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PREPARATION OF ORGANIC-INORGANIC NANOHYBRIDS BY USING SELF-ASSEMBLY REACTION OF AMORPHOUS METAL HYDROXIDES WITH ORGANIC COMPOUNDS.

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Organic-inorganic intercalation compounds were prepared by the self-assembly reaction of amorphous metal hydroxides including zinc hydroxide, copper hydroxide and cobalt hydroxide with carboxylic acids or substituted phenols. By the reaction, layered compounds modified by organic compounds were prepared. Interlayer spacing of the hybrids depended on the size and the quantity of reacted organic compounds. The layer compounds had different morphology depending on the kind of carboxylic acids. By the reaction with bulky organic carboxylic acid, fibrous compounds were prepared which were confirmed by SEM images.

Keyword: self assembly, layer, zinc hydroxide, substituted phenol.

1.Introduction

We have developed a new preparation method for organic-inorganic nanohybrids by the reaction of $Zn(OH)_2$ with various organic carboxylic acids as shown in Fig.1 [1]. Their layered structures are similar to layered double hydroxides (LDH). The interlayer spacing of the reaction products of $Zn(OH)_2$ with straight chain type mono carboxylic acids were 1.09nm to 4.33nm, and those of $Zn(OH)_2$ with di-carboxylic acids were 0.71 nm to 1.48nm. These values depended on the length of the organic compounds and the number of carboxyl groups. The SEM images of the reaction products of $Zn(OH)_2$ with carboxylic acids were plate like morphology similar to the LDH, except the fibrous morphology of the reaction product of $Zn(OH)_2$ with benzoic acid.

In this study, we tried to understand the reaction of metal hydroxide with substituted phenols.

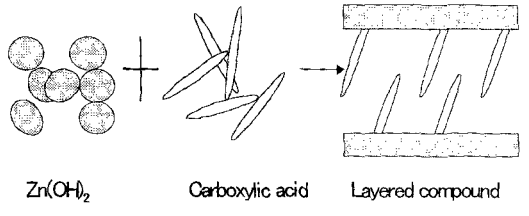

Fig.1 Image of self-assembly reaction.

2.Experimental

2.1.Preparation of $Zn(OH)_2$

$Zn(OH)_2$ was prepared by the following method. A solution containing $Zn(NO_3)_2 \cdot 6H_2O$ in deaerated water was added over 0.5 h to stirred deaerated water containing NaOH at 277K. The reactant was filtered and washed. The resulting white solid was dried at 333K.

2.2.Preparation of organic-inorganic nanocomposite

In typical conditions metal hydroxide such as $Zn(OH)_2$ and organic compounds such as substituted phenol were reacted at 333K for 5 h in water. After the reaction, the product was filtered and washed with water to remve unreacted acid. After then the product was dried under reduced pressure.

2.3.Characterization

X-ray powder diffraction (XRD) data ware collected on a Rigaku powder diffractmeter, using CuK α radiation at 40kV and 20 mA between 1.8° and 50° . FT-IR spectra were recorded on samples pressed into KBr disks using a Horiba FT-200. Thermal analyses (TG/DTA) of samples were performed on a Seiko SSC5000 thermal analysis system (heating rate : 10K/min, in the flow of N_2 gas). The morphology and microstructhre of the samples were examined using a scaninning electron microscope (JEOL,JSM-6330).

3.Results and discussion

3.1.Reaction of $Zn(OH)_2$ with substituted phenol

No reaction was observed between zinc hydroxide and phenol. However zinc hydroxide reacted with substituted phenols. The XRD patterns of reaction products of $Zn(OH)_2$ with substituted phenols are shown in Fig.2. $Zn(OH)_2$ doesn't have clear peaks at lower than 20 ° . The new peaks in XRD appeared by the reaction with substituted phenol as shown in Fig.2(a). The value of the reaction products of $Zn(OH)_2$ with *p*-nitrophenol , 2,6-dichlorophenol, and 2,4,6-trichlorophenol were 1.09nm, 1.42nm, and 1.44nm. These peaks were not those of phenols indicating the presence of the reaction of $Zn(OH)_2$ with phenols and Fig.2 indicated the production of layered compound.

