

Preparation of a new organic-inorganic nanocomposite by surface modification with inorganic compound

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We have examined a new surface modification reaction of metal hydroxide such as $Zn(OH)_2$ with organic compound. New surface modified inorganic compounds were prepared by the reaction of $Zn(OH)_2$ with organic oxychlorides. The IR spectrum of $Zn(OH)_2$ fairly decreased by the reaction with oxychloride and the peaks of COO-Zn bond were observed. It was confirmed by XRD and SEM measurements that the reaction products with aliphatic oxychlorides were layer composites. The layer structure were similar to those of the layered double hydroxides (LDHs). However, the reaction products of $Zn(OH)_2$ with benzoylchloride were crystalline forms of "fiber-shape like".

1. INTRODUCTION

By incorporation of a molecule into a crystalline inorganic host lattice, intercalation compounds are obtained as ordered materials. The metal phosphonates are useful for organizing molecules into lamellar structures. We have already reported that new surface modified inorganic layer compounds were prepared.¹ In the compounds the surface of the Zn/Al layered double hydroxides (LDHs) was

modified by the reaction with organic oxychloride and the compound was well organized inorganic - organic hybrid. LDH is inorganic layer compound and the LDH layer has positive charge. Therefore, It is an anion exchangeable clay. The surface modified LDH has also anionic compound between the layers. Recently, we have succeeded to prepare new surface modified inorganic layer compounds in which neutral amorphous compound, $Zn(OH)_2$, was reacted with organic oxychloride as shown in Fig. 1.² Not only di-oxychlorides but also mono-oxychlorides reacted with $Zn(OH)_2$ giving surface modified layer compounds. They were different from the surface modified Zn/Al LDH because they do not need to include any anionic compound between the layers. In this study, further reactions of $Zn(OH)_2$ were carried out.

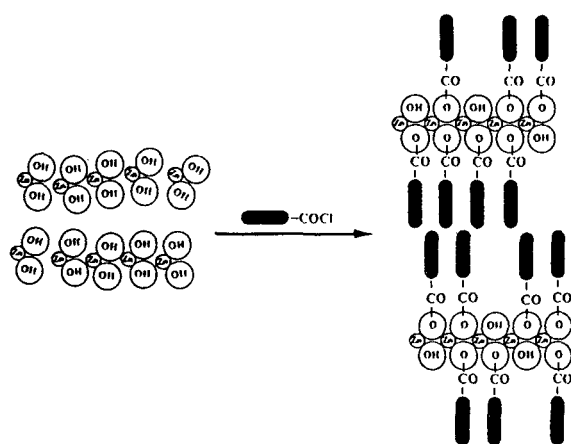


Fig.1 Preparation of surface modified $Zn(OH)_2$ with organic oxychloride to give inorganic-organic nanocomposites.

2. EXPERIMENTAL

2.1. Surface modification of metal hydroxides with organic compounds

0.2g (2.01 mmol) of zinc hydroxide (Aldrich, 99%) and 0.2g (3.43 mmol) of magnesium hydroxide (Wako, 97%) were reacted with 20% or 40% equivalent quantity of organic acid chlorides in acetonitrile for 5hr under stirring at 60°C. After the reaction, these reaction products were filtered and washed with acetonitrile to remove unreacted acid

chloride and impurities. After then these surface modified compound were dried under reduced pressure.

2.2. Characterization

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku powder diffractometer unit, using $\text{CuK}\alpha$ (filtered) radiation ($\lambda=0.154$ nm) at 40 kV and 20mA between 1.8 and 50° . FT-IR spectra (KBr disc method) were recorded on a Horiba FT-200. Thermal analyses (TG/DTA) of samples (5-10 mg) were performed on a Seiko SSC5000 thermal analysis system (heating rate: $10^\circ\text{C}/\text{min}$, in flowing N_2).

