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Intercalation of Cationic Fluorinated Surfactant into Interlayer Space of Montmorillonite through Ion-exchange Reaction

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Intercalation of cationic fluorinated surfactant into interlayer space of montmorillonite through ion-exchange reaction has been investigated. It was found that the surfactant is easily exchanged to form a new layer composite with basal spacing, d_{001} = 1.5 nm, in water / methanol suspension system. When the amount of the surfactant was increased over CEC, excess surfactant salts are also inserted together into the interlayer space to form an expanded phase with d_{001} = 3.0 nm, suggesting a strong guest-guest interaction in the interlayer space. The gas adsorption experiment revealed that the intercalated compound shows a weak interaction toward N_2 and CO_2 gases.

Key words : Fluorinated-surfactant, layered-clay, Intercalation, Structure of intercalates

1. INTRODUCTION

Fluorinated surfactant with perfluoro alkyl chain has attractive features, such as thermal stability, water- and oil-repellency, low surface tension, caused by stiff perfluoro chain[1-3]. On the other hand, layered clay with cation exchange ability is interesting as a host material serving a 2-dimensional space to give a regular array of this cationic surfactant[4]. Thus intercalation of stiff fluorinated surfactants into layered clay is considered to provide a new possibility to make pillared materials, or layer-stacked nano-composites. However, the knowledge on the intercalation reaction of fluorinated surfactant into layered clay is quite limited in literature, compared with usual hydrocarbon surfactants. To extend the field of application of this material, the intercalation reaction, as well as the structure of the resultant should be studied. In most of cationic fluorinated surfactants, the fluorinated hydrophobe is attached directly or indirectly to a quaternary ammonium group. Because of this combined character, one can expect not only coulombic interaction between the negatively charged aluminosilicate and the ammonium cation (host-guest), but also attractive interaction among the surfactants (guest-guest). The first purpose of the study is to demonstrate the ion-exchange reaction between Na-montmorillonite and perfluorooctanesulfonamido-surfactant at room temperature with a water / methanol suspension system through the ion-exchange reaction. The second part is to clarify the effect of the guest-guest interaction on the intercalation behavior of this surfactant. The gas adsorption behavior of the resultant products will be also presented.

2. EXPERIMENTAL SECTION

2.1 Materials.

A quaternary ammonium type cationic fluorinated surfactant, $C_8F_{17}SO_2NHC_3H_6N(CH_3)_3I$ [5], provided from Tohkem Products Corp., was used. The clay used for this study was Na-montmorillonite, KUNIPIA-F, provided by Kunimine Industries Corp.. The typical unit cell formula is represented as $(Na_{0.7}K_{0.02}Ca_{0.04})$ $(Si_{7.78}Al_{0.22})$ $(Al_{3.2}Fe_{0.16}Mg_{0.64})O_{20}(OH)_4{\cdot}nH_2O$. The cationic exchange capacity, CEC, was about 100 meq. / 100 g.

2.2 Synthesis.

The intercalation reaction of the cationic fluorinated surfactant into the Na-montmorillonite was carried out through ion-exchange reaction between Na^+ and $[C_8F_{17}SO_2NHC_3H_6N(CH_3)_3]^+$. One gram of the clay was added in 200 ml of deionized water under vigorous stirring. The suspension was mixed with 200 ml water / methanol mixed solution (the mixture ratio was 1 : 1) containing the surfactant with different amount 0.5-3.0 times of the CEC. Solubility of the surfactant in water is about 0.1 wt %, while that in methanol is more than 10 wt %. Thus we used the mixed solvent for ion-exchange. The suspensions were vigorously stirred for 3 hours under lowered pressures with suction. They were allowed to age overnight, and the products were separated by centrifugation, washed with deionized water and dried in vacuo. For preparation of preferentially oriented samples, 50 mg of the products dispersed in 3 ml of methanol with supersonic wave irradiation for 2 hours, were spread on glass plates.

Through this procedure, we obtained 6 composite samples containing different amount of the surfactant in the interlayer spaces. The following nomenclature will be used FSM-*R*, abbreviates as follows: *R* is the molar ratio of amount of the surfactant to CEC.

2.3 Characterization of the products.

X-ray diffraction (XRD) patterns for powder and oriented film samples were obtained with a Rigaku diffractometer RAD-C using Ni-filtered CuKα radiation.

FT-IR spectra were obtained with a Perkin-Elmer 1640 spectrometer. The sample was ground finely with KBr to make a pellet. Thermogravimetric analysis (TG) was performed with a Rigaku TG8120. The data were collected under N_2 flow at a scanning rate of 10 K / min. Gas adsorption experiments were carried out with N_2 and CO_2 at 77 K and 193 K, respectively. The samples were outgassed at 423 K overnight. Specific surface areas were estimated by fitting the data with BET equation.

