

## Thermal Deintercalation of Ethylammonium-Aluminosilicate Intercalates with Various Layer Charges

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Ethylammonium-layered aluminosilicates intercalates were prepared by ion exchange reaction between the layered silicates with different layer charge density of 0.32-0.41 e<sup>-</sup> per unit formula and ethylammonium chloride. A kinetic study on the thermal deintercalation of the ethylammonium-layered silicate intercalates was carried out by means of differential scanning calorimetry (DSC). A single step deintercalation was observed in the temperature range of 350°C to 480°C (heating rate of 10°C/min). Based on the Ozawa's method, the activation energies of the thermal deintercalation reaction were estimated as 171.2-133.0 kJ/mol, which increase linearly with the layer charge densities.

**Key words :** Aluminosilicate, Ion exchange reaction, Layer charge density, Deintercalation activation energy.

### I. Introduction

Due to the unique surface properties such as surface acidity or layer charge, pore size distribution, and high surface areas, the layered aluminosilicates are potentially useful for adsorbents and catalysts.<sup>1-4</sup> Among various layered aluminosilicates, generally used as host matrix, the 2:1 type layered silicates have charge deficiency due to its unbalanced charge distribution which is caused by isomorphous substitution of silicon in the tetrahedral sites or aluminum in the octahedral ones by other cations of lower valency.<sup>1</sup> As a result of isomorphous substitution, the layered silicates become negatively charged. A deficiency of positive charge may be compensated to some extent by internal substitution but the most part of electrical neutrality is maintained by inclusion of extraneous cations between silicate layers. The extent of isomorphous replacement influences the surface and colloidal properties of layer silicates. Thus the charge per formula unit, which is called layer charge density, is an important parameter which serves as a criterion for the classification of such minerals.

Since the interlayer cations such as Na<sup>+</sup> and Ca<sup>2+</sup> are weakly bound to silicate layer, they can be exchanged easily with other inorganic or organic cations, particularly surface active agents like *n*-alkylammonium cation in an aqueous solution. The alkylammonium ions intercalate into the interlayer space of the layered silicates and aggregate as monomolecular or bimolecular structures. The arrangement of the alkylammonium ions depends upon the layer charge and chain length. Therefore, the layer charge can be evaluated from the linear relationship between the basal spacing and the carbon number.<sup>5-10</sup> In the *n*-alkylammonium-layered silicates

complexes, since the excess negative charge is delocalized all over the oxygens of the silicate lattices, *n*-alkylammonium cations are held to the interlayer surface mainly *via* electrostatic interaction and partly *via* hydrogen bonding and/or van der Waals interaction. It is, therefore, expected that the bonding force of intercalated organic ions in the interlayer space is greater for the layers with greater charge density.

Several investigators including the present authors have studied the thermal behavior of clay-organic complexes to elucidate the dependency of deintercalation activation energy on the layer charge density and the decomposition mechanism.<sup>11-17</sup> In our previous works,<sup>17</sup> kinetic studies on deintercalation of the methylammonium intercalated layered silicates were performed and a good linearity between the layer charge density and the deintercalation activation energy was found. In the present study, the ethylammonium-aluminosilicate complexes were prepared by ion-exchange reaction between layered silicates with different charge density and ethylammonium ion. For the kinetic study of thermal deintercalation of organic molecules, differential scanning calorimetry (DSC) analyses were carried out and the activation energies were estimated.

### II. Experimental

#### 1. Materials

In this work, five kinds of natural aluminosilicates (denoted as sample A, B, C, D and E) were used as starting samples. Samples A and B (both are montmorillonites) were obtained from American Colloid Co., Ltd., U.S., C (montmorillonite) was from Pohang area in Korea, D (montmorillonite) from Junsei Chemical Co., Ltd., Japan

**Table 1.** Elemental Analysis of Aluminosilicates (wt%)

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Ig-loss	K <sub>2</sub> O	Na <sub>2</sub> O
A	56.78	20.65	3.46	1.37	2.47	tr	14.55	0.72	tr
B	60.34	19.28	3.48	0.38	1.67	tr	14.75	0.10	tr
C	56.83	18.88	4.44	0.36	3.95	tr	15.11	0.44	tr
D	52.49	16.28	tr	0.43	4.23	0.10	18.35	0.14	tr
E	50.16	3.54	0.06	1.46	23.69	0.24	17.18	0.24	tr

\*tr; trace

**Table 2.** Layer Charge Density of Selected Layered Aluminosilicates and Activation Energy of Deintercalation of Ethylammonium Derivatives

