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The structure of intercalation compound between a layered double hydroxide and an ethyl orange

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층상이중수산화물과 에틸오렌지의 삽입화합물의 구조

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Abstract We synthesized the intercalation compound between a layered double hydroxide and an ethyl orange. The orientation of the intercalated ethyl orange into the layered double hydroxide was investigated. The molecular plane of the ethyl orange and its N=N axis lie nearly perpendicular to the hydroxide layers with an antiparallel pattern.

요 약 층상이중수산화물과 에틸오렌지의 삽입화합물을 합성하였다. 층상이중수산화물에 삽입되는 에틸오렌지의 공간 배열을 조사하였다. 에틸오렌지는 서로 반대 방향으로 교차하는 배열을 가지며, 에틸오렌지의 분자 평면과 N=N 이중결합이 동시에 이중수산화물층에 수직되게 결합되고 있음을 확인하였다.

1. Introduction

Layered double hydroxides (LDHs) are minerals and synthetic materials with positively charged brucite-type layers of mixed-metal hydroxides. Exchangeable anions located in the interlayer spaces compensate for the positive charge of the brucite-type layers. The chemical composition of the LDH is generally expressed as $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}H_2O]^{x-}$ with $x=[M^{3+}]/([M^{2+}]+[M^{3+}])$. Here, $M^{2+}=Mg^{2+}$, Co^{2+}, Ni^{2+}, etc., $M^{3+}=Al^{3+}$, Cr^{3+}, etc., and A^{n-} is an interlayer exchangeable anion such as CO_3^{2-}, Cl^-, etc. These ionic layered materials also have been termed "hydrotalcite-like" compounds in the reference to the structural similarity to the mineral hydrotalcite, $[Mg_6Al_2(OH)_{16}][CO_3] \cdot 4H_2O$, or termed "anionic clays" in mirror image resemblance to the cationic clays whose negative charge of the alum-inosilicate layers are counterbalanced by the intercalated cations. LDHs are an important class of materials currently receiving considerable attention. The preparations, properties, and applications of LDH materials have been studied extensively [1,6]. They are used as adsorbents, catalysts, catalyst precursors, aninoic exchangers, and antacid drugs [7,10].

There have been several reports on the intercalation of organic anions into the LDH [11,12]. The main synthetic route has been performed by anionic exchange. Am-ong the various organic substances used as the interlayer guest species, dyes are one of the most interesting materials because their host-guest interaction may provide unique structural features and physicochemical properties. Intercalation compounds between a LDH and an anionic dye are expected to have several uses such as in pigments and in the recovery of anionic dyes from waste water. However, LDHs of aluminium with magnesium intercalated with naphthol yellow S, indigo carmine, and new coccine as anionic dyes have been reported so far [13,14]. In this study, the structure of the intercalation compound of an ethyl orange into the LDH of aluminium with zinc was investigated.

2. Experimental

The compounds $ZnCl_2$, and $AlCl_3$ were of guaranteed reagent grade. Ethyl ornage {4-(4-diethylaminophenylazo) benzene sulfonic acid} was obtained from Aldrich and used without further purification. Figure 1 shows the structure and size of an ethyl orange. The layered double hydroxide of aluminium with zinc (Zn-Al-Cl LDH) was synthesized by hydrolysis of the mixed aqueous solutions of $ZnCl_2$(1.0 mol dm^{-3}), $AlCl_3$(0.5 mol dm^{-3}) at pH $= 7.5 \pm 0.2$ by dropwise addition of an aqueous NaOH solution (1.0 mol dm^{-3}) with vigorous stirring under a nitrogen atmosphere. The molar ratio of aluminium is 0.33. The precipitate was aged at 60℃ for 24 hours, filtrated, washed with decarboxylated water, and air dried at 80℃ for 18 hours. Intercalation compound of an ethyl orange into the LDH of aluminium with zinc (Zn-Al-EO LDH) was directly synthesized by hydrolysis of the mixed aqueous solutions of $ZnCl_2$(0.05 mol dm^{-3}), $AlCl_3$(0.025 mol dm^{-3}), and an ethyl orange (0.03 mol dm^{-3}) at pH $= 7.5 \pm 0.2$ by dropwise addition of an aqueous

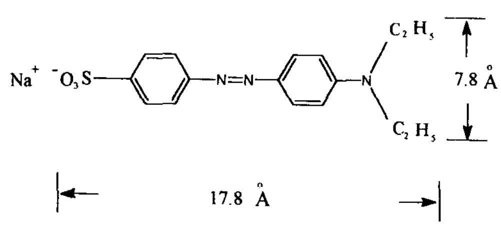

Fig. 1. Structure and size of an ethyl orange.

NaOH solution (1.0 mol dm^{-3}) with vigorous stirring under a nitrogen atmosphere. The precipitate was aged at 70℃ for 7 days, filtrated, washed with decarboxylated water, and air dried at 80℃ for 18 hours. Chemical analysis for Zn and Al was carried out by using an inductively coupled plasma emission spectrometer (ARL Model 3410 ICP-AES). The dye content of the product was determined using an Vario EL CHN analyzer. Infrared spectra were recorded on a Midac Prospect FT-IR spectrometer. X-ray diffraction spectrum was obtained with a Rigaku diffractometer using Cu-K_α radiation.

