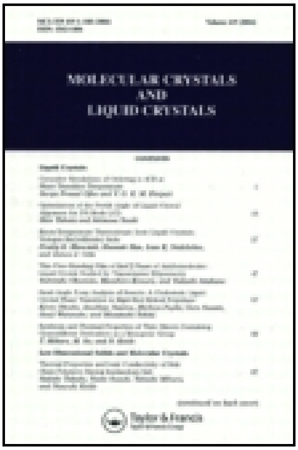


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation of New Inorganic—Organic Layered Compounds, Hydroxy Double Salts, and Preferential Intercalation of Organic Carboxylic Acids into Them

Hideyuki Tagaya [a], Naoki Sasaki [a], Hiroyuki Morioka [a] & Junichi Kadokawa [a]

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

Version of record first published: 27 Oct 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 413-418
Reprints available directly from the publisher
Photocopying permitted by license only

Preparation of New Inorganic – Organic Layered Compounds, Hydroxy Double Salts, and Preferential Intercalation of Organic Carboxylic Acids into Them

HIDEYUKI TAGAYA, NAOKI SASAKI, HIROYUKI MORIOKA and JUNICHI KADOKAWA

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

(In final form June 25, 1999)

New inorganic – organic layered compounds were prepared by ion-exchange reactions of zinc-nitrate and copper-nitrate HDSs with organic carboxylic acids whose interlayer spacings increased depending on the sizes of carboxylic acids. The amounts of ion-exchanged 2-naphthoic acid and 2,6-naphthalene dicarboxylic acid were larger than those of 1-naphthoic acid and 2,7-naphthalene dicarboxylic acid, respectively, indicating the molecule recognition ability of the HDSs.

Keywords: intercalation; hydroxy double salt; organic-inorganic nanocomposites

INTRODUCTION

Layered metal hydroxides are of great interests to both science and technology because of their possibility as an ion-exchanger, catalyst, antacid and magnetic materials [1,2]. Layered double hydroxide (LDH) consists of positively charged metal oxide / hydroxide sheets with intercalated anions in which various organic compounds were included into the layers giving new organic intercalation compounds[3,4]. Hydroxy double salts (HDSs) are also known as anion exchangeable layered compounds similar to the LDH. The formula of zinc-nitrate HDS and zinc-acetate HDS can be represented as $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and $Zn_5(OH)_8(OCOCH_3)_2 \cdot 2H_2O$, respectively. Interlayer spacings of them are 0.97 and 1.34 nm, respectively. In this study, new organic - inorganic layered compounds were obtained by the ion exchange reaction of HDSs.

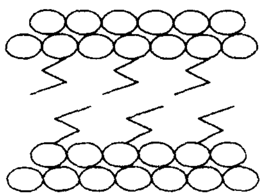
EXPERIMENTAL

Zinc-nitrate (copper-nitrate) HDSs were prepared by the reaction of zinc oxide (copper oxide) in an aqueous solution of zinc nitrate (copper nitrate). Powder X-ray diffraction (XRD) spectra were obtained by a Rigaku powder diffractometer unit, using CuKα radiation (λ= 0.154nm) at 20mA and 40KV. Characterization of ion-exchanged HDSs were carried out by using FT-IR (KBr disc method) and TG/DTA apparatus. The amounts of ion-exchanged naphthalene carboxylic acids were estimated by measuring GC after esterification.

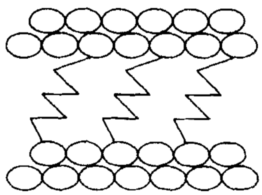
RESULTS AND DISCUSSION

Ion-exchange Reaction with Aliphatic Carboxylic Acid

By the ion-exchange reaction of nitrate ion of zinc-nitrate HDS with aliphatic mono- and di-carboxylic acids, interlayer spacing of the HDS increased to 1.22 - 3.71 nm depending on the sizes of carboxylic acids. IR spectra indicated the presence of RCOO-zinc bond and elemental analyses of the ion exchange reaction products indicated the complete exchange of nitrate ion with aliphatic carboxylic acids. In the case of mono-carboxylic acid, bilayer structure between the layers was suggested from the sizes of carboxylic acids and the value of interlayer expansion. Also bridged structure between the layers was suggested for the reaction products of HDS with di-carboxylic acids.



