Unexchangeable Interlayer Anions; Synthesis and Characterization of Zn/Al- and Mg/Al-Layered Double Hydroxides with Interlayer Alizarin red S

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Abstract

Zn/Al- and Mg/Al-layered double hydroxides with interlayer 9,10-anthraquinone-1,2- dihydroxy-3-sulfonate (Alizarin red S anion abbreviated as ARS) are synthesized (products are abbreviated as M/Al/ARS-LDH where M=Mg or Zn) and the solid-state properties are characterized. In powder X-ray diffraction measurements, basal spacings of the layered compounds are elucidated on the basis of the molecular size of ARS and its conformation at the interlayer gallery region. ^{27}Al MAS NMR spectra reveal that the Al^{3+} ions in the layers of Zn/Al/ARS-LDH or Mg/Al/ARS-LDH locate in the octahedral hexa-coordination sphere whereas some of the metal cations in the calcined Zn/Al/CO_3-LDH, the precursor in the synthesis of Zn/Al/ARS-LDH, locate in the penta- or the tetra-coordination sphere. FT-IR spectra and ^{13}C CP/MAS NMR spectra illustrate that the interlayer ARS anions are stable in both layered compounds and the coordination bond is formed in Zn/Al/ARS-LDH between the sulfonate of ARS and Al^{3+} in the layer. The interlayer ARS anions are not eliminated from the interlayer region of Zn/Al/ARS-LDH when the solid is immersed in an aqueous solution containing carbonate; the unexchangeable nature of the interlayer ARS with carbonate results from the coordination bond observed in FT-IR and ^{13}C CP/MAS spectra.

Introduction

Intercalation of organic anions having rigid molecular frameworks between layers of Al^{3+}-containing double hydroxide has been studied from the viewpoint that molecular size of these anions along the stacking axis, the *c*-axis in the hexagonal unit cell of the layered double hydroxide (LDH), governs the magnitude of the interlayer distance [1–10]. We have reported that some solid phases with different basal spacings are observed in X-ray powder diffraction (XRD) of the intercalated compounds when one of geometrical isomers of naphthalenedisulfonate (NDS) [5–7] or that of 9,10-anthraquinonedisulfonate (AQDS) [8–10] is intercalated between layers of double hydroxides. When one of these organic anions is intercalated, some tilted conformations against the two-dimensional development of the inner surface of the layer have been suggested for the anionic molecule since the basal spacing of the LDH is usually smaller than the estimated molecular size between two anionic groups in the molecule. The negative charges of the interlayer anions compensate the excess positive charges of the Al^{3+} ions which are substituted in place of the octahedral M^{2+} sites in the brucite-like structure, originally.

It has been accepted that the interlayer anions in LDH are sometimes exchanged with other anionic species (carbonate, etc.) in water and that this nature of the interlayer anions allows the intercalation of the desired anions into the interlayer region of LDH by anion-exchange. Nevertheless, the anion-exchange is not necessarily expected to occur because this results from the weakness in the attractive interaction between the interlayer anions and the layer in LDH [11]. When the interlayer anions make coordination bonds to the metal cations in the layer and thus are bound strongly to the layer in LDH, which takes place in the interlayer NDS and has been observed in FT-IR spectra [12, 13], it is plausible that the anions are unexchangeable except breaking the coordination bonds. The unexchangeable nature of the interlayer anions is important for the practical use of LDH to separate hazardous anion or valuable one from the water resources and to hold the anions firmly at the interlayer space against anion-exchanging and spreading them to the environmental water.

Two more methods have been reported for the intercalation of the desired anion between layers of double hydroxides; rehydration using the calcined LDH and coprecipitation with the constituent metal ions and the anions altogether. In this work, 9,10-anthraquinone-1,2-dihydroxy-3-sulfonate (Alizarin red S, abbreviated as ARS) is intercalated between layers of Zn/Al- or Mg/Al-double hydroxide. Solid-state properties are discussed by means of XRD, X-ray photoelectron spectroscopy (XPS), DTA/TG thermal analysis, ^{13}C and ^{27}Al solid state NMR spectroscopy and

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FT-IR absorption spectroscopy. Unexchangeable nature of the interlayer ARS anions in Zn/Al/ARS-LDH is discussed.

