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# Preparation and characterization of Mg–Al/Zn–Al layered double hydroxides intercalated with (+)-2,3-di(*p*-toluyl)-tartaric acid

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ABSTRACT

The intercalations of (+)-2,3-di(*p*-toluyl)-tartaric acid (DTTA) into three kinds of layered double hydroxides, such as Mg–Al–$CO_3$–LDH, Zn–Al–$CO_3$–LDH and Zn–Al–$NO_3$–LDH, have been prepared by ion-exchange. The solids have been characterized by X-ray powder diffraction, FT-IR spectroscopy, DSC/TG analyses and Elemental chemical analyses. The results show that the original interlayer inorganic ions can be replaced by the organic anions under the controlled conditions. After the intercalation of DTTA, the gallery heights range between 1.32 and 1.60 nm. FT-IR and DSC/TG curves reveal the presence of a complex system of supramolecular host–guest interaction and the increase of thermal stability of materials. The molecules of DTTA may stay in the layers in a bilayer with the carboxylate groups pointing towards the LDHs layers, the two planes associated with aromatic ring are parallel to each other and the orbits of bonds overlap partly, forming two big off-region Π bonds.



## 1. Introduction

Clay minerals are focused on the synthesis of new organic–inorganic hybrid materials in recent years. A kind of clay minerals, layered double hydroxides (LDHs) are widely known as hydrotalcite-like compound and often called anionic clay comparing with the more conventional cationic clay. The chemical composition of LDHs is represented by general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n}\cdot yH_2O]$, where $M^{2+}$ is a divalent cation such as $Mg^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$ and $Cu^{2+}$, $M^{3+}$ is a trivalent cation such as $Al^{3+}$, $Cr^{3+}$, $Co^{3+}$ and $Fe^{3+}$. $A^{n-}$ is an ion exchangeable anion such as $OH^-$, $Cl^-$, $NO_3^-$, $CO_3^{2-}$, $SO_4^{2-}$ and various organicanions. The $x$ value is equal to the ratio $M^{3+}/(M^{2+}M^{3+})$, generally ranging between 0.20 and 0.33. This value is attributed to the charge density of the hydroxide basal layer, namely, anion exchange capacity (AEC) [1]. LDHs basal layer possesses a positive charge due to the trivalent cation substituted for the divalent cation, and the interlayer space is neutralized by the intercalation of anions with water molecules. As a result, LDHs are now well established as excellent anion-exchange materials and their extensive intercalation chemistry has widespread applications in areas such as heterogeneous catalysis [2,3], optical materials [4,5], biomimetic catalysis [6,7], and separation science [8,9]. It is especially so, if the pillars are chiral, as these quasi two-dimensional channel systems are not only well defined structures with huge pore openings, but the optically active pillars create a chiral environment. Materials like these may easily find use in the chiral field [1,10–12].

Tartrate is an important ligand for asymmetric catalytic centers [13]. Tartrate intercalated LDHs are supposed to show potential and promising applications in the field of heterogeneous asymmetric catalysis. Some research efforts have been denoted to tartrate intercalated LDHs [14–18]. (+)-2,3-di(*p*-toluyl)-tartaric acid (DTTA), a derivative of D-tartaric acid, has been known as a acidic resolving agent. The intercalation of DTTA in the confined interlayer region of LDHs should give rise to a new type of stationary phase for liquid chromatography with high chiral selectivity and low degree of leaching [19]. Of course, it also could use as the heterogeneous asymmetric catalyst or the chiral sorbent. Our group has recently reported the intercalation behavior of (+)-dibenzoyl-D-tartaric acid (DBTA) into two kinds of MgAl–$CO_3$–LDH and MgAl–$NO_3$–LDH systems by the anion-exchange method [20].

In the present study, the intercalation behavior of DTTA into three kinds of LDHs (MgAl–$CO_3$–LDH, ZnAl–$CO_3$–LDH and ZnAl–$NO_3$–LDH) host by the ion-exchange method with a solution of DTTA, in ethanol. The intercalated materials were characterized by different physico-chemistry techniques.

## 2. Experimental

All reactants were of chemical reagent grade and used without further purification.

### 2.1. Precursors preparation

The Reichle method [21] was applied to synthesize precursor MgAl–$CO_3$–LDH and ZnAl–$CO_3$–LDH. Solution A was prepared by

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dissolving 0.08 mol $Mg(NO_3)_2{\cdot}6H_2O$ and 0.04 mol $A1(NO_3)_3{\cdot}9H_2O$ in distilled water. Solution B was prepared by dissolving 0.24 mol NaOH and 0.08 mol $Na_2CO_3$ in distilled water. The LDH was prepared by dropwise addition of solution A to solution B in 1 h with vigorous stirring, maintaining the pH between 9 and 10. The mixture was submitted to hydrothermal treatment at 100 °C for 6 h. The precursor ZnAl–$CO_3$–LDH was prepared similarly. Solution A was prepared by $Zn(NO_3)_2{\cdot}6H_2O$ and $A1(NO_3)_3{\cdot}9H_2O$, and the mixture was submitted to hydrothermal treatment at 80 °C for 8 h. The precursor ZnAl–$NO_3$–LDH was prepared by coprecipitation [22] in a $N_2$ atmosphere (to avoid incorporation of carbonate from atmospheric carbon dioxide) from aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ and $A1(NO_3)_3{\cdot}9H_2O$ at pH 10. The suspension was aged for 6 h at 80 °C and simultaneous stirring.

In all cases the $M^{2+}/M^{3+}$ molar ratio in the starting solution was 2.0. The precursors were centrifuged and washed several times with warm deionized water until neutral pH was reached and finally dried at 80 °C for 24 h.

