



Fourier Transform Infrared Spectra of Naphthalene Disulfonates between Layers of Mg and Al double Hydroxide: Intercalation by Means of Coprecipitation and Direct Observation of Coordination from the Interlayer Anion to the Metal Cation in the Layer

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Abstract. A Mg/Al-layered double hydroxide with interlayer naphthalene-2,6-disulfonate having a basal spacing of 1.68 nm was prepared by means of the coprecipitation method. The results of powder X-ray diffraction are compared with those of other intercalates which have interlayer naphthalene disulfonates. Fourier transform infrared spectra of the LDH intercalated compounds reveal that the organic molecules located in the interlayer region are stable. Coordination from the oxygen atom in the $-\text{SO}_3^-$ group of the interlayer molecules to the metal cation in the layer is observed.

Key words: intercalation, layered double hydroxides, FT-IR, layered compounds, naphthalene disulfonates

1. Introduction

Interest has been increasing in the intercalation of organic anions between layers of M and Al-layered double hydroxide (M/Al/X-LDH, where M and X are a divalent metal cation in the layer and an interlayer anion, respectively) [1–9]. The negative charges on the interlayer anions compensate the excess positive charges which result from the substitution of Al^{3+} for octahedral M^{2+} sites in the layer [10, 11]. The layered structure of Mg/Al/ CO_3 -LDH, a typical compound in the family, has been revealed in detail by means of in situ high temperature X-ray diffraction [12]. Intercalation of naphthalene disulfonates between layers of double hydroxides has been achieved using several methods; rehydration [4–6], coprecipitation [1] and ion-exchange [2, 3]. Two values of the basal spacing, 1.7 nm and 1.5 nm, have been observed only when calcined Zn/Al/ CO_3 -LDH is used as a starting material in the rehydration method [4–6]. However, only one value of 1.5 nm has

been observed when naphthalene-1,5-disulfonate (N15DS) is intercalated between layers of Mg/Al-LDH by means of the coprecipitation method [1]. IR absorption spectroscopy [2, 13–18] as well as UV-visible diffuse reflection spectroscopy [2, 4–8] have been used in order to characterize interlayer organic molecules.

In this work, a layered compound having a basal spacing of 1.7 nm (the 17 Å phase) is prepared for the first time when naphthalene-2,6-disulfonate (N26DS) is intercalated between layers of Mg/Al-LDH by means of the coprecipitation method. Fourier transform infrared (FT-IR) spectra indicate coordination of the oxygen in $-\text{SO}_3^-$ of the interlayer organic anion to the metal cation in the layer.

2. Experimental

During sample preparation, the atomic/molecular ratio Mg : NijDS ($i, j = 15, 26$ and 27) was kept at 4 : 3 and the ratio Mg : Al was changed by an order of magnitude. A typical condition to yield powdered compounds with high crystallinity is described below. An aqueous solution containing MgCl_2 (0.036 mol) and AlCl_3 (0.018 mol) was added to another aqueous solution of N15DS sodium salt or of N26DS sodium salt (0.027 mol), both from Tokyo Kasei Co., at room temperature keeping the pH at 10–11 by using NaOH aqueous solution (0.63 mol/dm^3) with vigorous stirring followed by aging for 42 h at 73–74 °C. After washing until a negative test for Cl^- with Ag^+ in the filtrate, the white precipitate of Mg/Al/N15DS-LDH or of Mg/Al/N26DS-LDH was dried overnight at 80 °C before measurement and analysis. All the chemicals were reagent grade and were used as received. Chemical analysis of the intercalated compounds has been frequently reported [4–8]. The chemical compositions of the synthetic compounds are listed in Table 1. Intercalation of naphthalene-2,7-disulfonate (N27DS) produced no crystalline powder under the synthetic condition used in this study.

Details of measurements for X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have been described previously [4–8]. A Rigaku Rint 1200 diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation and with its optional database was used to obtain and analyze the XRD patterns. FT-IR spectra of KBr disks were observed by means of a JASCO VALOR-III FT-IR spectrometer with a resolution of $\pm 4 \text{ cm}^{-1}$ after the data accumulation of 500 times. XPS spectra were measured by using a Shimadzu ESCA-1000 spectrometer with a Mg cathode.

