Effects of Anion Species on Deintercalation of Carbonate Ions from Hydrotalcite-like Compounds

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(Received March 22, 2005; CL-050385)

The deintercalation of carbonate ions from a hydrotalcite-like compound (MgAl-LDH) was investigated using salt-HCl mixed solutions with sodium salts containing various monovalent anion species. The deintercalation was influenced by the anion species, and the carbonate ions were deintercalated most easily for the system containing Cl^- or Br^- anions.

Layered double hydroxides (LDHs) consist of positively charged metal hydroxide layers (brucite-like sheets) and anions such as CO_3^{2-} located in the interlayer space for charge compensation.[1] The chemical formula is $M^{II}_{1-y}M^{III}_y(OH)_2(X^{n-})_{y/n}\cdot mH_2O$, where: $y = 0.2$–0.33, $m = 1$–$3y/2$, M^{II} = divalent cations, M^{III} = trivalent cations, and X^{n-} = n-valent anions.[2] The M^{II}/M^{III} mol ratio is in the range 2.0–4.0. Their use as a host for nano-composites has recently been focused on because LDHs incorporate various anions topotactically by anion exchange.[3] So far well-crystalline CO_3^{2-}-LDH is easily obtained.[4,5] However, the CO_3^{2-} ions have an exceptionally high affinity to LDHs, so it is extremely difficult to be anion-exchanged once carbonate ions are incorporated.[6]

Very recently, we found that the addition of NaCl dramatically enhanced the decarbonation of MgAl-LDH (Mg/Al ratio = 3) by the aqueous HCl solution.[7] By using the NaCl–HCl mixed solution, Cl^- form of LDH (Cl^--LDH) was successfully obtained under mild conditions without any weight loss and shape change. Because Cl^--LDH possesses high anion-exchangeability, this would be a very promising method to synthesize well-crystalline LDHs containing a variety of anions. The protonation of the interlayer carbonate into hydrogen carbonate followed by anion-exchange by excess Cl^- anions in the system was assumed to be the mechanism of the enhanced deintercalation using the mixed solution.[7] However, the effect of the anion species on the decarbonation rate still remained unclarified.

The aim of this study is to understand the effect of anion species on the deintercalation of carbonate ions from MgAl-LDH (Mg/Al ratio = 3) in order to clarify the optimum deintercalation conditions.

The starting CO_3^{2-}-LDH with Mg/Al = 3.0, which is a commercially available material (DHT-6, Kyowa Kagaku Kogyo Co., Ltd.), was used as the starting material as was used in our previous study.[7] From the chemical analysis, the Mg/Al mol ratio of the starting LDH (DHT-6), which contains carbonate ions, was determined to be 2.99, and the CHN analysis revealed the C(carbon) content of 2.14 wt % (theoretical: 1.93 wt %).[7] Its BET plot showed good linear relation, and the BET surface area was found to be 17.4 m^2/g. The grain size was 0.5–1.0 µm from the SEM observation. The reagents used were 1N, 0.1N, and 0.01N HCl solutions, which were diluted to prepare the solutions with the desired concentration, NaCl, Na_2SO_4, $NaNO_3$, $NaClO_4$, NaI, NaBr, H_2SO_4, and HNO_3 (reagent grade, Kanto Chemical Co., Ltd.). Degassed and deionized water was used for diluting the solutions and washing the filtered precipitates.

The typical deintercalation process is as follows: DHT-6, 20 mg (20.00 ± 0.04 mg, 0.662 mmol), was placed in a glass vessel, and then 10 mL of an aqueous solution adjusted to a given acid and salt concentration was added. We used 0.005N and 0.0025N HCl because the HCl concentration of less than 0.005N was found to be appropriate for the decarbonation without any weight loss due to dissolution. After purging with N_2 gas, the glass vessel was tightly capped and then subjected to ultrasonification for a thorough dispersion. With constant shaking, the vessel was stored at 25 °C for 1 day. The resulting suspension was filtered through a membrane filter having a pore size of 0.2 µm (Millipore) and thoroughly washed several times with degassed deionized water under a N_2 flow. The remaining precipitates on the filter were collected and immediately dried in a vacuum.

For determination of the carbonate and nitrate contents in the resulting materials, a CHN analysis data (Perkin-Elmer 2400 II) and a very strong absorbance at 1368 cm^{-1} for the C–O stretching vibration of CO_3^{2-} in the IR spectra[8] were used as previously reported.[7] In this paper, the carbonate content is expressed in the ratio to the carbonate content of the starting LDH (DHT-6).

The remaining carbonate content plotted versus the concentration of anions is shown in Figures 1 and 2 for two different HCl concentrations. The incorporation of the anions originating from sodium salts was confirmed by the FTIR spectra and weight change. The results clearly indicated that the decarbonation was

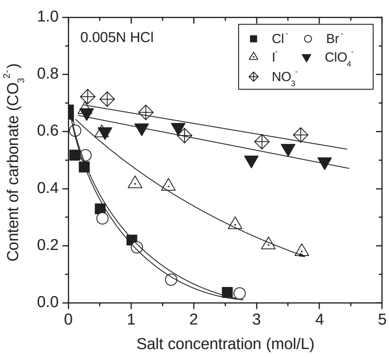

Figure 1. Carbonate content of CO_3^{2-}-LDH (Mg/Al = 3) after the treatment with 0.005N HCl–sodium salt (NaX) mixed solutions plotted versus concentration of anions (X^-). The carbonate content is expressed in the ratio to that of the starting LDH.

