Solvent-Mediated and Mechanochemical Methods for Anion Exchange of Carbonate from Layered Double Hydroxides Using Ammonium Salts

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ABSTRACT: Deintercalation of carbonate from layered double hydroxides (LDH) followed by intercalation of another anion (decarbonative intercalation) is a good method for the synthesis of crystalline LDH with different intercalated anions. We have carried out decarbonative intercalation of halides, nitrate, acetate, and sulfate by refluxing the carbonate-LDH with the corresponding ammonium salt in 1-butanol to obtain ordered LDH incorporating the desired anion. The crystallinity of the precursor LDH is retained in the anion-exchanged products, making this reaction a useful tool to prepare ordered LDH containing various anions. In addition, the morphology of the LDH is also retained after the exchange, making the reaction morphotactic. As the reaction is facilitated by the weak acidity of the ammonium salt, just grinding the carbonate-LDH in a mortar and pestle results in the decarbonation of the carbonate-LDH. When using a salt/organic solvent mixture, decarbonative intercalation is effective, even at high salt concentrations. It was proposed that decarbonation is enhanced due to the protonation of carbonate ions in the interlayer space and subsequent ion exchange of bicarbonate ions with a large excess of Cl− ions present in solution. However, here the decarbonated product showed small peaks due to carbonate ions present in the IR spectrum. It was found that decarbonation of CO3−-LDH is highly enhanced by adding NaCl to a dilute HCl solution to obtain chloride-intercalated LDH and that 0.005 N HCl with 13 wt % NaCl was required to obtain a pure chloride-intercalated LDH. It was easier to decarbonate Mg4Al2(OH)12(CO3)·mH2O compared to carbonate-richer Mg6Al2(OH)16(CO3)·mH2O. While the decarbonation of the former could be achieved with a NaCl concentration of ~2 mol L−1, the latter required a NaCl concentration of >4 mol L−1, and it proceeded slower than in the case of the former. When using a salt–acid mixed solution for decarbonation, almost complete substitution of carbonate ions was possible for the Cl− and Br− ions but not with I−, NO3−, and ClO4− ions even at high salt concentrations. Subsequently Iyi’s group used acetate buffer/NaCl mixture to obtain good-quality Cl− LDH. Later, they studied the decarbonation of carbonated LDH using acetate buffer/salt.

INTRODUCTION

Layered double hydroxides (LDH) or hydrotalcite-like compounds (HTLC) can be represented by the general formula [M1−x2+Mx3+(OH)2]y+(A−)z/2−n·mH2O, where M2+ is a divalent metal ion, M3+ is a trivalent metal ion, and A− is the charge-balancing interlayer anion.1 These compounds find applications in varied fields, including sorption, catalysis, electrochemistry, and drug delivery.2−10 Naturally occurring mineral hydrotalclite,11 whose formula is Mg6Al2(OH)16(CO3)4H2O, belongs to this class and has carbonate in its interlayer as the charge-balancing interlayer anion. Carbonate anions are known to be held tenaciously in the interlayer, which restricts its use in the synthesis of LDH with other interlayer anions, and thus, chloride- or nitrate-containing LDH are generally preferred as the starting precursors for the synthesis of other derived LDH through anion exchange.11 However, this results in products with low crystallinity and the products are generally subjected to postsynthesis hydrothermal treatment to obtain better crystallinity. Also, synthesis of LDH with anion other than carbonate requires prevention of contamination due to carbonate from atmospheric carbon dioxide by a suitable method. Intercalation of a suitable anion into a layered solid depends upon its selectivity/affinity for the layered solid. There have been various studies on selective intercalation of organic13−15 or inorganic16 anions in layered solids, but it is well known that the selectivity of carbonate toward LDH is very high, due to which its removal or intercalation of ions other than carbonate in its presence becomes difficult.

