doi:10.1246/cl.2010.591
Published on the web May 15, 2010

# One-step Conversion of $CO_3^{2-}$–LDH (Layered Double Hydroxide) into Anion-exchangeable LDHs Using an Acetate-buffer/Salt Method

Nobuo Iyi* and Hirohisa Yamada
*National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044*

(Received February 22, 2010; CL-100173; E-mail: iyi.nobuo@nims.go.jp)

By carrying out decarbonation of $CO_3^{2-}$-type MgAl-LDH (layered double hydroxide) using an acetate-buffer/salt solution under $N_2$ flow, $CO_3^{2-}$–LDH was successfully converted into $ClO_4^-$ and $NO_3^-$–LDHs, which contain only a little residual $CO_3^{2-}$, in one step under mild conditions. Due to the superior anion-exchangeability, they serve as suitable intermediates for the preparation of LDH hybrids.

Layered double hydroxides (LDHs) consist of positively charged metal hydroxide layers and anions in the interlayer spaces.[1,2] Because LDHs incorporate various anions, including organic anions, by anion exchange, they have recently been focused on as a host for nanohybrids.[3] LDHs containing interlayer carbonate ions ($CO_3^{2-}$) can be easily prepared, and commercially available LDH mostly contain carbonates; however, because of the high affinity of $CO_3^{2-}$ for LDHs, it is extremely difficult to deintercalate $CO_3^{2-}$ by anion exchange.[1,4] Therefore, conversion of $CO_3^{2-}$–LDHs into anion-exchangeable LDHs is an important process in LDH chemistry.

We have previously reported that aqueous HCl/NaCl mixed solution deintercalates $CO_3^{2-}$ from $CO_3^{2-}$–LDH to yield $Cl^-$–LDH without any weight loss or shape change.[5] However, such complete decarbonation was observed only for $Cl^-$ and $Br^-$, whereas other anions such as $NO_3^-$ and $ClO_4^-$, which have less affinity toward LDH, showed only partial exchange even when a salt solution of a very high concentration (ca. 8 M) was used.[5] Even in the case of $Cl^-$, NaCl concentration as high as 3 M was required for complete decarbonation. LDHs containing these low-affinity anions, $NO_3^-$ and $ClO_4^-$, are much easier to be anion-exchanged than $Cl^-$–LDH, so they are more suitable intermediates for preparing organo–LDH hybrids. Furthermore, exfoliation in formamide was observed only for $NO_3^-$ and $ClO_4^-$–LDHs;[6] therefore, there has been a strong need for one-step conversion of $CO_3^{2-}$–LDH into $NO_3^-$ and $ClO_4^-$–LDHs.

We have subsequently reported that acetate-buffer (hereafter referred to as "buffer") can replace HCl in the acid/salt solution.[7] In this buffer/salt solution, a lower concentration (1 M) of NaCl was enough for complete decarbonation.[8] These experiments have been conducted in closed vials; however, recent study showed that a much lower concentration of NaCl was enough for the decarbonation using the buffer/salt solution conducted under $N_2$ flow.

Figure 1 shows the residual $CO_3^{2-}$ content in the resulting $Cl^-$–LDH obtained using buffer/salt method. The $CO_3^{2-}$ content is expressed in percentage relative to that of the initial LDH. For this experiment, commercially available $CO_3^{2-}$–LDH with Mg/Al = 3 was used as the initial LDH.[9] The buffer was prepared from acetic acid (AcOH) and sodium acetate ($AcONa \cdot 3H_2O$), and NaCl was used for $Cl^-$ salt.[10] The buffer was 0.1 M in concentration, and its AcOH ratio ([AcOH]/[AcONa + AcOH]) was 0.10.[11]

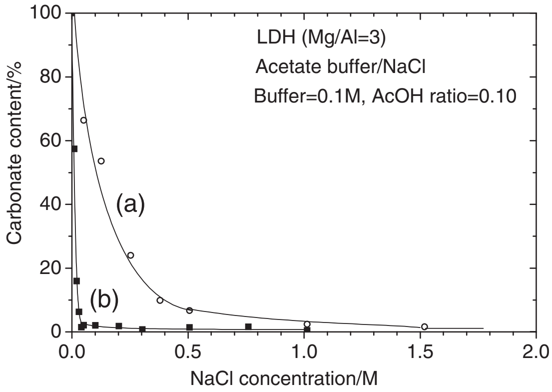

**Figure 1.** Carbonate content in the LDH after one-day treatment with acetate-buffer/NaCl solution (a) in a closed vial and (b) under $N_2$ flow.

