COMMUNICATIONS TO THE EDITOR

Thermal Analysis of n-Alkylammonium-layer Silicate Compounds: I. Surface Charge Heterogeneity

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The 2:1 type lattice-expanding silicates possess the structure in which the crystallites are made up of altering layers of negatively charged sheet and the interlayer cation. This layer charge is known to result from the replacement of tetrahedral Si^{4+} or octahedral Al^{3+}, Fe^{3+}, and Mg^{2+} by cations of lower charge. The interlayer space with the large internal surface area (ca. 800 m^2/g) occupied by the electrostatically bonded cations, which are readily exchangeable, can be increased by the uptake of water, alcohols, and the other polar molecules.[1-2]

A study on the ionic and covalent bonding contributions of interlayer cation was performed by Seyama and Soma[3], who employed the X-ray photoelectron spectroscopy to compare the binding energies of core electrons of the interlayer cation in various homoionic forms of 2:1 type layer silicate with the corresponding salts. But the studies on the charge heterogeneity and the isomorphous substitution site in silicate lattice were not performed systematically.[4-6] According to the report by Fripiat,[6] the partial replacements of Si^{+4} by M^{+3} (normally Al^{+3}) in the tetrahedral site could induce strongly localized electric field at the surface, especially at the three oxygen atoms directly connected to the replacement centre, which was enough to convert the symmetry of the adsorbed ammonium ion from tetrahedral T_d into C_{3v}. On the other hand, the ammonium ion adsorbed on the active site due to the octahedral substitution retained the Td symmetry, since in this case the induced field was considerably delocalized.

In this report, we have therefore attempted to confirm this fact that the heterogeneous electric field on the surface should be accessible to differenciate the pathway of the appropriately designed reaction occurring in interlayer space. This concept is demonstrated for the first time by the DSC results communicated herein for the thermal decomposition of n-hexylammonium derivatives of two kinds of silicate, one of which possesses only tetrahedral replacement and the other of which contains both sites, octahedral and tetrahedral replacement.

Natural montmorillonite from Japan (I) regarded as having both replacement sites has been selected,of which layer charge was determined to be 0.68 per approximate unit cell composition by n-alkylammonium method.[7] Synthetic sodium saponite offered by Hoechst lab. (Germany) (II) has been used in this work and the approximate unit cell formula was $Na_{0.80}Mg_6(Si_{7.20}Al_{0.80})\ O_{20}(OH)_4$, which shows there exist only tetrahedral replacements. These silicates were converted to their n-hexylammonium form by treating them with the aqueous solution of 2N n-hexylammonium chloride at 65°C. Excess salts and free amines were washed out with the mixture of distilled water and ethanol until no free chloride ion was detected by $AgNO_3$ solution. The ion-exchanged silicates were then centrifuged and dried at vacuum ($<10^{-3}$ torr).

From the X-ray diffraction data, the basal spacings were determined to be 13.6 Å in both n-hexylammonium silicates, which could be interpreted as the sum of van der waals thickness of alkylchain, 4.0 Å, and that of silicate, 9.6 Å. This indicates the intercalated cations are oriented with the flat-lying structure in the interlamella space of silicate.[7]

The thermal decomposition reaction was monitored by TG and DSC under nitrogen atmosphere. Figure 1. shows the DSC curves of these silicate derivatives, confirming the difference in reaction pathway between two samples. The thermogram of the II-complex shows only a single endothermic peak at 330-460°C except the dehydration peak of interlayer water around 100°C, whereas there exists an additional peak at 220-360°C in the I-complex. Correlating the peaks with the replacement sites, it is believed that the peak of 220-360°C is due to the octahedral substitution and that of 350-460°C results from the teterahedral one.

As a consequence, it could be proposed that the composition of the evolved gas might be varied between the first and second step. The validity of this assumption was demonstrated by the analyses of the evolved gas using gas chromatography. As shown in Figure 2-a, in the first step only n-hexylamine molecules were evolved which was identified by comparing

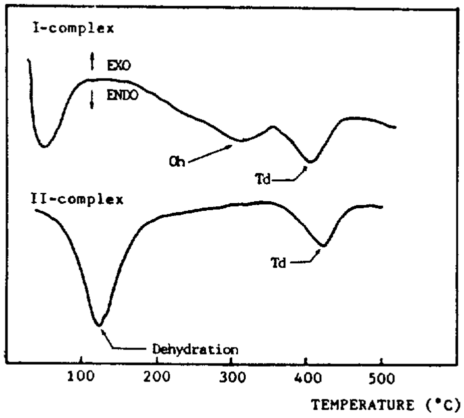


Figure 1. DSC curves of n-hexylammonium-layer silicate complexes with heating rate of 10°C/min under nitrogen atmosphere.