3. Results and Discussion

Figure 1 illustrates an XRD pattern of Mg/Al/N26DS-LDH where indexing of the major diffractions is included. A sequence of $00l$ lines follows the basal 001 diffraction showing that brucite-like layers of the double hydroxide have well developed stacking in the direction parallel to the c -axis [10]. The basal spacing (1.68 nm) in Figure 1 is compared with that of 0.78 nm in Mg/Al/ CO_3 -LDH reported

Table I. Summary of XRD and synthetic conditions of Mg/Al/NijDS-LDH (ij = 15, 26 and 27)

ij	L ¹ /nm	L ² /nm	M:Al:NijDS ³	M	Notes ⁶
26	1.266	1.23	4:2:5	Zn	17 Å phase [8], r
		1.06	4:2:1		15 Å phase [6], r
		1.20	4:2:3	Mg	17 Å phase This work ⁴
15	1.205	1.21	4:2:1	Zn	17 Å phase [6], r
		1.04	4:2:1		15 Å phase [8], r
		1.03	–		[5], r
		1.03	–	Mg	15 Å phase [3], c
		0.99	4:2:3		15 Å phase This work ⁵
		1.08	–	Ca	15 Å phase [5], i
27	1.208	1.17	4:2:1	Zn	17 Å phase [6], r

¹) Molecular size; twice the anionic radius of oxygen (0.28 nm) plus the interatomic distance between two anionic groups of an aromatic dianion whose geometry is optimized in MO calculation [6].

²) Interlayer distance; $d(001)$ in XRD patterns minus the thickness (0.4769 nm [11]) of a layer.

³) Molar/atomic ratio in preparation. See text about M.

⁴) $\text{Mg}_{0.61}\text{Al}_{0.39}(\text{OH})_{1.32}(\text{N26DS})_{0.07}(\text{CO}_3)_{0.46} \cdot 1.06\text{H}_2\text{O}$.

⁵) $\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_{1.63}(\text{N15DS})_{0.10}(\text{CO}_3)_{0.26} \cdot 0.92\text{H}_2\text{O}$.

⁶) Methods of intercalation: r, rehydration; c, coprecipitation; i, ion-exchange.

previously [10, 11]. The enhancement of the interplanar spacing results from the intercalation of N26DS between layers of Mg/Al-LDH.

Results of XRD and synthetic conditions are summarized in Table 1 for three kinds of Mg/Al/NijDS-LDH. On the intercalation of N26DS or N15DS, only one phase (the 17 Å phase for N26DS and the 15 Å phase for N15DS) is produced in the case of $\text{M} = \text{Mg}^{2+}$ whereas two phases with different values of basal spacing have been reported in the case of $\text{M} = \text{Zn}^{2+}$ [4–6]. The presence of two phases of different basal spacings results from two different orientations of the interlayer molecular anion relative to the internal surface of Zn/Al-LDH [4–8]. In other words, two spacings are observed when the interlayer anion is rigid enough to be geometrically anisotropic. The interlayer distance of the 17 Å phase in Table 1 approximately agrees with the calculated molecular size of the corresponding NijDS (ij = 15, 26 and 27) [4]. This agreement has been elucidated as the molecular axis connecting two anionic oxygen atoms in the two $-\text{SO}_3^-$ groups of the interlayer molecule perpendicular to the internal surface of Mg/Al- and Zn/Al-LDH [4–6]. In comparison to the 17 Å phase, it has been pointed out that the molecular axis of the interlayer molecule is tilted in the 15 Å phase [4, 6]. The result in Table 1 shows that the multiplicity in the magnitude of the interlayer distance is observed when Zn^{2+} is the divalent metal cation in LDH. This is in contrast with the result of