Bilayer structure



bridged structure

Ion-exchange Reaction with Naphthalene Carboxylic Acid

Zinc-nitrate and copper-nitrate HDSs were reacted with aromatic mono- and di-carboxylic acids. By the reaction of zinc-nitrate HDS with 1-naphthoic acid and 2-naphthoic acid, interlayer spacing increased from 0.98 nm to 1.6 nm and 2.4 nm, respectively, as shown in Figure 1. The size of 2-naphthoic acid and the value of layer expansion indicated the bilayer structure of naphthoic acid between the layers. Interlayer spacing of copper-nitrate HDS increased from 0.70 to 1.58 and 2.01nm by the reaction with 1-naphthoic acid and 2-naphthoic acid, respectively as shown in Table I.

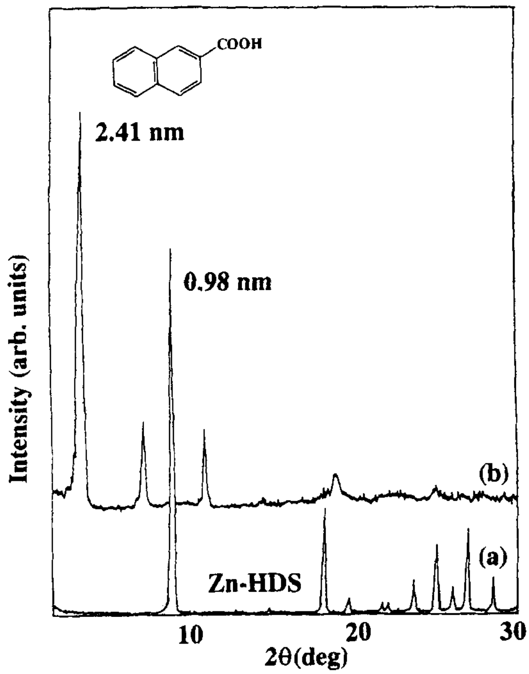
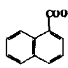
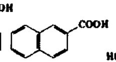
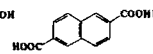
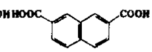


FIGURE 1 XRD patterns of (a) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and (b) the reaction product of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ with 2-naphthoic acid.

On the other hand by the reaction of zinc-nitrate HDS with 2,6- and 2,7-naphthalene di-carboxylic acids, interlayer spacing increased to 1.65 and 1.64

nm. The values of layer expansion were smaller than those of molecular sizes of di-carboxylic acids indicating the bridged structure of di-carboxylic acids between the layers.

TABLE I Interlayer spacing of ion-exchanged HDS with naphthalene carboxylic acids

	HNO_3				
Cu-HDS	0.70	1.58	2.01	1.28	1.33
Zn-HDS	0.98	2.09	2.41	1.65	1.64

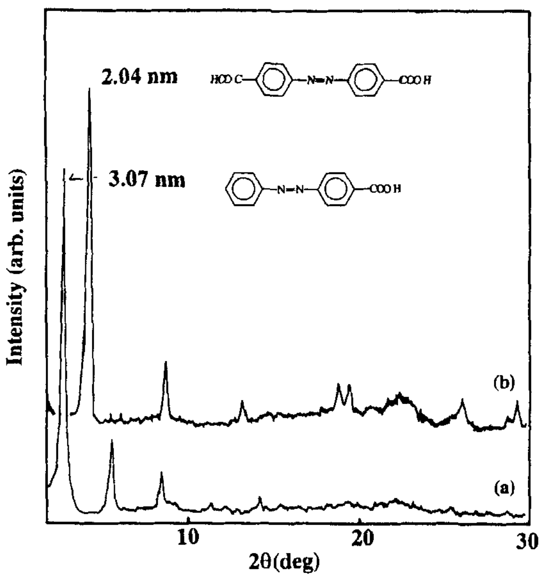


FIGURE 2 XRD patterns of the reaction products of zinc HDS with (a) azobenzene carboxylic acid and (b) azobenzene di-carboxylic acid.

