

Step-wise Anion-Exchange in Layered Double Hydroxide Using Solvothermal Treatment

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Synthetic layered double hydroxides (LDHs), $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]\text{CO}_3 \cdot n\text{H}_2\text{O}$, were prepared in the submicron size of plate-like polycrystals. Anion-exchange reactions with various linear dicarboxylic acids were performed to produce LDH/organic hybrid materials by solvothermal treatment in toluene. X-ray powder diffraction spectra for the products indicated that the interlayer spacings of LDHs remarkably changed, up to 20 Å when 1,10-decanedicarboxylic acid anions were intercalated as an organic guest. Dicarboxylates-LDHs samples could be also re-exchanged consecutively with other dicarboxylic acids or carbonate without serious destruction of layer structure under the scanning electron microscopic observation.

Key Words : Layered double hydroxides, Solvothermal, Anion exchange, Dicarboxylic acids

Introduction

The synthetic layered double hydroxides, also called as hydroxide-like compounds, have chemical composition expressed by the general formula $[\text{M}^{2+}_{(1-x)}\text{M}^{3+}_x(\text{OH})_2]\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal ions capable of occupying the octahedral holes of a brucite-like layer and A^{n-} is virtually any hydrated exchangeable anion positioned in the gallery between the layers.¹⁻³ The structure of layered double hydroxides consists of positively charged layers separated by the anions and water molecules.³ The LDHs are now widely studied materials due to their potential application in various researches and industrial purposes such as catalysts, catalysts precursors, anion exchanger, medicines, and nanometer-sized composite materials.^{1,3-6}

The extensive application of LDHs is expected by the reason of the anion exchange capacity toward inorganic and organic anions.⁷ Especially, layered organic/inorganic hybrid materials could be easily obtained by an ion-exchange reaction of interlayer ions with organic guest anions. In this study, two different dicarboxylic acids, 1,10-decanedicarboxylic acid and glutaric acid, were exchanged by stepwise reactions in toluene as a non-aqueous solvent. The former is vertically arranged, and the latter is horizontally oriented within the host layers. The stepwise anion exchange reactions of these two diacids are also investigated with respect to the intercalation properties such as lattice expansion and morphological change. The preparation of these hybrid materials is one of effective ways to exchange some large polyoxometalates.^{8,9}

Investigations of the ion exchange reactions of LDHs have been mostly obtained in aqueous solutions due to utilization of water-soluble ionic compounds^{7,10-12} and accomplished under inert gas atmosphere owing to the competitive incorporation of carbonate from carbon dioxide.³ However the anion-exchange reactions in aqueous solutions are not

able to prevent the equilibrium of dissolution-recrystallization reaction resulting from the hydrolysis of host layers of LDHs.¹³ When the non-aqueous solvents were used in anion exchange of LDHs, reconstruction of LDH crystals could be restrained and the morphology of LDH particles could be preserved during the anion-exchange reactions.¹⁴ We believe that the hydrolysis reactions could be effectively excluded when aprotic organic solvents were used in anion exchange reaction.

The exchange reactions demonstrated in this report generate the impression that layered double hydroxides react easily with linear dicarboxylates by solvothermal treatment in organic solvent. Our approach has overcome the drawback of dissolution and recrystallization of LDHs in aqueous solution, and we could observe the morphological change of the LDH crystals before and after the anion-exchange reaction by SEM and XRPD technique.

