Deintercalation of Carbonate Ions from a Hydrotalcite-Like Compound: Enhanced Decarbonation Using Acid−Salt Mixed Solution

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Received March 13, 2004. Revised Manuscript Received May 18, 2004

Because of the high affinity of the carbonate ion (CO_3^{2-}) to the hydrotalcite-like compounds or LDHs (layered double hydroxides), it was difficult to deintercalate carbonate ions and convert them into other LDHs with an easier anion-exchangeability. By treatment with dilute acids such as HCl, the conversion is limited, and, at higher concentrations, changes in shape and weight loss occurred. We found that the addition of NaCl dramatically enhanced the deintercalation of carbonate ions by dilute HCl solution (0.0025−0.005 N). It made the carbonate ions very rapidly deintercalate from the hydrotalcite-like compounds at 25 °C without any weight loss. Scanning electron microscopy (SEM) revealed that no morphological change occurred. Furthermore, by changing the HCl/NaCl ratio, it was possible to regulate the exchange ratio. Protonation of carbonate ions in the interlayer space and successive ion exchange with a large excess of Cl^- ions was assumed to be the mechanism for this enhanced deintercalation.

Introduction

Layered double hydroxides (LDHs) are anionic clays consisting of positively charged metal hydroxide layers with anions such as CO_3^{2-} located in the interlayer space for charge compensation of the cationic layers.[1] LDHs composed of Mg and Al hydoxyl sheets with carbonate ions (CO_3^{2-}) as counteranions are called hydrotalcites, and are commonly synthesized for use as catalysis substrates[2] and acid absorbents.[3] The general formula for MgAl-LDH is $Mg_{1-y}Al_y(OH)_2(X^{n-})_{y/n}\cdot mH_2O$, where $y = 0.1-0.34$, $m = 1-3y/2$, and X^{n-} is an n-valent anion.[4] LDHs are known as some of the few anion-exchangeable compounds, and the affinity of the LDH toward various anions is in the following order:[5]

$$CO_3^{2-} > SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$$

Carbonate ions are exceptionally difficult to anion-exchange because of their high affinity to LDHs. By utilizing this strong affinity toward carbonate, LDHs have been a candidate as a material for capturing carbon dioxide to prevent the emission of carbon dioxides into the ambient atmosphere.[6]

LDHs have been prepared by precipitation from a solution of Al and Mg chlorides by the action of NaOH solution while maintaining the pH of the solution at slightly alkaline.[1,7,8] It is usually followed by aging at high temperature for several hours to several days to obtain well-crystallized LDHs. The desired anions can be incorporated by adding them to the reaction system,[9] though the crystallinity and homogeneity of the obtained LDHs are not good. Recently, LDHs with a homogeneous size have been prepared by the urea method, in which the homogeneous nucleation of LDHs is realized by the hydrolysis of urea at high temperature.[10,11] If these well-crystallized LDHs would be converted into other LDHs with different anions, e.g., functional organic anions, these materials are very interesting from the viewpoint of nanotechnolgy because they serve as nanoscale interlayer space for the incorporated anions. However, the LDHs prepared by the urea method usually contain carbonate anions,[10,11] which cannot be easily converted by ion-exchange or other methods without changing their shapes and structure.

So far, a few trials were made to deintercalate carbonate ions from the interlayer space of hydrotalcite. Bish[12] reported the successful conversion of hydrotalcite and related LDH containing carbonate ion into other

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10.1021/cm049579g CCC: $27.50

types of LDHs using an aqueous solution of HCl or other inorganic acids. However, such an acid-treatment would lead to a weight loss despite the successful conversion as pointed out by Constatino et al.[10] Weight loss indicates degradation of the host LDHs. To prevent such weight loss, Constatino et al. tried an HCl-treatment in the gas phase at the high temperature about 150 °C.[10] This method is not, however, very versatile because of using corrosive high-temperature HCl gas. Heat-treatment and reconstruction is an alternate way. Elimination of carbonate from LDHs was attained by heating the hydrotalcite at a high temperature around 500 °C, and, at this temperature, a structure transformation takes place with the loss of CO_2.[13,14] The thus-formed materials are reconstructed into LDHs by hydration with an aqueous solution containing the desired anion to make the LDHs with the desired anions.[15] Anions also include functional organic compounds in an anionic form. However, heating at high-temperature poses a serious drawback; namely, the reconstruction ability is reduced by repeated heat cycles, which means that degradation of the crystals takes place due to the heat treatment.[16]

The aim of this study is to prepare LDHs with high anion-exchangeability by decarbonation (deintercalation of carbonate ion) of the well-crystallized hydrotalcite without any morphological change. In the present paper, we report that the addition of NaCl dramatically enhanced the decarbonation by aqueous HCl, and that the conversion of hydrotalcite into LDHs with high anion-exchangeability was successfully attained under mild conditions without any weight loss and shape change. The detailed optimal conditions for the deintercalation of carbonate and the plausible mechanism of the enhanced deintercalation using the HCl−NaCl mixed solution will be discussed.

