Transactions of the Materials Research Society of Japan 26 [2] 519-522 (2001)

Control of Interlayer Structure of the Reaction Products of Hydroxy Double Salt with Naphthoic Acid

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Hydroxy double salt (HDS) is an inorganic layered compound in which the space of the layer can intercalate organic anions. Such a compound has a possibility to be used as the catalyst, the adsorbent, and so on. HDSs having center metals more than three which were not reported at present were prepared in this study. It was tried to control the layer structure by adjusting centered metals such as Zn, Cu, Co and Ni with the various combinations, and intercalation of 1- naphthoic and 2-naphthoic acid was carried out. In the Zn-Cu,Co,Ni HDS, a peak at around about 2.00 nm was observed for the intercalation compound of 1-naphthoic acid even into the Zn rich Zn-Cu,Co,Ni HDS.

Key words: Hydroxy Double Salt, layer, hybrid materials, intercalation

1. INTRODUCTION

Some inorganic layered compound can intercalate various ions and molecules into their interlayers[1,2]. The Hydroxy Double Salt (HDS) is such an inorganic layered compound whose center metals are usually one or two divalent metals. The formula of zinc type HDS and copper type HDS can be represented as $[(Me'',M'')_5(OH)_8(X^{n-})_{2/n} \cdot 2H_2O]$ and as $[(Me'',M'')_2(OH)_3(X^{n-})_{1/n}]$ in which M and Me correspond to divalent metals such as Cu, Co, Ni and Zn. X^{n-} is an anion situated between the cation layer, and can be either monovalent, Cl^-, NO_3^-, Br^-, ClO_4^-, MnO_4^- and NO_3^-, or divalent, SO_4^{2-} and CO_3^{2-}[3]. In this study, we have prepared new HDSs whose center metals were two or more than three, and we characterized them by using XRD, TG etc. Anionic guest compound in HDS layers can be exchanged by anionic compounds including organic anions. Various organic compounds were exchanged into the layer of HDS confirming the expansion of interlayer spacing.

2. EXPERIMENTAL

Zinc type nitrate or copper type nitrate HDSs were prepared by the reaction of zinc oxide or copper oxide in an aqueous solution of zinc nitrate, copper nitrate, nickel nitrate and/or cobalt nitrate. Powder X-ray diffraction (XRD) patterns of HDSs

Table 1 Characterization of HDS prepared in this study

HDS	anion	d-spacing (nm)		Ratio of HDS center metal			
				Zn	Cu	Co	Ni
Zn – Zn	NO_3^-	1.00	0.50	1	0	0	0
Zn - Zn	Cl^-	0.80	0.40	0	1	0	0
Cu – Cu	NO_3^-	0.70	0.35	0	1	0	0
Zn - Cu, Ni	NO_3^-	0.70	0.35	1	3.4	0	1
Zn - Cu, Co	NO_3^-	0.70	0.35	1	14	0.8	0
Zn - Cu, Co, Ni	NO_3^-	0.70	0.35	1	1.6	0.3	0.6
Zn - Zn [b]	NO_3^-	0.80	0.40	1	1.7	0	0

a Zn – Zn (NO_3^-) HDS which was treated with $CuCl_2$.

were obtained by using a Rigaku powder diffractometer unit with CuK α radiation (λ =0.154 nm) at 20 mA and 40 kV. Nitrate HDSs were ion-exchanged by contacting an aqueous solution of naphthoic acid. Characterization of ion-exchanged HDSs were carried out by using TG/DTA. The amounts of ion-exchanged naphthalene carboxylic acids were estimated by measuring UV-Vis spectra of an aqueous solution of naphthoic acids and gas chromatography after esterification of the un-intercalated naphthoic acids.

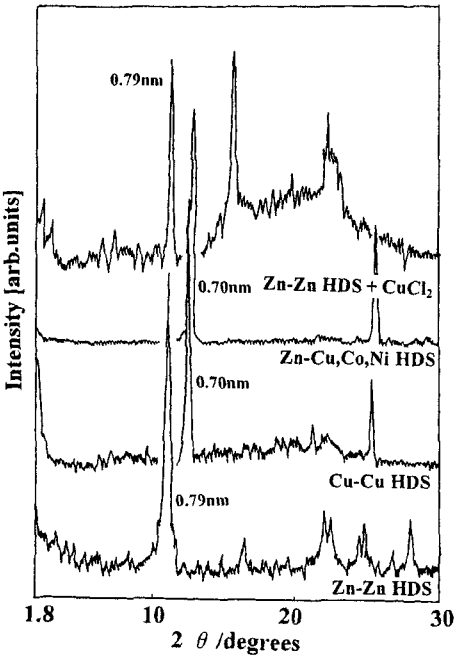


Figure 1 XRD patterns of HDSs.