Experimental Section

Synthesis of carbonate-LDH crystals. The pristine LDH, $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]\text{CO}_3 \cdot n\text{H}_2\text{O}$, denoted as carbonate-LDH, was prepared by the coprecipitation method.^{1,2} To an aqueous solution containing 0.02 M $\text{Mg}(\text{NO}_3)_2$ and 0.01 M $\text{Al}(\text{NO}_3)_3$ a mixed solution of 2.0 M NaOH and 0.2 M Na_2CO_3 was slowly added with vigorous stirring. During the titration the pH of solution was adjusted to 10.0 ± 0.1 at room temperature. The resulting precipitate was collected by centrifugation and washed with deionized water three times. Hydrothermal treatment was carried out in deionized water at 180 °C to obtain larger crystal size and improved crystallinity of carbonate-LDH crystals, followed by drying at 120 °C in a convection oven.¹⁵

Anion exchange of aliphatic α,ω -dicarboxylic acid. 100 mg of the carbonate-LDH and 400 mg of aliphatic dicarboxylic acids were dispersed in a Teflon-coated autoclave vessel containing 18 mL of toluene, and allowed to react for

2 days at 140 °C. The residual acids were washed out six times with 100 mL ethanol and the samples were dried at 70 °C in air. The consecutive exchange reactions using glutaric acids were performed in the similar conditions. The room temperature treatment of aqueous solution of 0.1 M Na₂CO₃ produced carbonate-LDH, washed with 100 mL deionized water six times and dried at 70 °C in air.

Characterization. X-ray powder diffraction (XRPD) patterns were measured with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, on $\theta\sim 2\theta$ scanning mode. The measurements were performed under the conditions of 40 kV, 30 mA, and Cu-K α ($\lambda = 1.5405 \text{ \AA}$). Infrared (IR) spectra were obtained in 4000-400 cm⁻¹ range using a Nicolet 1700 FT-IR spectrometer. The samples were ground with dry KBr and pressed into a transparent disk. Thermogravimetric analyses (TGA) were conducted on a TA instruments SDT 2960 in a nitrogen atmosphere using a heating rate of 10 °C/min from room temperature to 1000 °C.

Results and Discussion

Size effect of dicarboxylates. Figure 1 shows the XRPD spectra and basal spacings for the LDH samples exchanged with the various α,ω -dicarboxylic acids, indicating the layer expansions depend upon the chain lengths of each dicarboxylate for the general formula (CH₂)_n(COO⁻)₂. For the selected α,ω -dicarboxylates from $n = 5$ (pimelic acid) to $n = 10$ (1,10-decanedicarboxylic acid), the basal spacings suggest that the dicarboxylates were vertically arranged or slightly tilted within the host layers and the carbonate-LDH peaks disappeared. For $n = 3$, glutarate-LDH sample, denoted as GL-MgAl-LDH, gave a basal spacing close to 9 Å, which implies a horizontal arrangement in the interlayer space.¹⁶ For $n = 6$, one of the minor peaks having basal spacing of 15 Å indicates the nearly vertical arrangement of interlayer anions.¹⁷

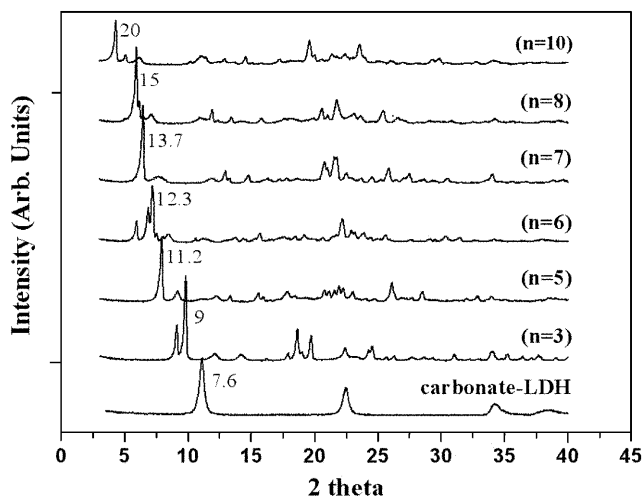


Figure 1. XRPD spectra and basal spacings (Å) for the various dicarboxylate-LDH products obtained by solvothermal anion exchange in toluene. The $n = 3$ (intercalate with glutarate) ~ $n = 10$ (intercalate with 1,10-decanedicarboxylate) are number of carbon of aliphatic chain in α,ω -dicarboxylates (CH₂)_n(COO⁻)₂.

