Preparation of a Clay Pillared with Rodlike Cationic Polysiloxane

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(Received September 1, 2004; CL-041029)

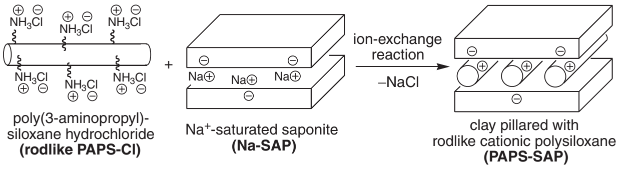
A clay pillared with a polymer was prepared by the ion-exchange of Na-saponite with a novel rodlike cationic polysiloxane. The present material had a *d*-value of ca. 1.8 nm, expanded by incorporation of the polysiloxane. It provided a micropore material with a relatively large surface area of more than $300\,m^2/g$ in the interlayer space.

There have been intense research activities on layered silicates pillared with inorganic or organic clusters, which are called pillared interlayer clays (PILCs).[1] PILCs have much higher surface areas, pore volumes, thermal stabilities, and better catalytic activities than the parent clays. Such superior properties make them useful catalysts, ion-exchangers, and adsorbents. These materials are normally prepared by the intercalative ion-exchange of layered clay minerals with a variety of nano-sized pillars, such as organic ions,[2] inorganic ions,[3] and sol particles.[4]

The preparations of various PILCs and various polymers/clay composites[5] have already been reported; however, there has been no study on the preparation of PILCs using polymers. Because the polymers usually have a flexible structure, expansion of the interlayer space of clays by polymer incorporation is not enough for providing more free space. For the preparations of porous materials using polymers, Carrado et al. attempted the direct intercalation of polymers such as hydroxypropyl methylcellulose,[6] hydroxyethyl cellulose,[6] poly(dimethyl diallyl ammonium chloride),[6] and polyvinylpyrrolidone[7] into clay minerals, followed by calcination. These polymers acted as reagents, not for pillaring, but for making space by removal of the polymers. One of the characteristics of polymers is the ability to form a space-morphology between the molecules. Therefore, the clays pillared with polymers would have interesting properties.

Recently, we prepared nanostructured polysiloxane materials; poly(3-aminopropyl)siloxane hydrochloride (PAPS-Cl) and poly(3-aminopropyl)siloxane nitrate ($PAPS\text{-}NO_3$) by the sol–gel reaction of 3-aminopropyltrimethoxysilane (APTMOS) in an inorganic-acid aqueous solution.[8,9] These polysiloxanes are water soluble with ammonium cations on the surface, and a rodlike structure with a hexagonal phase.[9] These materials have inspired us to develop new PILCs, because these polysiloxanes have both a rigidity to expand the interlayer of clays and an ability to intercalate molecules into the interlayer of clays by an ion-exchange reaction. We now report the preparation of a clay pillared with rodlike cationic polysiloxane (Scheme 1).

The synthesis was conducted by pouring the PAPS-Cl aqueous solution (0.15 g PAPS-Cl/10 mL-distilled water) into an aqueous suspension of Na^+-saturated saponite (Na-SAP)[10] (0.15 g Na-SAP/10-mL distilled water). After the mixture was vigorously stirred for 2 h at room temperature, the product was collected by filtration using a membrane filter (0.2 µm, Millipore), washed with distilled water, and then dried in a vacuum at room temperature. The obtained product (denoted as PAPS-SAP) was characterized by IR spectroscopy, CHN elemental analysis, X-ray diffraction (XRD), and nitrogen adsorption–desorption isotherm measurements.



Scheme 1.

