

Isomorphous Substitution Effects on the Thermally Induced Interlayer Reaction in *N*-Hexylammonium Layered Aluminosilicates

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Abstract. It was found that the variation in the thermally evolved gases obtained by decomposition of *n*-hexylammonium layered aluminosilicates is mainly due to the difference between octahedral and tetrahedral coordination of aluminium in the lattice and also to the contribution of the excess negative layer charges.

ESCA, TG-DSC, GC and MS results indicate that the layer charge originated from the octahedral substitution induces only desintercalation of *n*-hexylamine around 250–360 °C, whereas that from the tetrahedral substitution induces the catalytic decomposition reaction involving the cleavage of C—N and C—C bonds at 350–450 °C with the evolution of ammonia, ethylene, pentene and hexene.

It is therefore concluded that the former reaction step is a simple desintercalation, but for the latter one a Brönsted acid catalytic mechanism is proposed.

Key words. *N*-hexylammonium, montmorillonite, catalytic decomposition reaction, intercalate, layer charge.

1. Introduction

The layer charge in the 2 : 1 type lattice expanding layered aluminosilicates is known to result from isomorphous substitutions of tetrahedral Si⁴⁺ or octahedral Al³⁺, Fe³⁺ and Mg²⁺ by cations of lower charge [1].

The isomorphous substitution site distribution has been studied recently by employing MAS-NMR [2], X-ray photoelectron diffraction [3], IR [4], etc. These studies suggest that the character of the silicate surface should be differentiated according to the site where the isomorphous substitution occurred.

It has been also reported that the layer silicate intercalates can undergo an organic solid-state reaction within the interlayer region, such a reaction can be considered as highly regiospecific due to the distinct surface properties such as surface acidity or layer charge [5–7]. Moreover, size- and shape-selective layer silicates have been prepared [8, 9] and the catalytic properties investigated in recent years [10].

However, up to now, the possibility has not been well studied whether the difference in the surface character attributed to each type of isomorphous substitution can affect the chemical reaction. In this report, we have, therefore, attempted to con-

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firm this possibility for the first time and to determine the pathway of a specific decomposition reaction of *n*-hexylammonium derivatives of silicates with different layer charges.

2. Experimental

The natural montmorillonite (Junsei Chem. Co., Japan) and the synthetic saponite (Hoechst Lab., BRD) were used as starting materials. The sodium exchanged form of montmorillonite was prepared by treating with 1.0 N NaCl, centrifuging and discarding the supernatant liquid. The particle size was controlled below 0.2 μm according to the sedimentation rule. The approximate chemical composition of montmorillonite is $\text{Na}_{0.70}[\text{Al}_{3.92}\text{Mg}_{0.08}][\text{Si}_{7.38}\text{Al}_{0.62}]\text{O}_{20}(\text{OH})_4$ and that of saponite is $\text{Na}_{0.8}[\text{Mg}_{6.0}][\text{Si}_{7.2}\text{Al}_{0.8}]\text{O}_{20}(\text{OH})_4$. The latter shows only tetrahedral substitution in the lattice.

These two silicates were converted into their *n*-hexylammonium forms with an aqueous solution of 2.0N *n*-hexylammonium chloride at 65 °C.

The interlayer cation exchange capacity or the layer charge was estimated by the *n*-alkylammonium method [11].

X-ray diffractograms were obtained on a Jeol instrument using $\text{CuK}\alpha$ radiation with a Ni-filter; samples were examined as oriented aggregates in order to enhance the basal reflections.

ESCA spectra were recorded on a Perkin-Elmer PHI-558 with unmonochromatized $\text{MgK}\alpha$ radiation (1253.6 eV). The separation of an asymmetric peak into two symmetric ones was performed by using a reiterative curve fitting computer program provided by Perkin-Elmer.

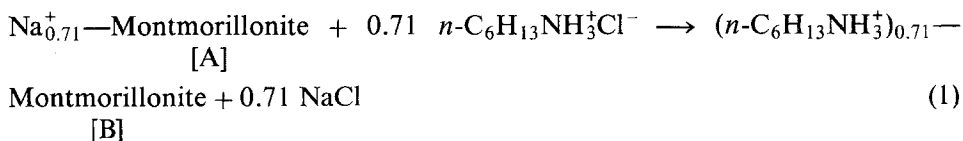
The thermally induced interlayer reaction of *n*-hexylammonium silicate complexes were studied by TG and DSC with a Dupont 1090 Thermal Analyzer. The dehydroxylation of lattice —OH groups, desintercalation and catalytic decomposition of *n*-hexylammonium in interlayer silicates were measured in a flowing atmosphere of N_2 with a flow rate of 1.0 cm^3/s . The heating rate was 10°/min. for both TG and DSC.

