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Intercalation of 2,2'-Bipyridine and Complex Formation in the Interlayer Space of Montmorillonite by Solid-Solid Reactions

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Solid-solid reactions that which occur between powders in the solid state have attracted much attention because of their ease of operation and the possibility of preparing compounds not accessible from solutions, among other reasons.[1-4] Solid-solid reactions can be applied to the preparation of various types of host-guest systems, for example, those of organic host-guest complexes (Toda et al.[5]). It is well-known that the smectite group of clay minerals, in particular montmorillonite, can form various intercalation compounds with a wide variety of organic substances.[6] Although these compounds have widely been prepared, no successful application of solid-solid reactions for smectite-organic systems has been published outside our previous reports.[7,8]

Several unusual physicochemical properties of transition metal-2,2'-bipyridine (bpy) complexes adsorbed onto smectite surfaces have been reported in this decade.[9] For example, $[Ru(bpy)_3]^{2+}$-smectite intercalation compounds have been studied as clay-modified electrodes[10] and as catalysts for the photodecomposition of water.[11] These compounds were prepared by ion exchange using aqueous solutions of complex salts. During our studies of the application of solid-solid reactions to prepare intercalation compounds, we found that bpy intercalates into the interlayer space of montmorillonite by a solid-solid reaction mechanism at room temperature. When the interlayer-exchangeable cation is Co(II), the intercalated bpy forms a coordination compound in the interlayer space. The formation of transition metal-bpy complexes within the cavities of zeolites[12] and in the interlayer space of layered zirconium phosphates has already been reported.[13] However, these reactions were carried out by solid-liquid or solid-gas reactions. The solid-solid reaction we report here is unique and may be applicable as a new method for the preparation of clay-complex intercalation compounds. The present paper describes the results of solid-solid reactions between homoionic montmorillonites and bipyridyl.

Experimental Section

Sodium montmorillonite (Kunipia F, Kunimine Industries Co., obtained from Aterazwa mine, Japan) was used; the cation-exchange capacity (CEC) is 119 mequiv/100 g of clay. Homoionic (sodium, calcium, and cobalt(II)) montmorillonites were prepared by treating sodium montmorillonite with aqueous solutions of appropriate metal chlorides, which were subsequently washed repeatedly with deionized water until chloride ion free. Homoionic montmorillonites were dried at 300 °C for 2 h in air to remove adsorbed water and then cooled to room temperature under reduced pressure. Cobalt(II) montmorillonite was dried under two different conditions in order to vary the hydrated state of interlayer Co(II): (a) 120 °C for 2 h under vacuum and (b) 300 °C for 2 h in air. The mixtures of dried montmorillonites and bpy were ground with an agate mortar and pestle for a few minutes at room temperature under a dry air atmosphere. Air-dried montmorillonites were also used, and reactions between these and bpy were carried out without considering the atmosphere. The molar ratios of bpy to interlayer-exchangeable cations varied from 1:1 to 6:1. The products were washed with *n*-hexane, which cannot penetrate into the interlayer space of montmorillonite, to remove excess bpy.

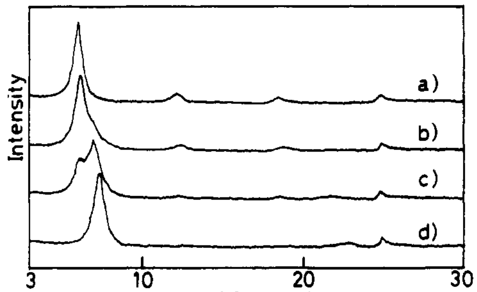

Figure 1. X-ray diffraction patterns of bpy-intercalated cobalt(II) montmorillonites prepared by solid-solid reactions from the mixtures at molar ratios of (a) 3:1, (b) 2:1, and (c) 1:1 for bpy:Co(II). Curve d: X-ray diffraction pattern for air-dried cobalt(II) montmorillonite.

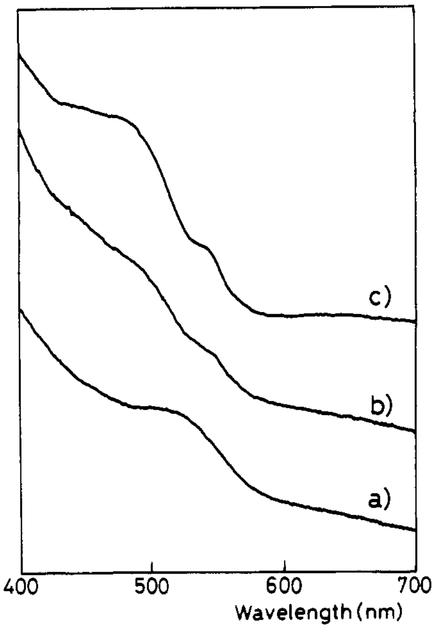

Figure 2. Diffuse-reflectance UV-vis spectra of (a) air-dried cobalt(II) montmorillonite, (b) bpy-intercalated cobalt(II) montmorillonite prepared by a solid-solid reaction, and (c) $[Co(bpy)_3]Cl_2{\cdot}6H_2O$.

