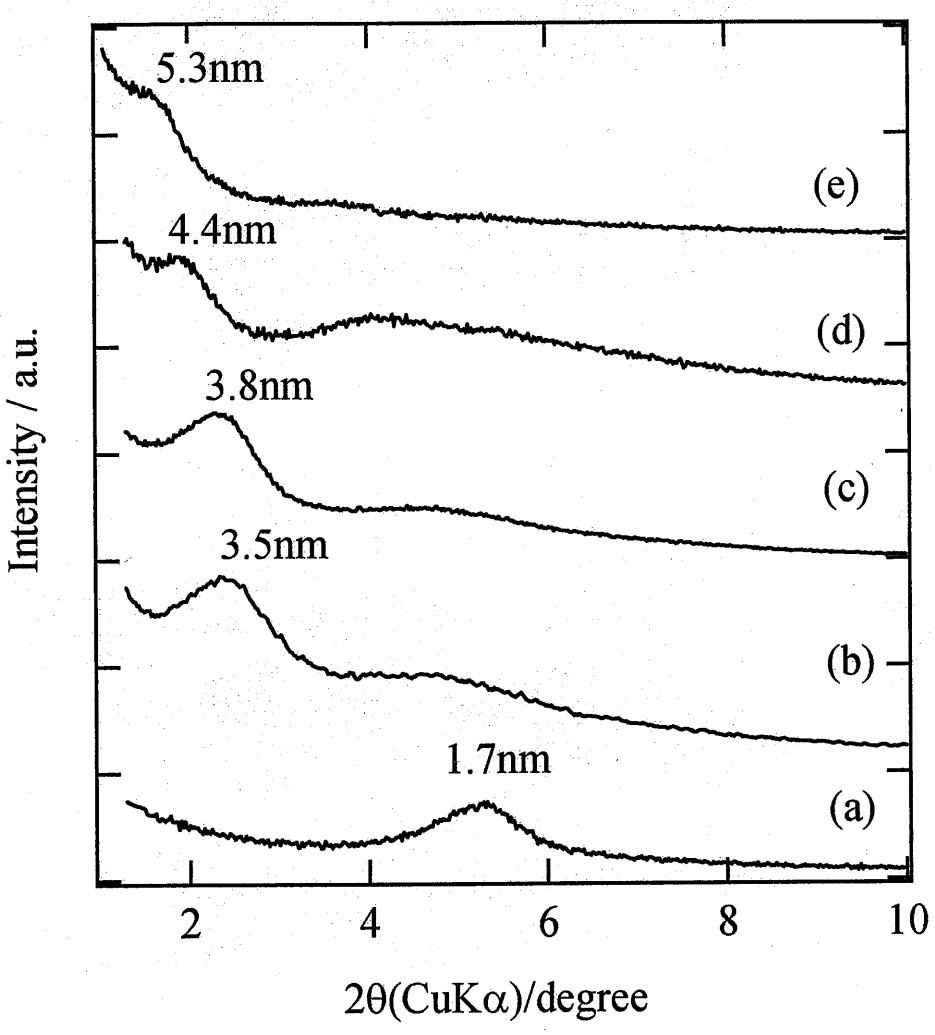


Fig. 4-1. XRD patterns of silica-pillared clays prepared at different PVA concentrations calcined at 873K for 3 hours. PVA concentration (wt%): (a) 0, (b) 1.4, (c) 2.0, (d) 4.0, (e) 6.0.

The detailed information of the pore structure in these pillared clays must be derived from nitrogen adsorption-desorption data. Fig.4-2 shows the pore distributions derived from the nitrogen adsorption isotherms of the pillared clays by intercalation of the polysiloxane at different PVA concentrations. These curves were obtained by the BJH method [11]. Based on nitrogen adsorption-desorption measurements, the pore distributions of the silica pillared clays increased with the increase PVA concentration. They gave the pore size distribution of mesopores and micropores, which had the peaks from 2.0 to 3.3 nm at 1.4-6.0 wt% of PVA. This result presented the same tendency as the increase of the pillaring heights determined from the XRD measurements which had a slight difference in the estimated data by an angstrom order. It appeared that the pore size depended on the intercalated PVA quantity, because the amount of intercalated silica pillar estimated by XRF measurement was scarcely dependent on the PVA concentration. The clay sheets were swollen by the simultaneous intercalation of the pillaring precursors and PVA. The clay sheets were expanded as PVA concentration increased. The silica pillar formation and PVA decomposition by calcination would result in pores composed of the silica pillars and clay sheets.

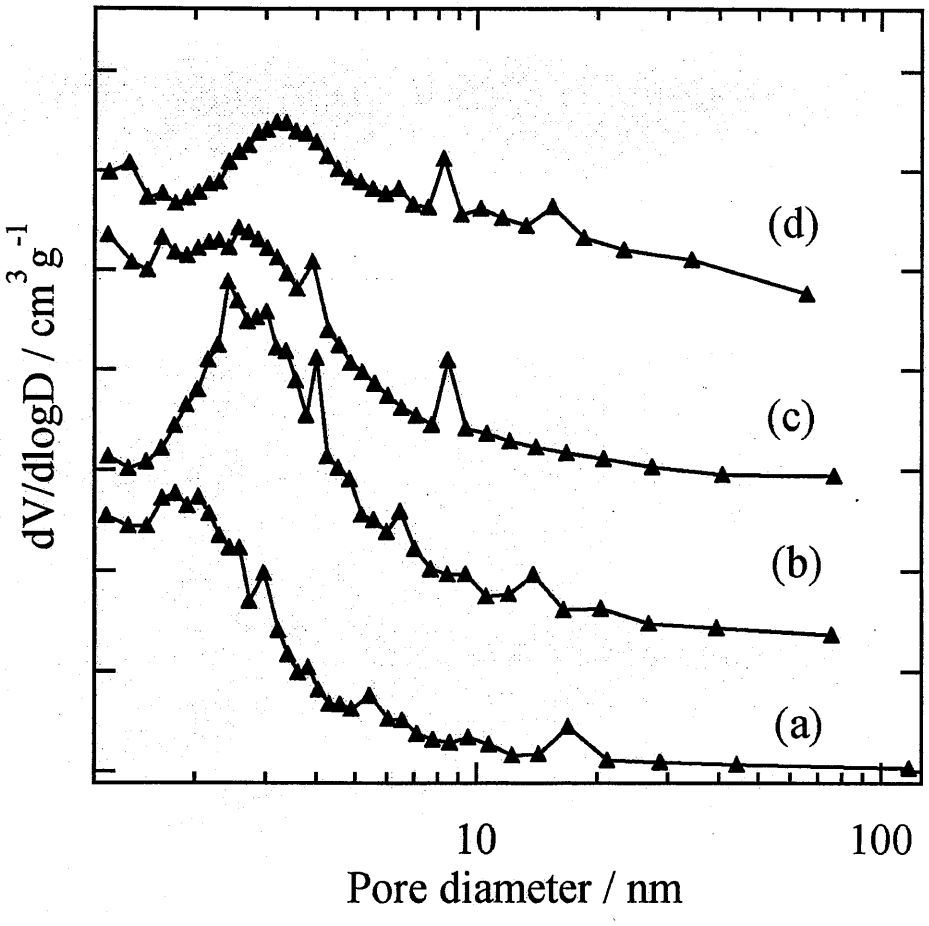


Fig.4-2. Pore size distribution curves of silica-pillared clays prepared at different PVA concentrations calcined at 873K for 3 hours. PVA concentration (wt%): (a) 1.4, (b) 2.0, (c) 4.0, (d) 6.0.

