

锌铝类水滑石的复原及表征

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本文采用焙烧复原法, 在 70 °C 以 80% 的乙醇溶液为分散介质, 有机酸阴离子与煅烧后的锌铝类水滑石的物质的量之比为 1:9 的条件下, 实现了苯甲酸及苯二甲酸异构阴离子与锌铝类水滑石的插层反应, 同时, 还进行了等物质的量的两种酸与锌铝类水滑石 (1:1:9) 的插层反应。利用 XRD 和 IR 测试技术对样品结构进行表征, UV 及 HPLC 对有机酸的反应量进行定量, 并采用 Gaussian-98 软件包中 *ab initio* 分子轨道法 (HF/6-31G) 计算了各有机酸阴离子的分子结构, 分析了其结构与插层行为的关系, 并理论结合实验给出了各有机酸阴离子在锌铝类水滑石层间可能的空间构型。研究表明, 苯甲酸及苯二甲酸异构阴离子在插层过程中表现出选择性, 其优先进入锌铝类水滑石层间的顺序是: 对苯二甲酸 > 邻苯二甲酸 > 间苯二甲酸 > 苯甲酸, 且锌铝类水滑石对对苯二甲酸表现出较高的选择性, 是环境友好的分离方法。

关键词: 苯甲酸阴离子 苯二甲酸阴离子 选择性插层 锌铝类水滑石
分类号: O614.24[†] O614.3[†]

Reconstruction and Characterization of Zn,Al Hydrotalcite Like Compound

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Intercalation of 1,2-,1,3-,1,4-benzenedicarboxylate or benzenecarboxylate ions into Zn,Al-HTlc was carried out by the reconstruction method in the molar ratio of organic acid: calcined HTlc=1:9, in 80 % alcoholic aqueous solution at 70 °C. Selective reaction was observed in competitive experiments involving an equal concentration pairs of acids. The structures of the intercalates formed by reaction of four guests with Zn, Al-HTlc were characterized by XRD and IR techniques. And the charge density on the oxygens of each of the carboxylate groups for each of the four anions was investigated utilizing *ab initio* (HF/6-31G) method by G98w. The orientation of 1,2-,1,3-,1,4-benzenedicarboxylate or benzenecarboxylate anions between the layers was also proposed. The results show that the preference order for intercalation of all guests in Zn,Al-HTlc was 1,4-benzenedicarboxylate > 1,2-benzenedicarboxylate > 1,3-benzenedicarboxylate > benzenecarboxylate. This material exhibits the preferential intercalativity for 1,4-benzenedicarboxylate from mixed pairs of organic acids and will be exploited as a method for the chemical separation of these anions from solution.

Keywords: benzenecarboxylate anion benzenedicarboxylate anions preferential intercalation
Zn,Al-HTlc

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0 Introduction

In recent years preferential intercalation in layered materials has been received considerable attention because of their potential applications, as molecular recognition, environmentally friendly separation and new organic-inorganic hybrid composites^[1-8].

Hydrotalcite like compounds (HTlcs) form an important class of lamellar hosts with positively charged layers and intercalated exchangeable anions. The empirical formula of HTlc is generally expressed as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are di- and tri-valent metal cations, respectively, that occupy octahedral positions in hydroxide layers. A^{n-} is an exchangeable anion, such as CO_3^{2-} , NO_3^- , Cl^- , etc. Hydrotalcite like compounds have been widely known as catalysts, catalyst supports, adsorbents, anion exchangers, etc.^[9]. Recently, there have been several reports on the preferential intercalation into the HTlc of $[LiAl_2(OH)_6]Cl \cdot H_2O$ ^[5-8] with the main synthetic route via anionic exchange. However, preferential intercalation of isomeric organic anions into Zn,Al-HTlc has scarcely been studied. In the present paper, we report the intercalation of 1,2-,1,3-,1,4-benzenedicarboxylate or benzenecarboxylate ions into Zn, Al-HTlc by the reaction of calcined Zn, Al-HTlc with solutions of the organic acids. The preferential isomer of anions intercalation into Zn, Al-HTlc was also observed.

