

Characterization of the Indigocarmine Intercalation Compound into the Layered Double Hydroxide which has Two Different Interlayer Spacings

Sumikazu Ogata, Tetsuro Hoshi, Sigetaka Matsumura, Masa Karasu,
Jun-ich Kadokawa, and Hideyuki Tagaya

Faculty of Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, Yamagata, 992-8510 JAPAN
Fax: 81-238-26-3413, E-mail: tc021@dipfr.dip.yz.yamagata-u.ac.jp

We have examined that the indigocarmine (IDC) intercalation compounds (LDH-IDC10 and LDH-IDC7) were treated by acidic or basic solution. By treatment of LDH-IDC10 in the acidic solution, interlayer spacing increased from 1.89nm to 2.25nm. On the other hand, by treatment of LDH-IDC7 in the basic solution, the peak in the XRD pattern of LDH-IDC7 completely changed from 2.25 to 1.85nm by base treatment. Furthermore, the acid treatment of LDH-IDC10 was also changed to 1.85nm by base treatment. The IR spectra and absorption spectra were changed according to acid or base treatment. Thus, we have confirmed that interlayer spacing of the IDC intercalation compound was reversibly changed by acid - base treatment.

Key words: Layered double hydroxide, Indigocarmine, Intercalation, Self-organization

1. INTRODUCTION

Intercalation of guest molecule such as organic spaces into an inorganic layered compound to form an intercalation compound can lead to organic-inorganic nanohybrids[1]. It could be expected that the various properties of intercalation compound were differ from similar properties of guest species itself. Therefore, these intercalation compounds were self-ordered materials and the potential of a new functional material. Layered double hydroxide (LDH) having positive charge is known as anion exchangeable clays [2] and intercalate various organic and inorganic anions.[3] We have already reported to intercalation of photo functional compound into the LDH[4] Their intercalation compounds gave to the possibility of a new photo functional material.

Recently, reversible change of interlayer spacing of intercalation compound was reported by Fujita et al. The intercalation compound of 8-((*p*-phenylazo) phenyl)oxy)octanoate in copper hydroxides occurred to the reversible structural transformation in interlayer spacing by the solvent such as methanol and acetonitrile.[5]

On the other hand, indigocarmine (IDC) is well known to representative dye compound, which has the intermolecular hydrogen bonding between the carbonyl groups and secondary amine groups. In this paper, we have prepared new intercalation compounds of IDC into the LDH. Furthermore, we have attributable the secondary interaction such as electric interaction, and examined the control of interlayer spacing by coordination action of the molecule. Here, we have found to a novel function such as reversible change of interlayer spacing for the intercalation compound in the LDH.

2. EXPERIMENTAL SECTION

2.1 Preparation of the Zn/Al LDH

The carbonate Zn/Al LDH $[(Zn_{1-x}Al_x(OH)_2)]^{x+} [(CO_3)_{x/2}]^{x-} \cdot nH_2O$: $x=0.25$ or 0.3) was prepared as follows. By dropwised the mixture solution (50ml) of $Zn(NO_3)_2 \cdot 6H_2O$ $[(1-x)/2$ mol/l] and $Al(NO_3)_3 \cdot 9H_2O$ $[x/2$ mol/l] to a 0.02M Na_2CO_3 solution (300ml) at 333K, a white precipitate was obtained. Here, 0.2M NaOH solution was appended simultaneously, and the pH was continuously adjusted to ca. 10 and stirring continued for 2 h at 333K. After the reaction, the precipitate was washed by using distilled water 3 times and dried for 24h at 333K.

2.2 Intercalation reaction of the Zn/Al LDH with IDC

We have carried out that the intercalation reaction method was a reconstruction method. The Zn/Al LDH was calcined at 773K for 3h. The calcined Zn/Al LDH was reacted with 2-fold excess the LDH anion exchange capacity (AEC) of indigocarmine (IDC). IDC was added in degassed and distilled water. The pH finally adjusted to ca. 7 (LDH-IDC7) or 10 (LDH-IDC10) by a NaOH solution. The calcined Zn/Al LDH was stirred into the IDC solution under N_2 at 333K for 5~10h.

After the reaction, the reaction product was filtered, washed using distilled water or boiling distilled water, and dried under reduced pressure at room temperature.

