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Preparation of Montmorillonite-Organic Intercalation Compounds by Solid-Solid Reactions

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Montmorillonite-organic intercalation compounds were prepared by solid-solid reactions using acrylamide, methacrylamide, and urea as the guest organic molecules. It took only a few minutes to complete the reaction even when dried montmorillonite was used.

Montmorillonite, which is a typical layered clay mineral, has been known to accommodate various organic substances in its interlayer space to form intercalation compounds.1) These intercalation compounds have generally been prepared by solid-liquid or solid-gas reactions.

During the course of our study on clay mineral-organic intercalation compounds, we found that solid-solid reactions were effective ways to the preparation of montmorillonite-organic intercalation compounds. Solid-solid reactions, which mean the formation of compounds by mixing solid components together, have attracted much interest because of their possibility to prepare compounds not accessible from solutions.2) Recently, Toda et al. have reported the formation of some organic host-guest complexes by solid-solid reactions.3) As to the clay-organic chemistry, Wada has already reported that kaolin minerals can form intercalation compounds with potassium acetate by solid-solid reactions.4) However, it has been noted that the attempts to prepare intercalation compounds using other hosts and guests by solid-solid reactions were unsuccessful.

In this paper we report the successful application of solid-solid reactions to the preparation of montmorillonite-organic intercalation compounds. During preparing this manuscript, we noticed that Vicente et al. reported the solid-state formation of a smectite-(N-methyl 8-hydroxy quinoline methyl sulfate) intercalation compound.5) They suggested the possible role of adsorbed water in this type of reaction. Our findings, however, show that intercalation compounds with some neutral molecules can form by solid-solid reactions from the dried components.

The clay used in this study was sodium montmorillonite (Kunipia F) obtained from Aterazawa mine (Yamagata, Japan). The chemical composition was the same as described in the previous report.6) Copper and calcium montmorillonites were prepared from sodium montmorillonite by cation exchange as described previously.[7)] At first, acrylamide (WAKO Pure Chemical Ind.) was selected as the guest substance, and was recrystallized from ethyl acetate before use. Urea and methacrylamide were selected as other guest molecules.

In order to exclude the effect of the adsorbed water, sodium montmorillonite was dried at 300 °C for 2 h in advance. The heat treated montmorillonite showed the basal spacing of ca. 9.6 Å even after being cooled to room temperature, which meant the adsorbed water had been almost removed. Then, various weight ratios of mixtures of the dehydrated sodium montmorillonite and acrylamide were ground with an agate mortar and a pestle under a dry air atmosphere in a glove box for a few minutes.

The variation in the XRD patterns is shown in Fig. 1. With the increase in the weight ratios of acrylamide to montmorillonite, the peaks due to d(001) shifted to lower 2θ angles. When the weight ratio of acrylamide to sodium montmorillonite was 1:2, the basal spacing was 19.1 Å, indicating the expansion of the interlayer space by 9.5 Å. (The basal spacing of sodium montmorillonite is 9.6 Å.) We have already reported the preparation of montmorillonite-acrylamide intercalation compounds by treating montmorillonite with acrylamide aqueous solutions.[7)] The basal spacing showed two typical values of ca. 15 Å and 20 Å, indicating monomolecular and bimolecular arrangements of the intercalated acrylamide in the interlayer space, respectively. The value observed here is close to 20 Å. Thus, it was thought that acrylamide was intercalated in a bimolecular arrangement. When copper and calcium montmorillonites were used, the basal spacings also increased, confirming the formation of intercalation compounds.

Since acrylamide has a vapor pressure of 0.007 mmHg at 25 °C, the reaction can be thought to be a solid-gas reaction. To exclude its possibility, both components were placed together in a vessel and analyzed. No intercalation was observed after a week. Therefore, it can be concluded that the intercalation occurred through the solid-solid interface.

In this reaction, acrylamide molecules were thought to migrate the solid-solid interface and diffuse at the surface of montmorillonite particles to be intercalated

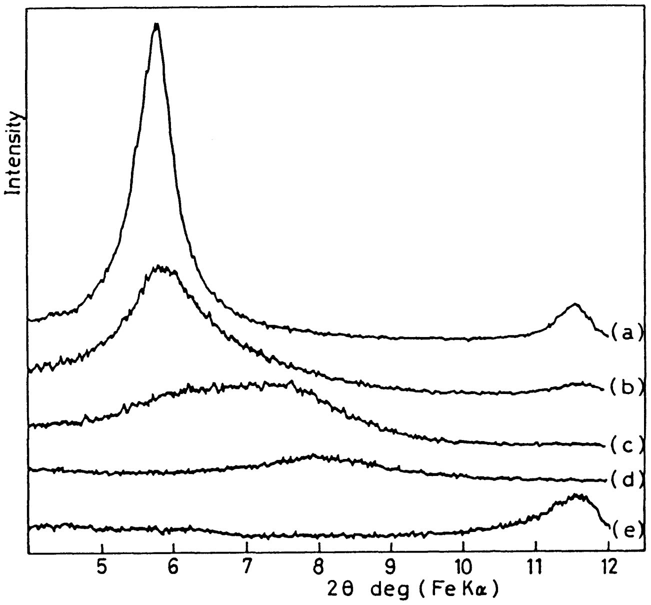

Fig. 1. X-Ray powder diffraction profiles (lower 2θ region) of montmorillonite-acrylamide intercalation compounds prepared from various mixtures with the weight ratios of acrylamide to montmorillonite; (a) 1:2, (b) 1:4, (c) 1:6, (d) 1:10, and (e) dried sodium montmorillonite.