It is well known that HTlcs decompose to mixed oxides solid solution by heating to 400~800 °C and the calcined products can rehydrate and combine with the anions in solutions to reconstruct the original hydrotalcite like structure^[9-14]. Hence, both HTlcs and their calcined products are expected to find applications in the uptake of anions from aqueous solutions. The anion exchange behaviour is governed by the electrostatic interaction between positively charged host layer and interlayer anions, and the selectivity of anion exchange can be influenced by temperature, shape of guest, charge density of guest, host layers and the solvent of the intercalation reaction^[5,15]. Therefore Zn,Al-HTlc seems to be useful for the separation

into their components of mixtures of benzenecarboxylate ions possessing different charge density and shape. In order to develop a greater understanding of the factors influencing the preferences exhibited by these hosts, we have investigated the intercalation of isomers of benzenedicarboxylate anions in Zn, Al-HTlc in the present paper.

1 Experimental

The raw material Zn,Al-HTlc was synthesized by the coprecipitation method. The mixed aqueous solution of $ZnSO_4 \cdot 7H_2O$ (0.8 mol·L⁻¹) and $Al_2(SO_4)_3 \cdot 18H_2O$ (0.13 mol·L⁻¹), and the mixed aqueous solution of NaOH (1.92 mol·L⁻¹) and Na_2CO_3 (0.53 mol·L⁻¹) were slowly added with stirring to 108 mL distilled water at the same time at pH 10. The resulting suspension was thoroughly stirred and refluxed for 6 h. The solid product was washed and dried, giving the carbonate HTlc. Elemental analysis indicated the HTlc composition was $[Zn_{0.72}Al_{0.27}(OH)_2](CO_3)_{0.14} \cdot 1.32H_2O$. Then, the Zn,Al-HTlc was calcined at 500 °C for 3 h to form its calcined oxide.

For the intercalation reaction, the 1,2-,1,3-,1,4-benzenedicarboxylate or benzenecarboxylate acids were respectively dissolved in 80 % alcoholic aqueous solution pH with 5~6, then zinc aluminum oxide powder was added to the solution, and the mixture was stirred at 70 °C for 5 h. The molar ratio of organic acid : calcined HTlc was 1:9. Then, the samples were filtered, washed with 80 % alcoholic aqueous solution, and dried at 70 °C for 24 h. UV spectroscopy was used to measure the concentration of each organic acid remaining in the filtrate, and the percentage of each anion intercalated in the HTlc could be calculated. The solids were characterized by powder X-ray diffraction and IR spectroscopy.

For two component competitive intercalation reactions, any two of the organic acids and calcined Zn, Al-HTlc in the molar ratio 1:1:9 were synthesized by a similar method as before. And the amount of each organic anion remaining in the filtrate was determined by HPLC and the percentage of each anion intercalat-

ed in the HTlc could be calculated.

Powder X-ray diffraction (XRD) measurement was performed on a Rigaku D/Max-3B powder X-ray diffractometer, using $\text{CuK}\alpha$ radiation, a scanning rate of $5^\circ \cdot \text{min}^{-1}$, and a 2θ angle ranging from 3° to 70° . Infrared spectra (IR) was obtained using a NICOLET 60SXB FTIR spectrophotometer from 200 cm^{-1} to 4000 cm^{-1} by the standard KBr disk method. HPLC was performed on Shimadzu LC-6A, UV detector at 250 nm. The column was a ZORBAX SB-Aq 4.6×150 (mm) (Agilent technologies), and the mobile phases were 90 % methanol and 10 % acetic acid solution ($0.017 \text{ mol} \cdot \text{L}^{-1}$) (elution speed: $1 \text{ mL} \cdot \text{min}^{-1}$).

