FORMATION OF SPINEL FROM A HYDROTALCITE-LIKE COMPOUND AT LOW TEMPERATURE: REACTION BETWEEN EDGES OF CRYSTALLITES

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Abstract—The thermal decomposition behavior of hydrotalcite-like compounds (HTlcs) prepared by reconstruction of calcined HTlcs is described. From the results of X-ray diffraction (XRD), it seems that dicarboxylate intercalates of HTlc calcined at 500 °C are completely reconstructed to Mg-Al-CO_3 HTlc by exposure to aqueous Na_2CO_3. However, the Mg-Al-CO_3 HTlc reconstructed under particular conditions yields spinel ($MgAl_2O_4$) at 400 °C. This temperature is very low, because Mg-Al-CO_3 HTlc that has been reported yields spinel at 900 °C after forming a Mg-Al double oxide. The reconstructed Mg-Al-CO_3 HTlc that yields spinel at 400 °C is obtained when the following conditions are fulfilled: the crystallites of the starting dicarboxylate intercalates are coagulated tightly and the calcined HTlcs and reconstructed materials are not ground. The Mg-Al-CO_3 HTlc reconstructed under these conditions contains only 55–70% of carbonate anions required by stoichiometry. Therefore, we conclude that the transformation of reconstructed Mg-Al-CO_3 HTlc to spinel at 400 °C is the result of a reaction occurring between edges of crystallites.

Key Words—Double Hydroxide, Grinding, Hydrotalcite, Reconstruction, Spinel, Thermal Decomposition.

INTRODUCTION

Hydrotalcite-like compounds are a layered double hydroxide, with the general formula $[M^{II}_{1-x} M^{III}_x(OH)_2][A^{n-}_{n/x} \cdot zH_2O]$. Here M^{II} and M^{III} are di- and trivalent metal cations that occupy octahedral positions in hydroxide layers, x is atomic ratio of $M^{III}/(M^{II} + M^{III})$, A^{n-} is an interlayer anion and z is the number of interlayer water molecules (Ingram and Taylor 1967; Allmann 1968). The atomic ratio of M^{II}:M^{III} varies from 4:1 through 2:1 ($0.20 \leqq x \leqq 0.33$) for the Mg-Al system (Miyata 1980). There is no limitation as to the nature of interlayer anions. Derivatives of HTlcs with various anions have been synthesized and their physicochemical properties studied from the viewpoint of a chemical curiosity, catalysis, microporous material and layered inorganic host of electroactive and photoactive anions (Giannelis et al. 1987; Itaya et al. 1987; Drezdzon 1988; Cavani et al. 1991; Constantino and Pinnavaia 1995; Yun et al. 1995).

The coprecipitation method was the first way discovered to prepare HTlcs, but this was useful to synthesize only compounds with simple intercalates like chloride and nitrate forms. Other anions were intercalated into these simple HTlcs by anion exchange. However, HTlcs are highly selective for carbonate anion and tend to incorporate carbonate resulting from CO_2 in air. This procedure of direct synthesis and ion exchange is cumbersome because CO_2 must be totally excluded at each stage. Reconstruction of calcined Mg-Al-CO_3 HTlc in aqueous solutions of appropriate anions has been reported to be a more facile method of intercalating various anions, particularly large ones, into HTlcs (Chibwe and Jones 1989a, 1989b; Dimotakis and Pinnavaia 1990; Narita et al. 1991). In this method, the thermal decomposition process is an important area for investigation.

There have been many studies of thermal decomposition, although their major purpose was to evaluate the potential use of calcined HTlc as a solid base-catalyst (Rouxhet and Taylor 1969; Miyata 1980; Pesic et al. 1992; Rey et al. 1992; MacKenzie et al. 1993; Hibino et al. 1995; Hudson et al. 1995). The thermal decomposition sequence of Mg-Al-CO_3 HTlc has been reported as follows. Mg-Al-CO_3 HTlc converts to Mg-Al double oxide at 400 °C. Migration of Al ions from the Mg-Al double oxide phase into a spinel phase ($MgAl_2O_4$) occurs at 900 °C, and then the double oxide decomposes to spinel and MgO at that temperature. Moreover, the double oxide obtained between 400 and 800 °C can be reconstructed to the HTlc structure by exposure to aqueous solutions. The reaction is applied for new intercalation method, as mentioned above. However, the decomposition behavior of the reconstructed HTlcs has scarcely been reported to date.

In a previous paper, we reported on the decarbonation behavior of reconstructed Mg-Al-CO_3 HTlcs (Hibino et al. 1996). During that study, we noted that some Mg-Al-CO_3 HTlcs reconstructed from the organic anion derivatives yielded spinel at 400 °C in 1 step, together with MgO phase. Spinel formation from HTlcs or other precursors at the lower temperature had not yet been reported.

