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Preparation method for organic–inorganic layered compounds including fibrous materials by the reaction of $Zn(OH)_2$ with organic compounds

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A preparation method of surface modified inorganic layered compounds including fibrous materials was established by the reaction of amorphous $Zn(OH)_2$ with organic oxychlorides. The resultant layer structures were similar to those of the layered double hydroxides (LDHs). Although the LDH layers have positive charges the layers of the reaction products obtained here are uncharged. IR spectra indicate that hydroxyl groups reacted with the organic oxychlorides, and new peaks assigned to RCO_2–Zn bonds appeared around 1400 and 1550 cm^{-1} and 40–98% of hydroxyl groups were reacted. Interlayer spacings of the reaction products of $Zn(OH)_2$ with dioxychlorides were 0.71–1.48 nm, and those of $Zn(OH)_2$ with monooxychlorides were 1.19–2.67 nm and depended on the length of organic compounds. SEM images showed that the reaction products of $Zn(OH)_2$ with organic oxychlorides had plate-like morphology similar to LDHs. However, the reaction product of $Zn(OH)_2$ with benzoyl chloride was fibrous.

Recently, the preparation of various organic–inorganic hybrid materials has been reported.[1] Incorporation of a molecule into a crystalline inorganic host lattice to form an intercalation compound can lead to ordered materials.[2,3] For example, it has been extensively reported that metal phosphonates are useful for organizing molecules into lamellar structures.[4] Their structures are very similar to those formed by Langmuir–Blodgett (LB) techniques, but have higher thermal stabilities than LB films.[5] Recently, attempts on the preparation of new organic derivative nanocomposites have been reported.[6,7] It is possible to bond organic molecules on the surface of metal phosphonate covalently by the reaction of phosphate hydroxyl groups with organic compounds. Thus, the reaction of hydroxyl groups with organic compounds leads to organic derivatived hybrid materials. These chemical modifications included reactions of inorganic compounds with alcohols.

We have already reported the preparation method for inorganic layered compounds the surfaces of which are modified by organic compounds. In this reaction, a water-treated Zn/Al layered double hydroxide (LDH) was prepared by placing the calcined Zn/Al LDH in degassed water and reacting with an organic oxychloride in organic solvent. The resultant compound is a well organized organic–inorganic hybrid material, and the interlayer space is hydrophobic. The LDH is an inorganic layered compound[8] and many organic intercalates into LDHs are known.[9–13] Since the LDH layer has a positive charge, the LDH undergoes anion exchange intercalation reactions with guests such as organic acids and inorganic anions. The surface modified LDH also has a positive charge and includes anionic compounds between the layers.[14,15]

On the other hand, chemical surface modification of $Zn(OH)_2$ was reported in which $Zn(OH)_2$ was reacted with methanol at 588 K. In this reaction hydroxy ions were substituted by methoxy ions.[16] Recently, we have described a method to prepare new surface modified inorganic layered compounds by the reaction of $Zn(OH)_2$ with organic oxychlorides at 333 K.[17] Not only monooxychlorides but also dioxychlorides reacted with $Zn(OH)_2$ giving surface modified layered compounds. The products differ from the surface modified Zn/Al LDHs since their layers are uncharged and inclusion of anionic compounds between the layers is not required.

In this study, we have prepared and characterized layered organic–inorganic compounds including fibrous materials by the reaction of amorphous $Zn(OH)_2$ with organic oxychlorides.

Experimental

Reagents

All reactions were carried out using commercial reagents. *n*-Butyryl chloride [$CH_3(CH_2)_2COCl$], hexanoyl chloride [$CH_3(CH_2)_4COCl$], glutaryl dichloride [$ClCO(CH_2)_3COCl$] and adipoyl chloride [$ClCO(CH_2)_4COCl$] were purchased from Tokyo Chemical Industry Co. $Zn(OH)_2$, suberoyl chloride [$ClCO(CH_2)_6COCl$], sebacoyl chloride [$ClCO(CH_2)_8COCl$] and dodecanedioyl dichloride [$ClCO(CH_{12})_{10}COCl$] were purchased from Aldrich Chemical Co. Phenylacetyl chloride [$C_6H_5CH_2COCl$], benzoyl chloride (C_6H_5COCl), $Mg(OH)_2$, $Cu(OH)_2$ and $Ni(OH)_2$ were purchased from Wako Chemical Co. $Al(OH)_3$ was purchased from Kanto Chemical Co.