Experimental

Synthesis of Zn/Al/ARS-LDH by means of rehydration

Zn/Al/ARS-LDH was obtained by means of the rehydration method in which calcined Zn/Al/CO$_3$-LDH was used as the precursor in the synthesis. Synthesis of Zn/Al/CO$_3$-LDH is omitted here since it has been described in detail previously together with its solid-state properties [6, 7]. The white solid of Zn/Al/CO$_3$-LDH with the formula of Zn$_{0.62}$Al$_{0.38}$(OH)$_{2.02}$(CO$_3$)$_{0.18}$·0.14H$_2$O was calcined at 500 °C in an electric furnace as long as the layered structure disappeared in the XRD measurement and the precursor was used immediately after cooling down to room temperature. A portion (*ca.* 0.6 g) of the precursor was finely ground using a mortar and a pestle and was added to an aqueous solution of NaOH (0.01 mol/dm^{-3}) containing a sodium salt of ARS (1.8 mmol; C$_{14}$H$_5$O$_2$(OH)$_2$SO$_3$Na, purchased from KISHIDA CHEMICAL Co., Ltd.). The reaction mixture was stirred vigorously overnight in dark followed by filtration and the precipitate was washed repeatedly with deionized water until the filtrate was colorless. Since the ARS sodium salt is very soluble in water, the adsorbed ARS at the external surface of the microcrystalline LDH is easily removed by the washing. A dark purple powder of Zn/Al/ARS-LDH was obtained with the typical composition of Zn$_{0.60}$Al$_{0.40}$(OH)$_{1.96}$(ARS)$_{0.17}$(CO$_3$)$_{0.05}$·0.44H$_2$O; carbonate co-intercalates inevitably together with other anions as has been reported previously [5–7]. Coprecipitation method was unsuccessful for the synthesis of Zn/Al/ARS-LDH.

Synthesis of Mg/Al/ARS-LDH by means of coprecipitation

Mg/Al/ARS-LDH was obtained by means of the coprecipitation method; an aqueous solution of the ARS sodium salt (3 mmol) was added dropwise to another aqueous solution containing MgCl$_2$ (0.01 mol) and AlCl$_3$ (0.004 mol) at room temperature keeping the pH at 10–11 by a NaOH aqueous solution (0.03 mol/dm^3). The suspension was stirred vigorously for 19 h and aged for 48 h at 80 °C in the dark. Precipitation was separated by centrifugation of the reaction mixture at 3000 rpm for 10 min and was washed repeatedly as in the synthesis of Zn/Al/ARS-LDH. A negative test for Cl$^-$ with Ag$^+$ in the final filtrate was also assured. A purple fine powder of Mg/Al/ARS-LDH with the typical composition of Mg$_{0.64}$Al$_{0.36}$(OH)$_{1.98}$(ARS)$_{0.10}$(CO$_3$)$_{0.09}$·0.13H$_2$O was obtained. In contrast to the synthesis of Zn/Al/ARS-LDH, the rehydration method using calcined Mg/Al/CO$_3$-LDH was unsuccessful in the synthesis of Mg/Al/ARS-LDH.

Other chemical procedures

All the chemicals were commercial reagent grade and were used as received. Solid samples of the intercalated products were dried at 80 °C in an electric furnace for a day before all measurements. Chemical formulae were determined by means of the chelatometric titration for metals, the BaSO$_4$ gravimetry for ARS and of ordinal C/H analysis. Elimination of the ARS anions from the solids was examined after the suspension of a weighed portion of the solid in the volume (100 mL) of a Na$_2$CO$_3$ aqueous solution (0.5 moldm^{-3}) or deionized water was stirred for 24 h or more and was centrifuged at 3000 rpm for 20 min. The absorbance at λ_{max} = 520 nm of the supernatant was measured using a Shimadzu UV-3000 spectrometer in order to determine the amount of ARS after the pH of the supernatant was adjusted at 10–11 using an NH$_3$ (0.1 moldm^{-3})-NH$_4$Cl (0.1 moldm^{-3}) buffer solution.

