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Characterization of Repeatedly Reconstructed Mg−Al Hydrotalcite-like Compounds: Gradual Segregation of Aluminum from the Structure

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Calcined hydrotalcite-like compounds (HTlcs) can be reconstructed to their original structure by exposure to an aqueous solution, provided that the original HTlcs contain volatile interlayer anions. In the present study, repetitive treatment consisting of calcination at 400 °C and subsequent reconstruction in an aqueous solution was carried out for Mg−Al−CO_3 HTlcs. Gradual changes in these HTlcs during repetitions of the treatment were observed. The quantity of interlayer carbonate anions decreased as the treatment was repeated. This finding indicates that the HTlcs were not completely reconstructed and that some Al was extracted from the structure during treatments, because the quantity of interlayer anions is proportional to Al content in HTlcs. The extracted Al increased with repetitions of the treatment, and spinel ($MgAl_2O_4$), whose Al content is much higher than HTlcs, was eventually detected after several repetitions as a consequence of segregation of the extracted Al phase. The spinel obtained by the repetitive treatments was highly crystalline and comparable to spinel obtained by calcination of Mg−Al coprecipitates above 1000 °C.

Introduction

Hydrotalcite-like compounds (HTlcs), which are also termed layered double hydroxides (LDHs), are a family of lamellar ionic compounds containing exchangeable anions. These compounds consist of positively charged hydroxide sheets with intercalated anions and water molecules, and can be represented by the general formula, $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}{}_{x/n}\cdot mH_2O]$, where M^{2+} and M^{3+} are di- and trivalent metal cations, respectively, that occupy octahedral positions in hydroxide layers, and A^{n-} is an interlayer anion.[1,2] HTlcs are an important class of materials currently receiving considerable attention as precursors of mixed oxide catalysts[3−7] and of microporous materials.[8−14] Regarding catalytic applications, discussion on the thermal decomposition materials of HTlcs has been extensively reviewed.[4,15,16] Also, calcined HTlcs have recently been found to be among the most effective catalysts for decomposition of N_2O, which is a contributor to the destruction of ozone and a relatively strong greenhouse gas.[17−20] In addition to these catalytic properties, thermal decomposition materials of HTlcs are utilized to synthesize novel intercalates of HTlc,[21,22] such as polyoxometalates that are expected to become a new class of microporous materials.[8−14] Mixed oxides obtained by calcination of HTlcs containing vaporizable anions at a moderate temperature can be reconstructed to the HTlc structure by exposure to an aqueous solution. The mixed oxides regenerate with water and the anions in the aqueous solution. Replacing vaporizable anions such as $CO_3{}^{2-}$ by the desired anions is an easy method of intercalating various anions. Therefore, thermal decomposition of HTlcs is a highly significant process for both synthesis of catalysts and reconstruction of intercalation.

Because of the interest in calcined materials of HTlc, many studies have been reported on the thermal decomposition behavior of HTlcs, especially in Mg/Al/

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CO_3 systems.[4,7,21,23−30] An MgO phase with rock-salt structure is detected by X-ray diffraction (XRD) when Mg−Al−CO_3 HTlc is heated at 400−800 °C; the smaller lattice parameter of the MgO phase than that of pure MgO indicates the presence of Al in the MgO lattice. When calcined above 900 °C, the HTlcs decompose to pure MgO and spinel ($MgAl_2O_4$). Products calcined below 800 °C are reported to rehydrate to HTlcs.[21] Further studies have generally supported the conclusions of earlier discussion on thermal decomposition, but suggest that it is more complex than previously thought. Lattice parameter ***a*** of Mg−Al−CO_3 HTlcs has been reported to increase at 300 °C, indicating that some Al has been extracted from the structure.[7] Moreover, tetrahedral Al was detected by solid-state NMR in MgO phases obtained by calcination of HTlcs.[7,26,27,29,30] These facts indicate the presence of a small amount of an amorphous phase of spinel-based aluminas such as γ-Al_2O_3.[7,29,30] It is reported that HTlc reconstruction from the MgO phase is not totally reversible as a result.[7] However, the segregated phase of Al, although its existence has been suggested, has not been observed directly.

We previously found that when HTlcs containing organic anions were used as the original HTlcs, the spinel phase formed at 400 °C from the reconstructed HTlcs as a consequence of reactions occurring between edges of crystallites in certain conditions.[31] Possibly, spinel formation at such low temperature is related to the extracted Al from thermal decomposition of HTlcs containing organic anions. However, we could not obtain spinel in the same way when Mg−Al−CO_3 HTlc was used as the original HTlc. In that study, we used only HTlcs with a Mg:Al ratio of 2:1, and made only one reconstruction. In the present study, we demonstrate that several repetitions of alternating calcination and reconstruction produce a spinel at 400 °C, even when Mg−Al−CO_3 HTlcs are used as the original HTlcs. The aim of the present study was to examine the complex thermal decomposition behavior in repeatedly reconstructed HTlcs by using HTlcs with various Mg:Al atomic ratios and crystallinities.

