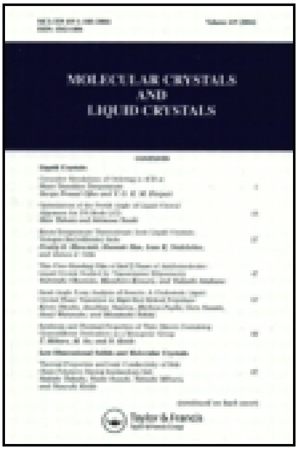

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Preparation of New Fibrous Organic-Inorganic Layered Compounds Derived from Zinc Hydroxyde

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A new preparation method of the fibrous organic-inorganic nanohybrids was established by the reaction of $Zn(OH)_2$ with various organic carboxylic acids. Interlayer spacings of the reaction products of $Zn(OH)_2$ with benzoic acid and *p*-phenyl azobenzoic acid were 1.46 and 2.04 nm, and these reaction products have layered structure. In IR spectra, new peaks of RCOO-Zn band appeared at around 1400 cm^{-1} and 1550 cm^{-1} indicating that hydroxyl groups reacted with organic carboxylic acids. SEM images of these reaction products showed fibrous morphology. The TEM image showed that the layer structure was constructed along the fiber direction.

Keywords: intercalation; self-assembly; organic-inorganic nanohybrid; layered compound; zinc hydroxide

INTRODUCTION

Incorporation of an organic molecule into a crystalline inorganic host lattice to form an intercalation compound can lead to organic-inorganic hybrid materials with highly ordered layered structures[1]. Recently, we have reported that $Zn(OH)_2$ reacted with organic oxychloride and organic carboxylic acids giving high ordered layered compounds[2, 3]. For the reaction of $Zn(OH)_2$ with bulky organic compounds such as benzoyl chloride or benzoic acid, fibrous organic-inorganic hybrids were obtained[2, 3]. In this paper, we have examined the reaction of $Zn(OH)_2$ with various bulky organic carboxylic acids such as *p*-phenyl azobenzoic acid leading to a new fibrous layered organic-inorganic nanohybrids. Furthermore, we have also examined the preparation of the fibrous compound by the reaction of $Cu(OH)_2$ with benzoic acid.

EXPERIMENTAL

A fibrous nanohybrid was prepared as follows. All organo derivatization reactions of $Zn(OH)_2$ with organic compounds [benzoic acid (99.5%, Kanto), *p*-phenyl azobenzoic acid (Guaranteed Reagent, Tokyo Kasei)] were carried out in the COOH/OH ratio of 0.5. For example, 0.2g (2.01×10^{-3}mol) of commercialized $Zn(OH)_2$ (99.0%, Aldrich) or synthesized $Zn(OH)_2$ was reacted with 2.01×10^{-3}mol of organic compounds in 10 ml of acetonitrile/water or acetone/water (the ratio was 1:1) for 5h under stirring at 333K.

After the reaction, the reaction products were filtered, washed by employing organic solvent to remove unreacted organic carboxylic acid and impurities, and dried under reduced pressure at normal temperature.

RESULTS AND DISCUSSION

SEM images of the reaction products of $Zn(OH)_2$ with benzoic acid or *p*-phenyl azobenzoic acid are shown in Figure 1(a) and (b), respectively. It shows that the reaction products have fibrous morphology.

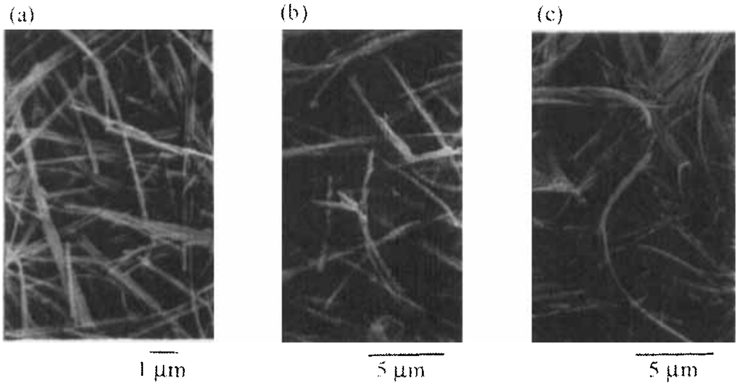

FIGURE 1 SEM images of the reaction products of (a) $Zn(OH)_2$ with benzoic acid, (b) $Zn(OH)_2$ with *p*-phenyl azobenzoic acid, and (c) $Cu(OH)_2$ with benzoic acid.