Instrumentation

Details of the instrumentation in XRD, XPS, DTA/TG thermal analysis and FT-IR spectroscopy have been published previously [5–9, 12–16]; a Rigaku Rint 1200 diffractometer with the CuKα radiation was used in XRD measurements, XPS was carried out on disk samples using a Shimadzu ESCA-1000 with a Mg cathode (hν = 1253.6 eV; 10 kV/30 mA) under the reduced pressure (0.1–1μPa), DTA/TG thermal analysis was done with a Shimadzu DTA-50 under N$_2$ flow with a heating rate of 3 °Cmin^{-1} and with a reference of α-Al$_2$O$_3$, and FT-IR spectra of KBr disks were observed using a JASCO VALOR-III FT-IR spectrometer with a resolution of 4 cm^{-1} after data accumulation of 500–1000 scans. ^{27}Al MAS NMR spectra and ^{13}C CP/MAS NMR spectra were obtained by using a Brucker Avance 300 solid state NMR spectrometer of the University of Tokushima with references of adamantane (chemical shift of ^{13}C is δ = 1.91ppm) and an Al(NO$_3$)$_3$ aqueous solution (1 moldm^{-3}, chemical shift of ^{27}Al is δ = −0.1 ppm), respectively. Sample powder was put in a capped ZrO-rotor (7mm or 4mm in diameter) spinning at a frequency in the rage of 4.0–13 kHz in order to distinguish spinning side bands. Molecular size of ARS was estimated in a semiempirical MO calculation using the MOPAC/PM3 software program which gives the optimal geometry having the lowest formation enthalpy change (ΔH$_f$) for the molecule under the NDDO approximation [5, 6, 8].

Results and discussion

Single basal spacing in XRD profile

Figure 1 shows XRD patterns of Zn/Al/ARS-LDH and Mg/Al/ARS-LDH together with basal spacings; two patterns are very similar to each other and the basal spacings are the same within the experimental error. The relative intensity of the two diffraction lines located at $2\theta < 10°$ is inverted in both figures, which has been discussed elsewhere [17]. On the other hand, the basal spacing is enhanced in Zn/Al/ARS-LDH than Zn/Al/CO$_3$-LDH (7.6–7.8 Å) [18], a raw material in the synthesis of Zn/Al/ARS-LDH, which enhancement originates in the larger molecular size of the
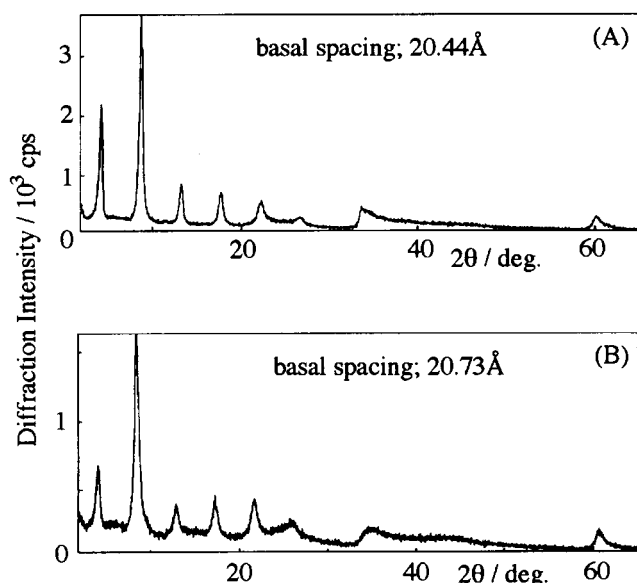
Figure 1. XRD patterns of Zn/Al/ARS-LDH(A) and of Mg/Al/ARS-LDH(B) in the range of diffraction angle $2° \leq 2\theta \leq 65°$ with basal spacings.
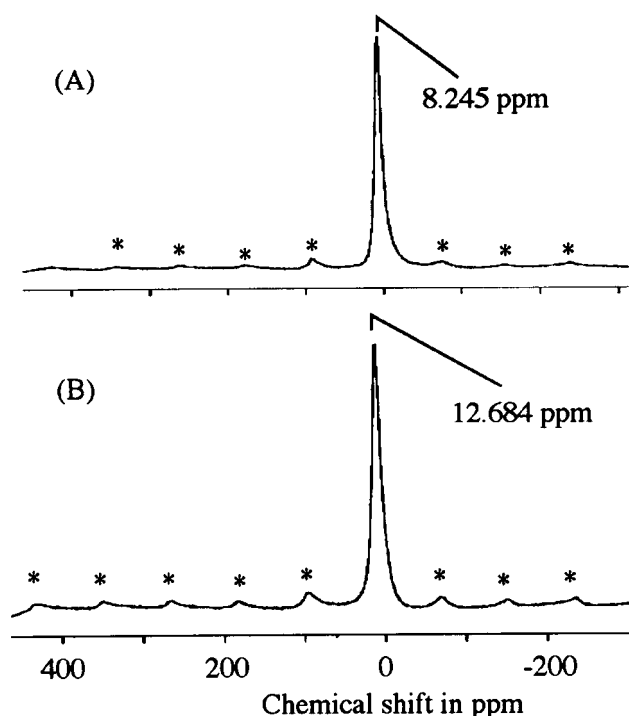

