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Preparation of New Organic-inorganic Nanohybrids by the Reaction of Metal Hydroxides with Organic Carboxylic Acids

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Layered organic-inorganic nanohybrids were obtained by the reactions of $Zn(OH)_2$, $Cu(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Mg(OH)_2$ or $Ca(OH)_2$ with various organic carboxylic acids. Structures of the products were similar to those of Layered Double Hydroxide (LDH) and Hydroxy Double Salts (HDS). Morphologies of the products were plate type or fibrous. It is clarified that interlayer spacing of the nanohybrids depended on the kinds of metal hydroxides and carboxylic acids.

Keywords: Layered organic-inorganic nanohybrid, Self-assembly, Intercalation, metal hydroxide

1. INTRODUCTION

We have already reported that layered structure can be prepared by the reaction of $Zn(OH)_2$ with carboxylic acid [1-7]. $Zn(OH)_2$ was amorphous, therefore, the reaction is self-assembly reaction of amorphous zinc hydroxide with organic carboxylic acid. This reaction is named as "organoderivatization reaction" because the organic compounds determine the structure of the hybrids.

The reaction is soft chemical reaction being carried out under mild conditions at near rt and the reaction of $Zn(OH)_2$ with carboxylic acid occurs smoothly compared to other preparation methods of layered compounds because the treatment such as calcinations and decarboxylation shouldn't be necessary in the case of $Zn(OH)_2$. It is clarified that, in the organoderivatization reaction, interlayer spacing and shape of the nanohybrid can be controlled.

In this study, reactions of various metal hydroxides with carboxylic acids were carried out and correlation between reaction conditions and morphology of the obtained nanohybrids was made clear.

2. EXPERIMENTAL

2. 1 Preparation of $Zn(OH)_2$

In this study, $Cu(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Mg(OH)_2$ and $Ca(OH)_2$ were commercial reagents, and $Zn(OH)_2$ was prepared in this study.

Preparation method of $Zn(OH)_2$ is as follows. 15.52g (5.22×10^{-2}mol) of $Zn(NO_3)_2 \cdot 6H_2O$ (99.0%) was dissolved in 300 ml of degassed distilled water. By adding 300ml of degassed 0.23M NaOH solution to $Zn(NO_3)_2$ solution at 277K, a white precipitate was obtained. Washed by using distilled water twice and dried for a few days at room temperature.

2. 2 Reaction of metal hydroxide with carboxylic acid

Reactions of metal hydroxides with organic carboxylic acids were carried out at 333K. In a typical reaction, 0.2g (2.01×10^{-3}mol) of $Zn(OH)_2$ was reacted with various quantity of carboxylic acids in water and acetonitrile for 5h.

3. RESULT AND DISCUSSION

3 .1 Reaction of various metal hydroxides with hexanoic acid

The reactions of $Zn(OH)_2$, $Cu(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Mg(OH)_2$ or $Ca(OH)_2$ with hexanoic acid were carried out. Preparation of layered compound was confirmed by XRD patterns of the product.

Layered structures were obtained in the reactions of $Zn(OH)_2$, $Cu(OH)_2$, $Co(OH)_2$, and $Ca(OH)_2$ with hexanoic acid as shown in Table I .

Table. I Reaction products of metal hydroxides with organic carboxylic acids

Metal		hexanoic acid	sebacic acid	benzoic acid
Hydroxide	ratio[a]	Interlayer spacing (nm)		
$Zn(OH)_2$	1:1	1.68	1.28	1.44
$Zn(OH)_2$	2:1	2.15,1.63	1.95	2.00, 1.47
$Zn(OH)_2$	4:1	2.16	1.95, 1.29	1.99
$Cu(OH)_2$	1:1	1.77	1.37, 1.10	1.49
$Cu(OH)_2$	2:1	1.78	1.39, 1.11	1.49
$Cu(OH)_2$	4:1	2.02	1.40	1.53
$Co(OH)_2$	1:1	1.50		1.53
$Co(OH)_2$	2:1	2.02, 1.52		1.52
$Co(OH)_2$	4:1	2.05		1.53
$Ni(OH)_2$	1:1		1.38	1.55
$Ni(OH)_2$	2:1		1.38	1.51
$Ni(OH)_2$	4:1		1.40	
$Mg(OH)_2$	1:1		1.83	1.81
$Mg(OH)_2$	2:1			
$Mg(OH)_2$	4:1			
$Ca(OH)_2$	1:1	2.04	1.61	1.28
$Ca(OH)_2$	2:1	2.04	1.60	
$Ca(OH)_2$	4:1		1.59	

