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New preparation method for organic–inorganic layered compounds by organo derivatization reaction of $Zn(OH)_2$ with carboxylic acids

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A new preparation method for organic–inorganic nanohybrids has been developed by the reaction of $Zn(OH)_2$ with various carboxylic acids. The resulting layered structures are similar to the reaction products of $Zn(OH)_2$ or layered double hydroxides (LDHs) with acyl chlorides. The interlayer spacings of the reaction products of $Zn(OH)_2$ with straight chain monocarboxylic acids were in the range 1.19–4.33 nm, and with dicarboxylic acids were 0.71–1.48 nm. These values depended on the length of the organic compounds and the number of carboxyl groups. IR spectra showed new peaks due to the RCOO–Zn vibration at *ca.* 1400 and 1550 cm^{-1} indicating that the hydroxy groups had reacted with the carboxylic acids. SEM images of the reaction products of $Zn(OH)_2$ with carboxylic acids showed that they were of plate-like morphology similar to the LDHs. On the other hand, the morphology of the reaction products of $Zn(OH)_2$ with bulky carboxylic acids were fibrous, although they also had layered structures.

Preparations of organic–inorganic hybrid materials with highly ordered layered structures have been reported.[1–4] It is well known that metal phosphonates are useful for organizing molecules into lamellar structures.[5] These lamellar structures are very similar to those formed by Langmuir–Blodgett (LB) techniques, but have better thermal stability.[6] It is possible to link guest molecules covalently by the reaction of the phosphate surface hydroxy groups with the organic compound leading to organic nanohybrid derivatives. Chemical internal surface modification of inorganic compounds has been extensively studied as a means of changing their chemical and/or physical properties.[7] Recently, attempts to prepare new organic nanocomposite derivatives by chemical modification have included reactions of inorganic compounds with alcohols.[8,9] We have already prepared surface modified inorganic layered compounds in which the internal surface of the Zn/Al layered double hydroxide (LDH) was modified by reaction with acyl chlorides although the reaction of Zn/Al LDH with organic carboxylic acids did not give ordered crystals.[10,11] The obtained compounds were well organized inorganic–organic hybrids, and the interlayer space was hydrophobic. LDHs are inorganic layered compounds whose layers are positively charged[12] and act as anion exchangeable clays which undergo anion exchange intercalation reactions with guests such as organic acids and inorganic anions. Many organic intercalates of LDHs are known.[13–20] Internally surface modified LDHs contain anionic compounds between their layers. Recently, we reported that organic–inorganic nanohybrids could be prepared by organo derivatization reactions of amorphous $Zn(OH)_2$ with aliphatic acyl chlorides[21] and the resulting compounds had plate-like structures. The morphology was similar to those of LDHs and internally surface modified LDHs.[10] Chemical surface modification of $Zn(OH)_2$ has also been reported in which $Zn(OH)_2$ was reacted with alcohols.[22] However, the characteristics of the resulting materials are different from those of internally surface modified Zn/Al LDHs because their layers are neutral and they do not need to include anionic compounds between the layers. Furthermore, we have reported that $Zn(OH)_2$ reacted with carboxylic acids giving similar compounds to the reaction products of $Zn(OH)_2$ and acyl chlorides.[23] However, the amounts of reacted carboxylic acids were small compared to acyl chlorides, and reaction conditions such as the nature of the solvent were important.

Here, we have established a preparation method and characterized new layered organic–inorganic nanohybrids by the organo derivatization reaction of $Zn(OH)_2$ with a variety of carboxylic acids. We have also clarified the formation of fibrous layered compounds whose production depended on the structure and the amounts of the organic compounds reacted.

Experimental

Reagents

We have carried out all reactions by using commercial reagents without further purification. $Zn(OH)_2$ was prepared as follows. 15.52 g (5.22×10^{-2} mol) of $Zn(NO_3)_2 \cdot 6H_2O$ (99.0%) was dissolved in 300 ml of degassed distilled water. Upon adding 300 ml of degassed 0.23 M NaOH solution to the $Zn(NO_3)_2$ solution at 277 K, a white precipitate was obtained. The pH was finally adjusted to *ca.* 7 and stirring continued for 0.5 h at 277 K. The precipitate was washed three times with distilled water and then dried for 24 h at 333 K. XRD measurement identified the product as β-$Zn(OH)_2$.[24]

Organo derivatization reaction of $Zn(OH)_2$ with carboxylic acids

All organo derivatization reactions of $Zn(OH)_2$ were carried out by using a CO_2H/OH ratio of 0.5. For example, 0.2 g (2.01×10^{-3} mol) of commercial $Zn(OH)_2$ (99.0%) or synthesized $Zn(OH)_2$ was reacted with 2.01×10^{-3} mol of a monocarboxylic acid or 1.00×10^{-3} mol of a dicarboxylic acid in 3–5 ml of solvent such as acetonitrile, diethyl ether, toluene or ethanol for 5 h under stirring at 333 K.

After the reaction, the reaction products were filtered off, washed to remove unreacted carboxylic acid and impurities, and dried under reduced pressure at normal temperature.

Characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku powder diffractometer unit, using Cu-Kα (filtered) radiation ($\lambda = 0.165$ nm) at 40 kV and 20 mA between 1.8 and 50° in 2θ. FTIR spectra (KBr disc method) were recorded on a Hiroba

FT-200 instrument. Thermogravimetry analysis (TG) and differential thermal analysis (DTA) of powdered samples up to temperatures of 873 K were carried out at a heating rate of 10 K min^{-1} in flowing N_2 using a Seiko SSC 5000 thermal analysis system. Scanning electron microscopy (SEM) was performed with a JEOL JSM-5300 instrument, operating at 20 kV.

Results and discussion

Characterization of the reaction products of $Zn(OH)_2$ with carboxylic acids

Upon reaction of $Zn(OH)_2$ with various carboxylic acids in acetonitrile or diethyl ether, crystalline products were obtained. We have already reported the preparation of layered compounds by the organo derivatization reaction of $Zn(OH)_2$ with various acyl chlorides.[21,25] The thermal analyses, IR spectra and XRD profiles of the reaction products of $Zn(OH)_2$ with various carboxylic acids were similar to those of the reaction products of $Zn(OH)_2$ with various acyl chlorides.[21b] In the IR spectra of the reaction products, no absorption peaks due to the carboxylic acid (*ca.* 1700 cm^{-1}) or its dimer (*ca.* 1765 and 1825 cm^{-1}) were observed. Moreover, Table 1 shows that the *d*-spacings of these reaction products were different from those of the carboxylic acids themselves. In the reaction of $Zn(OH)_2$ with straight chain carboxylic acids such as *n*-caproic acid and sebacic acid, the interlayer spacings increased linearly with an increase in methylene chain length of the organic carboxylic acid as shown in Fig. 1. For straight chain mono- and di-carboxylic acids, the interlayer spacing increased by 0.22 and 0.13 nm, respectively, per methylene chain. For a given carbon number, the interlayer spacing of the reaction product of $Zn(OH)_2$ with the monocarboxylic acid was larger than that with the corresponding dicarboxylic acid. For the intercalation of organic amines into smectic or layered titanic acid, the orientation of the organic compound in the interlayer space (galleries) was considered as of bilayer type.[26–28] Similarly, the layer expansion in comparison to the length of the carboxylic acid suggests that interdigitation did not occur and that the orientation of monocarboxylic acids in the interlayer space was of bilayer type. The layer expansion in relation to the length of dicarboxylic acids suggests that the orientation of the latter in the interlayer space was of bridging type.

SEM images

SEM images of $Zn(OH)_2$ and the reaction products of $Zn(OH)_2$ with carboxylic acids are shown in Fig. 2. $Zn(OH)_2$ itself has a plate-like morphology as shown in Fig. 2(a). The reaction product of $Zn(OH)_2$ with sebacic acid has a clear plate-like morphology as shown in Fig. 2(b). Similar plate-like crystals were also obtained by the reaction of $Zn(OH)_2$ with other straight chain mono- or di-carboxylic acids. This plate-like morphology was quite similar to those of the LDHs.[29,30] Furthermore, the XRD patterns of the reaction products of $Zn(OH)_2$ with carboxylic acids were similar to those of internally surface modified LDHs indicating that these reaction products were of CdI_2-like structure. On the other hand, the organo derivatization reaction product of $Zn(OH)_2$ with benzoic acid showed fibrous morphology [Fig. 2(c)].

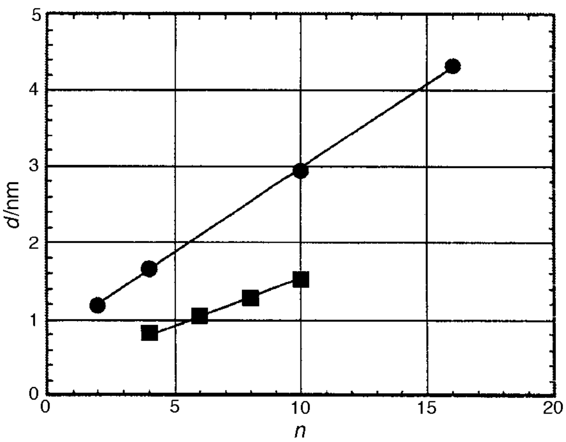

Fig. 1 Interlayer spacings (*d*) of the reaction products of $Zn(OH)_2$ with $HOOC(CH_2)_nCOOH$ (n=4, 6, 8 and 10) (■) and $CH_3(CH_2)_nCOOH$ (n=2, 4, 10 and 16) (●).

