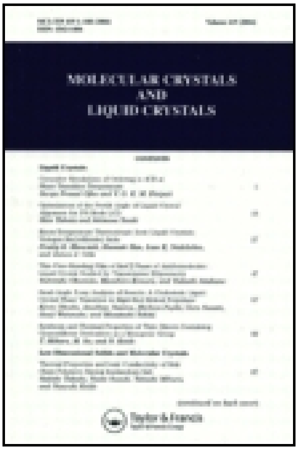

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Solid State Intercalation of 4,4′-Bipyridine into the Interlayer Space of Montmorillonites

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Solid State Intercalation of 4,4'-Bipyridine into the Interlayer Space of Montmorillonites

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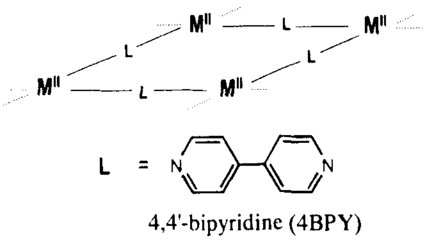
Intercalation of 4,4'-bipyridine into the interlayer spaces of cobalt(II), nickel(II) and copper(II)-montmorillonites by solid-solid reactions was investigated. The successful intercalation of 4,4'-bipyridine and the complex formation in the interlayer spaces of montmorillonites was confirmed by powder XRD (the change in the basal spacings) as well as IR and the thermal analysis of the products.

Keywords: intercalation; solid-solid reaction; montmorillonite; 4,4'-bipyridine

INTRODUCTION

Montmorillonite is a layered clay mineral which accommodates various organic substances in the interlayer space to form intercalation compounds.(1) These intercalation compounds have been studied widely from both fundamental and practical viewpoints.

Intercalation of cationic transition metal complexes in the interlayer space of montmorilllonite has been investigated in order to create novel inorganic-organic hybrid materials with specific functions including catalytic and optical ones.(2) There are two possible ways for the preparation of these intercalation compounds; one is cation exchange of the interlayer exchangeable cations and the other is the intercalation of ligands and the complex formation in the interlayer spaces. We have reported that a solid-state reaction is a useful way to prepare transition metal-2,2′-bipyridine complex montmorillonite intercalation compounds.(3) In this study, we apply the solid-solid reactions to the intercalation of 4,4′-bipyridine into Co(II), Ni(II) and Cu(II)-montmorillonites. The coordination of 4,4′-bipyridine leads to coordination polymers which are expected to exhibit novel functions such as molecular recognition.(4) The intercalation and the complex formation of 4,4′-bipyridine in the interlayer space of montmorillonite may lead novel two dimensional coordination polymer (Scheme 1) layered silicate hybrid materials.



SCHEME 1. Schematic model of two dimensional coordination polymer

EXPERIMENTAL

Materials

Sodium montmorillonite (Kunipia F, Kunimine Industries Co., cation exchange capacity (CEC) is 119 mequiv / 100 g of clay) was used as the host material. Cobalt(II), nickel(II) or copper(II)-montmorillonites was prepared from sodium montmorillonite by a conventional ion exchange reaction using an aqueous solution of cobalt(II), nickel(II) or copper(II) chloride. Quantitative cation exchange of the adsorbed cations was confirmed by the amounts of the adsorbed cations, 113, 115 and 118 mequiv / 100 g of clay for Co(II), Ni(II) and Cu(II)-montmorillonites, respectively.

Solid-solid reactions

The mixture of montmorillonite and 4BPY was ground with an agate mortar and a pestle at room temperature for 15-20 min. The molar ratio of 4BPY to the interlayer cations of montmorillonites was 3:1. After the reaction, the products were washed with n-hexane to remove unreacted 4BPY.