The other pore properties and d-basal spacings of the silica pillared clays are shown in Fig.4-3 – 4-6. It was shown that the increase of the PVA concentration trended to become a lager d-basal spacing. As shown in Fig.4-3, these pillared clay had from 500 to 750 $m^2/g$ of the BET surface area, which were the same or more than the other pillared montmorillonite [3,6,16]. The presence of PVA reduced the BET surface areas contrary to the extension of the d-spacing. The reductions may be due to decreasing micropores in pillaring silica penetrated by PVA molecules rather than the structural change of the clay sheets. Because it is assumed that a simple change in the pillar height gives not a change in surface area but an increase of the pore volume. On the other hand, the mesopore areas increased (Fig. 4-4), which were estimated by the t-plot method. The synthesized sample in 6 wt% of PVA gave 230 $m^2/g$ of the mesopore area, which accounted for approximately half of the surface area. It is possibly that the decrements of the micropores are more than that of the total surface areas. The pore volumes against the PVA concentrations are shown in Fig. 4-5. The pore volumes of pillared clays increased with increasing PVA concentration, which supports the expansion of the distance between the aluminosilicate layers. The pore volumes were found to become greater in proportion to the basal spacings based on XRD measurements. The average pore diameters are shown in Fig.4-6 with the basal spacings determined by XRD measurement as a function of the PVA concentration. The average pore diameters increased with the increasing concentration of PVA as with the mesopore area and pore volume. The average pore diameters were close to the pillaring heights, which were considered to subtract thickness of an aluminosilicate layer from d-spacing.

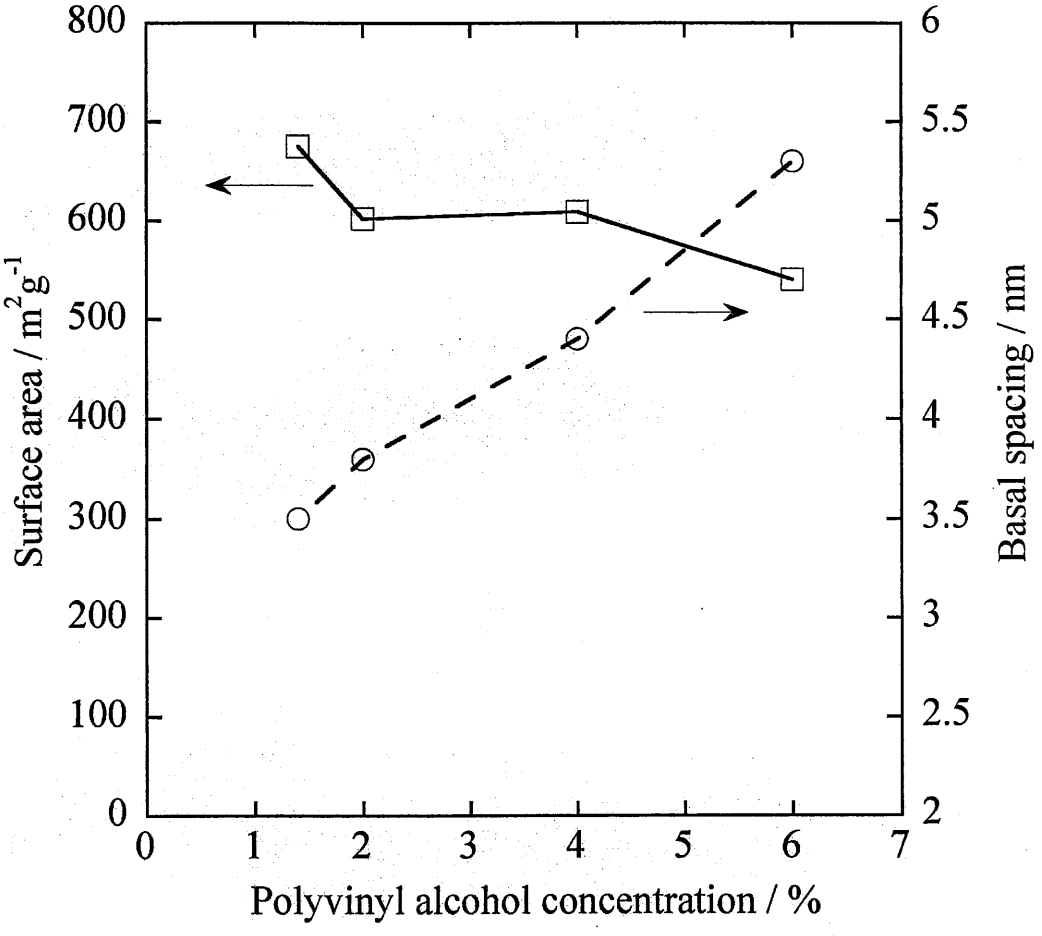


Fig.4-3. Effect of PVA concentration on the BET surface area and basal spacing from XRD data of the prepared pillared clay.

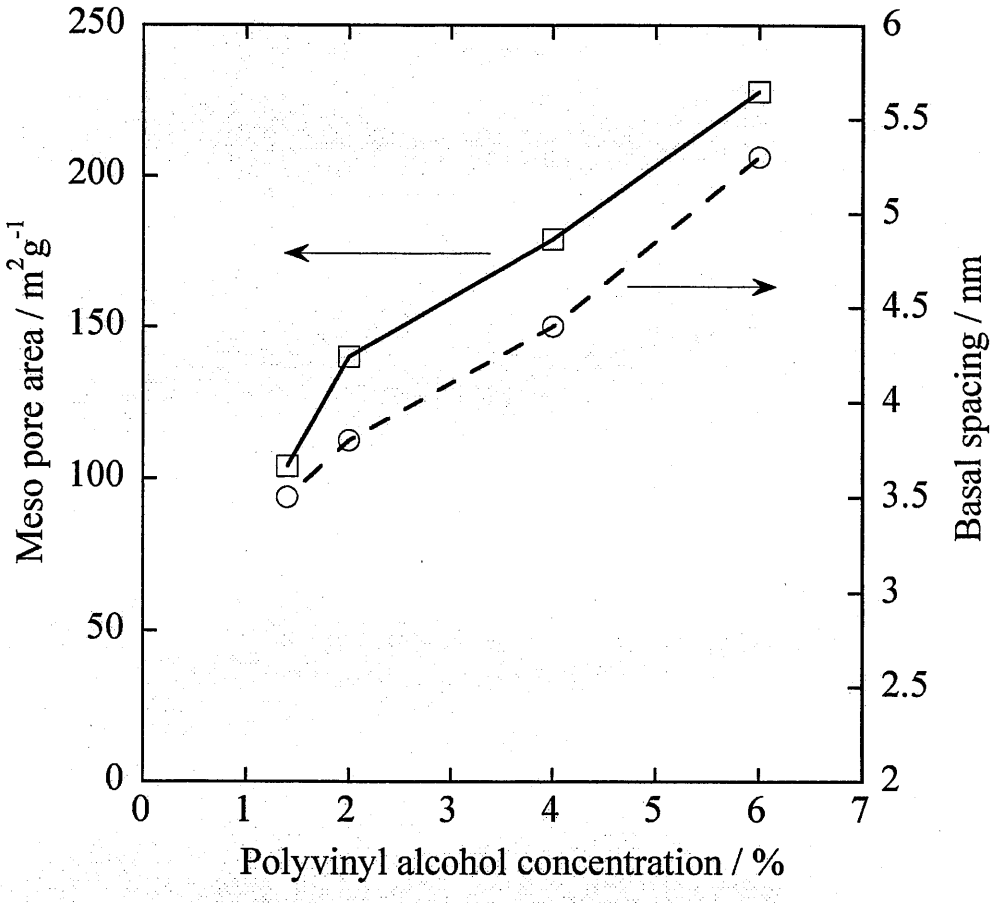


Fig.4-4. Effect of PVA concentration on mesopore area estimated by t-method, and on the basal spacing from XRD data of the prepared pillared clay.