2.3 Changing reaction of interlayer spacing of LDH-IDC by acid-base treatment

0.1g of LDH-IDC7 was added in 50ml of distilled water. The pH always adjusted to ca. 10 by dropwised a NaOH solution, and stirring continued for 84h at 298K. In the case of acid treatment, 0.1g LDH-IDC10 was added in 50ml of distilled water. The pH adjusted to ca. 4~5 by dropwised a HNO_3 , and stirring continued for 12~24h at 298K.

After the reaction, the reaction product was filtered,

washed by using distilled water and dried for 12h under reduce pressure.

2.4 Characterization

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku powder diffractometer unit, using CuK α (filtered) radiation ($\lambda=0.154$ nm) at 40kV and 20mA between 1.8 and 50° in two theta. FT-IR spectra (KBr disc method) were recorded on a Horiba FT-200. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of powdered samples up to 873K were carried out at a heating rate of 10K/min in flowing N₂ using a Seiko SSC 5000 thermal analysis system. Absorption spectra were recorded using a Shimadzu UV-2200A spectrophotometer.

All reactions were carried out by using commercial reagents (of analytical - reagents grade) without further purification.

3. RESULTS AND DISCUSSION

3.1 Characterization of the intercalation compounds

Thermal characteristics were determined by TG analysis. Two weight loss of LDH-IDC10 was observed up to 500K and between 700 and 800K. It was corresponded that the first region was the dehydration of absorbed water molecules and interlayer water molecules. The second region between 700 and 800 K corresponds to the desorption of IDC and the dehydration of OH group of the Zn/Al LDH layers. The total weight loss of the IDC intercalation compound was larger than that of the Zn/Al LDH. Therefore, we concluded that IDC was incorporated into the Zn/Al LDH.

The XRD pattern of the Zn/Al LDH was observed near 0.76nm as shown in Fig. 1(a). By calcination of the Zn/Al LDH at 773K, no clear peaks were observed. The d -spacing of the reaction product (LDH-IDC7) was increased from 0.76nm to 2.25nm by the intercalation reaction of the calcined Zn/Al LDH with IDC at pH7 as shown in Fig. 1(b). However, the d -spacing of the reaction product (LDH-IDC10) was also increased from 0.76nm to 1.89nm by those at pH10 as shown in Fig. 1(c). It indicated that the IDC intercalation compound has two different interlayer spacings.

The IR spectra of IDC, LDH-IDC7 and LDH-IDC10 were observed the sharp peaks at 1040cm⁻¹ and the broader peaks at 1196cm⁻¹ as shown in Fig. 2. These peaks are assigned to the characteristic of S-O vibrations in R-SO₃. Furthermore, the IR spectra of IDC and LDH-IDC7 were observed the sharp peaks at 1610cm⁻¹ and 1637cm⁻¹ which are assigned to the intermolecular hydrogen bonding between the carbonyl groups and secondary amine groups in IDC and the doubly conjugated carbonyl (C=O) band, respectively. It was noteworthy that the IR spectrum of LDH-IDC10 was not observed the peak at 1637cm⁻¹ as shown in Fig. 2(a). Therefore, it was mean that for LDH-IDC10 the intermolecular hydrogen bond of IDC was stable in the LDH interlayer. However, it was considered that for LDH-IDC7 the intermolecular hydrogen bond of IDC is inhibited. From these result, we have suggested that an another interaction between IDC molecules was formed in LDH-IDC7.

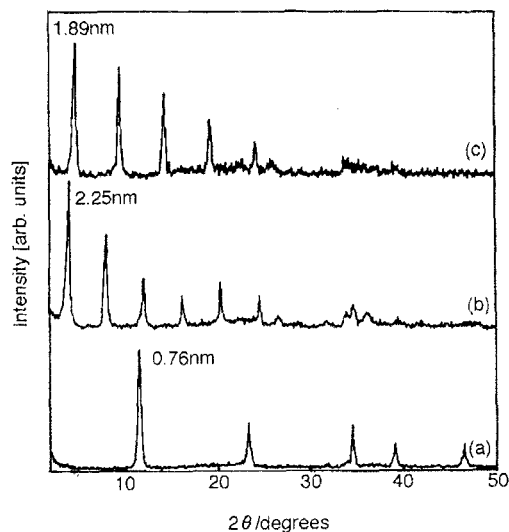


Fig. 1 XRD patterns of (a) Zn/Al LDH, (b) LDH-IDC7, and (c) LDH-IDC10.