Various methods for the deintercalation of carbonate ion to obtain another anion-intercalated LDH with higher crystallinity have been reported. It was observed that when takovite was treated with cold dilute HCl, interlayer carbonate could be deintercalated and chloride anions got intercalated.17 Decarbonative intercalation of chloride could also be achieved by passing a stream of water vapor and gaseous HCl through hydrotalcite sample maintained at 140−160 °C in a glass tube.18 It was found that the decarbonation was better in the presence of a salt with a common anion as that of the dilute acid used.19 It was proposed that decarbonation is enhanced due to the protonation of carbonate ions in the interlayer space and subsequent ion exchange of bicarbonate ions with a large excess of Cl− ions present in solution. However, here the decarbonated product showed small peaks due to carbonate ion in the IR spectrum. It was found that decarbonation of CO3−-LDH is highly enhanced by adding NaCl to a dilute HCl solution to obtain chloride-intercalated LDH and that 0.005 N HCl with 13 wt % NaCl was required to obtain a pure chloride-intercalated LDH.20 It was easier to decarbonate Mg4Al2(OH)12(CO3)·mH2O compared to carbonate-richer Mg6Al2(OH)16(CO3)·mH2O. While the decarbonation of the former could be achieved with a NaCl concentration of ~2 mol L−1, the latter required a NaCl concentration of >4 mol L−1, and it proceeded slower than in the case of the former.21 When using a salt–acid mixed solution for decarbonation, almost complete substitution of carbonate ions was possible for the Cl− and Br− ions but not with I−, NO3−, and ClO4− ions even at high salt concentrations.22

Subsequently Iyi’s group used acetate buffer/NaCl mixture to obtain good-quality Cl− LDH. Later, they studied the decarbonation of carbonated LDH using acetate buffer/salt.
mixture in a closed vessel and under N₂ flow.²³ It was found that N₂ flow gives better decarbonation and requires lower concentration of the salt for complete decarbonation. It has also been shown that acid—alcohol mixed solutions could be used for decarbonation of LDH to form the LDH intercalated with the corresponding conjugate base of the acid used.²⁴

Although there have been quite a few methods for the ion exchange of carbonate-LDH by other ions, many of them are limited to few anions, and in the methods involving acids, the yields would be low due to the dissolution of the LDH. Hence, it is important to find a universal method that could be employed to exchange the interlayer carbonate of LDH with a variety of anions.

In the IR spectrum of MgAl–CO₃ LDH heated to 100 °C, the water—carbonate IR absorption appearing around 3165 cm⁻¹ disappears and the antisymmetric stretching mode ν₂ of carbonate appearing at ~1365 cm⁻¹ splits into two bands at 1357 and 1391 cm⁻¹ and a sharp band around 1538 cm⁻¹ appears, which indicate a change in the carbonate symmetry upon dehydration of the hydrotalcite at 100 °C.²⁵ The loss of water molecules breaks the H-bonding network and weakens the bonding of interlayer carbonate with the layers. Olanrewaju et al. reasoned that the presence of ammonia in solution prevents carbonate from getting intercalated into the interlayer of LDH, as seen by them during their modified synthesis of nitrate-LDH.²⁶ Iyi et al. showed that chloride ion can replace the interlayer carbonate when the LDH is reacted with ammonium chloride or amine salts of HCl in methanol/alcohol mixed solutions could be used for decarbonative anion exchange using ammonium salt of the anion of interest at 120 °C in 1-butanol. Keeping these in mind, we have carried out decarbonative anion exchange using ammonium salt of the anion of interest at 120 °C in 1-butanol. This procedure is shown to be a general method for the synthesis of desired LDH with better crystallinity from carbonate-LDH in a single step. We have also carried out the reaction between carbonate-LDH with better crystallinity from carbonate-LDH in a single step. We have also carried out the reaction between carbonate-LDH with better crystallinity from carbonate-LDH in a single step. We have also carried out the reaction between carbonate-LDH with better crystallinity from carbonate-LDH in a single