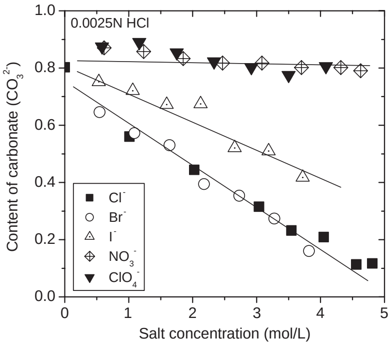

Figure 2. Carbonate content of CO_3^{2-}-LDH (Mg/Al = 3) after the treatment with 0.0025N HCl–sodium salt (NaX) mixed solutions plotted versus concentration of anions (X^-).

affected by the anion species and, from the view point of the decarbonation degree, three types of behaviors were observed. For the Cl^- and Br^- anions, at the higher salt concentration, the decrease in carbonate ions was remarkable (i.e., the effect of an excess amount of anions on the decarbonation was conspicuous); however, for I^-, the effect of excess anions was of a medium degree, resulting in a limited decarbonation. The decarbonation was most difficult for the systems containing the NO_3^-, and ClO_4^- anions. Especially, for the 0.0025N HCl series of NO_3^-, and ClO_4^- anions, the amount of residual carbonate remained almost constant regardless of the increase in the salt concentration. Thus, for the Cl^- and Br^- anions, a higher salt concentration leads to the almost complete substitution of carbonate ions; however, for the I^-, NO_3^-, and ClO_4^- anions, a thorough decarbonation was not attained under the present conditions. The order of decarbonation in the sodium salt–HCl system was: $Cl^- = Br^- > I^- > NO_3^- = ClO_4^-$. This is in good agreement with the order of the affinity of the LDH toward various anions reported by Miyata:[6] $CO_3^{2-} \gg Cl^- > Br^- > NO_3^- > I^-$. No information was available for ClO_4^-. This is also in rough accordance with the size (diameter) of the anions: The reported ionic sizes for Cl^-, Br^-, I^-, NO_3^-, and ClO_4^- are 0.336, 0.380, 0.422, 0.400, and 0.450 nm, respectively.[9] Namely, the order of anion size is: $Cl^- < Br^- < NO_3^- < I^- < ClO_4^-$. The anion becomes more difficult to be incorporated into the LDHs as the ionic size increases. This is in good agreement with the work by Miyata.[6]

According to the decarbonation mechanism we proposed,[7] the decarbonation consists of two processes: Protonation of carbonate ions into hydrocarbonate ions with the simultaneous incorporation of an anion, and ion exchange of hydrocarbonate as well as carbonate ions by the excess anions in the system. Such a protonation process was assumed to take place much faster than the dissolution of the LDH layers which would take place beyond the mol ratio $H^+/CO_3^{2-} > 2.0$. In the present system, 20 mg of LDH was used versus 10 mL of 0.005N and 0.0025N HCl solutions; i.e., the amounts of ionic species are: the proton is about 0.05 mmol for the 0.005N solution and 0.025 mmol for the 0.0025N solution, and the CO_3^{2-} ion in the LDH (M_w; 312.1) is approximately 0.032 mmol. For the 0.005N solution, the ratio of H^+/CO_3^{2-} in this reaction system is about 1.6 and, for the 0.0025N solution, the ratio of H^+/CO_3^{2-} is about 0.8. If there is no exchange of CO_3^{2-} by a certain anion (X^{n-}), an excess amount of anions would not have any effects, and the carbonate content remains constant at the same degree as that by the HCl treatment. This is the case with NO_3^- and ClO_4^-. On the other hand, if the CO_3^{2-} to X^{n-} exchange occurs to a certain extent, the excess amount of anion has an effect and the decarbonation reaction proceeds as the anion amount increases. This is the case with Cl^- and Br^-. In the second process of decarbonation, the incorporation of an anion by the anion exchange is included. Therefore, the affinity of the anions to LDH would play an important role, and it is reasonable that the decarbonation degree is in the order of the affinity. A higher acid concentration would lead to an increase in the better ion-exchangeable species (HCO_3^-) in the interlayer space, which makes the exchange much easier. The pH value calculated for the full decarbonation under 0.0025N HCl condition was about 8.3. The measured pH-values were 8.3–8.4 for Cl^- and Br^-, about 7.8 for I^-, and 6.4–7.0 for ClO_4^- and NO_3^- at about 4 mol/L anion concentration. These values are in accordance with the degree of exchange depending on the anion species.

Other factors which would have effects on the decarbonation are the acid species, and Mg/Al ratio etc. To clarify the effects of acid species, we conducted experiments using HNO_3 as well as HCl as the acid for decarbonation from LDH in the NO_3^- system. The experimental conditions were the same except for the acid species. The decarbonation rates were not so different from each other. Thus the effect of acid species on the decarbonation rate was not observed.

To see the effect of the Mg/Al ratio of LDH, preliminary decarbonation experiments were conducted by using LDH with Mg/Al ratio = 1.91 (LHD2) with similar grain size prepared by the hexamethylenetetramine method.[5] The result implied that LDH2 was more difficult to be decarbonated than LDH (Mg/Al = 3.0). For example, at 0.005N HCl, thorough decarbonation was attained by applying the concentration of 2.53 mol/L NaCl to LDH (Mg/Al = 3.0); however, this concentration was not enough for LDH2 and higher concentration up to 4.81 mol/L was needed. The higher layer charge of LDH2 would have made the deintercalation of carbonate more difficult.

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