into the interlayer space of montmorillonite, being the same as the case of organic solid-solid reactions.[2)]

As expected by the preparing procedure, there should be an excess of acrylamide in the sample. Then, it was washed with CCl_4 which cannot penetrate into the interlayer space to remove acrylamide. The XRD patterns of the montmorillonite-acrylamide intercalation compound (acrylamide:montmorillonite = 1:2) before and after washing are shown in Fig. 2, together with that of the compound prepared by treating sodium montmorillonite with a 20% acrylamide aqueous solution.[7)] In the XRD pattern of the product before washing, some sharp peaks due to an excess of acrylamide appeared, which disappeared after washing. In the DTA curve of sodium montmorillonite-acrylamide intercalation compound after washing, the two endothermic peaks around 80-120 °C due to melting and vaporization of acrylamide disappeared. All these results showed an excess of acrylamide was removed after washing. No change in the basal spacing was observed after washing, which showed that CCl_4 did not affect the intercalated acrylamide.

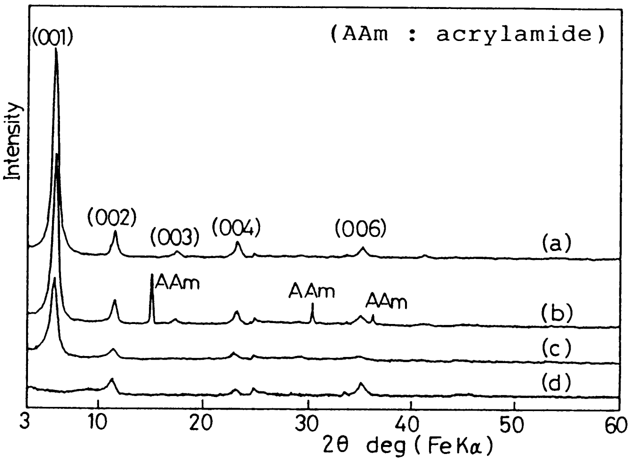

Fig. 2. X-Ray powder diffraction profiles of montmorillonite-acrylamide intercalation compounds prepared by solid-solid reactions (acrylamide:montmorillonite=1:2),(a) after washing with CCl_4, (b) before washing, (c) similar intercalation compound prepared from a 20% acrylamide aqueous solution, and (d) dried sodium montmorillonite.

In addition, the diffraction peaks of the sodium type compound were sharper than those of the intercalation compound prepared from a 20% acrylamide aqueous solution, although no sharpening in the XRD patterns of calcium and copper type compounds was observed. Vicente et al.[5)] reported that similar sharpening was observed. Yamanaka et al. reported that the sharpening occurred when montmorillonite was treated with a $TiCl_4$ aqueous solution.[8)] Although the reason why the present XRD peaks were so sharp is not clear at present, the intercalated acrylamide can take an ideal conformation in the interlayer space to cause a regular stacking between adjacent layers.

The DTA curve also showed that the endothermic peak due to desorption of adsorbed water was much weaker than those of the montmorillonite-acrylamide intercalation compounds obtained from acrylamide aqueous solutions.[7)] This finding suggested that the montmorillonite was almost free of water through the reaction.

The amounts of the intercalated acrylamide were 30, 35, and 36 g per 100 g clay for sodium, calcium, and copper type compounds, respectively, indicating that the occupied spaces by acrylamide were approximately constant, irrespective of the kinds of the interlayer cations.

The infrared absorption bands due to acrylamide appeared in the spectra of the compounds. Thus, the intercalation of acrylamide into montmorillonite was confirmed. The band due to C=O stretching and those attributed to N-H stretching appeared in a lower frequency region than those of acrylamide dissolved in $CHCl_3$.9) The spectrum of copper type compound showed the band due to C=O stretching appearing in a lower region than that of the sodium type compound. Copper acrylamide coordination complex, in which coordination occurs through the oxygen atom of carbonyl group, has already been reported.10) The absorption bands observed were similar to those of the complex. These observations suggested that acrylamide molecules were intercalated by ion-dipole interactions with the interlayer cations and hydrogen bonding with surface oxygen of silicate sheet.

In order to confirm the applicability of such solid-solid reactions, methacrylamide and urea were selected as other guest molecules and ground with montmorillonites in the same way as described above. Methacrylamide and urea gave the basal spacings of 14.7 Å and 17.1 Å for sodium montmorillonite, respectively. Urea also gave the intercalation compounds with calcium- and copper-montmorillonites, showing the basal spacings of 17.1 Å and 16.8 Å, respectively. The values of the urea compounds were different from those of the compounds prepared from an aqueous solution.11) This observation suggests that there are different types of interaction in the compounds prepared in the present study.

In conclusion, some montmorillonite-organic intercalation compounds were formed by mixing the solid components for only a few minutes. Besides the ease of the operation, it is advantageous because the adjustment of pH, the use of solvents, and their choice etc. are unnecessary. In order to elucidate the nature of solid-solid reactions, our research on this type of reaction with various guest substances are now in progress and will be reported subsequently.

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