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DECARBONATION BEHAVIOR OF Mg-Al-CO_3 HYDROTALCITE-LIKE COMPOUNDS DURING HEAT TREATMENT

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Abstract—Historically, the decarbonation of Mg-Al-CO_3 hydrotalcite-like compounds (HTlc) has been thought to occur between 400° and 500°C. The present work demonstrates that when HTlcs having the maximum Al content, Al/(Al + Mg) = 0.33, are heated to 500°C, 20–30% of the carbonates remain. The evolution of the remaining carbonates was observed as two maxima, at 600 and 900°C. At these temperatures, Al ions go into MgO, and spinel ($MgAl_2O_4$) forms. Therefore, the carbonates are released as the Al ions migrate.

At a lower Al content, Al/(Al + Mg) = 0.25, CO_2 evolution is almost complete at 500°C. This HTlc has no maximum of CO_2 evolution above 500°C. Lower charge densities, due to lower Al contents, lead to lower amounts of remaining carbonate anions.

Key Words—Decarbonation, Heat treatment, Hydrotalcite.

INTRODUCTION

In the literature there is extensive discussion of the properties of hydrotalcite-like compounds (HTlcs), with the general formula: $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}\cdot[A^{n-}_{x/n}\cdot m H_2O]^{x-}$. Here, M^{2+} and M^{3+} are di- and trivalent metal ions that occupy octahedral positions in brucite-like hydroxide layers, and A^{n-} is the interlayer anion. The value of x [x = Al/(Al + Mg)] ranges between 0.20 and 0.33 for the Mg-Al system (Miyata 1980). HTlcs consist of positively charged brucite-like layers alternating with negatively charged interlayers (Allmann 1968, Ingram and Taylor 1967). The interlayers contain anions and water molecules, and hydrogen bonding exists between them (Miyata 1975, Bish and Brindley 1977). Mg-Al-CO_3 HTlc are known to decompose to Mg-Al oxide solid solution upon heating to between 400°–800°C. The resulting oxides readily rehydrate and adsorb anions to reconstruct the original HTlc structure.

Recently, the reconstruction of calcined and decarbonated HTlcs in the presence of large anion solutions has been established as a method for synthesizing HTlcs intercalated with large anions, as shown by Chibwe and Jones (1989a, 1989b) and Narita *et al* (1991). Nevertheless, no detailed study on decarbonation behavior of HTlcs has been reported, though some studies have touch on it briefly in Mg-Al–CO_3 system. Ross and Kodama (1967) mentioned that nearly all the CO_2 was evolved by 600°C when the precipitate's composition was near those of manasseite and hydrotalcite (x = 0.25). Miyata (1980) reported about a chemical analysis of outgassed HTlc with x = 0.33. No carbonate was released at 400°C, and 77% of the carbonate was lost at 500°C. In other studies, the weight loss near 400°C is simply attributed to both dehydroxylation and decarbonation (Bish and Brindley 1977; Sato *et al* 1986a, 1986b).

In the present work, we measured the amounts of CO_2 evolved from Mg-Al-CO_3 HTlcs at various temperatures up to 1200°C.

EXPERIMENTAL

The HTlc was prepared by coprecipitation. An aqueous solution of $MgCl_2$ and $AlCl_3$ ($Mg^{2+} + Al^{3+} = 0.5$ mol/liter, x = 0.33) was continuously added to an aqueous solution of Na_2CO_3 ($CO_3^{2-}/Al^{3+} = 1$) at a flow rate of 50 ml/min. The mixture was maintained at 70°C, pH was adjusted to 10 by drop-wise addition of an NaOH solution, and the solution was vigorously stirred. The precipitate was washed ultrasonically with distilled water and then centrifuged. This operation was repeated until Cl^- was no longer detectable with $AgNO_3$. The washed precipitate was dried at 80°C and stored in a desiccator (Sample 1).

Well-crystallized HTlc (Sample 2) was prepared by hydrothermal treatment at 150°C and 500 kPa for 12 hours, with the previously mentioned solution of $MgCl_2$, $AlCl_3$ and Na_2CO_3. Other HTlcs with x = 0.20 and 0.25 were prepared in the same way as Sample 1.