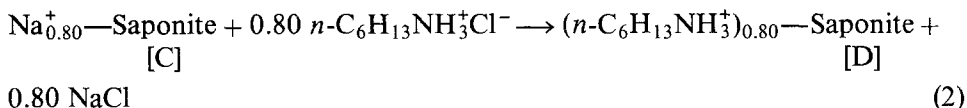
The evolved gas products at various temperatures were identified by GC using a Yanaco 180 G instrument and partly by MS using a Hewlett-Packard 5985B GC-MS system.

3. Results and Discussion

The layer charges of the montmorillonite and the saponite were determined by the *n*-alkylammonium method [11] as 0.80 and 0.71 per unit cell composition, respectively.

The ion exchange reactions for *n*-hexylammonium silicate complexes can be formulated as follows:





From the X-ray diffraction data, the basal spacings of [B] and [D] were estimated to be $\sim 13.6 \text{ \AA}$ in both cases, which can be interpreted as the sum of the van der Waals interval occupied by alkyl chains, 4.0 \AA , and of that of the silicate layer, 9.6 \AA , respectively. It shows that the intercalated cations are oriented with the flat-lying monolayer structure in the interlamellar space of the silicate. The interlayer surface area of a unit cell can be calculated as $a \times b = 5.14 \text{ \AA} \times 9.00 \text{ \AA} = 46.3 \text{ \AA}^2$ for montmorillonite and $5.28 \text{ \AA} \times 9.18 \text{ \AA} = 48.5 \text{ \AA}^2$ for saponite respectively. Since the effective surface area of one n -hexylammonium ion is 45.16 \AA^2 [11], the silicate surface is covered by n -hexylammonium cations up to about 69% in the montmorillonite and to 75% in the saponite.

From the ESCA spectra, the binding energies of Al-2*p* and -2*s* orbital electrons of both silicates have been obtained. The asymmetric line shape of the Al-2*p* signal, as shown in Fig. 1, was observed because of the octahedral and tetrahedral coordinations of aluminium in the lattice and it was separated into two peaks with the help of a curve fitting program. One of the separated peaks at 73.2 eV is attributable to Al-2*p* of a tetrahedrally coordinated aluminium atom, because it corresponds exactly to the Al-2*p* line of synthetic saponite, where all the aluminium atoms occupy the tetrahedral sites. The major peak at 74.3 eV is consequently assigned to the Al-2*p* of octahedrally coordinated atoms. The peak shift of about $1.0 \pm 0.1 \text{ eV}$

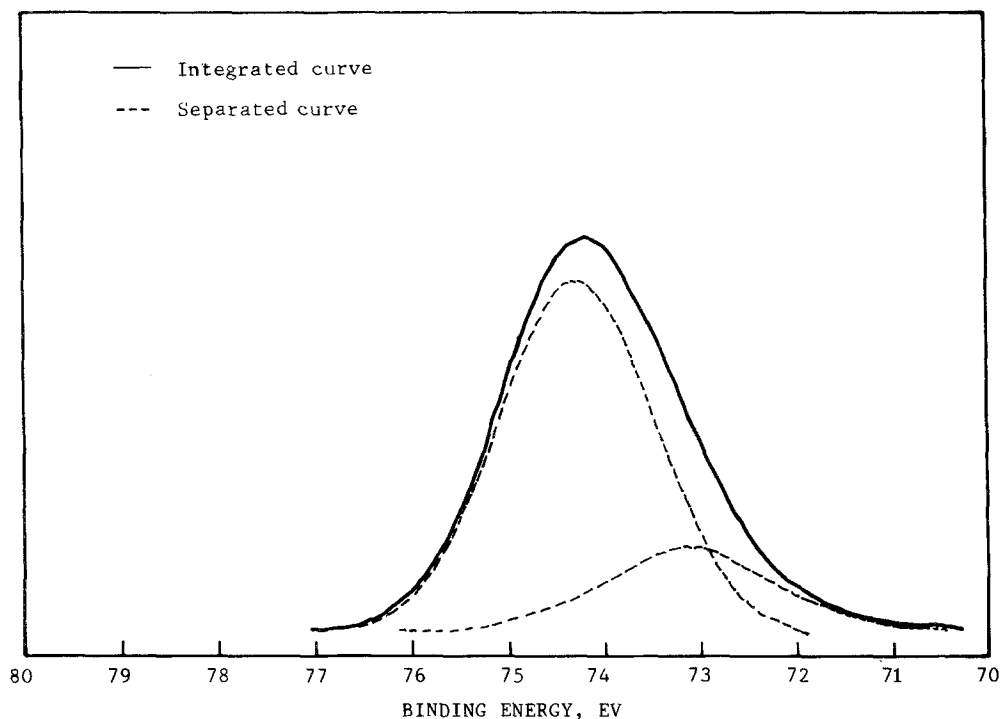


Fig. 1. ESCA spectrum of Al 2*p*-orbital electrons of the montmorillonite.