Experimental Section

Synthesis of Starting Materials. The initial HTlcs for reconstruction were prepared by the coprecipitation method. An aqueous solution of $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ ($Mg^{2+} + Al^{3+} = 0.5$ mol L^{-1}) was continuously added to a Na_2CO_3 aqueous solution ($CO_3^{2-}/Al^{3+} = 1$) at a flow rate of 50 mL h^{-1}. The mixture was maintained at pH 10 by dropwise addition of a NaOH aqueous solution with vigorous stirring. The Mg:Al atomic ratios in the initial solutions were adjusted to 1:2, 1:1, 2:1, 3:1, and 4:1. The precipitate was isolated by centrifuging, washing thoroughly with distilled water, and drying at 80 °C. When the Mg:Al ratios of the initial solutions were 1:2 and 1:1, the products were mixtures of Mg−Al−CO_3 HTlc and gibbsite, as mentioned later.

Well-crystallized Mg−Al−CO_3 HTlc with Mg:Al = 2:1 was prepared by hydrothermal treatment at 150 °C and 500 kPa for 12 h, with coprecipitation product and its mother liquor.

Reconstruction Procedure. First, we examined effects of crystallite size on the thermal reaction sequence in repeatedly reconstructed HTlcs, using Mg−Al−CO_3 HTlcs with Mg:Al = 2:1, that is, samples prepared by both coprecipitation and by coprecipitation with subsequent hydrothermal treatment. In addition, because sample powders became lumpy to some extent at each calcination, the difference between samples ground (with a mortar and pestle) and unground just after each calcination was also examined. Therefore, for samples with Mg:Al = 2:1, we conducted repetitive calcination and reconstruction in 3 ways. For the sample prepared by coprecipitation, repetition of calcination and reconstruction was performed in two ways: (a) each calcination was not followed by grinding and each reconstruction was performed using the as-calcined product (series I); and (b) each calcination was followed by careful grinding and each reconstruction was performed using the well-ground calcined product (series II). For well-crystallized sample, no grinding procedure, the same way as series I, was performed during the repeated treatments (series III). Each calcination was conducted at 400 °C for 2 h, followed by reconstruction in a Na_2CO_3 aqueous solution overnight (>18 h); the quantity of carbonate anions was more than twice that necessary for stoichiometric anion exchange. The calcination and reconstruction steps were repeated six times; carbonate content of the reconstructed samples was measured to monitor how well the samples were reconstructed to Mg−Al−CO_3 HTlc.

Second, we examined the effect of different Mg:Al atomic ratios. Coprecipitation samples with Mg:Al ratios between 1:2 and 4:1 (1:2-sample, 1:1-sample, 2:1-sample, 3:1-sample and 4:1-sample) were calcined at 400 °C for 2 h, followed by reconstruction in distilled water without grinding after each calcination. The calcination and subsequent reconstruction treatment was repeated several times.

Characterization. XRD patterns of samples were obtained using a Rigaku Geigerflex RAD-IIA with CuKα radiation. Calcined samples for XRD study were placed quickly in the sample holder and measured immediately to minimize any rehydration effect. The morphology of samples was observed using a Philips CM30 transmission electron microscope (TEM) operating at 200 kV; samples were prepared by deposition from an aqueous suspension onto a holey carbon film. The Mg:Al atomic ratios of samples were measured by X-ray microanalysis with an energy dispersive spectrometer (EDS) attached to the TEM using an EDAX PV9900. Surface areas were measured by the Brunauer−Emmett−Teller (BET) method with nitrogen, using a Carlo Erba Sorptomatic 1800; samples were evacuated at room temperature for 2 h before measurement. Carbonate contents were determined by titration, in which CO_2 that evolved from samples as they dissolved in a sulfuric acid solution was absorbed in an aqueous solution of NaOH and $BaCl_2$.

Results

Effects of Crystallite Size and Grinding on Repetitive Reconstruction. We observed changes related to crystallite size and grinding in Mg−Al−CO_3 HTlcs with Mg:Al = 2:1 during repetitive calcination at 400 °C and subsequent reconstruction in a Na_2CO_3 aqueous solution. Both the sample prepared by coprecipitation and the well-crystallized one were identified as Mg−Al−CO_3 HTlc by XRD. Crystallites of the sample prepared by coprecipitation were small (25−50 nm in diameter; surface area, 53 m^2 g^{-1}) and irregular flakes, whereas the well-crystallized sample consisted