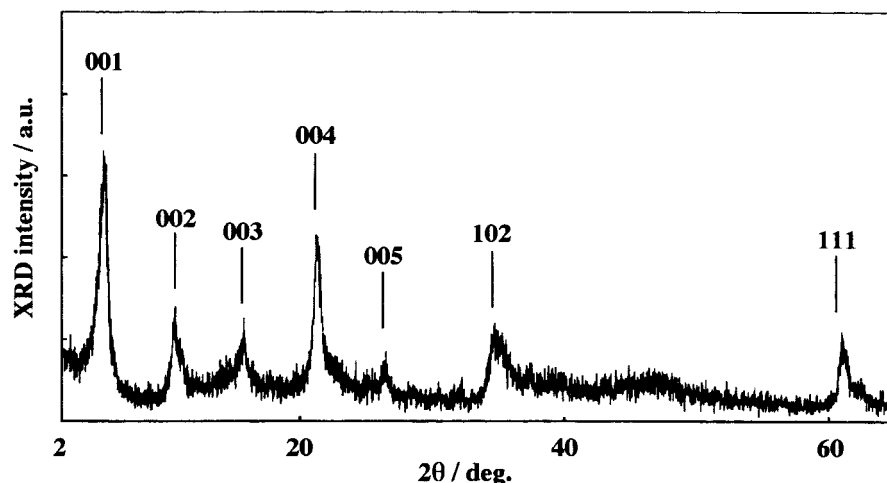


Figure 1. XRD pattern of Mg/Al/N26DS-LDH at room temperature; 2θ (hkl) = 5.26° (001), 10.56° (002), 15.86° (003), 21.24° (004), 26.44° (005), 34.68° (102) and 60.92° (110) indexed under the assumption of a hexagonal unit cell with lattice constants $a_0 = 3.04 \text{ \AA}$ and $c_0 = 16.77 \text{ \AA}$.

interlayer 9,10-anthraquinone disulfonates (AQ); three solid phases with different values of the interlayer distance have been observed between layers of Mg/Al-LDH [7, 8].

Figure 2 shows an FT-IR spectrum of Mg/Al/N15DS-LDH. Absorption bands indicated by arrows in this figure are those also observed both in the IR spectrum of Mg/Al/N26DS-LDH and that of Mg/Al/CO₃-LDH (neither is shown). At $3400\text{--}3500 \text{ cm}^{-1}$, a stretching vibration of the O–H group both in the hydroxide layer and in the interlayer water molecules is observed [12–14, 16–18]. Two bands at 1627 cm^{-1} and at 1367 cm^{-1} in this figure are observed at 1623 cm^{-1} and at 1361 cm^{-1} in the spectrum of Mg/Al/N26DS-LDH. These two bands correspond to bands at about 1600 cm^{-1} and at 1360 cm^{-1} in the spectrum of Mg/Al/CO₃-LDH, respectively. The former band has been assigned as an O–H bending mode of the interlayer water [12, 14, 16–18] and the broadness of this band results from overlapping with other bands of skeleton vibrations in the naphthalene moiety. The latter band has been assigned as an antisymmetric stretching mode of the interlayer carbonate [13, 14, 16–18]. The location of the latter band verifies the result of the elemental analysis listed in Table 1; carbonate coexists with N15DS or with N26DS at the interlayer of both intercalated compounds as has been observed in the case of $M = \text{Zn}$ [5, 6]. Two absorption bands at 449 cm^{-1} and at 555 cm^{-1} in Figure 2 are observed at 448 cm^{-1} and at 570 cm^{-1} in the spectrum of Mg/Al/N26DS-LDH and correspond to two bands at 449 cm^{-1} and at 593 cm^{-1} in the spectrum of Mg/Al/CO₃-LDH, respectively, all of which have been assigned to lattice vibrations in the layer [12, 15].