Experimental Section

Materials. The starting hydrotalcite-like compound was a commercially available material (DHT-6, Kyowa Kagaku Kogyo Co., Ltd.). The reagent used was 1 N HCl (reagent grade, Kanto Chemical Co., Ltd.), which was used by diluting to make the desired concentration. The other reagents were NaCl (Merck Co., Ltd.) and Na_2SO_4, $NaNO_3$, H_2SO_4, and HNO_3 (reagent grade, Kanto). Degassed and deionized water was used for diluting the solutions and washing the filtered precipitates.

Deintercalation Process. The typical deintercalation process is as follows. About 20 mg (20.0 ± 0.3 mg) of hydrotalcite (DHT-6) was placed in a glass vessel, to which 10 mL of an aqueous solution adjusted to a given HCl and NaCl concentration was added. After purging with nitrogen gas, the glass vessel was tightly capped, and, after ultrasonification, it was placed in a thermostatic chamber controlled at 25 °C. With constant shaking, the vessel was stored for 1 day. The resulting suspension was filtered through a membrane filter with a pore size of 0.2 μm (Millipore filter) and thoroughly washed several times with degassed deionized water under a nitrogen atmosphere. The remaining precipitates on a filter were collected and immediately dried in a vacuum, thus yielding a white solid.

For the experiment to examine the effect of concentration of HCl and/or NaCl, the weight of the starting DHT-6 and volume of the solution were always kept constant, and the reaction mixture was treated in the same way, unless otherwise stated.

Weight recovery (or weight loss) was measured to monitor the dissolution of the host LDHs. As a control experiment, the weight loss was measured for the DHT-6 after the treatment only by deionized water followed by the same filtration and drying procedures. The experimental data of weight recovery were compensated using this weight loss, i.e., handling loss.

Characterization Techniques. For determination of the carbonate ion content in the resulting materials, a CHN analysis was conducted using a Perkin-Elmer 2400 II CHN element analyzer. The amounts of Mg and Al were analyzed using a Seiko SPS1700HVR ICP-AES instrument for the diluted nitric acid solution after a decomposition treatment by acid. The wavelengths used for the Mg and Al analyses were 285.213 and 396.152 nm, respectively. The Cl^- ion content was analyzed by an ion chromatograph after extracting with hot sodium carbonate solution (Sumika Chemical Analysis Service, Co., Ltd.). The FT-IR transmittance spectra were recorded using a Perkin-Elmer 1600 FT-IR spectrometer at room temperature in the wavenumber range from 4000 to 450 cm^{-1}. The KBr pellet technique was used for the measurement.

Powder X-ray diffraction (XRD) of the products was conducted at a scanning speed of $2\theta = 2°$/min using a RINT 1200 (Rigaku Co., Ltd.) diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The measurement was conducted at 25 °C in the ambient atmosphere. The basal spacing corresponds to the d_{003} for the unit cell, which is the c-value of the subcell containing one interlayer space and one-third of that of the hydrotalcite unit cell. The pH of the solution was measured by using a TOKO TPX-90 pH meter with a glass electrode. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-5000 scanning electron microscope. Simultaneous thermogravimetry differential thermal analysis (TG-DTA) was conducted by a MAC TG-DTA2000 (MAC Science Co., Ltd.) at 10 °C /min under an Ar atmosphere in the range of room temperature to 1000 °C using Al_2O_3 powder as the standard material.

Results and Discussion

Nomenclature. The following nomenclature will be used in the remainder of this paper. MgAl-LDH is used for the LDH composed of Mg and Al cations with anions in the interlayer space being unspecified. MgAl-X-LDH expresses the LDH composed of Mg and Al cations with anions (X) in the interlayer space. The word hydrotalcite is used to express MgAl-CO_3^{2-}-LDH with Mg/Al = 3, so this name is also used to express the starting material, DHT-6. The Mg/Al mol ratio of the hydrotalcite, DHT-6, was found to be 2.99, and its C(carbon) content was 2.14 wt % (theoretical: 1.93 wt %).

Carbon Content and IR Profile. For quick estimation of the carbonate ion content of the treated LDHs, a very strong absorbance at 1368 cm^{-1} for the C−O stretching vibration of CO_3^{2-} in the IR spectra[13,17] was used. The absorbance ratio was taken against the absorption in the range 620−670 cm^{-1}, which was assigned to the vibrational modes of the hydroxide octahedral layers of the hydrotalcite,[18] because this absorption was not expected to change by ion-exchange.