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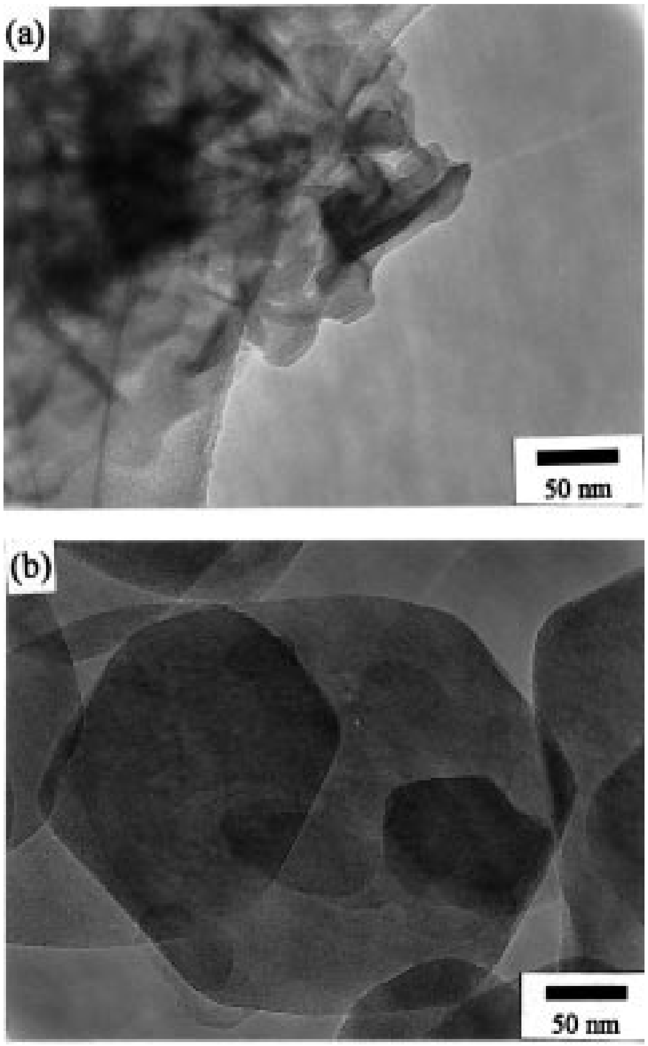

Figure 1. TEM of (a) HTlc prepared by coprecipitation and (b) well-crystallized HTlc.

of hexagonal crystals of 100–300 nm, with a surface area of <3 m^2 g^{-1} (Figure 1).

Figures 2 and 3 show changes in XRD patterns of samples with Mg:Al = 2:1 when the calcination and reconstruction steps were repeated. In series I, in which the sample prepared by coprecipitation was used and no grinding was performed, spinel formed at the fourth calcination and HTlc peaks became wider and lower with more repetitions, indicating that crystallite size was becoming smaller and that the quantity of reconstructed HTlc was decreasing (Figure 2). On the other hand, in series II and III, spinel formed at later repetitions of the calcination and subsequent reconstruction. In series II, which was different form series I in grinding procedure, spinel did not form at the fourth calcination, and XRD peaks of spinel were very faint even at the sixth calcination (Figure 3). In series III, which was different from series I in starting size of crystallites, spinel did form at the sixth calcination, although very weak spinel peaks were observed at the fifth calcination. In both series II and III, peaks of the HTlcs at the sixth reconstruction were sharper and larger than those in series I.

Observation by TEM indicates that crystallites of HTlc became smaller as calcination and reconstruction were repeated. In particular, the well-crystallized sample lost its hexagonal shape. No Al-rich phase that might be spinel nuclei or spinel was observed in any sample, even after spinel formation was observed by XRD. The Al-rich phase might be mixed in aggregated crystallites of HTlc, as seen in Figure 1, making it difficult to identify this phase from the aggregated mass. The latter seemed to be the same in all reconstructed samples, except in the size of platy crystallites, and their Mg:Al ratios were always nearly 2:1.