Surface modification reactions of metal hydroxides

$Zn(OH)_2$ (0.2 g; 2.01 mmol) and other metal hydroxides such as $Cu(OH)_2$, $Ca(OH)_2$, $Ni(OH)_2$, $Mg(OH)_2$ and $Al(OH)_3$ were reacted with 0.4 equivalents of organic oxychlorides in 3 or 5 ml of acetonitrile or diethyl ether for 5 h under stirring at 333 K. For benzoyl chloride the reaction product of $Zn(OH)_2$ with 0.4 equivalents of benzoyl chloride dissolved in the solvent. Therefore, the reaction was repeated using 0.2 equivalents of benzoyl chloride. After being filtered off, the reaction products were washed with the same solvent to remove unreacted organic oxychlorides and impurities, and dried under reduced pressure at room temperature.

Characterization

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku powder diffractometer unit, using Cu-Kα (filtered) radiation ($\lambda = 0.154$ nm) at 40 kV and 20 mA between 1.8 and 50°. FTIR spectra (KBr disc method) were recorded on a Horiba FT-200 apparatus. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of powdered samples up to 873 K were carried out at a heating rate of 10 K min^{-1} under flowing N_2 using a Seiko SSC5000 thermal analysis system. Scanning electron microscopy (SEM) was performed with a JEOL JSM-5300 instrument, operating at 20 kV.

Results and discussion

Thermal characteristics of the reaction products of $Zn(OH)_2$ with organic oxychlorides

Thermal characteristics of the reaction products of $Zn(OH)_2$ with organic oxychlorides were determined by TG analysis. For $Zn(OH)_2$, weight loss was observed up to 343 K as shown in Fig. 1(a) and corresponded to dehydration of $Zn(OH)_2$. For benzoyl chloride weight loss was observed up to 470 K as shown in Fig. 1(c). For the reaction product of $Zn(OH)_2$ with benzoyl chloride, two weight loss regions were observed between 450 and 720 K as shown in Fig. 1(b). The first weight loss near 450 K corresponded to the dehydration of OH groups of $Zn(OH)_2$ and desorption of organic groups reacted on the outer surface of $Zn(OH)_2$. The second weight loss at between 570 and 720 K corresponded to desorption of organic groups reacted on the inner surface of $Zn(OH)_2$. Certainly, the reaction product of $Zn(OH)_2$ with benzoyl chloride was more stable thermally than benzoyl chloride itself. Similar thermal stabilities were observed for other reaction products of $Zn(OH)_2$ with organic oxychlorides.

X-Ray powder diffraction patterns of the reaction products

No clear peaks were observed in the XRD pattern of $Zn(OH)_2$ alone as shown in Fig. 2(d). Upon reaction of this amorphous $Zn(OH)_2$ with 0.4 equivalents of hexanoyl chloride in acetonitrile, a crystalline product was obtained, although the reaction product dissolved in acetonitrile in the reaction of $Zn(OH)_2$ with 1.0 equivalents of hexanoyl chloride. Crystalline $Zn(OH)_2$ was prepared by the reaction of $Zn(NO_3)_2$ with NaOH, and was reacted with organic oxychlorides. The reactivity of crystalline $Zn(OH)_2$ with organic compounds is fairly low, and peaks of $Zn(OH)_2$ remained even after reaction with organic oxychlorides. In the reaction of amorphous $Zn(OH)_2$, similar crystalline products were obtained by the reaction with suberoyl chloride or benzoyl chloride in acetonitrile or diethyl ether. Interlayer spacings of these reaction products were 1.67, 1.08 and 1.48 nm as shown in Fig. 2(a), (b) and (c), respectively. The XRD peaks of these reaction products were different from those of the individual organic oxychlorides and carboxylic acids. We have already reported that water-treated Zn/Al LDHs reacted with various organic oxychlorides to give surface modified LDHs.[14,15] These were different from those of intercalation compounds of organic carboxylate anions.[18,19] Upon reaction of sebacic acid with calcined Zn/Al LDH in water, an intercalation compound was obtained, and the interlayer spacing increased to 1.88 nm (Table 1). This value is larger than the spacing of 1.28 nm for the surface modified LDH. XRD peak patterns of all reaction products except that of $Zn(OH)_2$ with benzoyl chloride were similar to those of the surface modified Zn/Al LDH in which the water-treated Zn/Al LDH was reacted with oxychlorides. In the reaction products of $Zn(OH)_2$ with straight chain oxychlorides such as hexanoyl chloride and suberoyl chloride, the interlayer spacings of the reaction products increased with an increase in

