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Intercalation in hydrotalcite-like layered Zn/Al-double hydroxides with naphthalenedisulphonates

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Hydrotalcite-like layered Zn/Al-double hydroxides (Zn/Al-HTs) with one of three naphthalenedisulphonates (NijDSs) as an interlayer guest dianion, were obtained as precipitates from weak alkaline solutions of NijDS admixed with calcined host powder. Two values of interplanar spacing were observed in the powder X-ray diffraction patterns of NijDS-intercalated Zn/Al-HTs with two guest isomers. Intercalated materials have been characterized by means of UV–vis diffuse reflectance spectroscopy, differential thermal analysis/thermogravimetry and X-ray photoelectron spectroscopy. A model has been proposed in which the organic dianion at the interlayer gallery region bridges two Al^{3+} cations in neighbouring layers of double hydroxides. The guest molecules have an orientation perpendicular to the internal surface of the layers for all NijDS-intercalated materials. Another orientation has been suggested in which the molecules tilt from the perpendicular position for two isomers of NijDS.

1. Introduction

Hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}xH_2O$), an anionic clay mineral, has a layered structure where carbonate dianions locate at the interlayer gallery spacing in brucite-type magnesium and aluminium layered double-hydroxides (LDH). The crystallographic *c*-axis is perpendicular to the two-dimensional development of the layer surface [1, 2]. It has been reported that the layered structure is maintained even when the Mg^{2+} ions in the layers are replaced by some other divalent metals ($M^{2+} = Ni^{2+}$, Zn^{2+}, etc.) isomorphously thus producing synthetic M/Al–HTs [3]. So far, some inorganic and organic dianions have been used as intercalating guests [3–13]. Enhancement of the interplanar spacing is observed in X-ray diffraction (XRD) patterns on the intercalation and it has been discussed in conjunction with relative orientation of the intercalating aliphatic dianions [3, 5]. This paper reports two different values of interplanar spacing are observed when two isomers of NijDS are intercalated between the layers of Zn/Al-HT. The duality in interplanar spacing is elucidated as a result of an alternative orientation of the interlayer guest dianions in the intercalated materials. This is significant, because naphthalene has such a rigid molecular plane that no flexible structure of this molecule is supposed, in contrast with aliphatic molecules. The results of diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS) and differential thermal analysis/thermogravimetry (DTA/TG) are also described.

2. Experimental procedure

Zn/Al-HT, the host compound, was obtained by hydrolysis of $ZnCl_2$ and $AlCl_3$ at pH 9–11 using NaOH and at room temperature followed by ageing overnight in aqueous Na_2CO_3 solution. Chemical analysis revealed the composition of the host as $Zn_6Al_{1.89}(OH)_{14.92}Cl_{0.02}(CO_3)_{1.37}\cdot 0.71H_2O$. The atomic ratio of the trivalent metal ion to the total one, Al/(Zn + Al), was 0.24 which is among the normal range of a series of hydrotalcite-like compounds [3]. The host compound was calcined at $T = 500\,°C$ in air for 3 h before use. Naphthalene-2,6-, -1,5- and -2,7-disulphonate (N26DS, N15DS and N27DS, respectively) disodium salts were employed as sources of organic dianions. The calcined powder of the host was admixed with an aqueous solution containing one of these organic salts at room temperature with vigorous stirring followed by ageing for 18 h at $T = 73$–$74\,°C$. Organic salts were added in stoichiometric equivalent to the amount of Al^{3+} ion in the powder unless otherwise specified. Typical pH values in the reaction mixture are listed in Table I. White precipitates were washed repeatedly with deionized water, dried overnight at 80 °C, and used in the measurements. Chemical analysis revealed that carbonate ions still coexist even after the intercalation of organic dianions, thus the carbonates take part in balancing the excess positive charge on the Al^{3+} cation. The molecular ratio of the guest dianion to Al^{3+} cation, NijDS/Al, in the intercalated materials is listed in Table I.

