CHEMISTRY LETTERS, pp. 1283-1286, 1993.

Preparation of a Self-Supporting, Multilayered Film of Montmorillonite

Munetoshi ISAYAMA,[†] Kanji SAKATA,[††] and Toyoki KUNITAKE*[†††]
Molecular Architecture Project, JRDC, Kurume Research Park, Kurume 830

A self-supporting, multilayered film which was prepared from an aqueous dispersion of montmorillonite and orthophosphoric acid (H_3PO_4) remained intact even in hot water and maintained the ion exchange capacity similar to that of the original montmorillonite powder. An ammonium surfactant (CTAB) was intercalated into this film readily to give a highly oriented composite film.

In order to broaden functional uses of clay minerals, introduction of inorganic pillars and intercalation of functional organic materials have been conducted by the ion exchange method.[1-6] These composite materials were obtained as powders, and the layer structure of clay minerals was not fully exploited. If modified clay minerals are available as self-supporting films, their uses such as ion exchange membranes and anisotropic optical materials will be much expanded.

The basic structure of montmorillonite consists of the octahedral aluminate layer that is sandwiched by the tetrahedral silicate layers. The aluminate layer exposed at the edge of this unit structure is reactive and assist various reactions.[8,9] Thus we attempted to take advantage of this reactive aluminate layer to improve the film-forming property of montmorillonite

Montmorillonite powder (0.02 g, Kunimine Kogyo Ind. Ltd.) was dispersed in water by sonication, and conc. orthophosphoric acid (1×10^{-2} mol) was added. The mixture was again sonicated to give a slightly turbid dispersion, cast on a fluorocarbon membrane filter, and dried for 3 days (at 25 ℃, 65% relative humidity). The resulting cast film was washed twice by water, and air-dried for 12 h at 35 ℃. It was self-supporting and flexible. Figure 1 shows its whole view and cross-sectional SEM views. The montmorillonite layers run parallel to the film plane, and the layer thickness is a few nanometers.

Table 1 summarizes the stability of this cast film against water at several temperatures. After soaking in 100 ml of water for 24 h at given temperatures, the remaining film was filtered, air-dried for 12 h at 35 ℃ and weighed. A cast film of untreated montmorillonite swelled in water and disintegrated. The H_3PO_4-treated cast film held the original film shape without swelling. Although slightly dissolved at higher temperatures, the cast film was basically stable in water even at 90 ℃.

The ion exchange capacity of montmorillonite films was then measured. The H_3PO_4-treated cast film was immersed in 1 M aqueous ammonium acetate for 24 h at 25 ℃, washed with ethanol, and pulverized. The organic

---

[†] Permanent address: Fukuoka Industrial Technology Center, Fukuoka 818.

[††] Permanent address: Tokuyama Soda Co., Ltd., Tokuyama 745.

[†††] Permanent address: Faculty of Engineering, Kyushu University, Fukuoka 812.

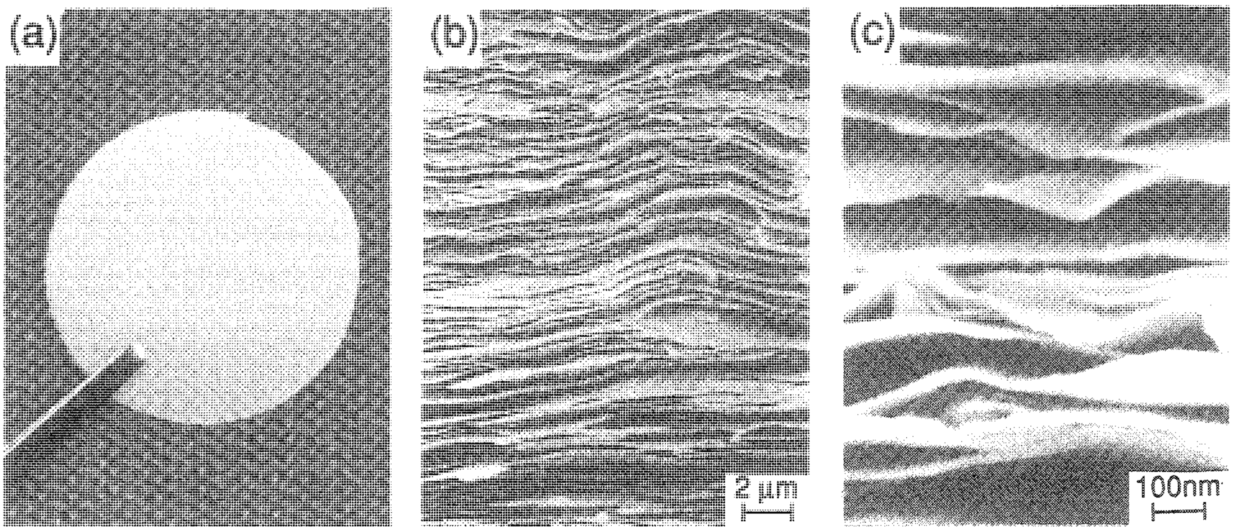

Fig. 1. A cast film of H_3PO_4-treated montmorillonite.
(a) Whole view, (b) SEM view of the cross section (Hitachi, S-900), (c) Expanded SEM view.

moiety in the powder was decomposed with conc. sulfuric acid in the presence of copper sulfide catalyst, and the amount of nitrogen was determined by the Kjeldahl method (instrument, Mitsubishi Kasei Kogyo KN-03). The resulting ion exchange capacity for the ammonium ion was 65 meq/100 g. The ion exchange capacity of the original montmorillonite powder estimated in the same manner was 98.5 meq/100 g. It is clear that the ion exchange capacity is mostly retained after the H_3PO_4 treatment.