2 Results and Discussion

2.1 Characterization of the Intercalation Compounds

The intercalation compounds were directly synthesized by the reconstruction method in the molar ratio of organic acid: calcined HTlc=1:9, in 80 % alcoholic aqueous solution pH with 5~6, at 70°C for 5 h. The X-ray diffraction patterns for the intercalated samples were displayed in Fig.1 and the interlayer space of each sample and percentage of each anion intercalated in the HTlc were listed in Table 1. Fig.1 showed that these products also presented the hydrocalcite-like structure. However, the (003) diffraction peaks of Zn,Al-1,4-benzenedicarboxylate and Zn,Al-1,2-benzenedicarboxylate shifted to lower 2θ angle compared to that of the Zn,Al-HTlc precursor in the carbonate and the large interlayer distances in Table 1

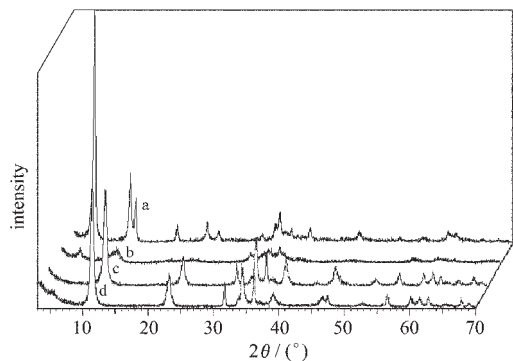


Fig.1 XRD patterns of Zn,Al-1,4- $\text{C}_8\text{H}_4\text{O}_4$ (a), Zn,Al-1,2- $\text{C}_8\text{H}_4\text{O}_4$ (b), Zn,Al-1,3- $\text{C}_8\text{H}_4\text{O}_4$ (c), and Zn,Al- $\text{C}_7\text{H}_5\text{O}_2$ (d)

Table 1 Interlayer Distance of Each sample and Percentage of Each Anion Intercalated in HTlc

HTlc	$2\theta / (^\circ)$	interlayer distance / nm	percentage / %
Zn,Al-1,4- $\text{C}_8\text{H}_4\text{O}_4$	6.16	1.433	96.4
Zn,Al-1,2- $\text{C}_8\text{H}_4\text{O}_4$	5.81	1.521	60.8
Zn,Al-1,3- $\text{C}_8\text{H}_4\text{O}_4$	11.64	0.760	12.1
Zn,Al- $\text{C}_7\text{H}_5\text{O}_2$	11.47	0.771	5.2

strongly indicated the intercalation of isomeric dicarboxylate anions into the HTlc^[9]. We believe that the percentage of benzenecarboxylate (5.2%) and 1,3-benzenedicarboxylate (12.1%) reacting with the HTlc were rather low so that the only phase observed in the XRD pattern was unreacted starting material containing carbonate ion in the interlayer region ($d_{003}=0.78 \text{ nm}$)^[9]. However, after intercalation of 1,2-(60.8%) and 1,4-benzenedicarboxylate ions (96.4 %), the measured interlayer spacings were 1.521 nm and 1.433 nm respectively for the new phases. The effective intercalation of anions could be confirmed by infrared spectroscopy in Fig.2. The characteristic bands of the carboxylate function, i.e. the asymmetric stretching vibration in the $1510 \sim 1575 \text{ cm}^{-1}$ and the symmetric stretching vibration in the $1391 \sim 1415 \text{ cm}^{-1}$, were clearly observed. At the same time, the phenyl group vibration at $700 \sim 880 \text{ cm}^{-1}$ was also seen. A broad absorption peak in the region $3600 \sim 3000 \text{ cm}^{-1}$ was assigned to O-H group stretches of both the hydroxide basal layer and interlayer water. However, in the IR spectrum of 1,3-benzenedicarboxylate or benzenecar-

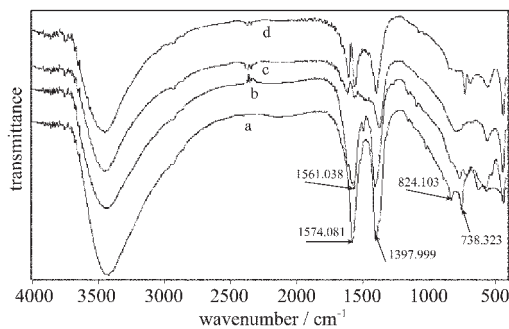


Fig.2 IR spectra of Zn,Al-1,4- $\text{C}_8\text{H}_4\text{O}_4$ (a), Zn,Al-1,2- $\text{C}_8\text{H}_4\text{O}_4$ (b), Zn,Al-1,3- $\text{C}_8\text{H}_4\text{O}_4$ (c), and Zn,Al- $\text{C}_7\text{H}_5\text{O}_2$ (d)