For reference, a normal ion-exchange method[14] was carried out with an aqueous solution of $[Co(bpy)_3]Cl_2$. A solid-solid reaction between sodium montmorillonite and $[Co(bpy)_3]Cl_2{\cdot}6H_2O$ was also carried out as a control experiment. In order to avoid intercalation during washing, the product was characterized as prepared. Here, the amount of the complex was equivalent to the CEC of the clay.

XRD patterns of the products were obtained on a Rigaku RAD II-A diffractometer using Mn-filtered Fe Kα radiation. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1640 Fourier-transform spectrometer by the KBr-disk method. Diffuse-reflectance UV-visible absorption spectra were recorded on a Hitachi U-3200 spectrophotometer.

Results and Discussion

When cobalt(II) montmorillonite dried at 300 °C is used, no solid-solid reaction is observed after grinding. In contrast, the mixture of cobalt(II) montmorillonite dried at 120 °C under vacuum with bpy (molar ratio of bpy to Co(II) was 6:1) gives a yellowish brown product after grinding for just a few minutes.

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Since the time for grinding was short, it did not cause the sample to heat up. The XRD pattern of this product is shown in Figure 1a. The mixture of air-dried cobalt(II) montmorillonite and bpy also results in a yellowish brown product. The basal spacings of both materials are 18.1 Å, which means the interlayer space expands by 8.5 Å. These observations suggest that bpy is intercalated into the interlayer space of cobalt(II) montmorillonite by a solid–solid reaction. The basal spacing of the product obtained by normal ion exchange of montmorillonite with an aqueous solution of $[Co(bpy)_3]Cl_2$ is also 18.1 Å. Formation of $[M(bpy)_3]^{n+}$–hectorite intercalation compounds ($M = Cu^{2+}, Fe^{2+}, Ru^{2+}$) with basal spacings of ca. 18 Å have been reported by Traynor et al.[14] These authors concluded that the complex ions were intercalated at monolayer coverage with their 3-fold axis perpendicular to the silicate sheet. This suggests that the intercalated bpy forms $[Co(bpy)_3]^{2+}$ during solid–solid reaction with a similar monolayer arrangement.

Figure 2 shows the UV–visible diffuse-reflectance spectrum of the products prepared by solid–solid reaction together with those of cobalt(II) montmorillonite and $Co(bpy)_3Cl_2 \cdot 6H_2O$. The spectrum of the product was in good agreement with that of $Co(bpy)_3Cl_2 \cdot 6H_2O$. The reflectance spectrum of the product prepared by solid–solid reaction was identical with that of the product obtained by conventional solid–liquid reaction. An IR spectrum of the product obtained by grinding reveals absorption bands due to bpy that are shifted from those of bpy dissolved in CCl_4 but that correlate with those of the product prepared by a normal ion-exchange method. The C:N ratios (found: C, 15.6; H, 1.8; N, 4.1) are in agreement with that of bpy (5:1). The amount of adsorbed bpy for the product obtained by solid–solid reaction after washing with *n*-hexane was 26 wt %, corresponding to a molar ratio of adsorbed bpy to interlayer Co(II) of 3.2:1. The amount of bpy for the product obtained by a normal ion-exchange method was 23%. All these results confirm that intercalated bpy forms $[Co(bpy)_3]^{2+}$ with the interlayer Co(II) of montmorillonite. Taking into account the result that cobalt(II) montmorillonite dried at 300 °C was unreactive, the intercalation of bpy was explained by a ligand displacement reaction between H_2O and bpy.