Compositions

Compositions were obtained from elemental analyses of the reaction products of $Zn(OH)_2$ with carboxylic acids (Table 2). About 70% of the OH groups of $Zn(OH)_2$ reacted with *n*-caproic acid (*i.e.* a host/guest ratio of 0.61/1.39) whereas 36–70% of OH groups reacted with straight chain monocarboxylic acids (*i.e.* host/guest ratios of 1.28/0.72–0.61/1.39). The values of y in $Zn(OH)_x(O–G)_y$ of the reaction products of $Zn(OH)_2$ with *n*-butyric acid and *n*-caproic (*n*-hexanoic) acid were larger than those with lauric acid and stearic acid while the z values in $Zn(OH)_x(O–G–O)_z$ were smaller than the y values indicating that the reactivity of OH groups toward dicarboxylic acids were lower than those towards monocarboxylic acids. Furthermore, with benzoic acid, 53% of OH groups in $Zn(OH)_2$ underwent reaction (*i.e.* host/guest ratio is 0.93/1.07). It was confirmed that the amount of reacted OH groups in $Zn(OH)_2$ depended on the structure of the carboxylic acid.

The composition of the reaction product of $Zn(OH)_2$ with benzoic acid was calculated as $Zn(OH)_{0.93}(C_6H_5COO)_{1.07}$ by elemental analysis. A 7.5% weight loss in the TG curve is

Table 1 Interlayer spacings of the organo derivatization reaction products of $Zn(OH)_2$ with organic compounds

		d/nm				
Carboxylic acid	Length[a]/nm	Acid	Zinc salt	$Zn(OH)_2$+RCOCl[b]	$Zn(OH)_2$+RCOOH[c]	Layer expansion/nm
n-Butyric acid	0.47	—		1.19	1.19	0.71
n-Caproic acid	0.72	—		1.67	1.67	1.19
Lauric acid	1.49	2.58			2.94	2.46
Stearic acid	2.25	4.09	4.20		4.33	3.85
Adipic acid	0.64	0.68		0.83	0.83	0.35
Suberic acid	0.89	0.89		1.08	1.06	0.58
Sebacic acid	1.14	1.12		1.28	1.28	0.80
Dodecanedioic acid	1.40	1.38		1.48	1.53	1.05
Benzoic acid	0.54	1.10	1.06	1.48	1.46	0.98

[a]Distance between carbonyl carbon and the furthest hydrogen (monocarboxylic acid) or between two carbonyl carbons (dicarboxylic acid). [b]The reaction product of $Zn(OH)_2$ with aryl chloride. [c]The reaction product of $Zn(OH)_2$ with carboxylic acid.

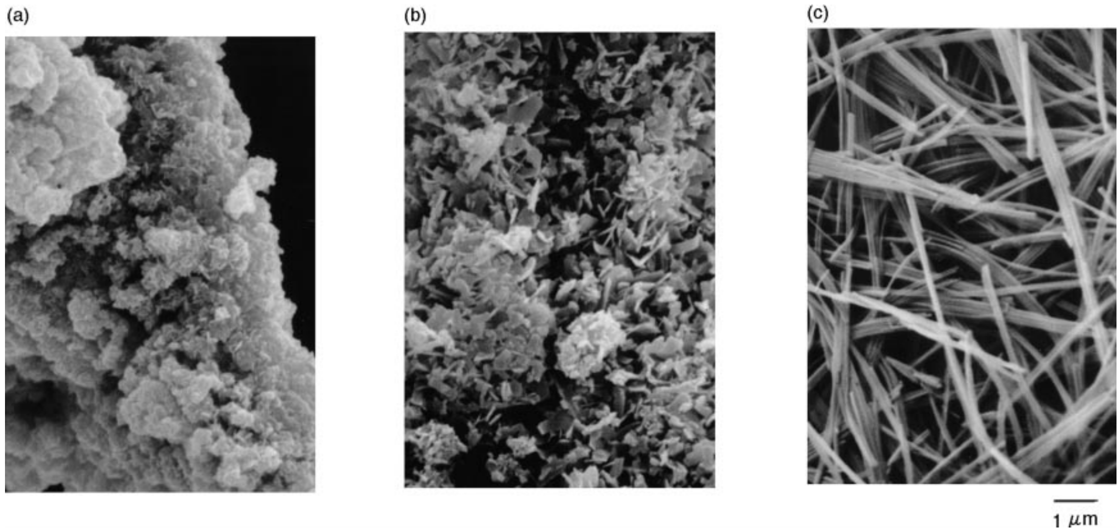

Fig. 2 SEM images (magnification 10000 ×) of (a) $Zn(OH)_2$ and the reaction products of $Zn(OH)_2$ with (b) sebacic acid and (c) benzoic acid.

predicted for the loss of OH groups and 61% for the loss of benzoic acid according to this composition. The predicted values were roughly similar to those obtained in TG measurements.

As already stated, Zn/Al LDH scarcely reacted with carboxylic acids, indicating that the reactivity of $Zn(OH)_2$ is higher than that of the LDH. We have also confirmed the absence of reaction of $Al(OH)_3$ with various acyl chlorides[21] and carboxylic acids; the presence of Al might be the reason for the low reactivity of the Zn/Al LDH toward acyl chlorides and carboxylic acids.

Characterization of fibrous organic–inorganic nanohybrids

We have already communicated that the reaction product of $Zn(OH)_2$ with benzoyl chloride was fibrous.[23] This is confirmed by an SEM image of the reaction product of $Zn(OH)_2$ with benzoic acid which has a fibrous morphology as shown in Fig. 2(c). The TEM image of the fibrous compound indicates that is a layered compound as shown in Fig. 3, the fibres being of thickness of *ca.* 120 nm. The layer structure is constructed along the fibre direction.