### EXPERIMENTAL SECTION

**Synthesis of MgAl LDH, Mg₂Al(OH)₆(CO₃)₀.₅·mH₂O and NiAl LDH, Ni₂Al(OH)₆(CO₃)₀.₅·mH₂O.** The crystalline carbonated LDH, Mg₂Al(OH)₆(CO₃)₀.₅·mH₂O, was prepared by modifying the method reported by Rao et al.²⁶ A 50 mL aqueous solution containing 5.13 g of Mg(NO₃)₂·6H₂O, 3.75 g of Al(NO₃)₃·6H₂O, and 9.12 g of urea was subjected to hydrothermal treatment at 180 °C for 2 h in a Teflon-lined stainless steel autoclave. The product was separated by centrifugation, washed with water, and dried at 65 °C in an air oven to constant weight. Ni₂Al(OH)₆(CO₃)₀.₅·mH₂O LDH was prepared by adding a solution containing 0.03 mol nickel nitrate, Ni(NO₃)₂·6H₂O, and 0.015 mol aluminum nitrate, Al(NO₃)₃·9H₂O, into 50 cm³ of a solution containing 0.11 mol sodium hydroxide and 0.05 mol sodium carbonate. The material obtained was hydrothermally treated at 130 °C for 48 h.²⁷ The product was then washed with deionized water and dried at 65 °C in an air oven to constant weight.

**Mechanochemical Anion Exchange Reactions.** For achieving nitrate exchange in MgAl LDH, a mixture containing 300 mg of Mg₂Al(OH)₆(CO₃)₀.₅·mH₂O LDH, 320 mg of ammonium nitrate (1.87 mmol, 3 times the anion exchange capacity) in a round-bottom flask and the mixture was refluxed for 24 h. The product was separated by centrifugation, washed with acetone, and dried in an air oven at 65 °C to constant weight. Same procedure was followed for the exchange by bromide and acetate ions [180 mg of ammonium bromide (1.84 mmol) and 140 mg of ammonium acetate (1.82 mmol) were used for bromide and acetate exchange, respectively]. For iodide exchange, the procedure was same except for the amount of ammonium salt used [368 mg (2.54 mmol), 6 times the anion exchange capacity]. For chloride and sulfate exchange, in addition to increased amount the ammonium salt (6 times the anion exchange capacity), the duration of refluxing was also doubled. The product after sulfate exchange needed additional washing by decarbonated water after acetone wash. Similar exchange reactions of NiAl LDH were also carried out.

**Anion Exchange Reactions of Carbonate-LDH with Various Anions in 1-Butanol.** For achieving nitrate exchange in hydrotalcite, 300 mg of the Mg₂Al(OH)₆(CO₃)₀.₅·mH₂O LDH was dispersed in 100 cm³ of 1-butanol containing 150 mg of ammonium nitrate (1.87 mmol, 3 times the anion exchange capacity) in a round-bottom flask and the mixture was refluxed for 2 h. The product was separated by centrifugation, washed with acetone, and dried in an air oven at 65 °C to constant weight. Same procedure was followed for the exchange by bromide and acetate ions [180 mg of ammonium bromide (1.84 mmol) and 140 mg of ammonium acetate (1.82 mmol) were used for bromide and acetate exchange, respectively]. For iodide exchange, the procedure was same except for the amount of ammonium salt used [368 mg (2.54 mmol), 6 times the anion exchange capacity]. For chloride and sulfate exchange, in addition to increased amount the ammonium salt (6 times the anion exchange capacity), the duration of refluxing was also doubled. The product after sulfate exchange needed additional washing by decarbonated water after acetone wash. Similar exchange reactions of NiAl LDH were also carried out.

**Figure 1.** Basal spacing region of XRD patterns (A) and carbonate absorption region of IR spectra (B) of the products obtained on the reaction of ammonium chloride with Mg₂Al(OH)₆(CO₃)₀.₅·mH₂O. The crystalline carbonate-LDH was dispersed in 100 cm³ of 1-butanol containing 150 mg of ammonium nitrate (1.87 mmol, 3 times the anion exchange capacity), and a few drops of cyclohexane was ground in a pestle and mortar for 45 min. The product was washed with ethanol followed by water to remove excess ammonium salt.
and dried at 65 °C. Halide and sulfate exchanges were also carried out by the same procedure.

Characterization. The chemical composition of the precursor MgAl LDH was arrived at by wet chemical analysis and thermogravimetry (TGA). Mg and Al contents were determined by atomic absorption spectrometry (AAS) using a Varion AA240 spectrometer, and the water content was estimated by TGA using a PerkinElmer STA 6000 thermal analyzer (30–900 °C, 10 °C/min). Powder X-ray diffraction (XRD) measurements were performed on a PANalytical X’pert Pro X-ray Diffractometer using Cu Kα radiation (λ = 0.154 nm) at 40 kV, at a scanning rate of 1° min⁻¹. The infrared (IR) spectra of samples were collected using a PerkinElmer Spectrum Two FT-IR spectrometer operated in ATR mode, in the range 4000–550 cm⁻¹ with 4 cm⁻¹ resolution. Scanning electron microscopy (SEM) images were recorded using a Zeiss, Ultra 55 SIRION field emission microscope.