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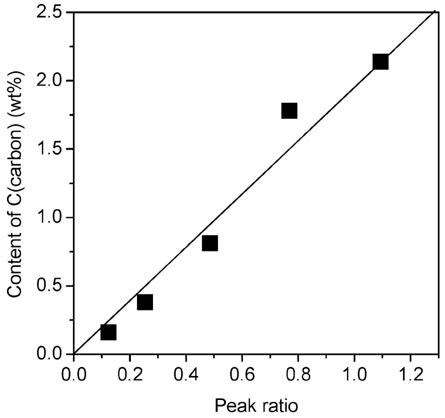

Figure 1. Relation between C(carbon)-content of MgAl-LDHs and peak ratio [Abs$_{max}$ (1368 cm^{-1})]/[Abs$_{max}$ (620−670 cm^{-1})] of a FTIR spectrum. Abs$_{max}$ (620−670 cm^{-1}) indicates the maximum absorbance within 620−670 cm^{-1}.

To certify the relation between the IR absorbance ratio and carbonate content, their C contents and FTIR spectra were measured for the MgAl-LDHs with different CO_3^{2-} contents which were prepared following the procedure described later (treatment by mixed HCl−NaCl solutions with 0.0025 N HCl and various NaCl concentrations).

The ratio [absorbance (1368 cm^{-1})]/[absorbance (620−670 cm^{-1})], hereafter abbreviated as peak ratio, derived from the IR data, was plotted vs the observed C content (Figure 1). The peak at 668 cm^{-1} for the LDH containing CO_3^{2-} ion shifts to about 626 cm^{-1} by substitution with Cl^- ion, so, in practice, the maximum absorbance in this range (620−670 cm^{-1}) was used. The relation was almost linear; therefore, this peak ratio can be used for estimating the amount of the remaining carbonate. In this paper, the carbonate content is expressed in the ratio to carbonate content of the starting hydrotalcite.

Deintercalation of Carbonate by HCl Solution. Acid treatment is known to cause a weight loss despite the successful decarbonation.[10] To clarify the effect of acid treatment, hydrotalcite was treated with different HCl concentrations and was examined with respect to the remaining carbonate and weight recovery (Figure 2). The weight recovery is the easiest way to monitor dissolution of LDH hosts. And no weight loss indicates no weathering and no morphological change during the decarbonation process. And also, no weight loss ensures the repeated use of the LDHs as a decarbonation−carbonation process for capturing carbon dioxide.

In this experiment, a 10-mL HCl aqueous solution was used for 20 mg of hydrotalcite at 25 °C. For the weight recovery calculation, the handling loss was taken into account as already mentioned in the Experimental Section. At concentrations less than 0.005 N HCl, the recovery was almost quantitative, though 65% of carbonate remained (Figure 2). A more concentrated solution caused substantial weight loss, e.g., for 0.015 N HCl the remaining carbonate is as low as 5% but the recovery was about 75%. For concentrated HCl of more than 0.1 N, the solid was completely dissolved.

The IR spectra of the starting hydrotalcite and the treated specimen are shown in Figure 3a. For the starting hydrotalcite, the absorption band at 1368 cm^{-1}, characteristic of the C−O antisymmetric stretching of CO_3^{2-}, was observed as previously reported,[13,17,19] but it almost disappeared for the treated hydrotalcite, e.g., the hydrotalcite treated with 0.025 N HCl; however, the weight recovery for this treatment is about 70% (Figure 2). The other IR absorptions were assigned according to the literature.[17−19] The hydrogen vibrations occur at 3400−3600 cm^{-1} (stretching), H_2O bending vibration occurs at 1600 cm^{-1}, and the broad shoulder at about 3100−3200 cm^{-1} is due to a carbonate−water interaction.

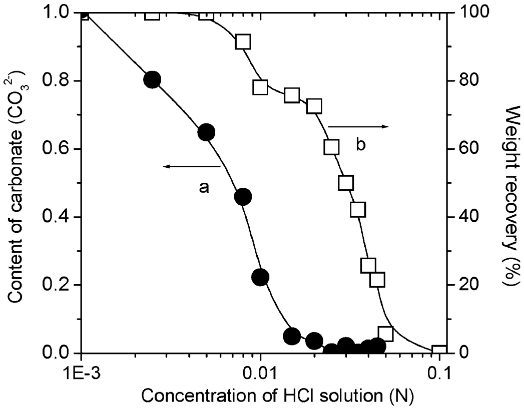

Figure 2. (a) Carbonate content of hydrotalcite, and (b) weight recovery plotted vs the HCl concentration after treatment for 24 h. The hydrotalcite amount was 20 mg, and solution volume used for this treatment was 10 mL. The carbonate content is expressed in ratio to that of the starting hydrotalcite.

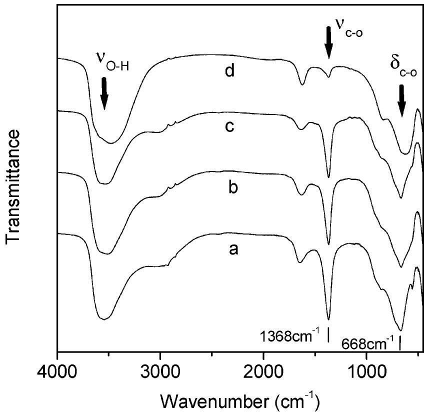

Figure 3. IR spectra for (a) starting MgAl-CO_3^{2-}-LDH (hydrotalcite), (b) the hydrotalcite after treated only with 0.005 N HCl, (c) the hydrotalcite after being treated only with 13 wt % NaCl solution, and (d) the hydrotalcite after treatment with a mixture of HCl−NaCl containing 0.005 N HCl and 13 wt % NaCl concentration.

