研究简报

锂铝水滑石对水杨酸及其异构体的选择性插层研究

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Competitive Intercalation of Geometric Isomers of Hydroxybenzoic Acid into [LiAl₂(OH)₆]Cl·yH₂O Layered Double Hydroxides

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Abstract: $[LiAl_2(OH)_6]Cl \cdot yH_2O$ was prepared by co-precipitation. The competitive intercalation of geometric isomers of hydroxybenzoic acid into the interlayer of layered double hydroxides (LDHs) was studied by the reaction of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ with various mixtures of *o*-hydroxybenzoic acid, *m*-hydroxybenzoic acid and *p*-hydroxybenzoic acid. Powder X-ray diffraction (XRD) results confirmed the intercalation of the isomers, and high performance liquid chromatography (HPLC) was used for the quantitative study. The order of the preferential intercalation of the three isomers was found to be: *o*-hydroxybenzoic acid $(1,2-C_7H_6O_3) \gg$ *p*-hydroxybenzoic acid $(1,4-C_7H_6O_3) >$ *m*-hydroxybenzoic acid $(1,3-C_7H_6O_3)$.

Key words: layered double hydroxides; competitive intercalation; hydroxybenzoic acids; geometric isomers

The preparation, properties and applications of Layered double hydroxides (LDHs) have been studied extensively [1]. LDHs are materials with positively charged, mixed-metal hydroxide sheets and negatively charged interlayer anions with water molecules [2]. In this role they have been used as ion-exchange materials, catalysts, sorbents and halogen absorbers [3,4]. The chemical composition of LDHs is generally expressed as $[M^{z+}_{1-x}M^{3+}_x(OH)_2]^{\xi+} X^{n-}_{\xi/n} \cdot mH_2O$. In the vast majority of cases, $z=2$ in which case $M^{2+}=Ca^{2+}$, Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, etc., and $M^{3+}=Al^{3+}$, Cr^{3+}, Mn^{3+}, Fe^{3+}, Ga^{3+},

Co^{3+}, etc., giving $\xi=x$ [5,6]. LDHs have also been prepared with $z=1$. In this case, M^+ is limited to Li^+ and $M^{3+}=Al^{3+}$. X^{n-} is an interlayer exchangeable anion such as CO_3^{2-}, Cl^-, NO_3^-, etc. [7~9].

LDHs have been found many applications from separation chemistry to gene reservoirs [10,11]. In particular, the cation and anion ordered LDH, $[LiAl_2(OH)_6]Cl \cdot yH_2O$, forms crystalline intercalation compounds with a range of organic anions. In recent years, OHare et al. have reported preferential ion-exchange intercalation in LDHs and examined the potential of these sys-

tems for isomer separation in organic chemistry[12~14]. It has been suggested that the affinity of anions for intercalation into LDHs is influenced by the charge density and chemical composition of host LDH lattices as well as the shape, size, and charge of guest anions[15,16]. Factors such as ionic strength, pH value, atmospheric conditions, molar fraction and concentration of isomers might affect the kinetic and thermodynamic processes for the anion-exchange reaction in aqueous systems. Therefore, a systematic investigation on such factors will be important in the understanding of the selectivity in the intercalation reaction from mixtures of geometric isomers.

In previous studies the organic isomers were dianions and so they were able to interact strongly with the positively charged metal-containing layers within the interlayer space[11,14,17]. In the present work, we expand our studies to the preferential intercalation of isomeric mixtures of mono anions, namely, hydroxybenzoic acids into $[LiAl_2(OH)_6]Cl \cdot yH_2O$. The structural properties and quantitative aspects of the intercalates were studied by elemental analysis, X-ray powder diffraction (XRD), and high performance liquid chromatography (HPLC).

1 Experimental

1.1 Reagents

All the chemicals used were of analytical grade, purchased from the Beijing Chemical Plant Limited and used without any further purification. All solutions were prepared using distilled and decarbonated water.