Results and Discussion

The chemical composition of the precursor carbonate-intercalated MgAl LDH is as expected from the nominal formula Mg₃Al(OH)₆(CO₃)₀.₅·mH₂O. The mass percentages of Mg, Al, and water in the sample are 20.1 (expected: 20.3), 11.6 (expected: 11.3), and 13.5 leading to the formula Mg₃Al(OH)₆(CO₃)₀.₅·1.₈H₂O. The slight excess of water is possibly due to adsorbed moisture. The net mass loss 44.6% (expected 45.2%) observed in TGA also matches with this formula.

We carried out the reaction between carbonate-intercalated MgAl LDH and ammonium chloride in 1-butanol for 8, 16, and 24 h to optimize the reaction time. Figure 1 compares the XRD patterns and IR spectra of the products obtained in these reactions. The basal reflection increases (Figure 1A) and the carbonate content decreases (Figure 1B) with reaction time. Based on the intensities of the carbonate absorption in IR spectra (Figure 1B), it is estimated that the reaction is ∼90% complete in 8 h. The exchange is ∼97% complete when the reaction was carried out for 24 h. There was no appreciable improvement when the reaction time was further increased. To optimize the amount of ammonium salt, the reaction was carried out for 24 h with the amount of ammonium nitrate varied from 1× to 6×, with × being twice the no of moles of carbonate in LDH. The evolution of XRD pattern with the amount of ammonium salt (Figure 2) suggests that complete exchange is achieved when the amount of ammonium salt is 3×. Thus, all of the reactions were carried out for 24 h with the amount of ammonium salt being 3×.

Success of the decarboxative anion exchange in LDH under the optimized reaction conditions could be corroborated from the changes observed in basal spacing along with the IR spectra of the final products. In Figure 3, the XRD pattern of the starting carbonate-intercalated MgAl LDH is compared to that of the products obtained on decarboxative anion exchange with halides. The starting carbonate-intercalated MgAl LDH with a basal spacing of 7.5 Å is crystalline and its set of reflections in the range 2θ = 30–65° suggests that the LDH is the 3R₁ polytype. The halide-exchanged LDHs show modified basal spacings ~7.7 Å for MgAl-chloride, 7.8 for MgAl-bromide, and 8.2 Å for MgAl-iodide obtained through decarbonation of the starting carbonate-intercalated LDH using the corresponding ammonium salts—confirming the conversion of the carbonated LDH to the desired anion-intercalated LDH. The XRD patterns of all of the halide-exchanged products could also be indexed to 3R₁ polytype, suggesting a topotactic transformation. In the halide-exchanged products, the full width at half-maximum (FWHM) of the 003
 reflections of the products remains the same as that of the precursor carbonate-LDH (Table 1), suggesting that the platelet thickness and ordering along the layer stacking direction are not altered during the anion exchange reaction. The FWHM of 011 and 111 reflections of chloride- and bromide-exchanged samples are also comparable to that of the precursor LDH (Table 1) suggesting that the ordering along the a and b directions are also retained in the anion exchange reaction. In the case of iodide-exchanged product, the pattern could be indexed to a three-layer polytype, but some of the prominent reflections of the 3R₁ polytype are missing. In addition, the reflections due to planes in which h or k ≠ 0 are broadened, indicating lower crystallinity compared to the precursor LDH. This may be attributed to the larger size of the iodide ion. There are also three weak reflections at 11.1, 5.5, and 3.7 Å (marked with a red star in Figure 3d) due to a possible layered impurity, the nature of which is unclear.