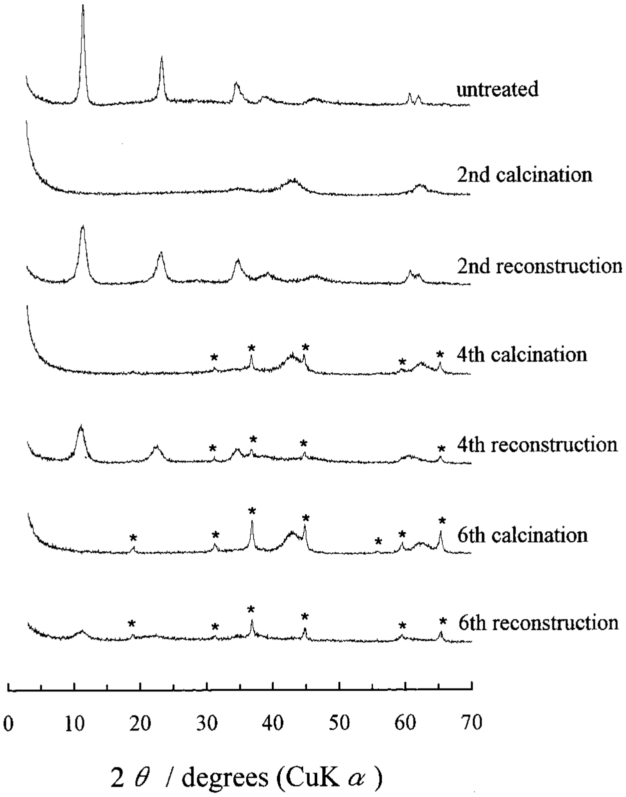

Figure 2. XRD patterns of products in series-I. Treatment by which each product was obtained is indicated, and diffraction peaks corresponding to spinel are labeled with an asterisk.

When samples in series I were put into a sulfuric acid aqueous solution, insoluble residues were observed in samples reconstructed more than 3 times. These residues were identified as spinel by XRD, and the spinel consisted of uniformly sized particles of about 30 nm (Figure 4). The quantity of spinel increased gradually with repeated calcination and subsequent reconstruction (Table 1). A sample reconstructed 3 times did not show XRD peaks of spinel, as shown in Figure 2, but this result was due to the extremely small amount of spinel present. When the spinel in the 3-times reconstructed sample was concentrated, the spinel showed sharp XRD peaks that indicated its high crystallinity; the Mg:Al ratio was 1:2 as in the spinel in the 4-times reconstructed sample shown in Figure 4.

Figure 5 shows the changes in carbonate contents in reconstructed products of series I, II, and III. As shown in Figure 2, until spinel formed, each sample was reconstructed to HTlc and no other phase was observed by XRD. However, carbonate content decreased with increasing numbers of reconstructions for all samples, indicating that samples were not completely reconstructed to Mg–Al–CO_3 HTlc and that an amorphous phase not detected by XRD was increasing. Curves of carbonate content for series II and III were almost the

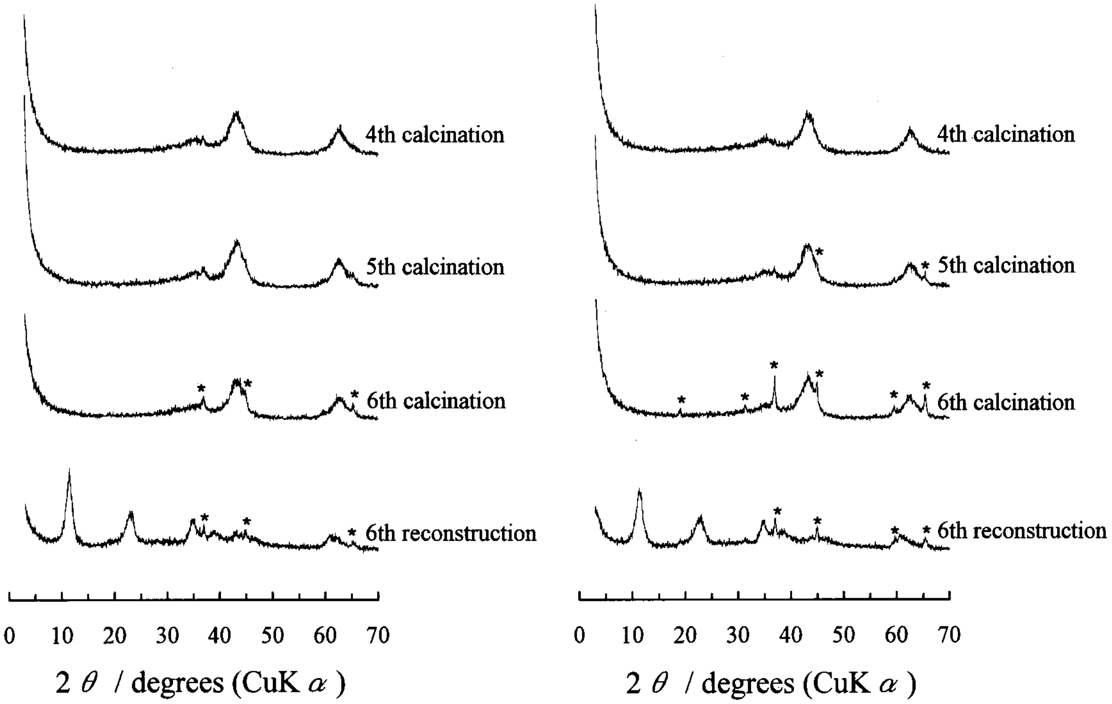

Figure 3. XRD patterns of products in series II (left series) and in series III (right series). Treatment by which each product was obtained is indicated, and diffraction peaks corresponding to spinel are labeled with an asterisk.

