

Selective Solid-State Intercalation of *cis-trans* Isomers into Montmorillonite

Makoto OGAWA, Masahiro HIRATA, Kazuyuki KURODA, and Chuzo KATO\*

Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169

Maleic and methylmaleic acids were intercalated into montmorillonite by solid-solid reactions, whereas their geometrical isomers (*trans*-forms), fumaric and methylfumaric acids, were not intercalated. Both maleic and fumaric acids were intercalated into Na-montmorillonite, when the ethanolic solutions were used. Both the difference in the crystal structures of the guest species and the ability of *cis*-isomer to form a chelate like structure with the interlayer cations are thought to be concerned for the novel selectivity in the solid-state.

Montmorillonite is a typical layered clay mineral to accommodate various organic substances in the interlayer space to form intercalation compounds.<sup>1)</sup> Recently, we have succeeded in solid-state intercalation of organic compounds into montmorillonites. Solid-state intercalation of organoammonium cations by cation exchange mechanism,<sup>2)</sup> and acrylamide,<sup>3)</sup> n-alkylamine,<sup>4)</sup> and 2,2'-bipyridine<sup>5)</sup> by adsorption mechanism have already been observed. Since the solid-solid reactions have advantages such as the ease of operation compared to conventional solution methods and the possibility to prepare compounds not accessible from solutions,<sup>6-9)</sup> further study on the solid-state formation of intercalation compounds is of great importance from both theoretical and practical viewpoints.

In our study on the solid-state intercalation of organic compounds into montmorillonite, we found a novel selectivity in the solid-state between *cis*- and *trans*-isomers upon intercalation into Na-montmorillonite. Although, maleic and methylmaleic acids were intercalated into montmorillonite by solid-solid reactions, their geometrical isomers (*trans*-forms), fumaric and methylfumaric acids, were not intercalated. Several unique phenomena upon intercalation into montmorillonite, such as chirality recognition of polypyridine chelate compounds from solutions<sup>10)</sup> and shape selective adsorption of organic compounds into organophilic montmorillonites from both vapor phase and solution,<sup>11,12)</sup> have already been reported. However, the selectivity observed in this study is of great interest since this is the first example to show selectivity of *cis*- and *trans*-isomers using naturally occurring layered clay minerals in the solid-state.

Sodium-montmorillonite (Kunipia F, Kunimine Ind. Co., Japan) was used as the host material. The cation exchange capacity of the clay was 119 mequiv./100 g clay and the chemical composition was described elsewhere.<sup>13)</sup> Maleic acid (*cis*-butenedioic acid, obtained from WAKO Pure Chem. Industries), methylmaleic acid (*cis*-1-methyl-butenedioic acid, Tokyo Kasei Industries Co.), fumaric acid (*trans*-butenedioic acid, WAKO Pure Chem. Industries Co.), and methylfumaric acid (*trans*-1-methyl-butenedioic acid, Tokyo Kasei Industries Co.) were used as the guest species. Solid-state intercalation was carried out according to the previous report.<sup>2-5)</sup> In order to avoid the effect of adsorbed water on the reactions, Na-montmorillonite was

dried at 300 °C in air for 2 h in advance. The mixtures of dried Na-montmorillonite and guest species were ground with a mortar and a pestle manually for a few minutes at room temperature under a dry air atmosphere (in a glove bag). The products were washed with chloroform in order to remove excess guest species. For comparison, intercalation of maleic and fumaric acids into Na-montmorillonite in ethanolic solutions was conducted.

X-Ray powder diffraction was performed on a Rigaku RADII-A diffractometer using Mn filtered Fe K $\alpha$  radiation. Infrared spectra were recorded on a Perkin Elmer FT-1640 Fourier-transform spectrophotometer by the KBr disk method. DTA curves were recorded on a Shimadzu DT-20B instrument at the heating rate of 10 °C / min using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a standard material. Thermogravimetric analysis was performed on a Shimadzu TGA-40 instrument at the heating rate of 10 °C / min.