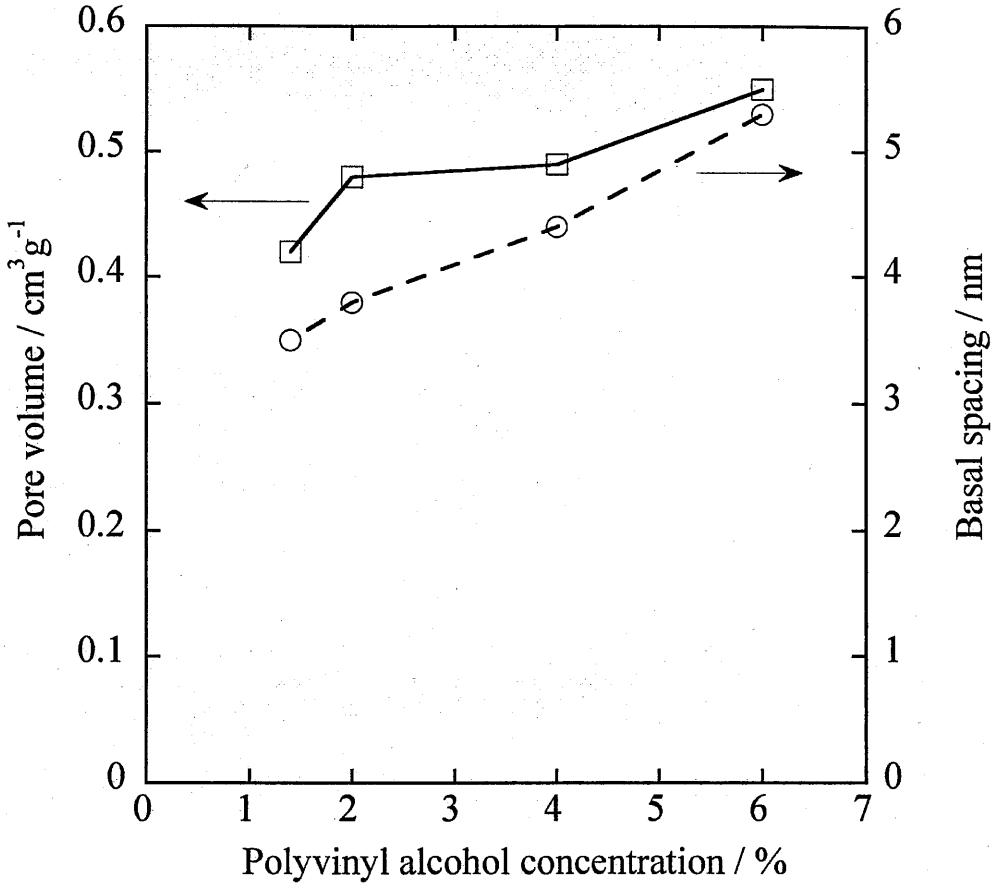


Fig.4-5. Effect of PVA concentration on the pore volume and basal spacing from XRD data of the prepared pillared clay.

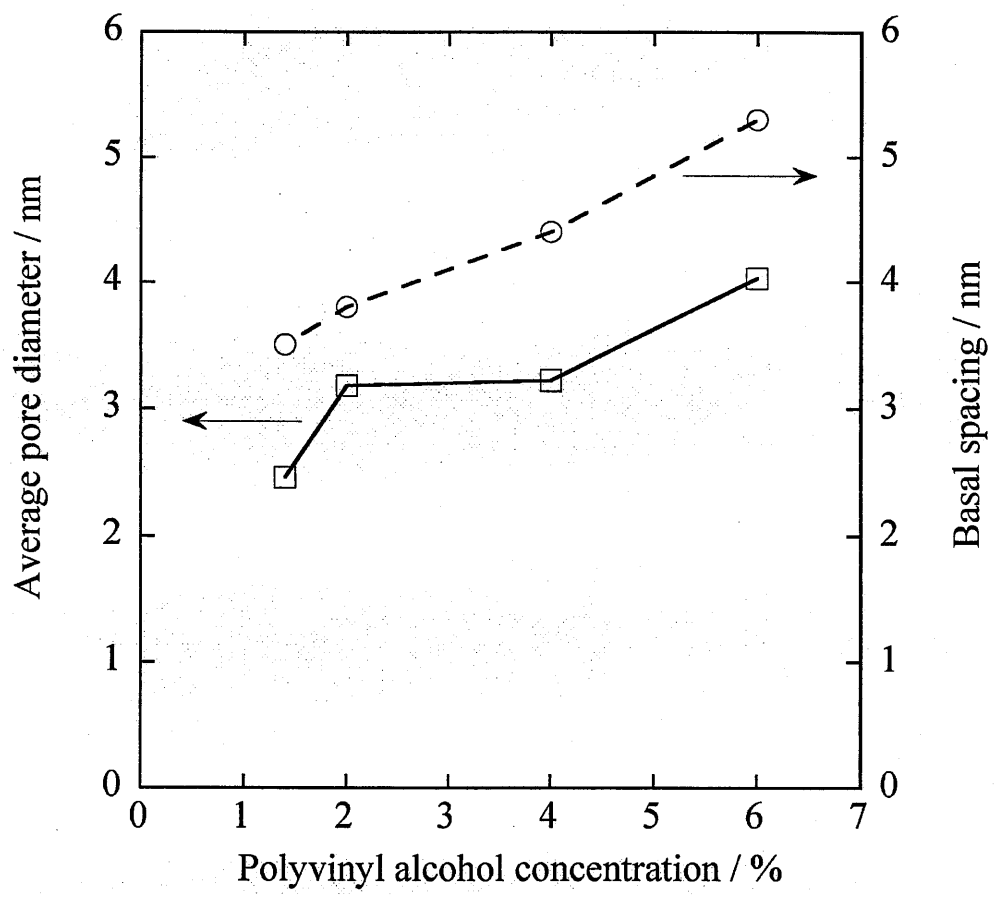


Fig.4-6. Effect of PVA concentration on the average pore diameter and basal spacing from XRD data of the prepared pillared clay.

The average pore diameters can happen to coincide with pillaring heights, nevertheless it is worth while to be consistency of the magnitude of the change. These results suggested the relation between the gallery height and pore properties. The behavior of such pore properties on pillared clay as pore volume, mesopore area and average pore diameter is consistent with the change of the gallery height. These results were similar to the behavior of the porous clays using surfactants [17,18]. The pore radius of the porous clays was proportional to not so much the surface areas as the pore volumes. As the alkyl chain of surfactants increased in length, the mean radius of the framework pores in the porous clays increased. It seems that PVA concentration would similarly contribute to the pore size of the pillared clays using the PVA method.

## 4.4. Summary of Chapter 4

The author synthesized silica pillared clays with a various mesopore sizes from montmorillonite using a polysiloxane in different PVA concentrations. In spite of adding the silica-pillaring precursor containing ten equivalents of ammonium group on basis of the CEC of the host clay, the pillaring precursor of more 80 mol% penetrated into the pillared clays over the range tested PVA concentration. PVA could expand clay sheets and stimulate the intercalation of the large amounts of polysiloxane which might be attributed to the ion exchange of parts of polysiloxane for sodium ions. It seems that the siloxane linkages between the silane molecules enable the incorporation of most silica-precursor which prepared from APS and TEOS by the sol gel method. Based on the XRD pattern, the pillaring height increased up to approximately 4 nm. The pillar height of the pillared clay was adjusted by varying the concentration of PVA. It was

found that the pore size distribution derived from the nitrogen adsorption isotherms gave the similar results to the XRD measurements. PVA concentrations had an influence on the other pore properties of the pillared clays. The pore volume and mesopore areas increased with increasing of PVA concentration as with the basal spacings estimated by XRD patterns. The average pore diameter agreed with the pillaring height. On the other hand, the increase in PVA concentration provided opposite results on the BET surface areas. The reduction of intricate micropores probably contributes to this result. It was found that the increase of PVA concentration caused the enlargement of interlayer spacing and the decrement of micropore. It was clarify that the PVA concentration contributed to the pore size for which the pillaring height depending on PVA concentration accounted.

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# CHAPTER 5

# PREPARATION OF SILICA PILLARED FLUOROHECTORITE BY COINTERCALATION OF POLYSILOXANE AND POLYVINYL ALCOHOL


## Abstract of Chapter 5

The fluorohectorite were used as a host compound. The silica pillared clays with mesopores were prepared from the fluorohectorite by means of the cointercalation of PVA and polysiloxane. 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.