Mg-Al spinel is known to have many prominent properties: high melting point, high hardness, high chemical stability and good optical transmission. Spinel ceramic has served as structural material for very high temperature, such as lining of rotary furnaces. Recently, it is also expected to be a transparent ma-
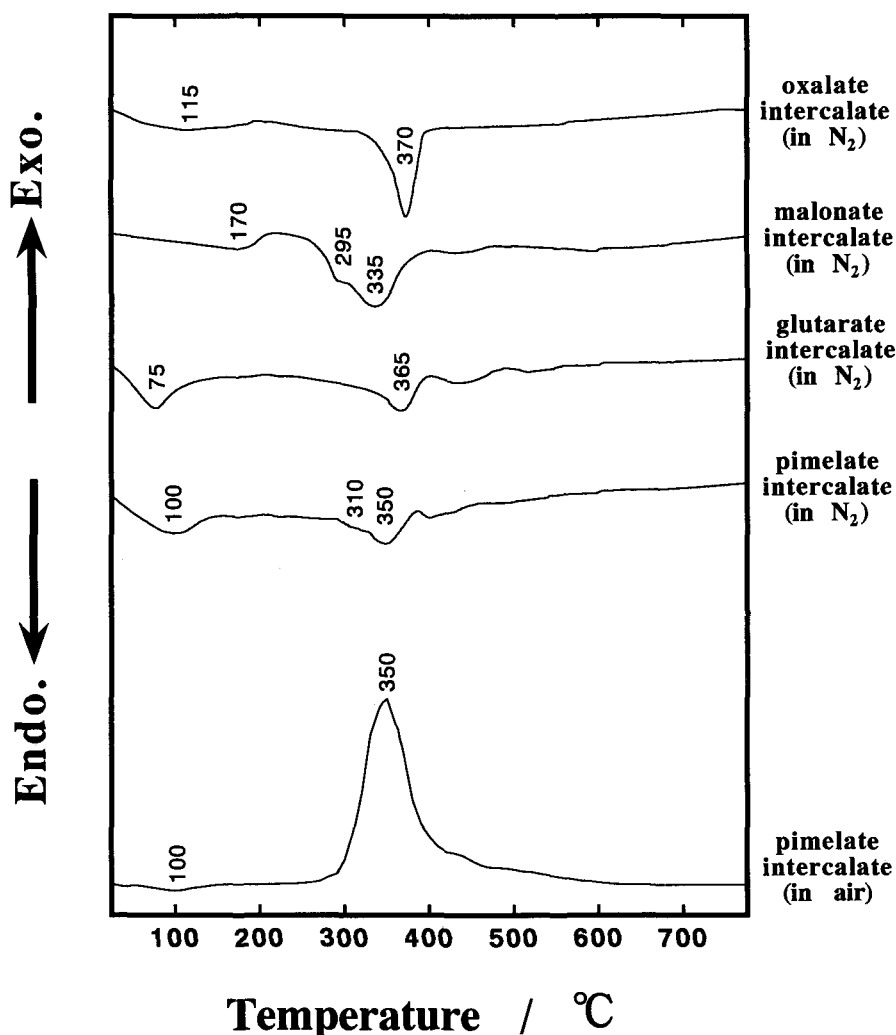
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Figure 1.　DTA curves (heating rate 3 °C min⁻¹) for dicarboxylate intercalates of HTlc. Scale of the DTA curve for pimelate intercalate in air is reduced to half that of the others.

terial for high temperature. Mg-Al spinel powders for sintering are often prepared by solid-state reaction between high purity MgO and Al_2O_3. The temperature required for this reaction is usually above 1600 °C in commercial practice and at least 1400 °C even when submicron reactants are used in the laboratory. Coprecipitated hydroxide mixture, hydrotalcite and gibbsite $Al(OH)_3$, is a more effective precursor to reduce the spinel-formation temperature. Calcining them above 800 °C affords reactive spinel powder for sintering (Bratton 1969; Gusmano et al. 1991; Hokazono et al. 1991): the spinel obtained by this reaction does not exhibit 6 relatively strong reflections of X-ray pattern until 800 °C, although 2 very small and broad peaks are detected at 400 °C. Note that it is 400 °C where our method of work provides highly crystalline spinel comparable to spinel obtained from coprecipitated hydroxide mixture at 800–1000 °C. Therefore, the prep-

aration method of our study is markedly beneficial to saving energy, compared with previous methods. In the present study, the conditions and mechanisms of spinel generation from reconstructed HTlcs at low temperature are investigated.