3. Results and discussion

Layered double hydroxide of Al and Zn (Zn-Al-Cl LDH) was directly synthesized by the hydrolysis of $ZnCl_2$, and $AlCl_3$, with a NaOH solution. The interlayer anion is Cl^-. Intercalation compound between an ethyl orange and a layered double hydroxide of Al and Zn (Zn-Al-EO LDH) was directly synthesized by the hydrolysis of $ZnCl_2$, $AlCl_3$, and the ethyl orange with a NaOH solution. Figure 2 shows the X-ray diffraction patterns of Zn-Al-Cl LDH and Zn-Al-EO LDH Figure 2-A shows the X-ray diffraction patterns of the Zn-Al-Cl LDH. The indexing of the diffraction peaks was obtained by comparison with the diagram reported for Mg-Al LDH [6]. The a parameter of the hexagonal cell unit corresponds to the distance between two metal cations in adjacent octahedra while the c parameter corresponds three times the distance between adjacent hydroxyl layers. The c-axis parameter was calculated to be 22.86 Å from averaging of the positions (003) and (006) peaks. The a-axis parameter was calculated to be 3.08 Å from the position (110) peak. The basal spacing of the Zn-Al-Cl LDH is 7.62 Å. The gallery height of Zn-Al LDH is 2.82 Å when the thickness of the $Zn(OH)_2$ layers (4.80 Å) is substracted [15].

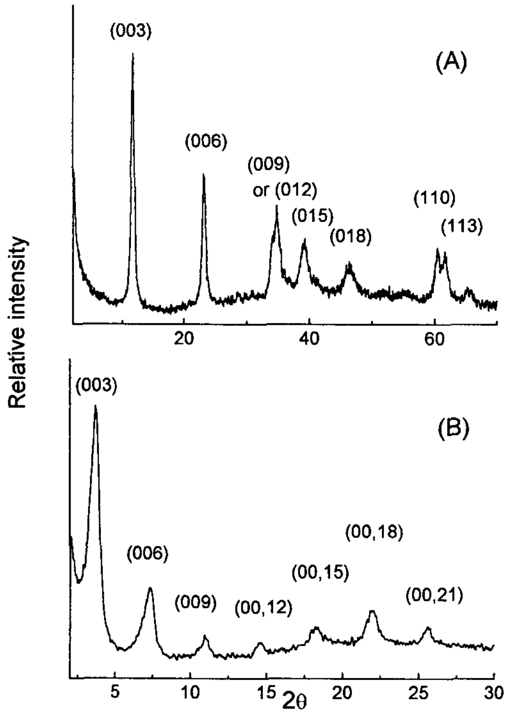

Fig. 2. X-ray diffraction patterns and Miller indices of (A) Zn-Al-Cl LDH and (B) Zn-Al-EO LDH.

Figure 2-B shows the X-ray diffraction

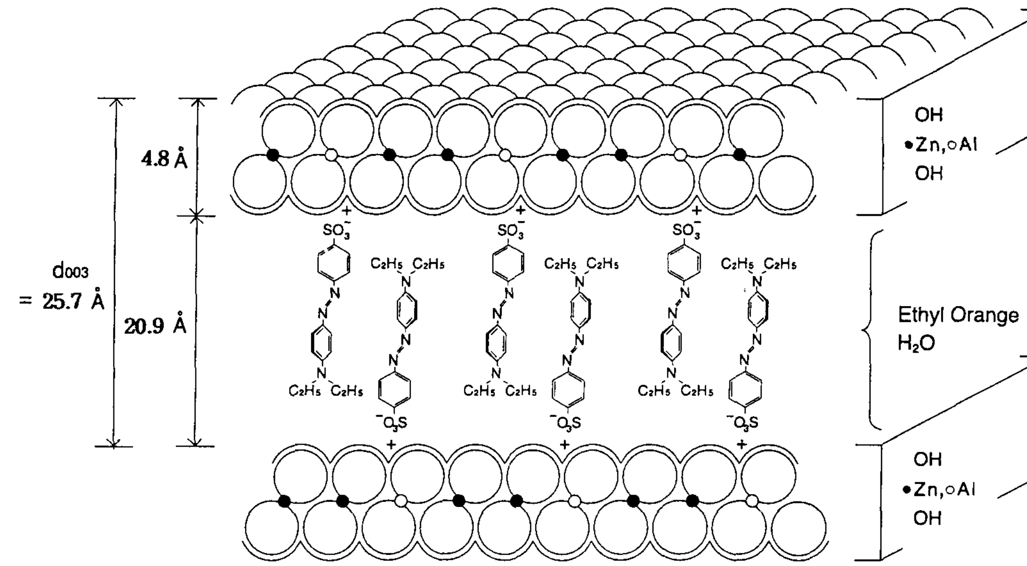

Fig. 3. Schematic illustration of the orientation of Zn-Al-EO LDH.