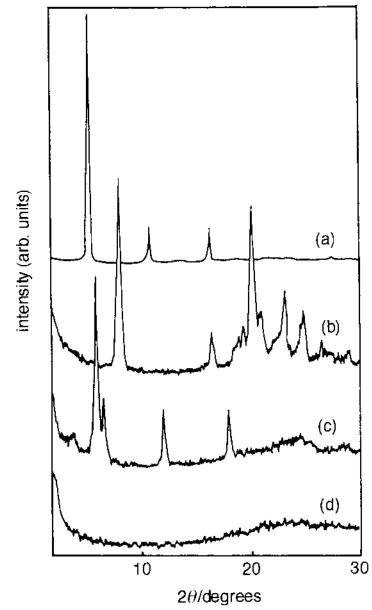

Fig. 2 XRD patterns of the reaction products of $Zn(OH)_2$ with (a) hexanoyl chloride, (b) suberoyl chloride, (c) benzoyl chloride, and (d) $Zn(OH)_2$ alone.

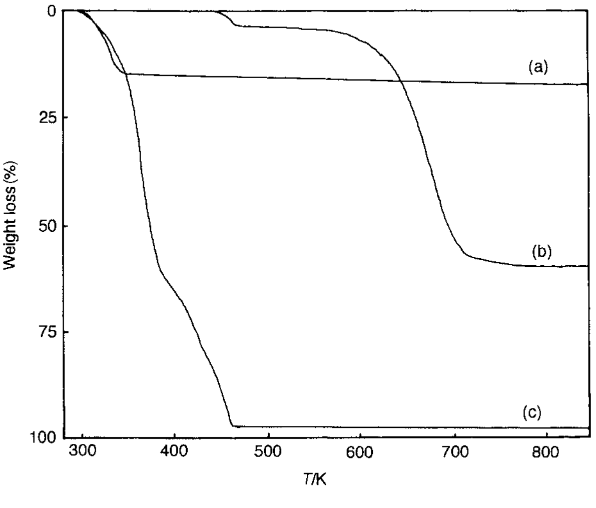

Fig. 1 Thermal analysis of (a) $Zn(OH)_2$, (b) the reaction product of $Zn(OH)_2$ with benzoyl chloride and (c) benzoyl chloride.

Table 1 XRD profiles of the reaction products of $Zn(OH)_2$ with organic oxychlorides

	d-value/nm			
Oxychloride	Length/nm	OH-LDH[a]	LDH[b]	$Zn(OH)_2$
n-Butyryl chloride	0.47	1.18		1.19
Hexanoyl chloride	0.72	1.61		1.67
Benzoyl chloride	0.54	1.12	1.54	1.48
Phenylacetyl chloride	0.61	1.54		1.53
p-Phenylazobenzoyl chloride	1.16	2.67	2.28	2.67
Glutaryl dichloride	0.51			0.71
Adipoyl chloride	0.64	0.77	1.48	0.83
Suberoyl chloride	0.89	1.07		1.08
Sebacoyl chloride	1.14	1.28	1.88	1.28
Dodecanedioyl dichloride	1.40	1.52	2.28	1.48

[a]The reaction products of the water-treated LDHs with various organic oxychlorides.[14] [b]The intercalation compounds of corresponding organic anions into the Zn/Al LDHs.