The IR spectrum of the PAPS-SAP showed an absorption band at ca. $1515\,cm^{-1}$ ascribed to the ammonium ion of the PAPS component. This absorption band was absent in the spectrum of the Na-SAP. These results indicate that the PAPS was inserted into the interlayer of SAP. On the basis of the CHN analysis data, the exchange amount of a repeating unit of the PAPS component in the PAPS-SAP was calculated to be 126 meq/100 g SAP (host material).[11] This value is greater than that of the cation exchange capacity (CEC) of Na-SAP (92 meq/100 g SAP).[10] The distance between the charges of PAPS would be shorter than that of SAP. Therefore, excess ammonium groups and counter anions (Cl^-) of PAPS-Cl were inserted into the interlayer of SAP, which was confirmed by a Cl elemental analysis (wt % of Cl; 0.78).

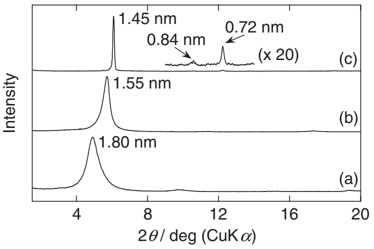


Figure 1. XRD patterns of PAPS-SAP (a), Na-SAP (b), and PAPS-Cl (c).

The XRD patterns of the PAPS-SAP, Na-SAP, and PAPS-Cl are shown in Figure 1. The XRD profile of PAPS-SAP was completely different from that of Na-SAP (Figure 1b) and PAPS-Cl (Figure 1c). Accordingly, the PAPS-SAP is not a mixture, but an intercalated nano-order material, i.e., a nanocomposite. The *d*-value of the PAPS-SAP was 1.80 nm. This indicates that the PAPS-pillared interlayer spacing is 0.84 nm because the thickness of each of the silicate layers of Na-SAP is 0.96 nm. The distance between the rods of PAPS-Cl was ca. 0.95 nm based on a TEM observation.[9] The interlayer spacing (0.84 nm) of PAPS-

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SAP is shorter than this distance, which is reasonable because the chloride anion size is included in the inter-rod distance for PAPS-Cl.

On the basis of the surface area for each cell (0.515 × 0.89 nm)[2b] and the interlayer spacing (0.84 nm), the theoretical volume of the interlayer space was determined to be $0.385\,\text{nm}^3$. On the other hand, we calculated the volume of a model compound for PAPS; $H_3N^+(CH_2)_3Si(OH)_3$, using a semi-empirical molecular dynamics program (MM2 in Chem3D, CambridgeSoft), taking the van der Waals radii into consideration. Consequently, this volume was $0.195\,\text{nm}^3$. The volume of the model compound in each cell was calculated to be $0.095\,\text{nm}^3$ ($= 0.195 \times 1/3 \times 126/86$) by considering the exchange amount of PAPS (126 meq/100 g SAP), the theoretical CEC of Na-SAP (86 meq/100 g SAP),[12] and the number of sodium ions in each cell (1/3). Therefore, the volume ratio of the model compound to the pore is 24.7:75.3 ([$0.095\,\text{nm}^3$] : [$0.385–0.095\,\text{nm}^3$]). Because 1 g of PAPS-SAP contains 0.123 g (1.106 mmol) of PAPS, the volume of PAPS is calculated to be $0.13\,\text{cm}^3/\text{g}$ ($= 1.106 \times 10^{-3} \times 6.02 \times 10^{23} \times 0.195 \times 10^{-21}$). Accordingly, the pore volume is $0.40\,\text{cm}^3/\text{g}$ ($= 0.13 \times 75.3/24.7$).

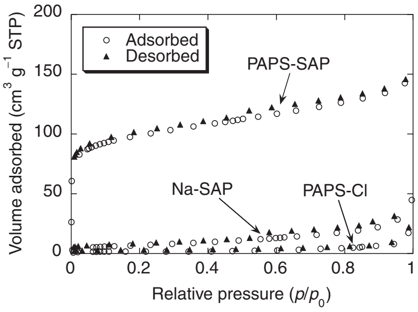

Figure 2. Nitrogen adsorption–desorption isotherms at 77 K of PAPS-SAP, Na-SAP, and PAPS-Cl.