EXPERIMENTAL

HTlcs intercalated with organic anions were prepared by the coprecipitation method. Aliphatic dicarboxylic acids chosen in this study were of the general formula $HOOC(CH_2)_nCOOH$, where $n = 0$ (oxalic), 1 (malonic), 2 (succinic), 3 (glutaric), 4 (adipic) and 5 (pimelic) acids. An aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ ($Mg^{2+} + Al^{3+} = 0.5$ mol l⁻¹) was continuously added (250 mL total) to 500 mL each of dicarboxylic acid aqueous solution at a flow rate of 50 mL h⁻¹. The Mg:Al ratio of this solution was adjusted to 2:1. The mixture was maintained at
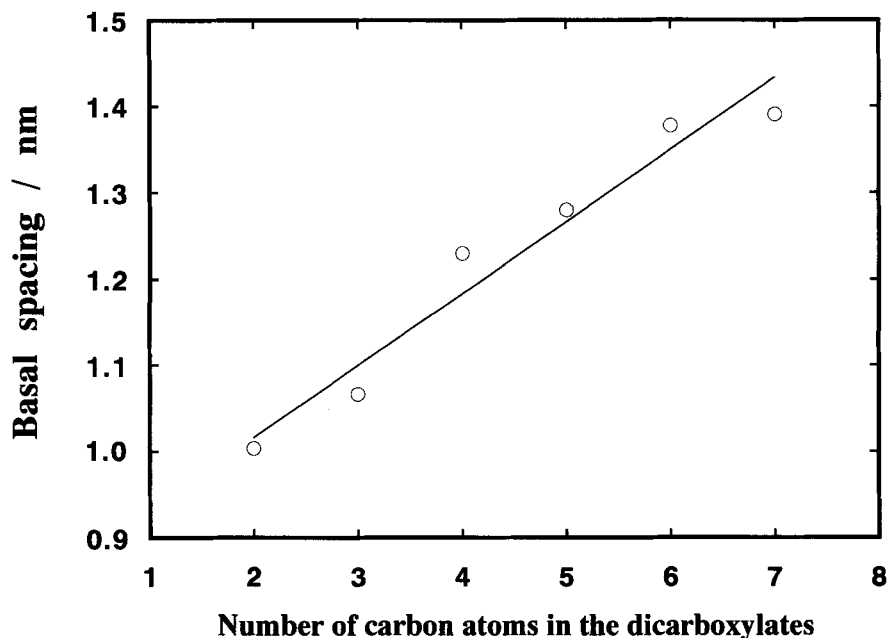
Figure 2. Basal spacing versus carbon number for dicarboxylates in HTlc.

pH = 10 by dropwise addition of a NaOH solution with vigorously stirring. The precipitate was washed ultrasonically with distilled water and then centrifuged. This washing procedure was repeated more than 10 times to wash thoroughly. Synthesis was performed under nitrogen flow to avoid contamination of carbonate from air. Also, the transferring of the materials and distilled water into centrifuge tubes and capping was carried out in N_2. The distilled water used for washing had been boiled to decarbonate it. The thoroughly washed precipitates were partially dried in N_2 and then completely dried in air at 80 °C. We tested whether drying the pimelate intercalate by another method altered its thermal decomposition behavior. In this alternative drying procedure, the wet precipitates, after the last distilled water wash had been poured off were twice washed with ethanol and centrifuged to replace remaining water, then dried at room temperature in N_2. The Mg-Al-CO_3 HTlc, which served as a reference, was prepared in the same way.

These dicarboxylate intercalates of HTlc were heated to 500 °C at a heating rate of 10 °C min^{-1} and kept at that temperature for 30 min. The calcination materials were then added to Na_2CO_3 aqueous solution for 1 d to reconstruct to the HTlc structure. The amount of Na_2CO_3 added corresponded to 200% of that needed for reconstruction to Mg-Al-CO_3 HTlc. Calcination of the starting HTlcs was carried out under 2 different atmospheres (N_2 and air), to examine the effect of dicarboxylate anion combustion on reconstructed HTlcs. Moreover, to examine mechanochemical effects, some calcined materials were hand-ground with an agate

mortar before reconstruction in Na_2CO_3 aqueous solution; others were not. Reconstructed HTlcs were washed with distilled water and air dried at 80 °C. Further, some reconstructed materials were also ground; others were not.

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) of samples was carried out under both N_2 and air at a heating rate of 3 °C min^{-1}. Powder XRD patterns were obtained with Cu$K\alpha$ radiation. Infrared (IR) absorption spectra were obtained for the range of wave numbers from 400 to 4600 cm^{-1} with the KBr pellet technique. Carbon and carbonate contents were measured by a combustion method. The morphology of samples was observed with a transmission electron microscope (TEM). The Mg:Al ratios of samples were measured by X-ray microanalysis with an energy dispersive spectrometer (EDS) attached to the TEM.

RESULTS

Thermal Decomposition of Dicarboxylate Intercalates

In nitrogen, the DTA curves of dicarboxylate intercalates showed 2 endothermic peaks, one below 200 °C and the other at 300–400 °C (Figure 1). In some cases, the second peak at 300–400 °C had shoulders. The DTA curve of pimelate intercalate in air exhibited a large exothermic peak at around 350 °C due to combustion of interlayer anions.