Figure 2. ^{27}Al MAS NMR spectra of Mg/Al/ARS-LDH(A) and Zn/Al/ARS-LDH(B) at spinning frequency of 7 kHz; chemical shifts of the maxima are indicated, peaks with asterisks are spinning side bands.

interlayer ARS than that of the carbonate. Since the molecular size of the interlayer anion along the stacking direction parallel to the c axis determines the interlayer distance which is calculated by subtracting the one-layer thickness of the double hydroxide (4.8 Å) [18] from the basal spacing, it is natural to conclude that the ARS anions have the same molecular conformation at the interlayer region of both LDHs. The interlayer distance calculated for the two LDHs is larger in common than the molecular size estimated along the long axis of ARS (13.85 Å) probably because of the zig-zag antiparallel conformation of the interlayer ARS anion as has been supposed for the interlayer 9,10-anthraquinone-2-sulfonate [10]. It is plausible that the zig-zag structure of the interlayer ARS anions results in the unique basal spacing observed in the XRD patterns for both compounds in Figure 1, which is contrast to the result of the layered double hydroxides with interlayer isomers of AQDS or NDS [5–10].

Octahedral coordination of Al^{3+} in the layer

Figures 2(A) and 2(B) show ^{27}Al MAS NMR spectra of Mg/Al/ARS-LDH and Zn/Al/ARS-LDH, respectively, with several spinning side bands; an intense absorption band corresponds to the transition between $m_I = 1/2$ and $-1/2$ of ^{27}Al nuclei. Since the chemical shift (δ = 8.245 ppm) of the band in Figure 2(A) is very near to that of Mg/Al/CO$_3$-LDH (δ = 8.305 ppm, obtained in our laboratory or δ = 8.1 ppm, reported by Hudson *et al.* [19]) and that of Mg/Al/B$_4$O$_5$(OH)$_4$-LDH (δ = 9.2 ppm) [20], the band in this figure is assigned to the ^{27}Al nuclei in O$_h$Al. On the other hand, the chemical shift (δ = 12.684 ppm) of the band in Figure 2 (B) is smaller by 1.8 ppm than that of Zn/Al/CO$_3$-LDH (δ =14.5 ppm) [21]; the ^{27}Al nuclei in the layer of Zn/Al/ARS-LDH are assigned to O$_h$Al and at the same time the resonance condition of the nuclei shifts to the higher magnetic field than that of Zn/Al/CO$_3$-LDH. The shift to the

higher magnetic field results from the diamagnetic shielding of the nuclei under the applied magnetic field in the NMR measurement; the shielding is due to the electron-donation from the oxygen atom in the sulfonate of the interlayer ARS to the ^{27}Al nucleus and will be further described in sections 3.4–3.6. The shift of δ to the higher magnetic field has been also reported previously for Zn/Al/SiO$_4$-LDH (δ = 12.5 ppm) [22] and for Zn/Al/PW$_{11}$O$_{39}$-LDH (δ = 7.1 ppm) [23]. The assignment of O$_h$Al is verified by the XPS spectra of the two LDHs (results are omitted), where several peaks are assigned to core-level electrons eliminated from constituent atoms of the LDHs except hydrogen. The binding energy of Al2p electrons for both LDHs in this study agrees with that of octahedrally coordinated Al^{3+} (O$_h$Al) previously reported [8, 24].