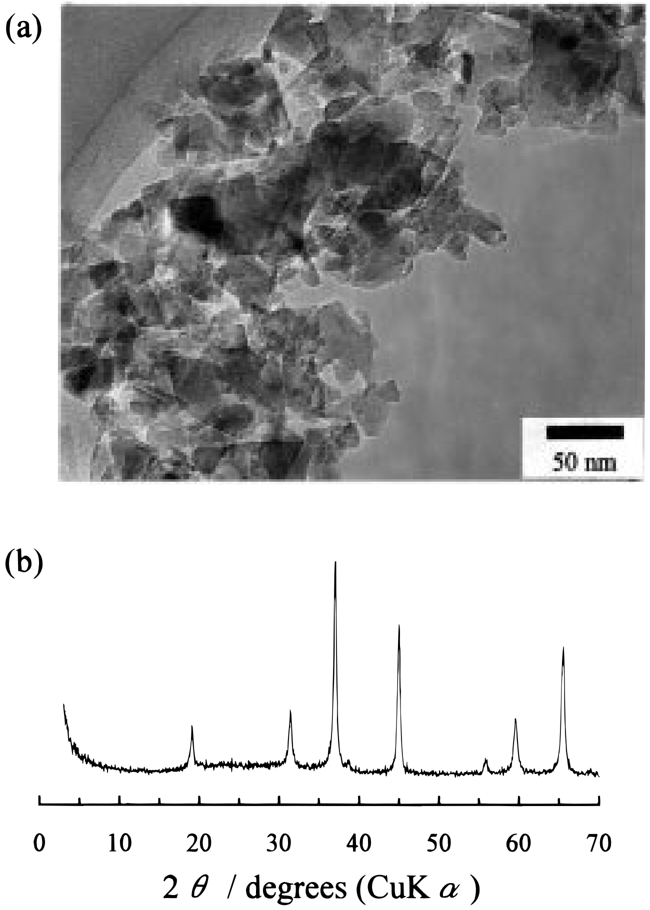

Figure 4. Residue insoluble in sulfuric acid solution, obtained from fourth reconstruction of samples in series I: (a) TEM photograph; (b) XRD pattern.

same. Carbonate content in series I showed the largest decrease after 4-times reconstruction, when spinel began to be observed by XRD.

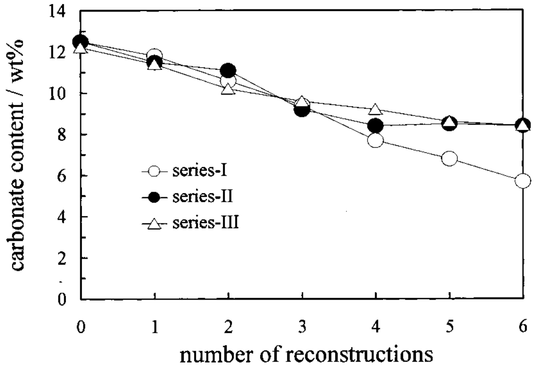

Figure 5. Changes in carbonate content in reconstructed products in series I, II, and III.

Table 1. Quantity of Spinel in Reconstructed Products in Series I

number of reconstructions	quantity of spinel (wt %)
3	0.7
4	3.0
5	11.5
6	15.9

Effect of Mg:Al Ratio on Repetitive Reconstruction. To examine the effect of Mg:Al ratios on changes in repeatedly reconstructed HTlcs, samples were calcined at 400 °C, followed by reconstruction in distilled water. The process was repeated several times. Grinding was not conducted at any step. The atomic ratio of Mg:Al was varied beyond the Mg:Al ratio of 2:1, which is the limit at which HTlc can be coprecipitated. Mg−Al coprecipitates with Mg:Al = 1:1 and 1:2, which were mixtures of HTlc and gibbsite, were also examined. These ratios are interesting because the stoichiometric Mg:Al atomic ratio of spinel is 1:2.

The result for the 2:1-sample was the same as that of series I shown in Figure 2, although there were differences between reconstruction in Na_2CO_3 aqueous