XRD analysis showed that basal spacing of dicarboxylate intercalates were in proportion to the number of carbon atoms in the dicarboxylates (Figure 2), as
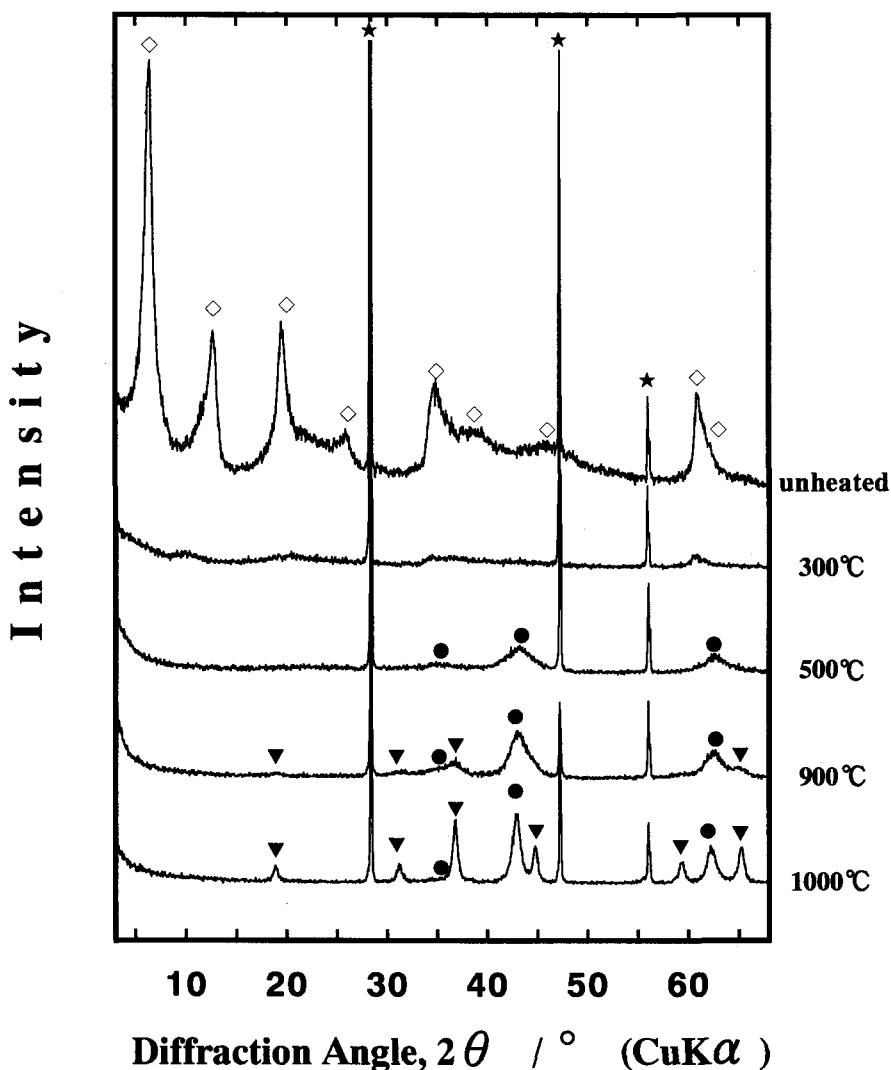
Figure 3. XRD patterns of pimelate intercalate calcined in nitrogen at various temperatures. (★) internal standard (Si), (◇) pimelate intercalate of HTlc, (●) MgO and (▼) spinel, $MgAl_2O_4$.

Miyata and Kumura (1973) have already reported. When samples were heated in N_2, the layer structure of the dicarboxylate intercalates collapsed at the second DTA peak temperature (300–400 °C). Between 400 and 800 °C, a MgO-like phase—which was a Mg-Al double oxide, to be precise—was detected. At 900 °C, the double oxide decomposed to spinel ($MgAl_2O_4$) and MgO (Figure 3). Thermal decomposition phases obtained by heat treatment in air were the same as the phases obtained by heat treatment in N_2. Moreover, this thermal decomposition behavior was the same as that of Mg-Al-CO_3 HTlc.

Morphology of Samples

Starting HTlcs which were air-dried at 80 °C after washing with distilled water and partial drying under nitrogen had distinctive morphologies (Figure 4).

Crystallites of malonate, succinate, glutarate, adipate and pimelate ($HOOC(CH_2)_nCOOH$, n = 1, 2, 3, 4 and 5) intercalates of HTlc were highly aggregated into rock-hard masses (Figures 4c, 4d and 4e). Alternatively, crystallites of the oxalate (n = 0) intercalate and the carbonate intercalate (Mg-Al-CO_3 HTlc) were clustered loosely (Figures 4a and 4b).