It should be noted that the recovery or weight loss depended not only on the concentration of the HCl solution used for the treatment, but also the volume of the HCl solution. In Figure 4, recovery was plotted vs the volume of HCl solution with the same concentration (0.005 N) for a 24-hr-treatment of 20 mg of DHT-6. A substantial weight loss was observed for the volume of HCl solution > 15 mL, and at this volume, the H^+/CO_3^{2-} ratio (in mol) is 2.2, which is more than two times the carbonate ion. This clearly indicates that it is due to the reaction of a proton (+1) in the solution with the carbonate ion (−2), i.e., protonation of carbonate ion, and that, for $H^+/CO_3^{2-} > 2.0$, successive degradation of

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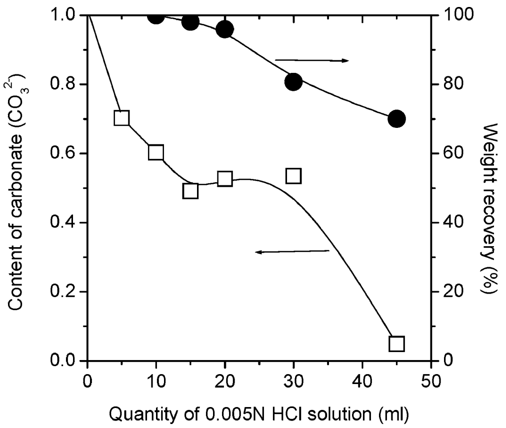

Figure 4. Effect of volume (mL) of HCl solution (0.005 N) for treating 20 mg of hydrotalcite. The remaining carbonate and weight recovery are plotted vs quantity of HCl solution.

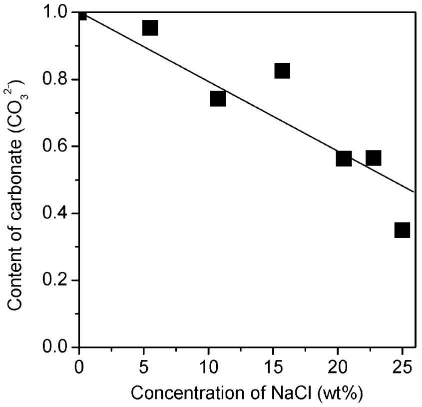

Figure 5. Effect of NaCl concentration in 10-mL solution used to ion-exchange 20 mg of hydrotalcite. The amount of remaining carbonate is plotted vs NaCl concentration.

the Mg–Al double hydroxide layer occurs due to excess protons, which would lead to the loss in weight. The substantial weight loss due to dissolution of the host layers always takes place when using HCl of high concentration and in high H^+/CO_3^{2-} mol ratio in the reaction system.

Ion-Exchange Reaction Using NaCl Solution. Carbonate ion shows strong affinity to the LDH interlayer; however, it is an equilibrium reaction of CO_3^{2-} and other anions between the LDH interlayer and the surrounding solution, so a large amount of other anions would cause a greater deintercalation of the carbonate ion. An ion-exchange experiment was conducted to examine the extent of the ion-exchange by using only NaCl solution. The results of the ion-exchange with NaCl solutions of various NaCl concentrations are shown in Figure 5, indicating the effect of the concentration of NaCl on the exchange ratio. This experiment was conducted at 25 °C and the treatment was for 24 h. The content of CO_3^{2-} in the treated LDHs was based on the peak ratio as already mentioned. For the highest-concentration NaCl solution (25 wt %; almost saturated solution), the remaining carbonate in the LDH was almost 35–40%. For this condition, the Cl^-/CO_3^{2-} mol ratio in the system was around 1500, which means an extreme excess of Cl^-. A large quantity of Cl^- shifted the equilibrium between CO_3^{2-} and Cl^- toward Cl^- in the LDH interlayer, though full conversion into Cl^--form could not be attained only by NaCl solution.

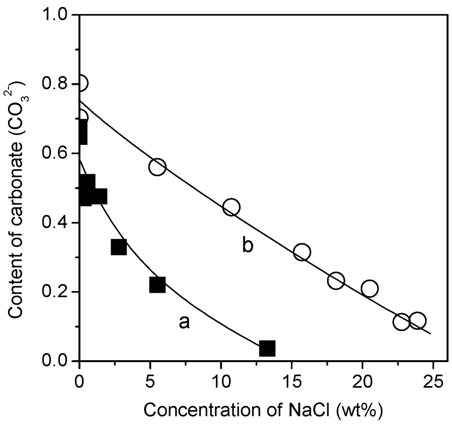

Figure 6. Effect of NaCl concentration of (a) 0.005 N HCl solution and (b) 0.0025 N HCl solution on deintercalation of carbonate ion from hydrotalcite. To 20 mg of hydrotalcite, 10 mL of solution was used.

