Intercalation of Methanol and Ethanol into Na-Fluorotetrasilicic Mica: Difference in Formation of Single and Double Layer Intercalates

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Intercalation of methanol and ethanol into Na-fluorotetrasilicic mica was traced dynamically by X-ray diffraction. The intercalation of methanol is much faster than that of ethanol. Methanol forms successively single and double layers between silicate sheets of the mica, while ethanol forms similar layers concurrently.

Layered clay minerals intercalate a variety of polar molecules and their intercalates have attracted considerable attention as a catalyst and an adsorbent of a new type.[1,2] The intercalation into clay minerals has been studied by many investigators especially on the intercalation-deintercalation of water[3-5] and on the structure and properties of intercalates.[6,7] However, the mechanism and the kinetics of intercalation have not been studied extensively. Breen et al.[8,9] measured the rate of intercalation of organic molecules including cyclic ethers and alcohols into Al^{3+}, Cr^{3+} and Fe^{3+}-exchanged montmorillonites by isothermal gravimetry flowing ether- or alcohol-saturated N$_2$ carrier gas onto the clay samples and suggested that the rate is controlled by diffusion of organic molecules in the N$_2$ carrier-gas. We studied intercalation of methanol or ethanol into Na-fluorotetrasilicic mica (Na-TSM) under reduced pressures to prevent the diffusion limitation, by tracing a change of the layer structure using a X-ray diffractmeter (XRD) equipped with a sample chamber sealed for evacuation.

Na-TSM was refined by sedimentation from a 10 wt% aqueous sol supplied by Toppy Ind. and a few drops of its water suspension was dried on a glass plate to prepare a thick film. The film of Na-TSM was dehydrated in the sample chamber of XRD at 573 K for 30 min by flowing Ar, evacuated to less than 6 pa, and exposed to methanol or ethanol vapor at 298 K. The diffraction peak corresponding to (001) plane of Na-TSM changed immediately after the exposure and was traced by scanning the range $3.00^\circ \le 2\theta \le 11.55^\circ$ in 3 min repeatedly.

The structures of intercalates formed were different by relative vapor pressures (vapor pressures relative to the saturated vapor pressure at 298 K) of alcohol. At relative pressures lower than 0.6, the diffraction peak corresponding to d(001) = 13.0 Å appeared and grew large by both of methanol and ethanol intercalations at the sacrifice of the peak intensity originally observed at d(001) = 10.0 Å. At a relative pressure of 0.9, a second peak newly appeared at d(001) = 16.0 and 16.4 Å in the intercalations of methanol and ethanol, respectively. The interlayer distances of the methanol intercalate and the ethanol intercalate are nearly equal in spite of the different molecular sizes and those of second intercalates are twice larger than those of the first ones. The fact suggested that the alcohol molecules lie between the silicate sheets of Na-TSM with the orientation, their axes parallel to the silicate sheet, and form a single layer and then a double layer as the relative vapor pressure is increased.

