Effects of Zinc on the New Preparation Method of Hydroxy Double Salts

Hiroyuki Morioka, Hideyuki Tagaya,* Masa Karasu, Jun-ichi Kadokawa, and Koji Chiba

Department of Materials Science and Engineering, Yamagata University, 4-3-16, Jonan,
Yonezawa, Yamagata 992-8510, Japan

Received October 15, 1998

In this study, a new preparation method of hydroxy double salts (HDSs) including organic compounds between layers has been established in which the HDSs were prepared by reacting ZnO with organic metal salts in water. This method does not need an anion-exchange reaction to incorporate organic compounds into the HDS layers. Moreover, the reaction proceeds under mild conditions around room temperature, and the obtained HDSs showed high crystallinity compared to those obtained by an anion-exchange reaction. We prepared ZnO crystals having a thin-plate structure by the thermal treatment of hydroxy zinc acetate at 873 K.

Introduction

The preparation and application of inorganic−organic nanocomposite materials are a recent matter of concern.[1,2] Much of the research interest in inorganic−organic nanocomposites is owed to the remarkably different properties displayed by these fascinating materials.

From the viewpoint of this concern, layered metal salt chemistry is rapidly becoming a well-developed branch of materials chemistry.[3,4] Furthermore, the inorganic layered metal salt may include organic compounds and allow them to exhibit new chemical and/or physical properties different from those alone as the bulk crystal.

Hydroxy double salts (HDSs) are known as anion-exchangeable inorganic layered compounds.[5] The general formula of HDSs is $[(M^{2+}{}_{1-x},Me^{2+}{}_{1+x})(OH)_{3(1-y)}]^{+}X^{n-}{}_{(1+3y)/n}\cdot zH_2O$ in which M and Me corresponds to divalent metals such as Cu, Co, Ni, Mn, or Zn. X^{n-} is the exchangeable anion. Usually, HDS was prepared by reacting a solid oxide such as ZnO with a solution of a solid salt such as $Zn(NO_3)_2\cdot 6H_2O$. Research in this area has been focused on the design of new materials by ion-exchange reaction, the key issue being the engineering of the interlayer space between these two-dimensional structures.

We have recently reported the preparation of a HDS whose interlayer anion was exchanged by an organic compound (HDS-organic).[6] Generally, two methods are known to prepare HDS-organic. In the first method, preparation starts from a mixture of a metal oxide and an aqueous solution of an inorganic metal salt.[7−9] The solid is transformed into the basic metal salt. Using this basic metal salt, HDSs exchanged by organic compounds were prepared by the anion-exchange reaction between the inorganic anion in their layers and the organic anion in the solution. Thus, the first preparation method needs two steps to obtain the HDS-organic. In the second method, preparation consists of a slow addition of sodium hydroxide into the solution of the inorganic or organic metal salt until the basic metal salt is precipitated.[10,11] The inorganic or organic metal salts may be hydrolyzed in this reaction. Corrosion of the inorganic or organic metal salts itself may dominate to the formation of inorganic or organic HDS. However, for the second method it is difficult to determine optimum reaction conditions.

In this study, we report a new and simple preparation method under mild conditions at around room temperature. The HDS structured compounds were prepared only by a one-step process in which a metal oxide was reacted with an organic metal salt in water. This method does not need the anion-exchange reaction to incorporate organic compounds into HDS layers.

Experimental Section

A HDS that includes organic compounds was prepared by the reaction of a metal oxide (MeO) with an organic metal salt (M−R; R = organic group). The obtained HDS was designed as Me/M R-HDS. For instance, Zn/Cu acetate-HDS is prepared from ZnO and copper acetate dispersed in solution.

In the case of Zn/Zn acetate-HDS, 0.41 g of ZnO (0.005 mol) and 1.10 g of zinc acetate (0.005 mol) were added to water (10 mL) with vigorous stirring at room temperature. The suspension was allowed to stand for 24 h at room temperature. The solid material was isolated, washed, and dried in vacuo at room temperature. The X-ray powder diffraction patterns of the products did not show the reflection peaks of ZnO. Also, Zn/Zn benzoate-HDS was prepared from 0.1 g of ZnO (0.001 mol) and 0.38 g of zinc benzoate (0.001 mol) in a mixture of water and ethanol (1:1, 10 mL) at room temperature. In the case of fatty acid metal salts having long chains and aromatic acid metal salts, reactants were suspended in the mixture of water and ethanol.

In a similar way, metal oxides such as CuO and NiO were reacted with organic metal salts such as fatty acid metal salts and aromatic

---

(1) Rao, C. N. R., Gopalakrishnan, J., Eds. *New directions in solid state chemistry,* 2nd ed.; Cambridge University Press: Cambridge, 1997.