a the molar ratio of $Zn(OH)_2$: carboxylic acid

When molar ratio of $Zn(OH)_2$: hexanoic acid was 1:1, interlayer spacing was 1.68 nm. By changing the molar ratio of $Zn(OH)_2$: hexanoic acid from 1:1 to 2:1 and 4:1, larger interlayer spacing, 2.2nm than 1.7nm was observed. Hexanoic acid is linear aliphatic mono-carboxylic acid.

The size of hexanoic acid and the value of layer expansion suggested that hexanoic acid was intercalated between the layers of $Zn(OH)_2$ forming bilayer structures. Interlayer spacing of 1.7nm was the similar value with that of Layered Double Hydroxide (LDH), and interlayer spacing of 2.2 nm was the similar value with that of Hydroxy Double Salt (HDS).

In the reactions of $Cu(OH)_2$ and $Co(OH)_2$, similar compounds with those of $Zn(OH)_2$ were obtained. However, in the reactions of $Ca(OH)_2$, large interlayer spacing was not observed.

3. 2 Reaction of various metal hydroxides with sebacic acid

Sebacic acid is linear aliphatic di-carboxylic acid. The reactions of $Zn(OH)_2$, $Cu(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$, $Mg(OH)_2$ or $Ca(OH)_2$ with sebacic acid were carried out. Various metal hydroxides except $Mg(OH)_2$ reacted with sebacic acid giving layered compounds. In the reaction of $Zn(OH)_2$, interlayer spacing increased to 1.3nm indicating the bridging structure of sebacic acid between the layers.

By increasing the ratio of $Zn(OH)_2$: sebacic acid from 1:1 to 2:1 and 4:1, larger interlayer spacing, 2.0nm than 1.3nm was observed. The results indicated the presence of two HDS structures. However, in the reactions of $Cu(OH)_2$, $Ni(OH)_2$, and $Ca(OH)_2$ with sebacic acid, one interlayer spacing for each metal hydroxide was obtained.

3 . 3 Reaction of various metal hydroxides with benzoic acid

Benzoic acid is aromatic carboxylic acid. All metal hydroxide reacted with benzoic acid giving layered structures. Only in the reactions of $Zn(OH)_2$, presence of two HDS structures was suggested from the peaks in XRD patterns. The reaction product of $Zn(OH)_2$ with benzoic acid in low metal hydroxide : benzoic acid ratio, fiber morphology was observed.

Similar fibrous structures were obtained even in the reactions of $Cu(OH)_2$ and $Co(OH)_2$ with benzoic acid as shown in Figure 1.

On the other hand, in the reaction product of $Zn(OH)_2$ with benzoic acid in high metal hydroxide : benzoic acid ratio, plate morphology was observed. In the reactions of $Mg(OH)_2$ or $Ca(OH)_2$, low ratio of metal hydroxide : benzoic acid was essential to obtain layered compounds.