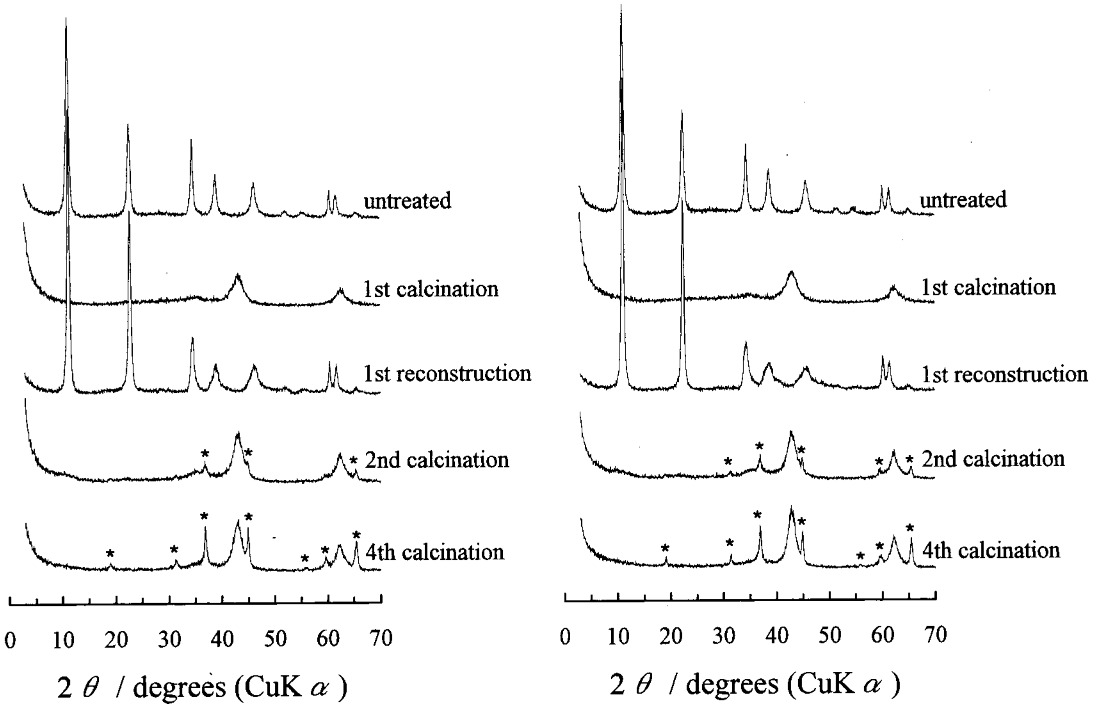

Figure 6. XRD patterns of products obtained from 3:1-samples (left series) and from 4:1-samples (right series). Treatment by which each product was obtained is indicated, and diffraction peaks corresponding to spinel are labeled with an asterisk.

solution and in distilled water. Figure 6 shows XRD patterns of products from 3:1- and 4:1-samples after repeated calcination at 400 °C and reconstruction in distilled water. These three samples (2:1, 3:1, and 4:1) contained only one phase of HTlc, based on XRD results. When these samples were calcined at 400 °C the first time, all were transformed to the MgO phase. On first reconstruction in distilled water, they were reconstructed to products with the same XRD patterns as the original ones. Those products from the 3:1- and 4:1-samples coagulated to a hard mass whereas the 2:1-sample became granular. When the samples were calcined and reconstructed repeatedly, spinel was observed by XRD at the second calcination in the 3:1- and 4:1-samples, and at the fourth calcination in the 2:1-sample. Spinel from the 4:1-sample gave slightly sharper XRD peaks than those from the 3:1-sample at the second calcination.

Figure 7 shows XRD patterns of products from the 1:1- and 1:2-samples. Both samples contained two phases of HTlc and gibbsite. When they were calcined at 400 °C, the 1:2-sample converted to a poorly crystallized spinel with very broad and indistinct XRD peaks, whereas the 1:1 product showed very broad and vague XRD peaks of both the MgO phase and poorly crystallized spinel. At subsequent reconstruction, the 1:1-sample product showed XRD patterns of HTlc with much broader and smaller peaks than those of the original sample, and gibbsite peaks were lost. The first reconstruction of the 1:2-sample produced an XRD pattern with broad and weak peaks identified as poorly crystallized spinel and HTlc. During repetitive treatment of calcination and reconstruction, both 1:1- and 1:2-samples gradually became granular, and crystalline spinel did not form even when alternate calcination at 400 °C and reconstruction were repeated 7 times. These coprecipitates did not provide a crystalline spinel until they were calcined at higher temperatures, as Bratton[32] reported (Figure 8). Note that a temperature of 1000 °C was necessary to obtain from the 1:2-sample a well-crystallized spinel comparable to that obtained from 2:1-, 3:1-, and 4:1-samples by repetitive calcination at 400 °C and subsequent reconstruction (see Figures 4b and 8).

Discussion

The present study confirmed that reconstruction of calcined Mg−Al−CO_3 HTlc is not totally reversible because:

(1) carbonate content in reconstructed materials decreases with increasing repetitions of calcination at 400 °C followed by reconstruction in a Na_2CO_3 aqueous solution; and

(2) spinel is formed from Mg−Al−CO_3 HTlcs when calcination at 400 °C and subsequent reconstruction are repeated several times.

The first fact indicates that Al is extracted from the structure of HTlc. The quantity of interlayer anions is proportional to that of Al in the structure of HTlc. Because HTlcs have a high affinity for carbonate anions, intercalation of anions other than carbonate into repeatedly reconstructed HTlcs is unlikely to occur when enough carbonate anions are present in the solution used for reconstruction.