(2) Bruce, D. W., O'Hare, D., Eds. *Inorganic materials;* 2nd ed.; John Wiley & Sons: New York, 1996.

(3) Müller-Warmuth, W., Schöllhorn, R., Eds. *Progress in intercalation research;* Kluwer Academic Publishers: Dordrecht, 1994.

(4) Lagaly, G.; Beneke, K. *Colloid Polym. Sci.* **1991**, *269*, 1198−1211.

(5) Bruschini, C. S.; Hudson, M. J. in *Access in Nanoporous Mater.;* Pinavaia, T. J., Thorpe, M. F., Eds.; Plenum Press: New York, 1995; pp 161−172.

(6) Morioka, H.; Tagaya, H.; Karasu, M.; Kadokawa, J.; Chiba, K. *J. Mater. Res.* **1998**, *13* (4), 848−851.

(7) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1993**, *32*, 1209−1215.

(8) Hayashi, H.; Hudson, M. J. *J. Mater. Chem.* **1995**, *5* (1), 115−119.

(9) Hayashi, H.; Hudson, M. J. *J. Mater. Chem.* **1995**, *5* (5), 781−783.

(10) Jiménez-López, A.; Rodríguez-Castellón, E.; Olivera-Pastor, P.; Maireles-Torres, P.; Tomlinson, A. A. G.; Jones, D. J.; Rozière, J. *J. Mater. Chem.* **1993**, *3* (3), 303−307.

(11) Choy, J.-H.; Kwon, Y.-M.; Song, S.-W.; Chang, S. H. *Bull. Korean Chem. Soc.* **1997**, *18* (4), 450−453.

10.1021/ic9812149 CCC: $18.00

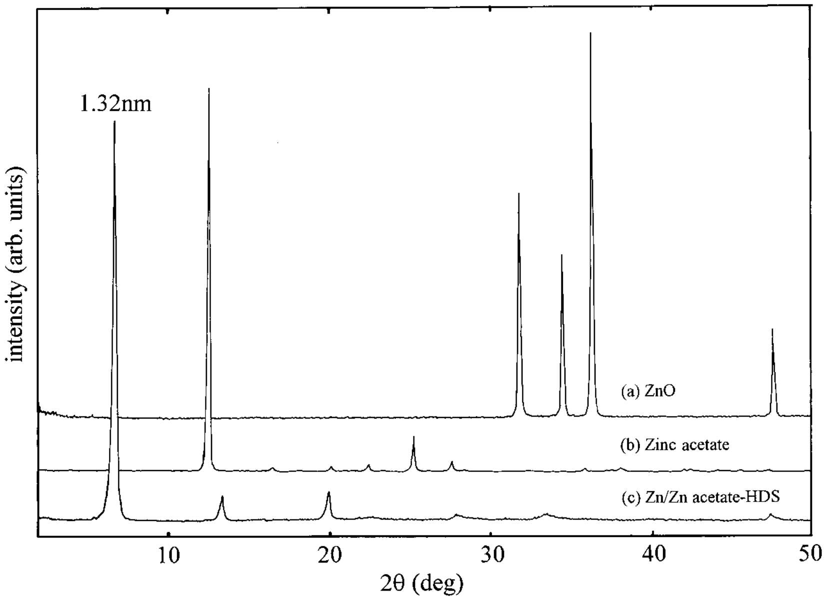
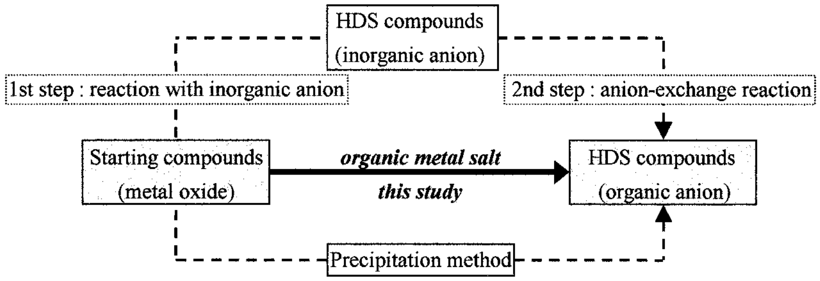


Figure 1. XRD patterns of (a) ZnO, (b) zinc acetate, and (c) Zn/Zn acetate-HDS.

Scheme 1. Three Preparation Methods of HDS Whose Interlayer Anion Was Exchanged by Organic Compounds (HDS-Organic)



acid metal salts. In most cases, the ratio of metal oxide:organic metal salt was 1.0:1.0−1.5.