3. RESULT AND DISCUSSION

The XRD profile of $\text{Zn}(\text{OH})_2$ is shown in Fig. 2 (a). No clear peaks were observed in the XRD pattern of $\text{Zn}(\text{OH})_2$, as received. By the reaction of a small excess of amorphous $\text{Zn}(\text{OH})_2$ with suberoylchloride

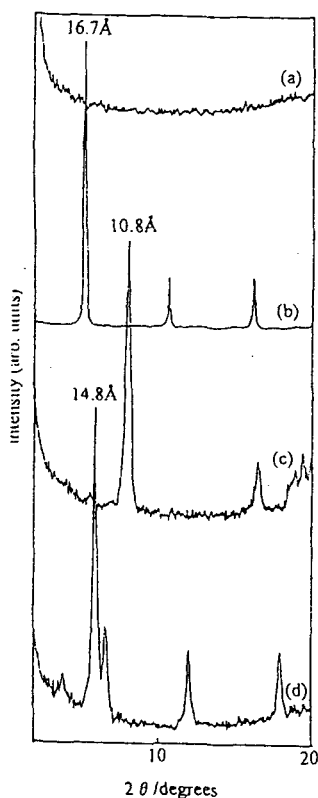


Fig.2 XRD patterns of (a) $\text{Zn}(\text{OH})_2$, and the reaction products of $\text{Zn}(\text{OH})_2$ with (b) hexanoylchloride, (c) suberoylchloride, and (d) benzoylchloride.

($\text{ClCO}(\text{CH}_2)_6\text{COCl}$) in acetonitrile, crystalline product was obtained. The interlayer spacing was 10.8\AA . The XRD peaks of the reaction products were different from those of organic di-oxychloride, and almost similar to those of the surface modified Zn/Al LDH in which the Zn/Al LDH was reacted with organic oxychloride. Similar XRD peaks to those of the surface modified Zn/Al LDHs were observed in the reaction products of $\text{Zn}(\text{OH})_2$ with various kind of oxychlorides, as shown in Table 1.

The IR spectra of the surface modified $\text{Zn}(\text{OH})_2$ by the organic oxychlorides were shown in Fig. 3. OH absorption at near 3500 cm^{-1} for $\text{Zn}(\text{OH})_2$ fairly decreased by the reaction with organic oxychlorides and new peaks appeared around 1540 and 1400 cm^{-1} . The peaks at 1400 cm^{-1} and 1550 cm^{-1} were assigned to the symmetric stretching vibration of carboxylate. These two peaks indicates the formation of COO-Zn bond. Also, in various surface modified

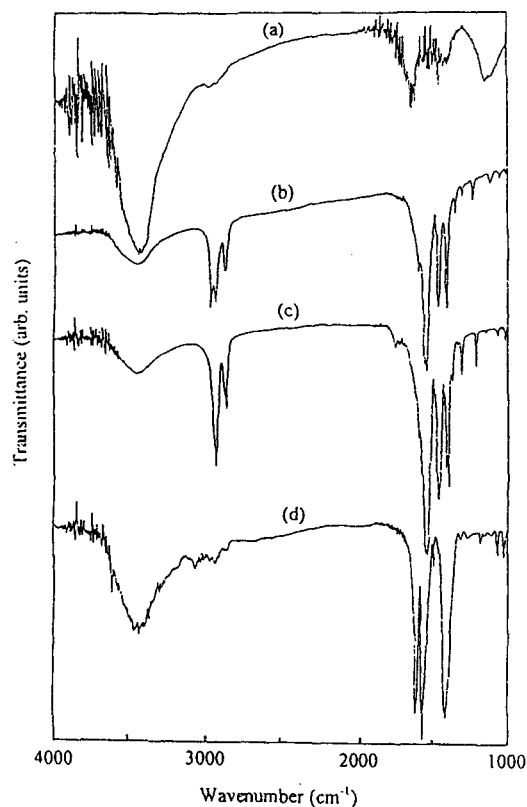


Fig.3 IR spectra of (a) $\text{Zn}(\text{OH})_2$, and the reaction products of $\text{Zn}(\text{OH})_2$ with (b) hexanoylchloride, (c) suberoylchloride, and (d) benzoylchloride.