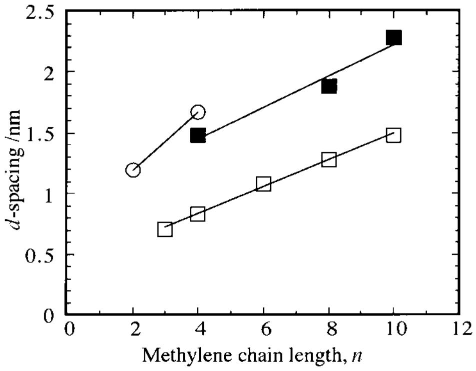

Fig. 3 Interlayer spacings of the intercalation compound of Zn/Al LDH (■), the reaction products of $Zn(OH)_2$ with $ClCO(CH_2)_nCOCl$ ($n=4$, 6, 8 and 10) (□), and $CH_3(CH_2)_nCOCl$ ($n=2$ and 4) (○).

methylene chain length as shown in Fig. 3. However, the interlayer spacings of the reaction product of $Zn(OH)_2$ with monooxychlorides were larger than those of $Zn(OH)_2$ with dioxychlorides. The interlayer spacing and the length of oxychlorides suggested that the reaction products from monooxychlorides were bilayer structures and the reaction products from dioxychlorides were bridging structures.

The interlayer spacing of the reaction product of $Zn(OH)_2$ with phenylacetyl chloride was 1.53 nm. The value was similar to that (1.54 nm) of the reaction product of the water-treated Zn/Al LDH with phenylacetyl chloride. However, in the reaction product of $Zn(OH)_2$ with benzoyl chloride, the interlayer spacing was 1.48 nm and larger than that of the reaction product of the water-treated LDH with benzoyl chloride (1.12 nm). The *d*-spacing of zinc benzoate $[Zn(C_6H_5CO_2)_2]$[20] was 1.10 nm.[21] The XRD pattern of the reaction product of $Zn(OH)_2$ with benzoyl chloride was different to that of zinc benzoate.

IR spectroscopy

The IR spectra of $Zn(OH)_2$ and its reaction products with organic oxychlorides are shown in Fig. 4. In all reaction products, no absorption peaks corresponded to carboxylic acids or dimers of the organic reactants. In the IR spectra of the reaction products of $Zn(OH)_2$ with straight chain type oxychlorides such as hexanoyl chloride and suberoyl chloride, ν(C–H) at *ca.* 2900 and 2800 cm^{-1} as well as δ(C–H) at *ca.* 1470 cm^{-1} were observed. In the IR spectrum of the reaction product of $Zn(OH)_2$ with benzoyl chloride a new peak at 1600 cm^{-1} was observed and assigned to ν(C=C) of the benzene ring.

ν(OH) absorptions at *ca.* 3500 cm^{-1} in the IR spectrum of $Zn(OH)_2$ decreased upon reaction with organic oxychlorides and new peaks at *ca.* 1540 and 1400 cm^{-1} appeared. The absorption peak at 1540 cm^{-1} is assigned to the asymmetric stretching vibration of carboxylate, and the absorption at 1400 cm^{-1} assigned to the symmetric stretching vibration of carboxylate. The presence of these two peaks suggest the formation of RCO_2–Zn bonds by reaction of $Zn(OH)_2$ with organic oxychlorides. These results indicate the formation of surface modified layered compounds as shown in Fig. 5.

To clarify the mechanism of the formation of the layered compounds, $Zn(OH)_2$ was reacted with an excess of oxychloride and the product was dissolved in an organic solvent such as acetonitrile or diethyl ether. Upon evaporation of acetonitrile or ether, powders were obtained the IR spectrum of which indicated the presence of RCO_2–Zn bonds while XRD showed the formation of carboxylic acid.