Sample	Layer charge density (eq./ $(\text{Si}, \text{Al})_4\text{O}_{10}$ )	Activation energy (kJ/mol)
A	0.32	133.0
B	0.34	145.1
C	0.34	146.4
D	0.38	159.8
E	0.41	171.2

and E (hectorite) from California, U.S. At first, the silicate samples were fractionated by sedimentation based on the Stokes' law (the particle size with  $<2 \mu\text{m}$ ). To remove the residual carbonate, the samples were treated with sodium acetate-acetic acid buffer solution (pH=5) in a boiling water bath, then organic matters were removed with 6% H<sub>2</sub>O<sub>2</sub> in the same bath as described in the literature.<sup>100</sup> Na activated layered silicates were prepared by treating the colloidal fractions with 1N sodium chloride solution. Then they were washed several times with distilled water until the chloride test with silver nitrate was negative.

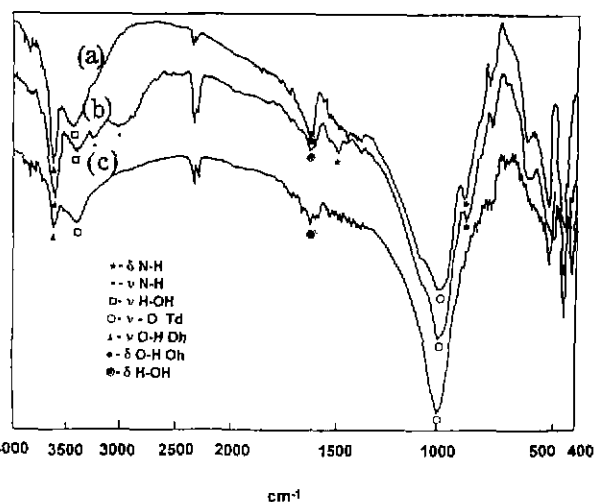
Elemental analyses for A, B, C, D and E were carried out by X-ray fluorescent spectroscopy (XRF) with PW1600 (Phillips).

### 2. Determination of layer charge density

The layer charge densities of starting samples were determined by *n*-alkylammonium method.<sup>61</sup> To ensure the complete ion exchange reaction, Na activated samples were reacted with excess *n*-alkylammonium ions, which is about 10 times larger than the cation exchange capacities of the Na activated samples, at 65°C for five days. After the supernatant being decanted, the samples were washed repeatedly for three times with 50% ethanol solution and then with distilled water until the chloride test was negative. Finally, the samples were dried at 65°C for 24 hours and kept under vacuum. To evaluate the variation of basal spacing of *n*-alkylammonium intercalates, the samples finely ground were investigated with powder X-ray diffractometer (XRD) with Cu-K $\alpha$  radiation ( $\lambda=1.5405\text{\AA}$ , JEOL JDX-5P).

### 3. Preparation of ethylammonium-aluminosilicate intercalates

Ethylammonium-aluminosilicate complexes were also prepared by ion-exchange reaction between alu-



**Fig. 1.** FT-IR spectra for raw material (sample C) (a), the ethylammonium derivative before (b) and after (c) thermal analysis.

minosilicates and ethylammonium salts in an aqueous solution using the same procedure as described in the section 2.2. In order to ensure the complete ion-exchange reaction of ethylammonium ion, the exchange reaction was performed for a month with renewing the reactant every 6 days.

### 4. Sample characterization

To characterize the layered silicates and ethylammonium derivatives before and after the thermal analysis, the samples were dispersed in KBr and pressed into thin disks and examined with infrared (FT-IR) spectroscopy (Bruker IFS 88). Simultaneous thermogravimetry-differential thermal analyses (TG-DTA) were carried out to investigate the thermal behavior of starting raw materials with Rigaku TAS-100. For kinetic study with differential scanning calorimetry (DSC), the heating rate was only varied while the other experimental conditions were kept as constant as possible, that is, a same amount of sample, constant N<sub>2</sub> flow rate (80 ml/min), and so on. In this study, the maximal deintercalation peak temperature was monitored with varying the heating rate in 5°C/min intervals in the range of 5 to 20°C/min.