Time dependence of the ion-exchange was also investigated using a 25 wt % NaCl solution by changing the ion-exchange duration, and it was found that the ion-exchange reaction is rapid and almost complete in 1 min without any further change to 72 h (the final remaining carbonate = 35–40%).

Enhanced Decarbonation Using HCl–NaCl Mixed Solution. As already pointed out, protonation of the carbonate ion to form HCO_3^- would take place in the LDH interlayer. The change in intercalated species would alter the ion-exchangeability, but HCl solution can afford only a small amount of anions; Cl^- (from HCl) and far less OH^- (from H_2O). Excess anions in the reaction system would lead to much more ion-exchange. On the basis of this idea, a HCl–NaCl mixed solution was used to supply the reaction system with excess Cl^- anions. The experiments were conducted in the same manner as already described except for the use of the mixed solution. The IR spectra for (i) hydrotalcite treated with a 0.005 N HCl solution, (ii) that treated with a 13 wt % NaCl solution, and (iii) that treated with a mixed solution of 0.005 H HCl and 13 wt % NaCl, are shown in Figure 3. The spectra were denoted as b, c, and d, respectively. The change in the IR absorption band at 1368 cm^{-1}, characteristic of the carbonate ion, clearly indicates that the mixed solution has a significant effect on the deintercalation of carbonate ions from the LDHs. Thus, remarkable enhancement of decarbonation was observed when a mixed solution of HCl and NaCl was used.

To clarify the dependence of NaCl concentration on decarbonation ratio, a systematic experiment with different NaCl concentrations was conducted for two HCl concentration series (0.005 N and 0.0025 N; 10 mL), and these results are shown in Figure 6. For both HCl concentration series, decarbonation was apparently enhanced by an increase in the NaCl concentration and also no weight loss was observed.

For practical use of this decarbonation reaction, the time needed for this reaction is important. The reaction rate of the ion-exchange process was examined by changing the treatment duration using 10 mL of a 0.005 N HCl solution containing 13 wt % NaCl against 20 mg of hydrotalcite. The treatment time, which is the time from the addition of the solution to the hydrotalcite until filtration, was changed, and the resulting powder was

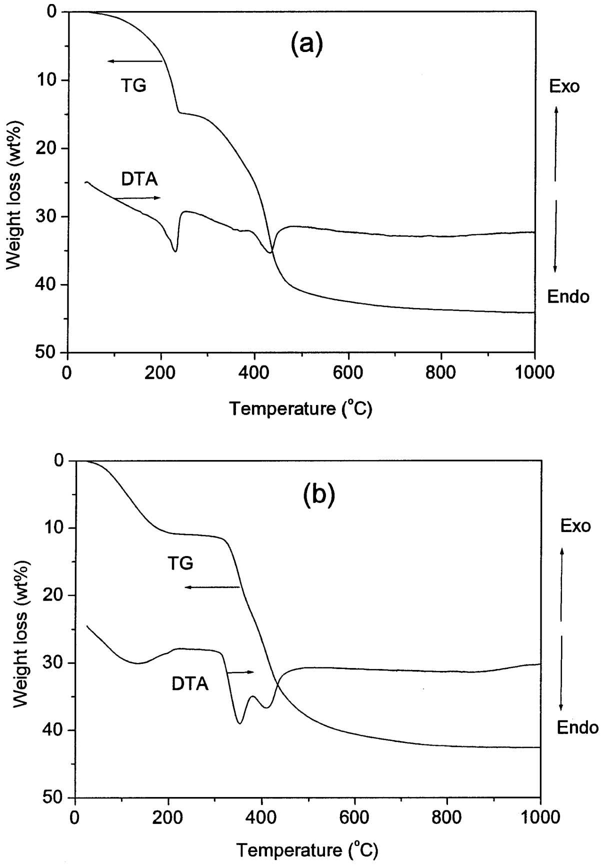

Figure 7. DTA-TG diagrams for (a) the starting material (hydrotalcite), and (b) hydrotalcite treated by HCl−NaCl mixed solution with 0.005 N HCl and 13 wt % NaCl.

characterized by FT-IR spectroscopy, which showed that even a 15-second treatment of the hydrotalcite with the mixed solution is enough for the elimination of carbonate ion from the interlayer space of the hydrotalcite. The remaining carbonate < 10% did not change by a longer treatment up to 48 h. This is probably due to protonation of the carbonate ion into HCO_3^- in the interlayer space. Other inorganic acids such as HNO_3 and H_2SO_4 also showed the same effect as HCl when mixed with NaCl. Here, the concentration is the same as that of HCl. This fact also implies that the amount of protons in the reaction system released from the acid is the key factor of this process.