Table 1 Surface modified zinc hydroxide with organic oxychlorides, $Zn(OH)_x(O-G)_y$ or $Zn(OH)_x(O-G-O)_z$

acid chloride	size(Å)	d-value (Å)				x	y	z
		acid	OH-LDH	LDH	$Zn(OH)_2$			
butanoylchloride	4.7	----	11.8		11.9	0.31	1.69	----
						(C, 32.94; H, 4.80%)		
hexanoylchloride	7.2	----	16.1		16.7	0.58	1.42	----
						(C, 42.80; H, 6.49%)		
benzoylchloride	6.1	10.9	11.2	15.4	14.6	1.00	1.00	----
						(C, 41.26; H, 2.83%)		
phenylacetylchloride	6.1	14.2	15.4		15.3	0.46	1.54	----
						(C, 52.57; H, 3.88%)		
p-phenylazobenzoylchloride	11.6	15.7	26.7	22.8	26.7	1.19	0.81	----
						(C, 47.23; H, 3.07%)		
adipoylchloride	6.4	6.8	7.7	14.8	8.3	0.04	----	0.98
						(C, 34.10; H, 3.83%)		
suberoylchloride	8.9	8.9	10.7		10.8	0.54	----	0.73
						(C, 34.89; H, 4.29%)		
sebacoylchloride	11.4	11.2	12.8	18.8	12.8	0.50	----	0.75
						(C, 40.50; H, 5.41%)		
dodecanedioylchloride	14.0	13.8	15.2		14.8	0.52	----	0.74
						(C, 43.82; H, 6.04%)		

nanocomposites, the IR absorption peaks of carboxylic acid or dimer of the guests were not observed. These results indicate that $Zn(OH)_2$ reacted with organic oxychlorides giving surface modified layered compounds. The interlayer spacings of the reaction products from di-oxychlorides, $Zn(OH)_x(O-G)_y$, increased in proportion to the methylene chain length, and the same tendency was observed in the case of the reaction products from mono-oxychlorides, $Zn(OH)_x(O-G)_y$, as shown in Table 1. However, the interlayer spacings of $Zn(OH)_x(O-G)_y$ were larger than those of $Zn(OH)_x(O-G-O)_z$. It is considered with their molecular sizes that reaction products from mono-oxychlorides have bilayer structures. On the other hand, the products from di-oxychlorides were of bridging structures. On these surface modification reactions by the addition of an excess amount of organic acid chlorides, the product of $Zn(OH)_2$ was dissolved in acetonitrile. By evaporation of the acetonitrile, a powder product was obtained. The IR spectrum and XRD profile of the powder have suggested the presence of surface modified $Zn(OH)_2$ and carboxylic acid. Whereas, XRD peaks corresponding to the layer structures were not observed. It is considered that the layer structure of surface modified $Zn(OH)_2$ is broken by

hydrochloric acid generated in the reaction. Also, we have examined the same reaction with oxychloride as for the other metal hydroxides, $Mg(OH)_2$ and $Al(OH)_3$. We have already reported that water-treated Zn/Al LDHs react with organic oxychlorides to give a surface modified LDHs.¹ They were different from those of intercalation compounds of organic carboxylate anions as shown in Table 1.^{3,4} Furthermore, we were not able to obtain water-treated Mg/Al LDHs, and it hardly reacted with organic oxychloride. $Al(OH)_3$ did not react with oxychlorides. $Mg(OH)_2$ reacted with oxychlorides. However, the decrease of the OH group adsorption of $Mg(OH)_2$ at IR spectrum was small by the reaction. And the XRD peaks of the reaction product of $Mg(OH)_2$ with organic oxychloride were not clear.

The elemental analysis of these surface modified $Zn(OH)_2$ were shown in Table 1. In the cases of aliphatic oxychlorides, 71% to 98% of OH groups of $Zn(OH)_2$ reacted with the oxychlorides. However, in the cases of aromatic oxychlorides, 40% to 77% of OH groups of $Zn(OH)_2$ reacted. The amounts of reacted OH groups of $Zn(OH)_2$ with aromatic oxychlorides were smaller than those of aliphatic oxychlorides. The aromatic oxychlorides were bulky molecules. Therefore, it has been considered that