The morphology of crystallite aggregation changed with different dispersing media in which the HTlcs were soaked before drying (see Figures 5 and 6). When pimelate intercalate was soaked in ethanol before drying, the face–face clustering of the platy crystallites was loosened, and the morphology of the dried form (Figure 5b) was similar to those of oxalate and carbonate intercalates (Figures 4a and 4b). However, soaking in distilled water and drying this dry pimelate intercalate, of which crystallites were loosely clustered
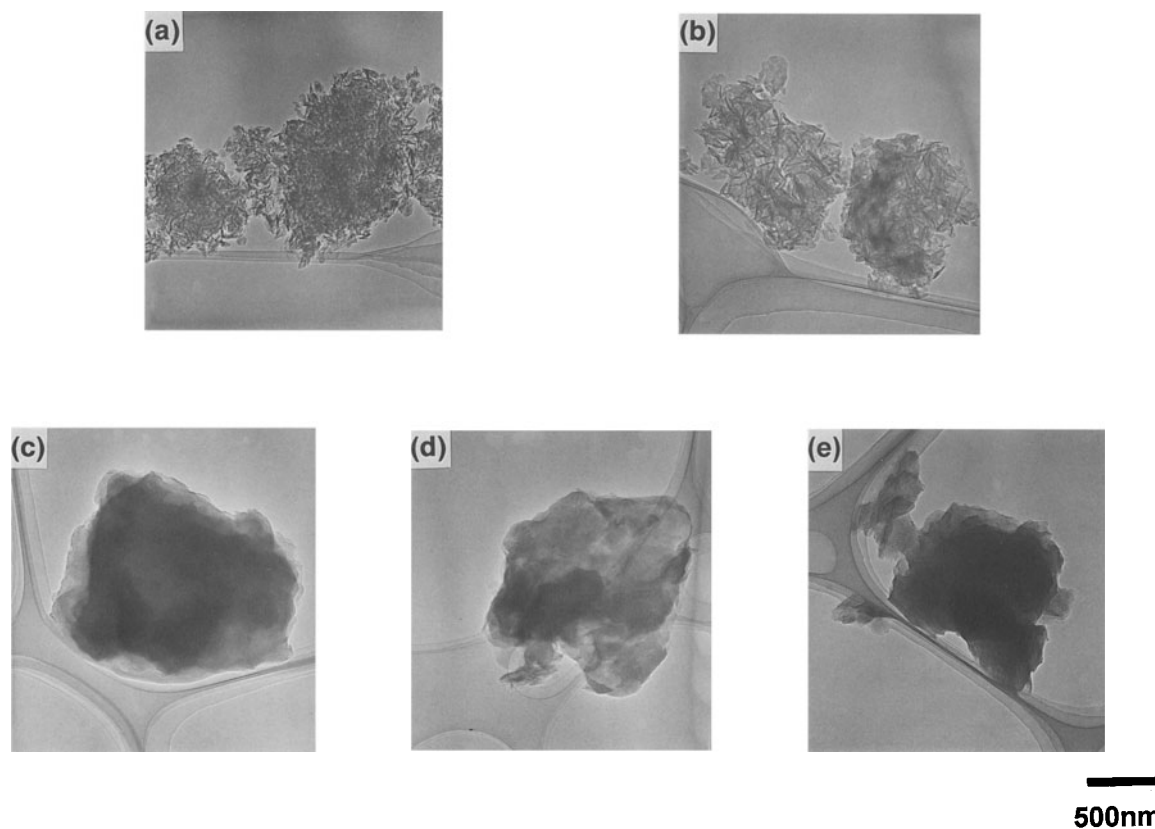
500nm

Figure 4.   Transmission electron micrographs of HTlcs. a) Mg-Al-CO$_3$ HTlc, b) oxalate intercalate, c) malonate intercalate, d) succinate intercalate and e) pimelate intercalate, each washed with distilled water and dried at 80 °C.
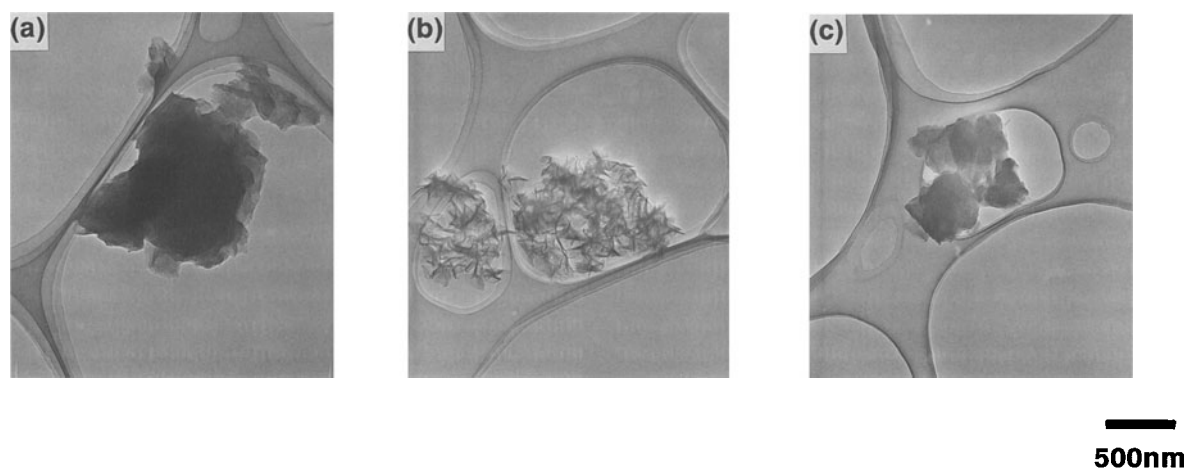