The nitrogen adsorption–desorption isotherms at 77 K of the PAPS-SAP, Na-SAP, and PAPS-Cl, which were dehydrated at 110 °C under vacuum for more than 5 h, are shown in Figure 2. The adsorption of PAPS-SAP almost follows a type I isotherm and shows a microporosity for nitrogen with only a small macropore contribution, probably due to the external surfaces. The surface area and pore volume of PAPS-SAP derived from the *t*-plot were $370\,\text{m}^2/\text{g}$ and $0.15\,\text{cm}^3/\text{g}$. This indicates that a porous material was prepared from the starting materials with dense structures (BET surface areas of Na-SAP and PAPS-Cl were ca. 26 and $5\,\text{m}^2/\text{g}$, respectively). The actual pore volume is smaller than the theoretical volume ($0.40\,\text{cm}^3/\text{g}$). Because of the dead spaces formed by the side chain conformation of PAPS and the chloride ions due to extra PAPS in the interlayer, nitrogen could not completely permeate into the interlayer space. The pore size of 0.92 nm, which was also obtained from a *t*-plot, was almost consistent with the interlayer spacing of PAPS-SAP (0.84 nm). The pore structure of PAPS-SAP has not yet been clarified; however, the results obtained from the isotherms are almost compatible with the XRD results.

When clay minerals with a high CEC, such as Li^+-saturated taeniolite,[13] were used, such a porous material was not obtained by combination with PAPS-Cl (BET surface area of the obtained material was ca. $53\,\text{m}^2/\text{g}$), although a sufficient interlayer spacing existed as confirmed by an XRD measurement (*d*-value of the obtained material was ca. 1.83 nm). Because the distance between the rods of PAPS in the interlayer of taeniolite is short due to the higher CEC of the Li^+-saturated taeniolite (exchange amount of a repeating unit of PAPS was calculated to be 140 meq/100 g taeniolite), sufficient space was not provided. Furthermore, when we used polyallylamine hydrochloride (PAA-Cl; weight-average molecular weight is ca. 70,000) —a common cationic polymer— for pillaring in the SAP interlayer, a porous structure was not obtained (BET surface area of the obtained material was ca. $52\,\text{m}^2/\text{g}$). It was difficult for PAA-Cl to pillar the interlayer of SAP due to the lack of rigidity. From these results, we consider that both the rigidity of the guest polymers and a sufficient distance between charges in the host layered clay minerals are necessary for preparing clays pillared with polymers. Detailed studies on the effect of the layer charge density of the clay minerals are now in progress.

To summarize, we have prepared a pillared interlayer clay (PILC) composed of a rodlike cationic polysiloxane and a layered clay mineral (Na-saponite) by an ion-exchange reaction. The obtained material provides nano-sized micropores in the interlayer space.

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10 Ideal formula; $Na_{1/3}[(Si_{11/3}Al_{1/3})(Mg_3)O_{10}(OH)_2]\cdot nH_2O$. Details of the source and characterization of the Na^+-saturated saponite have been given in the following papers: J. Bujdák, N. Iyi, J. Hrobáriková, and T. Fujita, *J. Colloid Interface Sci.*, **247**, 494 (2002).

11 Calculation was conducted using the CHN elemental analysis data (wt % of nitrogen; 1.55), taking molecular weight of one repeating unit for PAPS ($H_3N^+(CH_2)_3SiO_{1.5} = 111.2$) into consideration.

12 Theoretical CEC of Na-SAP was determined from the ideal formula[10] without the water content being considered.

13 Li^+-saturated taeniolite was kindly supplied by Topy Industries Co., Ltd., Japan. Ideal formula; $LiMg_2Li(Si_4O_{10})F_2\cdot nH_2O$. BET surface area: ca. $54\,\text{m}^2/\text{g}$.

Published on the web (Advance View) October 16, 2004; DOI 10.1246/cl.2004.1486