In Figure 4, the XRD patterns of the nitrate-, acetate-, and sulfate-exchanged products are compared to that of the precursor carbonate-LDH. The pattern of the nitrate-exchanged product could be indexed to a three-layer polytype, but some of the prominent reflections of the 3R₁ polytype are missing. In addition, the reflections due to planes in which h or k ≠ 0 are broadened, indicating lower crystallinity compared to the precursor LDH. This may be attributed to the larger size of the iodide ion. There are also three weak reflections at 11.1, 5.5, and 3.7 Å (marked with a red star in Figure 3d) due to a possible layered impurity, the nature of which is unclear.

Table 1. Basal Spacing and FWHM of Select Bragg Reflections and Polytypic Form of the Precursor and Anion-Exchanged LDH

| MgAl LDH             | basal spacing (Å) | FWHM (deg) | polytype |
|----------------------|-------------------|------------|----------|
| precursor carbonate-LDH | 7.53              | 0.29, 0.31, 0.41, 0.33 | 3R₁     |
| chloride-LDH          | 7.67              | 0.22, 0.33, 0.47, 0.35 | 3R₁     |
| bromide-LDH           | 7.81              | 0.22, 0.32, 0.39, 0.47 | 3R₁     |
| iodide-LDH            | 8.21              | 0.22, 0.28, 0.32 | 3R₁     |
| nitrate-LDH           | 8.90              | 0.19, 0.22, 0.26, 0.28 | 3R₁     |
| acetate-LDH           | 12.7              | 0.22, 0.21, 0.63, 1.15 | 3R₁     |
| sulfate-LDH           | 8.78              | 0.24 | 3H₁     |
| carbonate-LDH after 2nd cycle | 7.53              | 0.32, 0.31, 0.35, 0.32 | 3R₁     |
| carbonate-LDH after 4th cycle | 7.54              | 0.29, 0.31, 0.35, 0.32 | 3R₁     |

Figure 4. XRD patterns of carbonate-intercalated MgAl LDH (a) and its nitrate- (b), acetate- (c), and sulfate (d)-exchanged products. The expanded pattern in the region 2θ = 30–65° has been overlaid in each case.

Figure 5. IR spectra of carbonate-intercalated MgAl LDH (a) and its bromide- (b), acetate- (c), and sulfate (d)-exchanged products.
ν₂, and symmetric stretching mode ν₁, respectively, for the sulfate anion.³¹

If the anion exchange reaction occurs by a topotactic mechanism, the morphology of the starting carbonate should be preserved. In Figure 6, we compare the SEM images of the anion-exchanged products with that of the precursor carbonate-LDH. The precursor LDH (Figure 6a) presents a near-uniform morphology with the crystallites being hexagonal platelets of near-uniform dimensions. The diameters of the platelets range from 1.5 to 2 μm. In the bromide- (Figure 6b) and nitrate (Figure 6c)-exchanged samples also, the hexagonal platelet morphology is retained, and the average diameter of the platelets is the same as that of the precursor LDH. Thus, the anion exchange reaction here is morphotactic.

To check if the crystallinity of the LDH would be retained if we reexchange the anion with carbonate, we carried out carbonate exchange on the nitrate- and bromide-exchanged LDH by stirring the anion-exchanged LDH in sodium carbonate solution for 24 h. The XRD patterns of the reexchanged products match that of the precursor LDH, and the FWHM values of the Bragg reflections are comparable (Figure 7, Table 1). In fact, even after a few cycles of carbonate-to-bromide-to-carbonate exchanges, the crystallinity is intact (Figure 7d,e). The hexagonal platelet morphology of the platelets is also retained after four cycles of anion exchange (Figure 6d).

Once we ascertained the versatility with respect to the incoming anion, we wanted to check if the method works well for LDH other than MgAl LDH. When the decarboxylative anion exchange was carried out for NiAl−CO₃-LDH, we obtained similar results. In Figure 8, XRD patterns of carbonate-intercalated NiAl LDH and its ion-exchanged products are shown. The basal spacing of 7.6 Å for the starting carbonate NiAl LDH changes to 8.9 Å for nitrate, 7.8 Å for chloride, and 8.7 Å for sulfate-exchanged products, confirming anion exchange. The absence of characteristic absorptions of carbonate in the IR spectra of the anion-exchanged products (data not shown) suggests complete exchange in all of the three cases. This indicates that the method could be used for all LDH.