Table 1. Stability of montmorillonite films against water[a)]

Cast film	weight loss(%) after soaking in water at				
	20 °C	40 °C	50 °C	70 °C	90 °C
H_3PO_4 -treated	0	2.1	2.9	3.6	8.1
not treated[b)]	100	—	—	—	—

a) See text for procedures.
b) A reference film was prepared by casting an aqueous dispersion of the original montmorillonite powder.

Figure 2 shows a ^{31}P-MAS-NMR spectrum of H_3PO_4-treated montmorillonite. This montmorillonite gives several ^{31}P peaks at 18.4 ppm to -24.7 ppm. These chemical shifts relative to that of H_3PO_4 suggest that orthophosphoric acid is tightly bound to montmorillonite, and that the bound phosphate unit is coordinated to elements other than hydrogen.[10)] We assume that the aluminate edge of montmorillonite fragments is bridged extensively with each other by the phosphate unit, as illustrated in Fig. 3.

Alkylammonium ions can be intercalated into montmorillonite readily, and the alkyl chain is oriented in montmorillonite layers.[12-14)] These composites possess unique properties including dispersibility in organic solvents. It would be interesting if these properties can be imparted to the free-standing montmollironite film. Thus, the H_3PO_4-treated montmorillonite film was soaked in 15 mM aqueous CTAB (cetyltrimethylammonium bromide) in an autoclave for 12 h at 150 °C, washed with water, and air-dried at 35 °C. The film kept its morphology even under these conditions, and was transparent and slightly yellow. The molar percentage of bound CTAB per anionic site as determined by thermogravimetry was 98%.

X-Ray diffraction of the H_3PO_4-treated cast film shows a pattern corresponding to the long spacing (12.8 Å) of the montmorillonite layer (Fig. 4-a). On the other hand, the long spacing of the montmorillonite / CTAB composite film is 38.6 Å, and is observed up to the 14th order (Fig. 4-b). The extended molecular length of CTAB is ca. 25 Å and the thickness of the montmorillonite unit layer is 11.5 Å.[15] The observed long spacing of 38.6 Å is very close to the sum of these two lengths. Transmission X-ray diffraction (edge view) of the composite film gives equatorial diffractions in the small-angle region which correspond to the long spacing observed in the reflection diffraction, along with the axial diffraction of the aligned alkyl chain. It is clear that the H_3PO_4-treated montmorillonite film keep the original layer structure and that CTAB molecules are intercalated into the film in an alternate, perpendicular array.

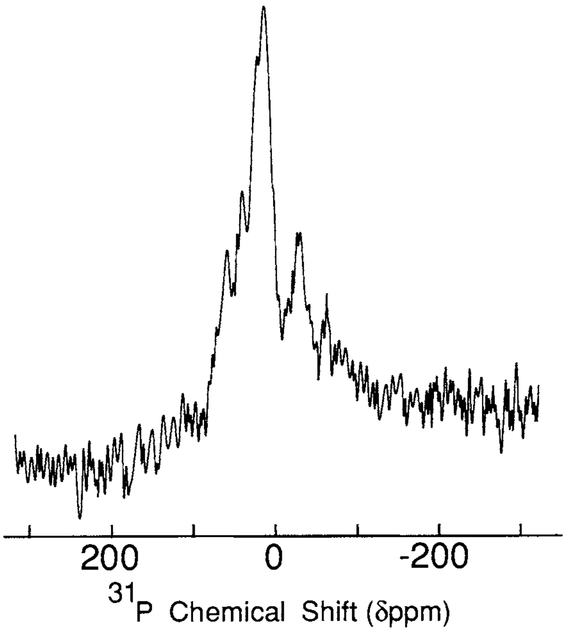

Fig. 2. ^{31}P-MAS-NMR spectrum of a powdered cast film prepared from H_3PO_4-treated montmorillonite. (reference, H_3PO_4 : instrument, Bruker AC-250P).