In Figure 3, three absorption bands are observed in ^{27}Al MAS NMR spectrum of Zn/Al/CO$_3$-LDH calcined at 500 °C, the precursor in the synthesis of Zn/Al/ARS-LDH. A sharp band located at δ = 8.890 ppm, a shoulder at δ = 50.015 ppm and a broad band at δ = 72.289 ppm have been assigned to O$_h$Al, the penta-coordinated Al [21, 23] and the tetra-coordinated one (T$_d$Al) [19, 21, 23–25], respectively. Both bands of the non-octahedrally coordinated Al^{3+} in Figure 3 disappear in Figure 2(B); all of the Al^{3+} ions uniformly locate in the octahedral coordination sphere after the intercalation of ARS in the rehydration process to synthesize Zn/Al/ARS-LDH. Although this uniformity has also been reported previously for some intercalated anions [21, 23], no definite explanation has been made; abundant resources of donating atoms in aqueous solution of ARS likely cover
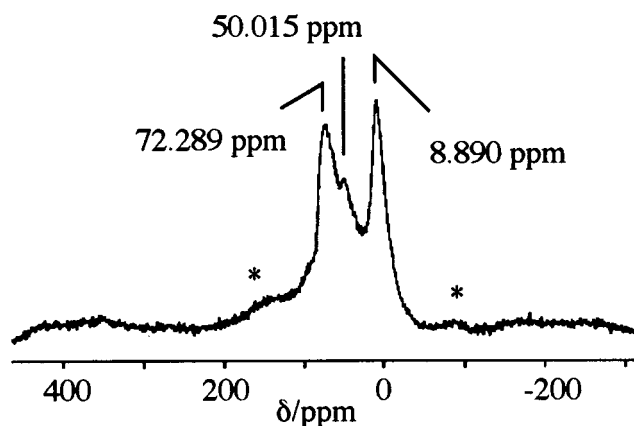
Figure 3. ^{27}Al MAS NMR spectrum of Zn/Al/CO$_3$-LDH calcined at 500 °C measured with the spinning frequency of 7 kHz; chemical shifts of three maxima are indicated, peaks with asterisks are spinning side bands.
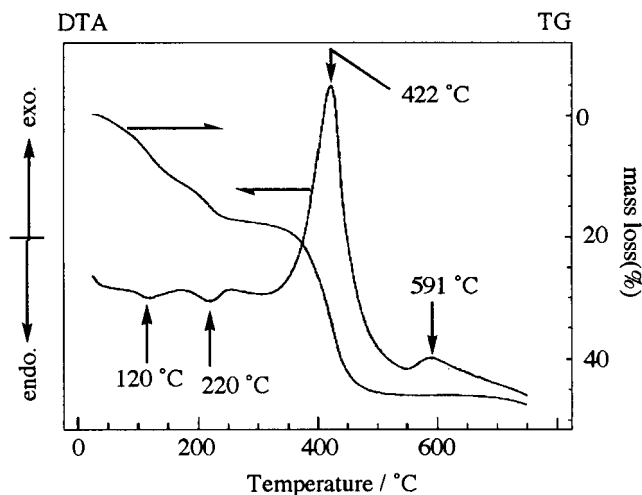

Figure 4. DTA/TG thermogram of Zn/Al/ARS-LDH between room temperature and 750 °C; temperatures of the exothermic peaks and endothermic peaks are displayed.

the deficiency in the donating atom of non-octahedral Al^{3+} upon the rehydration.

Thermal analysis

Two endothermic peaks and two exothermic peaks are observed in the DTA thermogram of Zn/Al/ARS-LDH with significant mass loss in the TG thermogram (Figure 4). Two endotherms located at 120 °C and at 220 °C are due to the elimination of interlayer water and the collapse of the layered structure of the double hydroxide (dehydroxylation), respectively, and have been also reported previously in the thermal analysis of Zn/Al/NDS-LDH [5-7]. The collapse of the layer just above 200 °C is observed in the high temperature *in situ* XRD measurement of Zn/Al/CO$_3$-LDH, and ZnO and a spinel phase are formed up to 1000 °C (result is omitted). The intense exotherm at 422 °C is also observed in the thermogram of a free sodium salt of ARS at 455 °C (thermogram is omitted) and therefore is assigned to the thermal decomposition of the interlayer ARS anion. The other exotherm at 591 °C is a new peak which does not appear in the thermograms of the free salt, and likely results from a phase change since the thermal mass loss is not observed at the temperature. Mg/Al/ARS-LDH shows the similar thermograms although the layer collapses at 380 °C–400 °C, as has been reported in the DTA/TG thermograms and *in situ* high temperature XRD measurement of Mg/Al/CO$_3$-LDH [10–16, 26], which temperature is very near to the exotherm of thermal decomposition of the inetrlayer ARS (thermograms are omitted).