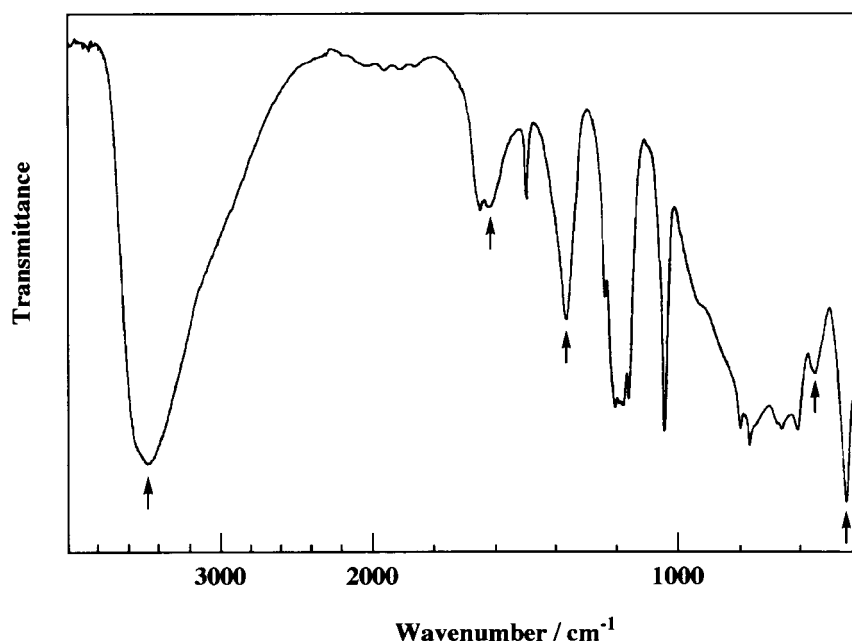


Figure 2. FT-IR spectrum of Mg/Al/N15DS-LDH in KBr disks in the 400–4000 cm^{-1} region: absorption bands with an arrow, see text.

It is thus plausible that the other sharp bands located in the region between 1500 cm^{-1} and 600 cm^{-1} in Figure 2 are due to molecular vibrations of interlayer N15DS. Table 2 lists the band location of two intercalated compounds in this region in comparison with that of the free sodium salts with possible assignment [13, 18, 19]. Each band of the interlayer N15DS or N26DS has the corresponding counterpart of the free ion. Apart from weak overtone and combination bands at 1300–1400 cm^{-1} for the free ions, a band at 923 cm^{-1} for free N15DS and two bands at 973 cm^{-1} and at 887 cm^{-1} for free N26DS are missing in the spectra of the corresponding interlayer molecules. Both bands at 923 cm^{-1} for free N15DS and at 973 cm^{-1} for free N26DS have been assigned to a stretching ν_3 vibration of S–O in the $-\text{SO}_3^-$ group and a shift to lower frequency owing to the coordination through an oxygen atom [13, 19]. This is the case with interlayer N15DS and N26DS and the shifted band may be hidden behind the intense bands located below 800 cm^{-1} . Namely, one of the three oxygen atoms in the $-\text{SO}_3^-$ group of interlayer N15DS or N26DS coordinates to a metal ion (probably to Al^{3+}) in the double hydroxide in substitution for an originally coordinated OH group. In contrast, bands at 1043 cm^{-1} and at 1206 cm^{-1} of the interlayer N15DS and at 1037 cm^{-1} and at 1234 cm^{-1} for interlayer N26DS are of non-coordinating oxygen atom(s) in this group and have the same frequencies for the free N15DS and free N26DS, respectively. Therefore, it is concluded that the $-\text{SO}_3^-$ group of the interlayer molecule has two kinds of oxygen atoms; one coordinates to Al^{3+} in the layer and the other does

Table II. Location¹⁾ of IR absorption bands of Mg/Al/N15DS-LDH and Mg/Al/N26DS-LDH in the 1500-600 cm⁻¹ region compared with the bands of the free sodium salts with a possible assignment.