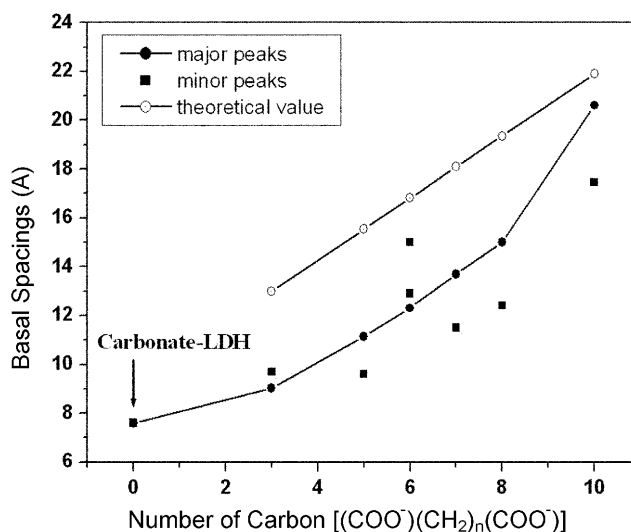


Figure 2. Plot for interlayer separation of the various dicarboxylate-LDH products against the number of carbon atoms, n , in the chain of (CH₂)_n(COO⁻)₂. The black circles (●) and the squares (■) are observed values, and the hollow circles (○) are theoretical ones. The black circles (●) indicate the major peaks for the XRPD spectra in Figure 1.

1,10-Decanedicarboxylate-LDH ($n = 10$), denoted as DC-MgAl-LDH, presents the basal spacing of 20 Å, which indicates the vertical arrangement of interlayer anions.¹⁶ Assuming the thickness of brucite layer including the hydrogen bonding is approximately 6.8 Å,³ the gallery height is 13.2 Å in DC-MgAl-LDH. Given that the size of 1,10-decanedicarboxylate anion is approximately 13.3 Å,¹⁸ such value is generally associated with the vertical arrangement of interlayer anion within the interlayer space. The dicarboxylates-LDH samples present the mixed phases which may be ascribed to low dispersion of LDH crystals and low solubility of dicarboxylic acids in toluene. In the previous study for the dicarboxylates-MgAl-LDH on Si substrate, all dicarboxylates¹⁷ were exchanged with vertical arrangements in the interlayer space, since the LDH crystals on Si could have kept in easier contact than the powder samples with dicarboxylic acid during the exchange reaction, as well as a high solubility of dicarboxylic acids in alcohol/toluene mixture.

Figure 2 presents a plot for the interlayer separation (Å) against the carbon number (n) in (CH₂)_n(COO⁻)₂. The basal spacing values (d) in major peaks of each XRPD spectra linearly increase with the chain length, n . Compared with the theoretical d -values, assuming the mean increase $\Delta d = 1.27 \text{ \AA}/\text{CH}_2$ from glutarate to 1,10-decanedicarboxylate, the basal spacings for all samples have the lower basal spacings than those of the corresponding to theoretical d -values.^{7,19-21}

Figure 3 shows time dependency upon the exchange reaction of DC-MgAl-LDH by solvothermal treatment at 140 °C. In Figure 3b, the 1,10-decanedicarboxylates were slightly exchanged into the interlayer spaces, and the carbonate-LDH was remained. For the Figure 3c, the 1,10-decanedicarboxylates were exchanged into the interlayer