The anion exchange was conducted (a) in a closed vial and (b) in a flask under $N_2$ flow at room temperature (25 °C). In the closed vial system, 20.0 mg of LDH (0.066 mmol) was placed in a glass vial, and 10 mL of the buffer/salt solution was added. After purging with $N_2$, the vial was tightly capped and stored with constant shaking for 1 day. On the other hand, for the reaction under $N_2$ flow, LDH (100 mg) and buffer/salt solution (50 mL) were mixed in a three-necked flask equipped with a cooler and $N_2$ inlet. The reaction was conducted with stirring under $N_2$ flow ($500\,mL\,min^{-1}$).[12] In both procedures, the resulting suspension was filtered and washed with degassed deionized water under $N_2$ flow. The precipitates were dried in vacuum. The residual $CO_3^{2-}$ content was determined as described previously.[5]

As shown in Figure 1, $CO_3^{2-}$–LDH was converted into $Cl^-$–LDH much more efficiently under $N_2$ flow (b) than in a closed vial (a): In the case of the closed vial system, a higher NaCl concentration ($\geq 1$ M) was required to obtain $Cl^-$–LDH with residual $CO_3^{2-} \leq 5\%$, whereas a NaCl concentration as low as 0.05 M was enough to obtain the same result in the $N_2$-flow system. FTIR spectrum and powder XRD profile of the product indicated complete decarbonation under optimum conditions (Figure S1; SI).[15] The $d_{003}$ value of the obtained $Cl^-$–LDH was 0.793 nm at 10% RH, which is in good agreement with the previously reported value ($d_{003} = 0.795$ nm at 10% RH).[13]

The possible mechanism of decarbonation of $CO_3^{2-}$–LDH by using acid/NaCl solution was proposed previously,[5,7] and it may be expressed as follows:

$$H^+(aq) + Cl^-(aq) + \{CO_3^{2-}\}(LDH) \rightleftharpoons \{HCO_3^-, Cl^-\}(LDH) \qquad (1)$$

$$\{HCO_3^-, Cl^-\}(LDH) + H^+(aq) + Cl^-(aq) \rightleftharpoons \{2Cl^-\}(LDH) + H_2O + CO_2(aq) \quad (2)$$

Here, (aq) indicates aqueous solution phase; (gas), gas phase; and { }(LDH), interlayer space of LDH.

Acetate ions are not included because of its low affinity to LDH. In the present case, most of $H^+(aq)$ are supplied from the acetate buffer. $CO_2(aq)$ is in equilibrium with $CO_2$ in gas phase. According to Henry's law, the amount of $CO_2(aq)$ is proportional to $[CO_2(gas)]$, i.e., the concentration of $CO_2(gas)$:

$$CO_2(aq) \rightleftharpoons CO_2(gas) \quad (3)$$

These equilibrium equations indicate that the increase in $[CO_2(gas)]$ leads to increase in $[CO_2(aq)]$ (eq 3), and subsequently increase in incorporation of carbonate ions in the LDH interlayer (eqs 1 and 2). This is reverse to decarbonation. Thus, $CO_2(aq)$ and $CO_2(gas)$ are in equilibrium with the interlayer anions of LDH; therefore, higher $[CO_2(gas)]$ results in incorporation of more carbonate ions in the LDH interlayer.

In a closed vial, $CO_2$ gas generated by decarbonation remains in the vial. The total amount of the $CO_2$ species in the system is equal to the amount of $CO_3^{2-}$ in the initial $CO_3^{2-}$LDH. The estimated concentration of $CO_2$ was ca. 5% if the free space volume is the same as that of the solution and if all $CO_3^{2-}$ ions go into the free space (gas phase) as $CO_2$. This concentration is much higher than that in the ambient air (ca. 0.04%). Thus $[CO_2(gas)]$ becomes very high for the closed vial system, which leads to the incorporation of carbonate ions in the interlayer of LDH. On the other hand, by applying continuous $N_2$ flow, $CO_2$ in the gas phase is removed with $N_2$ flow, and $[CO_2(gas)]$ is maintained very low. This leads to the shift of the equilibrium for more decarbonation and consequently decrease in the carbonate ions in the LDH interlayer as indicated by the equilibrium equations (eqs 1 and 2). Thus, the incorporation of carbonate ions by the LDH interlayer is prevented.