In the XRD patterns of the fibrous products of $Zn(OH)_2$ with benzoic acid or *p*-phenyl azobenzoic acid, new peaks were observed at 1.46 and 2.04 nm respectively as shown in Figure 2 (b) and (d). The *d*-values of zinc benzoate and benzoic acid were 1.06 and 1.10 nm, suggesting that the peaks of the reaction products of $Zn(OH)_2$ with benzoic acid were not those of zinc benzoate or benzoic acid. TEM image of the reaction product of $Zn(OH)_2$ with benzoic acid shows the product has a fibrous morphology (Figure 3). The thickness of the fiber was about 120 nm. The layer structure was constructed along the fiber direction. The TEM image showed that the layers were parallel to the axis of fiber.

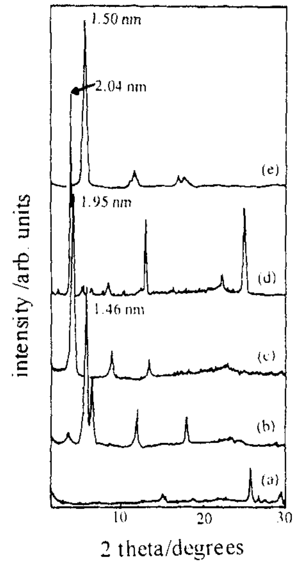

FIGURE 2 XRD patterns of (a) $Zn(OH)_2$, and the reaction products of $Zn(OH)_2$ with benzoic acid [(b) 1/2 and (c) 1/4 equivalent], and (d) *p*-phenyl azobenzoic acid, and (e) the reaction products of $Cu(OH)_2$ with benzoic acid.

When the IR spectra of the reaction products of $Zn(OH)_2$ with organic carboxylic acids were measured, the new peaks at near 1540 and 1400 cm^{-1} were observed (data not shown). The absorption at 1540 cm^{-1} is assigned to the asymmetric stretching vibration of carboxylate, and the absorption at 1400 cm^{-1} is assigned to the symmetric stretching vibration of carboxylate. These two peaks indicated the formation of RCOO-Zn bond.

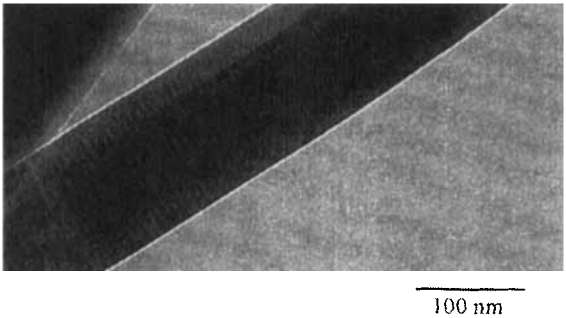

FIGURE 3 TEM image of the reaction product of $Zn(OH)_2$ with benzoic acid.

Thermal properties of the reaction products of $Zn(OH)_2$ with benzoic acid indicated two weight loss regions at 450 K (3.13%) and 570-720 K (46.9%) (data not shown). In the elemental analysis of the reaction products of $Zn(OH)_2$ with benzoic acid, the host/guest ratio was 0.93/1.07. The formula of the reaction product of $Zn(OH)_2$ with benzoic acid was calculated as $Zn(OH)_{0.93}(C_6H_5COO^-)_{1.07}$. We have estimated the expected weight loss in TG curve from the composition as 7.5% for the loss of OH group and 61% for the loss of benzoic acid. The values were roughly similar to those in TG measurement. Therefore, it was considered that the first weight loss (450K) corresponded to the dehydration of OH groups of $Zn(OH)_2$, and the second weight loss (570-720 K) corresponded to desorption of organic groups between the layers of $Zn(OH)_2$.

For the reaction product of $Zn(OH)_2$ with 1/4 molar equivalent amount (COOH/OH=0.25) of benzoic acid, the *d*-value in XRD pattern was 1.95 nm as shown in Figure 2 (c). The host/guest ratio of the reaction product was 1.57/0.43. The SEM image of the reaction product showed a plate-like structure. Furthermore, TEM image of the product showed the clear layer structures (data not shown). The *d*-value of $Zn_5(OH)_8(C_6H_5COO^-) \cdot 2H_2O$ was about 1.93 nm. The value roughly corresponded to the *d*-value of the plate-like compound obtained in this study. Therefore, we considered that the plate-like compound was $Zn_5(OH)_8(C_6H_5COO^-) \cdot 2H_2O$. When the plate-like compound reacted with benzoic acid further, fibrous compound was obtained which was confirmed by SEM image and XRD pattern of the reaction product. Moreover, the reaction product of the fibrous compound with an excess amount of carboxylic acid was the organic zinc salt. These results indicated that the morphology of the reaction product depended on the quantity of reacted organic compound.