500nm

Figure 5.   Transmission electron micrographs of pimelate intercalates of HTlc: a) pimelate intercalate washed with distilled water and dried at 80 °C, b) pimelate intercalate soaked in ethanol before drying and c) pimelate intercalate shown in (b) after subsequent soaking in distilled water and drying.
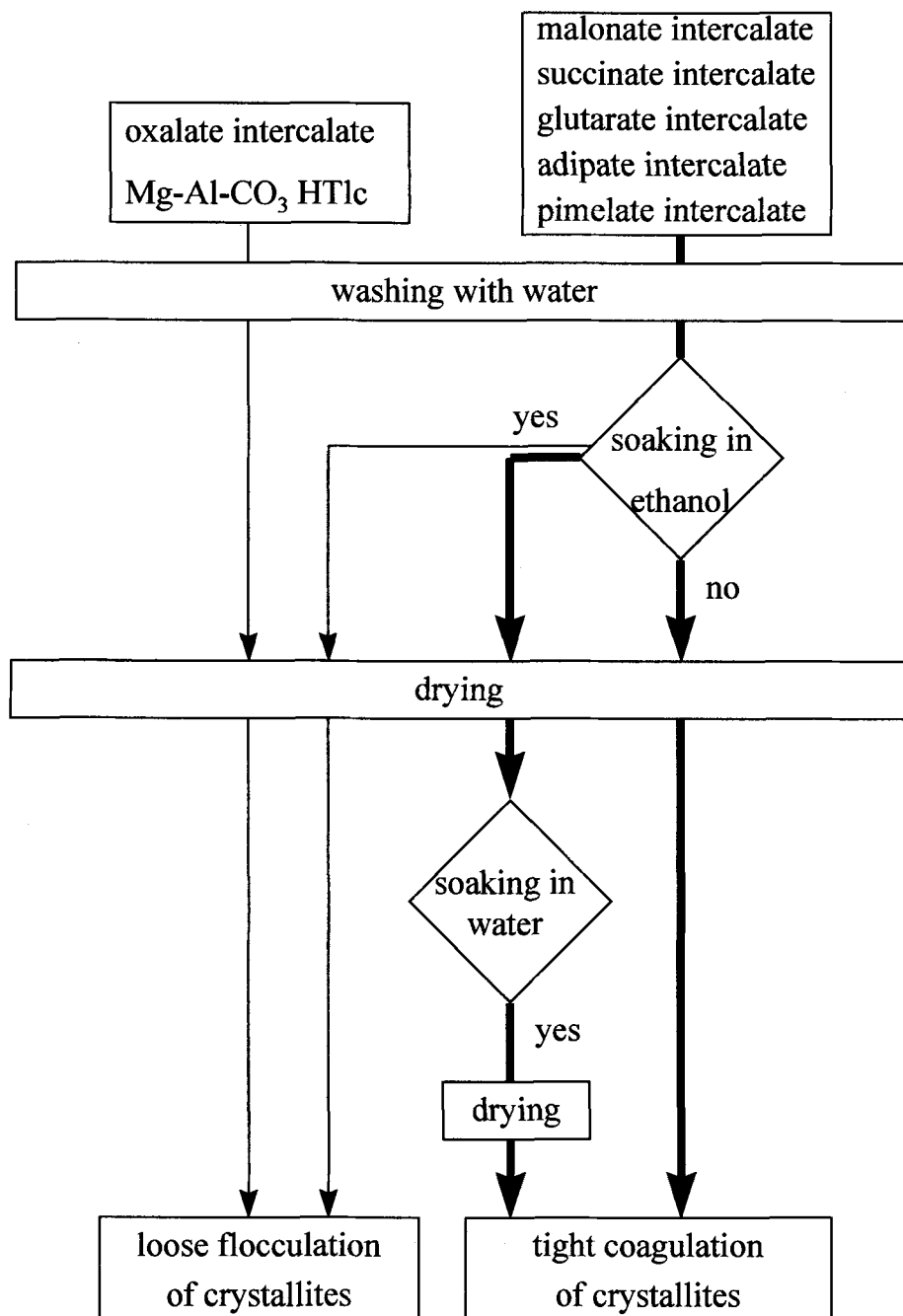
Figure 6.   Diagram illustrating various routes followed for washing and drying samples.

in a face–edge fashion, coagulated the crystallites tightly once again (Figure 5c). In summary, tight coagulation of sample crystallites occurred only when procedures on the thick line shown in Figure 6 were performed.

In addition, Mg-Al-CO₃ HTlc did not change its aggregation morphology whether the dispersing medium was water, ethanol or acetone.

Thermal Decomposition of Reconstructed HTlc and Formation of Spinel

The atmospheric conditions during calcination of the starting HTlcs, whether in N_2 or in air, did not affect reconstruction and thermal decomposition of reconstructed HTlcs. When dicarboxylate intercalates of HTlc were heated, small amounts of carbonaceous res-

Table 1. Preparation procedures for reconstructed Mg-Al-CO₃ HTlcs and their thermal decomposition phases.