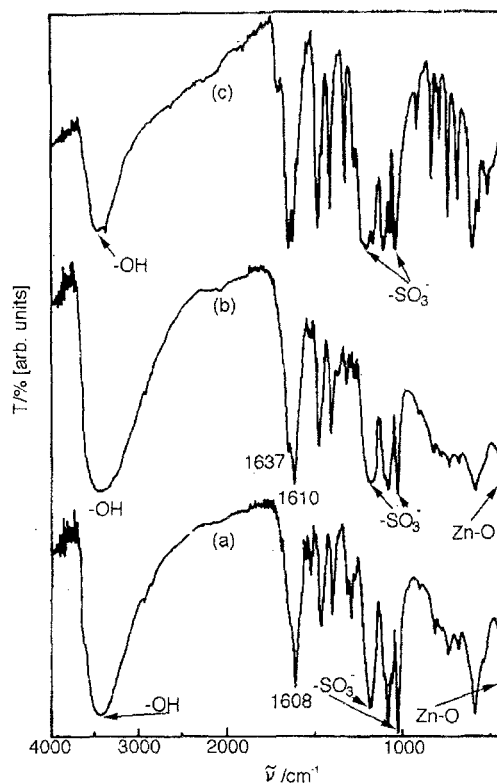


Fig. 2 IR spectra of (a) IDC, (b) LDH-IDC7, and (c) LDH-IDC10.

The host/guest ratios of LDH-IDC7 and LDH-IDC10 calculated by elemental analyses. The host/guest ratios of LDH-IDC7 and LDH-IDC10 were 0.126 and 0.133 indicating that 84% and 89% of the anion exchangeable capacity was occupied by IDC respectively. It indicated that the amount of incorporated IDC was not

influenced to the orientation states.

The absorption spectra of IDC and the IDC intercalation compounds (LDH-IDC7 and LDH-IDC10) were recorded shows that Fig. 3. The absorption peak of IDC alone was showed at 547nm as shown in Fig. 3(broken line). For the absorption spectrum of LDH-IDC7, the peak was observed at 588nm, indicating red shift was occurred as shown in Fig. 3 (dot-dash line). Furthermore, the peaks in the absorption spectrum of LDH-IDC10 indicated that further red shift was occurred to 652nm, and new peak at 795nm was appeared as shown in Fig. 3 (solid line). It is well known that the red shift was reflected by the aggregation state of dye compounds at interlayer space. Thus, we have suggested that the orientation of IDC for LDH-IDC7 differ from that of LDH-IDC10.

We also examined the influence of the reaction condition such as reaction time, reaction temperature, the ratio of $[Al/(Zn+Al)]$ in the Zn/Al LDH, and the concentration of IDC solution. Although, these reaction conditions did not essentially concern with the difference of interlayer spacings

3.2 Acid-base treatment of the IDC intercalation compounds

The intercalation reaction of IDC with the calcined Zn/Al LDH were given two difference interlayer spacing by the dependence of pH as mention above. We have examined that the interlayer spacing of the IDC intercalation compounds may be reversibly changed by acid or base treatment.

We have treated LDH-IDC10 in water adjusting the pH at 4-5 using HNO_3 solution at 298K for 24h. pH of the starting solution increased to about 7 by adding LDH-IDC10, therefore, HNO_3 solution was added

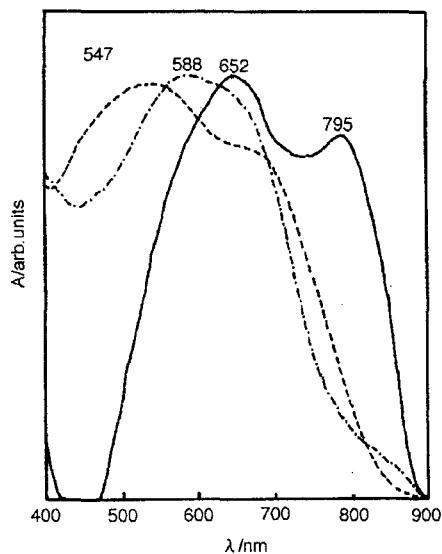


Fig. 3 Absorption spectra of (a) IDC [broken line], (b) LDH-IDC7[dot-dash line], and (c) LDH-IDC10 [solid line].