These results were obtained for the products prepared in the presence of excess bpy. In our previous report on the preparation of montmorillonite–acrylamide intercalation compounds by solid–solid reaction, ratios of the mixtures were found to affect the XRD patterns of the products.[5] Hence, solid–solid reactions between cobalt(II) montmorillonite and bpy at mixing ratios of 1:1 or 2:1 (bpy:Co(II)), which is too low for all Co(II) ions to form stoichiometric tris(bipyridine) complexes, were carried out. The resulting products display two distinct basal spacings of ca. 13 and 18 Å (Figure 1b,c). The basal spacing of 18 Å is the same as when excess bpy is used, indicating that the intercalated bpy forms $[Co(bpy)_3]^{2+}$ and that the complex is arranged as a monolayer with its 3-fold axis perpendicular to the silicate sheet. The value of 13 Å corresponds to that of air-dried cobalt(II) montmorillonite. These products are also yellowish brown and show similar UV–visible diffuse-reflectance spectra and IR spectra irrespective of the ratios of the mixtures. These also indicate that the intercalated bpy forms $[Co(bpy)_3]^{2+}$. Although the existence of mono- and bis(bipyridine)cobalt(II) complexes ($[Co(bpy)_2]^{2+}$ and $[Co(bpy)]^{2+}$) has been observed,[15] these are not observed in UV–visible reflectance spectra. It is postulated that the intercalated bpy expands only some layers at first, with the remaining bpy tending to intercalate into the expanded interlayers preferentially. This occurs when the amount of bpy used for sample preparation is not enough to fully occupy the interlayer space.

Bipyridine was also intercalated into sodium and calcium montmorillonites both dried at 300 °C and air-dried. The basal spacings of all the washed products are 18.5 Å Infrared spectra show absorption bands corresponding to bpy, confirming its intercalation. The adsorption of bpy onto sodium and calcium montmorillonites from solution has been reported previously.[16-18] However, no detailed conformation of the intercalated bpy was described. In this study, the change in the *d*(001) values is in agreement with the radius of interlayer-exchangeable cations. In addition, there is a linear relationship between pyridine ring frequencies ($\nu_{C=C}$ and $\nu_{C=N}$) and the polarizing power of the interlayer-exchangeable cations (shown in Figure 3). The $[Mn(bpy)_3]^{2+}$–montmorillonite complex was also prepared by a solid–solid reaction between manganese(II) montmorillonite and bpy, and its frequencies were plotted together with those of the Na–, Ca–, and Co(II)–montmorillonite systems. The polarizing power is defined as Z/R, where Z and R denote charge and ionic radius of interlayer cations, respectively, and it has a direct relation to the strength of the electrostatic field around the cations. Judging from the above results, it was thought that the intercalated bpy was bound to the interlayer cations through nitrogen atoms to make an arrangement similar to that of $[Co(bpy)_3]^{2+}$.

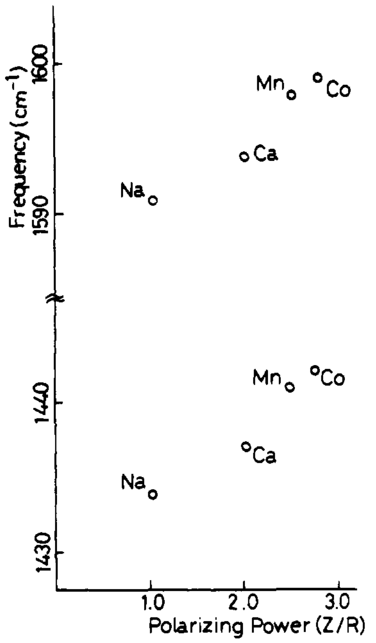

Figure 3. Relationships between polarizing power of the interlayer-exchangeable cations and $\nu_{C=N}$, $\nu_{C=C}$ frequencies of the montmorillonite–bpy intercalation compounds.

In addition to the results obtained by adsorption of bpy, we prepared the $[Co(bpy)_3]^{2+}$–montmorillonite complex by ion exchange of sodium montmorillonite with $[Co(bpy)_3]Cl_2$ in the solid state. A mixture of sodium montmorillonite dried at 300 °C and $[Co(bpy)_3]Cl_2$ (the amount was equivalent to the CEC of sodium montmorillonite) under solid–solid reaction was unsuccessful. However, the mixture of air-dried sodium montmorillonite and $[Co(bpy)_3]Cl_2$ gave an intercalation compound. The basal spacing and the IR spectrum of the product were in agreement with those of the product obtained by a normal method using an aqueous solution of $[Co(bpy)_3]Cl_2$. The ion exchange can be monitored by not only the change in the basal spacing but also by the formation of sodium halides as byproducts. Sodium chloride was observed in the XRD pattern of the product and no diffraction peaks due to $[Co(bpy)_3]Cl_2$ were detected. These results confirmed the intercalation of the $[Co(bpy)_3]^{2+}$ ion. The difference in the reactivity with the drying state cannot be explained well at this stage. The difference in basal spacings of air-dried sodium montmorillonite and the mineral dried at 300 °C (ca. 12.5 and 9.6 Å) is thought to be relevant. Finally, it can be concluded that solid–solid reactions can be applied for the preparation of various clay–complex intercalation compounds.

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