CHARACTERIZATION OF 2:1 TYPE LAYERED ALUMINOSILICATE VIA INTERCALATION REACTION

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+ Dedicated to Prof. Yun-Myung Hong in memory of his retirement

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Abstract—The stable intercalation compounds were synthesized by ion exchange reaction of the cations (Ca^{2+}, Mg^{2+}, etc.) existing in the interlayer of the 2:1 type layered natural aluminosilicate with n-decylammonium ion and by successive molecular intercalation reaction of the primary n-alcanol (ROH, R = $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$).

The charge densities were calculated from the basal spacings of n-decylammonium derivatives under primary n-alcanol.

As the result, the aluminosilicates used in this study have the charge density of 0.25, 0.34 per formula unit and interlayer cation exchange capacity of 69.3, 92.4 meg./100g, respectively.

INTRODUCTION

The mica type of layer silicate can be described by a general formula as follows:

$$M^{n+}_{\frac{x+y}{n}}[\{(Me^{+}Me^{2+}Me^{3+})_{2-3}\}^{(6-x)+}(OH)_2(Si_{4-y}Al_y)0_{10}]^{(x+y)-} \quad \cdots\cdots (1)$$

where, M; interlayer cation Me; octahedral cation In this formula, x + y represents the magnitude of the negative charges in the silicate layer unit, layer charge. The layer charge can also occur in nature via isomorphous replacement reaction that the silicon atoms in the tetrahedrons of $(SiO_4)^{4-}$ are replaced by Al^{3+} or Me^{3+} in the octahedrons by divalent or monovalent cations. For the compensation of layer charge, exchangeable cations (K^{+}, Na^{+}, H^{-}, Mg^{2+}, Ca^{2+} etc.) are occupied in the interlayer of aluminosilicate and polar organic molecules can also incorporate with silicate surface to form organo-aluminosilicate complex. The magnitude of cation density or layer charge density or layer charge (x + y) can more significantly influence on many colloid chemical properties and chemical reactivity than the type of cations (Me^{3+} and Me^{2+} within the silicate sheet), particle size and morphology.

A number of workers[1-9] have particularly been interested in the ion exchange type intercalation reaction and its reaction mechanism. Slabaugh[10] and Bradley[11] have also studied on the swelling mechanism of alkylammonium montmorillonite system. Brindley[12] has reported on the complex of the montmorillonite with long chain primary alcohol, and suggested the molecular orientation model of alkyl chain in between the layered aluminosilicate. Many others[13-17] have observed the organo-aluminosilicate intercalation complex with ethylene glycol, alkylammonium, fatty acid, polyglycol ether, acrylonitrile etc.

But, as yet, no systematic investigation was performed on the domestic aluminosilicate for the purpose mentioned above. The study on the chemical characterization of the aluminosilicate has been inevitable for the development and usage of the domestic raw materials. Therefore, in this study, the charge density of Young-il montmorillonite was determined by ion exchange reaction with RNH_3^{+} and molecular intercalation of ROH, and discussed with the systematic chemical treatment.

The conventional methods to evaluate the layer charge are chemical analysis and C. E. C. (cation exchange capacity),[18,19], but these are time-consuming and inac-

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curate because the raw minerals are usually complex in chemical composition and contain a lot of impurities.

Present paper deals with a simple method to predict the layer charge from the basal spacings of organo-silicate complexes[20]. As it based on the selective reactivity of swelling layer silicate with n-alkylammonium and n-alcanol, the charge density and charge distribution on the silicate layer surface could be easily determined even in existence of the other mineral impurities.

EXPERIMENTAL

Sample preparation

The bentonites studied were obtained from Young-il area. Sample A was pinkish and from the upper region of the main bentonite horizon, sample B brownish and from Keumkwangdong formation.

The starting materials with < 0.2μm fraction of bentonite were obtained by sedimentation and centrifuging at appropriate condition (3500 r.p.m) in accordance with Stokes' law. Sedimentation impurities and quartz were discarded simultaneously, and the fractionated aluminosilicate (raw sample) was found to be Ca- or Mg-montmorillonite. Their basal spacings were 1667, 1536 pm at room temperature and 1211, 1245 pm at 110°C, respectively.