The XRD pattern of the product obtained by the solid-solid reaction between Na-montmorillonite and maleic acid is shown in Fig. 1b together with that of dried Na-montmorillonite. By grinding for a few minutes, the basal spacing increased to 1.25 nm, indicating the expansion of the interlayer space by 0.29 nm. (The basal spacing of dried Na-montmorillonite was 0.96 nm.) Since the observed basal spacing was close to that of air dried Na-montmorillonite (ca. 1.25 nm), the basal spacing can be assigned to Na-montmorillonite hydrated through the XRD measurement. In order to eliminate this possibility, the product was dried at 100 °C in air and the XRD pattern was recorded. The basal spacing of the product did not change after the heat treatment, suggesting that the increase in the basal spacing was caused by intercalation of maleic acid.

More intriguing is the difference in the reactivity between *cis*- and *trans*-isomers. In contrast to the reaction between Na-montmorillonite and maleic acid, fumaric acid (*trans*-isomer of maleic acid) was not intercalated into Na-montmorillonite by solid-solid reaction mechanism. Even after the solid-solid reaction for 30 min, the mixture of Na-montmorillonite and fumaric acid did not react at all. The XRD pattern showed the diffraction peaks due to

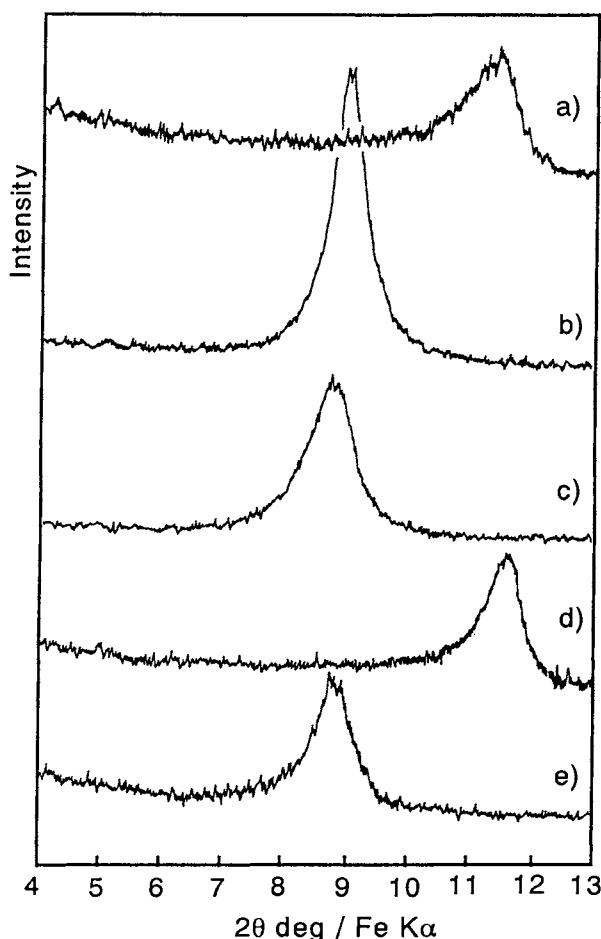


Fig. 1. X-Ray powder diffraction patterns of a) dried Na-montmorillonite, b,c) the Na-montmorillonite-maleic acid intercalation compounds prepared b) by solid-solid reaction and c) by solid-liquid reaction, and d,e) the reaction products between Na-montmorillonite and fumaric acid d) by solid-solid reaction and e) by solid-liquid reaction.

unreacted Na-montmorillonite (Fig. 1d) and fumaric acid (in higher  $2\theta$  angle), and the infrared spectrum showed the absorption bands due to both of the components without any shifts of the peak positions. Moreover, methylmaleic acid was intercalated into Na-montmorillonite to form an intercalation compound with the basal spacing of 1.27 nm, while no evidence of intercalation of methylfumaric acid (*trans*-isomer of methylmaleic acid) into Na-montmorillonite was obtained.