FT-IR Spectra

In the FT-IR spectrum of Zn/Al/ARS-LDH (Figure 5), three absorption bands indicated by asterisks are those also observed in the spectrum of Zn/Al/CO$_3$-LDH (not shown); a broad band at 3400–3500 cm^{-1} is the O–H stretching vibration of the hydroxide in the layer and of the interlayer water molecules [25–30], two intense bands at 1637 cm^{-1} and at 1348 cm^{-1} are assigned to the O–H bending of the interlayer water [25, 28–30] and the antisymmetric stretching of

carbonate [27–31], respectively. The stretching vibrations of two carbonyl groups of the interlayer ARS lie over the band at 1637 cm^{-1} in Figure 5. The complete assignment of the other bands is out of scope in this work and we focus our attention to the bands due to the sulfonate in ARS as has been done in the study of the interlayer NDS [12–13]. It has been reported that three stretching vibrations of –SO$_3^-$ locate in the range of 1260–1150 cm^{-1} (ν_{OSO}), 1090–1010 cm^{-1} (ν_{SO}) and of 700–600 cm^{-1} (ν'_{SO}) [30]; the bands at 1261 cm^{-1}, 1039 cm^{-1} and at 639 cm^{-1} of the free sodium salt of ARS correspond to these vibrations, respectively (spectrum is omitted). In the spectrum of Zn/Al/ARS-LDH, they locate at 1259 cm^{-1}, 1043 cm^{-1} and very broad at 600 cm^{-1}, respectively, as indicated by arrows in the figure; the former two bands locate very near to those of the free salt though the band at 600 cm^{-1} locates in the lower wavenumber side significantly and at the same time is broader than the corresponding band of the free ARS salt at 639 cm^{-1}. It has been accepted that the coordination of the oxygen atom in the sulfonate group decreases the electron density in the S–O bond and thus also decreases the force constant in the vibration along this bond and accordingly shifts the location of the S–O vibration band to the lower wavenumber side [30], which has been observed in the FT-IR spectra of the interlayer NDS [12, 13]. Therefore, it is concluded that the shift of the ν'_{SO} band to 600 cm^{-1} in Figure 5 results from the coordination of the oxygen atom in the sulfonate group of the interlayer ARS to the Al^{3+} ion in the layer of Zn/Al/ARS-LDH.

These assignments are supported in the FT-IR spectrum of the Zn/Al/ARS-LDH calcined at 250 °C (result is omitted) at which temperature ARS anions are still present even though the layers of the double hydroxide disappear as described in the previous section. In the spectrum of the LDH calcined at 250 °C, the three vibrations of –SO$_3^-$ are observed at 1255 cm^{-1}, 1043 cm^{-1} and at 639 cm^{-1} together with other bands observed in the spectrum of the free salt; the location of these characteristic bands of sulfonate in
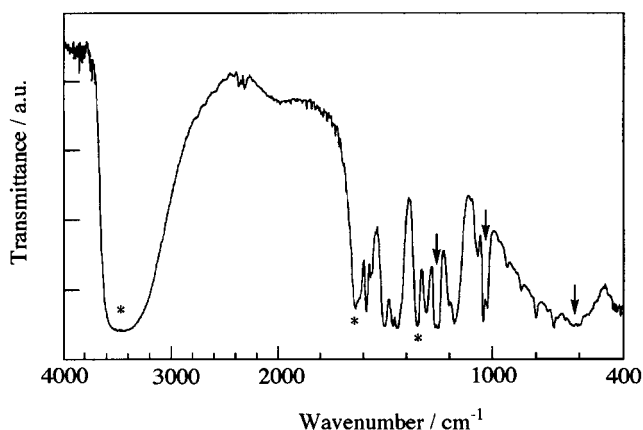
Figure 5. FT-IR spectra of Zn/Al/ARS-LDH in a KBr disk at room temperature; for bands denoted by asterisks or by arrows, see text.