further to adjust pH of the solution at 4 to 5. As expected, by treatment of LDH-IDC10 in the acidic solution, the interlayer spacing increased from 1.89nm to 2.25nm as shown in Fig. 4 (b). Furthermore, the acid treatment of LDH-IDC10 was changed to 1.85nm by the base treatment as shown in Fig. 4 (c). It indicated to the IDC intercalation compound is reversible change of interlayer spacing by pH control.

We have also treated LDH-IDC10 in acidic solution of an other pH values. By treatment of LDH-IDC10 in the solution at $pH < 4$, LDH-IDC10 dissolved in the solution. It suggested that the Zn/Al LDH structure was destroyed under acidic conditions. For the treatment of LDH-IDC10 in the solution at $pH = 5-7$, interlayer spacing of LDH-IDC10 also changed. However, the interlayer spacing was not completely changed.

On the other hand, we have also treated LDH-IDC7 in water adjusting the pH at 10 using NaOH solution at room temperature. The XRD pattern of LDH-IDC7 was observed 2.25nm as shown in Fig. 5 (a). By the base treatment for 2h and 10h, the peak in the XRD pattern observed at ca. 2.20 and 1.85nm, indicating layered structure was two phase as shown in Fig. 5 (b) and (c), respectively. After the treatment for 84h, the peak in the XRD pattern of LDH-IDC7 completely changed from 2.25 to 1.85nm by the treatment as shown in Fig. 5 (d).

These results indicated new intercalation compound was prepared in which interlayer spacing changed reversibly by the control of pH. Additionally, the IR spectra and the absorption spectra implied that the orientation states of IDC between LDH layers were

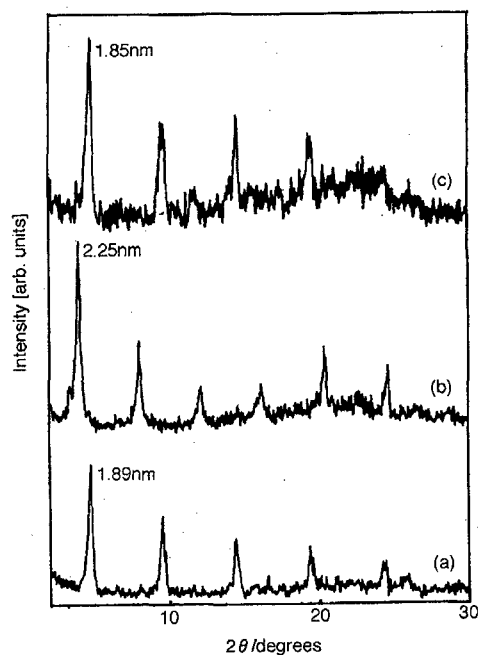


Fig. 4 XRD patterns of (a) LDH-IDC10, (b) acid treatment of (a), and (c) base treatment of (b).

reversibly changed by the control of pH.

From these results, we have suggested that reversibly changes of interlayer spacing by acid or base treatment is concerned in protonation of secondary amine groups in IDC as shown in Scheme 1. Therefore, it is suggested that the orientation state of LDH-IDC7 and LDH-IDC10A was interdigitate structure by forming electrostatic interaction between the protonation of secondary amine groups in IDC and the sulfonate anions. Because, the intermolecular hydrogen bonding between the carbonyl groups and secondary amine groups in IDC was not formed by forming electrostatic interaction. Actually, the IR spectra of LDH-IDC7 and LDH-IDC10A appeared new peak at near 1637cm^{-1} which are assigned to the doubly conjugated carbonyl ($\text{C}=\text{O}$) band.

4 CONCLUSION

We have succeeded to new organic-inorganic nanohybrids such as intercalation compound of IDC with the Zn/Al LDH, which is reversible change of interlayer spacing by pH control. They have potential as chemical sensor, new response material, and photofunctional materials. Furthermore, the method of not only electrostatic interaction but also coordination action of molecule is also useful for controlling the organization of organic molecules in the solid state, and the preparation of new organic-inorganic nanohybrids which have controlled interlayer spacing.