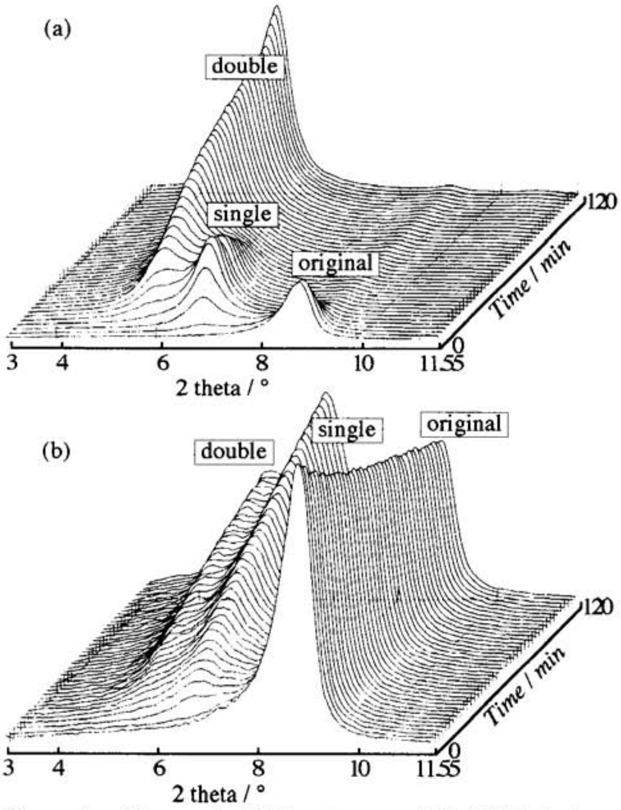

Figure 1. Change in XRD patterns of Na-TSM during intercalation of methanol (a) and ethanol (b). Relative vapor pressure, 0.9.

The changes in the (001) diffraction peaks with the exposure time were completely different when Na-TSM was exposed to methanol and ethanol at the relative vapor pressure 0.9. The results obtained by the repeat scan for 120 min were illustrated in Figure 1. In the intercalation of methanol (Figure 1(a)), the diffraction peak (d(001) = 10 Å) observed originally decreased in intensity and kept its intensity very weak after 15th scan suggesting that a few original stacks of Na-TSM silicate sheets were not able to afford the methanol intercalation. The intensity of the diffraction peak for the single layer intercalation (d(001) = 13 Å) increased initially and then decreased through maximum at 6th scan, while that for the double layer intercalation (d(001) = 16 Å) increased monotonously after a short induction period. The changes of the intensities of three diffraction peaks show a typical feature of successive reaction, that is, methanol is intercalated into Na-TSM to form the single layers and intrudes subsequently into the single layers to form the double layers.

The changes in the three diffraction peaks during the intercalation of ethanol are illustrated in Figure 1(b). The intensity of the original (001) diffraction peak decreased at the rate much lower than that observed for the methanol intercalation. The diffraction peak for the double layer intercalate grew simultaneously with that for the single layer intercalate showing no appreciable induction period. It is likely that the intercalation of ethanol forms two layers concurrently. After the measurement shown in Figure 1(b), the sample was evacuated at the same temperature observing the diffraction peaks. The diffraction peak for the single layer intercalate grew up to a steady size , while that for the double layer intercalate shrank with the evacuation time and finally disappeared. The observation is rather strange, because it shows the deintercalation proceeds successively although the intercalation does concurrently.

As described above, the intensity of the diffraction peak for the single layer intercalate increased to a plateau value by the evacuation. The value agreed well with the sum of the intensities of the single and the double layer intercalates observed immediately before the evacuation. The fact suggests that the peak intensity for the intercalates is in a linear relationship and the peak intensity relative to that for fully intercalated sample represents the concentration of each intercalate. Figure 2 shows the time course of the relative peak intensity for the original stacking (I_o), the single layer intercalate (I_s), and the double layer intercalate (I_d). I_o, I_s, and I_d are defined by the following equations.

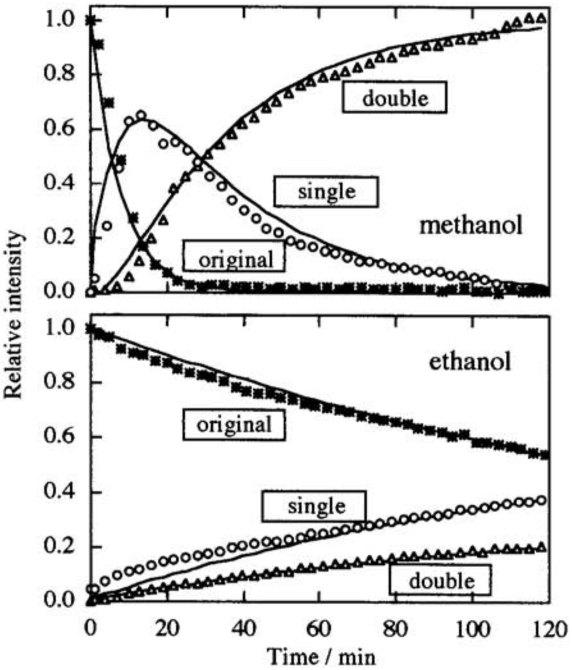

Figure 2. Time course of relative intensity of (001) reflection.