XRD patterns of the fibrous compound showed five peaks [Fig. 4(a)] the layered structure having a *d*-value of 1.46 nm. Two weight loss regions at 450 and 570–720 K in TG of the reaction product of $Zn(OH)_2$ with benzoic acid were observed. The structure of zinc benzoate [$Zn(C_6H_5COO)_2$] has already been reported in which it is shown that it is not a layered compound.[31–33] In TG analysis of zinc benzoate only one weight loss region between 553 and 774 K was observed indicating decomposition and desorption of benzoate anions.[31] As shown in Fig. 4(b) and (d), the *d*-values of zinc benzoate and benzoic acid were 1.06 and 1.10 nm, respectively, suggesting that the product was not zinc benzoate or benzoic acid since the *d*-value of the reaction product of $Zn(OH)_2$ with benzoic acid was 1.46 nm. The peak at 1.30 nm in the XRD pattern corresponded to that of benzoylbenzoic acid,[34] the dimer of benzoic acid. We could not completely remove this impurity, however, no peaks of the carboxylic acid or dimer were observed in the IR spectrum.

Table 2 Elemental analyses of the reaction products of $Zn(OH)_2$ with carboxylic acids, $Zn(OH)_x(O\text{–}G)_y$ and $Zn(OH)_x(O\text{–}G\text{–}O)_z$ ($x+y=2$, $x+2z=2$)

Carboxylic acid	C%	H%	x	y	z
Monocarboxylic acid					
n-Butyric acid	33.70	4.78	0.63	1.37	—
n-Caproic acid	42.67	6.44	0.61	1.39	—
Lauric acid	37.68	6.56	1.28	0.72	—
Stearic acid	59.47	9.97	0.99	1.01	—
Benzoic acid	42.68	2.90	0.93	1.07	—
Dicarboxylic acid					
Adipic acid	19.08	2.24	1.26	—	0.37
Suberic acid	21.96	2.71	1.34	—	0.33
Sebacic acid	25.88	3.58	1.33	—	0.33
Dodecanedioic acid	34.48	4.95	1.11	—	0.44

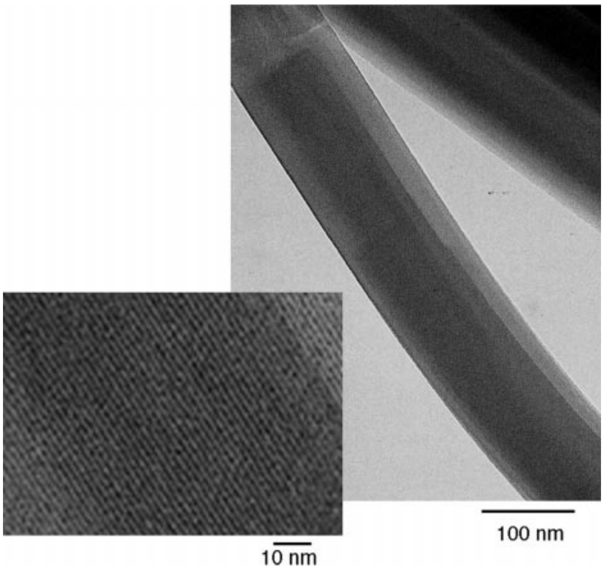

Fig. 3 TEM image of the reaction product of $Zn(OH)_2$ with benzoic acid.

In the XRD pattern of the reaction product of $Zn(OH)_2$ with benzoic acid for 0.5 h, two peaks at 1.48 and 1.38 nm were observed, although the peak at 1.48 nm was of low intensity. The SEM image showed that the product was not fibrous. The XRD pattern of the reaction product of $Zn(OH)_2$ with benzoic acid for 1 h showed a strong peak at 1.50 nm and a weak peak at 1.38 nm. The product was a mixture of fibrous and plate-like material. We suggest that the product with a peak at 1.38 nm was of CdI_2-like $Zn(OH)_2$ structure incorporating the organic compound.

Organo derivatization reaction of ZnO

We have also confirmed the production of a layered compound by the organo derivatization reaction of ZnO with benzoic acid in water. The host/guest ratio of the reaction product of ZnO