## 5.1. Introduction

As discussed in previous chapters, the cointercalation of PVA and polysiloxane consisting from APS and TEOS provided fairly well the transformation of structure for montmorillonite which was natural resources clay. Polysiloxane, which are polycondensation of APS molecules, has been incorporated into the clay layers in the absence of PVA [1]. The polysiloxane pillared clay provided micropores below 1 nm without template agents. The method that improves the pore properties can employ the cointercalation of nonionic templates, which are water-soluble polymer [2-5] or are nonionic surfactants[6-8], other than the cationic surfactants. PVA as polar polymer can easily penetrate into swelling clay such as montmorillonite, because of charged layer surface. The Chapter 2 already described that the silica pillared clays with larger surface areas and pore volumes using polysiloxane and PVA were prepared. It was concluded in Chapter 2 that the presence of PVA in the interlayer space left the distance between the aluminosilicate layers expanded [9]. It was note in it that PVA could be incorporated into the interlayer region of expandable clays without interfering with the ion exchange process. The author proposed the production of pillared clays with long basal spacings, large surface areas and pore volumes using APS and TEOS with the PVA method [10], which is discussed in Chapter 3. The pore sizes enlarged up to the meso region by changing the mole ratio of TEOS to APS. The gallery heights of the pillared clays shifted up to approximately 3 nm.

This chapter discusses the preparation of the silica pillared fluorohectorite, which does not include iron oxide included approximately 3 wt% in montmorillonite. The porous material which transition metal is free is required in some industrial fields,

because the transition metals of the kind cause unexpected alteration to chemical production. Then the fluorohectorite is swelling clay, which has the ion exchange capacity in the order of 1 meq/g as with montmorillonite. It consequently seems that montmorillonite can be replaced in the same pillaring process as the fluorohectorite. In this examination, the silica pillared fluorohectorite are synthesized 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.

## 5.2. Experimental Section

### 5.2.1 Syntheses and characterization of pillaring precursor

APS (2.32 g, Shin-Etsu Chemical Co.,Ltd.) was neutralized by 5 mol/dm$^3$ HCl solution (2.10 cm$^3$). 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 hours 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 μm, Millipore), washing the water-soluble siloxane and excess surfactant, and then air

drying. The water-insoluble product was calcined at 1073 K, and then the weight of the calcine was measured.

5.2.2 Reaction with clay

Fluorohectorite ($Na_{0.33}Mg_{2.67}Li_{0.33}Si_4O_{10}F_2$, 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 wt%;20g). Different amounts of distilled water were added to the suspension followed by stirring for 2 hours. 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 hours. The determined PVA concentrations of the solutions were 0.0, 2.0, 4.0, 6.0, and 8.0 wt%. 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 hours. Next, the silica-intercalated clay was calcined at 873 K for 3 hours in order to remove the organic components.

5.2.3 Characterization of pillared fluorohectorite

The X-ray diffraction measurements were carried out using a Rigaku RINT 2200 X-ray diffractometer with Cu-Kα 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 hours under vacuum before analysis. The

pore size distributions were estimated by the BJH method [11] 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 [12]. Elemental analysis of the silica content of the sintered samples was carried out by X-ray fluorescence spectroscopy 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 hours. The surface of pillared fluorohectorite was observed by scanning electron microscope (SEM).

## 5.3. Results and Discussion

The infrared spectra of APS monomer and the silica precursor before dissolution are respectively shown in Fig.5-1. The spectrum of APS monomer (a) in Fig.5-1 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.5-1 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. The author cannot clarify the degree of polymerization and the molecular weight of the silica precursors. The calcined water-insoluble silica precursor, which was organized by oleic acid, weighed 1.22 g.

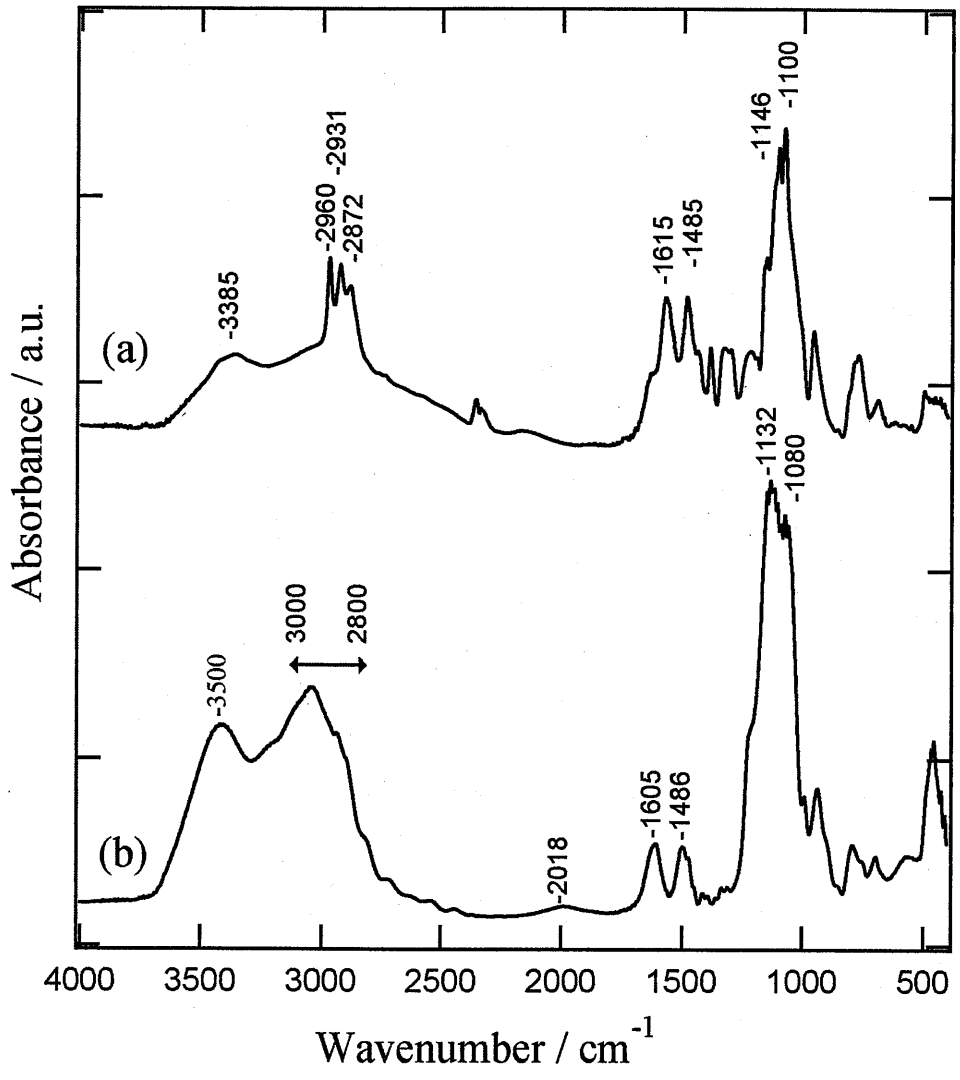


Fig.5-1. FTIR spectra of (a) APS monomer and (b) the polysiloxane consisting of APS and TEOS.

It 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 $Cl^-$ [13].

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 [1,13,14], which provides the reactivity with clay. Table 5-1 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 wt%, and the silica contents of pillared fluorohectorite. The author 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 5-1. 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[15]. It is probable that the silica precursor is a cationic

polysiloxane like polyaminopropylsiloxane hydrochloride [13]. 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. The author presumes that the reason for the adsorption of the silica-pillaring precursor containing an excess amount of the ammonium group is as follows.