To evaluate the effect of the difference of preparation method on characteristics, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ was prepared by the method of Stälin and Oswald.[12] In this method, ZnO powder was added to an aqueous $Zn(NO_3)_2$ solution with vigorous stirring at room temperature. Cu/Cu acetate-HDS (drop) was prepared by dropwise titration of a copper acetate solution with an aqueous NaOH solution up to OH:Cu = 1.0 at room temparature.[13,14]

Obtained compounds were calcined at 873K for 60 min, and their morphologies before and after thermal treatment were measured by scanning electron microscopy (SEM).

Powder X-ray diffraction (XRD) spectra were determined on a Rigaku powder diffractometer unit, using Cu Kα radiation ($\lambda = 0.154$ nm) at 20 mA and 40 kV. FT-IR spectra (KBr disk method) were recorded on a Horiba FT-200.

Results

In traditional preparation methods, the first step is to prepare a layered compound including the inorganic ion between the layers. The second step is to exchange ions in the layers and organic ions in the layers and organic ions in the solution. Thus, the preparation of layered compounds which include organic compounds needs two steps (Scheme 1). A one-step method to obtain layered compounds which include organic compounds was known, although it was a precipitation method. However, in this method it is difficult to control dropwise speed, pH, and concentration of alkali compounds. In this study HDS-organic was prepared by reacting a metal oxide with an organic metal salt. This method does not need two-step anion-exchange reactions to obtain HDS-organic.

In the first study, ZnO was reacted with zinc acetate. The XRD patterns of ZnO and zinc acetate are shown in Figure 1, traces a and b, respectively. The XRD pattern of the obtained product is shown in Figure 1c. The XRD pattern of the obtained product did not show the reflections of ZnO and zinc acetate. We confirmed the presence of acetate ion in the interlayer space of the obtained product by IR, as shown in Figure 2a, in which the peak at 1550 cm^{-1} was assigned to the symmetric stretching vibration of carboxylate. XRD patterns and the elemental analysis data found (H, 3.08; C, 7.89; N, 0.00) suggested that the obtained product was $Zn_5(OH)_8(OCOCH_3)_2 \cdot 2H_2O$ (H, 2.94; C, 7.79; N, 0.00). These results indicate that all ZnO transformed to Zn/Zn acetate-HDS. The peak at 1.32 nm in the XRD pattern corresponds to the interlayer distance of HDS, and the presence of several orders of harmonic reflections demonstrates that the product was highly oriented crystallites. ZnO was also reacted with monocarboxylic acid zinc salts, $(C_nH_{2n+1}COO)_2Zn$ (n = 0, 1, 11, 17). By the reaction of ZnO with $(C_nH_{2n+1}COO)_2Zn$, new peaks appeared in the XRD patterns indicating the formation of HDS crystals. The basal spacing of the reaction products of ZnO with $(C_nH_{2n+1}COO)_2Zn$ increased in the alkyl chain length n (Table 1); the mean increase is 0.18 nm/n, as shown in Figure 3. Interlayer distances of the products agree

---

(12) Stählin, W.; Oswald, H. R. *Acta Crystallogr.* **1970**, *B26*, 860−863.

(13) Yamanaka, S.; Sako, T.; Hattori, M. *Chem. Lett.* **1986**, 1869−1872.

(14) Yamanaka, S.; Sako, T.; Seki, K.; Hattori, M. *Solid State Ionics* **1992**, 53−56, 527−533.

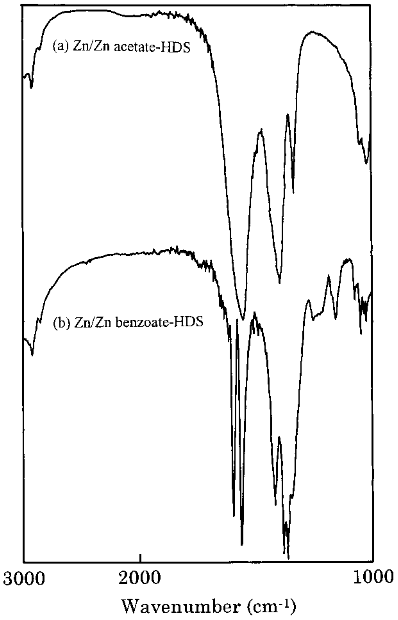


Figure 2. IR spectra of (a) Zn/Zn acetate-HDS and (b) Zn/Zn benzoate-HDS.