3. RESULTS AND DISCUSSION

3.1 XRD study.

XRD patterns for the ion-exchanged powder products and the pristine montmorillonite are shown in Fig. 1a. The patterns of the lightly loaded products (FSM0.5, 0.75) showed (001) diffraction at $2\theta = 5.8°$ corresponding to a basal spacing of 1.5 nm. It indicated that the interlayer space expanded in comparison with the original clay. Assuming the thickness of the host layer is approximately 0.96 nm, the interlayer space height is calculated to be to 0.54 nm. On the other hand, diffraction appeared at $2\theta = 2.9°$ (d = 3.0 nm), 5.8° (1.5 nm), 8.8° (1.0 nm) for the heavily loaded products (FSM1.0-3.0). These were harmonic reflections from a basal plane with spacing of 3.0 nm. Hence, the interlayer space expanded as increasing amount of the surfactant, suggesting that a phase transition occurred depending on the amount of the loading of the surfactant. However, it seems difficult to describe the conformation of the products from only the value of 3.0 nm, which will be discussed later.

The XRD pattern for an oriented sample with methanol treatment is shown in Fig. 1b. It was found from TG experiment that almost all the surfactant remained in the interlayer space even after the methanol treatment. The pattern exhibited 11 harmonic reflections, indicating fairly high crystallinity. This means that the treatment is effective for progress in regularity of the arrangement of the composite particles.

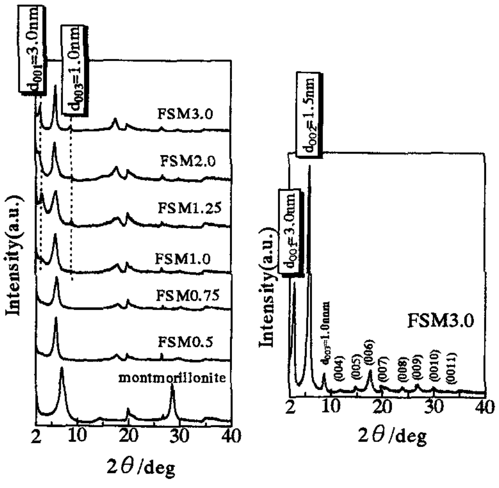

Fig. 1 XRD patterns for the composite products obtained by the ion-exchange reaction between the fluorinated surfactant and the montmorillonite, the original montmorillonite (a) and the oriented film sample of FSM3.0 (b).

3.2 FT-IR study.

The FT-IR spectra for the products are summarized in Fig. 2. In this profile, we can distinguish at least 4 absorption bands originated from the surfactant. The assignment to these bands are as follows: (1) stretching vibration of C-F bond at 1150 and 1210 cm^{-1}; (2) stretching vibration of S=O double bond at 1370 cm^{-1}; (3) bending vibration of C-H bond at 1480 cm^{-1}. These spectra are the evidence for the presence of the surfactant in the product composites. As we pay our attention to the bands of the C-F bond, it is apparent that the absorbance increases with increasing amount of the surfactant.

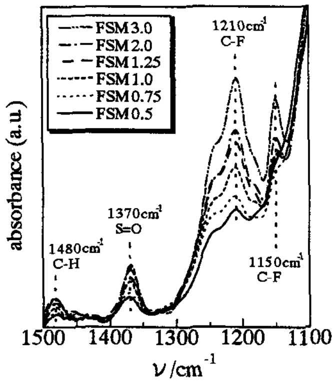

Fig. 2 FT-IR spectra for the composite products obtained by the ion-exchange reaction between the fluorinated surfactant and the montmorillonite in the difference of the amount of the surfactant.

3.3 TG study.

TG data for the composite products are shown in Fig. 3. For comparison, those for the montmorillonite and the original fluorinated surfactant iodide salt are also presented. The weight of the original surfactant began to drop suddenly at approximately 448 K and almost the entire sample decomposed by 553 K. On the other hand, the TG profile of the clay showed two typical transitions below 360 K and at around 903 K. The former is

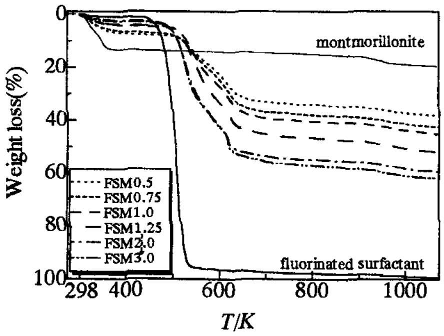

Fig. 3 TG curve for the composite products obtained by the ion-exchange reaction between the fluorinated surfactant and the montmorillonite, the original montmorillonite and fluorinated surfactant.

attributed to dehydration of physisorbed water molecules and interlayer water molecules, and the latter is attributed to dehydroxyl of the aluminosilicate structure. Comparing of these results, however, we can distinguish at least 3 transitions involved in thermal processes of the composite products. The dehydration at low temperatures and the dehydroxyl at high temperatures coincide with those of the clay. The transition temperature region corresponding to the decomposition of the surfactant is higher and broader than that of the original surfactant itself. This difference in temperature of the decomposition indicates that the surfactant is intercalated into the interlayer space of the clay. The weight loss due to decomposition of the surfactant seems to increase as increasing amount of the surfactant, while that of solvent decreases on the contrary.