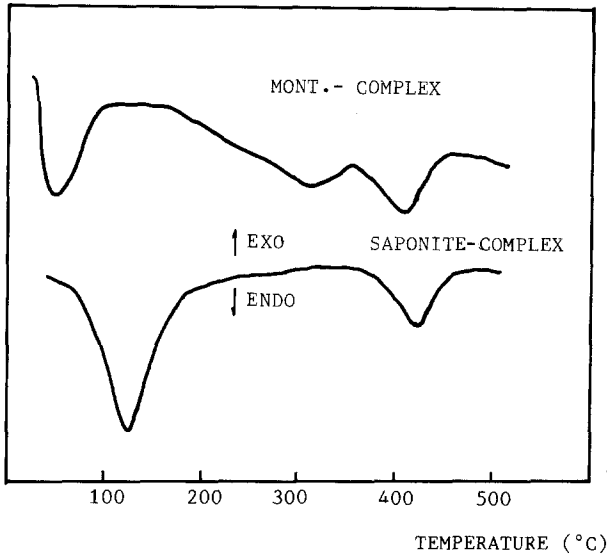
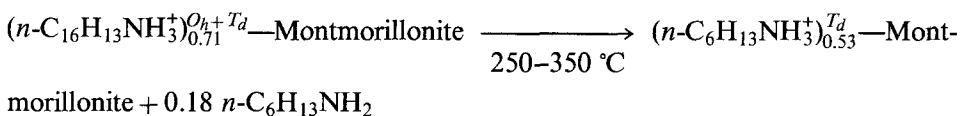


Fig. 2. DSC curves for *n*-hexylammonium complexes of (a) montmorillonite, and (b) saponite under a N_2 -flowing atmosphere with the temperature elevating rate of $10^\circ C/min$.

is associated with the difference of the coordination number of aluminium [12] and also with formation of the excess negative layer charge by isomorphous substitution.

Figure 2 shows the DSC curves of the silicate complexes. The thermogram of the saponite complex indicates only a single endothermic peak at $350\text{--}450^\circ C$, whereas an additional peak appears at $250\text{--}350^\circ C$ in the montmorillonite complex. Correlating the endothermic peaks with the substitution site, it is strongly believed that the peak around $250\text{--}350^\circ C$ is due to the octahedral substitution and that of $350\text{--}450^\circ C$ results from the tetrahedral one. This consideration is reasonable since the ionic bonding character between *n*-hexylammonium ion and the surface oxygen can be considered to be stronger in the tetrahedral substitution than in the octahedral one.

The evolved gas of the first step around $300^\circ C$ of the montmorillonite complex was identified as *n*-hexylamine by GC-analysis (Fig. 3), which indicates the simple desintercalation of amines. According to the TG-analysis of the first step, approximately 25% of the total weight decrease was measured, and this indicates that the layer charge originating from the octahedral substitution might be 0.18 per unit cell composition. On the basis of this result, along with that of the layer charge estimation by the *n*-alkylammonium method, the chemical equation of the first step can be formulated as follows;



The protons left on the silicate surface after desintercalation of the first step seem to be combined with the ---OH group of the octahedral sheet to form H_2O , because