Table 5-1. Pillaring silica components of the pillared fluorohectorite prepared in different PVA concentrations.

| PVA concentration | Component mixed [1)] | | Uptake silica found[1),2)] |
|---|---|---|---|
| /wt% | APS | TEOS | $SiO_2$ |
| 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 wt%) and the synthesized pillared clays by XRF measurement

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 873K are shown in Fig.5-2. The pillared clay without PVA (b) shows about 1.7 nm of the 001 basal spacing. It is apparent that the distance becomes larger than 1.2 nm of the raw material hectorite (a). 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 $2\theta = 1.91°$ (d=4.62nm), $2\theta = 1.71°$ (d=5.16nm), $2\theta = 1.64°$ (d=5.38nm), and $2\theta = 1.53°$ (d=5.77nm) respectively. The author 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[2-5], 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

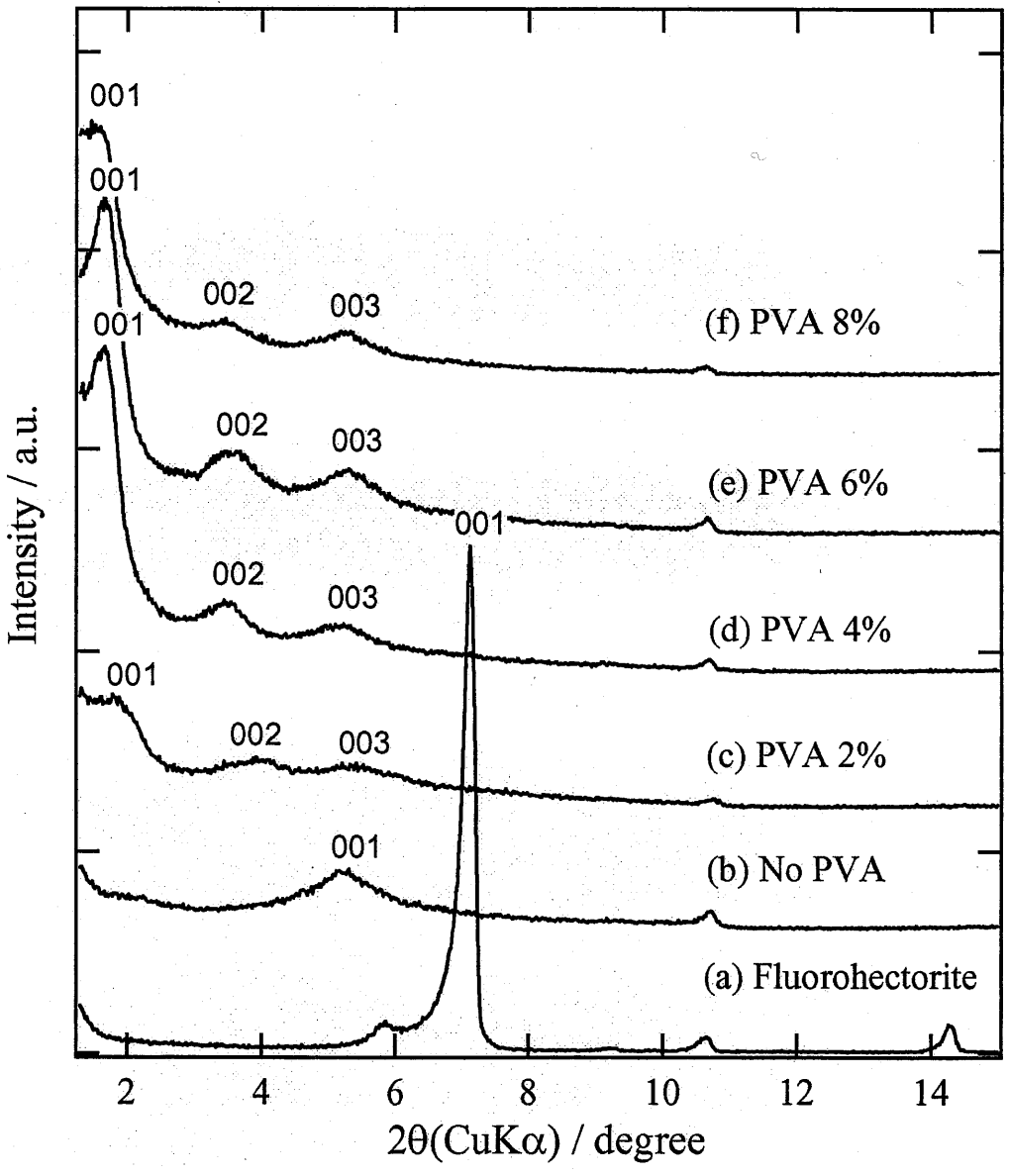


Fig. 5-2. X-ray diffraction pattern of (a) the original fluorohectorite, and the silica pillared fluorohectorites prepared in (b) 0.0%, (c) 2.0%, (d) 4.0%, (e) 6.0% and (f) 8.0% PVA concentration after calcination at 873 K for 3 hours.

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 wt% PVA is estimated to be 4.8 nm by subtracting the 0.96nm thickness of the silicate layer [15] 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 wt% 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 APS[16] or of the polyaminopropylsiloxane hydrochloride[1,9] 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[2].

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 wt% are shown in Fig.5-3. 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%(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.5-3 is attributed to the existence of mesopores. Figure 5-4 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 [11]. 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 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 [1].

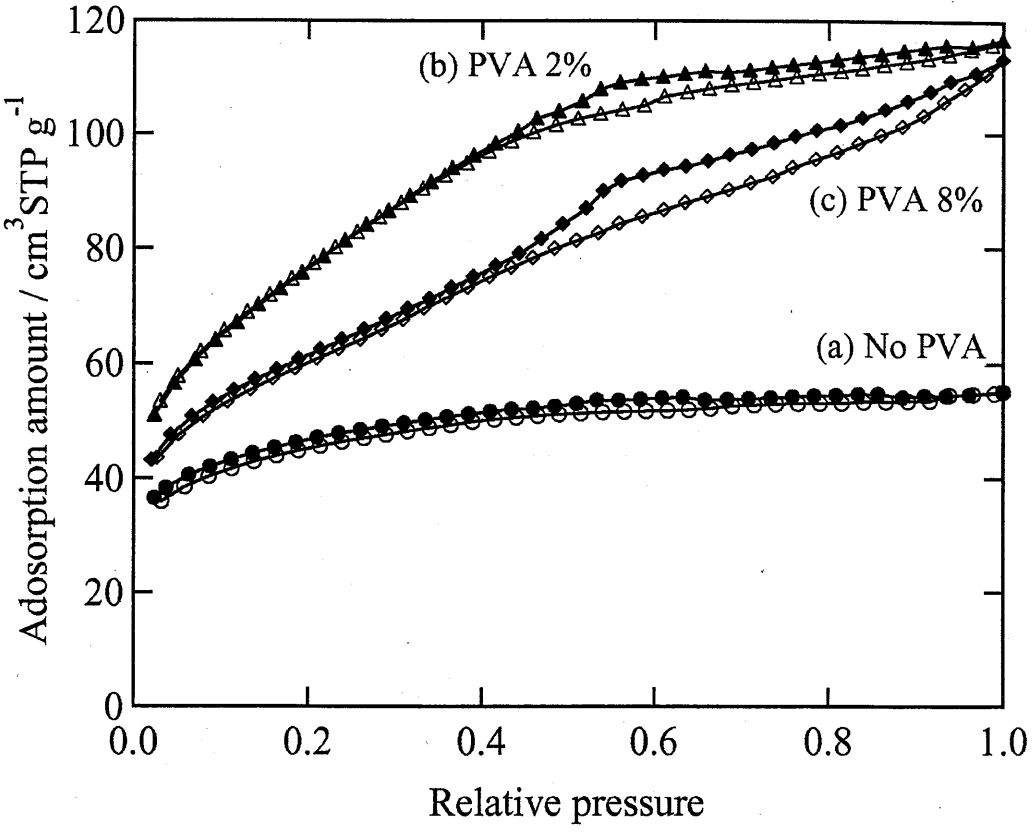


Fig.5-3. Nitrogen adsorption-desorption isotherms at 77K for the silica pillared fluorohectorite prepared in (a) 0.0 %, (b) 2.0 % and (c) 8.0 % of PVA concentration.