## III. Results and Discussion

From the variation of basal spacing of *n*-alkylam-

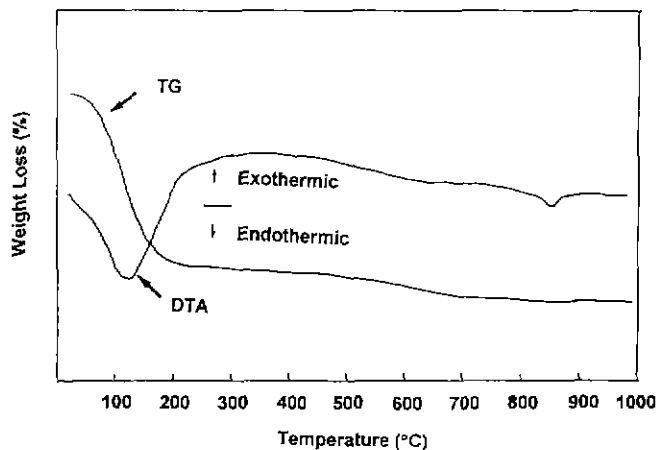


Fig. 2. Simultaneous thermogravimetry-differential thermal analysis for raw material (sample C).

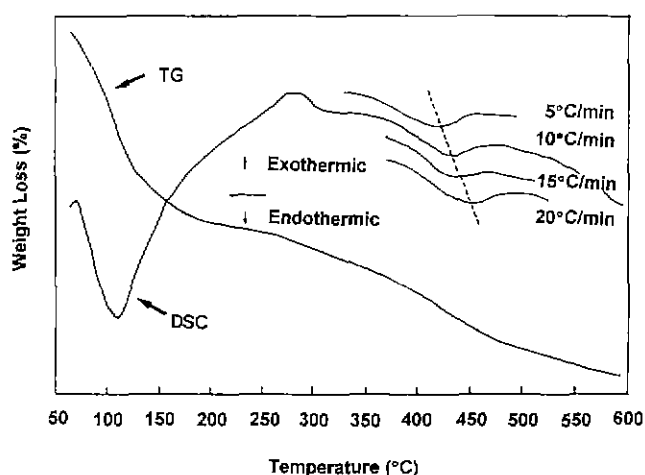


Fig. 3. TG-DSC curves for the ethylammonium derivative of sample C with respect to the heating rate.

monium intercalates, the average charge densities of the samples A, B, C, D and E were estimated as 0.32~0.41 e<sup>-</sup> per unit formula (Table 2). Infrared (FT-IR) absorption spectra were taken for natural silicates and their ethylammonium derivatives in the absorption range of 400~4000 cm<sup>-1</sup>. The absorption patterns of all the samples are nearly identical, and the patterns of sample C and its ethylammonium intercalate before and after thermal analysis are shown in Fig. 1. Before the thermal analysis, the absorption spectra due to the N-H stretching at 3290 and 3050 cm<sup>-1</sup> ( $\nu_{\text{avg}}=3170$  cm<sup>-1</sup>) and the N-H symmetric deformation at near 1515 cm<sup>-1</sup> can be seen, indicating the presence of ammonium group in the interlayer space. After the thermal analysis, however, the characteristic absorption peaks originated from ammonium group are disappeared, implying the deintercalation of ammonium group from the layered silicate.

TG-DTA curves of the sample C and TG-DSC curves of its ethylammonium intercalates are shown in Figs. 2 and 3, respectively. Endothermic peaks in DTA and DSC curves with drastic weight loss at around 100°C is likely attributed mainly to the dehydration. In TG-DSC curves

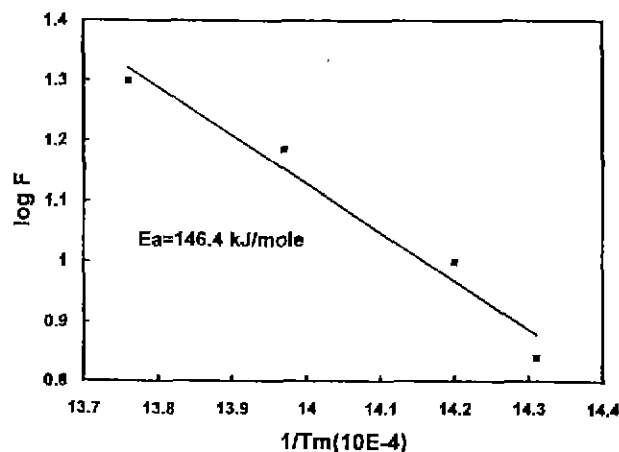


Fig. 4. Plots of Ozawa's equation and activation energy (sample C).