It is proposed that the first step of the reaction of $Zn(OH)_2$ with monooxychlorides (RCOCl) is a dehydration reaction between OH groups of $Zn(OH)_2$ and RCOCl to give RCO_2–Zn–OH or RCO_2–Zn–OCOR. The cross-sectional area of one HO–Zn–OH unit[22] is calculated to be 0.96 nm^2. It is proposed that the layered structure is assembled by interacting RCO_2–Zn–OH or RCO_2–Zn–OCOR units as shown in Fig. 5. However, the cross-sectional area of RCO_2–Zn–OCOR is >0.96 nm^2 and therefore, an excess amount of RCO_2–Zn–OCOR might interfere with the assembly reaction owing to steric repulsion.

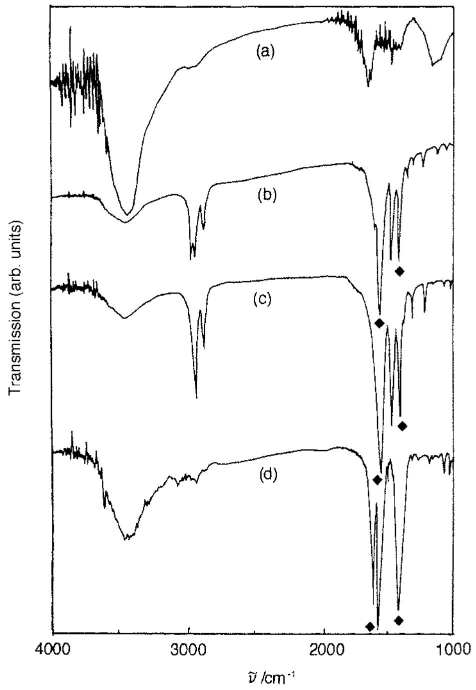

Fig. 4 IR spectra of (a) $Zn(OH)_2$, the reaction product of $Zn(OH)_2$ with (b) benzoyl chloride, (c) suberoyl chloride, and (d) hexanoyl chloride. ◆: RCO_2–Zn band.

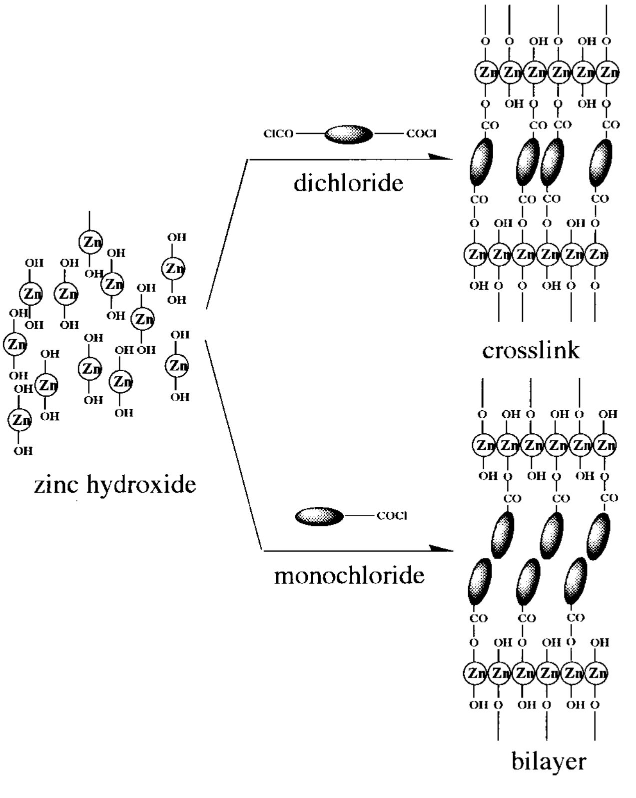

Fig. 5 Reaction of $Zn(OH)_2$ with organic oxychlorides to give organic–inorganic hybrid layered compounds.