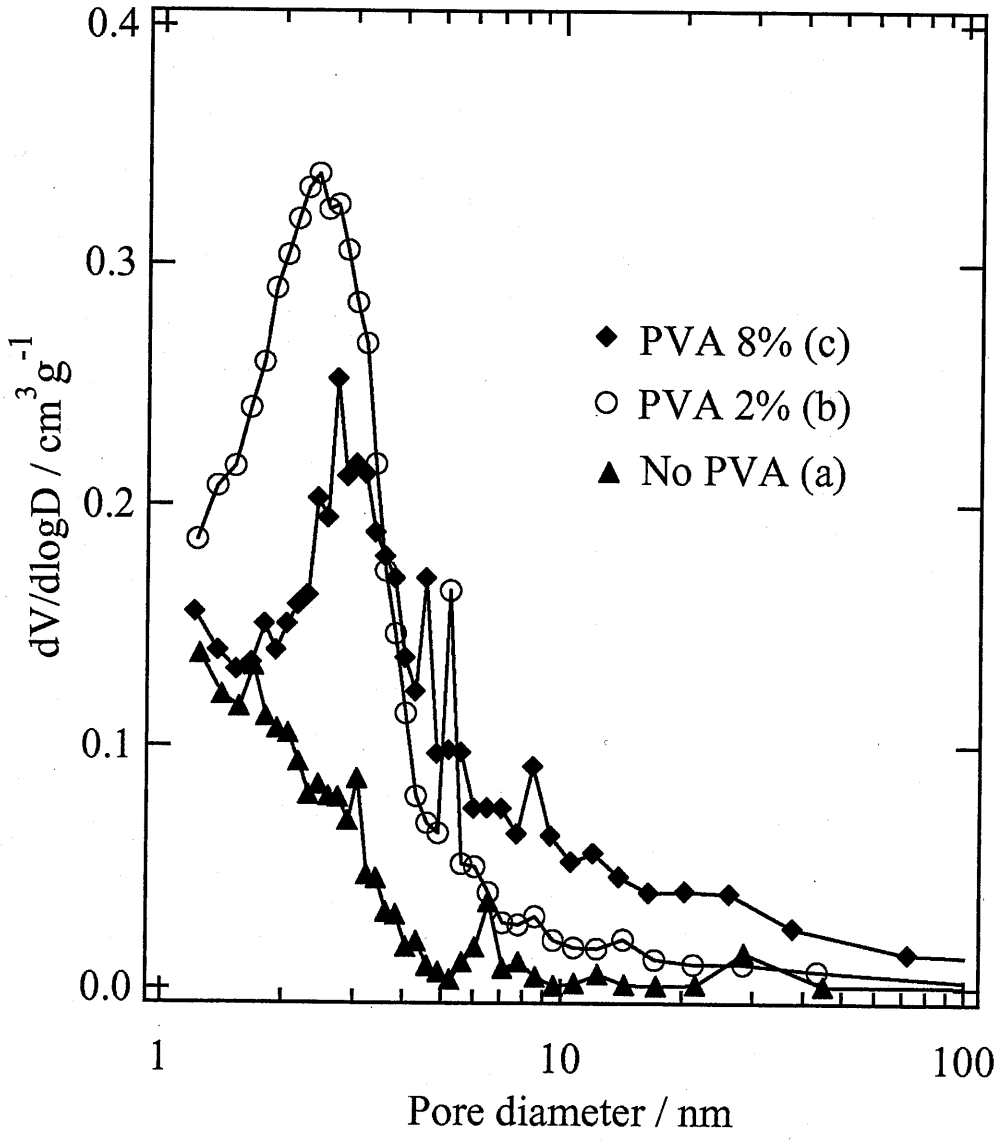


Fig.5-4. Pore size distribution curves of silica pillared fluorohectorites prepared (a) without PVA, (b) in 2.0% PVA, and (c) in 8.0% PVA.

The other pore properties of the silica pillared fluorohectorites are shown in Fig.5-5—5-8. As shown in Fig.5-5, these pillared clays had BET surface areas from 160 to 270 $m^2/g$ of which were half that of the other pillared montmorillonite[2,16,17]. This result also conformed to that of fluorine mica [4,5]. 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.5-6), 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.5-3. The synthesized sample in 8.0 wt% PVA gave an external surface area of 53 $m^2/g$ 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.5-7. 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

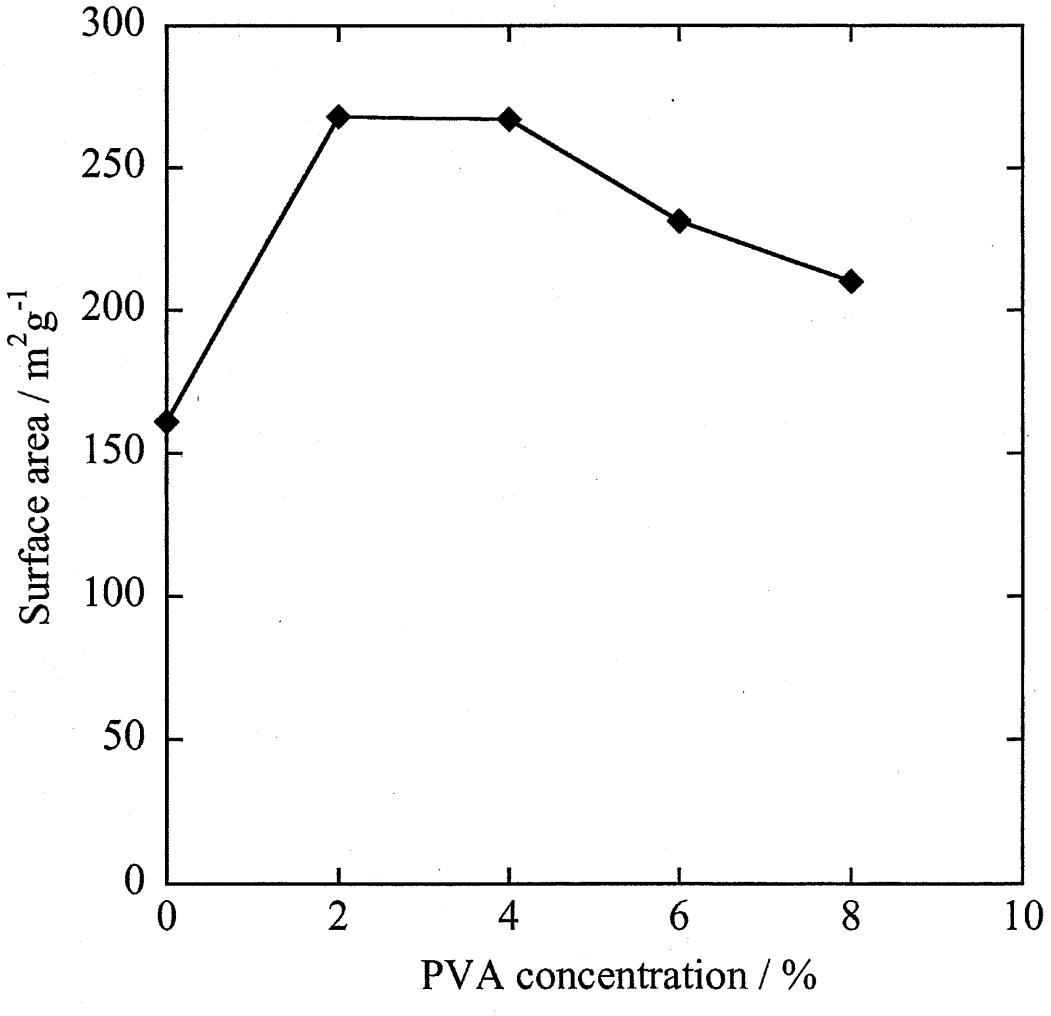


Fig.5-5. BET surface area of the silica pillared fluorohectorites plotted against PVA concentration.