Preparation of decylammnoium derivatives

Each fractionated sample was made to decylammonium derivatives by cation exchange reaction, that the interlayer cations were replaced by $C_{10}H_{21}NH_3^+$ in 0.1N $C_{10}H_{21}NH_3Cl$ aqueous solution. The pH of the aqueous solution was adjusted to 6.5 by titration with 1N hydrochloric acid.

In a 20 ml testtube, 1000 mg of the aluminosilicates was treated with 10 ml of the $C_{10}H_{21}NH_3Cl$ aqueous solution at 65°C for 72 hours. After decantation and washing, the same amount of the solution was twice added in the same condition for the purpose of the quantitative exchange reaction. To get rid of Cl^- and free amine on the surface or interlayer of the silicate, the sample was washed five times with ethanol and ten times with the mixture of ethanol and water (1:1). After the sample was slightly dried in vacuum, carefully ground, and dried again in vacuo (10^{-3} Torr), and then used for measurement of basal spacings by XRD.

Preparation for n-alcanol intercalates

In order to obtain the paraffine type structure of alcanol intercalation compound, excess alcanol was added to alkylammonium derivatives at 65°C for 72 hours. Decanol (99% purity), dodecanol (98% purity), tetradecanol (97% purity) as commercial products from Aldrich Chem. Co. were used without purification. After reaction, samples were slowly cooled to room temperature with the cooling rate of 0.2°C/min so as to avoid the formation of high temperature phase, namely, conformational isomers.

Apparatus

The X-ray diffraction patterns were obtained with the X-ray diffractometer JEOL JDX-5P, the diffractometer was used under the following conditions; source Cu-K_α (Ni filter), scanning speed 1200 mm/hr, counting range 4 × 10^2 cps, and time constant 4 sec.

Infrared absorption spectra (4000-400 cm^{-1}) were recorded with Perkin Elmer Model 283.

The microstructures were observed by SEM, after deposition with platinium, and the deposition depth of the sample was 600 A under high vacuum.

Thermal analysis was carried out under the N_2 purging gas (50 ml/min) with DuPont Instrumental, Model DSC 910, TGA analyser, Analyser 1090.

RESULTS AND DISCUSSION

By applying the oriented sample mounting technique, the fractionated raw samples and the amine salt treated were observed by transmission and scanning electron microscopes. The results show that montmorillonite is approximately 0.1-0.2μm in size and almost round or irregular in shape, but their curled edges are characteristic. (Fig. 1)

And the images of microstructure were not altered throughout the n-$C_{10}H_{21}NH_3^+$ ion exchange adsorption,which means the reaction proceeds topochemically.

Thermal analysis (DTA, TG, DTG) supports the X-ray results that the samples chosen are montmorillonitic. For both samples, a broad endothermic peak is observed between ~50°C and ~200°C. In this temperature region, heat is absorbed by the clay for the interlayer water. The shoulder on the peak, indicating an incompletely resolved double peak, shows that a part of the water is more strongly adsorbed than the other one. Such dual dehydration effect of Ca-montmorillonite has been commonly observed.[21] (Fig. 2-a) The dehydration energies of the montmorillonite A and B can be obtained by integrating the endothermic areas. The

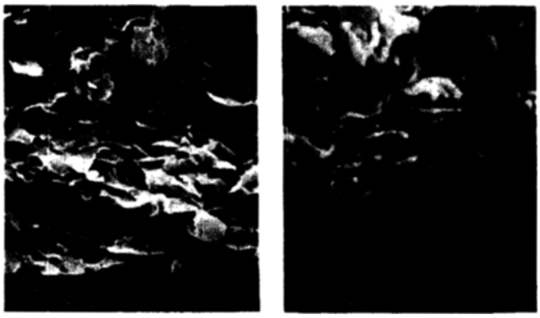

Fig. 1. Scanning electron micrographs of a) fractionated sample A < 0.2 μm, b) $C_{10}H_{21}NH_3^+$ ion intercalalated.

area enclosed by the DSC curve peak is directly proportional to the enthalpy change,

$$A = k\,\Delta H \cdot m \quad \cdots\cdots (2)$$

if k is independent of temperature.[22] The coefficient k is calculated by the quantity of 60 B.E Δqs for any given set of instrument condition, which can be also used to convert area directly into heat of reaction as follows.