Table 2 Elemental analysis of the reaction products of $Zn(OH)_2$ with organic oxychlorides, $Zn(OH)_x(O{-}G)_y$ or $Zn(OH)_x(O{-}G{-}O)_z$

Oxychloride	C(%)	H(%)	x	y	z
n-Butyryl chloride	32.94	4.80	0.31	1.69	—
Hexanoyl chloride	42.80	6.49	0.58	1.42	—
Benzoyl chloride[a]	41.26	2.83	1.00	1.00	—
Phenylacetyl chloride	52.57	3.88	0.46	1.54	—
p-Phenylazobenzoyl chloride	47.23	3.07	1.19	0.81	—
Glutaryl dichloride	23.68	2.48	0.74	—	0.63
Adipoyl chloride	34.10	3.83	0.04	—	0.98
Suberoyl chloride	34.89	4.29	0.54	—	0.73
Sebacoyl chloride	40.50	5.41	0.50	—	0.75
Dodecanedioyl dichloride	43.82	6.04	0.52	—	0.74

[a] Fibrous.

Composition of organic–inorganic layered compounds

Elemental analyses of the reaction products of $Zn(OH)_2$ with organic oxychlorides are shown in Table 2. About 85% of the OH groups of $Zn(OH)_2$ reacted with hexanoyl chloride to assemble a layered structure and for cases of straight chain oxychlorides and phenylacetyl chloride, 63–98% of OH groups reacted. However, for bulky oxychlorides, such as benzoyl chlorides and *p*-phenylazobenzoyl chloride ($C_6H_5NNC_6H_4COCl$), only *ca.* 50 and 40%, respectively, of OH groups react. The results indicate that the extent of reaction of OH groups in $Zn(OH)_2$ depends on the structure of the oxychloride.

Reaction of $Cu(OH)_2$, $Mg(OH)_2$, $Ni(OH)_2$ and $Al(OH)_3$ with oxychloride

We have already reported that water-treated Zn/Al LDHs react with organic oxychlorides to give surface modified LDHs.[14,15] However, we could not obtain a water-treated Mg/Al LDH, and Mg/Al LDH scarcely reacted with oxychlorides. Furthermore, $Al(OH)_3$, $Cu(OH)_2$ and $Ni(OH)_2$ did not react with oxychlorides. We confirmed reaction of $Mg(OH)_2$ with oxychlorides, however, the amounts of reacted OH groups were small, and XRD peaks of the products were not clear.

Morphology of the reaction product of $Zn(OH)_2$ with organic compounds

$Zn(OH)_2$ has a plate-like morphology as shown in Fig. 6(a). Upon reaction of $Zn(OH)_2$ with hexanoyl chloride and suberoyl chloride, clear plate morphologies were obtained as shown in Fig. 6(b) and (c). Similar plate-like crystals were also obtained by the reactions of $Zn(OH)_2$ with other straight chain organic oxychlorides. The plate-like morphologies were quite similar to those of LDHs.[23,24] By contrast, the reaction product of $Zn(OH)_2$ with benzoyl chloride had a fibrous morphology as shown in Fig. 6(d).

A TEM image of the reaction product of $Zn(OH)_2$ with benzoyl chloride indicates that the fibrous compound was a layered compound as shown in Fig. 7. The reaction products of $Zn(OH)_2$ with phenylacetyl chloride and *p*-phenylazobenzoyl chloride were not fibrous although their structures are similar to that of benzoyl chloride. The distance between Zn centres of the inorganic layer and the benzene ring in $C_6H_5CH_2CO_2{-}Zn$ bond was larger than that in $C_6H_5CO_2{-}Zn$. However, the distance between Zn of the inorganic layer and the benzene ring of $C_6H_5NNC_6H_4CO_2{-}Zn$ was the same as that for $C_6H_5CO_2{-}Zn$. The molecular length of *p*-phenylazobenzoyl chloride (1.16 nm) is about twice as large as that of benzoyl chloride (0.54 nm). These results suggest that steric repulsion between organic moieties between layers is important in determining the morphology.