RESULTS AND DISCUSSION

The color of montmorillonites due to hydrated interlayer transition metal ions changed by the solid-solid reactions as shown in Table 1, suggesting the change in the coordination states of the interlayer exchangeable cations. The change in the XRD pattern of Ni(II)-montmorillonite by the reaction with 4BPY is shown in Figure 1 as a typical example. The basal spacings of the products increased to ca. 1.5 nm irrespective of the interlayer cations, indicating the expansion of the interlayer space by ca. 0.5 nm. Since the observed basal spacings of the products were close to those of hydrated montmorillonites, the increase in the basal spacing could be attributed to the hydration of montmorillonite during the solid-solid reactions. In order to eliminate this possibility, the products were dried in the sample holder in an XRD instrument at 60℃ under a reduced pressure.(5) The basal spacings of the products did not change by the heat treatment, while the basal spacings of the transition metal exchanged montmorillonites decreased as shown in Figure 1. This observation indicates that the increase in the basal spacings was caused by the intercalation of 4BPY.

TABLE 1 Color of the products

Host	Hydrated	After the reaction with 4BPY
Co(II)-montmorillonite	Pink	Brown
Ni(II)-montmorillonite	Green	Pale Green
Cu(II)-montmorillonite	Pale Blue	Blue

The formation of the intercalation compounds was confirmed by thermal analyses and infrared spectroscopy. In the DTA curves of the products, an endothermic peak due to melting of 4BPY was absent and an exothermic peak which accompanies a weight loss in the corresponding TG curve was observed at around 250-480℃ in each sample. The exothermic reactions were attributed to the oxidative decomposition of the intercalated 4BPY.

In the infrared spectra of the products, the absorption bands due to 4BPY were observed even after washing with n-hexane. The pyridine ring frequencies ($\nu_{C=C}$ and $\nu_{C=N}$) shifted depending on the polarizing power (6) of the interlayer exchangeable cations, confirming that the intercalated 4BPY coordinate to the interlayer cations.

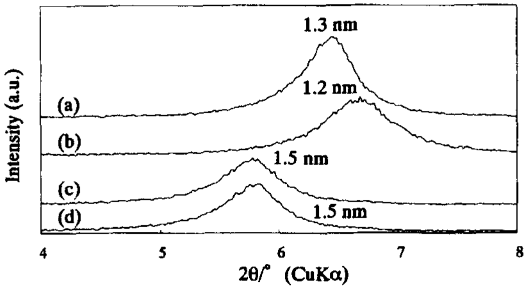


FIGURE 1. The XRD Patterns of (a) Ni-montmorillonite, (b) Ni-montmorillonite at 60℃, (c) Ni(II)-montmorillonite-4BPY and (d) Ni(II)-montmorillonite-4BPY at 60℃

The composition of the products was determined by CHN analysis to be ca. 2:1 (4BPY:interlayer cation), suggesting that the intercalated 4BPY form complex ions with the formula of ($[M(4BPY)_2]^{2+}$).

The coordination polymers with bridging organic ligands have extensively been investigated to prepare porous microstructures.(7) Since it seems to be very difficult to introduce presynthesized 4,4'-bipyridine-transition metal coordination polymers into the interlayer space, the intercalation of 4,4'-bipyridine and the complex formation in the interlayer space is a promising way to prepare two dimensional coordination polymer in the interlayer space of layered solids. Further studies on the preparation of intercalation compounds using bridging ligands with variable molecular structures and layered solids with different cation exchange capacities are now underway in order to construct two dimensional coordination polymer-layered silicate hybrid materials.

CONCLUSION

4,4′-bipyridine molecules have successfully been intercalated into the interlayer space of Co(II), Cu(II) and Ni(II)-montmorillonites by solid-solid reactions. The intercalated 4,4′-bipyridine molecules form complex cations with the interlayer cations.

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[5] See detailed experimental set up, H. Hashizume, S. Shimomura, H. Yamada, T. Fujita and H. Nakazawa, *Powder Diffraction,* **11,** 288 (1996).
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