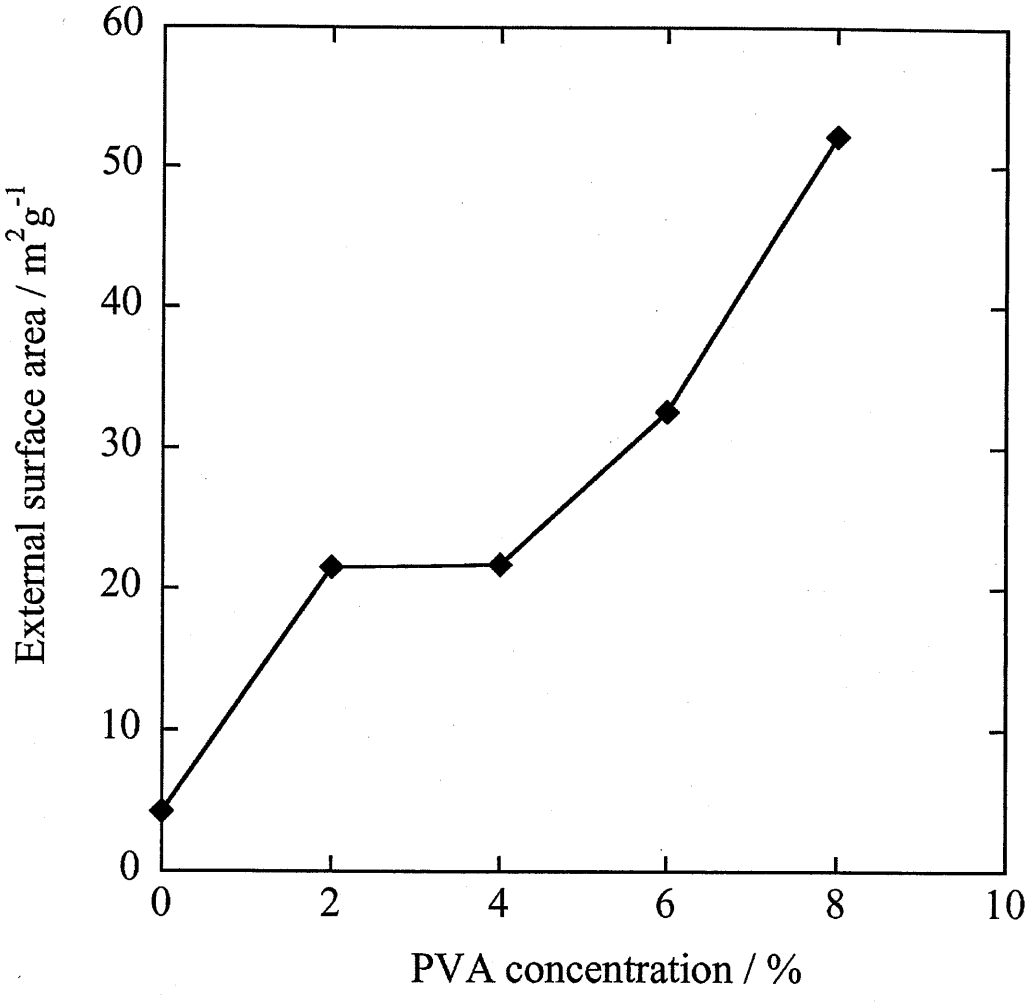


Fig.5-6. Effect of PVA concentration on the external surface area estimated by t-method of the silica pillared fluorohectorites.

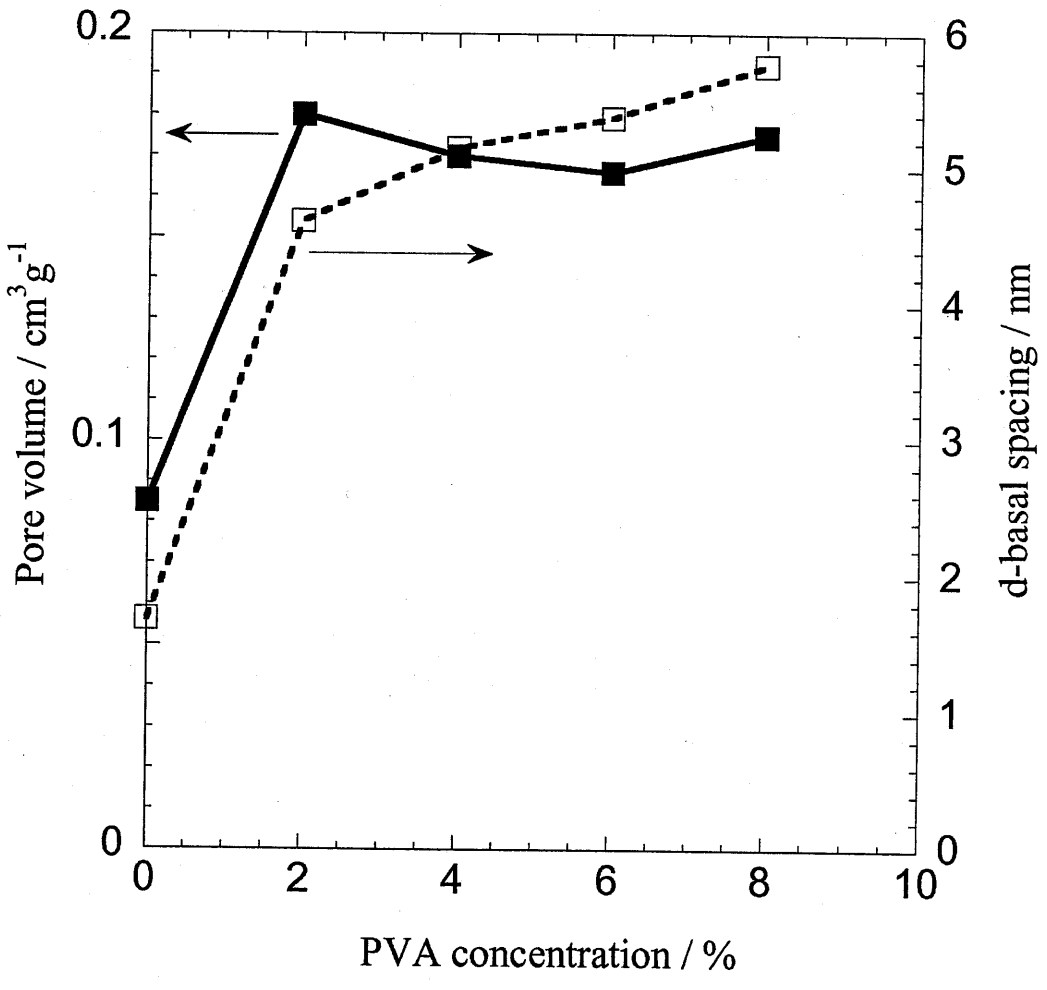


Fig.5-7. Effects of PVA concentration on the basal spacing from XRD data and pore volume of the silica pillared fluorohectorite.