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TABLE I Interlayer distances of naphthalenedisulphonate (NijDS)-intercalated hydrotalcite-like compounds and calculated molecular sizes of guest anions

Guest	l^a_M (nm)	l^b_L (nm)	NijDS/Al^c	pH^d	Host	Notes	
N26DS	1.266	1.06 ± 0.04	0.39	11.9	Zn/Al	n-form	This work
		1.23 ± 0.07	0.29	11.9	Zn/Al	w-form	This work
N15DS	1.205	1.04 ± 0.05	0.25	11.9 12.5	Zn/Al	n-form	This work
		1.21 ± 0.04	0.26	11.9	Zn/Al	w-form	This work
		1.05	–	–	Mg/Al		Drezdzon [4]
N27DS	1.208	1.17 ± 0.03	0.15	11.9	Zn/Al		This work

[a] Molecular size: twice the anionic radius of oxygen (0.28 nm) plus the interatomic distance between two anionic oxygen atoms in two $-SO_3^-$ groups of an aromatic dianion whose geometry is optimized in MO calculation, see text.

[b] Interlayer distance: the interplaner spacing $d(0\,0\,1)$ obtained in XRD patterns minus the thickness of a layer (0.48 nm); deviation is estimated from the full-width of half value of (0 0 1).

[c] Molar ratio of guest dianion to Al^{3+} cation based on the chemical analysis of the intercalated products.

[d] Typical value during synthesis.

XRD, DRS and DTA/TG measurements were done as described before [14, 15]. XPS was carried out by using a Shimadzu ESCA-1000 X-ray photoelectron spectrometer equipped with a magnesium cathode ($h\nu = 1253.6$ eV) in an X-ray gun (10 kV/30 mA) under the reduced pressure of 10^{-5}–10^{-6} Pa. A semiempirical MO calculation with the MOPAC/PM3 program software was used to obtain optimal geometries of the organic molecules [16, 17]. The initial C–C bond lengths in the naphthalene moiety were the values previously reported [18]. Conformation was discussed which gave the lowest value of the formation enthalpy change, ΔH_f.

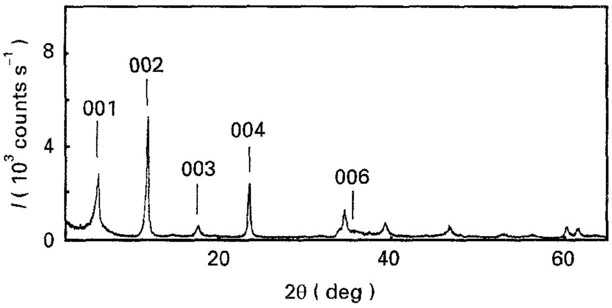

Figure 1 A powder X-ray diffraction pattern for the n-form of N15DS-intercalated Zn/Al-HT. Indexing is attempted for some $(0\,0\,l)$-type diffraction lines with $2\theta = 5.820°$, 11.68°, 17.58°, 23.48° and 35.60°.

3. Results and discussion

The XRD pattern of the host compound has the interplanar spacing $d = 0.761$ nm which agrees with the value reported previously [3]. Two kinds of XRD pattern were observed where the interplanar spacing is differently enhanced when N26DS and N15DS are intercalated, although only one enhanced value is observed when N27DS is intercalated. Fig. 1 shows one of the two patterns of the N15DS-intercalated Zn/Al-HT in which pattern (0 0 1) appears at $2\theta = 5.82°$. Some $(0\,0\,l)$-type diffractions are prominently observed in Fig. 1, which is indicative of predominant crystal growth in the direction of the crystallographic c-axis. The (0 0 1) diffraction shifts to a slightly lower angle at $2\theta = 5.24°$ when the concentration of all reactants in the synthesis is decreased commonly to about 29%. This sample is termed the wide spacing form (w-form) of the N15DS-intercalated Zn/Al-HT, whereas the sample in Fig. 1 is termed the narrow spacing form (n-form). The n-form is also obtained after leaving the solid in the reaction mixture for 40 days; a similar d value has been reported with the Mg/Al-HT host by Drezdzon [4]. In the N26DS-intercalated Zn/Al-HT, the (0 0 1) diffraction of n- and w-forms appears at $2\theta = 5.74°$ and 5.18°, respectively; the w-form was obtained when the organic salt was added about 6.8 times as much as in the synthesis of the n-form. The corresponding interlayer distance calculated for each intercalated materials are listed together in Table I. Although synthesis was done under the same carefully adjusted pH value (pH 11.94 ± 0.05) in Table I, different forms were observed in both cases, which is in contrast with the previous result [5]. Under the synthesis conditions for the n-form of the N15DS-intercalated Zn/Al-HT, a slightly increased pH (pH 12.5) did not affect the result. However, the relation between the form and the molar ratio of guest dianion of Al^{3+} cation is not clear in Table I.