The chemical compositions were determined by inductively coupled plasma emission spectrochemical analysis (ICP). Surface areas were measured by the BET method with nitrogen. The morphology of samples was observed with a transmission electron microscope (TEM). Simultaneous thermogravimetry differential thermal analysis (TG-DTA) of the samples was carried out under nitrogen gas at a heating rate of 3°C/min. X-ray powder diffraction (XRD) patterns were observed with CuKα radiation. Lattice constants were

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Table 1. Structural formulae, d_{003} spacings and surface areas for Samples 1 and 2.

Sample no.	Structural formula	Surface area (m^2/g)	d_{003} spacing (nm)
Sample 1	$[Mg_{0.67}Al_{0.33}(OH)_2]$ $[(CO_3)_{0.18} \cdot 0.64\ H_2O]$	53	0.765
Sample 2	$[Mg_{0.68}Al_{0.32}(OH)_2]$ $[(CO_3)_{0.17} \cdot 0.55\ H_2O]$	<3	0.764

determined using silicon as an internal standard. CO_2 evolution from the TG experiment (heating rate 3°C/min) was measured by gas chromatography (GC) with nitrogen carrier gas. Infrared (IR) absorption spectra were obtained in the range of 4600 to 400 wavenumbers (cm^{-1}) using the KBr pellet technique.

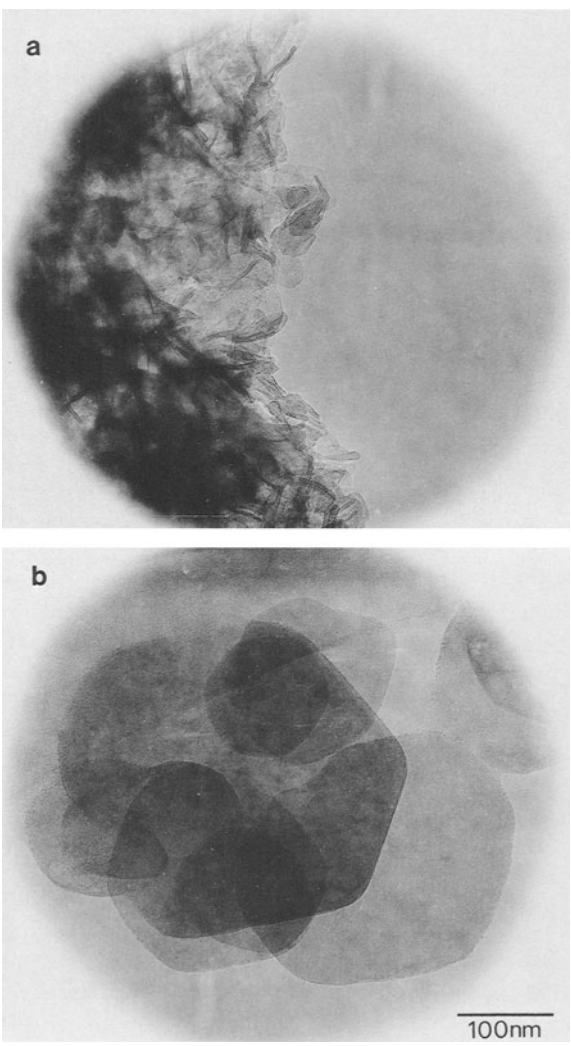

Figure 1. Transmission electron micrographs. (a): Sample 1, (b): Sample 2.

RESULTS

Crystallochemical characteristics of the samples

Table 1 shows the structural formulae, basal spacings (d_{003}) and specific surface areas of the samples. The ratio of x [Al/(Mg + Al)] for the samples was close to that of the starting aqueous solutions. In each sample, the carbonate content was slightly greater than the amount necessary to compensate for the net positive charge of the brucite-like layer.

The XRD patterns of samples were completely indexed as hydrotalcite. Sample 1 consists of thin, plate-like crystals of 25 to 50 nm in size (Figure 1a). The hydrothermally treated Sample 2, on the other hand, consists of well crystallized, hexagonal and plate-like crystals of 100 to 300 nm (Figure 1b).