Table 1. XRD Data and Layer Expansion of Obtained HDSs

organic Zn salt	calcd length of acid (nm)	interlayer distance of HDS (nm)	layer expansion (nm)
carboxylic acid Zn salt			
$(HCOO)_2Zn$	0.29	1.12	0.65
$(CH_3COO)_2Zn$	0.41	1.33	0.86
$(CH_3(CH_2)_{10}COO)_2Zn$	1.65	2.98	2.51
$(CH_3(CH_2)_{16}COO)_2Zn$	2.42	4.09	3.62
aromatic carboxylic acid Zn salt			
$(C_6H_5COO)_2Zn$	0.71	1.87	1.40
$(1\text{-}C_{10}H_7COO)_2Zn$	0.71	1.62	1.15
$(2\text{-}C_{10}H_7COO)_2Zn$	0.95	2.44	1.97

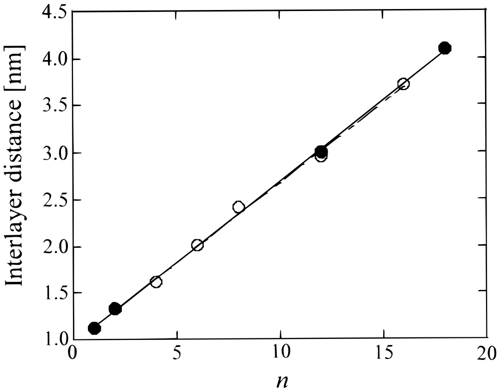


Figure 3. Interlayer distance of the $Zn_5(OH)_8(C_nH_{2n+1})_2{\cdot}2H_2O$ which were obtained by one-step reaction or by anion-exchange reaction: (●) obtained in this study; (○) anion-exchange reaction.

Table 2. Reaction of Metal Oxide with Metal Acetate

compds		interlayer distance (nm)	assigned
metal oxide	metal acetate		
divalent metal			
ZnO	$(CH_3COO)_2Zn$	1.32	HDS
ZnO	$(CH_3COO)_2Ni$	1.28	HDS
ZnO	$(CH_3COO)_2Co$	1.31	HDS
ZnO	$(CH_3COO)_2Cu$	0.94	HDS
NiO	$(CH_3COO)_2Zn$	0.21[a]	oxide
NiO	$(CH_3COO)_2Ni$	0.21[a]	oxide
NiO	$(CH_3COO)_2Co$	0.21[a]	oxide
NiO	$(CH_3COO)_2Cu$	0.21[a]	oxide
CuO	$(CH_3COO)_2Zn$	0.23[b]	oxide
CuO	$(CH_3COO)_2Ni$	0.23[b]	oxide
CuO	$(CH_3COO)_2Co$	0.23[b]	oxide
CuO	$(CH_3COO)_2Cu$	0.23[b]	oxide
monovalent metal			
ZnO	CH_3COONa	0.25[c]	oxide
ZnO	CH_3COOK	0.25[c]	oxide

[a] NiO. [b] CuO. [c] ZnO.

with those obtained by ion-exchange reactions between nitrate ion in $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ and monocarboxylate ion.[6] Ordinarily, ion-exchange reactions proceed between pre-incorporated counterions and objective ions in the interlayer. The new preparation method in this study showed a high exchange capacity the same as in the case of ion-exchange reactions. However, one of the important points of the new preparation method is that pre-incorporated inorganic counterions such as carbonate ion or nitrate ion and organic counterions do not need to exist in the reacting solution without the objective ion. Therefore, this method can protect coexistence with the objective ion and the pre-incorporated inorganic or organic counterion in the interlayer. The interlayer spacing of the products and the calculated length of the carboxylate ion indicated that the carboxylate ions are aggregated in the bilayer and tilted between the layers. We have already reported the conformation of mono- and dicarboxylate ions in the interlayer space of HDS in a previous paper.[6] In the paper, we postulated a bilayer structure for monocarboxylate ions and a bridged structure for dicarboxylate ions in which the two ends of the guest have reacted with cationic layers of opposing inner planes.

ZnO was also reacted with the zinc salts of aromatic carboxylic acids such as benzoic acid. In the reaction of ZnO with the zinc salt of an aromatic carboxylic acid, the production of HDS was confirmed in the XRD patterns. The IR spectrum indicates the appearance of a new peak at 1600 cm^{-1}, which was assigned to the symmetric stretching vibration of the aromatic ring as shown in Figure 2b.

We have also confirmed that even bulky organic compounds such as naphthoic acid could be incorporated. However, a large difference of interlayer distances between Zn/Zn 1-naphthoic-HDS (1.62 nm) and Zn/Zn 2-naphthoic-HDS (2.44 nm) was observed. This difference may be attributed to the difference of conformation between the layers, which was caused by the difference of the position of the carboxylate group.

