CHEMISTRY LETTERS, pp. 71-74, 1990.

Formation of Organoammonium-Montmorillonites by Solid-Solid Reactions

Makoto OGAWA, Tokuhiko HANDA, Kazuyuki KURODA, and Chuzo KATO*
Department of Applied Chemistry, Waseda University,
Ohkubo 3, Shinjuku-ku, Tokyo 169

Organoammonium-montmorillonites were formed from dehydrated sodium montmorillonite and organoammonium halides by solid-solid reactions. The formation depended on the sizes and counter anions of the ammonium ions used. The behavior was different from that observed in a conventional solution method.

So-called solid-solid reactions, which mean the formation of compounds through solid-solid interfaces, have attracted much interest because of the possibility to prepare compounds not accessible from solutions.[1,2] Recently, Toda et al. reported the formation of some organic host-guest complexes by solid-solid reactions.[3] Hence, solid-solid reactions can be applied to other types of host-guest systems.

Clay mineral-organic intercalation compounds have widely been prepared from various host and guest substances.[4] Although Wada reported a kaolin mineral-potassium acetate intercalation compound by a solid-solid reaction,[5] no successful applications for the preparation of clay-organic intercalation compounds have been published except for our report on the preparation of montmorillonite-organic intercalation compounds with some polar molecules by solid-solid reactions.[6] Montmorillonite has the interlayer exchangeable cations and can intercalate various organic cations by ion exchange. The mechanism is different from that of the adsorption of polar molecules. Thus, it seems interesting to investigate the possibility of the ion exchange by solid-solid reactions. Recently, Vicente et al. have reported the intercalation of N-methyl 8-hydroxy quinoline methyl sulfate into smectite.[7] However, they mentioned that the adsorbed water might have played a role as a neutral medium for the ion exchange. Our previous report showed that the adsorbed water was not essential for adsorption of polar molecules. This work aims at the application of solid-solid reaction to the ion exchange of interlayer exchangeable cations under dehydrated condition. Various organoammonium ions were selected as the guest substances for this study, since these ions have widely been studied in intercalation chemistry and they are industrially important.

The clay used in this study was montmorillonite (Kunipia F) obtained from Aterazawa mine, Japan. Sodium montmorillonite was prepared by treating with an excess of a sodium chloride aqueous solution. Sample preparation was carried out according to the previous paper.6) In order to exclude the effect of adsorbed water, sodium montmorillonite was heated at 300 °C for 2 h in advance. Heat treated sodium montmorillonite showed the basal spacing of ca. 9.6 Å even after being cooled to room temperature under reduced pressure, indicating the adsorbed water was removed. All the organic salts were dried under reduced pressure before use. The absence of adsorbed water was checked by DTA. The mixtures of dehydrated sodium montmorillonite and organoammonium salts were ground with an agate mortar and a pestle for a few minutes under a dry air atmosphere in a glove box at ambient temperature. The amounts of organic salts were equivalent to the cation exchange capacity of sodium montmorillonite (119 mequiv. / 100 g). As a reference, normal ion exchange was also carried out using aqueous solutions of the organic salts.

Figure 1 shows the XRD pattern of the product obtained by grinding propylammonium chloride and sodium montmorillonite. The basal spacing of the product was 13.1 Å, showing the expansion of the interlayer space by 3.5 Å. A similar expansion was observed in the product obtained by normal ion exchange method using an aqueous solution of propylammonium chloride. The infrared spectrum of the product also showed that the bands due to νNH_3^+ were shifted from those of propylammonium chloride. The spectrum was the same as that of the product obtained by normal ion exchange method. These results showed that ion exchange of the interlayer exchangeable cations could easily occur by solid-solid reactions. The XRD pattern of the product also showed that sodium chloride was formed. This observation supported that the interlayer sodium cations were desorbed through the grinding to balance the electrical charge with the propylammonium ions. The product obtained by grinding was not washed in order to avoid the formation of an intercalation compound during washing. Consequently, the amount of the adsorbed species was not determined. However, the XRD pattern of the product showed no diffraction peaks due to propylammonium chloride, suggesting that most propylammonium ions used were intercalated.

Alkylammonium-montmorillonite intercalation compounds have been studied extensively.4) Since montmorillonite has small cation exchange capacity, intercalated alkylammonium ions (from C_1 to C_{10}) are thought to be lying flat in the interlayer space.8,9) The basal spacings of these compounds are ca. 13.5 Å, whose increments are approximately consistent with the van der Waals radii of carbon chain. Since the basal spacing observed in the present study was in accordance with the reported value,8) the intercalated propylammonium cations were lying flat in the interlayer space of montmorillonite.

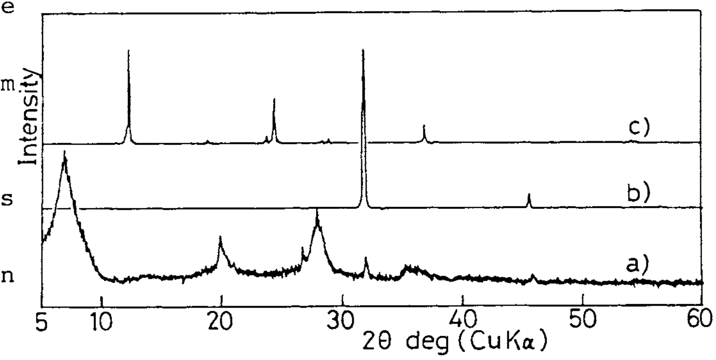

Fig. 1. X-Ray powder diffraction patterns of (a)propylammonium-montmorillonite intercalation compound, (b)sodium chloride, and (c)propylammmonium chloride.