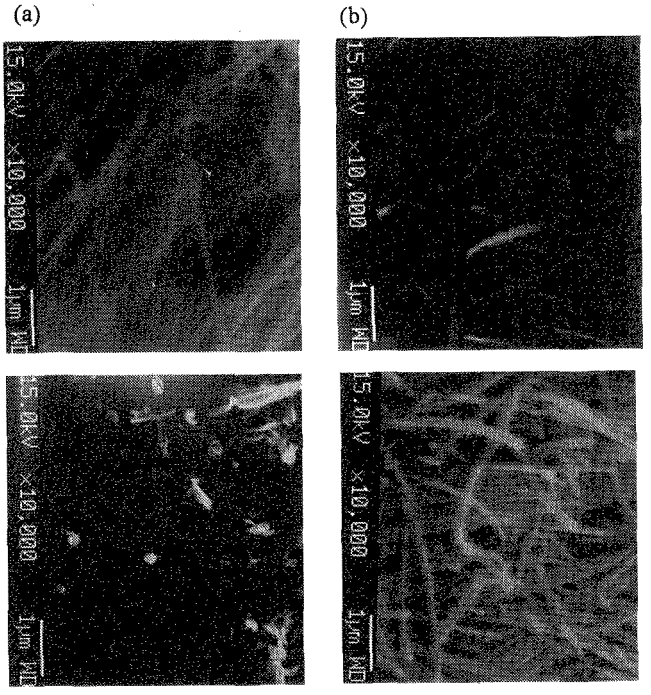

Figure 1 SEM images of the reaction products of (a) $Cu(OH)_2$ with benzoic acid ($Cu(OH)_2$: benzoic acid = 1 : 1), (b) $Cu(OH)_2$ with benzoic acid ($Cu(OH)_2$: benzoic acid = 4 : 1), (c) $Co(OH)_2$ with benzoic acid ($Co(OH)_2$: benzoic acid = 1 : 1), and (d) $Co(OH)_2$ with benzoic acid ($Co(OH)_2$: benzoic acid = 4 : 1).

3 . 4 Morphology of the reaction product of metal *hydroxide with carboxylic acid*

As described above, in the reaction of $Zn(OH)_2$ with benzoic acid, preparation of fibrous compound was confirmed. Benzoic acid is bulky compared to hexanoic and sebacic acids. Therefore, to obtain information on the preparation of fibrous structures, various carboxylic acids were reacted with $Zn(OH)_2$.

It was confirmed that bulky carboxylic acids shown in Figure 2 reacted with $Zn(OH)_2$ giving fibrous structures.

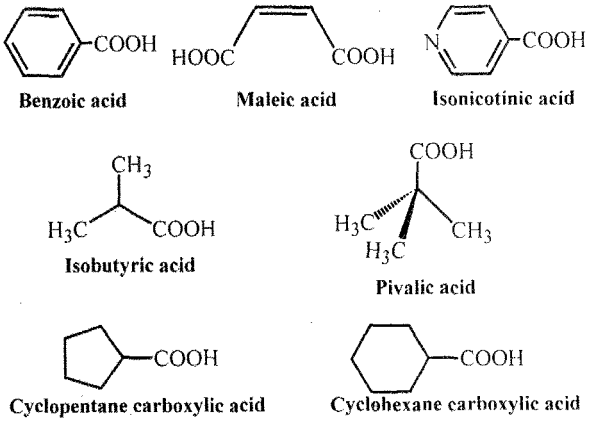

Figure 2 Bulky carboxylic acids reacted with $Zn(OH)_2$

Steric repulsion between organic carboxylic acids should cause curling of the layers giving fibrous structures as shown in Figure 3.

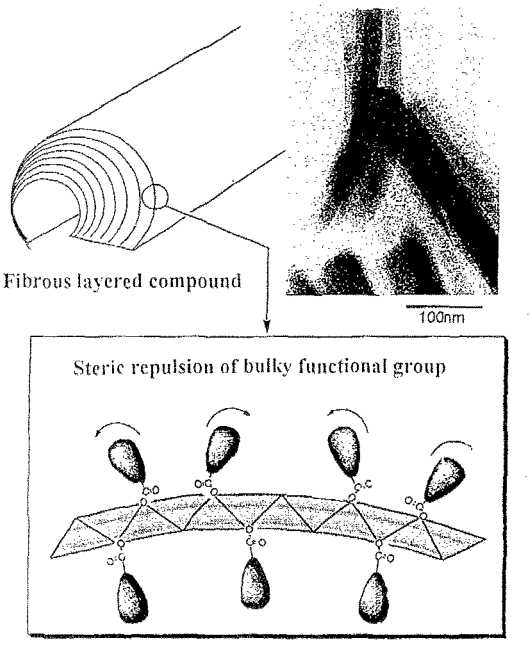

Figure 3 Speculative mechanism to give fibrous structures.

4 . CONCLUSIONS

In this study preparation of layered compounds was confirmed in the reactions of various metal hydroxides with organic carboxylic acids. It was also confirmed that fibrous compounds were prepared in the reactions of $Zn(OH)_2$, $Cu(OH)_2$ and $Co(OH)_2$ with bulky organic carboxylic acids such as benzoic acid. The self-assembly reaction contributes to obtain various organic-inorganic nanohybrids.

5 . ACKNOWLEDGMENTS

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