Analysis of thermal behavior

The phases at various temperatures were determined by XRD analysis (Figure 2). The structure of HTlcs was retained up to 350°C, with decreasing basal spacing (d_{003}). The layer structure collapsed to an amorphous phase at 350°C. MgO began to form above 400°C. The value of the MgO lattice constant *a* decreased with a rise in calcination temperature up to 500°C (Figure 3). In the temperature range of 500° to 800°C, the lattice constants *a* for both samples increased gradually, and

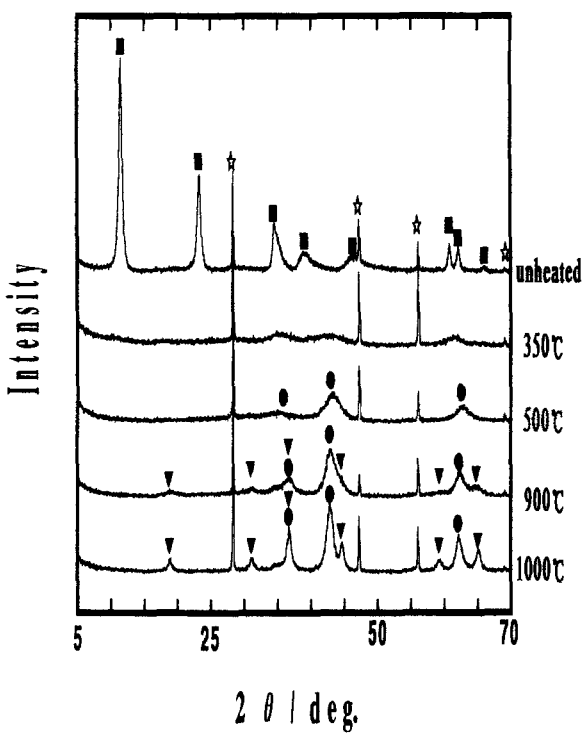

Figure 2. X-ray diffraction patterns of HTlc (Sample 1) heated at various temperatures: (■) HTlc, (☆) internal standard; Si, (●) Mg-Al oxide solid solution, (▼) spinel.

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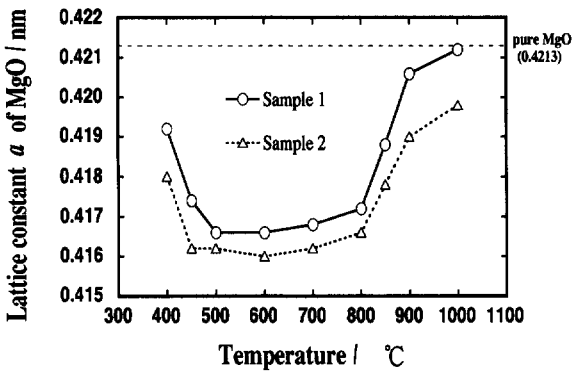

Figure 3. The relation between lattice constant a of MgO and calcination temperatures.

they increased rapidly above 800°C. These results reveal that Al ions, which have a smaller ionic radius than Mg ions, enter into MgO between 500° and 800°C, and are then released to spinel ($MgAl_2O_4$) above 800°C, as Miyata (1980) reported. Finally, spinel was detected above 900°C.

TG and DTA curves are shown in Figure 4. The first endothermic peak, due to the dehydration of interlayer water, was observed at 210°C for Sample 1 and at 220°C for Sample 2, accompanied by a shoulder around 175°C. The second peak appeared at 320°C for Sample 1, and at 305°C for Sample 2; the third at 375°C for Sample 1 and at 400°C for Sample 2. The second peak is attributed to the dehydroxylation of OH bound with Al (Miyata 1980, Sato *et al* 1986), and the third to the dehydroxylation of OH bound with Mg and the main CO_2 evolution which is mentioned later. Three weight loss steps were observed in the TG curves for both samples. Each step corresponded to the reaction mentioned above.

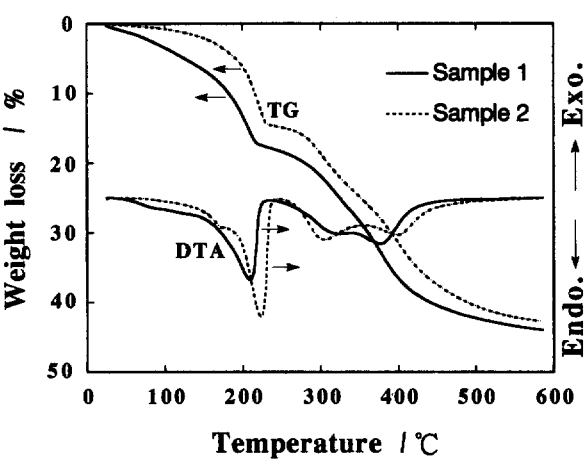

Figure 4. TG and DTA curves for Samples 1 and 2 under nitrogen.