Disperse medium before drying of starting HTlc	Starting HTlc	Grinding before reconstruction	Detected phase after reconstruction	Phase after heating to 400 °C†
Water				
	malonate, succinate, glutarate, adipate and pimalate intercalates	yes	Mg-Al-CO₃ HTlc	Mg-Al double oxide
		no	Mg-Al-CO₃ HTlc	spinel + Mg-Al double oxide
	oxalate intercalate and Mg-Al-CO₃ HTlc	yes	Mg-Al-CO₃ HTlc	Mg-Al double oxide
		no	Mg-Al-CO₃ HTlc	Mg-Al double oxide
Ethanol				
	pimelate intercalate	yes	Mg-Al-CO₃ HTlc	Mg-Al double oxide
		no	Mg-Al-CO₃ HTlc	Mg-Al double oxide
	Mg-Al-CO₃ HTlc	yes	Mg-Al-CO₃ HTlc	Mg-Al double oxide
		no	Mg-Al-CO₃ HTlc	Mg-Al double oxide
Ethanol → water				
	pimelate intercalate	yes	Mg-Al-CO₃ HTlc	Mg-Al double oxide
		no	Mg-Al-CO₃ HTlc	spinel + Mg-Al double oxide

† None of the samples was ground after reconstruction.

idues remained in the resulting Mg-Al double oxide (about 0.5 wt% of carbon when calcined in air, 0.6–3.7 wt% of carbon when calcined in N_2). The carbonaceous residues also remained in the reconstructed Mg-Al-CO₃ HTlcs. However, only the Mg-Al-CO₃ HTlc phase was detected by XRD. The IR spectral patterns of these reconstructed Mg-Al-CO₃ HTlcs were the same as that of Mg-Al-CO₃ HTlc prepared by the coprecipitation method. Moreover, difference in amounts of carbonaceous residues did not affect the subsequent spinel formation at all.

The phases appearing during heat treatment of the reconstructed Mg-Al-CO₃ HTlcs depended on the starting HTlc, the dispersing medium in which the starting HTlcs were soaked before drying and the grinding operation after calcination of the starting HTlcs. Table 1 shows phases detected by XRD when the reconstructed Mg-Al-CO₃ HTlcs were heated to 400 °C. A spinel phase appeared at 400 °C together with the MgO phase when all of the following conditions, which were described on the path of thick line shown in Figures 6 and 7, were fulfilled: 1) starting HTlcs were dicarboxylate intercalates other than oxalate intercalate, namely malonate, succinate, glutarate, adipate or pimelate ($HOOC(CH_2)_nCOOH$, $n = 1, 2, 3, 4$ and 5) intercalates; 2) the dispersing medium in which HTlcs were soaked before drying was water; 3) calcined starting HTlcs were not ground before reconstruction and reconstructed Mg-Al-CO₃ HTlcs were also not ground.

The XRD peaks of spinel generated at 400 °C by thermal decomposition of the Mg-Al-CO₃ HTlc reconstructed under these conditions were very sharp (Figure 8). This fact indicates the spinel was highly crystallized. In our previous study (Hibino et al. 1995), Mg-Al-CO₃ HTlc prepared by the coprecipitation method (virgin Mg-Al-CO₃ HTlc) yielded spinel at 900 °C. Also, in the present study, dicarboxylate in-

tercalates yield spinel at 900 °C (Figure 3). These spinel phases were not as well-crystallized as the spinel shown in Figure 8, although the calcination temperature was much higher than the temperature at which the spinel shown in Figure 8 was obtained. The positions of X-ray reflections of the highly crystalline spinel obtained at 400 °C corresponded to values for stoichiometric spinel (JCPDS card No. 21-1152). The value of lattice parameter a for MgO phase accompanied with the spinel (0.418 nm) is slightly lower than that of pure MgO (0.421 nm), indicating substitution of Al into the MgO lattice (Miyata 1980).

When reconstructed Mg-Al-CO₃ HTlc was prepared without fulfilling the conditions mentioned above, as when the samples were ground before or after reconstruction, the reconstructed Mg-Al-CO₃ HTlc converted to Mg-Al double oxide at 400 °C, and decomposed to spinel and MgO at 900 °C, just as virgin Mg-Al-CO₃ HTlc has been reported to do. In addition, Mg-Al-CO₃ HTlcs reconstructed from virgin Mg-Al-CO₃ HTlc did not yield spinel at low temperatures regardless of preparation method, dispersing medium or sample grinding.