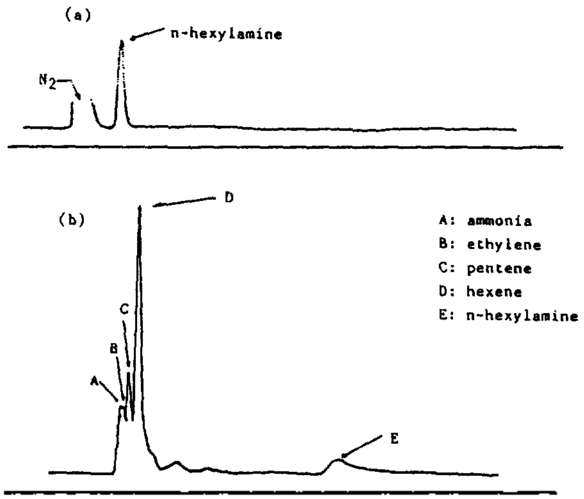


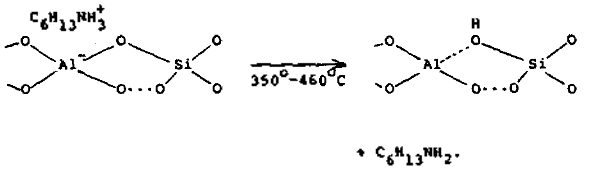
Figure 2. Gas chromatography results of the evolved gas from n-hexylammonium-layer silicate(I): (a) at 300°C using carbowax 20M stainless column (5mm×3m) with TCD; (b) at 400°C using OV-1 (10% doped) stainless column (5mm×3.6m) with FID.

the retention time with standard n-hexylamine. This indicated it was simple deamination, and according to the TG data of this process, approximately 25% of weight decrease of the thermal decomposition except the dehydration step was made. On the basis of this result, the chemical equation of the first step can be simply formulated as follows:

$$(n\text{-}C_6H_{13}NH_3^+)_{0.68}-\text{silicate}\xrightarrow[220-360^\circ C]{}(n\text{-}C_6H_{13}NH_3^+)_{0.51}$$
$$-\text{silicate}+0.17\,n\text{-}C_6H_{13}NH_2$$

The protons left in the silicate lattice after deamination were considered to combine with the $-OH$ of the octahedral unit to form water because the interlayer oxygens affected by the octahedral replacement were apparently not negative enough to trap protons.[6]

For the second step in which the tetrahedral replacement is participated, the gas chromatography result at 400°C supported that the catalytic alkylchain cleavage was involved in this step, though the fact that the small amount of n-hexlyamine was evolved suggested the deamination reaction was also simultaneously preceded(Figure 2-b). In this case, the protons are attached to the oxygen atoms bridging Si and Al atoms in tetrahedral sheet where the negative charges are strongly localized to form silanol groups, that is, Brϕnsted acid sites on the silicate surface.[6,8]



These active sites and the Lewis acid sites, that is, the tetrahedral replacement centres are considered to catalize the evolved n-hexylamine diffusing out from the interlayer space. The catalytic alkylchain cracking is related with the reaction temperature, which is necessary to obtain the thermal energy for the activation of silicate surface. Because the tetrahedral replacement exhibits stronger ionic bonding character than in the case of the octahedral replacement, the adsorption site originated from the tetrahedral replacement can hold the intercalated n-hexylammonium ion on the silicate surface even at the high temperature, which is hardly expected for the site due to octahedral replacement.

In summary, the decomposition reaction pathway of n-hexylammonium derivatives can be differenciated by the replacement site determining the nature of the electric field generated on the interlayer surface of layer silicate. The octaheral substitution site induces only deamination at 220-360°C. But the alkylchain cracking catalysis is observed at higher temperature around 350-460°C, which might be strongly affected by the site resulting from tetrahedral replacement.

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Syntheses of Polymer-Bound Hemin, Biliverdin and Bilirubin

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The exact nature of binding between bilirubin and albumin is not known clearly[1], although several types have been suggested: covalent bonding[2,3], hydrophobic and electrostatic bonding[4], and salt linkage and hydrogen bonding.[5,6] In order to study the binding type the polymer bound hemin, biliverdin and bilirubin were synthesized. Only a few papers have ap-