Although the exchange method does not involve an acid, the exchange is probably facilitated by acids produced when the

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**Figure 6.** SEM images of carbonate-intercalated MgAl LDH (a); its bromide- (b) and nitrate (c)-exchanged products; and MgAl carbonate-LDH obtained by reexchanging of bromide-exchanged LDH (d).

**Figure 7.** XRD patterns of the precursor carbonate-intercalated MgAl LDH (a); MgAl carbonate LDHs obtained by reexchange of nitrate (b) and bromide (c) LDH. XRD patterns of MgAl carbonate LDHs obtained after two (d) and four (e) cycles of carbonate-to-bromide-to-carbonate exchange.

**Figure 8.** XRD patterns of carbonate-intercalated NiAl LDH (a); its nitrate- (b), chloride- (c), and sulfate (d)-exchanged products.
ammonium salt undergoes hydrolysis. The adsorbed and interlayer water released by LDH on heating hydrolyzes the ammonium salt. The mechanism of the exchange reaction may be represented in the following reaction sequence

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{H}_3\text{O}^+ \\
\text{LDH} - \text{CO}_3^{2-} + \text{H}_3\text{O}^+ + \text{A}^- \rightarrow \text{LDH} - \text{A}^- + \text{H}_2\text{O} + \text{CO}_2
\]

The formation of \(\text{NH}_3\) and \(\text{CO}_2\) in the reaction was confirmed by passing the vapor generated during the reaction through Nessler's reagent and lime water, respectively. The ammonium ion hydrolyzes to form \(\text{H}_3\text{O}^+\). The carbonate-intercalated LDH reacts with \(\text{H}_3\text{O}^+\) and \(\text{A}^-\) to give the anion-exchanged product. The fact that there is no anion exchange when the reaction is carried out at room temperature or at 60 °C suggests that there is no solvolysis of the ammonium ion by 1-butanol.

If the mechanism of the reaction is as described above, there is no major role for 1-butanol except providing a medium for reaction at an elevated temperature. Hence, it should be possible to obtain similar results when the reaction is carried out between carbonate-LDH and ammonium salt of the desired anion in the absence of a solvent. Such a reaction could be carried out mechanochemically—simply by grinding the reactants together. Mechanochemical synthesis and anion exchange reactions of LDH are known. However, no attempts have been made so far to use carbonate-intercalated LDH as precursors for mechanochemical anion exchange. XRD patterns of the products obtained on the mechanochemical reaction of MgAl carbonate-LDH with ammonium salts of different anions are shown in Figure 9. Anion exchange occurs in all of the cases as evidenced by the change in basal spacing 7.7, 7.7, 8.3, 8.8, and 8.8 Å for the products obtained on reaction with \(\text{NH}_4\text{Cl}, \text{NH}_4\text{Br}, \text{NH}_4\text{I}, \text{NH}_4\text{NO}_3\), and \((\text{NH}_4)_2\text{SO}_4\) respectively. The IR spectra of the halide-exchanged products (Figure 10) show trace amounts of carbonate unlike in the 1-butanol medium synthesis. The fwhm of the XRD peaks of the products is similar to that of the precursor carbonate-LDH, indicating retention of crystallinity. The SEM images of the products (Figure 11) indicate that the morphology is not retained. Possibly, the LDH crystallites break into smaller ill-defined pieces during the mechanochemical reaction.

CONCLUSIONS

Carbonate could be deintercalated from MgAl/NiAl LDH and quantitatively replaced by a variety of monovalent anions such as chloride, bromide, iodide, nitrate, acetate, and a divalent sulfate anion by treating the carbonate-intercalated LDH with the corresponding ammonium salt in 1-butanol at 120 °C. The method does not use acid, and the products obtained retain the crystallinity and morphology of the precursor LDH in most
cases. The versatility and quantitative exchange for all of the anions makes this method a useful tool in the preparation of crystalline LDH with anions other than carbonate. The same reaction could be carried out in the absence of 1-butanol under mechanochemical condition. The products retain the crystallinity of the precursor, but the morphology is lost. If one is not particular about the morphology of the products, the mechanochemical method is good enough for the exchange of carbonate ion by other anions in LDH. The mechanochemical method is greener (as it involves no solvent), faster, and simpler.

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**Notes**

The authors declare no competing financial interest.

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