The thermal analyses curves of $Zn(OH)_2$, *p*-nitrophenol, and reaction products were shown in Fig3.

A weight loss of *p*-nitrophenol alone was observed up to 120℃ as shown in Fig.3(a). For $Zn(OH)_2$, a weight loss was observed up to 110℃. This weight loss corresponded to the reduction of H_2O. For the reaction product of $Zn(OH)_2$ with *p*-nitrophenol, two weight loss regions were observed between 160℃ and 400℃ as shown in Fig.3(c). It was considered that the first weight loss near 160℃ corresponds to the condensation of the OH groups of $Zn(OH)_2$ and desorption of organic groups which reacted on the outer surface of $Zn(OH)_2$. The second weight loss between 280 ℃ and 400 ℃ corresponded to desorption of the *p*-nitrophenol between the layers of $Zn(OH)_2$[2]. Therefore, the reaction product of $Zn(OH)_2$ with *p*-nitrophenol was more stable thermally than that of *p*-nitrophenol itself.

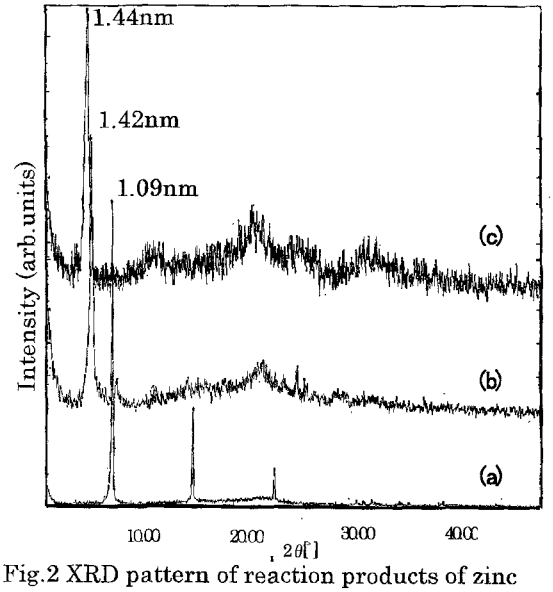

Fig.2 XRD pattern of reaction products of zinc hydroxide with (a)*p*-nitrophenol, (b)2,6-dichrolophenol, and (c)2,4,6-trichlorophenol

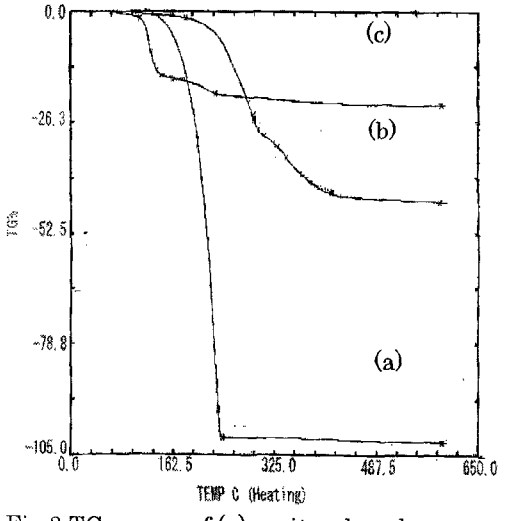

Fig.3 TG curves of (a) *p*-nitrophenol, (b)reaction product of zinc hydroxide with *p*-nitrophenol, and (c)zinc hydroxide.

The IR spectra of $Zn(OH)_2$, *p*-nitrophenol, and the reaction product of $Zn(OH)_2$ with *p*-nitrophenol were shown in Fig.4 In the spectra of the reaction product of $Zn(OH)_2$ with *p*-nirophenol, the C-O vibration(▲) at near 1200cm^{-1} of *p*-nirophenol decreased. Its suggested that hydroxyl groups reacted with and free movement of organics was prevented.