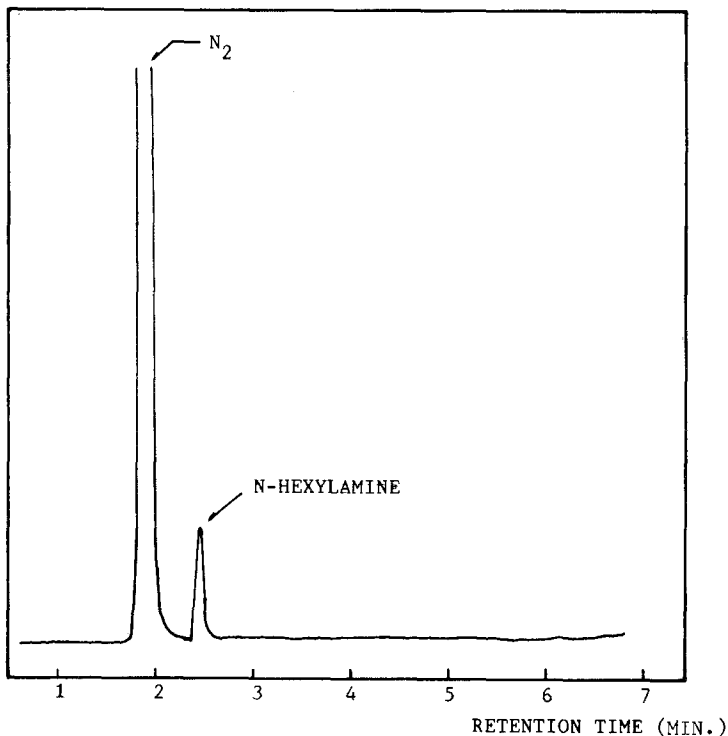


Fig. 3. G.C. results for the evolved gas from the *n*-hexylammonium montmorillonite complex at 300 °C.

the interlayer oxygen atoms affected by the octahedral substitution were apparently not negative enough to trap protons [4].

The results of TG analysis of montmorillonite and its hexylammonium derivative support this concept; the weight loss in the latter case in the temperature range 550–710 °C, (where the former undergoes dehydroxylation), reaches only 52% of that of the former, however, the expelled H₂O was not detected in GC analysis. As a consequence, the Brønsted acid sites which might catalyze the interlayer reaction of *n*-hexylamine diffusing out from the silicate lattice cannot be formed on the surface.

On the other hand, GC results on the decomposition of the saponite complex at 350, 380 and 420 °C indicate that catalytic alkylchain cleavage is involved in this step, in which the tetrahedral substitution participates (Fig. 4). It is noteworthy that deintercalation of amine occurs as the first step, even though the amount of evolved *n*-hexylamine is almost negligible. In this case, the protons left on the surface are attached to the oxygen atoms bridging Si and Al atoms in the tetrahedral sheet, on which the negative charges are strongly localized, to form silanol groups, namely, Brønsted acid sites on the silicate surface. These proton sites are considered to catalyze the evolved substrate diffusing out from the interlayer space.

It is also interesting to note that the ratios of evolved gas components varies as the temperature increases. The relative content of *n*-hexylamine and hexene has increased while the other components such as pentene, ammonia and ethylene have decreased. These results can be understood as following a mechanism including a carbocation intermediate (Fig. 5).