Characterization of the Treated Hydrotalcite. The hydrotalcite treated by 0.005 N HCl solution with a 25% NaCl concentration for 1 day was used for characterization such as chemical composition. The Mg/Al mol ratio was 2.91 by chemical analysis, which is comparable to that of the starting hydrotalcite (2.99). The C content measured by the CHN analysis was <0.05 wt %, which was remarkably less than 2.3% of the initial carbonate ion in the starting hydrotalcite. The Cl content was revealed to be 11 wt %, and this is consistent with the theoretical value (11.5 wt %) for the Cl^--form. It implies the successful conversion into Cl^--form. The DTA-TG profiles for the starting hydrotalcite and the treated hydrotalcite are shown in Figure 7a and b, respectively.

The DTA-TG profiles of DHT-6 exhibited two apparent endothermic events at 230 and 432 °C with a minor broad endothermic peak at about 350 °C. The first one can be assigned to the loss of interlayer water, and the second and minor ones can be assigned to the loss of hydroxyl ions and removal of carbonate ions,[20−22] though the temperature is slightly lower than the reported values.[20−22] The thermal behavior of the treated hydrotalcite is somewhat different. It showed a broad endothermic peak at about 130 °C, and two apparent endothermic peaks at 354 and 410 °C. For the thermal behavior of MgAl-Cl^--LDH, Miyata[13] assigned the 430 and 480 °C to the loss of OH^- and Cl^-, respectively. Following this assignment, the observed endothermic peaks were assigned to the loss of OH^- and Cl^-, though the temperature is slightly lower than the reported value also in this case. In the diagram of DHT-6, a 14.8 wt % loss was observed for the first stage (r.t. ∼250 °C). On the basis of this value, the water content was estimated to be 2.56 per chemical formula (i.e., the z value for $Mg_3Al(OH)_8 1/2CO_3 \cdot zH_2O$) for the starting hydrotalcite. The observed total weight loss by heating to 1000 °C was 44.2 wt %, which was consistent with the expected value (44.9 wt %). Also, a 10.8 wt % loss was observed for the treated specimen, and the amount of water was estimated to be 1.82 per chemical formula (i.e., the z value for $Mg_3Al(OH)_8Cl \cdot zH_2O$). The observed total weight loss, 42.6 wt %, was in good agreement with the expected value of 43.5 wt %. The SEM photos (Figure 8a and b) indicate that no weathering of the surface or changes in the shape and grain size for the hydrotalcite occurred by treatment with the 0.005 N HCl/25% NaCl concentration. Quantitative weight recovery is consistent with this SEM observation.

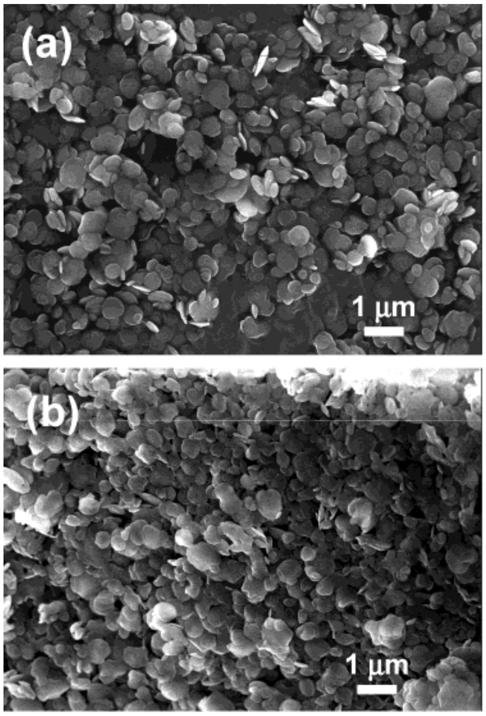

Figure 8. SEM photos for (a) the starting material (hydrotalcite), and (b) the hydrotalcite treated by HCl−NaCl mixed solution with 0.005 N HCl and 13 wt % NaCl. No corrosion seemed to occur.

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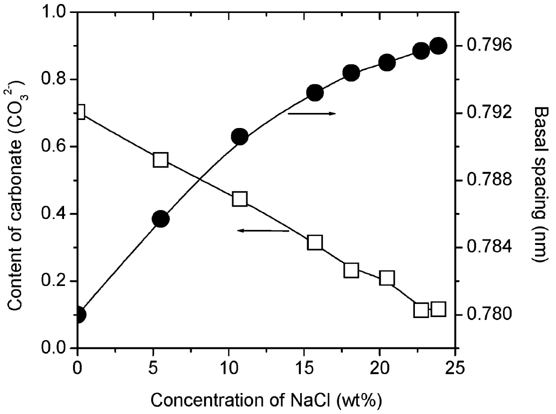

Figure 9. Basal spacing (d_{003}) and C-content of treated hydrotalcite plotted vs NaCl concentration used for the ion-exchange.