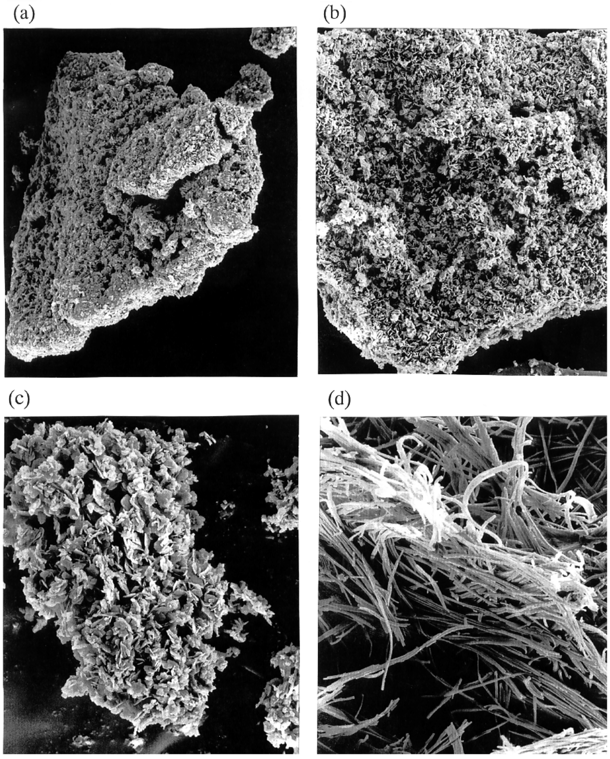

Fig. 6 SEM images (5000 ×magnification) of (a) $Zn(OH)_2$ and the reaction products of $Zn(OH)_2$ with (b) hexanoyl chloride, (c) suberoyl chloride and (d) benzoyl chloride.

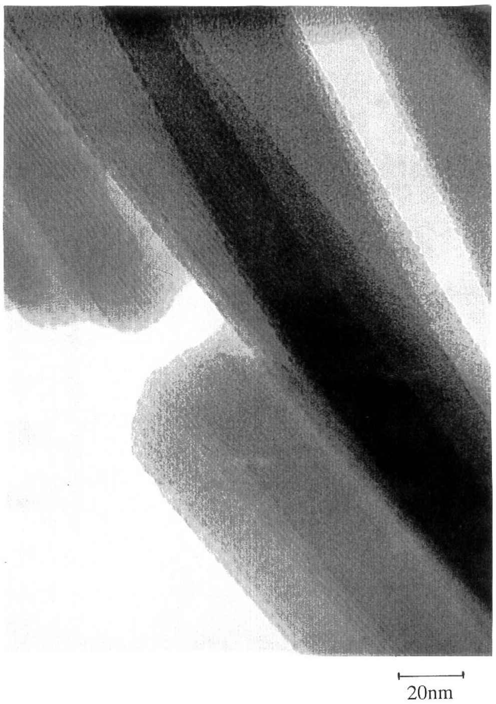

Fig. 7 TEM images (500 000 ×magnification) of the reaction product of $Zn(OH)_2$ with benzoyl chloride.

Conclusions

We have established a preparation method of organic–inorganic layered compounds by the reaction of $Zn(OH)_2$ with various organic oxychlorides. The IR spectra of the reaction products of $Zn(OH)_2$ with organic oxychlorides indicated the formation of $CO_2{-}Zn$ bonds. 40–98% of OH groups reacted with the organic compounds. SEM images showed that the structures of the reaction products were plate-like, whereas that of the reaction product with benzoyl chloride was fibrous. These results suggest that the structure of the nanomaterial depends on the structures of the organic compounds incorporated. Chemical surface modification of inorganic compounds has been studied extensively to change their chemical and/or physical properties in a controlled manner.[25,26] The present work describes a viable preparation method of surface-modified inorganic layered compounds. Organic intercalation compounds of smectite clays are known as organic sorbents and since the interlayer space of surface modified $Zn(OH)_2$ is hydrophobic the hybrid materials have potential as shape-selective sorbents and catalysts. The method is also useful for controlling the organization of organic molecules in the solid state, and preparation of microporous materials which have controlled morphology.

Acknowledgments

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