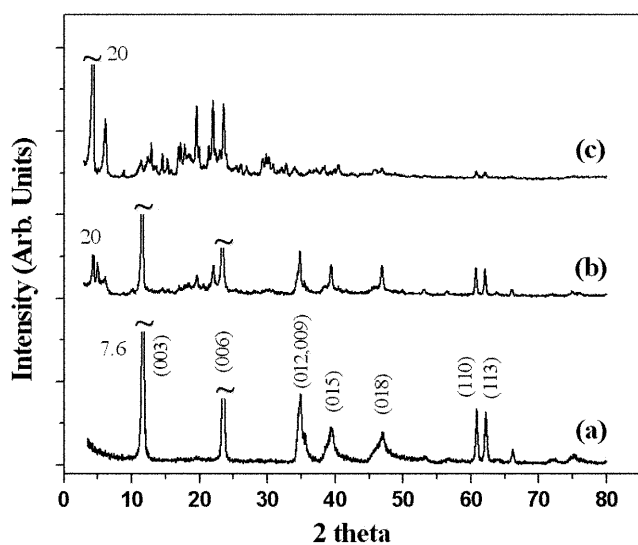


Figure 3. XRPD spectra and basal spacings (Å) for (a) carbonate-LDH, (b) DC-MgAl-LDH obtained at 140 °C for 12 hrs, and (c) DC-MgAl-LDH obtained at 140 °C for 2 days.

galleries of LDH, and also the carbonate-LDH peaks almost disappeared, but the (110) reflection show a low intensity. The intensities of (110) reflection ($d = 1.52$ Å) with regards to hexagonal axes³ decreased with increasing time of anion exchange, which is used for the calculation of the parameter a ($= 2d_{(110)}$) in natural and synthetic hydrotalcite-like compounds. The basal (00 l) reflections correspond to the successive orders of the layer stacking since these reflections depend on the layer stacking. The (110) reflection is independent of the kind of layer stacking, and then the value of parameter a depends on the ionic radii of metal cations in LDHs.^{3,22,23}

Step-wise anion exchange. Carbonate-LDH crystals exhibit plate-like particle morphologies together with the diameter ranging from 100 nm to 500 nm and the thickness of about 100 nm determining by scanning electron microscope (SEM) as shown in Figure 4a. The SEM image in Figure 4b shows the slightly changed layer expansions of LDH crystals prepared by anion exchange reaction with 1,10-decanedicarboxylate ions in toluene, and that the layer structure of LDH was constantly maintained after the reactions, but the residual acids were not clearly removed from the surface of LDH crystals. In the solvothermal

reaction the toluene prevents dissolution of LDH and preserves the layer crystal structure of LDH during the anion exchange reactions.

The XRPD spectra in Figure 5b indicate that the 1,10-decanedicarboxylate ions were intercalated as a guest molecule into the interlayer spaces of LDH. The XRPD spectra show that the DC-MgAl-LDH involves two basal spacings of 20 Å and 14 Å, and the carbonate-LDH peaks disappeared. The basal spacing of 20 Å was close to 21 Å where the 1,10-decanedicarboxylate ions were vertically arranged within the layers of LDHs visualized in Figure 4b.¹⁶ The existence of multi phases of DC-MgAl-LDH are ascribed to slow kinetic rates of equilibrium states.

The stepwise solvothermal reactions in toluene were performed using two different dicarboxylic acids. First, 1,10-decanedicarboxylic acid was solvothermally exchanged into the carbonate-LDH in toluene at 140 °C for 2 days. Then, the DC-MgAl-LDH powder samples and glutaric acid were applied under the similar condition for 2 days, resulting in the glutarate-LDH having the basal spacings of 9.7 and 9

