Preparation of New Fibrous Layered Compounds by the Reaction of Zinc Hydroxide with Organic Compounds

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(Received November 12, 1997; CL-970862)

Organic-inorganic layered nano-hybrids were prepared by the reactions of amorphous $Zn(OH)_2$ with organic oxychlorides and organic carboxylic acids, and fibrous layered compounds were obtained by the reaction with bulky organic compounds.

Chemical surface modification of inorganic compounds has been extensively studied in order to change their chemical and/or physical properties.[1] Recently we have prepared organic - inorganic nano-hybrids by the reaction of $Zn(OH)_2$ with organic oxychlorides.[2] The compounds had plate-like morphologies except the reaction product with benzoylchloride.[2b] The plate-like morphologies were similar to those of layered double hydroxides (LDHs)[3] and the surface modified LDHs. The surface modified LDHs were obtained by the reaction of the water treated Zn/Al LDH (W-LDH) with organic oxychlorides in which W-LDH was prepared by standing calcined LDH in degassed water.[4] Dehydration reaction of hydroxyl groups with carboxylic acid was not easy. Certainly, W-LDH did not react with carboxylic acid. In this study we have prepared layered compounds by the reactions of $Zn(OH)_2$ with carboxylic acids and also prepared new fibrous layered compounds by the reactions with bulky organic compounds.

Figure 1. TEM image (15000 × magnification) for the reaction product of zinc hydroxide with benzoylchloride in acetonitrile.

Fibrous nano-hybrid as shown in Figure 1 was obtained by the reaction of $Zn(OH)_2$ with benzoyl chloride at 333 K for 5 h in acetonitrile (ACN). Such fibrous compounds were not obtained in the reaction of $Zn(OH)_2$ with aliphatic oxychlorides and dioxychlorides.[2] However, similar fibrous compound was obtained by the reaction with benzoic acid. Although $Zn(OH)_2$ was amorphous, new peaks in XRD appeared by the reaction

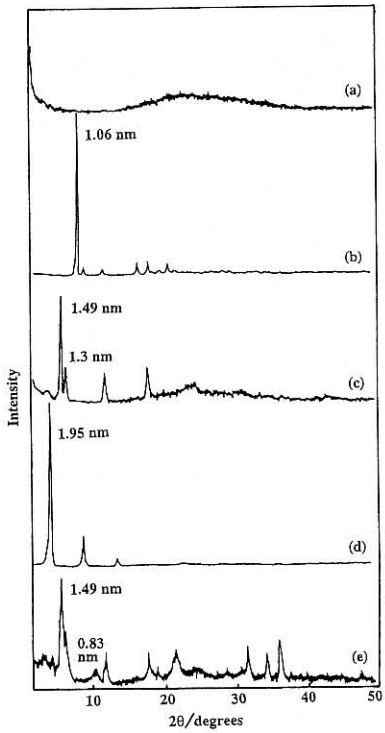

Figure 2. XRD patterns of (a) zinc hydroxide, (b) zinc benzoate and the reaction products of (c) zinc hydroxide with benzoylchloride in acetonitrile, (d) zinc oxide with benzoylchloride in water and (e) zinc hydroxide with the mixture of benzoic acid and adipic acid.

with benzoylchloride or benzoic acid as shown in Figure 2 (c). The d-values of zinc benzoate and benzoic acid were 1.06 and 1.09 nm, respectively. The d value of the reaction product of $Zn(OH)_2$ with benzoyl chloride was 1.49 nm suggesting that the reaction product was not zinc benzoate and benzoic acid. OH absorption of $Zn(OH)_2$ at near 3500 cm^{-1} in IR spectrum fairly decreased by the reaction with benzoic acid and a new peak appeared at near 1540 and 1400 cm^{-1}. These peaks indicates the formation of COO-metal bond.[6] The peak at near 1.3 nm in XRD patterns corresponded to the peak of benzoylbenzoic acid[7] which is dimer of benzoic acid. However, peaks of carboxylic acid or dimer were not observed in IR spectrum and TG analyses showed that the quantity of the organic by-product was small. Elemental analysis showed that 50-54% of hydroxyl groups reacted with benzoylchloride and benzoic acid. Interlayer spacing, 1.49 nm, was the same with that of the surface modified Zn/Al LDH which was prepared by the reaction of W-LDH with benzoyl chloride. The value of interlayer distance indicated tilted bilayer structure of organic compound between the layers. TEM image of the reaction product shows that the layer planes were parallel to the surface planes of fiber as shown in Figure 3(a).

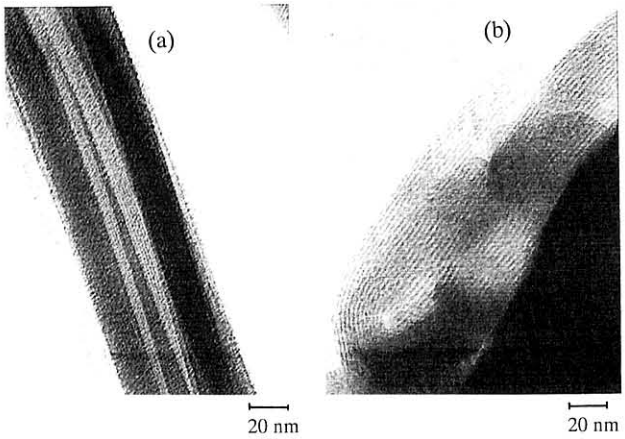

Figure 3. TEM images (500000 × magnification) for (a) the reaction product of zinc hydroxide with benzoylchloride in acetonitrile and (b) the reaction product of zinc oxide with benzoylchloride in water.