$$\Delta H = \frac{A}{m}(60\ B \cdot E \cdot \Delta qs) \quad \cdots\cdots (3)$$

where,

A = peak area in cm^2

m = sample mass in mg

B = time base setting in min/cm

E = cell calibration coefficient at the room temperature of the experiment in mW/mV

Δqs = Y-axis range setting in mV/cm

ΔH = heat of reaction in J/g

The dehydration enthalpies (ΔH) for the sample A and B are 45.6 and 73.3 cal/g respectively and their values are more or less variable depending on the amount of hydrated water and layer charge. A second inflection point around 650°C in TG and DTG curves indicates the loss of structural hydroxyl groups in the form of water, dehydroxylation. (Fig. 2-b)

IR-spectra of hydrated montmorillonite and n-decylammonium derivatives in the range of 4000-400 cm^{-1} are shown Fig. 3. In the upper trace, the strong absorption at 3400 (broad) and 1600 cm^{-1} are due to the presence of hydrogen-bonded water molecules on the silicate surface[23, 24] and the narrow band around 3600 cm^{-1} distinguished from the broad bands is attributed to structural OH group which is not disappeared by n-decylammonium intercalation and succesive evacuation. Seratosa[25] has also reported that the absorption band at 3610 cm^{-1} for nontronite (Fe^{3+} in octahedral), one of the montmorillonite group was clearly isolated

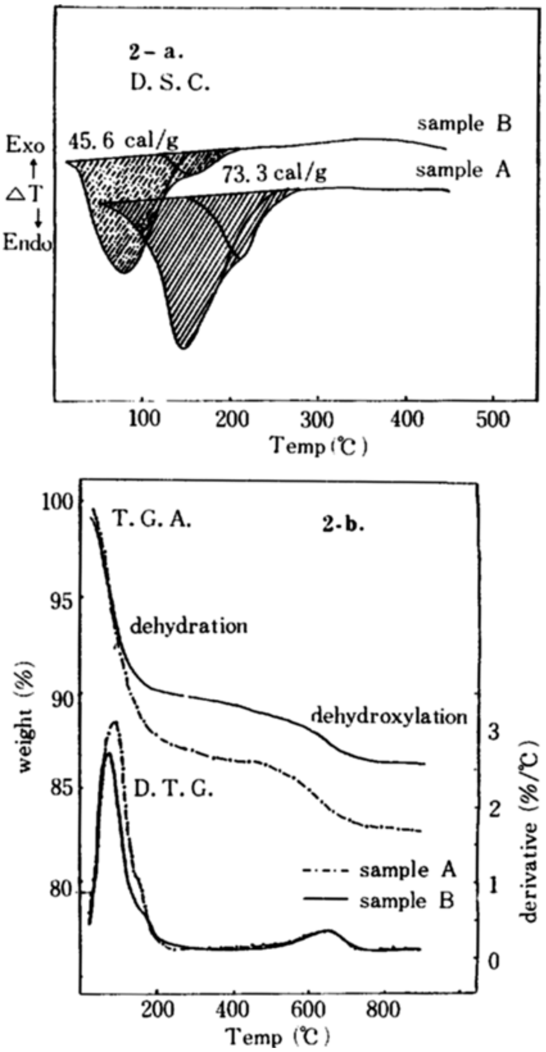

Fig. 2-a. DSC curves for aluminosilicates (sample A and B) in an atmosphere of nitrogen gas of 1 atm.

2-b. TG and DTG curves for aluminosilicates (sample A, and B) in an atmosphere of nitrogen gas of 1 atm.