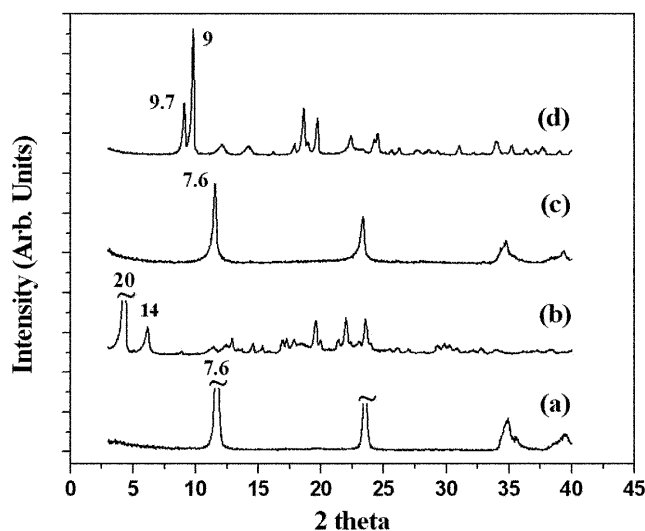


Figure 5. XRPD powder spectra and basal spacings (Å) for the products of stepwise reaction with 1,10-decanedicarboxylate (DC) and glutarate (GL), and for the product of re-exchange reaction; (a) carbonate-LDH, (b) DC-MgAl-LDH, (c) carbonate-LDH prepared by re-exchange reaction in a solution of 0.1 M Na₂CO₃, and (d) GL-MgAl-LDH. The scales of the XRPD spectra of (a) and (b) are multiplied by 10 to be compared with those of (c) and (d).

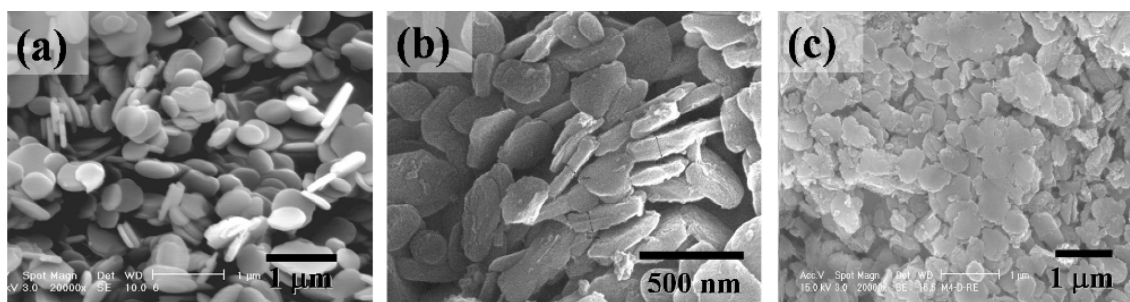


Figure 4. Typical SEM images of (a) carbonate-LDH powder sample, (b) DC-MgAl-LDH sample, and (c) carbonate-LDH sample prepared by re-exchange reaction in an aqueous solution of 0.1 M Na₂CO₃.