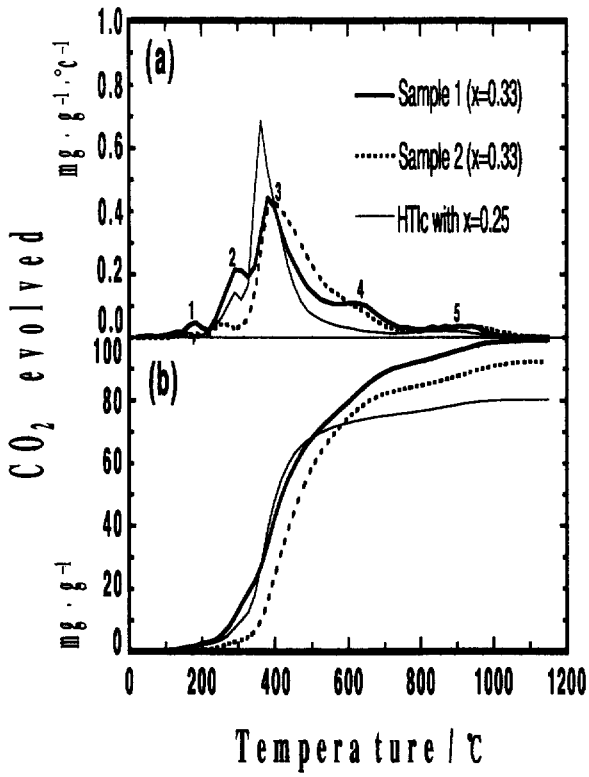

Figure 5. Amounts of CO_2 evolved from HTlc at various temperatures (a), and integrated amounts of CO_2 evolved up to various temperatures (b). The CO_2 evolution from the TG experiment (heating rate 3°C/min) was measured by gas chromatography with nitrogen carrier gas. Five maxima observed on the CO_2 evolution curves for Sample 1 and 2 are numbered.

Decarbonation behavior upon heating

Five maxima were observed on the CO_2 evolution curve for Samples 1 and 2 (Figure 5a). The first and second maxima on each CO_2 evolution curve appeared at about 180°C and 280°C, respectively. The third maximum of CO_2 evolution appeared at 380°C for Sample 1, and at 400°C for Sample 2. These temperatures correspond to the third endothermic peak temperatures on the DTA curves. At 500°C, after the CO_2 evolution of the third maximum, 30% of the carbonates still remained in the calcined material of both samples (Figure 5b). The fourth maxima of both samples were observed at 600°C. The fourth maximum of Sample 2 appeared as a shoulder. At this temperature, Al ions enter into MgO. The fifth maxima were observed for both samples at 900°C, at which temperature the oxide solid solution decomposed to MgO and $MgAl_2O_4$).

The third maximum occurred at a higher temperature for Sample 2 than for Sample 1, and the third maximum overlapped the fourth one in the case of Sample 2. However, the decarbonation behaviors for Samples 1 and 2 are nearly the same, although there is the difference of crystallite size between them.

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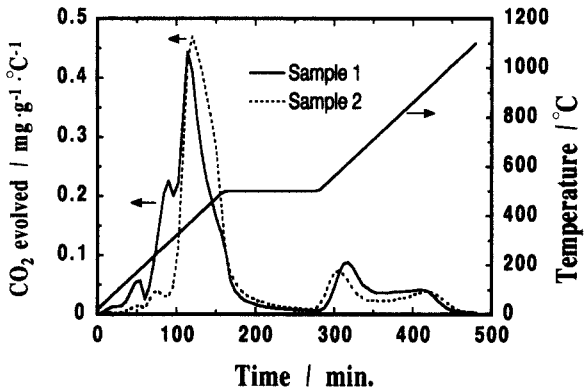

Figure 6. CO_2 evolution curves for HTlcs in the isothermal experiment at 500°C, on the way up to 1200°C at a heating rate of 3°C/min.