Table 2 Interlayer Space of Each Sample and Percentage of Mixed Organic Anions Intercalated in HTlc

product	$2\theta / (^{\circ})$	interlayer distance / nm	percentage of acid / %
Zn,Al-1,4-/1,2-C ₈ H ₄ O ₄	6.19	1.427	92.0, 42.1
Zn,Al-1,4-/1,3-C ₈ H ₄ O ₄	6.12	1.442	60.2, 26.0
Zn,Al-1,4-C ₈ H ₄ O ₄ /C ₇ H ₅ O ₂	6.11	1.446	97.8, 22.1
Zn,Al-1,2-/1,3-C ₈ H ₄ O ₄	11.61	0.761	54.7, 37.3
Zn,Al-1,2-C ₈ H ₄ O ₄ /C ₇ H ₅ O ₂	11.41	0.775	62.2, 3.0
Zn,Al-1,3-C ₈ H ₄ O ₄ /C ₇ H ₅ O ₂	11.65	0.759	18.0, 4.1

boxylate, the characteristic absorption peaks for -COO⁻ were also observed, it indicated that a small amount of 1,3-benzenedicarboxylate or benzenecarboxylate ions were most likely on the external surface of the HTlc crystallites. From the results of percentage of each anion intercalated in HTlc in Table 1, it can be seen that selective reaction was observed during calcined Zn,Al-HTlc reacting with 1,2-,1,3-,1,4-benzenedicarboxylate or benzenecarboxylate acids.

2.2 Competitive Intercalation Studies

When calcined HTlc was stirred with equimolar mixed pairs of organic acids in 80% alcoholic aqueous solution, the X-ray powder diffraction patterns in Fig.3 were very similar to those in Fig.1. The interlayer space of each sample and the percentage of each organic anion intercalated in the Zn, Al-HTlc were listed in Table 2. It could be seen that the ions were preferentially intercalated in the order 1,4-benzenedicarboxylate > 1,2-benzenedicarboxylate > 1,3-benzenedicarboxylate > benzenecarboxylate, so the measured interlayer spacings in Fig.3 (a), (b), and (c) were about 1.44 nm of 1,4-benzenedicarboxylate intercalated phase. The results are consistent with those in the literature where it was found that ion-exchange reaction of HTlcs Ca₂Al(OH)₆NO₃·2H₂O^[8] and LiAl₂(OH)₆Cl·H₂O^[7] in the aqueous mixture of benzenedicarboxylate anions afforded selective intercalation of the 1,4-isomer on the thermodynamically favoured product. However, the results differ from those of Mg,Al-HTlc reported by us before, which stated 1,2-benzenedicarboxylate was the most preferred guest of the four different anions^[16]. It seems that the nature of the HTlcs can affect the intercalation preferences. The further work is being investigated now.

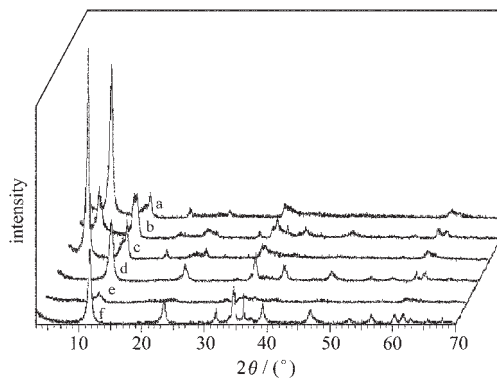


Fig.3 XRD patterns of Zn,Al-1,4-/1,2-C₈H₄O₄ (a), Zn,Al-1,4-/1,3-C₈H₄O₄ (b), Zn,Al-1,4-C₈H₄O₄/C₇H₅O₂ (c), Zn,Al-1,2-/1,3-C₈H₄O₄ (d), Zn,Al-1,2-C₈H₄O₄/C₇H₅O₂ (e), and Zn,Al-1,3-C₈H₄O₄/C₇H₅O₂ (f)

We recently reported^[17] that the strength of the hydrogen bonding interaction in the layered structures of HTlcs is connected with the charge density of oxygen atoms in the guest. In order to explain the observed selectivities, we have performed quantum chemical calculations on the guest ions using an *ab initio* (HF/6-31G) method by G98w. A summary of the results of these calculations was given in Table 3. According to the measured interlayer spacing and calculated results of the guest ions, the orientation of 1,2-,1,3-,1,4-benzenedicarboxylate or benzenecarboxylate anions between the layers was showed in Fig.4.

