

Novel Preparation Method for Organic-Inorganic Layered Compounds by the Organo Derivatization Reaction

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We have established a preparation method of new organic-inorganic compound by the organo derivatization reaction of $Zn(OH)_2$ with various organic oxychlorides. These reaction products were confirmed as layer structures by XRD measurement and similar to the reaction products of layered double hydroxide (LDH) with organic oxychlorides. Interlayer spacing of the reaction products of $Zn(OH)_2$ with di-oxychlorides was 0.71 nm to 1.48 nm, and those of $Zn(OH)_2$ with mono-oxychlorides were 1.19 nm to 2.67 nm. They depended on each molecular size of organic compound. In IR spectra, new peaks appeared at around 1400 cm^{-1} and 1550 cm^{-1} indicating formation of RCOO-Zn band by the reaction of hydroxyl groups of $Zn(OH)_2$ with organic oxychlorides. SEM images of the reaction products of $Zn(OH)_2$ with benzoyl chloride showed that the reaction products were fibrous morphology. Incorporation of photochromic compound into the layered compound was attained and photo chemical property of the reaction product was deferent from those of photochromic compound itself.

Keywords: Surface modification, Organic-inorganic nanohybrid, $Zn(OH)_2$, Intercalation, Self-organization

1. INTRODUCTION

Intercalation of an organic molecule into a crystalline inorganic host lattice to form an intercalation compound can lead to high ordered materials.[1] It has been well known that the Layered Double Hydroxide (LDH) is an anion exchangeable clay which undergoes anion exchange intercalation reactions with guests such as organic acids and inorganic anions. Many organic intercalates into the LDHs are known.[2] It is possible to express new function such as photo functional material, separation material, and catalyst etc.[3]

Chemical surface modification of inorganic compounds has been extensively studied to change their chemical and/or physical properties. We have already prepared the surface modified inorganic layered compounds in which the surface of the Zn/Al LDH was modified by the reaction with organic oxychloride.[4] Furthermore, we have reported that organic-inorganic nanohybrids were prepared by the reaction of $Zn(OH)_2$ with aliphatic oxychlorides.[5] The interlayer space of these compound is hydrophobic, and it was self-ordered inorganic-organic hybrids which was formed by the help of organic molecules.

In this paper, we have prepared and characterized new layered organic-inorganic nanohybrids by the reaction of $Zn(OH)_2$ with various organic oxychlorides. We have also examined that incorporation of dye compound into these organic-inorganic nanohybrids.

2. EXPERIMENTAL SECTION

2.1 Preparation of $Zn(OH)_2$

$Zn(NO_3)_2 \cdot 6H_2O$ (5.22×10^{-2} mol) was dissolved in 300 ml of degassed distilled water. By adding 300 ml of degassed 0.23M NaOH solution to $Zn(NO_3)_2$ solution at 277K, a white precipitate was obtained and stirring for 1 h at 277K. The precipitate was washed using distilled water 2 times and dried for 24h at 333K. In XRD measurement, the product was identified as β - $Zn(OH)_2$.

2.2 Organo derivatization reaction of $Zn(OH)_2$ with organic oxychlorides.

$Zn(OH)_2$ (2.01×10^{-3} mol) was reacted with 40 % equivalent quantity of organic oxychlorides in 3 or 5 ml of acetonitrile or ether for 5h under stirring at 333K. When $Zn(OH)_2$ was reacted with 40 % equivalent quantity of benzoyl chloride, the reaction product was dissolved in solvent. Therefore, the reaction was carried out by using 20% equivalent quantity of benzoyl chloride. After the reaction, all reaction products were filtered, washed with employing solvent to remove unreacted organic oxychlorides and impurities, and dried under reduced pressure at normal temperature.

2.3 Incorporation of dye compound into layered compound

$Zn(OH)_2$ (2.01×10^{-3} mol) was reacted with 40 % equivalent quantity of organic oxychlorides

in 5 ml of saturated nitrobenzene solution of thioindigo for 5h under stirring at 333K. After the reaction, they were filtered, washed, and dried as mentioned above.