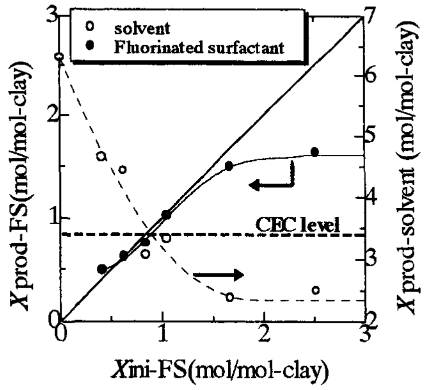

Fig. 4 Contents of the surfactant and solvent molecules in the products(Xprod-FS and -solvent) per $O_{20}(OH)_4$ unit as a function of the molar ratio of surfactant salts to the clay unit in the initial suspension(Xini-FS).

We tried to estimate the amount of the solvent molecules and the surfactant in the composite products from the weight loss between room temperature and 423 K, and that between 423 K and 773 k, respectively. In the calculation, we temporarily used the molar weight of H_2O for that of the solvent molecules in the interlayer. The contents of the surfactant and solvent molecules per clay $O_{20}(OH)_4$ unit in the composite products, Xprod, are present in Fig. 4 as a function of the molar ratio of the surfactant to the clay in the initial suspensions, Xini. In this figure, we inserted a dotted line for representing the CEC level and also a linear line that is expected when the all surfactant molecules are incorporated in the composite products. From this figure, we can point out three features as follows: (1) in the light loading regions, almost all the surfactants in the initial solution were taken into the composite products; (2) even in the heavy loading regions over CEC level, the occlusion continued to occur but finally show a saturation; (3) solvent molecules behaved in the opposite way. The observed, good correspondence between uptake of the surfactant and release of the solvent is considered to be the result of ion-exchange reaction in the interlayer space. In general, the internal surface of clay is hydrophobic and solvent molecules are introduced into the interlayer space mainly due to hydration to metallic cations. Since organic cations have less power of hydration, the solvent molecules have a tendency to be released out of the interlayer space by cation-exchange with organic cations.

It is surprising that the uptake of the surfactant continued to occur beyond the CEC level up to the maximum point almost twice as much as the CEC. In the case of quaternary ammonium ions with hydrocarbon chain, the uptake is limited by the CEC[6]. However our results showed an excess uptake of the surfactant. Moreover, the existence of the iodide ions in the heavily loaded composite was confirmed qualitatively by UV method. These facts suggest a strong attraction between perfluoro chains of this surfactant, which may cause self-assemblies of the surfactant inside the interlayer space. In this respect, it is interesting that Inoue et al. have recently reported that perfluorinated surfactant, $(CF_3)n\text{-}CONH(CH_2)_2N^+(CH_3)_2C_{15}H_{33}[n=1\text{-}3]$, of amount 5 times as much as the CEC were intercalated into the interlayer space of synthetic-Saponite[7].

3.3 Gas adsorption study.

N_2 adsorption isotherms for the products and montmorillonite are presented in Fig. 5a. The isotherms for the products were very similar to the type III

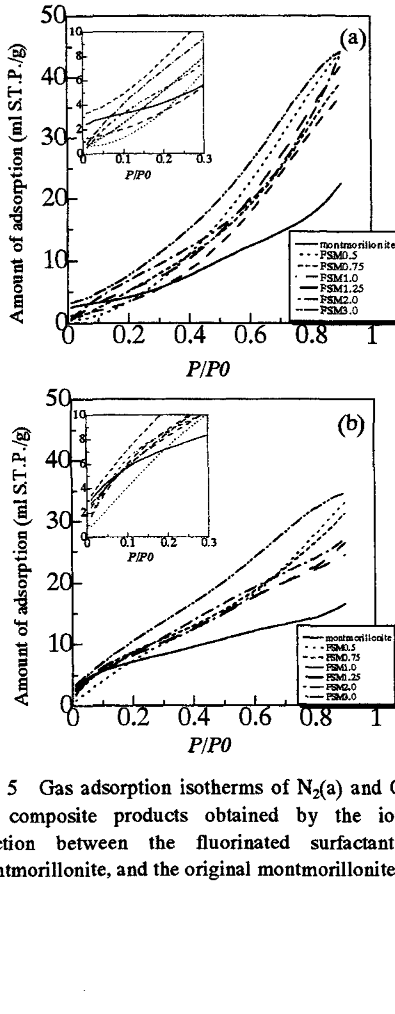

Fig. 5 Gas adsorption isotherms of N_2(a) and CO_2 (b) for the composite products obtained by the ion-exchange reaction between the fluorinated surfactant and the montmorillonite, and the original montmorillonite.