1.2 Synthesis

1.2.1 Preparation of $[LiAl_2(OH)_6]Cl \cdot yH_2O$

The precursor $[LiAl_2(OH)_6]Cl \cdot yH_2O$ ([Li-Al-Cl] LDH) was synthesized by a procedure similar to that described previously[17]. $[LiAl_2(OH)_6]Cl \cdot yH_2O$ was prepared by slowly dropping a solution of LiCl and $AlCl_3$ with molar ratio of 3:1 into a NaOH solution with vigorous stirring under a nitrogen atmosphere. The pH value of the solution was 10.5 at the end of the reaction. The slurry was aged at 65 ℃ for 6 h, and the product was washed extensively with decarboxylated

water, centrifuged and dried at 60 ℃ for 8 h. Elemental analysis gave Li/Al molar ratio of 1:2.02.

1.2.2 Preparation of LDH-[1,2-$C_7H_5O_3$], LDH-[1,3-$C_7H_5O_3$] and LDH-[1,4-$C_7H_5O_3$]

The ion exchanged intercalates were synthesized by the reaction of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ with a 4-fold excess of 1,2-, 1,3- or 1,4-$C_7H_5O_3^-$, respectively, in aqueous solution at 100 ℃ for 10 h under a nitrogen atmosphere. The pH value was kept 8.0 by adding 0.1 mol·L^{-1} NaOH solution during reaction. The product was washed with decarboxylated water, centrifuged and dried at 60 ℃ for 8 h.

1.2.3 Studies on the preferential intercalation

Four samples were prepared in order to carry out the preferential intercalation of the three isomers of hydroxybenzoic acid.

Sample 1: The intercalation compound from a mixture of m-hydroxybenzoic acid (1,3-$C_7H_6O_3$) and p-hydroxybenzoic acid (1,4-$C_7H_6O_3$) ions (1:1 molar ratio) into the LDH directly synthesized by the reaction of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ with a 4-fold excess of hydroxybenzoic salts in aqueous solution.

Sample 2: A method similar to that for sample 1 was used to obtain the intercalation compound from a mixture of o-hydroxybenzoic acid (1,2-$C_7H_6O_3$) and p-hydroxybenzoic acid (1,4-$C_7H_6O_3$) (1:1) ions into the LDHs.

Sample 3: The intercalation compound was prepared using the method in the preparation of sample 1 from a mixture of o-hydroxybenzoic acid (1,2-$C_7H_6O_3$) and m-hydroxybenzoic acid (1,3-$C_7H_6O_3$) (1:1 molar ratio) ions into the LDHs.

Sample 4: The intercalation compound from a mixture of o-hydroxybenzoic acid (1,2-$C_7H_6O_3$), m-hydroxybenzoic acid (1,3-$C_7H_6O_3$) and p-hydroxybenzoic acid (1,4-$C_7H_6O_3$) ions (1:1:1 molar ratio) into the LDHs was directly synthesized by the reaction of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ with a 4-fold excess of hydroxybenzoic salts in aqueous solution.

1.3 Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu $K\alpha$ radiation (λ=0.154 18 nm, Ni-filter)

at 40 kV, 30 mA. The samples without preferred orintations were scanned in steps of 0.02° in the 2θ range 3° to 70° using a count time of 4 s per step.

The quantitative analysis was carried out on a Shimadzu HPLC system with LC-10ATvp pump, a VP-ODS C18 column (250 × 4.6 mm) and SPD-10Avp UV-Vis detector (285 nm) at 40 ℃ and a flow rate of 1.0 mL·min⁻¹. The mobile phases were prepared by mixing 40% methanol, 58% deionized water and 2% phosphoric acid. All samples were filtered through 0.20 μm nylon filters prior to injection into the HPLC system. Injection volume was always 10 μL.