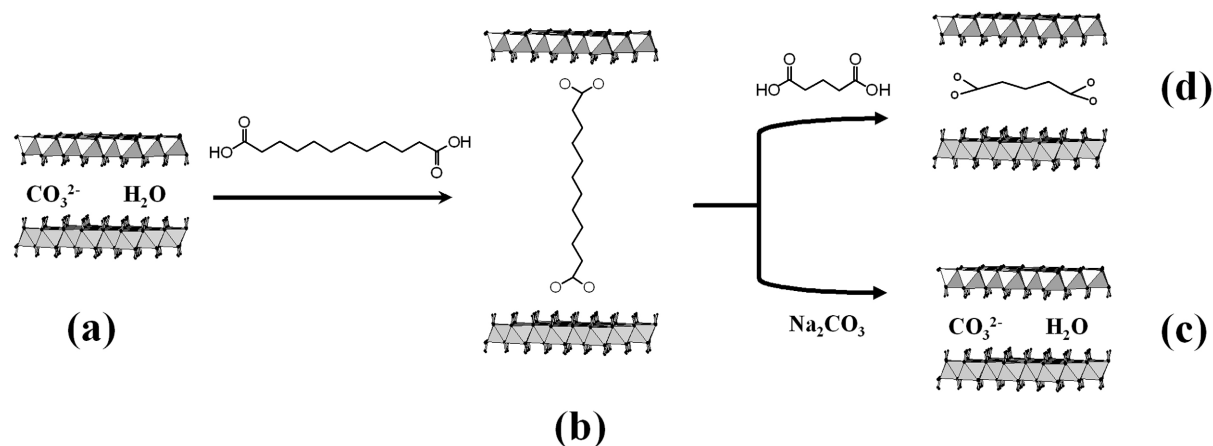


Figure 6. Scheme for the stepwise anion exchange reactions with 1,10-decanedicarboxylate (DC) and glutarate (GL), and for the re-exchange reaction; (a) carbonate-LDH, (b) DC-Mg-Al-LDH, (c) carbonate-LDH prepared by re-exchange reaction in a solution of $0.1 \text{ M Na}_2\text{CO}_3$, and (d) GL-Mg-Al-LDH.

Å as shown in Figure 5d. The horizontal arrangements of glutarates are expected in the interlayer spaces of LDHs, which are in agreement with previously reported XRPD studies for the exchange reactions of LDH on Si substrate demonstrating the intercalation properties of linear dicarboxylates in organic solvent systems.¹⁶ This result may come from the fact that interlamellar arrangement depends strongly on the area available to each interlayer anion.⁷ The interlayer anions such as short-chain linear dicarboxylates and terephthalate in LDH compounds present horizontal arrangement.^{16,24}

The XRPD spectra in Figure 5c indicate that the reconstruction of carbonate form from DC-MgAl-LDH was easily performed in an aqueous solution of $0.1 \text{ M Na}_2\text{CO}_3$ at room temperature, and the reformation of the layered structure of carbonate-LDH was confirmed with the basal spacing of 7.6 Å (Figure 6). However the reformed carbonate-LDH crystals have a low crystallinity after the re-exchange reaction as shown in Figure 4c, which is presumably expected to result from dissolution of LDH crystals in aqueous solution.

FT-IR. All possible vibrational modes for carbonate groups in the infrared and Raman spectra are at 1064 cm^{-1} , 844 cm^{-1} , 1415 cm^{-1} , and 680 cm^{-1} .²⁵ The intercalated carbonate has D_{3h} symmetry and lies flat between two hydroxide layers, and only three bands are expected to be present in the infrared spectra. The FT-IR spectra of carbonate-LDH in Figure 7b showed three carbonate related singlet frequencies at 1361 , 970 and 680 cm^{-1} . The band at $\sim 1640 \text{ cm}^{-1}$ may associate with the deformation of (H-O-H) angle of water molecule, and the band at 780 cm^{-1} is attributed to the deformation of water molecules in the interlayer.²⁶ The very broad band centered around 3500 cm^{-1} is assigned to overlapping stretching modes of hydroxyl groups present, both those in the brucite-type layer (Mg/Al-OH) and the interparticle and interlayer water molecules.¹⁵ The bands below 1000 cm^{-1} are due to M-O vibration modes (Mg-O, Al-O) in the brucite layer,²⁷ the peak at 451 cm^{-1} is assigned to Mg-O, and the peak at 551 cm^{-1} is assigned to

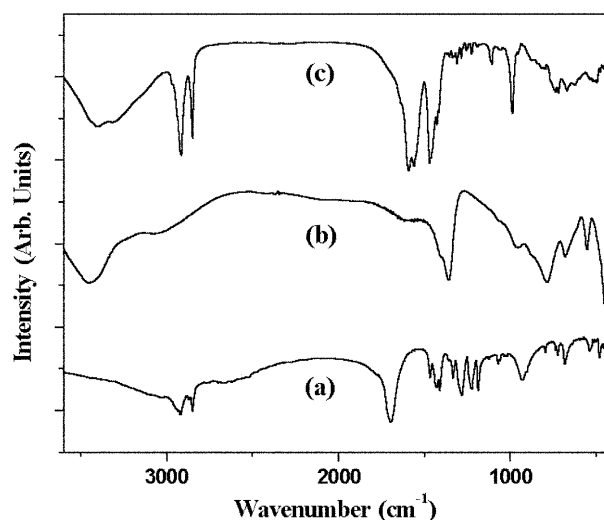


Figure 7. FT-IR spectra for (a) 1,10-decanedicarboxylic acid, (b) carbonate-LDH, and (c) DC-MgAl-LDH.