Figure S2 shows the time-dependent changes in the residual $CO_3^{2-}$ in LDH and in the $CO_2$ concentration in the outlet $N_2$. The $CO_2$ concentration reached its peak 4 min after mixing, and the residual $CO_3^{2-}$ was ca. 8% at this instant.

Thus, the salt concentration required was drastically reduced by carrying out the reaction under $N_2$ flow.[14] This strongly suggests the feasibility of direct conversion of $CO_3^{2-}$LDHs into $NO_3^-$ or $ClO_4^-$LDHs if the buffer/salt method is implemented under $N_2$ flow. As expected, $ClO_4^-$ and $NO_3^-$ LDHs with low residual $CO_3^{2-}$ were successfully obtained under $N_2$ flow.

The decarbonation experiments were conducted in the same way, and the salts used were $NaNO_3$ and $NaClO_4$, respectively.[10] The residual $CO_3^{2-}$ content in the treated LDH was determined by FTIR and CHN analyses: In the case of $ClO_4^-$, the $CO_3^{2-}$ content was determined by FTIR as before.[5] A strong absorbance for the C–O stretching vibration of $CO_3^{2-}$ at 1368 cm$^{-1}$ in the FTIR spectrum was used. In the case of $NO_3^-$, the $CO_3^{2-}$ content was estimated from the $NO_3^-$ content obtained by the elemental analysis because the characteristic bands of $CO_3^{2-}$, acetate, and $NO_3^-$ overlap in the FTIR profile.

For the decarbonation using buffer/$NaClO_4$, the buffer concentration was 0.1 M (AcOH ratio = 0.127). The residual $CO_3^{2-}$ content is plotted against $NaClO_4$ concentration up to ca. 8 M for a closed vial system (a), and for a $N_2$-flow system (b) (Figure 2). In the closed vial system, the residual $CO_3^{2-}$ was less than 5% for the buffer/salt solution with a $NaClO_4$ concentration of more than 7 M (Figure 2a). On the other hand, under $N_2$ flow, the residual $CO_3^{2-} \leq 5\%$ was achieved for a $NaClO_4$ concentration as low as 0.8 M (Figure 2b). Thus, about 1/10th of the $NaClO_4$ concentration used in the closed vial was enough for the reaction conducted under $N_2$ flow. FTIR spectrum of the obtained $ClO_4^-$LDH is shown in Figure 3, in which no characteristic absorption due to $CO_3^{2-}$ was observed. Powder XRD profile and SEM image of the obtained $ClO_4^-$LDH are shown in Figure S4. The $d_{003}$ value was 0.919 nm at 10% RH, which is in good agreement with the previously reported value ($d_{003} = 0.917$ nm at 10% RH).[13] SEM images showed that the original morphology of the initial LDH was retained without any sign of dissolution such as holes.

Figure 4 presents time-dependent changes in the residual $CO_3^{2-}$ in LDH, and time-dependent change in $CO_2$ concentration in the outlet $N_2$ is shown in Figure S5. The $NaClO_4$

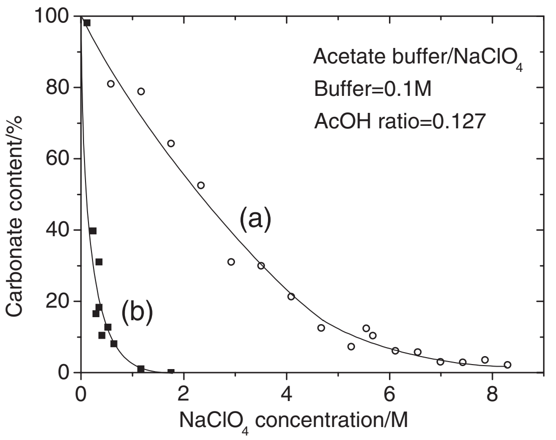

**Figure 2.** Residual carbonate content in the LDH treated by acetate-buffer/$NaClO_4$ solution (a) in a closed vial and (b) under $N_2$ flow.