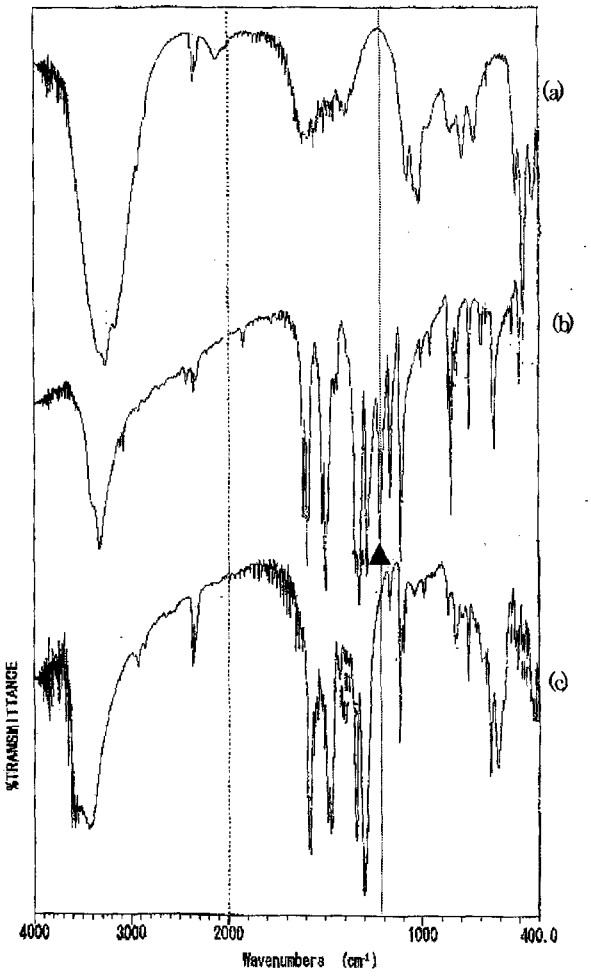

Fig. 4 IR spectra of (a)zinc hydroxide, (b)*p*-nitrophenol and (c)reaction product of zinc hydroxide with *p*-nitrophenol.

SEM images of reaction products of $Zn(OH)_2$ with the substituted phenols were shown in Fig.5. The reaction products of $Zn(OH)_2$ with *p*-nitrophenol was a plate-like structure. This plate like morphology was quite similar to that of the LDH. However, the reaction products of $Zn(OH)_2$ with 2,6-dichlorophenol, and with 2,4,6-trichlorophenol were fibrous structures. We have already reported that reaction products of $ZnOH)_2$ with some carboxylic acid was fibrous structure. Therefore, it is considered that the fibrous of reaction products of $Zn(OH)_2$ with substituted phenol was formed by similar mechanism of those carboxylic acids with $Zn(OH)_2$.

The reaction product of $Zn(OH)_2$ with carboxylic acid was fibrous structure, when the reaction products was prepared by metal hydroxide with organic acid. So it was suggested that the steric repulsion between organic compounds between the layers determined the morphology.

3.2.Reaction of p-nitrophenol with $Co(OH)_2$, and $Cu(OH)_2$

We have reported the reaction of carboxylic acid with various metal hydroxide. So we studied reaction of substituted phenol with copper hydroxide and cobalt hydroxide. As the result, cobalt hydroxide didn't react with p-nitrophenol. However XRD pattern of reaction product of copper hydroxide with p-nitrophenol showed a new peak as shown in fig.6.

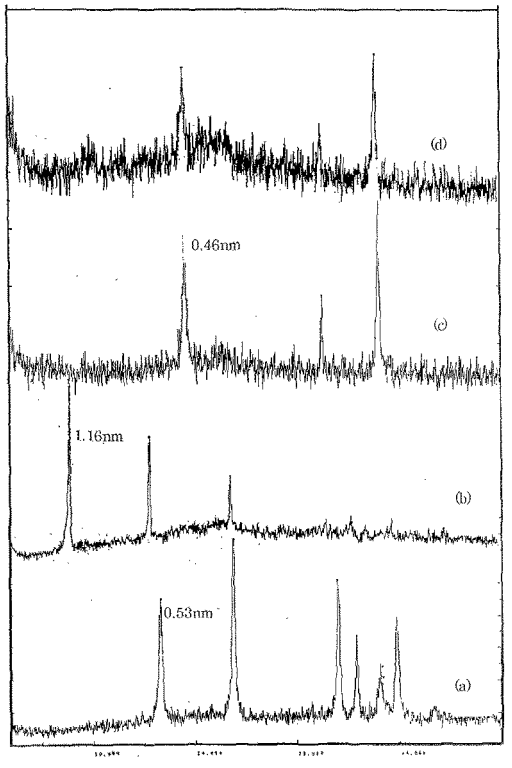

Fig.6 XRD patterns of (a)$Cu(OH)_2$, (b)reaction product of $Cu(OH)_2$ with *p*-nitrophenol, (c)$Co(OH)_2$, and (d)reaction product of $Co(OH)_2$ with *p*-nitorophenol