Al-O vibration.

The FT-IR spectra in Figure 7c showed the expected characteristic peaks of deprotonated carboxylic groups for DC-MgAl-LDH at 2914 and 2580 cm^{-1} (CH_2 stretching mode), at 1592 , 1560 and 1413 cm^{-1} (CO asymmetric and symmetric stretching mode), at 1467 cm^{-1} (CH_2 scissoring mode), and at 991 cm^{-1} (CH_2 rocking mode) comparing with those peaks observed for 1,10-decanedicarboxylic acids. The peak at 1108 cm^{-1} of DC-MgAl-LDH is associated with the presence of carbonate in the interlayer of LDH corresponding to C_{2v} symmetry.²⁸

TGA and DTA. The TGA curves of carbonate-LDH and DC-MgAl-LDH include the thermal dehydration and decomposition processes as shown in Figure 8. For the carbonate-LDH, the weight loss at below 280 °C is attributed to the desorption of water intercalated in the LDH galleries and adsorbed extracrystalline water on LDH sheets.²⁸ The broad shoulder around at 350 °C in TGA curves is attributed

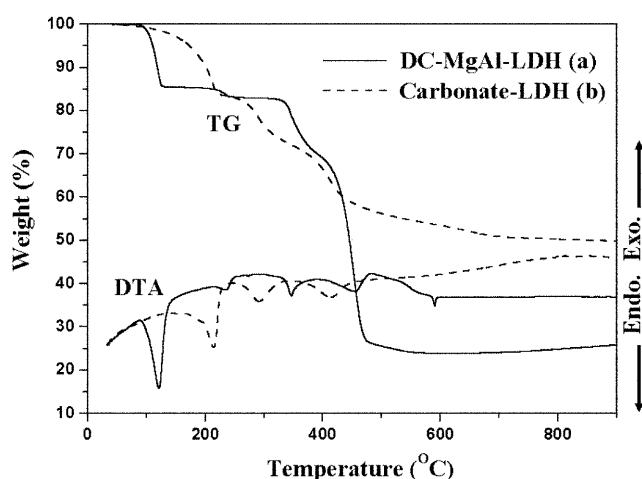


Figure 8. TGA and DTA curves for (a) DC-MgAl-LDH (solid line) and (b) carbonate-LDH (dash line) under nitrogen atmosphere.

to the dehydroxylation of OH bound with Al, and the sharp endothermic peak at 410 °C in DTA to the dehydroxylation of OH bound with Mg, and the weight loss above 450 °C corresponded to the CO₂ evolution of the carbonate-LDH.³⁰

For the DC-MgAl-LDH, the first and second endothermic peaks were observed at 120 and 230 °C assigned to the dehydration of interlayer water. Above 300 °C the DC-MgAl-LDH begins to undergo dehydroxylation of the brucite-like layers³¹⁻³³ and the decomposition of 1,10-decanedicarboxylate in interlayer gallery.³⁴

Conclusion

The results presented here demonstrated that the CO₃²⁻ anions in carbonate-LDH were exchanged with linear dicarboxylates by solvothermal reaction in toluene, which gave the layered organic/inorganic hybrid materials involving interlayer dicarboxylates with vertical, horizontal or tilted arrangements against host LDH layers. The 1,10-decanedicarboxylate has the vertical arrangement with basal spacing of 20 Å, but the glutarate has the horizontal arrangement with basal spacing of 9 Å within the interlayer spaces. The 1,10-decanedicarboxylate and glutarate was successfully intercalated through the consecutive two step solvothermal reactions. Therefore, the non-aqueous solvothermal media are very useful for exchange reactions of organic acids and also play an important role in the preservation of LDH crystallinity in the reaction.

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