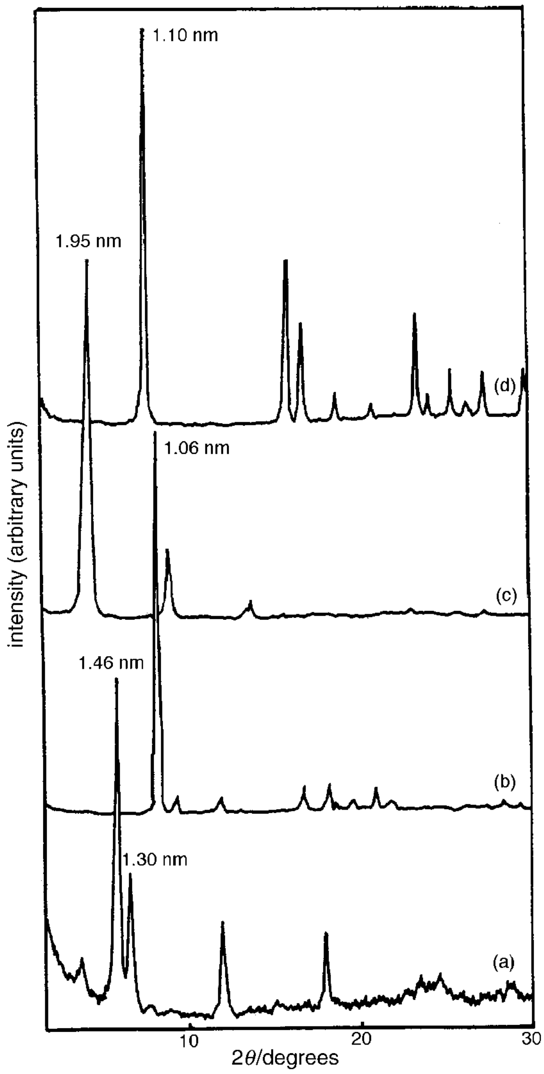

Fig. 4 XRD profiles of (a) the reaction products of $Zn(OH)_2$ with benzoic acid, (b) zinc benzoate, (c) the reaction products of $Zn(OH)_2$ with 0.25 equivalents of benzoic acid (1.00×10^{-3} mol) and (d) benzoic acid.

with benzoic acid was 1.35/0.65, and two series of peaks were observed in the XRD patterns corresponding to peaks of fibrous and plate-like products.

Mechanism for the self-assembly reaction

In the reaction of $Zn(OH)_2$ with an excess of benzoyl chloride, the product was found to dissolve in the solvent.[21] However, the reaction product of $Zn(OH)_2$ with an excess of benzoic acid was a powder. The IR spectrum and XRD pattern of the powder indicated the production of zinc benzoate. In the reaction of $Zn(OH)_2$ with 0.25 mol equivalent of benzoic acid in acetonitrile a powder was obtained and the host/guest ratio of the powder was 1.57/0.43. The weight loss of the compound observed by TG occurred at lower temperatures than that of the reaction product of $Zn(OH)_2$ with 0.5 mol equivalent of benzoic acid and the *d*-value was 1.95 nm as shown in Fig. 4(c). The reaction product had a plate-like structure as shown in Fig. 5(a). A TEM image of the product showed a clear layer structure as shown in Fig. 6. Also, the layer distance of the plate-like compound was larger than that of the fibrous compound.

Hydroxy double salt

The *d*-value of $Zn_5(OH)_8(C_6H_5COO)_2{\cdot}2H_2O$, a hydroxy double salt (HDS), was reported as 1.85–1.93 nm[35] close to the *d*-value of the plate-like compound obtained in this study. HDSs are layered inorganic compounds which show anion exchangeability.[36,37] The general formula of an HDS is

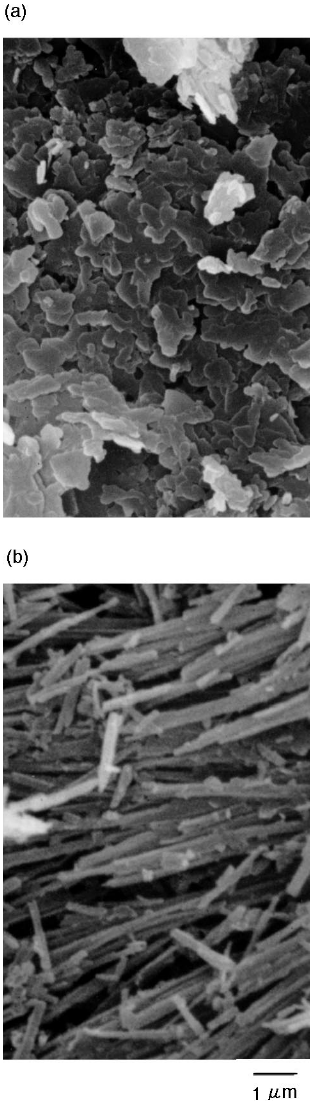

Fig. 5 SEM images (magnification 10000 ×) of the reaction products of $Zn(OH)_2$ with (a) 0.25 equivalents of benzoic acid (1.00×10^{-3} mol), and (b) cyclopentane carboxylic acid.

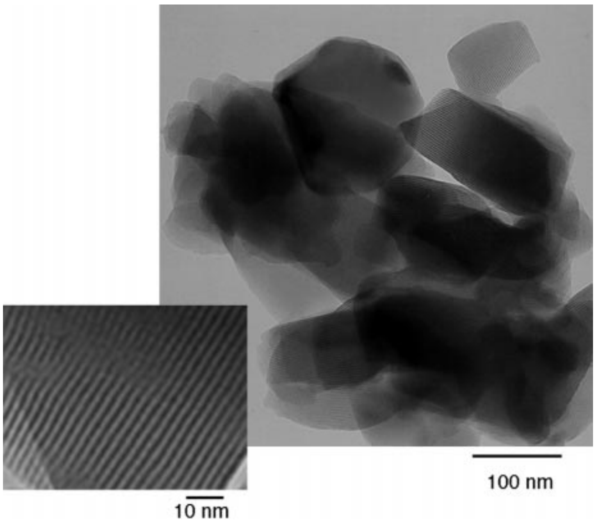

Fig. 6 TEM image of the reaction product of $Zn(OH)_2$ with 0.25 equivalents of benzoic acid (1.00×10^{-3} mol).