In order to observe the differences depending on Al contents, the decarbonation behavior of the HTlc with x = 0.25 was measured, and shown in Figure 5 together with the results from Samples 1 and 2. It can been seen that it was similar to that of Sample 1 up to 350°C. At the third maximum, the HTlc with x = 0.25 evolved nearly all the CO_2. Above 500°C, no maximum of CO_2 evolution was observed, although the CO_2 evolution curves of Samples 1 and 2 had two additional maxima at 600 and 900°C.

The amounts of CO_2 released from Samples 1 and 2 at 500°C decreased during a pause in heating at that temperature (Figure 6). After heating at 500°C for 2 hours, however, 20% of the carbonates still remained in the calcined material of both samples. This value agrees with that of Miyata (1980). When samples were heated again above 500°C, the fourth and fifth maxima on the CO_2 evolution curves were found. This result reveals that the remaining carbonate anions are trapped firmly inside the calcined material.

Infrared examination

The results of Samples 1 and 2 were nearly the same (Figure 7). The absorption bands for carbonate anions in the unheated HTlc are observed at 1360 (ν_3), 850 (ν_2) and 690 cm^{-1} (ν_4). Another ν_3 band also exhibits a shoulder near 1400 cm^{-1}. A very weak ν_1 band is observed at about 1080 cm^{-1}, although this vibration is inactive in the free anion. The asymmetry that is introduced into the simple trigonal structure of CO_3^{2-} by either mono- or bidentate ligand formation causes the ν_1 vibration to become infrared active, and the double degenerate ν_3 vibration to split into two components. Although the splitting of the ν_3 band and the appearance of the ν_1 band are observed, the effect is small. Therefore, we conclude that the symmetry of carbonate anions in the interlayer is close to that of the free anions [1415 (ν_3), 880 (ν_2) and 680 cm^{-1} (ν_4)], and that the shift of the ν_3 vibration from 1415 to 1370 cm^{-1} is due to a decrease in the force constant, as a result of hydrogen bonding between the carbonate anion and interlayer water.

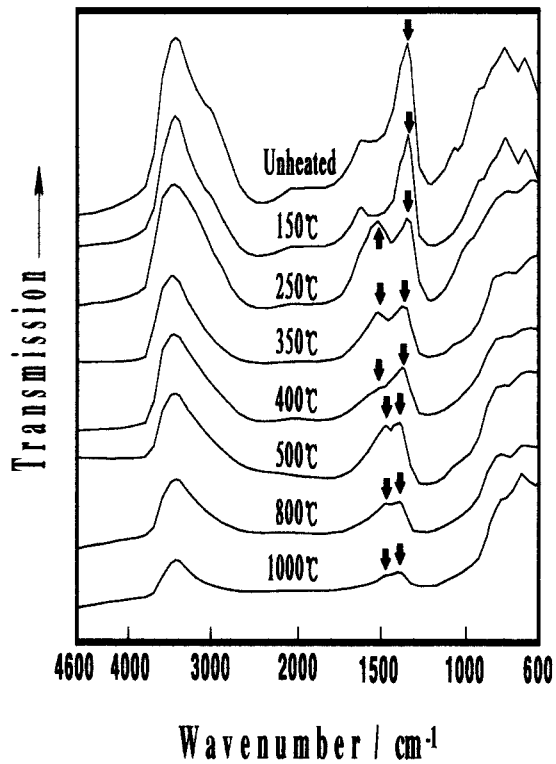

Figure 7. Infrared absorption spectra for Sample 1 heated at various temperatures in air for 0.5 h. The ν_3 bands of carbonate are marked.

Three other absorption bands are observed in the unheated HTlc spectra; the absorption band between 3200 and 3700 cm^{-1} is attributed to stretching vibrations of the OH groups of the brucite-like layer, the shoulder at around 3000 cm^{-1} to hydrogen bonding between water molecules and carbonates in the interlayer (Miyata 1975, Bish and Brindley 1977), and the band at 1625 cm^{-1} to the bending vibration of interlayer water.