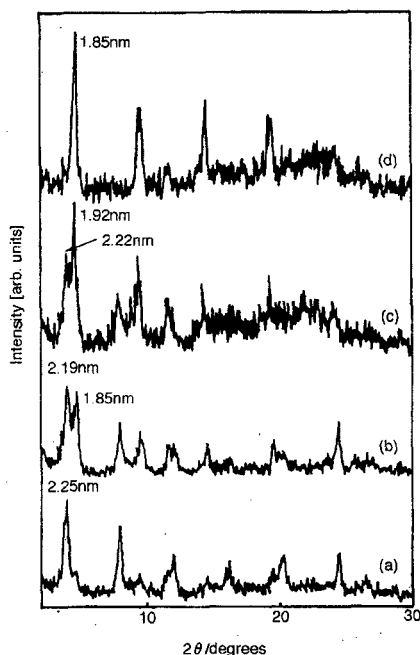
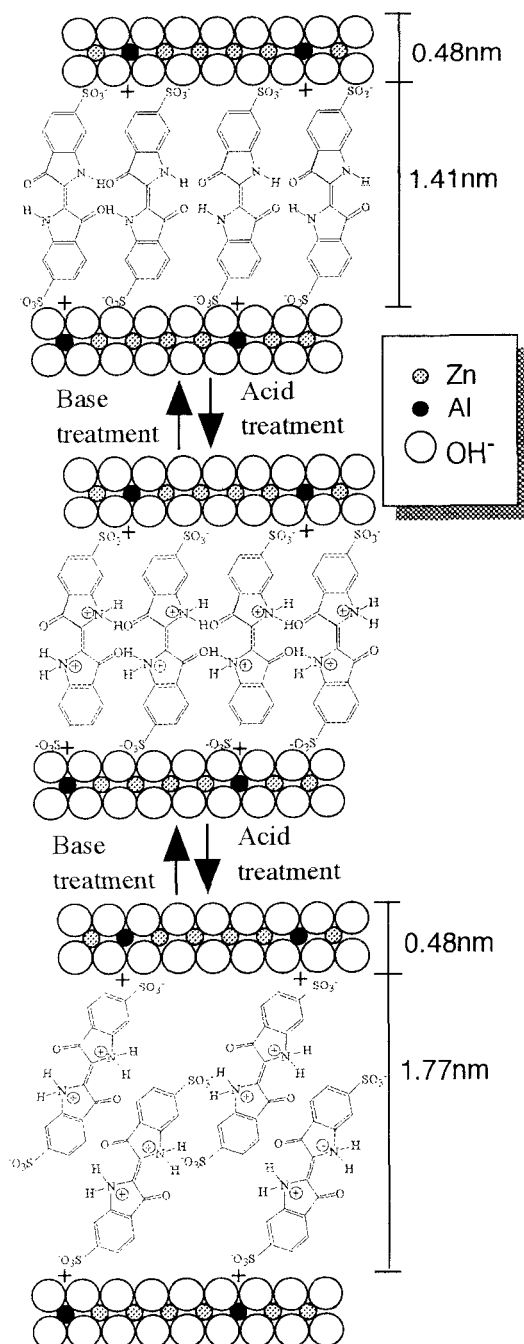


Fig. 5 XRD patterns of (a) LDH-IDC7, the base treatment of LDH-IDC7 for (b) 2h, (c) 10h, and (d) 84h.



Scheme 1. The proposed orientation of indigocarmine intercalation compound.

1. D. O'Hare, in *Inorganic Materials*, 2nd ed., edited by D. W. Bruce and D. O'Hare (John Wiley & Sons, Chichester, 1996), pp. 171.
2. S. Miyata and T. Kumura, *Chem. Lett.*, 843. (1973)
3. M. Meyn, K. Beneke, and G. Lagaly, *Inorg. Chem.*, **29**, 5201 (1990).
4. H. Tagaya, S. Sato, T. Kuwahara, M. Karasu, J. Kadokawa, and K. Chiba, *J. Mater. Chem.*, **4**, 1907 (1994).
5. W. Fujita and K. Awaga, *J. Am. Chem. Soc.*, **119**, 4563 (1997).

REFERENCES

(Received December 16, 1999; accepted February 29, 2000)