Microanalysis of metals was performed by ICP emission spectroscopy on a Shimadzu ICPS-7500 instrument using solutions prepared by dissolving the samples in dilute HNO_3. Analysis was carried out by the standard curve method.

2　Results and discussion

2.1　Preparation of LDH-[1,2-C₇H₅O₃], LDH-[1,3-C₇H₅O₃] and LDH-[1,4-C₇H₅O₃]

$[LiAl_2(OH)_6]Cl \cdot yH_2O$ has been shown to undergo a wide range of facile anion-exchange reactions with a variety of inorganic and organic guests. Reaction of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ with either hydroxybenzoic salts of o-hydroxybenzoic acid, m-hydroxybenzoic acid and p-hydroxybenzoic acid in water yields the intercalation compounds LDH-[G] (G=1,2-C₇H₅O₃, 1,3-C₇H₅O₃, 1,4-C₇H₅O₃), respectively. Fig.1 displays the XRD patterns of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ and the intercalation products of the three isomers, and Table 1 lists the basal spacing and lattice parameters.

Fig.1a shows the XRD pattern of the precursor $[LiAl_2(OH)_6]Cl \cdot yH_2O$. The a parameter of the hexago-

nal unit cell corresponds to the distance between two metals in adjacent octahedral sites while the c parameter corresponds to three times the distance between adjacent hydroxy layers. As shown in Table 1, the basal spacing (d_{003}) of the LDH is 0.761 nm. The gallery height of the LDH is 0.283 nm when the thickness of the mixed aluminium / lithium hydroxide layers (0.478 nm) is subtracted, which is consistent with the previous work[18].

As shown in Fig.1b, the (003) and the higher-order reflections of the LDH-[1,4-C₇H₅O₃] shifts to lower 2θ angles compared to those of the [Li-Al-Cl] LDH. After the intercalation, the basal spacing (d_{003}) increases from 0.761 nm ([Li-Al-Cl] LDH) to 1.524 nm (LDH-[1,4-C₇H₅O₃]). As a result, the gallery height of the LDH-[1,4-C₇H₅O₃] increases to 1.046 nm, which strongly indicates the intercalation of 1,4-C₇H₆O₃ into the LDHs. As shown in Fig.1c, the (003) reflection of LDH-[1,2-C₇H₅O₃] shifts to much lower 2θ angles compared to that of LDH-[1,4-C₇H₅O₃] with the value of d_{003} 1.730 nm. However, in the case of the interca-
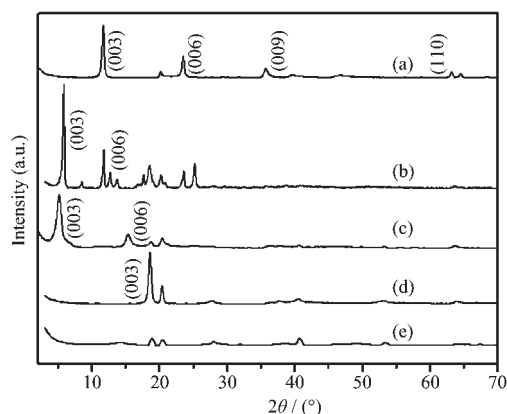
Fig.1　XRD patterns of (a) $[LiAl_2(OH)_6]Cl \cdot yH_2O$, (b) LDH-[1,4-C₇H₅O₃], (c) LDH-[1,2-C₇H₅O₃], (d) LDH-[1,3-C₇H₅O₃] and (e) Al(OH)₃