It was considered that the first step of the reaction was a dehydration reaction between the OH groups of $Zn(OH)_2$ and RCOOH. When the amount of carboxylic acid was the COOH/OH ratio of 0.25, the reaction gave the mixture of HO-Zn-OH and RCOO-Zn-OH. And the $Zn_5(OH)_8(R\text{-}COO^-) \cdot 2H_2O$ was formed by gathering a RCOO-Zn-OH and HO-Zn-OH unit. When the amount of reacted carboxylic acid was the COOH/OH ratio of 0.5, the reaction gave the mixture of HO-Zn-OH, RCOO-Zn-OH, and/or RCOO-Zn-OCOR. The CdI_2-type layered compound, $Zn(OH)_x(R\text{-}COO^-)_y$ was formed by gathering those units. Moreover, further reaction of $Zn_5(OH)_8(R\text{-}COO^-) \cdot 2H_2O$ with organic carboxylic acid gave an CdI_2-like layered compound, $Zn(OH)_x(R\text{-}COO^-)_y$. The structure of $Zn_5(OH)_8(R\text{-}COO^-) \cdot 2H_2O$ consists of brucite-type $[Zn_3(OH)_8]^{2-}$ layers with 25% of the octahedral positions remaining unoccupied. Above and below the unoccupied octahedral positions, two further zinc ions per formula unit occupy tetrahedral positions[4]. However, the further reaction of $Zn_5(OH)_8(R\text{-}COO^-) \cdot 2H_2O$ with organic carboxylic acid occurred with a disruption of tetrahedral units by the dehydration reaction between the OH groups of tetrahedral positions. Therefore, we have considered that the further reaction of $Zn_5(OH)_8(R\text{-}COO^-) \cdot 2H_2O$ gave $Zn(OH)_x(R\text{-}COO^-)_y$ structure. When the amount of reacted carboxylic acid was the COOH/OH ratio of over 0.5, the organic zinc salt, i.e. $Zn(RCOO^-)_2$, was obtained. The cross-sectional area of one OH-Zn-OH unit[5] was calculated to be 0.96 nm^2. However, RCOO-Zn-OCOR is larger than 0.96 nm^2. Therefore, An excess amount of RCOO-Zn-OCOR might interfere the assembly to form the layered structure by steric repulsion and the organic zinc salt was formed.

In the reaction of $Zn(OH)_2$ with other bulky organic carboxylic acids such as cyclopentane carboxylic acid, a fibrous compound was obtained. Its interlayer spacing was 1.37 nm and about 45 % of hydroxyl groups were reacted.

Fibrous structures were also obtained by the reaction of $Zn(OH)_2$ with bulky aliphatic acids such as pivalic acid, isobutyric acid and cyclohexane carboxylic acid. Also in the reactions of $Zn(OH)_2$ with *p*-methyl or *p*-nitro substituted benzoic acids, fibrous compounds were obtained. For the reaction products of $Zn(OH)_2$ with various straight chain type aliphatic oxychloride or carboxylic acid, however, the fibrous compound were not obtained[2]. These results indicated that the fibrous morphology depended on the nature of the organic compounds. Furthermore, TEM images showed that the ends of the fibrous compound of $Zn(OH)_2$ with benzoic acid were curl-like shaped (data not shown). Therefore, we have suggested that the steric repulsion between bulky organic compounds in the layers of the fibrous compound[3].

It was already reported that benzoate anion was exchanged into layered $Cu(OH)_2$ giving the composition, $Cu(OH)_{1.5}(C_6H_5COO^-)_{0.5}$[6]. Its interlayer spacing was 1.57 nm. They have plate-like structures. An azo compound intercalated into the layered $Cu(OH)_2$ indicated reversible structural transformation and a change of drastic magnetic property[7]. We have also examined the preparation of a new fibrous layered compound by the reaction of $Cu(OH)_2$ with benzoic acid. SEM image showed that the reaction product of $Cu(OH)_2$ with benzoic acid was a fibrous morphology and was similar to that of $Zn(OH)_2$ with benzoic acid as shown in Figure 1 (c). In XRD pattern, the *d*-value of the reaction product of $Cu(OH)_2$ with benzoic acid was observed at 1.50 nm as shown in Figure 2 (e). We have considered that the fibrous structure of $Cu(OH)_2$ with benzoic acid was similar to those of $Zn(OH)_2$ with benzoic acid.

In this study, we have established a preparation method of new fibrous layered compounds. The present work shows the possibility to design optional layered materials.

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