$[(M^{II}_{1-x}M'^{II}_{1+x})(OH)_{3(1-y)}]^{+}X^{n-}_{(1+3y)/n}$ in which M and M′ correspond to divalent metals such as Cu, Co, Ni, Mg, Zn,[38,39] Cd, Fe or Mn and X is an anion which is situated between the cationic layers. These compounds also show plate-like structures.[40] It has already been reported that benzoic anion can be exchanged into an HDS giving the composition $Cu(OH)_{1.5}(C_6H_5COO)_{0.5}$.[36] The interlayer spacing of this compound was 1.57 nm, and a large weight loss was observed between 500 and 600 K according to TG analysis. Therefore, we conclude that in our instance the plate-like compound of $Zn(OH)_2$ with benzoic acid is an HDS, *i.e.* $Zn_5(OH)_8(C_6H_5COO)_2 \cdot 2H_2O$.

We have further reacted the plate-like compound with benzoic acid and the SEM image and XRD pattern of the reaction product indicated the formation of a fibrous compound. It is suggested that the first step of the reaction between $Zn(OH)_2$ and a carboxylic acid is a dehydration reaction between the OH groups of $Zn(OH)_2$ and RCOOH. At a carboxylic acid COOH/OH ratio of 0.25, the reaction gives a mixture of HO–Zn–OH and RCOO–Zn–OH bonds with $Zn_5(OH)_8(RCOO)_2 \cdot 2H_2O$ being formed as shown in Fig. 7. At a COOH/OH ratio of 0.5, the reaction gives a mixture of HO–Zn–OH, RCOO–Zn–OH and/or RCOO–Zn–OCOR bonds with formation of the CdI_2-type layered compound $Zn(OH)_x(RCOO)_y$. Further reaction of $Zn_5(OH)_8(RCOO)_2 \cdot 2H_2O$ with carboxylic acid gave a CdI_2-type layered compound, $Zn(OH)_x(RCOO)_y$. The structure of $Zn_5(OH)_8(RCOO)_2 \cdot 2H_2O$ consists of brucite-type $[Zn_3(OH)_8]^{2-}$ layers with 25% of the octahedral positions remaining unoccupied. Above and below the unoccupied octahedral positions, two further zinc ions per formula unit occupy the tetrahedral positions.[37,39] Further reaction of $Zn_5(OH)_8(RCOO)_2 \cdot 2H_2O$ with carboxylic acid results in a disruption of the tetrahedral units by the dehydration reaction between the OH groups attached to Zn at tetrahedral positions. Since the layer distance of the fibrous compound was smaller than that of the HDS as shown in Fig. 3 and 6, we propose that the further reaction of $Zn_5(OH)_8(RCOO)_2 \cdot 2H_2O$ with RCOOH leads to the $Zn(OH)_x(RCOO)_y$ structure.

When the COOH/OH ratio was >0.5, the organic zinc salt, *i.e.* $Zn(RCOO)_2$, was obtained. The cross-sectional area of one OH–Zn–OH unit[41] is calculated to be 0.96 nm^2 whereas that of RCOO–Zn–OCOR is >0.96 nm^2. Therefore, an excess amount of RCOO–Zn–OCOR might interfere in the assembly process to form the layered structure owing to steric factors and thus the organic zinc salt is formed.

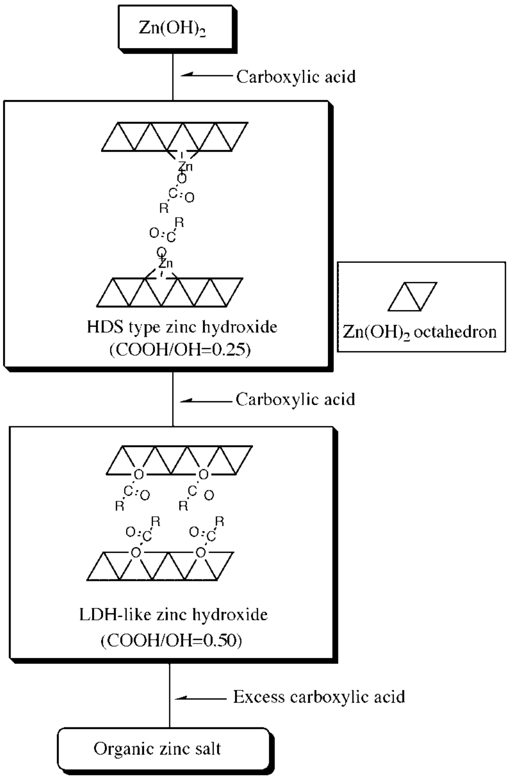

Fig. 7 A representative scheme of the organo derivatization reaction.