Table 1　Indexing of XRD patterns of the precursor and the intercalated products

	d_{003} / nm	Lattice parameter a / nm	Lattice parameter c / nm	Gallery height / nm	Size of guest / nm
[Li-Al-Cl]LDHs	0.761	0.294	2.283	0.283	—
LDH-[1,4-C₇H₅O₃]	1.524	—	4.572	1.046	0.701
LDH-[1,2-C₇H₅O₃]	1.730	—	5.190	1.252	0.620
Sample 1	1.528	—	4.584	1.050	—
Sample 2	1.749	—	5.247	1.271	—
Sample 3	1.819	—	5.457	1.341	—
Sample 4	1.777	—	5.331	1.299	—

lation of $1,3$-$C_7H_5O_3^-$ into [Li-Al-Cl] LDH, the expected intercalated product is not obtained (Fig.1d), while the reflections are similar to those of $Al(OH)_3$ (Fig.1e). This indicates that the affinity of $1,3$-$C_7H_5O_3^-$ to the LDH host lattice is rather low, and the reaction process results in the transformation of the precursor LDHs to $Al(OH)_3$.

From X-ray diffraction studies, the orientation of the intercalated species can be roughly estimated. The length of $1,4$-$C_7H_5O_3^-$ and $1,2$-$C_7H_5O_3^-$ was calculated to be 0.701 and 0.620 nm, respectively, by the method of molecular mechanics (shown in Table 1). As for the LDH-[$1,4$-$C_7H_5O_3$], comparison of the size of guest with a gallery height of 1.046 nm suggests that the $1,4$-$C_7H_5O_3^-$ anions are accommodated in the interlayer region as a crossing bilayer arrangement with the carboxyl group of individual anion attaching alternately to the upper and lower hydroxide layers. A hydrophilic area was formed through the interaction between hydroxyl groups of the guest and the interlayer water. A schematic representation of the probable arrangement for LDH-[$1,4$-$C_7H_5O_3$] is shown in Fig.2A. In the case of LDH-[$1,2$-$C_7H_5O_3$], the gallery height of 1.252 nm is approximately two times of the length of the interlayer guest, as a result of a bilayer antiparallel pattern can be anticipated (as shown in Fig.2B). The guests strongly interact with each other via π-π interactions of phenyl rings, which provides sufficient energy for the observed large interlayer expansion.
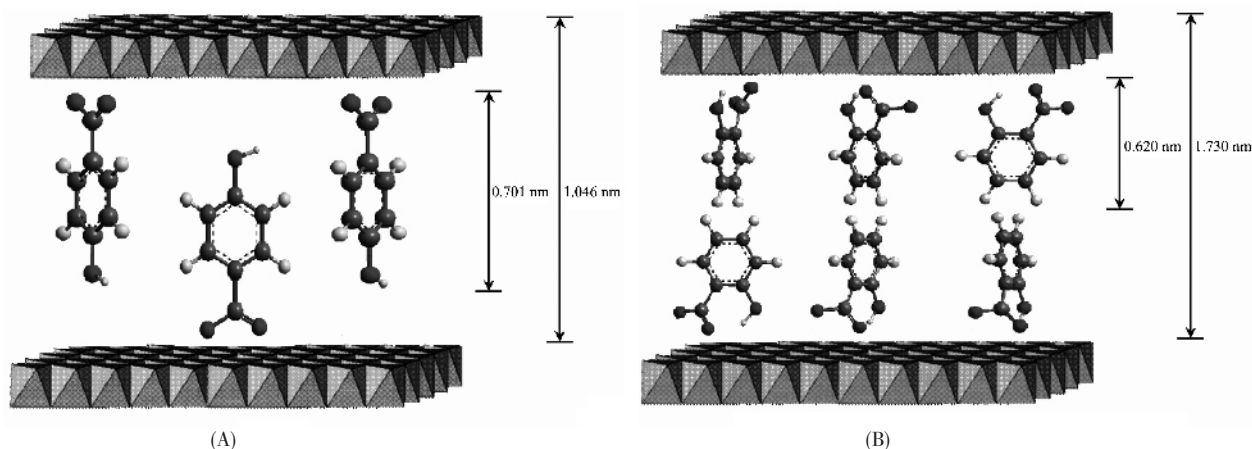

Fig.2　Schematic representations of the possible arrangements for (A) LDH-[$1,4$-$C_7H_5O_3$] and (B) LDH-[$1,2$-$C_7H_5O_3$]