2.4 Characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku powder diffractometer unit, using $\text{CuK}\alpha$ (filtered) radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV and 20 mA between 1.8 and 50° . FT-IR spectra (KBr disc method) was recorded on a Horiba FT-200. Thermo-gravimetric analysis (TG) and differential thermal analysis (DTA) of powdered samples up to temperatures of 873K were carried out at a heating rate of 10 K/min in flowing N_2 using a Seiko SSC 5000 thermal analysis system. Scanning electron microscopy (SEM) was performed with a JOEL JSM-5300, operating at 20 kV.

3. RESULTS AND DISCUSSION

3.1 Characterization of the reaction product of $\text{Zn}(\text{OH})_2$ with organic oxychloride.

Thermal characteristics of the reaction products of $\text{Zn}(\text{OH})_2$ with organic oxychlorides were determined by TG analysis. The TG curve of all reaction products indicate that the products were more stable thermally than those of organic compounds themselves.

Fig. 1 shows that interlayer spacing of the reaction products of $\text{Zn}(\text{OH})_2$ with n-hexanoyl chloride ($\text{CH}_3(\text{CH}_2)_4\text{COCl}$), suberoyl chloride ($\text{ClCO}(\text{CH}_2)_6\text{COCl}$), and benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$) were 1.67, 1.08, and 1.48 nm, respectively. The XRD peaks of these reaction products were different from those of carboxylic acids. By the intercalation reaction of sebacic acid with calcined Zn/Al LDH [6], the interlayer spacing increased to 1.88 nm as shown in Table I. The value is larger than the spacing of 1.28 nm for the surface modified LDH and the reaction product of $\text{Zn}(\text{OH})_2$ with sebacyl chloride. They were

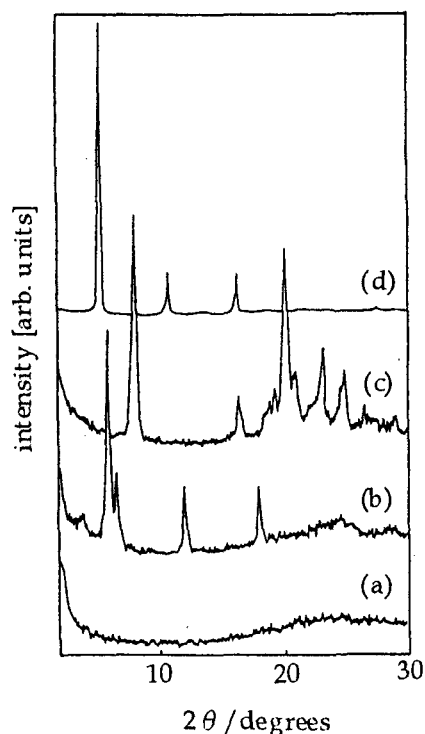


Fig. 1 XRD patterns of (a) $\text{Zn}(\text{OH})_2$, the reaction product of $\text{Zn}(\text{OH})_2$ with (b) n-hexanoyl chloride, (c) suberoyl chloride, and (d) benzoyl chloride.

different from those of intercalation compounds of organic carboxylate anions.

XRD patterns of all reaction products except the reaction product of $\text{Zn}(\text{OH})_2$ with benzoyl chloride were similar to those of the surface modified LDH. In the reaction products of $\text{Zn}(\text{OH})_2$ with straight chain oxychlorides, the interlayer spacing of the reaction products increased with an increase in methylene chain length as shown in Table I. However, the interlayer spacing of the reaction product of $\text{Zn}(\text{OH})_2$ with mono-oxychlorides was larger than those of $\text{Zn}(\text{OH})_2$ with di-oxychlorides. It was suggested that the reaction products of

Table I. XRD profiles of the reaction products of $\text{Zn}(\text{OH})_2$ with organic oxychlorides, $\text{Zn}(\text{OH})_x(\text{O-G})_y$ or $\text{Zn}(\text{OH})_x(\text{O-G-O})_z$