When a 1:1 mixture of maleic and fumaric acids was ground with Na-montmorillonite, the diffraction peaks due to maleic acid decreased distinctly. After the solid-solid reaction, the relative ratio of the intensity of the most intense diffraction peak due to maleic acid to that due to fumaric acid decreased to 0.7 : 1 from 2.9 : 1, indicating maleic acid was selectively intercalated into the interlayer space of Na-montmorillonite. It is supposed that the difference in the crystal structures between *trans*- and *cis*-isomers is a reason for the different reactivities in the solid-state. Maleic acid molecules are linked by longer intermolecular hydrogen bonds (0.275 nm)<sup>14)</sup> than those of fumaric acid (0.2682 nm)<sup>15)</sup> to form rows, and these rows are interlinked by still weaker hydrogen bonds (0.298 nm) to form layers. On the other hand, fumaric acid molecules are linked together by a double hydrogen-bonding system (0.2682 nm) to form chains.<sup>15)</sup> Thus, maleic acid molecules are interlinked each other by weaker interactions than those between fumaric acid molecules so that the diffusion of maleic acid at a molecular level is thought to be easier than that of fumaric acid to cause the selectivity. The geometry of *cis*-isomer to form stable chelate like structure with interlayer exchangeable cations may also be concerned with the difference in the reactivity. Anyhow, the observed selectivity between *cis*- and *trans*-isomers upon intercalation into montmorillonite is worth noting as a novel solid-state molecular recognition.

In the XRD pattern of the product prepared by the reaction between Na-montmorillonite and maleic acid, the diffraction peaks due to excess maleic acid were observed. The peaks due to excess maleic acid were decreased by washing with chloroform without affecting the basal spacing, suggesting excess maleic acid was preferentially removed by the washing. However, repeated washing with chloroform caused deintercalation of maleic acid. The observation suggests that the interactions between Na-montmorillonite and maleic acid are weak. From the change in the intensities of the diffraction peaks due to the excess maleic acid, the amount of intercalated maleic acid was estimated to be no less than 15 g / 100 g clay.

The infrared spectrum of the washed product showed the absorption band due to C=O stretching of maleic acid at 1720  $\text{cm}^{-1}$  and the position shifted compared with that of maleic acid (1710  $\text{cm}^{-1}$ ) in KBr. In the DTA curve of the product, an endothermic peak accompanying a weight loss was observed around 150  $^{\circ}\text{C}$ . Since maleic acid itself melts at 130  $^{\circ}\text{C}$  and vaporize subsequently, the endothermic peak can be ascribed to desorption of intercalated maleic acid. All these observations confirmed the intercalation of maleic acid into montmorillonite. From the observed basal spacing (1.25 nm) and the amount of the adsorbed maleic acid (15 g / 100 g clay), the intercalated maleic acid molecules were lying flat with their molecular planes parallel to the silicate sheets.

When ethanolic solutions were used, both maleic and fumaric acids were intercalated into the interlayer space of Na-montmorillonite. The XRD patterns of the products are shown in Figs. 1c and 1e for maleic acid and fumaric acid, respectively. The infrared spectrum and the DTA curve of the Na-montmorillonite maleic acid intercalation compound prepared by the solution method were similar to those of the product obtained by the solid-solid reaction. In the infrared spectrum of the product obtained by the reaction between Na-montmorillonite and an ethanolic solution of fumaric acid, the absorption band due to C=O stretching band

appeared at  $1717\text{ cm}^{-1}$  and the position shifted compared with that of fumaric acid in KBr ( $1674\text{ cm}^{-1}$ ). This confirmed the formation of the Na-montmorillonite fumaric acid intercalation compound. The difference between the reactions in the solid-state and those in the liquid-state confirms the important role of the crystal structure on the geometrical selectivity. Therefore, we can conclude that the solid-state intercalation is a novel way of molecular recognition taking advantage of crystal structure.

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