patterns of the Zn-Al-EO LDH. The (003) diffraction peak and the higher order peaks of the Zn-Al-EO LDH shifted to lower 2θ angles compared to those of the Zn-Al-Cl LDH. The c-axis parameter of the Zn-Al-EO LDH was calculated to be 77.1 Å from averaging of the positions (003) and (006) peaks. The basal spacing of the Zn-Al-EO LDH increased to 25.7 Å from 7.62 Å of the Zn-Al-Cl LDH. Therefore, the gallery height of the Zn-Al-EO LDH was 20.9 Å. This increase in the gallery height strongly indicated the intercalation of the ethyl orange into the Zn-Al-Cl LDH. The infrared spectra of the Zn-Al-EO LDH was similar to those of the ethyl orange in the range of 1700 ~1000 cm^{-1}. These indicated also that the ethyl orange was intercalated into the Zn-Al-Cl LDH.

The formula of the Zn-Al-EO LDH was checked by ICP-AES and C,H,N,S elemental analysis. The ratio of zinc to aluminium in the Zn-Al-EO LDH synthesized directly was 0.65:0.35, which was slightly different from the initial mixing ratio. The ideal formula of the intercalation compound, based on the zinc to aluminium ratio, can be expressed as $[Zn_{0.65}Al_{0.35}(OH)_2][(EO)_{0.35} \cdot mH_2O]$. The validity of this formula was confirmed by C, H, N and S elemental analysis. The H data could not be utilized because of the presence of water. The contents of ethyl orange exactly equal to the stoichiometric aluminium contents of LDH. Since the interlayer of LDH posseses top and bottom cationic surfaces, the sulfonate group of the ethyl orange attach with positively charged LDH layers with an alternate antiparallel pattern. By taking into account the molecular size and rigid shape of the ethyl orange, the H_2O were inserted into the interlayer site of the pillared ethyl orange with LDH.

From X-ray diffration studies, the orientation of the intercalated species can be roughly estimated. The size of the ethyl orange was calculated by using Alchemy program. The length between sulfonate group and diethyl amine group of the ethyl orange is 17.8 Å, when the van der Waals radius of oxygen and hydrogen are to assumed to be 1.4 Å and 1.2 Å, respectively [17]. The gallery height of the Zn-Al-EO LDH measured from the X-ray diffraction peaks is 20.9 Å. The estimated length of the ethyl orange is slightly less than the gallery height. Therefore, the molecular plane of the ethyl orange and its N=N axis lie nearly perpendicular to the hydroxide layers. Schematic illustration of the arrangement of the ethyl orange into the Zn-Al-Cl LDH are shown in Fig. 3.

4. Conclusions

We synthesized the intercalation compound of an ethyl orange into the LDH of aluminium with zinc. From the X-ray diffraction data, the orientation of the intercalated ethyl orange into the Zn-Al-Cl LDH was determined. The molecular plane of the ethyl orange and its N=N axis lie nearly perpendicular to the hydroxide layers with an alternate antiparallel pattern.

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References

[1] M. Orgawa and K. Kuroda, Chem. Rev. 95 (1995) 399.
[2] W.T. Reichle, Chemtech. (1986) 58.
[3] V.R.L. Constantino and T.J. Pinnavaia, Inorg. Chem. 34 (1995) 883.
[4] K. Itaya, H.C. Chang and I. Uchida, Inorg. Chem. 26 (1987) 624.
[5] S. Cooper and P.K. Dutta, J. Phys. Chem. 94 (1990) 114.
[6] S.W. Rhee, M.J. Kang and H.C. Moon, J. Korean Chem. Soc. 39 (1995) 627.
[7] C. Busetto, G. Del Piero, G. Manara, F. Trifiro and A. Vaccari, J. Catal. 85 (1984) 260.
[8] A. Cervilla, A. Corma, V. Fornes, E. Llopis, P. Palanca, F. Rey and A. Ribera, J. Am. Chem. Soc. 116 (1994) 1595.
[9] C.J. Serna, J.L. White and S.L. Hem, J. Pharma. Sci. 67 (1978) 324.
[10] M.J. Climent, A. Corma, S. Iborra and J. Primo, J. Catal. 151 (1995) 60.
[11] K. Chibwe and W. Jones, J. Chem. Soc. Chem. Commun. (1989) 926.
[12] H. Tagaya, S. Sato, H. Morioka, J. Kadokawa, M. Karasu and K. Chiba, Chem. Mater. 5 (1993) 1431.

[13] I.Y. Park, K. Kuroda and C. Kato, J. Chem. Soc. Dalton Trans. (1990) 3071.

[14] S. Miyata, Clays Clay Miner. 31 (1983) 305.

[15] S. Miyata and A. Okada, Clays Clay Miner. 25 (1977) 14.

[16] R.C. Weast, Handbook of Chemistry and Physics, 70th ed., p. D-190.