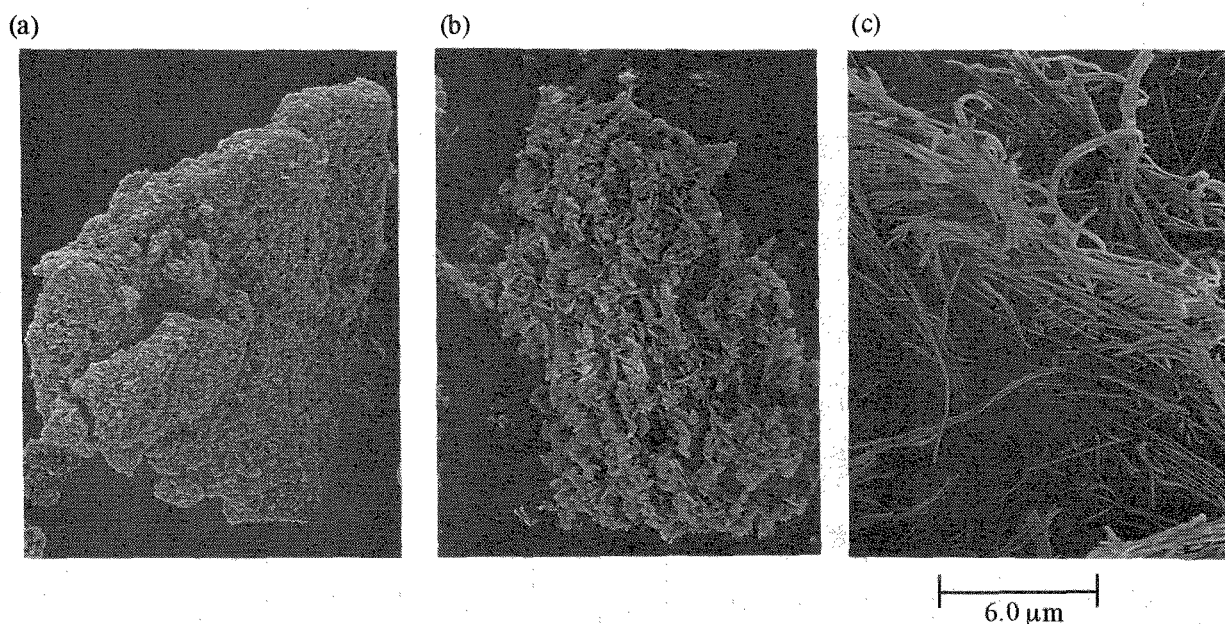


Fig.5 SEM images (5000 \times magnification) of (a) $\text{Zn}(\text{OH})_2$, (b) the reaction products of $\text{Zn}(\text{OH})_2$ with suberoyl chloride, and (c) the reaction products of $\text{Zn}(\text{OH})_2$ with benzoyl chloride

steric repulsion among aromatic oxychlorides occurred more than those of aliphatic oxychlorides.

The thermal behavior of $\text{Zn}(\text{OH})_2$, suberoylchloride, and the reaction products was measured by TG/DTA. 20% weight of $\text{Zn}(\text{OH})_2$ decreases up to 60 °C, suggesting the evolution of absorbed water. Only TG analysis of suberoylchloride shows weight loss between 150 and 260 °C. In contrast, it was confirmed that the reaction products from suberoylchloride were observed between 360 and 540 °C, and were more thermally stable than that of oxychloride itself. The same phenomenon was observed for other reaction products from oxychlorides. SEM images indicate that the clear plate crystals were obtained by the reaction of $\text{Zn}(\text{OH})_2$ with suberoylchloride as shown in Fig. 5. The similar plate crystals were obtained for all the reaction products of $\text{Zn}(\text{OH})_2$ with various kinds of organic oxychlorides. The plate crystals showed the quite similar feature to those of the LDHs. Particularly, the reaction products of $\text{Zn}(\text{OH})_2$ with benzoylchloride were very interesting, which was obtained as a crystalline form of fiber-shape like. The structure of Zinc benzoate ($[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2]_x$) was already reported in which the d-spacing of Zinc benzoate was 11.0 Å and the crystalline belonged to monoclinic.⁵ The d-value of the reaction products of $\text{Zn}(\text{OH})_2$ with benzoylchloride in this study was

14.8 Å. Therefore, it was considered that the crystal structure of the reaction products of $\text{Zn}(\text{OH})_2$ with benzoylchloride was different from the structure of Zinc benzoate. It is suggested that the crystal structure of reaction products from benzoylchloride were rhombic or trigonal, different from the hexagonal crystalline form. Distortion by the steric interaction derived from benzene ring might cause such a different feature.

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