$Zn(OH)_2$ also reacted with phenylacetyl chloride. By the reaction, 77% of hydroxyl groups reacted and interlayer spacing of the product was 1.53 nm. However, the product was plate-like morphology. Fibrous morphologies were also obtained by the reaction with pivalic, isobutylic and cyclohexane carboxylic acids. In the reactions, 53-71% of hydroxyl groups reacted as shown in Table 1. Fibrous compounds were also obtained by the

Table 1. Reaction products of $Zn(OH)_2$ with organic oxychloride or organic carboxylic acid

Organic compound (G)	d-value[a]	x[b]	y[b]	Morphology
benzoylchloride	1.49	1.00	1.00	fibrous
benzoylchloride[c]	1.96	1.81	0.19	plate-like
phenylacetylchloride	1.53	0.46	1.54	-[d]
benzoic acid	1.48	0.93	1.07	-[d]
benzoic acid[c]	1.96, 1.48	1.35	0.65	-[d]
pivalic acid	1.33	0.73	1.27	fibrous
isobutyric acid	1.24	0.94	1.06	fibrous
cyclohexanecarboxylic acid	1.41	0.85	1.15	fibrous
hexanoylchloride	1.67	0.58	1.42	plate-like
p-toluic acid	1.34	0.94	1.06	fibrous
p-hydroxybenzoic acid	1.63	1.13	0.87	-[d]
p-nitrobenzoic acid	1.52	1.09	0.91	fibrous
p-aminobenzoic acid	1.12	1.29	0.71	-[d]
1-naphthoic acid	1.61	0.92	1.08	-[d]
2-naphthoic acid	2.01	0.90	1.10	-[d]

[a] nm. [b] x, y in $Zn(OH)_x(O\text{-}G)_y$. [c] ZnO was used instead of $Zn(OH)_2$. [d] unclear images.

reaction with methyl and nitro substituted benzoic acids. However, in the reaction of para-amino or para-hydroxyl benzoic acids, the products were not fibrous. 1-Naphthoic and 2-naphthoic acids also reacted with $Zn(OH)_2$, and interlayer spacings were 1.61 and 2.01 nm, respectively. They were not fibrous. It was considered that proper steric interaction between bulky organic moieties might cause bending of the inorganic plane as shown in Figure 4 resulting in fibrous morphologies.

Hydroxy doubles salts (HDSs) have positively-charged layers and are known as anion exchangers.[8] They are plate-like morphologies.[6] Benzoate anion was exchanged into HDS giving the composition, $Cu(OH)_{1.5}(C_6H_5COO)_{0.5}$.[9] Its interlayer spacing was 1.57 nm. The host/guest ratio of the HDS was 1.5/0.5. We have reacted ZnO with benzoic acid in water to suppress the reaction. The host/guest ratio of the reaction product was

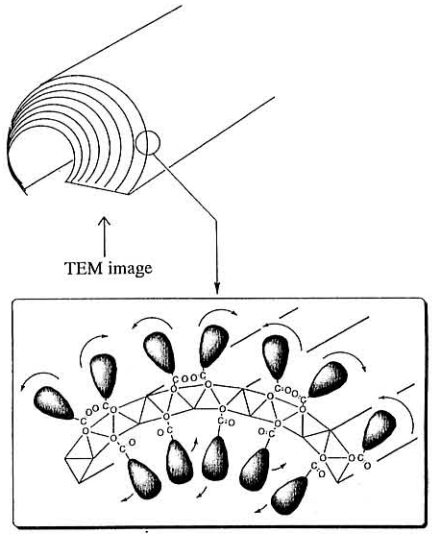

Figure 4. A schematic representation of organic - inorganic nanohybrid.

1.8/0.2. The product was plate-like morphology and weight loss occurred at lower temperatures than the reaction product of $Zn(OH)_2$ with benzoylchloride. Interlayer spacing of the compound was 1.95 nm. As shown in Figure 3(b), TEM image indicated the product was layer structure. These results suggested that the reaction product of ZnO with benzoic acid in water was HDS of zinc.

In the reaction of ZnO with benzoic acid in ACN, host/guest ratio of the product was 1.35/0.65 and two series of peaks were observed in XRD patterns. They corresponded to the peaks of the product of $Zn(OH)_2$ with benzoylchloride in acetonitrile and the peaks of the product of ZnO with benzoic acid in water. These results indicated that the morphology of the reaction product depended on the quantity of reacted benzoic acid.

The reaction product of $Zn(OH)_2$ with benzoic acid was fibrous and the reaction product of $Zn(OH)_2$ with adipic acid was plate-like morphology. We have reacted $Zn(OH)_2$ with the mixture of benzoic acid and adipic acid. SEM image of the product showed the co-presence of fibrous and plate-like morphologies. XRD patterns also indicated presence of two different series of peaks in which 1.49 nm corresponded to the peak of product from benzoyl chloride and 0.83 nm corresponded to the peak of product from adipic acid.

It is note worthy that the nano-hybrid could be prepared by the reaction with organic carboxylic acid and the morphology of the self-assembled nano-hybrid depends on the structure, kinds and quantity of organic compounds.

References and Notes

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