Fig. 2 shows a DTA/TG thermogram of the n-form of the N15DS-intercalated Zn/Al-HT, where two endotherms and two exotherms are observed. These two endotherms result in 22% weight loss, which agrees roughly with the sum of the calculated weight loss (21%) by H_2O and CO_2 elimination, based on the chemical analysis. Although the exact assignment of the exotherms is beyond the scope of this paper, it is tentatively concluded that the exotherms are due to the thermal decomposition of adsorbed organic dianions because such peaks are observed in neither the separate thermogram of the host powder nor in that of the guest organic salt only. The thermogram of the uncalcined host Zn/Al-HT and that of re-hydrolysed calcined host, commonly show no prominent

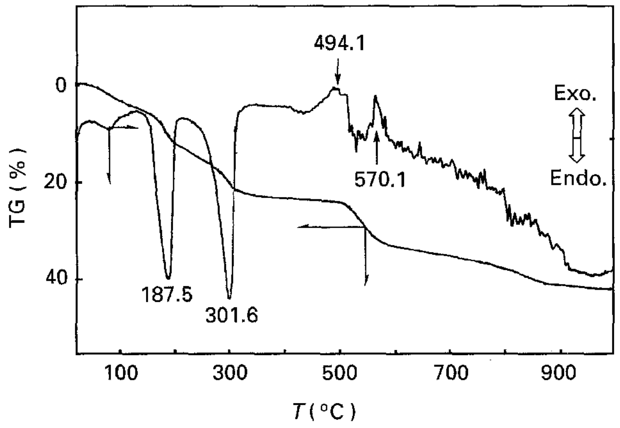

Figure 2 DTA/TG thermal analysis for the same sample as in Fig. 1. Figures in the DTA curve indicate temperatures of some prominent exo- and endotherms both of whose directions are displayed altogether. The scale in the TG curve shows the weight loss of the sample.

exotherms but do show an intense endotherm at around $T = 200\,^\circ C$ due to de-hydroxylation. NijDS salts commonly show intense and sharp endotherms at $T = 596$–$620\,^\circ C$ due to sublimation of some naphthalene-associated weak endotherms at lower temperature. Weight loss by the exotherms in Fig. 2 is 18%, whereas the organic component calculated for the sample based on chemical analysis is 15%. This discrepancy corresponds to the observation that the host compound alone shows 4–5% weight loss in this temperature range. The doubly-split figure of the exotherms in Fig. 2 suggests at least two kinds of organic species are located in this sample. The profile in this thermogram is identical to that of the w-form within experimental error; two endotherms at $T = 190.0$ and $306.3\,^\circ C$, two exotherms at $T = 522.2$ and $576.1\,^\circ C$. This similarity is also observed in the case of the N26DS-intercalated Zn/Al-HT; endotherms at $T = 185.3$ and $308.4\,^\circ C$, exotherms at $T = 486.8$ and $564.7\,^\circ C$ in the n-form; endotherms at $T = 177.9$ and $285.8\,^\circ C$, exotherms at $T = 525.0$ and $580.8\,^\circ C$ in the w-form. For the N27DS-intercalated Zn/Al-HT, endotherms appear at $T = 195.3$ and $282.8\,^\circ C$, exotherms appear at $T = 519.9$ and $565.2\,^\circ C$. These results indicate that the peak location in thermograms is insensitive to the variation in the interplanar spacing in both cases of the intercalated materials.

Two forms of the N15DS-intercalated Zn/Al-HT commonly have two absorption maxima at $\lambda_{max} = 274$–278 nm and at $\lambda_{max} = 314$–325 nm. These band locations agree well with those of the free organic salt corresponding to the transition to a ${}^1B_{2u}(\pi, \pi^*)$ and that to a ${}^1B_{3u}(\pi, \pi^*)$ in the naphthalene moiety, respectively [19], although the possibility of the aggregate formation cannot be excluded. This result suggests strongly that the interlayer dianions still maintain the conjugated π-electron system, thereby retaining the two-dimensional molecular skeleton of naphthalene.