The isolated band around 1645 cm^{-1}, due to OH bending frequency, gives the direct information on the presence of adsorbed water before and after the ion exchange and intercalation reaction. In IR pattern for $C_{10}H_{21}NH_3^+$ intercalated, N-H stretching and deformation bands around 3220, 1600, 1500

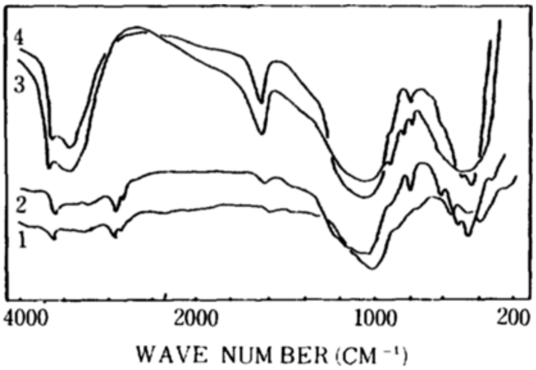

Fig. 3. IR spectra of the sample (1, 2 ; $C_{10}NH_3^+$ ion intercalated A, B, 3, 4 ; fractionated A, B).

cm^{-1} indicate clearly that decylammonium ions are located in the interlayer space of layer silicate[26,27] And X-ray measurement provides the explanation on the lattice expansion (Δ∼450pm) due to the ion exchange type intercalation of organic cation corresponding to an interlayer separation of ∼450 pm (the van der Waals thickness of methyl or methylene group).

The basal spacings (d) of the alkylammonium derivatives after swelling with long chained alcanols depend on the dimension of guest molecule. If the interlayer distance of intercalates is plotted against the alkyl chain length, the linear relationship between 2 parameters is generally found when the guest molecules arranged well in the interlayer region of host matrix. The basal spacings of alcanol intercalates increase linearly by 240±5 pm for each additional -CH$_2$-group in the alkyl chain (Fig. 4). This indicates that a bimolecular film of extended molecules in all trans conformation is tilted at 72.3±0.3° with respect to the silicate layer. (Fig. 5)

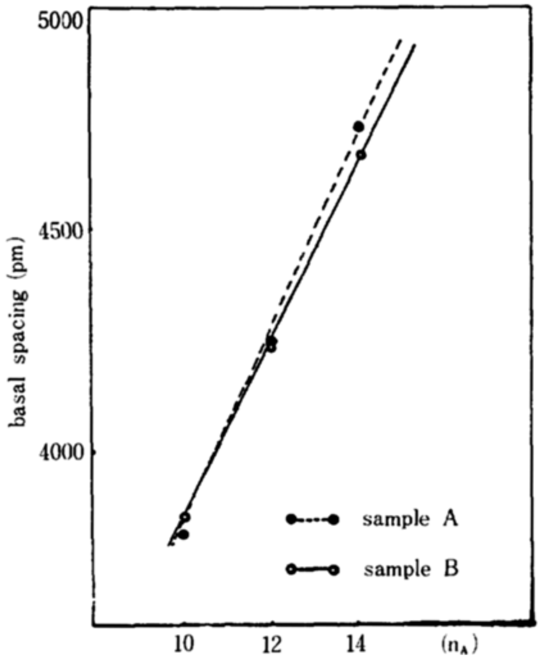

Fig. 4. Increment of basal spacings (d) in n-decylammonium derivatives under the primary n-alcanol with increasing the number of carbon atoms in alkyl chain(n_A)

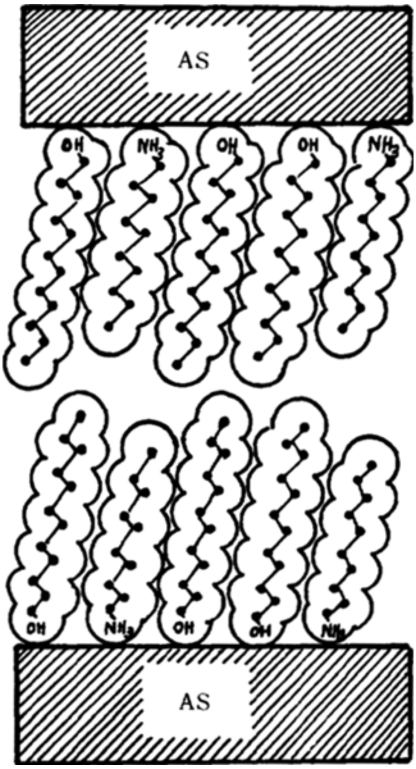

Fig. 5. Structure of the organomolecule- intercalated aluminosilicate (AS).