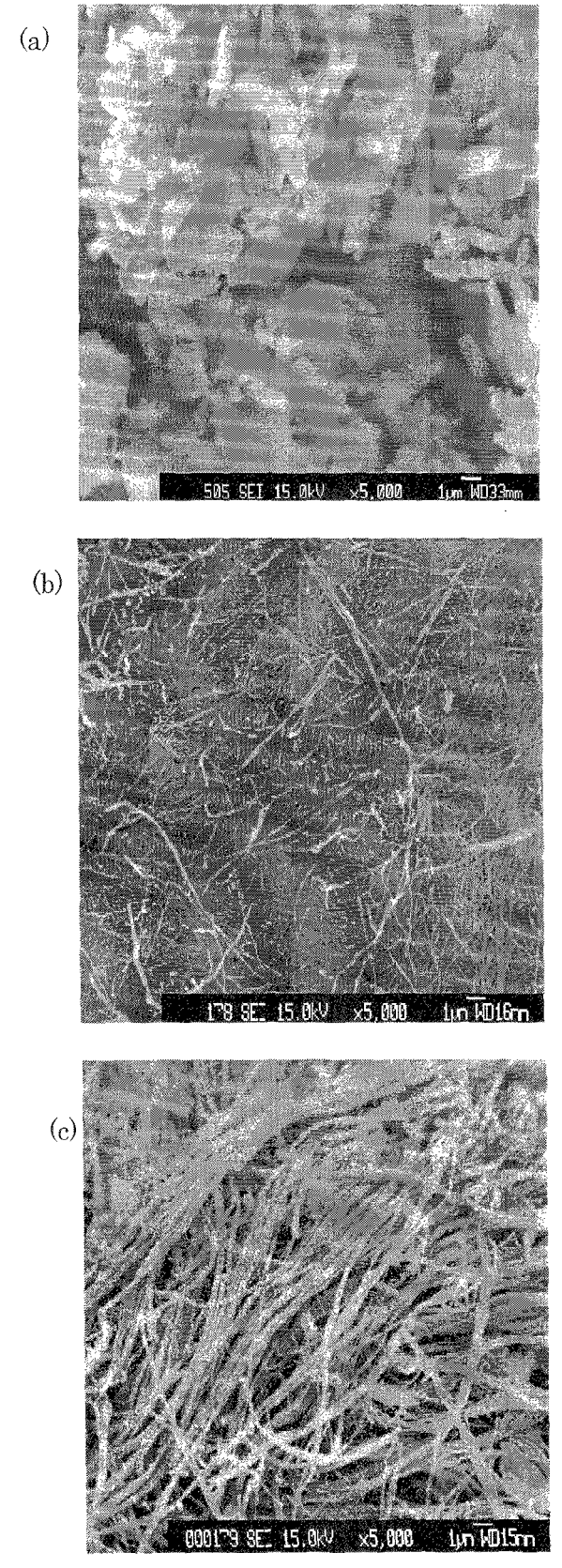

Fig.5 SEM images of reaction products of $Zn(OH)_2$ with (a)*p*-nitrophenol, (b)2,6-dichlorophenol, and (c)2.4.6-trichlorophenol

4. Conclusion

We prepared organic-inorganic nano composites by the reaction of $Zn(OH)_2$ with p-nitrophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol. SEM image of reaction product of $Zn(OH)_2$ with *p*-nitrophenol indicated plate-like structure. IR and TG spectra showed that the product was nano composite. SEM images of the reaction products of $Zn(OH)_2$ with 2,6-dichlorophenol or 2.4.6-trichlorophenol indicated fibrous structures.
We also confirmed that $Cu(OH)_2$ reacted with p-nitrophenol.

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