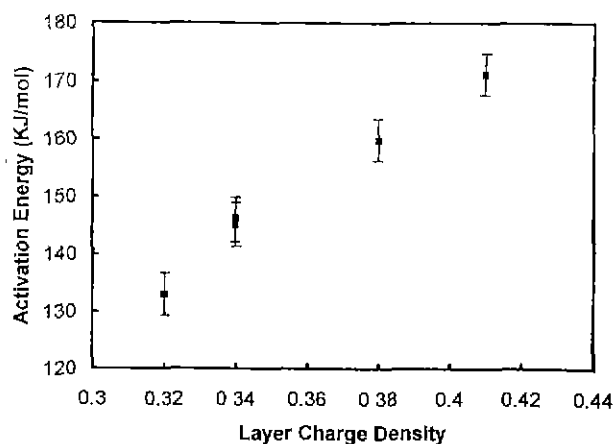


Fig. 5. Activation energy vs. layer charge density of alkylammonium derivatives.

of the ethylammonium derivative (Fig. 3), the additional endothermic peak with gradual weight loss in the range of 350~480°C is assigned to the deintercalation of ethylammonium ions from the layered silicate.

According to the Ozawa's method<sup>8,19)</sup> the activation energy of thermal deintercalation can be estimated from the temperature shift of maximal point of deintercalation on DSC curve with the various heating rate. The estimation is based on the general equation;

$$-dx/dt = Zf(x) \exp(-E/RT) \quad (1)$$

where  $x$  the fraction of the sample unreacted ( $0 \leq x \leq 1$ ),  $t$  the reaction time,  $Z$  the pre-exponential factor,  $E$  the activation energy,  $R$  the gas constant and  $f(x)$  the general function of  $x$ . Assuming a constant heating rate, the integration of eq. (1) gives;

$$\int dx/f(x) = (Z/F) \int \exp(-E/RT) dT \quad (2)$$

Using the approximation of  $\int \exp(-E/RT) dT = (E/R) \times p(E/RT)$  and by introduction the Doyle's approximation<sup>19)</sup> for  $E/RT > 20$ , the series expansion of  $p(E/RT)$  can be writ-

ten as follows,

$$\log p(E/RT) = -2.315 - 0.4567(E/RT) \quad (3)$$

The left hand side of eq. (2) is independent of the heating rate. Thus, the following linear relation for a given value of  $x$  is derived from eq. (3);

$$\log F + 0.4567(E/RT) = \text{constant} \quad (4)$$

where  $F$  is the heating rate. A linear plot of  $\log F$  versus  $1/T_m$  gives the slope of  $-0.4567E/R$ , from which the activation energy ( $E$ ) can be calculated.

To determine the activation energy the temperatures at maximal point of deintercalation peak,  $T_m$ , were determined for each sample by varying the heating rates at 5, 10, 15, 20°C/min under an inert atmosphere. Fig. 3 shows the variation of  $T_m$  with the heating rate for the ethylammonium complex of sample C. As can be seen in Fig. 3, the shape of absorption peaks due to the ethylammonium deintercalation becomes sharper and peak position ( $T_m$ ) shifts toward higher temperature as the heating rate increases.

The Ozawa's plot for the sample C is shown in Fig. 4 and the activation energy calculated from the regression analysis is 146.4 kJ/mol. The calculated activation energies for the other systems are summarized in Table 2 with the layer charge densities. The activation energies of ethylammonium deintercalation are plotted as a function of layer charge density in Fig. 5. As can be seen, the activation energy of deintercalation process increases monotonically as the layer charge density increases, indicating that the deintercalation activation energy is closely related to the layer charge density. That is, the tighter the organic species bond to host lattice, the more the energy is required to surmount an energy barrier. Despite of identical charge density, however, some samples (B and C), have slightly different activation energy. Such a small deviation from the linearity might be due to the inhomogeneity in charge distribution in the interlayer space and the extent of structural site substitution. Recently the result on GC-MS, which is not included here, indicates that the major decomposition product is not the simple ethylamine but the N-methylhydroxyl amine ( $\text{HONHCH}_3$ ,  $m/z=47$ ) and hydroxylamine ( $\text{HONH}_2$ ,  $m/z=33$ ). The GC-MS experiment is underway and details of the results will be published elsewhere.

#### IV. Conclusions

The layer charge densities of mica-type aluminosilicates were determined by the  $n$ -alkylammonium method and the upper and lower limits of layer charge were estimated as 0.41 and 0.32 eq./ $(\text{Si}, \text{Al})_4\text{O}_{10}$ , respectively. Ethylammonium derivatives of the aluminosilicates were prepared by ion exchange reaction between the layered aluminosilicates and ethylammonium chloride. From the kinetic study using DSC,

the deintercalation activation energies were estimated as 133.0 to 171.2 kJ/mol based on the Ozawa's method and the deintercalation activation energy was closely related to the layer charge density.

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