If the cation and alcanol have the same chain length, basal spacing is not dependent on layer charge, but only dependent on the alkyl chain length. Therefore, the number of methylene group in interlayer space per formula unit is independent on the layer charge, 2.03.[20,28,29] But if the alkyl chain length in cation and alcanol is different, on the contrary, the basal spacing is dependent on layer charge Since (x + y) cations with n_B carbon atoms per cation and (2.03 − (x + y)) alcanol molcules with n_A carbon atoms per alcanol in the alkyl chain are contained in a formula unit,

$[(x+y)n_B + \{2.03(x+y)\}n_A]CH_2$ — or CH_3 groups are bonded to a silicate formula unit. Therefore, from the linear regression as shown in Fig. 4, $d = 140\,[(x+y)n_B + \{2.03-(x+y)n_A] + 960$ pm can be derived.

With simple expression,

$$n_{CH_2} = -\xi \cdot n_C + 2.03 n_A \quad \cdots\cdots (4)$$

$$d = 140\, n_{CH_2} + 960 \text{ pm} \quad \cdots\cdots (5)$$

where, $n_C = n_A - n_B$, ξ ; charge density

Hence, the charge density can be simply obtained from only one basal spacing measurement of each sample using the above experimental equations (4) and (5).

Basal spacings of the aluminosilicates under various specified conditions are listed in Table 1. Raw samples have the basal spacings about 1530-1650 pm at room temperature, 1430 pm for the dried at 65°C. Decylammonium intercalates under high vacuum of ~ 10^{-3} Torr show the almost constant d-value of ~1430 pm. It means that the decylammonium ions in the interlayer space are oriented almost parallel to the silicate sheet. The value of ~1430 pm is nearly in accordance with sum of the van der Waals thickness of the decylammonium and the aluminosilicate sheet distance.

Table 1. The basal spacings under the various specified conditions.

	$C_{10}-\bar{C}_{10}AS$		Δd_1	$C_{10}-\bar{C}_{12}AS$		Δd_2	$C_{10}-\bar{C}_{14}AS$		Δd_3	layer charge density	C. E. C. (meq. /100g) for divalent cation
	a	b		a	b		a	b			
A	2	3805.7±50	2845.7	2	4248.5±25	3288.5	2	4738.2±25	3778.2	0.254±0.01	69.3±0.25
B	2	3853.8±25	2893.8	2	4224.9±5	3264.9	2	4688.8±5	3728.8	0.340±0.01	92.4±0.5

a ; No. of (001) b ; Mean basal spacing (in pm)

$\Delta d_1 = d_{decanol\ complex} - d_{AS}$ (in pm) $\Delta d_2 = d_{dodecanol\ complex} - d_{AS}$ (in pm)

$\Delta d_3 = d_{tetradecanol\ complex} - d_{AS}$ (in pm)

With decanol treatment to the decylammonium derivatives, the basal spacing of each sample increases stiffly to 3830±25 pm. Decylammonium derivatives have about 4235±15 pm under dodecanol and 4700±35 pm under tetradecanol. Hereby, the (001) reflections under specified conditions shifted to the lower angles due to the lattice expansion. These values indicate that the decylammonium chains are arranged in the interlayer space parallel along the silicate sheet at first and rearranged perpendicularly to the paraffine type double layer structure under alcanol. With the variation of the charge density, alkyl chains are arranged more or less inclined to the aluminosilicate layer. From the results of basal spacings, the mean charge density of the samples was obtained as listed in Table 1.

Considering the aluminosilicate as Ca^{2+}-montmorillonite, for the fixed homoionic divalent Ca^{2+}, the unit cell formula can be ideally represented as follows:

$$\underset{\vdots \atop z/2\ Ca^{2+}}{Si_8(Al_{4-z}Mg_z)O_{20}(OH)_4} \quad \cdots\cdots (6)$$

Then, the cation exchange capacity (C.E.C.) is calculated from the following eq. (7). [21].

$$\text{C. E. C.} = (\xi/\text{unit cell wt.}) \times 1000 \times 100 \text{ meq. per } 100\text{g} \quad \cdots\cdots (7)$$

where, ξ represents the charge density obtained from the experiment of the two aluminosilicates.

In consequence of the experimental data, the aluminosilicates have the cation exchange capacities of 69.3, 92.4 meq./100 g, respectively.

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