Bulky carboxylic acids such as azobenzene carboxylic acid and azobenzene dicarboxylic acid were also ion-exchanged with zinc-nitrate HDS, and interlayer spacing increased to 3.07 nm and 2.04 nm, respectively as shown in Figure 2.

The Reaction of Mixtures of Naphthalene Carboxylic Acids

We have already reported on preferential intercalation of isomers of naphthalene carboxylate ions into the LDHs [5]. In the preferential intercalation of the LDH, charge densities of carboxylic acids were important. Therefore, di- and tetra-carboxylic acids were incorporated easily more than mono-carboxylic acids.

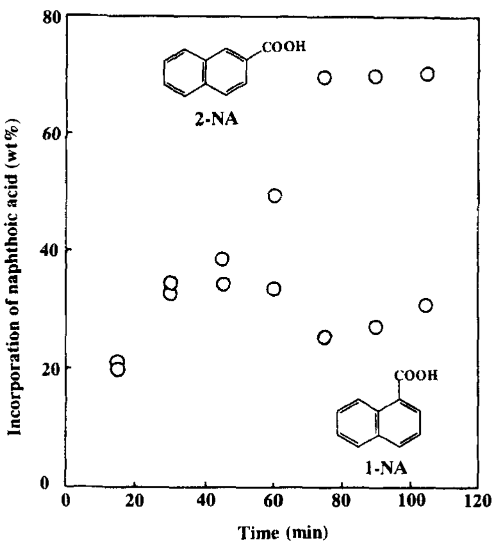


FIGURE 3 Incorporation of 1-naphthoic acid and 2-naphthoic acid into the zinc HDS.

In this study the mixture of 1-naphthoic acid and 2-naphthoic acid was reacted with zinc-nitrate HDS. As shown in Figure 3, 2-naphthoic acid was incorporated into the HDS more than 1-naphthoic acid. We also confirmed the preferential incorporation of naphthalene mono- and di-carboxylic acids into copper-nitrate and zinc-nitrate HDSs. Interestingly, 2-naphthoic acid was intercalated into copper-nitrate and zinc-nitrate HDSs more than 2,7-naphthalene di-carboxylic acid. It indicated that the charge densities of the carboxylic acids were not so important in the incorporation reaction into HDS and three-dimensional structure of carboxylic acid was important indicating that the presence of a molecular recognition ability of the HDS.

Acknowledgments

The authors are grateful to Miss Masa Karasu and Mr. Sumikazu Ogata for their technical assistance. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan

References

[1] S. Ogata, I. Miyazaki, Y. Tasaka, H. Tagaya, J. Kadokawa and K. Chiba, *J. Mater. Chem.*, **8**, 2813 (1998).
[2] H. Tagaya, S. Ogata, H. Morioka, J. Kadokawa, M. Karasu and K. Chiba, *J. Mater. Chem.*, **6**, 1235 (1996).
[3] H. Tagaya, S. Sato, T. Kuwahara, J. Kadokawa, M. Karasu and K. Chiba, *J. Mater. Chem.*, **4**, 1907 (1994).
[4] H. Tagaya, A. Ogata, T. Kuwahara, S. Ogata, M. Karasu, J. Kadokawa and K. Chiba *Microporous Materials*, **7**, 151 (1996).
[5] H. Tagaya, S. Sato, H. Morioka, J. Kadokawa, M. Karasu and K. Chiba, *Chem. Mater.*, **5**, 1431 (1993).