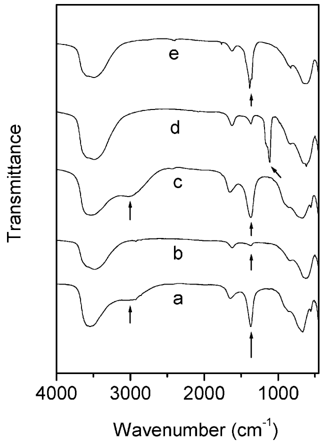

Figure 10. Ion exchange of the Cl$^-$-form LDH derived from hydrotalcite by treatment with HCl−NaCl mixed solution. FTIR spectra for (a) the starting material (hydrotalcite), (b) hydrotalcite treated by HCl−NaCl mixed solution with 0.005 N HCl and 13 wt % NaCl, (c) the Cl$^-$-LDH treated with Na_2CO_3 solution, (d) the Cl$^-$-LDH treated with Na_2SO_4 solution, and (e) the Cl$^-$-LDH treated with $NaNO_3$ solution, are shown. The arrows indicate the characteristic absorptions.

Powder XRD revealed the basal spacing of 0.780 nm for the starting hydrotalcite and 0.797 nm for the treated one. The basal spacing of the starting material is consistent with the reported values (0.778 and 0.781 nm)[7,11,21] for the specimen prepared by the coprecipitation method. The increase in the basal spacing by converting CO_3^{2-} to Cl$^-$ is 0.017 nm, and the basal spacing was the same as the reported value (0.797 nm) by Miyata[13] for MgAl-Cl$^-$-LDH with Mg/Al = 3. The change in the basal spacing for the specimens treated under the conditions of 0.0025 N HCl solution (10 mL) with different NaCl concentrations is shown with the carbonate content derived from the IR absorbance peak ratio (Figure 9). A gradual change in the peak intensity ratio in the IR and also the change in the basal spacing were observed, though the relation is not strictly linear.

Ion-Exchange of the Obtained Cl$^-$-LDH. To examine the exchangeability of the resulting MgAl-Cl$^-$-LDH, it was further treated with a Na_2CO_3 solution, a saturated Na_2SO_4 solution, and 36.5 wt % $NaNO_3$ solution at 25 °C for 1 day. As shown in Figure 10, the Cl$^-$-LDH treated with a Na_2CO_3 solution exhibited the same IR profile as the starting hydrotalcite: a strong absorption peak at the wavelength of 1368 cm^{-1} was observed for the Cl$^-$-LDH treated with Na_2CO_3. On the other hand, a strong absorption peak at 1112 cm^{-1} was for the Cl$^-$-LDH treated with Na_2SO_4, which is consistent with the previous reports about MgAl-SO_4^{2-}-LDH.[12,23] The Cl$^-$-LDH treated with $NaNO_3$ showed a strong peak at 1384 cm^{-1} attributable to N−O stretching vibration. The powder XRD results are as follows. The obtained CO_3^{2-}-LDH showed the basal spacing of 0.778 nm. The basal spacing of NO_3^--treated LDH was 0.839 nm, and the reported value for NO_3^--LDH was 0.834 nm.[13] The basal spacing of SO_4^{2-}-treated LDH was 0.867 nm, which is consistent with that reported for SO_4^{2-}-LDH (0.866 nm).[8]

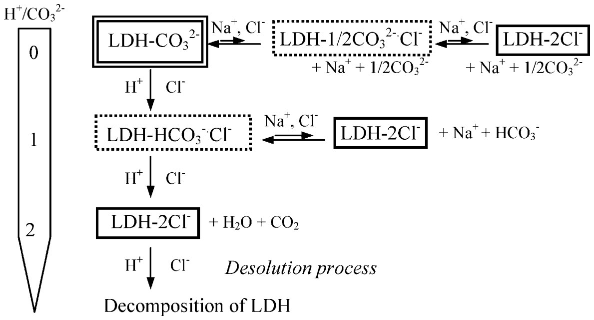

Figure 11. Diagram showing the proposed mechanism of deintercalation of carbonate from hydrotalcite by the action of proton (H$^+$) and Cl$^-$ ion. The ratio of H$^+$/CO_3^{2-} (in mol) indicates the initial mol ratio of proton in the solution to the carbonate in the interlayer of hydrotalcite.

Thus, the complete ion-exchange of Cl$^-$ in Cl$^-$-LDH with desired anion could be conducted under mild conditions. It indicates that a variety of MgAl-LDHs with the same particle size and crystallinity as the starting hydrotalcite can be obtained by two simple procedures: decarbonation and ion-exchange. At present, well-crystallized hydrotalcites can be easily available, so this conversion would be very useful to obtain a variety of MgAl-LDHs with good crystallinity. For direct conversion, preliminary experiments using acid−salt mixed solutions such as Na_2SO_4−H_2SO_4, Na_2SO_4−HCl, Na_2SO_4−HNO_3, $NaNO_3$−HNO_3, and $NaNO_3$−HCl, were conducted. Anion exchanges took place, though the exchange was partial in some cases. A detailed study is now in progress.