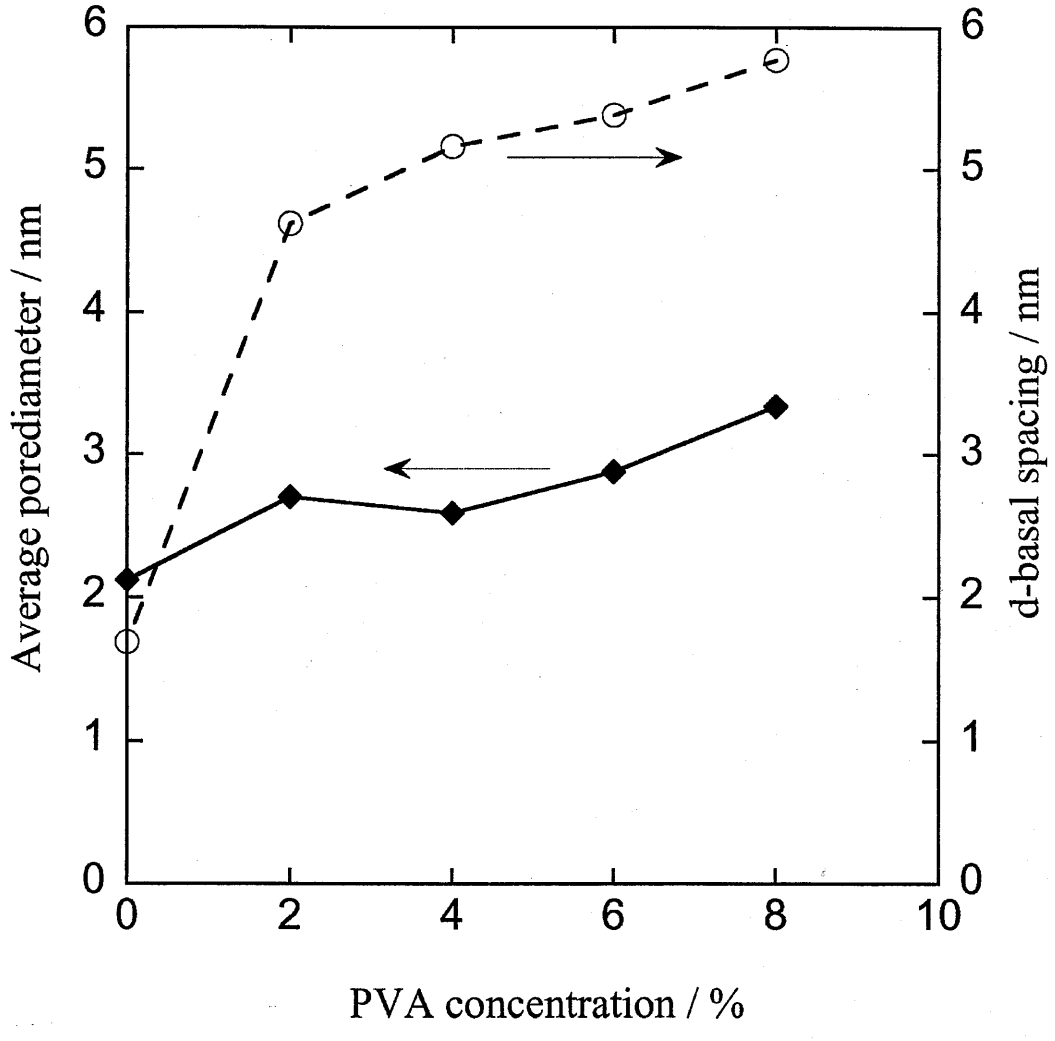


Fig.5-8. Effects of PVA concentration on the basal spacing from XRD data and average pore diameter of the silica pillared fluorohectorite.

the silicate layers. The average pore diameters are shown in Fig.5-8 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 [6,18]. 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. The author reported that there were few differences between the pore size

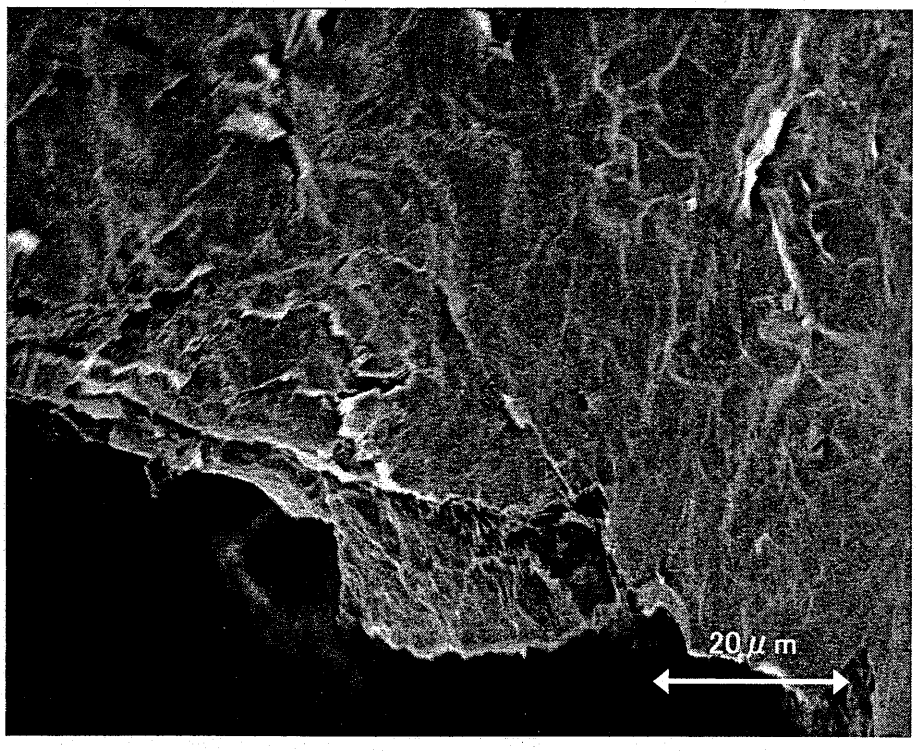


Fig.5-9. SEM image of the surface of the silica pillared fluorohectorite prepared in 2 wt% PVA.

estimated by the adsorption isotherm and the gallery height estimated by XRD in the silica pillared montmorillonite [10]. 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.5-9. 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.5-9.

## 5.4. Summary of Chapter 5

The silica pillared fluorohectorite with a various mesopore sizes using a polysiloxane with different PVA concentrations were synthesized. 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 cointercalation 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 montmorillonites[10] 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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# CHAPTER 6

# CONCLUSION AND FUTURE WORK

This study is done to prepare and characterize the silica pillared clay with micro and meso pores. The author studies the effect of PVA on the synthesis of pillared clays and the intercalation of large pillaring precursors, which are condensed outside clay sheets. The present study introduces a synthetic method of the mesoporous pillared clay without the usage of organic template. This is quite a new approach and has not recognized in previous work on pillared clays. It has already been shown that the addition of PVA on pillaring is available to enlarge interlayer distance [1-5]. It was noted that the layer structures of the clay corresponded to the pore structure in the region of micropore [2]. However, the present work achieves the production of pillared clay with mesopore and proves the correspondence of the pore size with clay structure. And then the intercalation of the large precursors with PVA causes more enlargement of pore size unlike many of the other intercalation of polyhydroxocations. The consistency in the pore distribution curve and large gallery height of clay has been made clear in the previous work [6,7]. In those cases, the use of organic template and the synthesis in hydrothermal condition was in large part due to give the mesopore. It must be considered that the synthesis and processing of porous materials generally require hydrothermal condition and the organic template molecule such as the alkylammonium. The appropriate synthetic condition and expensive reagent can be a limiting economic factor in the industrial production of pillared clays. The new approach proposes the

synthetic method that the use of PVA during pillaring facilitates the clay exfoliation and the intercalation of the large polysiloxane. Consequently, the cointercalation of PVA and polysiloxane provides mesoporous pillared clays in an economically available manner. By controlling the amounts or size loading of polysiloxane, they were able to vary gallery height of silica pillared clay over the range 0.7 to 4 nm.

For something unsatisfactory, this study does not allow us to make the pore size larger and did not give homogeneity of pore owing to the irregularity of clay structure. Furthermore, it is thought that the existence of the chlorine ion in the system is undesirable for environmental problems. Further study may dissolve the elimination of the chlorine ions as counter ions of polysiloxanes, because the polysiloxane from APS are the anion-exchange products and have the ion exchange reactivity with the anionic compound [8].

This work demonstrates that the polysiloxanes condensed outside clay sheets by sol gel method in advance can be incorporated into clay sheets and PVA affects the pillar arrangement of the polysiloxanes. This thesis gives the new approach of mesoporous silica pillared clay, and the added diversification to strategies for controlling the pore structure of silica pillared clay.

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