To establish the new preparation method, various metal oxides were reacted with various metal acetates as shown in Table 2. Only ZnO reacted with several metal acetates. In the reactions of CuO and NiO, unreacted metal oxides were obtained. We also reacted ZnO with monovalent metal acetates such as CH_3COONa and CH_3COOK as shown in Table 2. However, ZnO did not react with monovalent metal salts.

Although many studies on morphologies of inorganic–organic nanocomposites have been reported, there are few reports on morphologies for HDS and its oxide obtained by thermal decomposition. Figure 4 shows the SEM images of Zn/Zn acetate-HDS and $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$. $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ had a plate structure, although Zn/Zn acetate-HDS had a thin-plate-like structure.

ZnO and ZnO film are widely used as electrooptic and piezoelectric devices such as optical modulators and surface acoustic wave devices.[15] These applications require structured ZnO and ZnO films in which the *c* axis of the ZnO unit cell is

---

(15) Koch, M. M.; Hartmann, A. J.; Lanb, R. N.; Neaber, M.; Walz, J.; Granze, M. *Surface Rev. Lett.* **1997**, *4* (1), 39–44.

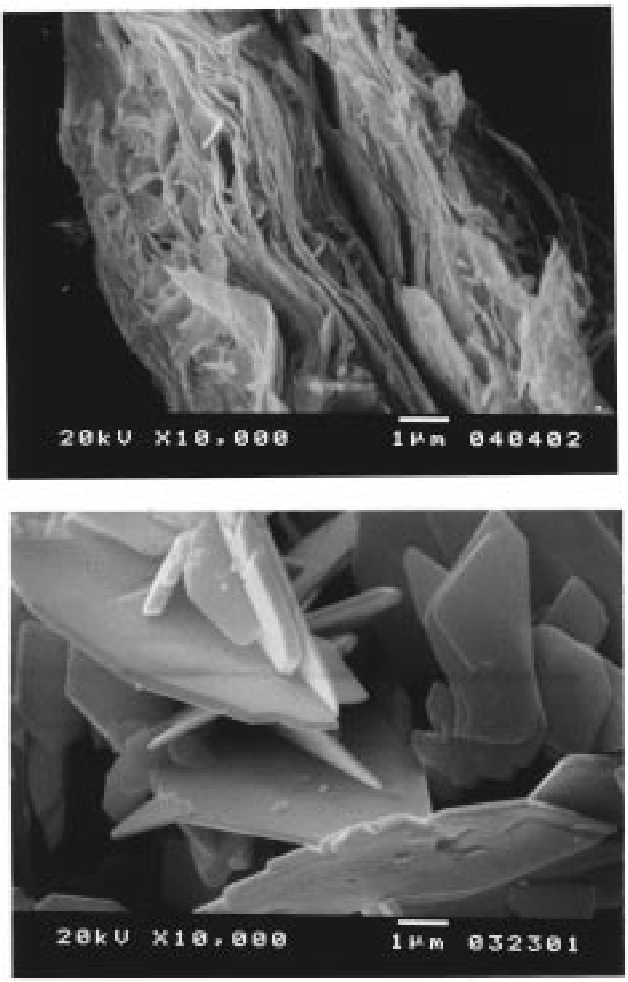


Figure 4. SEM images of (a) Zn/Zn acetate-HDS and (b) $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$.

perpendicular to the substrate/contact layer. Rykl et al.[16] reported a preparation method of thin-plate-structured ZnO. However, to prepare thin-plate-structured ZnO requires severe preparation conditions such as an autoclave with NH_4Cl at 723 K, 600 atm. In this study, characteristic ZnO powder was obtained by the thermal decomposition of Zn/Zn acetate-HDS at 873 K in an electric furnace. By the thermal treatment of Zn/Zn acetate-HDS and $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$, ZnO's were obtained as shown in Figure 5. Their XRD patterns were drastically different. The thermal decomposition product of Zn/Zn acetate-HDS shows an intense peak at 0.26 nm, and the other peaks are weak compared to those of ZnO obtained by the thermal decomposition reaction of $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$. The XRD patterns of characteristic ZnO agreed with the reported XRD patterns by Rykl et al.[16] $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ had a plate structure; however, Zn/Zn acetate-HDS had a thin-plate structure. It might be the reason for the discrepancy of peak intensities of ZnO as shown in Figure 5. The shape of the starting materials, as well as their compositions, affected morphologies of ZnO obtained by thermal treatment.[17] Figure 6 shows the SEM image of ZnO obtained from thermal treatment of Zn/Zn acetate-HDS and commercially available ZnO. These SEM images of ZnO suggested that the discrepancy of the XRD patterns between the thermal decomposition product of Zn/Zn acetate-HDS and $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ is a discrepancy of the shape of the starting materials.