The quantity of extracted Al increases with repetition of calcination and reconstruction, as indicated by the carbonate content. Spinel formation from HTlcs needs condensation of Al, because the Mg:Al ratio of spinel is 1:2 compared with a ratio of 2:1 even in HTlcs containing the maximum Al content. Extracted Al can be a source of spinel formation, although that phase is not detected by XRD at first calcination and subsequent reconstruction. We conclude that the extracted Al phase

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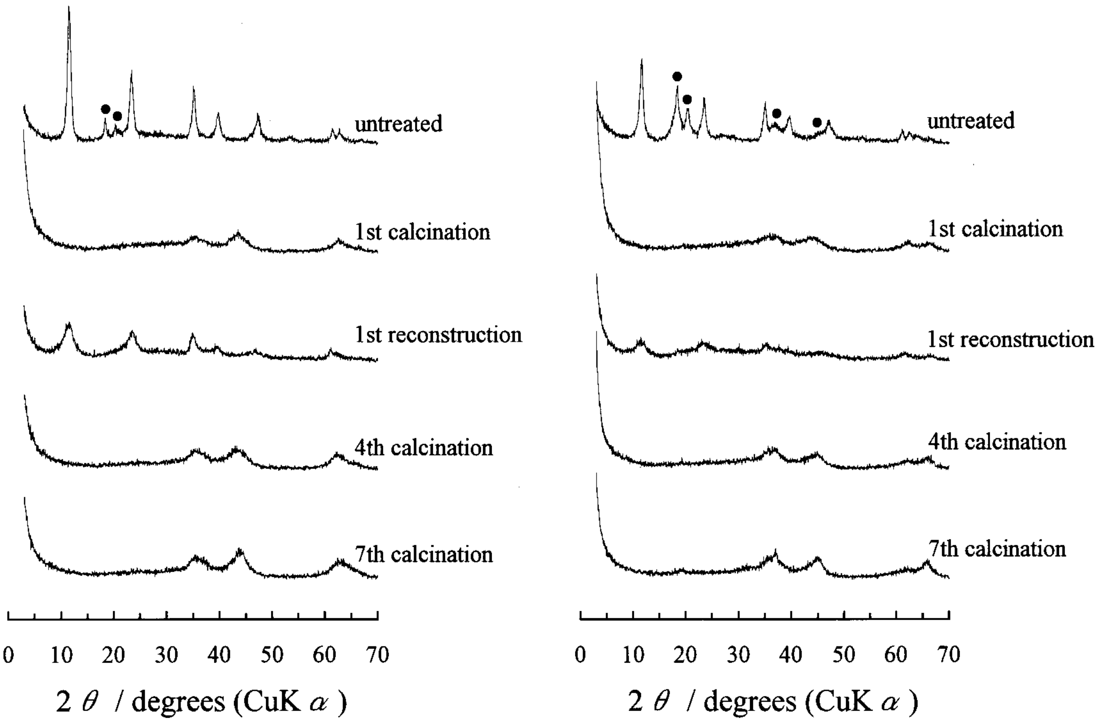

Figure 7. XRD patterns of products obtained from 1:1-samples (left series) and from 1:2-samples (right series). Treatment by which each product was obtained is indicated, and diffraction peaks corresponding to gibbsite are labeled with a solid circle.

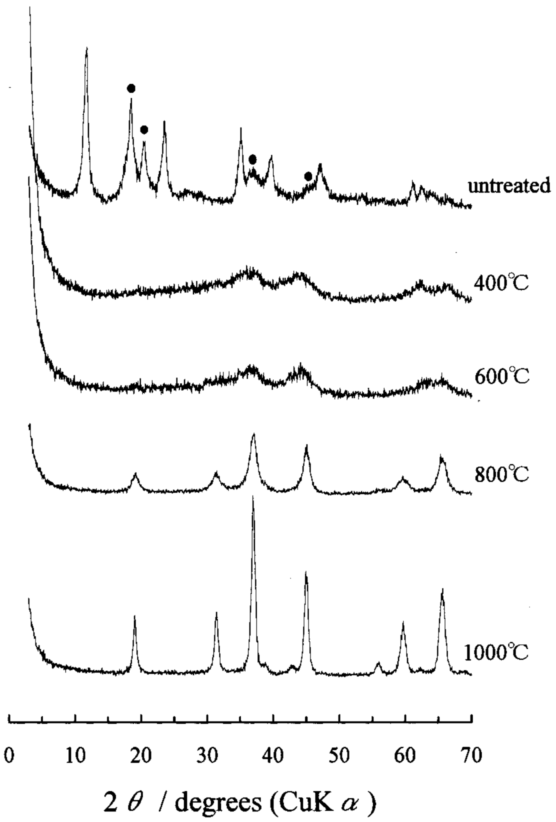

Figure 8. XRD patterns of 1:2-samples calcined at the temperatures indicated. Diffraction peaks corresponding to gibbsite are labeled with a solid circle.