2.2　Study on the preferential intercalation of isomers

Fig.3 displays the XRD patterns of samples 1~4, and the basal spacing and lattice parameters are listed in Table 1. As shown in Fig.3a, the d_{003} of sample 1 (1.528 nm) from an equimolar aqueous mixture of m-hydroxybenzoic acid ($1,3$-$C_7H_6O_3$) and p-hydroxybenzoic acid ($1,4$-$C_7H_6O_3$) is rather close to that of LDH-[$1,4$-$C_7H_5O_3$] (Fig.1b) (1.524 nm), which possibly indicates that the intercalation ability of $1,4$-$C_7H_5O_3^-$ is stronger than that of $1,3$-$C_7H_5O_3^-$. The XRD pattern of sample 2 (Fig.3b) from an equimolar aqueous mixture of $1,2$-$C_7H_6O_3$ and $1,4$-$C_7H_6O_3$ is a superposition of LDH-[$1,2$-$C_7H_5O_3$] and LDH-[$1,4$-$C_7H_5O_3$], and the intensity of (003) reflection of the former (2θ 5.05°) is much stronger than that of the latter (2θ =6.06°, marked with asterisk). This indicates that $1,2$-$C_7H_5O_3^-$ has preferential intercalation ability than that of $1,4$-
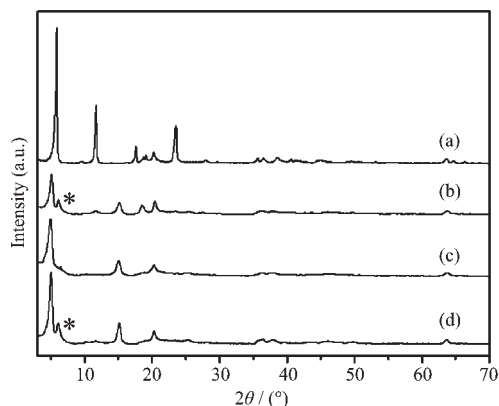

Fig.3　XRD patterns of (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4

$C_7H_5O_3^-$ in two LDH phases formed in sample 2. In the case of sample 3 from a mixture of 1,2-$C_7H_6O_3$ and 1,3-$C_7H_6O_3$, the XRD pattern (Fig.3c) is very similar to that of LDH-[1,2-$C_7H_5O_3$] (Fig.1c), while the d_{003} value of sample 3 (1.819 nm) is larger than that of the pristine LDH-[1,2-$C_7H_5O_3$] (1.730 nm), indicating the influence of 1,3-$C_7H_5O_3^-$ during the intercalation process.

Fig.3d shows the XRD pattern of the intercalation compound of equimolar mixture of the three isomers into the LDH, which is similar to that of sample 2 (Fig.3b), presenting the superposition of (003) reflection of both 1,2- and 1,4-$C_7H_5O_3^-$ intercalated LDH phases. However, the d_{003} value corresponding to the 1,2-$C_7H_5O_3^-$ (1.777 nm) intercalated phase is a little larger than that of LDH-[1,2-$C_7H_5O_3$] (1.730 nm). This might imply the co-intercalation of 1,3-$C_7H_5O_3^-$ into the host lattice. This will be further confirmed by HPLC results in the next section.