isotherm characteristic of little adsorption at low relative pressures. It suggested that micropores in which N_2 gas could enter were very few within the composites. Since the type Ⅲ isotherm arises from a weak interaction between the gases and the surface, the isotherms observed also suggested that the interaction between the products surface and N_2 gas was very weak. While, as shown in Fig. 5b, CO_2 gas was easier to adsorb on the surface at the low relative pressures as compared with N_2 gas, but the amount of adsorption was still not so large. By fitting the data with BET equation, specific surface areas and constant values, C, were estimated as shown in Table Ⅰ. The constant C gives a measure for the interaction between the gases and the surface. From this table, we can also see that the composites have lower interaction between the gas and the solid as well as few micropores. From the results, it is likely that the intercalation of the fluorinated surfactant into the montmorillonite is effective to lower the surface energy, but is not effective to make microporous materials.

Table Ⅰ Specific surface area(S) and constant values(C) estimated by fitting the data with BET plots

Sample	C_{N_2}	S_{N_2}(m^2/g)	C_{CO_2}	S_{CO_2}(m^2/g)
Montmorillonite	19.5	19.8	40.2	32.6
FSM0.5	-[a]	-[a]	5.8	50.8
FSM0.75	2.6	44.5	13.2	47.0
FSM1.0	10.8	25.4	16.0	42.8
FSM1.25	3.8	37.3	21.0	42.5
FSM2.0	8.1	37.2	12.3	47.5
FSM3.0	17.3	31.6	11.4	58.1

$C = \exp[(Q_1 - Q_L) / RT]$; Q_1 is heat of adsorption on the surface, Q_L is heat of liquefaction to the second layers.

[a] not determined because of too large deviation from BET equation.

3.4 Model structure of the composites

Finally, gathering the above results, we discuss about the conformation of the surfactants in the interlayer space. The surfactant used here is composed of three parts; (1) a cation head with the diameter of about 0.57 nm, (2) a perfluorinated normal chain with length of 0.9nm and thickness of 0.55 nm, (3) an alkyl chain with sulfonamide group bonding the above two parts. The former two parts are hard whereas the last part is relatively flexible for topological deformation. The d = 1.5 nm phase appeared in the lightly loaded samples is considered to be a result of lying of the surfactant ions along the a-b plane of the alumionosilicate sheet as shown in Fig. 6a. In this conformation, the surfactant ion form a monolayer sheet and the head part would act as the pillar.

On the other hands, the interpretation of the height of the interlayer space, 2.04 nm (d = 3.0 nm), appeared for the heavily loaded samples, allows several different possibilities. Some of them are presented in Fig. 6b-d. It is difficult to determine the precise structure from the basal spacing value only. However, in any structure, the interlayer space could accommodate the surfactants twice as many as CEC. In addition, the maximum capacity is naturally limited for geometrical reason. In order to obtain more detailed structure model, we are now studying the Fourier analysis with the aid of the intensity of the series of basal reflections of XRD.

4. CONCLUSION

It was found that ion-exchange reaction of cationic fluorinated surfactant with sodium ion of montmorillonite progressed quite easily in water / methanol suspension system. Furthermore, it was also found that excess surfactant over CEC can be introduced into the interlayer space due to interaction among surfactant molecules.

ACKNOWLEDGEMENT

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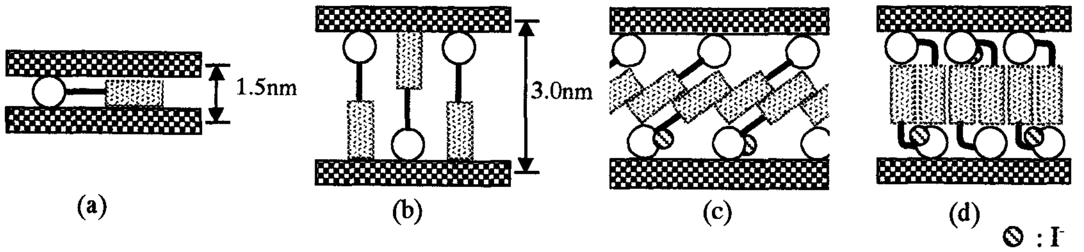

Fig. 6 Schematic structure model for the composite products obtained by the ion-exchange reaction between the fluorinated surfactant and the montmorillonite: (a) d=1.5nm phase, (b-d) d=3.0nm phase.

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