becomes spinel nuclei not detected by XRD at first, and that the nuclei form spinel gradually during the repetitions of calcination and reconstruction. In the present study, the following observations affected formation of spinel, and are helpful to understand the mechanism of spinel formation:

(1) spinel formation from HTlcs with larger crystallite sizes needs more repetitions of calcination and subsequent reconstruction;

(2) grinding after each calcination hinders spinel from forming;

(3) coprecipitates with Mg:Al = 1:1 and 1:2 that contain two crystalline phases of HTlc and gibbsite do not produce crystalline spinel by repetitive calcination at 400 °C and subsequent reconstruction; and

(4) spinel formation from 4:1- and 3:1-samples occurs at earlier repetitions of calcination and subsequent reconstruction than from 2:1-samples.

When some amount of Al is extracted from the structure, it is possible that the extracted Al is present around the edges of crystallites of calcined HTlcs. Indeed, Rebours et al. reported that Al-rich phases, likely aluminas or magnesium aluminates, are found in the surface region of the calcined Mg−Al HTlc using XPS measurements and alkaline reaching, and that tetrahedral Al, which has been reported in many other previous works,[7,26,27,29,30] is concentrated in the surface region.[33] Therefore, high Al-content regions are generated between the crystallites, and nuclei of spinel can form there. If the crystallites are isolated or separated (although complete isolation and separation of crystallites is virtually impossible), extracted Al might easily reenter the structure when reconstructed. Thus, we conclude that contact among platelets of crystallite is needed to form spinel nuclei at calcination. Observation 1 does not favor nuclei formation: the contact area becomes small when crystallites are large because their surface area is small, as already mentioned in the *Results*. The reason for delay of spinel formation for well-crystallized HTlc is that crystallites of well-crystal-

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lized HTlc need more repetitions of calcination and reconstruction to become a smaller size, comparable to that of HTlc prepared by coprecipitation. Indeed, the crystallite size decreases with repetitions of calcination and reconstruction, as mentioned in the *Results*.

Observation 2 might result from a cause related to regions between crystallites. In this case, the weak bonding between adjacent crystallite platelets could be broken by grinding. Alternatively, spinel nuclei formed between the edges could be weak enough to be broken mechanochemically, just like deformation of the crystal structure of kaolinite by grinding.[34,35]

From Observation 3 we conclude that overabundance of spinel nuclei hinders further crystal growth. Migration of Mg and Al cations is needed for crystal growth of spinel nuclei. Calcination is undoubtedly accompanied by migration of Mg and Al cations, because double hydroxide layers of HTlcs lose nearly half of oxygen atoms by calcination at 400 °C due to dehydroxylation. Also, reconstruction is accompanied by migration of cations, because, when reconstructed, calcined HTlcs resume the same quantity of oxygen atoms that are lost at the calcination. Therefore, migration of Mg and Al ions occurs actively every time samples are calcined or reconstructed, and the effect of the migration by the repetitive treatment can be comparable to that of calcination at a high temperature. Indeed, spinel obtained from the 2:1-sample by the repetitive treatment was as highly crystallized as that obtained by calcination of the 1:2-sample at 1000 °C (Figures 4 and 8). In the 1:1- and 1:2-samples, HTlc reacts with gibbsite when calcined, and most of the material is converted to very small poorly crystallized spinel particles at first calcination; the portion that can be reconstructed to HTlc becomes very low, as shown in Figure 7. Thus, in Observation 3, migration of cations is negligible during further repetitions of calcination at 400 °C and reconstruction, such that further crystal growth of spinel nuclei does not occur.

Observation 4 suggests that Mg and Al cations migrate more easily at calcination and reconstruction when the Al content decreases, because the property of reconstruction originates from magnesium oxide, not from aluminum oxide, as Sato et al. reported.[36] Therefore, we conclude that Al cations in HTlc with lower Al content are extracted from the structure of HTlc more easily because of the more active migration of cations. In addition, the large contact area of crystallites caused by tight coagulation of the 4:1- and 3:1-samples would help earlier formation of spinel.

Conclusions

The present study demonstrates that spinel is formed from Mg−Al−CO_3 HTlcs when calcination at 400 °C and subsequent reconstruction are repeated. Some Al is extracted from the structure at calcination, and the amount of the extracted Al increases with repetitions of calcination and reconstruction. A high-Al-content phase originating from the extracted Al provides spinel nuclei. Migration of Mg and Al cations occurs both when HTlcs are calcined and reconstructed, and leads to crystal growth around the nuclei. Spinel formation is enhanced by smaller crystallite size and by higher Mg:Al atomic ratios. Grinding after each calcination and mixing with gibbsite hinders crystalline spinel formation.

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