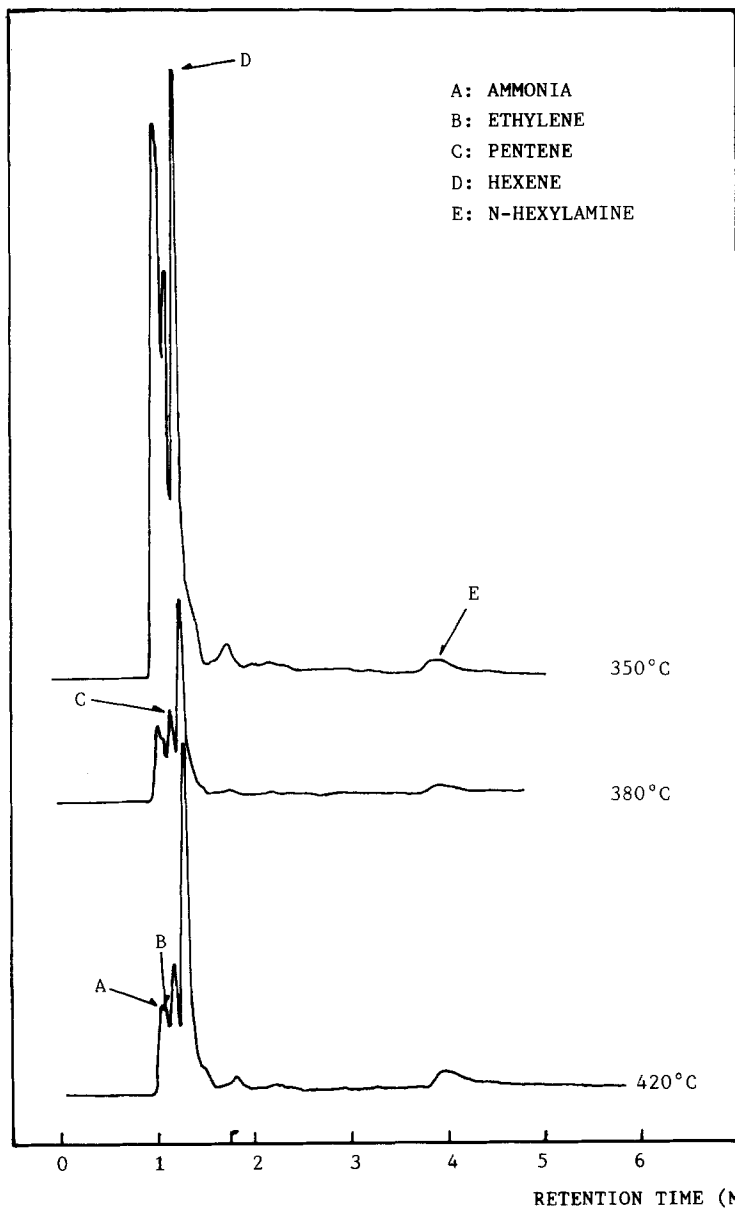


Fig. 4. GC results for the evolved gas from the *n*-hexylammonium saponite complex at 350 °C, 380 °C and 420 °C. (The identifications were also confirmed by mass spectroscopy.)

4. Conclusions

- (1) Deintercalation of amine occurs as the first step. The *n*-hexylamine molecules then diffuse out through the pathway blocked by the *n*-hexylammonium ion pillars.
- (2) As the reaction proceeds, the diffusion path length becomes shorter, since the surface concentration of *n*-hexylammonium ion pillars is decreased.
- (3) The *n*-hexylammonium cation is cleaved into 1-hexene and ammonium ions, which converts into ammonia leaving a proton on the surface.

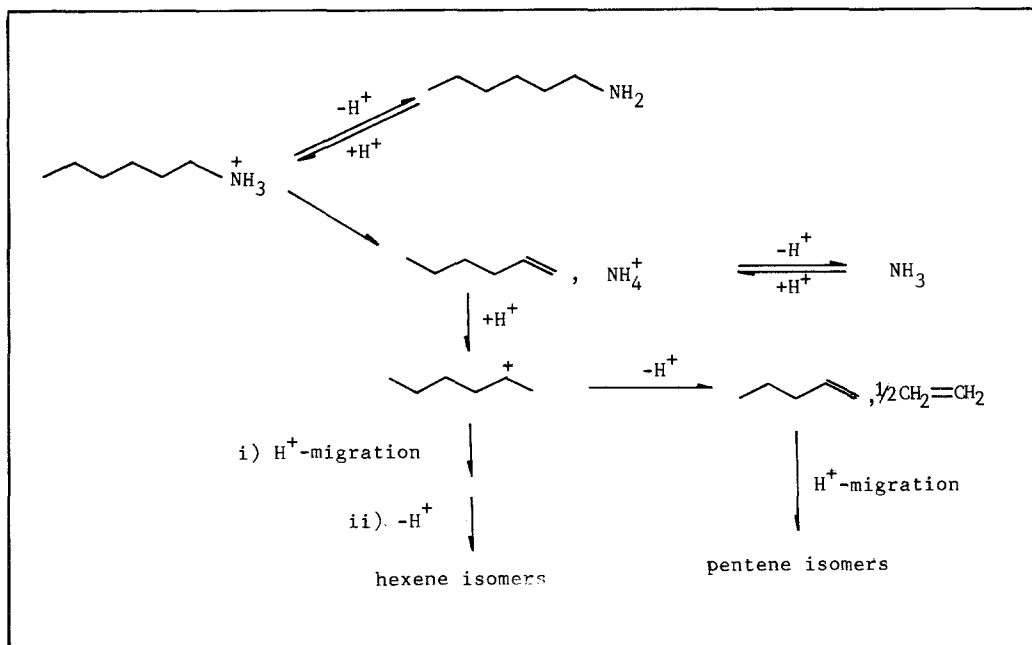


Fig. 5. Proposed mechanism of the catalytic interlayer reaction in the *n*-hexylammonium silicate complex.

(4) 1-hexene molecules can be protonated on the Brönsted acid sites to form carbocation intermediates on the silicate surface. The isomers of hexene can be produced by proton migration.

(5) The two carbocations produce two 1-pentene and one ethylene molecules leaving two protons on the surface.

(6) The equilibria of steps 1 and 4 become in favor of reactant sites as the temperature increases, because the probabilities of *n*-hexylamine and 1-hexene contacting the Brönsted acid sites decrease, as the surface concentration of the pillars that control the diffusion pathlength is diminished.

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