When HTlc was heated to 250°C, the ν_3 band of carbonates split into two bands at 1330 and 1540 cm^{-1}. These two bands are in excellent agreement with those found for bridged bidentate CO_3 complexes. The carbonates exist as bridged bidentate ligands, between 200 and 400°C, at which interlayer water is lost. Above 500°C, the temperature at which the third step of CO_2 evolution is complete, the two ν_3 bands shifted to 1415 and 1480 cm^{-1}. The small degree of splitting of the ν_3 bands (65 cm^{-1}) indicates that the remaining carbonates coordinate weakly with cations.

The changes in HTlcs with lower Al contents (x = 0.20 and 0.25) were similar to those of Samples 1 and 2. However, the absorption band of the carbonate an-

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ions at 800°C was weaker than those of Samples 1 and 2.

Intercalation of HTlc derivatives with large anions via the calcined HTlc

Using HTlcs calcined at various temperatures, the effects of the remaining carbonates on the reconstruction was observed. Sample 1 was calcined in air for 0.5 hour, and the calcined material was then exposed to a solution of malonic acid and potassium ferrocyanide.

The basal spacings of the HTlcs intercalated with these anions increased with calcination temperature up to 800°C. Above 800°C, the basal spacings decreased with calcination temperature (Table 2).

The coexistence of the carbonate anion and the larger anion in the interlayer impedes orientation of the long axis of the larger anions perpendicular to the brucite-like layers. When the amount of remaining carbonates decreases with calcination temperature up to 800°C, the basal spacings of the reconstituting HTlcs then increase. On the other hand, calcination at temperatures above 800°C leads to the migration of Al ions from the Mg-Al oxide solid solution to spinel ($MgAl_2O_4$), and the Al content in the oxide solid solution then decreases. Consequently, since the charge density decreases, the malonate or ferrocyanide anions prefer to be oriented with their long axes parallel to the brucite-like layers, and the basal spacings of the reconstituting HTlcs decrease.

Table 2. Basal spacings of the HTlc intercalated with large anions.

Calcination temperature /°C	Basal spacing/nm	
	Malonate	Ferrocyanide
500	0.850	1.046
800	0.884	1.093
900	0.839	1.024

DISCUSSION

Upon the measurement of CO_2 evolved from Samples 1 and 2 during heating, two maxima were observed below 350°C, at which the structure of HTlc is maintained. Since the samples have excess carbonates as shown in Table 1, and the fact that Sample 1, which has a larger surface area, releases more CO_2 up to 350°C than does Sample 2, we attribute the CO_2 evolved in this temperature range to the excess carbonates that exist as CO_2 adsorbed on the surface.

The CO_2 evolution at the third maximum corresponds to the loss of CO_2 reported in previous papers, and represents the main CO_2 evolution in the present work. Before the main decarbonation occurs, the dehydroxylation of OH bound with Al occurs and the layered structures of HTlcs collapse. Some carbonate is then trapped inside decomposed material, thus impeding the decarbonation.

After heating for two hours at 500°C, just above the temperature of the third maximum, 20% of the carbonates still remain. The existence of the remaining carbonates is also confirmed by IR analysis and by the basal spacings of the reconstituted HTlcs mentioned above. These carbonates were evolved at the fourth and fifth maxima, at 600° and 900°C, respectively. The remaining carbonates are released when the migration of Al ions occurs brought on by the entrance of Al into MgO and the formation of $MgAl_2O_4$. The results of the IR analysis suggest that the carbonates are coordinated with cations, presumably Mg ions. The migration of Al ions can affect this coordination.

No maximum of CO_2 evolution above 500°C for HTlc with $x = 0.25$ is observed. This result indicates that a lower charge density, due to a lower Al content, leads to lower amounts of remaining carbonate anions. Accordingly, the positive charge in the local area around the Al ions can capture carbonates.

CONCLUSION

Twenty percent of the carbonates remain when HTlcs whose Al content is maximum, Al/(Mg + Al) = 0.33, are heated at 500°C for two hours. The remaining carbonates are released as Al ions in the calcined material migrate. An HTlc with lower Al, Al/(Mg + Al) = 0.25, released its carbonates more readily at 500°C.

In the method for reconstructing calcined and decarbonated HTlcs in the presence of solutions of large anions, it is desirable that no carbonate remains in the calcined material. The remaining carbonates affect the basal spacings of reconstituted HTlcs, for instance. Therefore, precautions must be taken with the reconstruction method.

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