The content of each isomer intercalated in [LiAl$_2$(OH)$_6$]Cl·yH$_2$O during the competition reaction was determined by HPLC. Table 2 lists the relative content of respective isomer in samples 1~4, in which a remarkable property of preferential intercalation into LDH layers of the three isomers can be obtained. It should be noted that a small amount of 1,3-$C_7H_5O_3^-$ was determined in sample 1, sample 3 and sample 4, although no 1,3-$C_7H_5O_3^-$ intercalated LDH phase was observed in the XRD patterns of the three samples, confirming that 1,3-$C_7H_5O_3^-$ was co-intercalated into the host lattice. From the present data, preferential intercalation was observed for [LiAl$_2$(OH)$_6$]Cl·yH$_2$O, and the intercalation ability into [LiAl$_2$(OH)$_6$]Cl·yH$_2$O of the three isomers is in the order: o-hydroxybenzoic acid (1,2-$C_7H_6O_3$) ≫ p-hydroxybenzoic acid (1,4-$C_7H_6O_3$) > m-hydroxybenzoic acid (1,3-$C_7H_6O_3$). Since 1,4-$C_7H_6O_3$, 1,2-$C_7H_6O_3$ and 1,3-$C_7H_6O_3$ are isomers with the same negative charge, this preferential intercalation indicates the presence of a molecular recognition ability of the [LiAl$_2$(OH)$_6$]Cl·yH$_2$O, resulting from the interaction between the host and guest.

Hydroxybenzoic ions contain two functional groups: -COO$^-$ and -OH. It is generally expected that the principal energy consideration is based on the electrostatic interaction between the positively charged metal hydroxide layer and the interlayer anions, as well as hydrogen bonding formed among the carboxyl group in the guest anions, hydroxyl in the host, and interlayer water. The preferential intercalation of 1,2-$C_7H_5O_3^-$ among the three isomers can be explained by both geometric and electronic effect. Firstly, 1,2-$C_7H_5O_3^-$ is capable of forming intramolecular hydrogen bonding, which is helpful to the formation of a ball-like structure, resulting in the increase of its mobility for intercalation. However, 1,3-$C_7H_5O_3^-$ and 1,4-$C_7H_5O_3^-$ can form intermolecular hydrogen bonding, which could militate against the intercalation reaction. As a result, the geometric effect resulting from the formation of hydrogen bonding is a crucial factor in the selective intercalation. Secondly, the conjugated π-π interactions from the bilayer orientation (Fig.2B) may play an important role in controlling the long-range physical interaction by electronic communication. Based on the experimental results above, it can be proposed that, the LDH-[1,2-$C_7H_5O_3$] is the thermodynamically most stable product, consequently, it shows the strongest ability for intercalation. In the case of the other two isomers, 1,4-$C_7H_5O_3^-$ and 1,3-$C_7H_5O_3^-$, it has been reported that the more linear, rod-like structure is able to interact more strongly with cationic metal hydroxide layers in the study of other geometric isomers [19]. In this work, 1,4-$C_7H_5O_3^-$ is preferred in competition intercalation compared with 1,3-$C_7H_5O_3^-$, which is in accordance with previous reports.

Table 2　Results of HPLC for the hydroxybenzoic acids intercalates

Isomer	Sample 1 / %	Sample 2 / %	Sample 3 / %	Sample 4 / %
1,2-$C_7H_6O_3$	—	82.7	80.6	86.8
1,3-$C_7H_6O_3$	14.9	—	19.4	4.0
1,4-$C_7H_6O_3$	85.1	17.3	—	9.2

The identification of the molecular recognition of the LDHs is still not very clear at present. To elucidate the mechanism of preferential intercalation, a series of theoretical calculations should be carried out. The effects of concentration of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ and the isomers, temperature, pH value, solvent, and atmospheric conditions are under investigation to optimize the other experimental parameters.

3 Conclusions

The intercalation compounds of hydroxybenzoic ions isomers into $[LiAl_2(OH)_6]Cl \cdot yH_2O$ have been synthesized. The host material exhibits a remarkable sequential series of intercalation preferences for these isomer anions in aqueous solution. The intercalation preference order for the hydroxybenzoic acids is: *o*-hydroxybenzoic acid $(1,2\text{-}C_7H_6O_3) \gg p$-hydroxybenzoic acid $(1,4\text{-}C_7H_6O_3) > m$-hydroxybenzoic acid $(1,3\text{-}C_7H_6O_3)$. The hydrogen bonding plays an important role in the selective intercalation.

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