Binding energies (BEs) of the core level electrons in zinc, aluminium, carbon and oxygen atoms of the solids are obtained in XPS measurements. It is found that the interlayer dianions are bound electrostatically to the trivalent metal cation in double hydroxides [1–3]. The BE of Al(2p) electrons in the host compound (BE = 74.4 ± 0.6 eV) agrees with that of the octahedrally coordinated aluminium ions [20]. The BE in the n- and w-forms are 74.9 ± 0.6 and 75.0 ± 0.6 eV for the N26DS-intercalated Zn/Al-HT; 74.6 ± 0.7 and 74.9 ± 0.6 eV for the N15DS-intercalated Zn/Al-HT, respectively. These observations reveal that (1) the chemical shift for the BE of Al(2p) electrons is negligibly small upon the intercalation of NijDSs, and also (2) no significant shift results between the w- and n-forms within experimental error. In addition to CO_3^{2-} anions, the anionic charges on $-SO_3^-$ groups balance the cationic charges on Al^{3+} cations in the intercalated materials. The chemical circumstances around the trivalent ions are thereby kept unchanged on intercalation of NijDS, provided that we neglect the small difference in electron density on the oxygen atoms between the two kinds of dianion.

Early crystallographic works by Allman have revealed that the intercalating carbonates locate at the interlayer gallery with its molecular plane parallel to the two-dimensional development of the gallery spacing in Mg/Fe-HT [21, 22]. It is reported that the layer with a thickness of 0.48 nm is built by sharing one edge of the octahedron unit in which a metal cation is coordinated by six –OH groups [2, 21, 22].

A model for the intercalating NijDS dianions can be proposed from the above results where the dianion bridges a pair of Al^{3+} cations in the neighbouring layers, acting like a fastener which connects two layers of double hydroxides. Considering that no successful results with enhanced interplanar spacing have been observed on the intercalation of naphthalene *mono*sulphonates so far, this bridging model of the guest naphthalene is reasonable. Variation in the magnitude of the enhanced interplanar spacing of two forms is explained in the N26DS- or N15DS-intercalated materials as a result of the variation in the interlayer distance, which results from taking a conformation alternative by the aromatic guest dianions. Another possibility, that the difference in the thickness of the layer is responsible, is abandoned, because the difference in the interplanar spacing between the two forms is commonly 0.17 nm, which cannot be explained by the change of stacking number of the octahedron unit. Table I lists the interlayer distance, l_L, and the calculated molecular size, l_M, of the guest dianions. It is to be noted that both l_L values in the w-form of the two guests (N26DS and N15DS) and the value of N27DS agree with the l_M value of each isomer, within experimental error. This agreement is elucidated by assuming that the guest dianions commonly locate with their molecular planes perpendicular to the inner surface of the layer. The situation is slightly different in the n-forms. The guest dianions in this form have another conformation that the molecular plane tilts so much from the perpendicular position that the molecular size along the crystallographic *c*-axis decreases. There are two points which should be made clear; first, the reason why the interlayer distance is determined as 1.04 ± 0.05 nm in the n-form of N15DS, for example, should be known. Considering the sharpness and the predominancy of the diffraction sequence of diffraction in Fig. 1, the distance is solely and explicitly determined. The author's opinion is that the atomic ratio of two metals Al/Zn (= 0.315 in this study) in the layer of the double hydroxides should be important. Second, is there an n-form of the guest of N27DS dianion? Although synthesis was attempted under some different conditions, no successful result has been obtained so far.

Although more experimental results should be accumulated in order to explain why the selective choice in conformation of the interplanar NijDS results, it is interesting that the conformation of the aromatic dianion between the layer of Zn/Al-HT is changeable, in particular. With this changeable interlayer distance it would be possible to design molecular sieves for variable and desirable pore dimensions. Furthermore, it has been a traditional interest how large the guest size can be at the interlayer gallery spacing of LDH. Additional experiments on these points are now in progress.

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