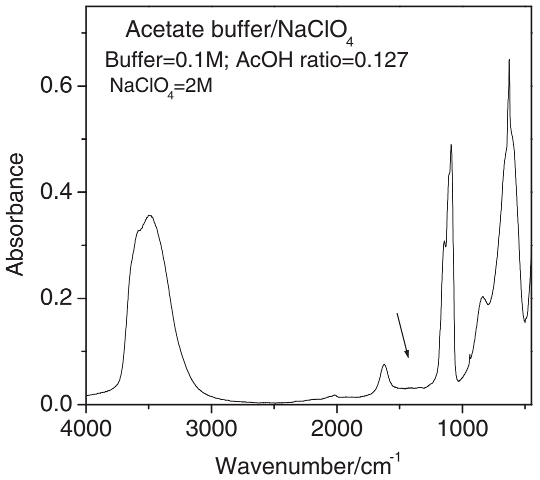

**Figure 3.** FTIR spectrum for the sample treated by buffer/$NaClO_4$ solution under $N_2$ flow for 18 h. The $\nu_{C\text{–}O}$ absorption peak due to $CO_3^{2-}$ was not detected as indicated by an arrow. Strong characteristic absorption peaks in the region of 1000–1250 cm$^{-1}$, are due to $ClO_4^-$.

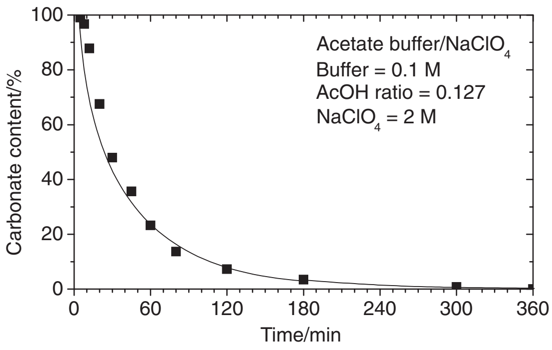

**Figure 4.** Time-dependent changes in the carbonate content in the LDH by treatment with acetate-buffer/NaClO$_4$ solution under $N_2$ flow.

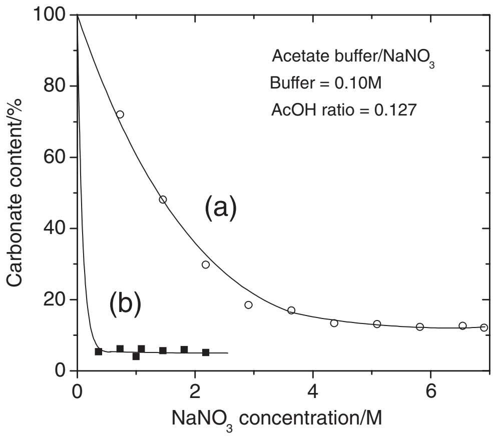

**Figure 5.** Residual carbonate content in the LDH after one-day treatment with acetate-buffer/NaNO$_3$ solution (a) in a closed vial and (b) under $N_2$ flow.

concentration in these experiments was 2 M. The maximum $CO_2$ concentration was observed after ca. 8 min (Figure S5); however, the residual $CO_3^{2-}$ gradually decreased and became less than 3% after 5 h (Figure 4). Compared with $Cl^-$, more salt concentration was required and the reaction was much slower.

Similar experiments were conducted for the system using $NaNO_3$, and the changes in the residual $CO_3^{2-}$ content plotted against the $NaNO_3$ concentration are shown in Figure 5. The buffer concentration was 0.1 M and its AcOH ratio was 0.127. After the closed vial reaction, ca. 12% $CO_3^{2-}$ remained for a $NaNO_3$ concentration as high as 7 M. On the other hand, under $N_2$ flow, a much lower $NaNO_3$ concentration (0.4 M) was enough, and the product contained only about 6% $CO_3^{2-}$. This residual $CO_3^{2-}$ content did not decrease even if $NaNO_3$ concentration was increased up to 2 M. Powder XRD profile and SEM image are also shown in Figures S6a and S6b respectively. The $d_{003}$ value was 0.833 nm at 10% RH, which is consistent with the previously reported value ($d_{003} = 0.829$ nm at 10% RH),[13] though slightly larger. Small difference would be due to the trace amount of anions such as acetate incorporated as impurity in the LDH interlayer, which would have affected the hydration of LDHs and caused expansion. Time-dependent changes in the residual $CO_3^{2-}$ in LDH for the case of $NO_3^-$ are shown in Figure S7. The decarbonation behavior is similar to that for $ClO_4^-$; however, the residual $CO_3^{2-}$ was slightly higher than that in the case of $ClO_4^-$ under the same decarbonation conditions. The residual $CO_3^{2-}$ content could be reduced by increasing the AcOH ratio or buffer concentration; however, the reason of comparatively higher amount of residual $CO_3^{2-}$ in the case of $NO_3^-$ is not clear.