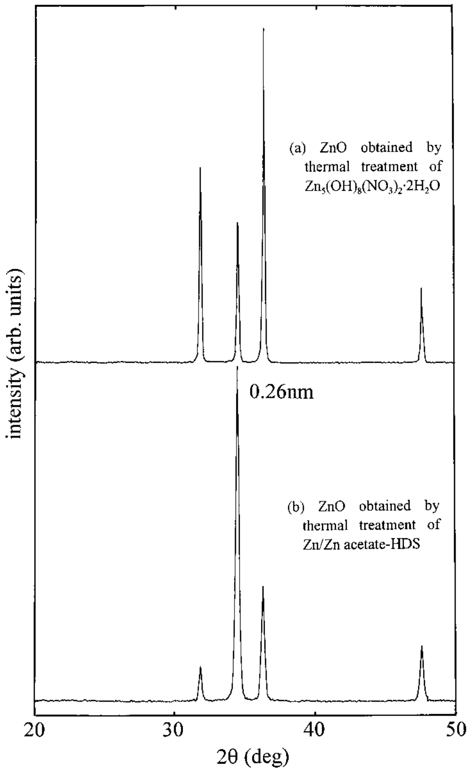


Figure 5. XRD patterns of ZnO obtained (a) by thermal treatment of $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ and (b) by thermal treatment of Zn/Zn acetate-HDS.

Discussion

We have shown that the HDS type compounds were prepared by reacting ZnO with organic metal salts in solution. This new preparation method does not need an ion-exchange reaction to incorporate organic compounds into the layers. Furthermore, this reaction proceeds only with ZnO and organic metal salts. However, CuO and NiO did not react with organic metal salts.

Some researchers reported that HDSs have two structures as shown in Figure 7. The first type of structure is prepared when the anion is NO_3^-; the compounds may be derived from $[Cu_2(OH)_3NO_3]$ by substituting Cu^{2+} for other divalent metal ions.[5] The structure of $[Cu_2(OH)_3NO_3]$ consists of $[Cu_2(OH)_4]$ layers where 25% of the OH^- ions are replaced by NO_3^- anions.[8,9] One oxygen ion of the NO_3^- group occupies the position of one hydroxide ion of the layer whereas the two further oxygen ions of NO_3^- lie between the hydroxide layers. These oxygen ions of the NO_3^- form single layers between the $[Cu_2(OH)_3]$ layers. Hence, the copper ions are octahedrally coordinated in a distorted form by $4OH^- + 2X^-$ and $5OH^- + X^-$ where X^- is NO_3^-. The Cu^{2+} ions occupy two nonequivalent positions with Cu(1) coordinated by four equatorial OH groups and two ionic oxygen atoms belonging the NO_3^- in the axial directions. Cu(2) is coordinated by four equatorial OH^- anions and by one OH^- plus one other oxygen from the NO_3^- in the axial directions.

The second type of HDS is derived from basic zinc hydroxide: $[Zn_5(OH)_8](NO_3)_2{\cdot}2H_2O$ and $[Zn_5(OH)_8]Cl_2{\cdot}2H_2O$.[12,18] The structure consists of brucite type $[Zn_3(OH)_8]^{2-}$ layers with 25% of the octahedral positions remaining unoccupied. Above

---

(16) Rykl, D.; Bauer, J. *Krist. Techn.* **1968**, *3*, 375−380.

(17) Kawai, A.; Sugahara, Y.; Park, I. Y.; Kuroda, K.; Katou, C. *Ceramic Powder Science IV*; The American Ceramic Society: Westerville, Ohio 1991; pp 75−80.

(18) Stählin, W.; Oswald, H. R. *J. Solid State Chem.* **1971**, *3*, 256−264.