### 2.2. Intercalation of DTTA into LDHs by ion-exchange method

The ethanol solution comprising a certain amount of DTTA was added to the solutions suspending a portion of LDHs in ethanol, respectively. The mixtures were magnetically stirred for 24 h at 80 °C (Mg–Al system at 140 °C). ZnAl–$NO_3$ system was under nitrogen atmosphere to avoid a contamination by atmospheric $CO_2$. The pH of mixtures was regulated to 5–6 by dropwise addition of 0.1 mol/L NaOH solution. The resulting precipitates were collected by centrifugal after aging for 12 h and washed several times with ethanol and decarbonated water until neutral pH was reached and dried at 80 °C for 24 h.

### 2.3. Characterization

Powder XRD measurements were performed on a Rigaku Rint 6000 powder X-ray diffractometer, using Cu/Kα radiation at 30 mA, 40 kV. FT-IR spectra were obtained using a NICOLET AVATAR 360 FT-IR spectrophotometer by the standard KBr disk method. DSC/TG were recorded on a NETZSCH STA 449C instruments, under a flux of 130 $cm^3$/min of synthetic air, with a heating rate of 10 °C/min, from room temperature to 800 °C. Elemental chemical analyses for Mg, Zn and Al were carried out in a model IRIS Advantage 1000 ICP-AES spectrophotometer after dissolving the sample in nitric acid. C, H, O and N were detected in an Elemental Analyzer from Germany in a model Elementar vario $EL^{III}$.

## 3. Results and discussion

### 3.1. X-ray powder diffraction

The XRD patterns of samples are similar for all series of samples. The observed basal spacing of MgAl–$CO_3$–LDH, ZnAl–$CO_3$–LDH and ZnAl–$NO_3$–LDH ((003) in Fig. 1a, c and e) are 0.76, 0.76 and 0.90 nm, respectively, and composed of a LDH host layer approximately 0.48 nm thick [25], with an interlayer spacing of 0.28, 0.28 and 0.42 nm. As a result of intercalation, the reflections diffraction peaks have been noticed at a lower angles with an increase in the basal spacing; the interlayer distance of (003) peak increases from 0.76 nm in the case of MgAl–$CO_3$–LDH (Fig. 1a) to 2.08 nm for DTTA–MgAl–$CO_3$–LDH (Fig. 1b). The other series have changed similarly. The basal spacing of ZnAl–$CO_3$–LDH and ZnAl–$NO_3$–LDH are increased to 1.80 nm, 2.07 nm. This is most likely caused by the intercalation of DTTA, which is larger than $CO_3^{2-}$ or $NO_3^-$, into the interlayer space of LDHs. Notablely, the ZnAl–LDHs have some obvious peaks between 30° and 50° which are assigned to metallic oxide out of layer. These peaks indicate that the ZnAl–LDHs are impure. The intensity of (003) peaks of DTTA–ZnAl–LDHs are impacted by the impurity, especially for the ZnAl–$CO_3$–LDH, of which the (003) peak is weaker than other pillared-LDHs.

The XRD peaks observed for MgAl–$CO_3$–LDH are ascribed to hydrotalcite (JCPDS card 22-700) [23], a hydroxy carbonate of Mg and Al, which occurs naturally and has the structure of a layered double hydroxide. The XRD peaks of LDH are generally indexed on the basis of a hexagonal unit cell, the basal spacing of which is equivalent to 1/*n*th of the *c* parameter, where *n* is the number of the repeat layers in the unit cell [24]. The basal spacing is composed of Al-bearing, brucite-like octahedral layers with interlayer spacing, which is affected by the size and orientation of the intercalated anion. Fig. 1 shows the XRD patterns for all the samples.

The lattice parameter of samples, calculated from the positions of maxima due to reflection by planes (003) for parameter *c*, and (110) for parameter *a*, are included in Table 1. The values of parameter *a* are almost identical for all series of samples as the different cations exist in the layers in almost the same molar ratio; the *a* values (Table 1) are in the range generally reported for LDHs with $M^{2+}$

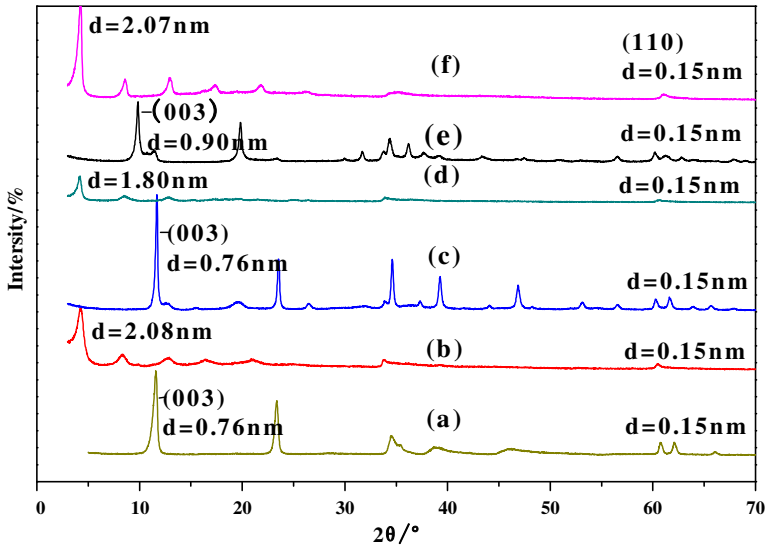


**Fig. 1.** XRD patterns for (a) MgAl–$CO_3$–LDH, (b) DTTA–MgAl–$CO_3$–LDH, (c) ZnAl–$CO_3$–LDH, (d) DTTA–ZnAl–$CO_3$–LDH, (e) ZnAl–$NO_3$–LDH, (f) DTTA–ZnAl–$NO_3$–LDH.