acid chloride	size (nm)	<i>d</i> -value (nm)				C%	H%	x	y	z
		acid	LDH ^a	OH-LDH ^b	$\text{Zn}(\text{OH})_2$					
butanoyl chloride	0.47	—	—	1.18	1.19	32.94	4.80	0.31	1.69	—
hexanoyl chloride	0.72	—	—	1.61	1.67	42.80	6.49	0.58	1.42	—
benzoyl chloride	0.54	1.09	1.54	1.12	1.48	41.26	2.83	1.00	1.00	—
phenylacetyl chloride	0.61	—	—	1.54	1.53	52.57	3.88	0.46	1.54	—
<i>p</i> -phenylazobenzoyl chloride	1.16	1.57	2.28	2.67	2.67	47.23	3.07	1.19	0.81	—
adipoyl chloride	0.64	0.68	1.48	0.77	0.83	34.10	3.83	0.04	—	0.98
suberoyl chloride	0.89	0.89	—	1.07	1.08	34.89	4.29	0.54	—	0.73
sebacyl chloride	1.14	1.12	1.88	1.28	1.28	40.50	5.41	0.50	—	0.75
dodecanedioyl chloride	1.40	1.38	2.28	1.52	1.48	43.82	6.04	0.52	—	0.74

^aLDH is the intercalation compounds of various organic anions into the Zn/Al LDHs. [6,7] ^bOH-LDH is the reaction products of the water-treated LDHs with various organic oxychlorides.

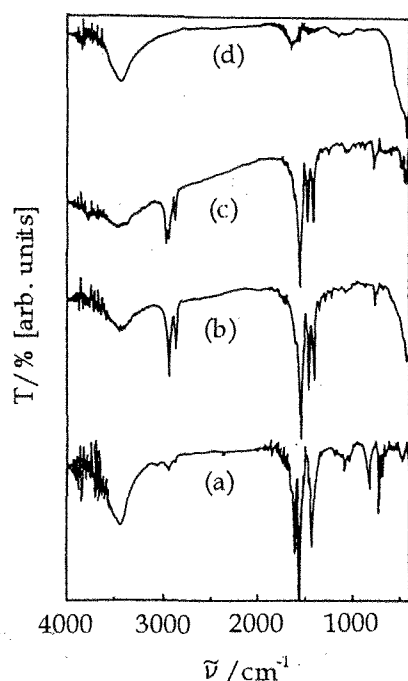


Fig. 2 IR spectra of the reaction product of $\text{Zn}(\text{OH})_2$ with (a) benzoyl chloride, (b) suberoyl chloride, and (c) n-hexanoyl chloride, and (d) $\text{Zn}(\text{OH})_2$.

$\text{Zn}(\text{OH})_2$ with mono-oxychlorides were bilayer structures, and the reaction products from di-oxychlorides were bridging structures.

Interlayer spacing of the reaction product of $\text{Zn}(\text{OH})_2$ with benzoyl chloride was 1.48 nm. It was not zinc benzoate ($\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$) [8], because the main peak in the XRD pattern of zinc benzoate was 1.10 nm. [9]

The IR spectra of $\text{Zn}(\text{OH})_2$ and the reaction products were shown in Fig. 2. In all reaction products, the new peaks at near 1540 and 1400 cm^{-1} appeared. The absorption at 1540 cm^{-1} is assigned to the symmetric stretching vibration of carboxylate, and the absorption at 1400 cm^{-1} is assigned to the asymmetric stretching vibration of

carboxylate. These two peaks indicate the formation of COO-Zn bond. Furthermore, the absorption peaks of carboxylic acid or dimer of the guest compounds were not observed. In IR spectra of the reaction products of $\text{Zn}(\text{OH})_2$ with straight chain oxychlorides, the carbon-hydrogen stretch absorption at near 2900 and 2800 cm^{-1} , and the carbon-hydrogen bending band at near 1470 cm^{-1} were observed (Fig. 2b, 2c). In the IR spectrum of the reaction product of $\text{Zn}(\text{OH})_2$ with benzoyl chloride the new peak at 1600 cm^{-1} was observed (Fig. 2a). The peak is assigned to the C=C stretch vibration of benzene ring.

These results indicate that $\text{Zn}(\text{OH})_2$ reacted with organic oxychlorides giving layered compounds by organo derivatization reaction. We have also reacted $\text{Zn}(\text{OH})_2$ with an excess amount of oxychlorides. However, the product was dissolved in solvent. By evaporation, powder was obtained. The IR spectrum of the powder indicated the presence of RCOO-Zn bond and carboxylic acid. Whereas, XRD peaks corresponded to the layer structures were not observed. It was considered that the first step of the reactions of $\text{Zn}(\text{OH})_2$ with mono-oxychlorides (RCOCl) was a dehydration reaction between the OH groups of $\text{Zn}(\text{OH})_2$ and RCOCl. The reaction gives RCOO-Zn-OCOR or RCOO-Zn-OH. The cross-sectional area of one OH-Zn-OH unit was calculated to be 0.96 nm^2 . [10] It was considered that the layered structure was assembled by gathering RCOO-Zn-OH or RCOO-Zn-OCOR unit. However, RCOO-Zn-OCOR is larger than 0.96 nm^2 . Therefore, an excess amount of RCOO-Zn-OCOR might interfere the assembly to the layered structure by steric repulsion.