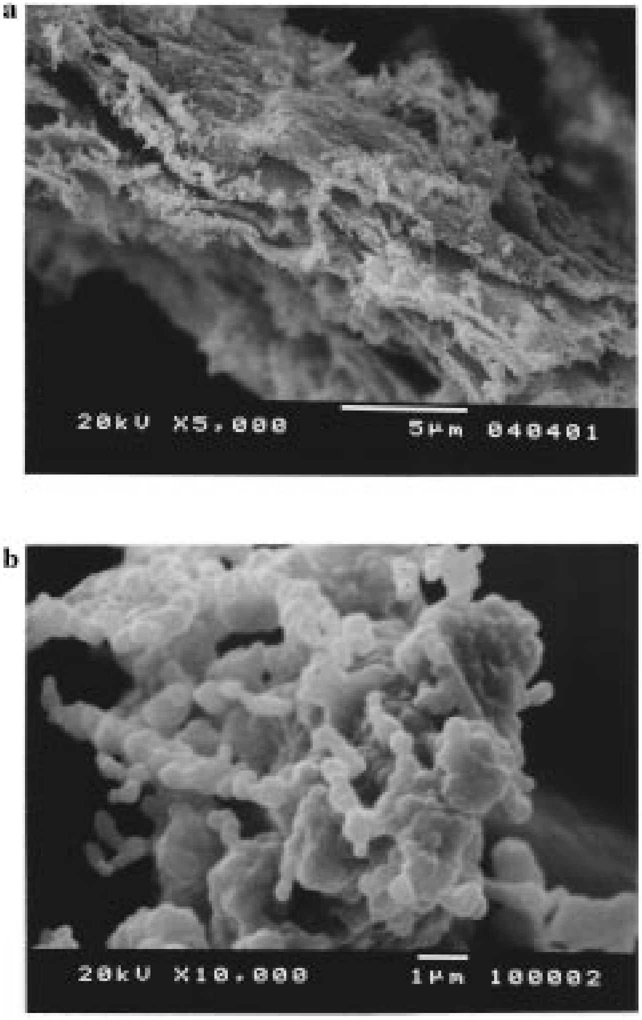


Figure 6. SEM images of (a) ZnO obtained from Zn/Zn acetate-HDS and (b) ZnO obtained from $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$.

and below the unoccupied octahedral positions, two further zinc ions per formula unit occupy tetrahedral positions. The tetrahedra are completed by water molecules or chloride ions lying between the $[Zn_5(OH)_8]^{2+}$ layers. After all, the structure of $[Zn_5(OH)_8](NO_3)_2 \cdot 2H_2O$ can be regarded as a variation of a hypothetical $Zn(OH)_2$ structure in the CdI_2 type group. One-quarter of a zinc atom is removed from the octahedral interstices of the sheet. Each occupied octahedron shares its edges with two unoccupied and four occupied octahedra. The resulting sheet is negatively charged: $[Zn_3^{oct}(OH)_8]^{2-}$. Tetrahedrally coordinated zinc atoms are located above and below the empty octahedron. Three corners of the tetrahedron are occupied by hydroxide ions belonging to the sheet described above, the fourth by a water molecule. The complex sheet so formed is positively charged, $[Zn_3^{oct}(OH)_8Zn_2^{tetr}(H_2O)_2]^{2+}$. In addition, the sheets are held together by hydrogen bonds; two oxygen atoms of the nitrate group are hydrogen bounded with water, and the third forms a bond with two hydroxide ions of the sheet.

As mentioned above, the first type of HDS including Cu and Ni is composed of octahedral coordination, but the second type of HDS including Zn metal is composed of octahedral and tetrahedral coordination. This discrepancy about the crystal structure of HDS was caused by the difference of the crystal structures of starting compounds. The crystal structure of Zn acetate dihydrate is monoclinic ($Z = 4$) and belongs to the space group $C2/c$.[20] The dihydrate is a six-coordinate structure, and the coordinating geometry around the Zn atom is approximately octahedral. The Zn atom is bonded to the two O atoms of the water molecules and the four O atoms of the acetate ligands. The crystal structures of copper and nickel acetate are approximately octahedral, too. The structure of CuO and NiO is a distorted octahedral or octahedral crystal structure in a rock salt type structure. However, only the crystal structure of ZnO is tetrahedral coordination in a wurtzite type structure. This is a reason for the difference of reactivities between zinc metal and other metals under their reaction conditions. The first type of HDS needs two types of octahedral coordination such as Cu(1) and Cu(2) in the same layer (Figure 7a); however, the second type of HDS need octahedral and tetrahedral coordination, octahedral coordination such as Zn^{oct} and tetrahedral coordination such as Zn^{tetr} in the same layer (Figure 7b). Tetrahedrally coordinated zinc atoms (Zn^{tetr}) are located above and below the empty octahedrally coordinated zinc atom (Zn^{oct}) layer.