3. RESULTS AND DISCUSSION

3.1 Preparation of Hydroxy Double Salts

Preparation of HDS was confirmed by XRD patterns. Figure 1 shows the XRD patterns of the reaction products obtained by the reaction of metal oxides and metal nitrates or metal chloride. Clear peaks suggesting the preparation of layered structures were observed. They were Zn-Zn (Cl^-) HDS, Cu-Cu (NO_3^-) HDS and Zn-Cu,Co,Ni (NO_3^-) HDS. Also Zn-Zn (Cl^-) HDS which was treated with $CuCl_2$ was shown. HDSs containing copper

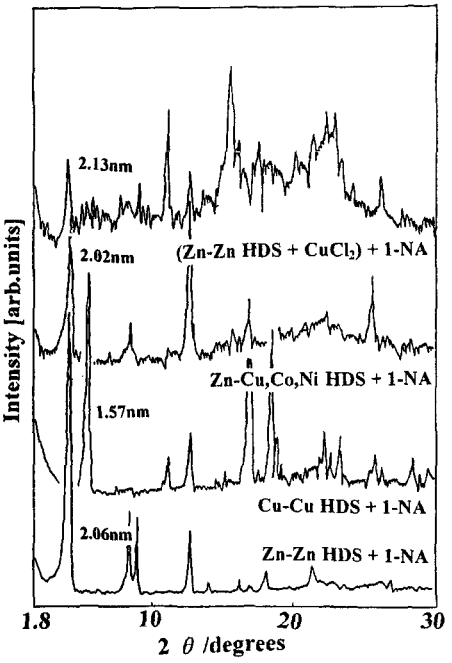


Figure 2 XRD patterns of 1-NA intercalated HDSs.

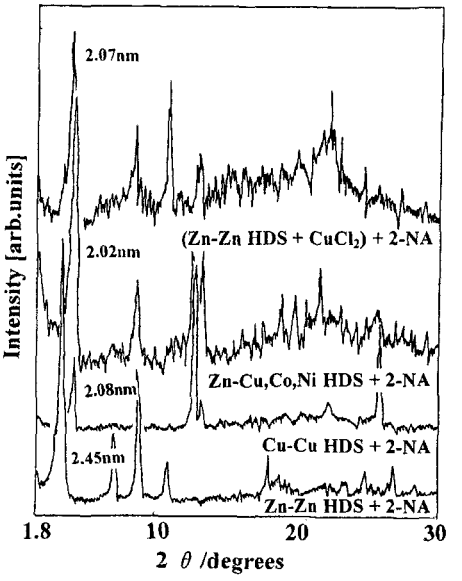
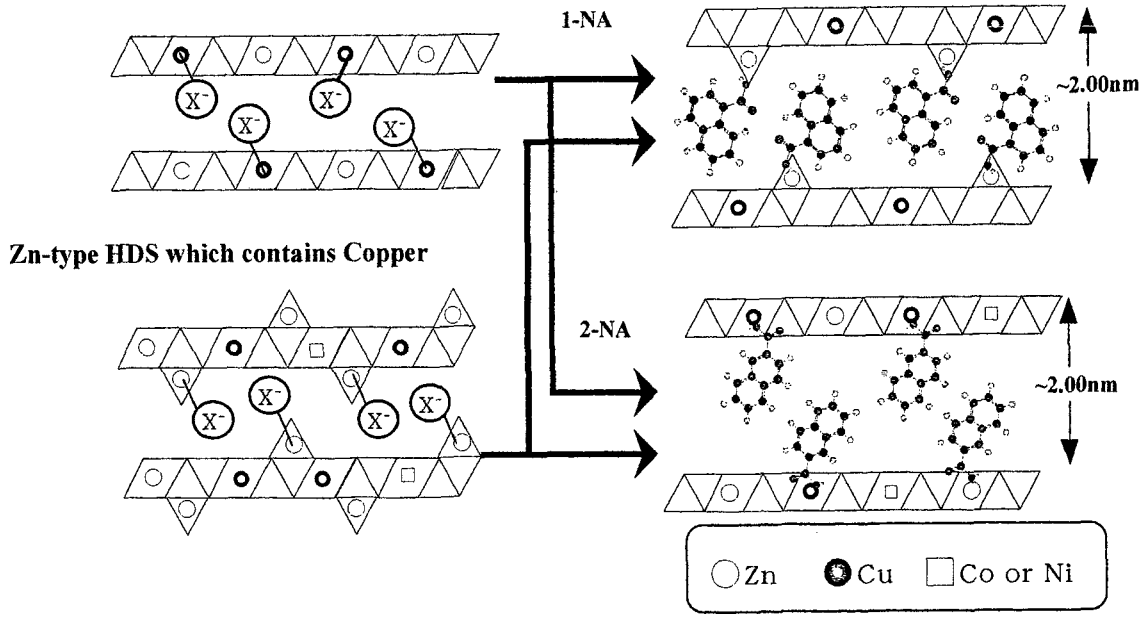