In conclusion, by employing a $N_2$ flow, one-step conversion of $CO_3^{2-}$LDHs into $NO_3^-$ and $ClO_4^-$LDHs containing only low amount of residual $CO_3^{2-}$ was achieved using buffer/salt method. The highly efficient decarbonation for the $N_2$-flow system was attributed to removal of $CO_2$ gas which will be incorporated in the LDH interlayer as $CO_3^{2-}$.

Besides the inorganic anions, the incorporation of organic anions is also a very interesting subject; hence, we conducted preliminary experiments on the incorporation of organic anions such as *p*-toluenesulfonate by employing the same method. Simply replacing inorganic salts with organic salts resulted in a partial exchange even under $N_2$ flow, probably due to their large anion size. However, by addition of $ClO_4^-$ as the coexisting anion, organo–LDH hybrids with low residual $CO_3^{2-}$ content were obtained in one step from $CO_3^{2-}$LDH (Figure S8). This also highlights the general versatility of the improved buffer/salt method presented in this paper.

This work was partly supported by Grant-in-Aid for Scientific Research (c) (No. 20550142) of JSPS (Japan Society for the Promotion of Science), and by Japan-Slovakia Research Cooperative Program of JSPS.

## References and Notes

1 F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* **1991**, *11*, 173; S. Miyata, *Clays Clay Miner.* **1975**, *23*, 369.
2 The chemical formula of LDH used is $M^{II}{}_yM^{III}(OH)_{2y+2}(X^{n-})_{1/n}\cdot mH_2O$, where $y = M^{II}/M^{III} = 2.0$–$4.0$, $m \approx 2$, $M^{II}$ = divalent cations, $M^{III}$ = trivalent cations, and $X^{n-}$ = *n*-valent anions. The "$CO_3^{2-}$LDH" stands for the LDH with carbonate ($CO_3^{2-}$) as the interlayer anion. The LDH used in this study is: $M^{III}$ = Al, $M^{II}$ = Mg.
3 S. P. Newman, W. Jones, *New J. Chem.* **1998**, *22*, 105.
4 The selectivity of anions in LDH is: $CO_3^{2-} \gg SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$; the selectivity of $ClO_4^-$ would be similar to that of $NO_3^-$. S. Miyata, *Clays Clay Miner.* **1983**, *31*, 305.
5 N. Iyi, T. Matsumoto, Y. Kaneko, K. Kitamura, *Chem. Mater.* **2004**, *16*, 2926; N. Iyi, K. Okamoto, Y. Kaneko, T. Matsumoto, *Chem. Lett.* **2005**, *34*, 932.
6 L. Li, R. Ma, Y. Ebina, N. Iyi, T. Sasaki, *Chem. Mater.* **2005**, *17*, 4386.
7 N. Iyi, T. Sasaki, *J. Colloid Interface Sci.* **2008**, *322*, 237.
8 No incorporation of acetate anion was observed, which is due to its extremely low affinity toward LDH as described before.[7]
9 DHT-6 (Kyowa Kagaku Kogyo Co., Ltd.) was used. Its Mg/Al mol ratio was 2.92 (±0.06), and BET surface area was 17.4 $m^2\,g^{-1}$. The grain size was 0.2–1 µm based on the SEM observations.
10 All reagents used were reagent grade (Kanto Chemical Co., Ltd.).
11 We have already reported that the weight loss of the LDH is negligible for the acetate-buffer with AcOH ratio $\leq 0.150$ at buffer concentration of 0.1 M. All experiments were conducted within this AcOH-ratio range to avoid the dissolution of LDHs.[7]
12 From the specification of the quality, $CO_2$ content of the $N_2$ gas used is estimated to be <5 ppm.
13 N. Iyi, K. Fujii, K. Okamoto, T. Sasaki, *Appl. Clay Sci.* **2007**, *35*, 218.
14 Since ambient air contains much less $CO_2$ than the gas phase of a closed vial, even by using air instead of $N_2$, the decarbonation could be conducted successfully in the case of $Cl^-$ (Figure S3).
15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.