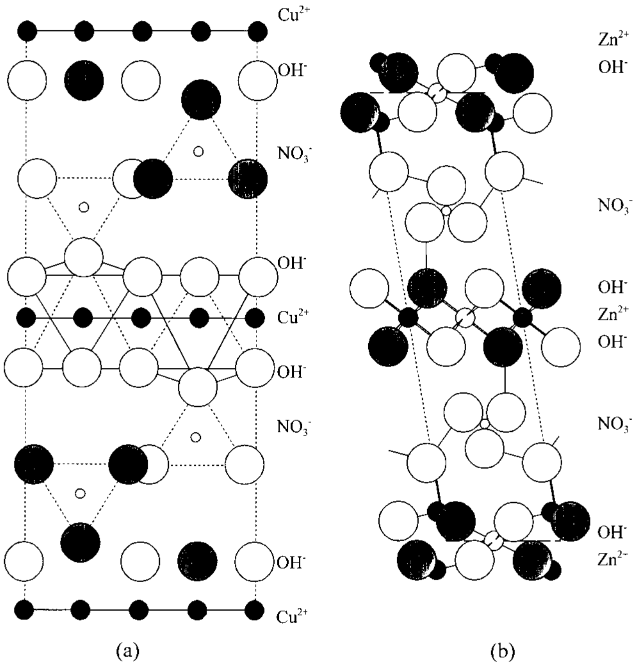


Figure 7. Schematic representation of HDS structure: (a) $Cu_2(OH)_3NO_3$ and (b) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$. Small, open circles are nitrogen atoms; medium, filled circles are metal atoms; and large, open circles are oxygen atoms.

Moreover, the reaction of ZnO with monovalent organic metal salts such as acetate potassium salt or sodium salt did not give layered compounds. Ordinarily, HDSs including organic ions in their layers were obtained from reactions with HDSs including inorganic ions and monovalent organic metal salt solutions via ion-exchange reactions. However, our reaction did not need monovalent organic metal salts to obtain HDSs including organic ions in their layers. It indicated that this reaction did not occur through the anion-exchange reaction.

Zn/Zn acetate-HDS was prepared from ZnO with zinc acetate in solution. The SEM image showed that the obtained compounds had thin-plate-like structures. Cu/Cu acetate-HDS (drop) was prepared by a dropwise titration method of copper acetate solution. Cu/Cu acetate-HDS (drop) had a plate structure as shown in Figure 8. A thin-plate-like structure was not obtained

---

(19) Fogg, A. M.; Dunn, J. S.; Shyu, S.-G.; Cary, D. R.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 351−355.

(20) Ishioka, T.; Murata, A.; Kitagawa, Y.; Nakamura, K. T. *Acta Crystallogr.* **1997**, *C53*, 1029−1031.

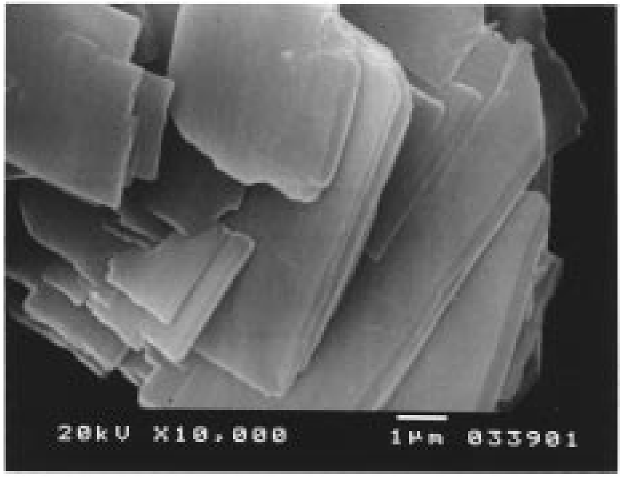


Figure 8. SEM image of $Cu_2(OH)_3(CH_3COO)$.

even though the reactions were carried out for various aging times, titration, and stirring speed. The analogous dropwise titration method was carried out for cobalt acetate and nickel acetate solutions, but no precipitation occurred. These results showed that Cu^{2+} ion was a strong complexing metal ion, but the Zn^{2+} ion was not strong, which was contemplated from the Irving–Williams complexation stability series.

Irving–Williams series of complexation stability:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The complexation tendency of Co^{2+} and Mn^{2+} was lower than that of Zn^{2+}. Low complexation ability of Co^{2+} and Mn^{2+} might be the reason for no precipitation reaction.

Conclusion

In this study, we report a new preparation method of HDS under mild conditions via one step in which the HDS structured compounds were prepared by reacting ZnO with organic metal salts. We have also found that Zn/Zn acetate-HDS is thin-plate structure and ZnO after thermal treatment of it has also a thin-plate structure. Thin-plate-like structure has potential for functional materials such as separation materials[19,20] and electrical devices.[21]

IC9812149

---

(21) Tagaya, H.; Sato, S.; Morioka, H.; Kadokawa, J.; Karasu, M.; Chiba, K. *Chem. Mater.* **1993**, *5*, 1431–1433.

(22) Ehisisen, K. T.; Delahaye-Vidal, A.; Genin, P.; Figlarz, M.; Willmann, P. *J. Mater. Chem.* **1993**, *3* (8), 883–888.