ARS agrees well with that of the free ARS sodium salt. This agreement indicates that the coordination bond between sulfonate and Al^{3+} is lost after Zn/Al/ARS-LDH is calcined at 250 °C and that a free ARS (in the acid form or a simple metal salt) is included in the calcined LDH. Since it is natural that the thermal energy at 250 °C is smaller than the bonding energy of the coordination between the sulfonate and Al^{3+} the coordination bond is lost presumably because the Al^{3+} ion loses the octahedral symmetry in the coordination sphere at 250 °C, which is suggested from ^{27}Al NMR spectra of Zn/Al/CO_3-LDH calcined at 500 °C (Figure 3). Contrary to the result of Zn/Al/ARS-LDH, the vibrations of $-SO_3^-$ locate at 1258 cm^{-1}, 1044 cm^{-1} and at 639 cm^{-1} in the FT-IR spectrum of Mg/Al/ARS-LDH (not shown) are very close to the location of the vibration a free sodium salt. The result of the interlayer sulfonate in Mg/Al/ARS-LDH is in a contrast to that of the interlayer thiosulfate in Mg/Al/thiosulfate-LDH; interlayer thiosulfate makes strong bonding with some of the Mg^{2+} ions in the layer and withdraws the metal cation into the interlayer space thus produces lattice defects in the microcrystalline LDH as has been reported previously [32]. The difference in the FT-IR spectra between the two layered compounds in this study well corresponds to the result of ^{27}Al NMR spectra described in section 3.2; a definite coordination bond between Al^{3+} and the sulfonate of ARS locates in Zn/Al/ARS-LDH whereas it does not in Mg/Al/ARS-LDH.

Solid state ^{13}C NMR spectra of interlayer ARS

Figures 6 compares two ^{13}C CP/MAS NMR spectra of free sodium salt (A) and the interlayer anion in Zn/Al/ARS-LDH (B), respectively. Although the complete assignment of the complicated spectra is out of scope in this work, the absorption bands in the spectrum of the free salt are classified in four groups; two bands located at δ = 149.387 ppm and at 152.435 ppm, a band at δ = 136.439 ppm, two bands at δ = 179.131 ppm and at 188.019 ppm, and four bands at δ = 115.716 ppm, 121.560 ppm, 128.687 ppm and at 132.531 ppm. They are due to C1 and C2 carbon nuclei (indicated totally as C1/C2 in Figure 6(A)), C3 nucleus (indicated as C3), C9 and C10 nuclei (indicated totally as

C9/C10), and the other nine carbon nuclei (indicated totally as Others) in ARS, respectively. In addition to four bands of Others in Figure 6(A), all bands of C3 and of C9/C10, two bands of C9/C10 and a band of C3 are also observed in the spectrum of 1,2-dihydroxy-9,10-anthraquinone, 9,10-anthraquinone and sodium naphthalene-1,5-disulfonate (results are omitted), respectively, though small deviation in the chemical shift is observed in the spectra of these compounds and some bands are lacking in the spectrum of the last compound. The assignment for C9/C10 in Figure 6(A) is consistent with that by Komori *et al.* [33] for the intercalated poly(vinylpyrrolidone) into kaolinite and that by Whilton *et al.* [34] for reactive species of asparatic acid at the interlayer of Mg/Al double hydroxide and the assignment for Others is based on that of anthraquinone derivatives [35, 36]. Two bands of C9/C10 have the separation of 8.888 ppm in Figure 6(A) because of the through-space interaction with the hydroxyl group at the C1 atom. Three points are noticed in particular when two spectra in Figure 6 are compared; first, the band of C3 in the spectrum of free ARS salt is not identified in that of the interlayer ARS, secondly, the two bands of C1/C2 shift commonly to the lower magnetic field in the spectrum of the interlayer ARS with enhanced band separation (δ = 163.915 ppm and δ = 171.302 ppm), thirdly, all bands of Others and C9/C10 remain their locations almost unchanged. The first point is elucidated as the electron density on the C3 atom in the interlayer ARS changes so largely that the band of C3 shifts out of the scope in Figure 6(B), which change originates in the coordination of the oxygen atom in the sulfonate group substituted on this carbon atom to the Al^{3+} ion in the layer as described in the previous section. The second point is elucidated as the electron densities on the C1 and C2 atoms are susceptible to the change of the electron density on the C3 atom. The separation of the chemical shift between the bands of C1/C2 is larger in the spectrum of the intercalated ARS (7.399 ppm in Figure 6(B)) than that of the free salt (3.144 ppm in Figure 6(A)) probably due to the mesomeric effect. The third point is a proof that the anthraquinone moiety is least influenced by the intercalation and locate stable at the interlayer region which is further discussed in the next section. The separation between two bands of C9/C10 is slightly smaller in the spectrum of the intercalated ARS (7.871 ppm in Figure 6(B)) than that of the free sodium salt (8.888 ppm) presumably because the hydrogen bond between the carbonyl group on the C9 atom and the hydroxyl group on the C1 atom of the free salt is broken in the intercalated ARS since the hydroxyl group dissociates to form ARS dianion. In the ^{13}C CP/MAS NMR spectrum of Mg/Al/ARS-LDH, bands of C1/C2 and bands of C9/C10 are broad considerably whereas bands of 'Others' in Figure 6 are observed distinctly (band of C3 is also missing) and no quantitative argument could be fixed for this compound.