Mg/Al/N15DS-LDH ²			Mg/Al/N26DS-LDH ²		
Interlayer anion	Free salt	Assignment ³	Interlayer anion	Free salt	Assignment ³
1500	1501 (m)	Skeleton	1508	1497 (m)	Skeleton
–	1395 (w)	607 + 771	1362	1361 (m)	–
–	1336 (w)	662 × 2	–	1338 (m)	666 × 2
1238	1237 (w)	d_{C-H}	1264	1271 (m)	δ_{C-H}
1206	1209 (s)	ν_{O-S-O}	1234	1236 (s)	ν_{O-S-O}
1181	1184 (sh)	δ_{C-H}	1197	1197 (s)	δ_{C-H}
1159	1162 (sh)	δ_{C-H}	1182	1192 (s)	δ_{C-H}
1043	1047 (s)	ν_{S-O}	1141	1146 (w)	δ_{C-H}
–	923 (m)	ν_{S-O}	1092	1101 (s)	δ_{C-H}
799	788 (s)	δ_{C-H}	1037	1046 (s)	ν_{S-O}
770	771 (s)	δ_{C-H}	–	973 (w)	ν_{S-O}
663	662 (w)	–	892	909 (m)	δ_{C-H}
611	607 (s)	ν_{S-O}	–	887 (w)	–
			802	829 (m)	δ_{C-H}
			661	666 (s)	–
			624	627 (s)	ν_{S-O}

¹ In cm⁻¹.

² s; strong, m; medium, w; weak and sh; shoulder.

³ ν ; stretching, δ ; bending.

not. This conclusion does not only ensure the idea that the anionic oxygen atom in the $-SO_3^-$ groups of the interlayer molecules are electrostatically attracted to the Al^{3+} cations in the layers [6] but also proves the presence of the coordination bond between the oxygen and Al^{3+} .

In an XPS spectrum of Mg/Al/N15DS-LDH (in Figure 3), several photoelectron peaks which are assigned to core level electrons emitted from Mg, Al, C, S and O atoms in the intercalated compound are observed. The binding energy of the Al 2p electron of this compound and of Mg/Al/N26DS-LDH before/after the bombardment is 75.0 eV/74.1 eV and 74.6eV/74.4eV, respectively, which are the same values in an experimental error of ± 0.6 eV. These values agree with the binding energy of octahedrally coordinated Al^{3+} [20], which is the same result as has been also observed in the XPS spectra of Zn/Al/NijDS-LDH ($i = 15, 26$ or 27) and in those of Mg/Al/AQ-LDH [7, 8].

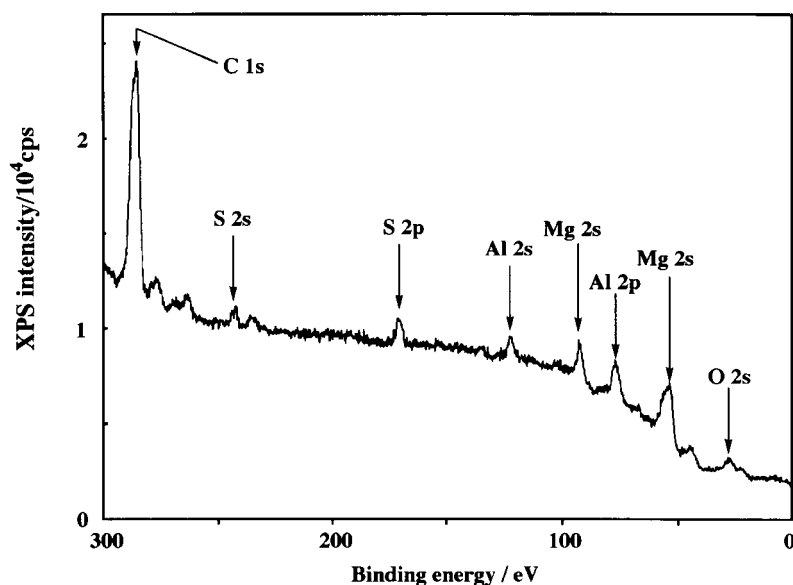


Figure 3. XPS spectrum of Mg/Al/N15DS-LDH after etching the surface of the sample disk by Ar^+ bombardment for 60 s; an assignment of major peaks using an energy reference of C(1s) is included.

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