$$I_o = \mathrm{I_o} / (\mathrm{I_{oi}} - \mathrm{I_{o\infty}}), \quad I_s = \mathrm{I_s} / \mathrm{I_{s\infty}}, \quad I_d = \mathrm{I_d} / \mathrm{I_{d\infty}} = \mathrm{I_d} / \mathrm{I_{s\infty}}.$$

In the equations, Io, Is, and Id are the peak intensities for the peaks observed in Figure 1, $\mathrm{I_{oi}}$ and $\mathrm{I_{o\infty}}$ are $\mathrm{I_o}$ observed before the intercalation and after the termination of the intercalation, respectively, and $\mathrm{I_{s\infty}}$, namely $\mathrm{I_{d\infty}}$, is $\mathrm{I_s}$ obtained by the evacuation after the observation shown in Figure 1. The solid lines illustrated in Figure 2 are the simulation curves calculated for $\mathrm{I_o}$, $\mathrm{I_s}$, and $\mathrm{I_d}$ assuming that those values change in the first order kinetics with respect to $-I_o$, I_s , and I_d, respectively, in the

$$-\mathrm{d}I_o / \mathrm{dt} = \mathrm{k_s} I_o \quad (1)$$
$$\mathrm{d}I_s / \mathrm{dt} = \mathrm{k_s} I_o - \mathrm{k_d} I_s \quad (2)$$
$$\mathrm{d}I_d / \mathrm{dt} = \mathrm{k_d} I_s \quad (3)$$

intercalation of methanol (eqs. (1)-(3)); $\mathrm{I_s}$ and $\mathrm{I_d}$ increased proportionally to $\mathrm{I_o}$ in the intercalation of ethanol (eqs. (4)-(6)).

$$-\mathrm{d}I_o / \mathrm{dt} = (\mathrm{k_s} + \mathrm{k_d}) I_o \quad (4)$$
$$\mathrm{d}I_s / \mathrm{dt} = \mathrm{k_s} I_o \quad (5)$$
$$\mathrm{d}I_d / \mathrm{dt} = \mathrm{k_d} I_d \quad (6)$$

Although the assumptions contain some ambiguities, the calculated curves well simulates the observed changes of relative peak intensities. The value of $\mathrm{k_s}$ calculated from the simulation independent of the eqs. (2) and (3) was 0.13 $\mathrm{min^{-1}}$, while the values of $\mathrm{k_s}$ and $\mathrm{k_d}$ obtained from the simulation based on the eqs. (2) and (3) were 0.11 and 0.033 $\mathrm{min^{-1}}$, respectively, meaning that the rate constant of the peak intensity decrease corresponding to the original stacking destruction is nearly equal to and slightly larger than that of the peak intensity increase corresponding to the single layer formation. This is reasonable because only a small amount of intercalated methanol destroys the regularity of original stacking and the regularity of the single layer stacking may be constructed after further intercalation. The values of $\mathrm{k_s}$ and $\mathrm{k_d}$ suggest that the single layer formation is about 4 times faster than the double layer formation. This is also acceptable because the former proceeds through the chemical interaction between the interlayer Na ion and methanol while the latter may proceed through the physical absorption into the single layers.

In the case of ethanol, the values I_s and I_d are not meaningful and the simulation curves for eqs. (5) and (6) as well, because the intercalation equilibrium was not attained in the observation period 120 min. The rate constant, that is $\mathrm{k_s}$ + $\mathrm{k_d}$, obtained from the simulation for the change of I_o was 0.006 $\mathrm{min^{-1}}$, suggesting that the intercalation rate of ethanol is about one twentieth slower that of methanol. We are now investigating the relationship between the change of the relative peak intensity observed with XRD and that of the intercalated amount measured by isothermal gravimetry.

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