Unexchangeable interlayer ARS

When a small portion (*ca.* 0.50 g) of Zn/Al/ARS-LDH is dispersed into an aqueous solution of Na_2CO_3 at room temperature, no elimination of ARS is observed from the solid to
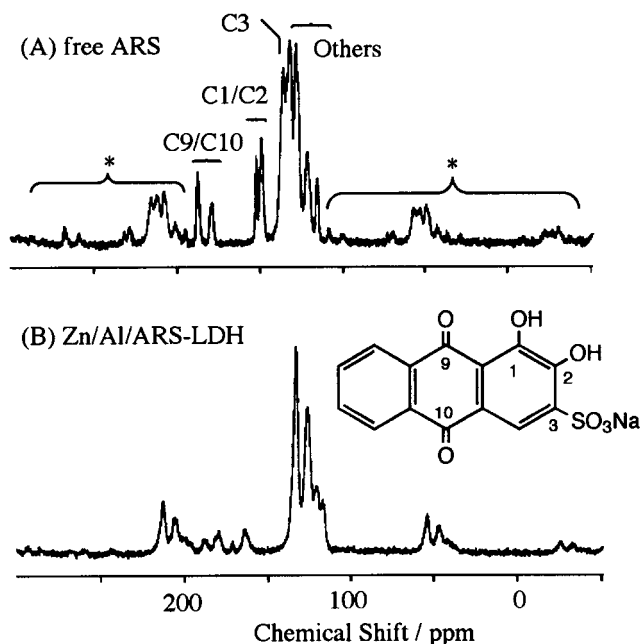
Figure 6. ^{13}C CP/MAS NMR spectra of the free sodium salt of ARS (A) and ZN/Al/ARS-LDH(B) associated with spinning side bands indicated totally by asterisks; numbering of the carbon atoms in ARS is depicted altogether and for the assignment, see text.

the solution; the interlayer ARS anions in Zn/Al/ARS-LDH do not deintercalate through the mechanism of the anion-exchange with carbonate in water. This is in contrast to the result of recent works by O'Hare *et al.* who have reported that series of interlayer carboxylate are easily exchanged with carbonate in water [37]. The unexchangeable nature of the interlayer ARS anions in Zn/Al/ARS-LDH agrees with the results of FT-IR spectra (section 3.4) and ^{13}C NMR spectra (section 3.5); the interlayer anions make the coordination bond so strongly with the Al^{3+} ions in the layer of the double hydroxide that the anions are stable and unexchangeable with carbonates in the surrounding water. On the other hand, significant elimination was observed when a small portion of Zn/Al/ARS-LDH calcined at 250 °C (*ca.* 0.35 g that is equivalent to 0.50 g of the uncalcined solid) was dispersed into deionized water. As much as 90% of the ARS anion was eliminated from the calcined solid when a larger volume (2 × 200 mL) of water was used and more several % of the anion also removed into additional volume (500 mL) of deionized water. This elimination results from losing the coordination bond between the sulfonate and the Al^{3+} ion upon heating the LDH up to 250 °C as described in section 3.4. For Mg/Al/ARS-LDH, however, 3–5% of the total amount of the ARS anion was eliminated from the LDH after stirring for 24 h and more 1-3% was also eliminated after additional 24 h when the LDH was dispersed in the aqueous solution of Na_2CO_3 at room temperature, presumably owing to the anion-exchange with the carbonate in water; the interlayer ARS is weakly bounded to the layer in this LDH through the electrostatic attraction between its negative charge and an excessive positive charge on Al^{3+} in the layer.

Making coordination bond to the metal cations in the layer, water-soluble anions can be immobilized at the interlayer region of LDH without oozing out to the surrounding water, which can be applied in practical use to separate hazardous anions or valuable anions from water resources, for example. Furthermore, the calcination of the intercalated LDH at the temperature just above the collapse of the layer but below the decomposition of the organic anions followed by immersing the calcined LDH in water to dissolve the anions is useful to extract the separated anions with the molecular structure unchanged as it was before the separation and to utilize the anions repeatedly. The combination of the making coordination bond and the thermal treatment will hopefully open the possibility to recycle not only the LDH as the precursor to separate organic anions by the intercalation but also the anion for further utilization.

Acknowledgements

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