From Table 1, the measured interlayer spacing of

Table 3 Calculated Charges for the Anions

anions	calculated charges	
	O1	O2
C ₇ H ₅ O ₂	-0.764	-0.764
1,2-C ₈ H ₄ O ₄	-0.564	-0.856
1,3-C ₈ H ₄ O ₄	-0.770	-0.803
1,4-C ₈ H ₄ O ₄	-0.788	-0.788

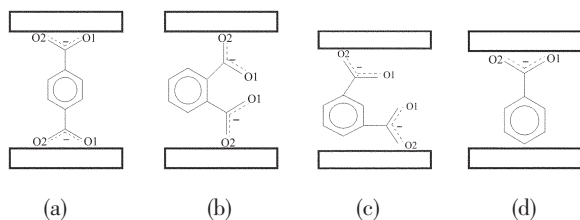


Fig.4 Schematic illustration of the proposed orientation of organic anions between the layers for Zn,Al-1,4- $\text{C}_8\text{H}_4\text{O}_4$ (a), Zn,Al-1,2- $\text{C}_8\text{H}_4\text{O}_4$ (b), Zn,Al-1,3- $\text{C}_8\text{H}_4\text{O}_4$ (c), and Zn, Al- $\text{C}_7\text{H}_5\text{O}_2$ (d)

Zn,Al-1,4-benzenedicarboxylate was 1.43 nm. As the thickness of the HTlc hydroxide basal layer was 0.47 nm, the gallery height was calculated as 0.96 nm. According to the calculated size and charges of 1,4-benzenedicarboxylate, the proposed orientation was that the plane of 1,4-benzenedicarboxylate ion was perpendicular to the plane of the host layer. We believe it is reasonable the more linear, rod-like dicarboxylates are able to interact strongly with both cationic metal hydroxide layers, since all the negatively charged oxygen atoms in this isomer are in close contact with the positively charged layers and form four hydrogen bonds with the positively charged layers. Therefore, 1,4-benzenedicarboxylate is the most highly favoured. 1,2-benzenedicarboxylate is the next most preferred guest of the four different anions. The reason is that although its oxygen atoms have the greater negative charge and can form the stronger hydrogen bonds with the positively charged layers, there is only two hydrogen bonds to be formed. So the measured interlayer spacing of Zn,Al-1,2-benzenedicarboxylate (1.521 nm) is bigger than that of Zn, Al-1,4-benzenedicarboxylate (1.43 nm). Based on the basal spacing of Zn,Al-1,2-benzenedicarboxylate of 1.521 nm in Table 1, we think that the plane of 1,2-benzenedicarboxylate ion is also perpendicular to the plane of the host layer, unlike the description of two 1,2-benzenedicarboxylate anions lying parallel to the layers in the literature^[8]. 1,3-benzenedicarboxylate and benzenecarboxylate anions are much more difficult to intercalate in Zn,Al-HTlc because of the lower symmetry and the block of the space structure for 1,3-benzenedicarboxylate ion

and the lower anionic charges for benzenecarboxylate ion.

3 Conclusions

We succeeded in establishing a preferential intercalation of 1,2-,1,3-,1,4-benzenedicarboxylate or benzenecarboxylate ions into Zn, Al-HTlc indicating the existence of a molecular recognition ability of the layered double hydroxide. This material exhibits the preferential intercalativity for 1,4-benzenedicarboxylate from mixed pairs of organic acids. The preferential intercalation suggests that this host material could be exploited as a method for the chemical separation of these anions from solution.

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