Figure 3 XRD patterns of 2-NA intercalated HDSs.

have interlayer spacing of ~0.70 nm and HDS without copper has that of ~1.00 nm, as shown in Table 1. HDSs having interlayer spacing of ~0.70 nm and ~1.00 nm were named as copper type HDS and zinc type HDS, respectively. By the ion exchange reaction of NO_3^- of zinc type HDS with Cl^-, interlayer spacing increased to 0.80 nm. Compositions of center metals in HDSs were calculated by ICP. They are shown in Table 1. The content of copper was also confirmed. As mentioned above, interlayer spacing of the $CuCl_2$ treated zinc type HDS was 0.80 nm and different with those of copper type HDS.

3.2 Ion-exchange Reaction of HDS with Naphthoic Acid

HDSs were reacted with 1-naphthoic acid (1-NA) and 2-naphthoic acid (2-NA). XRD patterns of obtained reaction products with 1-NA and 2-NA were shown in Figure 2 and 3, respectively. By the reaction of zinc type HDS with 1-NA and 2-NA, interlayer spacing increased from ~1.00 to ~2.00 and ~2.40 nm, respectively. By the reaction with naphthoic acids, interlayer spacing of copper type HDS increased from ~0.70 to ~1.60 and ~2.00 nm with 1-NA and 2-NA, respectively. In the case of Zn-Cu,Co,Ni HDS, interlayer spacing increased from ~0.70 to ~2.00 nm by the reaction with 1-NA or 2-NA. Interlayer spacing of zinc type HDS increased to ~2.00 nm by the reaction with 1-NA. This interlayer spacing is the same with that of zinc type HDS with 1-NA. It was confirmed by ICP analysis that zinc/copper ratio in Zn-Cu,Co,Ni HDS is larger than those in the other HDSs. These results suggested that the Zn-Cu,Co,Ni HDS structure changed from copper type HDS to zinc type HDS, as shown Scheme 1. Zn-Zn HDS was treated with $CuCl_2$. Interlayer spacing of the $CuCl_2$ treated Zn-Zn HDS increased from ~0.80 to ~2.00



Scheme 1 Reaction of zinc type HDS and copper type HDS with 1-NA or 2-NA.

nm by the reaction with 2-NA. This interlayer spacing is the same as that of zinc type HDS with 2-NA. In the same way, the $CuCl_2$ treated Zn-Zn HDS changed from zinc type HDS to copper type HDS by the intercalation of 2-NA, as shown in Scheme 1. When metal ratio of Zn-Cu,Co,Ni HDS was compared with the other copper type HDS, the amounts of metals are larger than the other copper type HDS. Copper type HDS hardly reacts with 1-NA, therefore it is suggested that structure of copper type HDS changed to the structure of zinc type HDS which easily reacts with 1-NA. In the same way, $CuCl_2$ treatment of Zn-Zn HDS structure of zinc type HDS to that of copper type HDS.

Acknowledgments

The authors are grateful to Miss Masa Karasu and Mr. Naoki Sasaki for their technical assistance.

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(Received December 7, 2000; Accepted March 23, 2001)