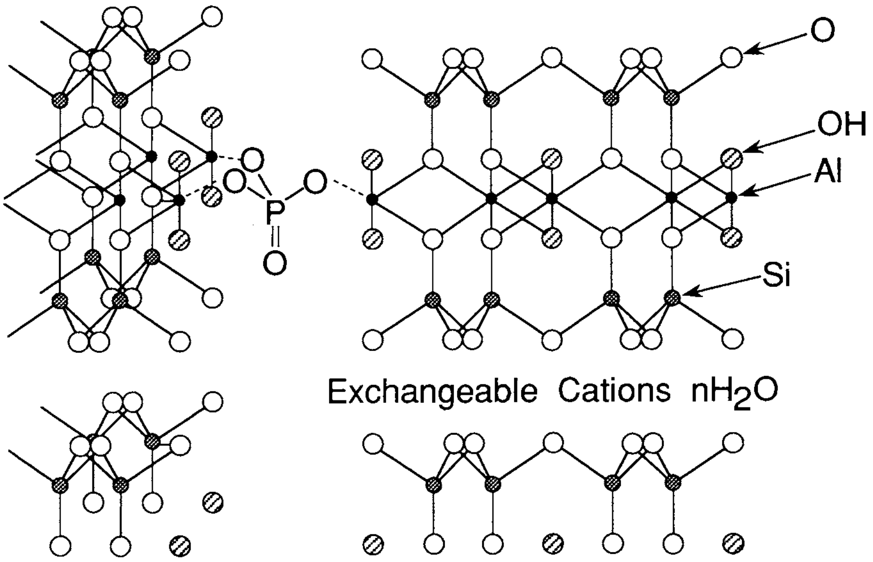

Fig. 3. The structure of montmorillonite [11] and a probable mode of immobilization with H_3PO_4.

In conclusion, we prepared a multi-layered, free-standing montmorillonite film by immobilizing montmorillonite fragments with orthophosphoric acid. The resulting film retains unique properties of the original montmorillonite powder. Therefore, the H_3PO_4-treated montmorillonite in the form of powder and film should be interesting as novel functional materials.

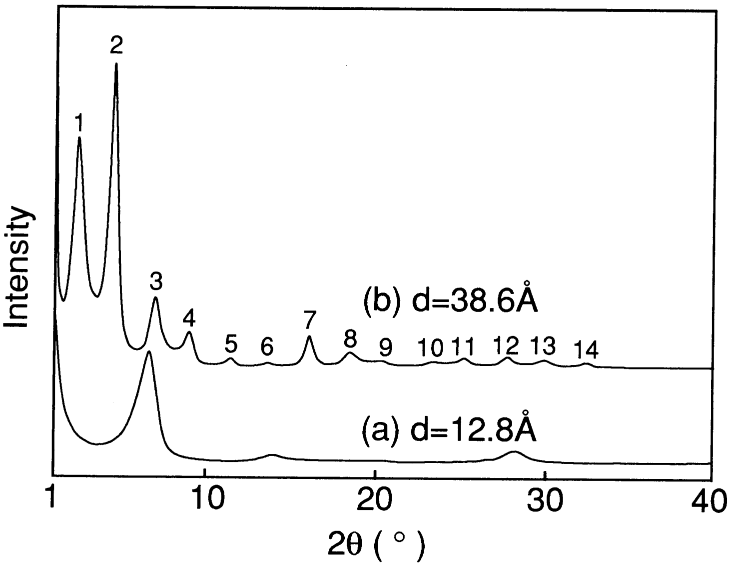

Fig. 4. Reflection X-ray diffraction of montmorillonite cast films. (Rigaku Denki, RAD-32, Cu Kα (50 KV, 200 mA))
(a) A cast film prepared from H_3PO_4-treated montmorillonite.
(b) A composite cast film of CTAB and H_3PO_4-treated montmorillonite.

Reference

1) V. E. Berkheiser and M. M. Mortland, *Clays and Clay Minerals.*, **25**, 105(1977).
2) T. Nakamura and J. K. Thomas, *J. Phys. Chem.*, **90**, 641(1986).
3) J. M. Serratosa, *Clays and Clay Minerals*, **14**, 385 (1966).
4) S. S. Cady and T. J. Pinnavaia, *Inorg. Chem.*, **17**,1501 (1978).
5) H. Hasegawa, *J. Phys. Chem.*, **65**, 292 (1961).
6) M. B. McBride, *Clays and Clay Minerals*, **33**, 510 (1985).
7) S. L. Swartzen-Allen and E. Matijevic, *Chem. Rev.*, **74**, 385(1974).
8) N. Murase and K. Gonda, *J. Biochem.*, **92**, 271 (1982).
9) B. Siffert and J.J. Trescol, *Clays and Clay Minerals*, **30**, 185 (1982).
10) S. Nakata, S. Asaoka, H. Takahashi, and K. Deguchi, *Anal. Sci.*, **2**, 91 (1986).
11) U. Hofmann, *Angew. Chem., Int. Edit. Engl.*, **7**, 681(1968)
12) A. Weiss, *Angew. Chem., Int. Edit. Engl.*, **2**, 134 (1963)
13) G. Lagaly, *Angew. Chem., Int. Edit. Engl.*, **15**, 575 (1976)
14) G. Lagaly and R. Witter, *Ber. Bunsenges. Phys. Chem.*, **86**, 74 (1982)
15) R. E. Grim, "Clay Mineralogy," McGraw-Hill Book Co., NY (1968).

(Received April 20, 1993)