Proposed Mechanism for Enhanced Decarbonation. Considering these facts, we propose a plausible mechanism for the enhanced effect using a mixture of HCl and NaCl (Figure 11). By adding HCl, the protons in the solution increase and they begin to react with the carbonate ion (CO_3^{2-}) to form the hydrogen carbonate ion (HCO_3^-). For charge compensation, Cl$^-$ ions in the solution would be incorporated into the interlayer space. The latter anion is a monovalent anion, so the exchange tendency is different from the divalent carbonate ion. Probably Cl$^-$ ions can be ion-exchanged with this monovalent ion much easier than with the divalent carbonate ion. A large amount of Cl$^-$ ions in the solution shift the equilibrium to the Cl$^-$-form formation, leading to the enhancement of the deintercalation of carbonate and HCO_3^-. The further addition of the protons for the system would lead to the protonation of HCO_3^- to form

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(23) Kloprogge, J. T.; Wharton, D.; Hickey, L.; Frost, R. L. *Am. Mineral.* **2002**, *87*, 623.

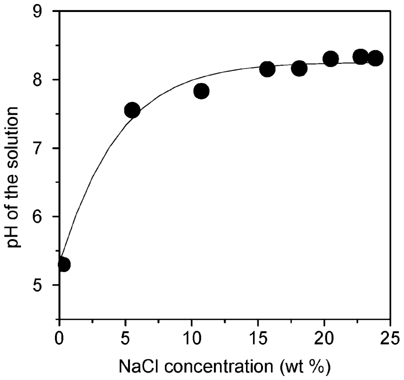

Figure 12. pH of the resulting solution when 20 mg of hydrotalcite were treated using 0.0025 N HCl solution (10 mL) with different NaCl concentrations.

neutral CO_2, which will be expelled from the interlayer space. This reaction would also make the hydrotalcite incorporate Cl^- ions in the solution. Beyond this amount, i.e., the mol ratio $H^+/CO_3^{2-} > 2.0$, the protons would begin to vigorously attack the Mg–Al layers, leading to an apparent weight loss. Under the typical experimental conditions of 20 mg of hydrotalcite against 10 mL of 0.005 N HCl solution, the amounts of ionic species related to this mechanism are as follows: the proton is about 0.05 mmol and CO_3^{2-} ion in the hydrotalcite (mw 312.1) is approximately 0.032 mmol. The ratio of H^+/CO_3^{2-} in this reaction system is about 1.6, which corresponds to the stage of coexisting CO_2 and HCO_3^-. Without NaCl addition, the amount of Cl^- ion, originating from HCl, is only 0.05 mmol. However, when the solution is at the concentration of 25 wt % NaCl, the amount of Cl^- ion is 50 mmol, which is an excessive amount.

As a supporting experiment for this mechanism, the pH values were measured for the resulting solutions by NaCl–HCl treatment (20 mg of DHT-6 and 10 mL of 0.0025 N HCl solution with different NaCl concentrations from 0 to 24 wt %; the same conditions as that for Figure 9). In Figure 12, the measured pHs of the resulting solutions are plotted vs the NaCl concentration. In this system, the CO_3^{2-} ion in the hydrotalcite is about 0.032 mmol, and HCl amount is 0.025 mmol. The ratio $H^+/CO_3^{2-} = 0.78$ is less than 1.0. So neither dissolution of the host LDH nor further protonation of HCO_3^- in the LDH interlayer would take place. Most of the protons of HCl would be consumed for protonation of carbonate ions into HCO_3^- ions in the interlayer space, which will be ion-exchanged with Cl^- ion to liberate HCO_3^- ion in the solution. Accordingly, the equilibriums we have to consider for the solution without NaCl addition are equivalent to an aqueous system containing hydrogen carbonate ions. The calculated pH value was about 5.3 for this system[24] and it is in good agreement with the pH of the solution after treatment only by the HCl solution (i.e., NaCl = 0 in Figure 12). For the treatment with HCl–NaCl solution, Cl^- ion is also incorporated in the interlayer of LDH by ion-exchange, which causes the excess Na^+ ion compared with Cl^- ion. It is equivalent to an aqueous system containing $NaHCO_3$. The calculated pH for this solution was about 8.3 according to the literature.[24] For less Cl^- incorporation, the excess Na^+ would decrease, which makes the pH approach 7.0. This is also in good agreement with the observed pHs (Figure 12).

The above-mentioned mechanism illustrates only the main reaction pathway of the over-all deintercalation reactions, and, in reality, these reactions may proceed in a more complex way. However, the enhanced decarbonation can be explained by this simplified model. This mechanism suggests that the key points for the optimal decarbonation are (i) the concentration of HCl, (ii) the mol ratio of H^+/CO_3^{2-}, and (iii) the presence of large excess Cl^- ion in the reaction system.

Acknowledgment. We thank Ms. H. Aoki of our institute for the SEM observations. Thanks are also due to Mr. S. Takenouchi of our institute for the chemical analyses of Mg and Al, to Dr. T. Fujita for the CHN analysis, and to Dr. K. Fujii for the DTA-TG analysis. Hydrotalcite, DHT-6, was kindly supplied by Kyowa Kagaku Kogyo Co., Ltd.

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