In all, these results indicate that the morphology of the reaction product depends on the quantity of reacted organic compound.

We have found that the fibrous compound was formed by the reaction of $Zn(OH)_2$ with benzoic acid and benzoyl chloride. Further reactions of $Zn(OH)_2$ with other bulky carboxylic acids, such as pivalic acid, isobutyric acid, cyclohexane carboxylic acid, cyclopentane carboxylic acid, terephthalic acid, *p*-toluic acid, *p*-hydroxybenzoic acid, *p*-nitrobenzoic acid, *p*-aminobenzoic acid, 1-naphthoic acid, 2-naphthoic acid and *p*-phenylazobenzoic acid were carried out.

In the reaction of $Zn(OH)_2$ with cyclopentane carboxylic acid, a fibrous compound was obtained as shown in Fig. 5(b) with an interlayer spacing of 1.37 nm and *ca.* 45% of reacted hydroxy groups. By contrast, the reaction product of $Zn(OH)_2$ with *n*-caproic acid yielded a plate-like structure as mentioned above. Fibrous structures were also obtained upon reaction of $Zn(OH)_2$ with other bulky aliphatic acids such as pivalic acid, isobutyric acid and cyclohexane carboxylic acid.

Reaction with various carboxylic acids

Upon reaction of $Zn(OH)_2$ with terephthalic acid 56% of the hydroxy groups reacted and the interlayer spacing was increased to 1.33 nm as shown in Table 3. However, the product was not fibrous. The reaction product of $Zn(OH)_2$ with terephthalic acid was considered to have a cross-linked structure. As expected the product was not fibrous owing to an anticipated lack of steric hindrance. Bulky aromatic compounds such as 1-naphthoic acid, 2-naphthoic acid and *p*-phenylazobenzoic acid were also reacted with $Zn(OH)_2$ and the interlayer spacings of the products increased to 1.61, 2.01 and 2.63 nm, respectively, while naphthoic acids and *p*-phenylazobenzoic acid are bulky aromatic compounds their reaction products with $Zn(OH)_2$ were not fibrous. The molecular lengths of 1-naphthoic acid (0.64 nm), 2-naphthoic acid (0.76 nm) and *p*-phenylazobenzoic acid (1.16 nm) are larger than that of benzoic acid (0.54 nm). Optimal distance between the layers may be achieved by formation of a fibrous morphology.

Clearly the morphology depends on the nature of the organic compounds. In the reactions of $Zn(OH)_2$ with *p*-methyl- or *p*-nitro-substituted benzoic acid, fibrous compounds were obtained whereas in reactions with *p*-amino- or *p*-hydroxybenzoic acids, plate-like structures were obtained suggesting the importance of functional groups in determining the morphology.

TEM images showed that the ends of the fibrous compound obtained by the reaction of $Zn(OH)_2$ with benzoic acid were curled suggesting that steric repulsion between organic moieties between the layers determined the morphology. From these results, we have proposed a construction scheme of the fibrous compounds as shown in Fig. 8.

Reaction with a mixture of two acids

The reaction product of $Zn(OH)_2$ with benzoic acid was fibrous while the reaction product of $Zn(OH)_2$ with adipic acid has a plate-like structure. Upon reaction of $Zn(OH)_2$ with the mixture of benzoic acid and adipic acid SEM images of the products showed the presence of both fibrous and plate-like structures. In XRD patterns, two different series of peaks were observed at 1.49 nm and 0.83 nm corresponding to the peaks of the products with benzoic acid and adipic acid respectively.

Table 3 Organo derivatization reaction products of $Zn(OH)_2$ with bulky carboxylic acids, $Zn(OH)_x(O{-}G)_y$ and $Zn(OH)_x(O{-}G{-}O)_z$ ($x+y=2$, $x+2z=2$)

		d/nm					
Carboxylic acid	Length[a]/nm	Acid	$Zn(OH)_2+RCOOH$[b]	*x*	*y*	*z*	Morphology
Aliphatic							
Pivalic acid	0.35	0.45	1.33	0.73	1.27	—	Fibrous
Isobutyric acid	0.35	—	1.24	0.94	1.06	—	Fibrous
Cyclohexane carboxylic acid	0.54	0.82	1.41	0.85	1.15	—	Fibrous
Cyclopentane carboxylic acid	0.45	—	1.37	1.05	0.95	—	Fibrous
Aromatic							
Terephthalic acid	0.58	0.51	1.33	0.88	—	0.56	Non-fibrous[c]
p-Toluic acid	0.63	0.71	1.34	0.94	1.06	—	Fibrous
p-Hydroxybenzoic acid	0.61	0.51	1.63	1.13	0.87	—	Non-fibrous[c]
p-Nitrobenzoic acid	0.65	0.62	1.52	1.09	0.91	—	Fibrous
p-Aminobenzoic acid	0.63	0.94	1.12	1.29	0.71	—	Non-fibrous[c]
Benzoic acid[d]	0.54	1.10	1.95, 1.48	1.35	0.65	—	Fibrous
Benzoic acid[e]	0.54	1.10	1.95	1.57	0.43	—	Plate-like
1-Naphthoic acid	0.64	1.57	1.61	0.92	1.08	—	Plate-like
2-Naphthoic acid	0.76	1.52	2.01	0.90	1.10	—	Plate-like
p-Phenylazobenzoic acid	1.16	1.57	2.63	1.20	0.80	—	Plate-like