The elemental analysis indicated that about 85% of the OH groups of $\text{Zn}(\text{OH})_2$ reacted with n-hexanoyl chloride to assemble a layered structure. Thus, in the cases of straight chain oxychlorides and phenylacetyl chloride, 63 to 98% of OH groups reacted. However, in the case of bulky oxychlorides, such as benzoyl chloride and *p*-phenylazobenzoyl chloride, the reacted OH groups were 50% and 40%, respectively. It indicated that the amounts of

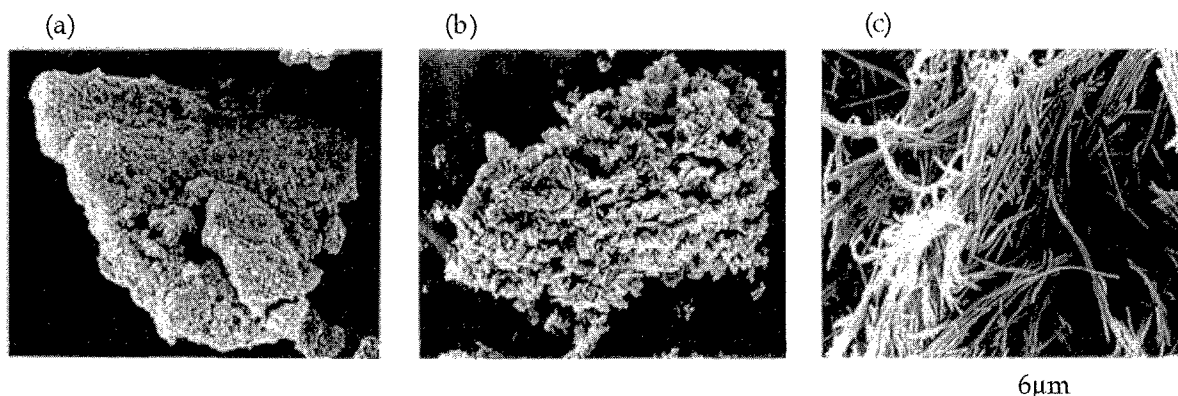


Fig. 3 SEM images of (a) $\text{Zn}(\text{OH})_2$, the reaction products of $\text{Zn}(\text{OH})_2$ with (b) suberoyl chloride and (d) benzoyl chloride.

reacted OH groups in $\text{Zn}(\text{OH})_2$ depended on the structure of oxychloride.

3.2 Morphology of the reaction product of $\text{Zn}(\text{OH})_2$ with organic compound

SEM images shows that $\text{Zn}(\text{OH})_2$ was plate morphology (Fig. 3a). By the reaction of $\text{Zn}(\text{OH})_2$ with suberoyl chloride, clear plate morphologies were obtained (Fig. 3b). The plate-like morphologies were quite similar to those of the LDHs.[11] Whereas, the reaction product of $\text{Zn}(\text{OH})_2$ with benzoyl chloride was fibrous morphology (Fig. 3c).

TEM image of the reaction product of $\text{Zn}(\text{OH})_2$ with benzoyl chloride indicates that the fibrous compound was layered compounds. The layer structure was constructed along the fiber direction (Fig. 4). The reaction products of $\text{Zn}(\text{OH})_2$ with phenylacetyl chloride and *p*-phenylazobenzoyl chloride were not fibrous although they are aromatic compounds. The distance between $\text{Zn}(\text{OH})_2$ layer and benzene ring of phenylacetyl chloride were larger than that of benzoyl chloride. And the distance between $\text{Zn}(\text{OH})_2$ layer and benzene ring of *p*-phenylazobenzoyl chloride were the same with that of benzoyl chloride. The molecular size of *p*-phenylazobenzoyl chloride (1.16 nm) is about twice as large as that of benzoyl chloride (0.54 nm). These results suggested that the steric repulsion between organic compounds in layers determines the morphology.