When methylammonium and hexylammonium chlorides were used as the guest substances, the intercalation compounds were obtained similarly. The basal spacings of the products prepared by solid-solid reactions and by normal exchange method using various alkylammonium salts were listed in Table 1. Although alkylammonium ions (from C_1 to C_6) were intercalated, larger ions (beyond C_8) were not intercalated. Steric hindrance seems to inhibit the ion exchange, though other factors should also be considered.

Table 1. Basal spacings of various organoammonioum-montmorillonite intercalation compounds

Guest species	Basal spacing a)(Å)	b)(Å)
Methylammonium chloride	11.9	12.7
n-Propylammonium chloride	13.1	13.1
n-Hexylammonium chloride	13.1	13.5
n-Octylammonium chloride	9.7c)	13.8
n-Decylammonium chloride	9.8c)	16.2
n-Dodecylammonium chloride	9.8c)	17.2
n-Octadecylammonium chloride	9.8c)	18.9
Dimethylammonium chloride	12.8	13.0
Trimethylammonium chloride	13.4	13.3
Tetramethylammonium chloride	13.8	14.1
Tetramethylammonium bromide	13.5d)	14.1
Tetraethylammonium bromide	14.0	14.4
Tetrapropylammonium bromide	14.0	15.3
Tetrabutylammonium bromide	18.6d)	17.1

a) Prepared by solid-solid reactions.
b) Solution method.
c) Not intercalated.
d) Obtained after grinding for 30 min.

To confirm the possibility of ion exchange by solid-solid reactions, secondary(dimethyl), tertiary(trimethyl), and quaternary(tetramethyl) ammonium chlorides were used as other guest substances. For these samples, the basal spacings were also listed in Table 1. The values were consistent with those obtained by normal exchange methods by using aqueous solutions of the salts. Sodium chloride was also detected in the XRD patterns, supporting the intercalation.

As described above, the size of monoalkylammonium ions seemingly affected the reactivity on ion exchange in the solid state. In order to investigate the influence of the size of the guest species further, various quaternary alkylammonium salts (tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutyl-ammonium bromides) were used. The basal spacings of the products were also listed in Table 1. The expansion in the interlayer space and the appearance of sodium bromide were also observed for these products. When tetramethyl- and tetrabutyl-ammonium bromides were used, however, apparent intercalation were not observed after grinding for 2 min, and further grinding gave intercalation compounds. When tetramethylammonium bromide was used, grinding for 10 min gave a partly intercalated compound. After grinding for 30 min, the basal spacing expanded to 13.5 Å, indicating the formation of the intercalation compound. The difference in the behavior was not clear at present.

In order to investigate the factors other than the size of guest cations, the effect of the counter anions was examined by the use of various tetramethylammonium halides (chloride, bromide, and iodide). When tetramethylammonium chloride was used, intercalation easily occurred (the basal spacing was 13.5 Å) after grinding for a few minutes. When the bromide was used, however, the intercalation was not observed apparently for a few minutes of grinding and the basal spacing increased to the reported value (13.5 Å) after grinding for 30 min. In addition, the iodide gave no intercalation compound even after grinding for 30 min. These observations suggested that counter anions had a certain effect for the ion exchange in the solid state. Although it is difficult to ascertain the effect at present, the size of counter anions and the lattice energy of both reactants and products seem to be concerned. Further investigations should be made to elucidate the nature of the ion exchange.

As this study have been carried out using aliphatic ammonium salts, anilinium chloride was used as another type of the guest substance. The basal spacing increased to 14.5 Å after grinding for 2 min. Sodium chloride was also detected in the XRD pattern of the product. A similar basal spacing was observed for the product obtained by normal exchange method. These results indicate the formation of the intercalation compound. Montmorillonite-aniline or anilinium ion intercalation compounds have already been prepared. The basal spacing observed here is similar to the reported value (15.0 Å).10) According to the report,10) intercalated anilinium ions existed in the interlayer space with their aromatic planes perpendicular to the silicate sheet. Intercalated anilinium ions of the compounds prepared by solid-solid reactions seem to have similar conformation in the interlayer region of montmorillonite.

In conclusion, solid-solid reactions were applied to the ion exchange of interlayer exchangeable cations. In some cases, the reactions proceeded rapidly. Because of some advantages such as the ease of the operation, solid-solid reactions should be applied to the preparation of other types of intercalation compounds. Further investigation is in progress in order to elucidate the nature of solid-solid reactions and to investigate the application.

References

1) R. P. Rastogi, J. Sci. Ind. Res., 29, 177 (1970).
2) A. O. Patil, D. Y. Curtin, and I. C. Paul, J. Am. Chem. Soc., 106, 348 (1984) and the references cited therein.
3) F. Toda, K. Tanaka, and A. Sekikawa, J. Chem. Soc., Chem. Commun., 1987, 279.
4) B. K. G. Theng, "The Chemistry of Clay-Organic Reactions," Adam Hilger, London (1974).
5) K. Wada, Am. Miner., 46, 78 (1961).
6) M. Ogawa, K. Kuroda, and C. Kato, Chem. Lett., 1989, 1959.
7) M. A. Vicente, M. Sanchez-Camazano, M. J. Sanchez-Martin, M. Del Arco, C. Martin, V. Rives, and J. Vicente-Hernandez, Clays Clay Miner., 37, 157 (1989).
8) J. W. Jordan, J. Phys. Colloid Chem., 53, 294 (1949).
9) Ref.4, Chap. 5.
10) R. Green-Kelly, Trans. Faraday Soc., 51, 412 (1955).

(Received October 2, 1989)