[a]Distance between carbonyl carbon and the furthest hydrogen (monocarboxylic acid) or between two carbonyl carbons (dicarboxylic acid. [b]The reaction product of $Zn(OH)_2$ with carboxylic acid. [c]The morphology was unclear. [d]Zinc oxide was used instead of $Zn(OH)_2$. [e]The reaction product of $Zn(OH)_2$ with benzoic acid (1.00×10^{-3} mol).

This indicates that the two acids react with $Zn(OH)_2$ separately.

In the reactions of $Zn(OH)_2$ with bulky organic compounds such as benzoyl chloride or bulky carboxylic acids, fibrous layered nanohybrids were obtained and can be considered as self-assembled nanocrystals. It is noteworthy that the morphology of the reaction products depends on the nature and the amounts of the reacted organic compounds.

Recently, many researchers have investigated architectures of inorganic and/or organic frameworks. The preparation of such frameworks in the presence of assemblies of template compounds[42] or *via* secondary interactions[43] is determined by various factors such as molecular size, and number or position of functional groups. This present work suggests possibilities for the preparation of layered compounds with control of interlayer spacings. Furthermore, the presence of plate-like and fibrous morphologies indicates the possibility to control morphology of layered compounds depending upon the organic compound.

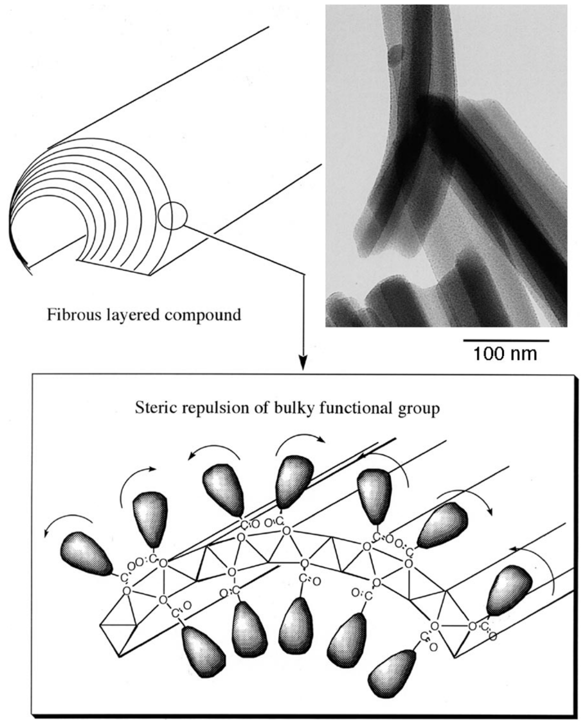

Fig. 8 Schematic representation of a fibrous organic–inorganic nanohybrid.

Conclusions

We have established a new preparation method for organic–inorganic layered compounds by the organo derivatization reaction of $Zn(OH)_2$ and ZnO with acyl chlorides and carboxylic acids. The IR spectra of the reaction products of $Zn(OH)_2$ with carboxylic acids indicate the formation of RCOO–Zn bonds. In XRD patterns, layered structures of the products were confirmed. SEM images showed that the main reaction products were of plate-like morphology, whereas reaction products with bulky carboxylic acids were fibrous. However, when the amount of reacted organic compound was low, the reaction products of $Zn(OH)_2$ with bulky carboxylic acids were of plate-like morphology. These results indicated that the structure of nanomaterials assembled by organo derivatization reactions depended on the structure and the amounts of reacted organic compounds.

In usual organic esterification reactions, removal of water is critical. However, the reaction of $Zn(OH)_2$ and ZnO with carboxylic acids occurred even in the presence of water, and the reaction products were stable in water. This indicates that the formation of RCOO–Zn bonds leading to organic–inorganic nanohybrids is energetically favorable. A possible driving force for assembly is given by hydrophobic–hydrophobic interactions between organic compounds and/or between $Zn(OH)_2$ and organic compounds.

Our reaction conditions are mild, and carboxylic acids are more convenient compounds than acyl chlorides. Therefore, this preparation method of organic–inorganic nanohybrid compounds promises to provide a variety of combinations of $Zn(OH)_2$ with organic compounds.

Chemical surface modification of inorganic compounds has been studied extensively to alter their chemical and/or physical properties in a controlled way.[7] The present reaction is a new preparation method of surface-modified inorganic layered compounds. The products have potential as shape-selective sorbents, catalysts and photofunctional materials. The present preparation method is also useful for controlling the organization of organic molecules in the solid state, and the preparation of new microporous materials with controlled morphology.

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