3.3 Incorporation of dye compound into layered compound

We have examined to incorporate a photochromic compound such as thioindigo into organic-inorganic layered compounds. By the reaction of $\text{Zn}(\text{OH})_2$ with straight chain oxychlorides in thioindigo saturated nitrobenzene solution, white powder was obtained. For the reaction product of $\text{Zn}(\text{OH})_2$ with suberoyl chloride, however, blue powder was obtained. The absorption spectra of thioindigo was observed at 504 nm. However, that of the reaction product of $\text{Zn}(\text{OH})_2$ with suberoyl chloride, the peak appeared at 598 nm. It was indicated that red shift occurred. This phenomenon was not caused by the functional group substitution of thioindigo. Because by extracting thioindigo from the reaction product of $\text{Zn}(\text{OH})_2$ with suberoyl chloride, color of thioindigo completely returned. The layer expansion (0.60 nm) of reaction product of $\text{Zn}(\text{OH})_2$ with suberoyl chloride was similar to molecular size of thioindigo (0.50 nm). Thus, it was considered that thioindigo was shape-selectively incorporated into the layered compound, and surrounded by methylene chain. We have guessed that the red shift occurred by conjugation of chromophore (carbonyl group of thioindigo) and auxochrome (hydroxy group of $\text{Zn}(\text{OH})_2$) at interlayer space.

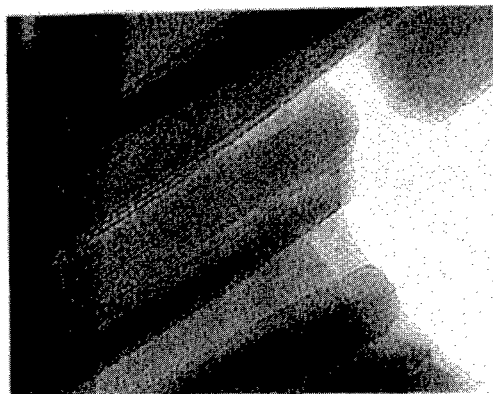


Fig. 4 TEM image of the reaction product of $\text{Zn}(\text{OH})_2$ with benzoyl chloride.

4. CONCLUSIONS

We have established new preparation method of inorganic-organic layered compounds by organo derivatization reaction of $\text{Zn}(\text{OH})_2$ with various organic oxychlorides. These results suggested that the structure of nano material by self-assembly reaction depended on the structure of organic compounds. They have potential as shape-selective sorbents, useful for controlling the organization of organic molecules in solid state, and preparation of new functional materials.

REFERENCES

- 1 D. O'Hare, "Inorganic Materials 2nd Edition", Ed, by D. W. Bruce and D. O'Hare, Wiley, Chichester, (1996) pp. 171.
- 2 H. Tagaya, S. Sato, H. Morioka, M. Karasu, J. Kadokawa and K. Chiba, *Chem. Mater.*, **5**, 1431 (1993)
- 3 F. Cavani, F. Trifiro, and A. Vaccari, *Catal. Today.*, **11**, 173 (1991).
- 4 H. Morioka, H. Tagaya, M. Karasu, J. Kadokawa and K. Chiba, *J. Solid State Chem.*, **117**, 337 (1995).
- 5 H. Tagaya, S. Ogata, H. Morioka, J. Kadokawa, M. Karasu, and K. Chiba, *J. Mater Chem.*, **6**, 1235 (1996).
- 6 S. Miyata and T. Kumura, *Chem Lett.*, 843 (1973).
- 7 M. Meyn, K. Beneke, and G. Lagaly, *Inorg. Chem.*, **1990**, **29**, 5201.
- 8 ASTM card., No. 30-1998
- 9 G. A. Guseinov, F. N. Musaev, B. T. Usabaliev, I. R. Amiraslanov, and Kh. S. Mamedov, *Koord. Khim.*, **10**, 117 (1984)
- 10 R. Allmamm, *Acta. Crystallogr.*, Sect. B, **24**, 972 (1968)
- 11 J. M. Fernandez, C. Barriga, M. Ulibarri, F. Labajos and V. Rives, *J. Mater Chem.*, **4**, 1117 (1994).

(Received December 11, 1998; accepted January 18, 1999)