Carbonate Content in Reconstructed HTlc

From the results of EDS, the Mg:Al ratio remained constant at 2:1 during each stage of the reconstruction procedure, from preparation of dicarboxylate intercalate to Mg-Al double oxide to reconstructed Mg-Al-CO₃ HTlcs. A close relationship was observed between carbonate content in reconstructed Mg-Al-CO₃ HTlc and formation of spinel at 400 °C (Table 2). The ideal formula for Mg-Al-CO₃ HTlcs can be written as $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O$, where $m = 1 - 3x/2$ (Miyata 1975). When the Mg:Al ratio is 2:1 ($x = \frac{1}{3}$), the stoichiometric carbonate content required by the formula is 12.8 wt%. The carbonate contents of all of the reconstructed Mg-Al-CO₃ HTlcs that yielded spinel and MgO
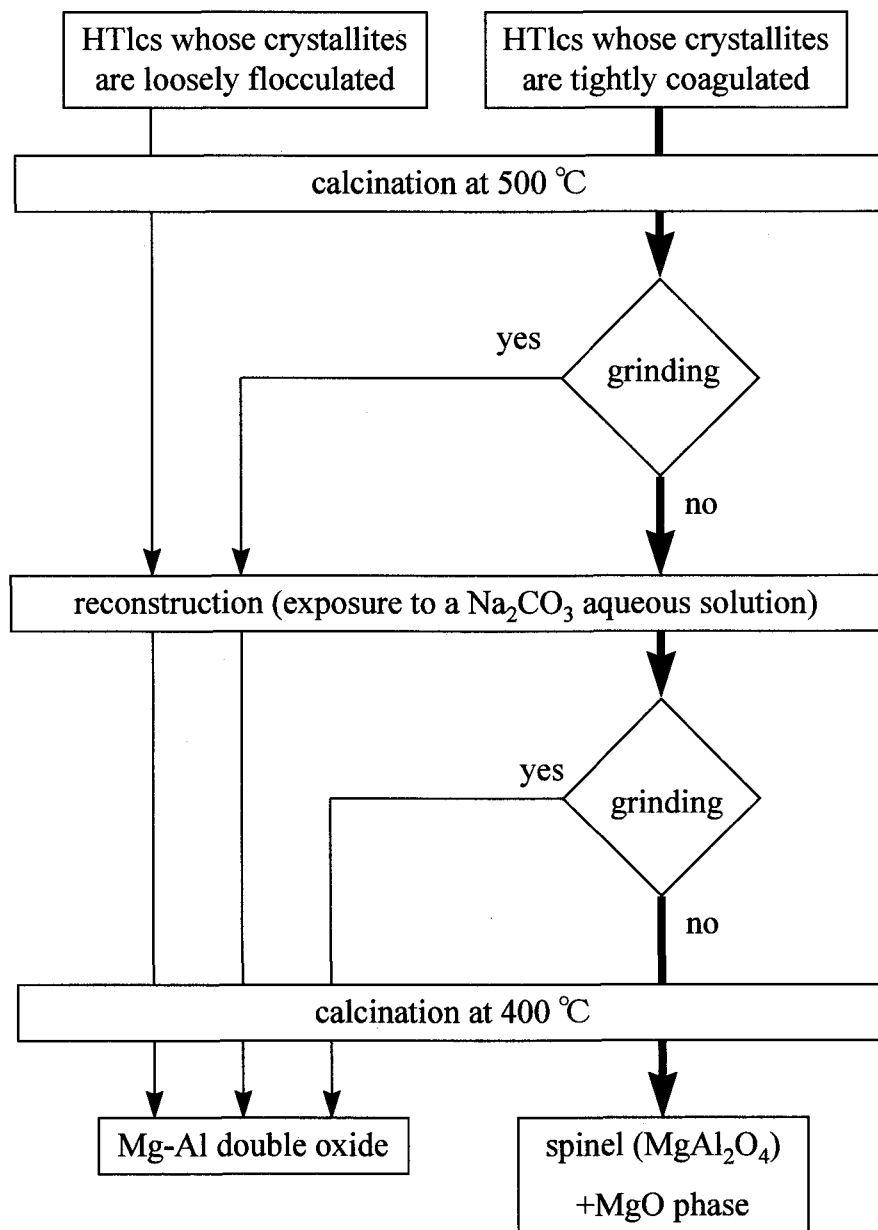
Figure 7.   Diagram illustrating various routes followed for calcination and reconstruction of samples.

phase at 400 °C were very low (55–70% of that calculated by the formula). In contrast, the carbonate contents of all of the reconstructed Mg-Al-CO$_3$ HTlcs that yielded only Mg-Al double oxide at 400 °C and decomposed to spinel and MgO only at 900 °C were equal to or a little less than that calculated by the formula (83–99% of the stoichiometric carbonate content).

DISCUSSION

The proportional relationship between basal spacing and anion sizes (Figure 2) strongly implies that the dicarboxylic anions were in the HTlc interlayers. Re-

sults of DTA and XRD show that the thermal decomposition behavior of dicarboxylate intercalates was similar to that of the Mg-Al-CO$_3$ HTlc reported previously, and that no product was generated between host layers and interlayer anions during heat treatment. XRD and IR data suggest that Mg-Al-CO$_3$ HTlc was completely reconstructed from calcined materials of dicarboxylate intercalates. However, some reconstructed Mg-Al-CO$_3$ HTlcs yielded spinel at 400 °C during heat treatment, and others yielded spinel at 900 °C, the same temperature at which virgin Mg-Al-CO$_3$ HTlc yields spinel.
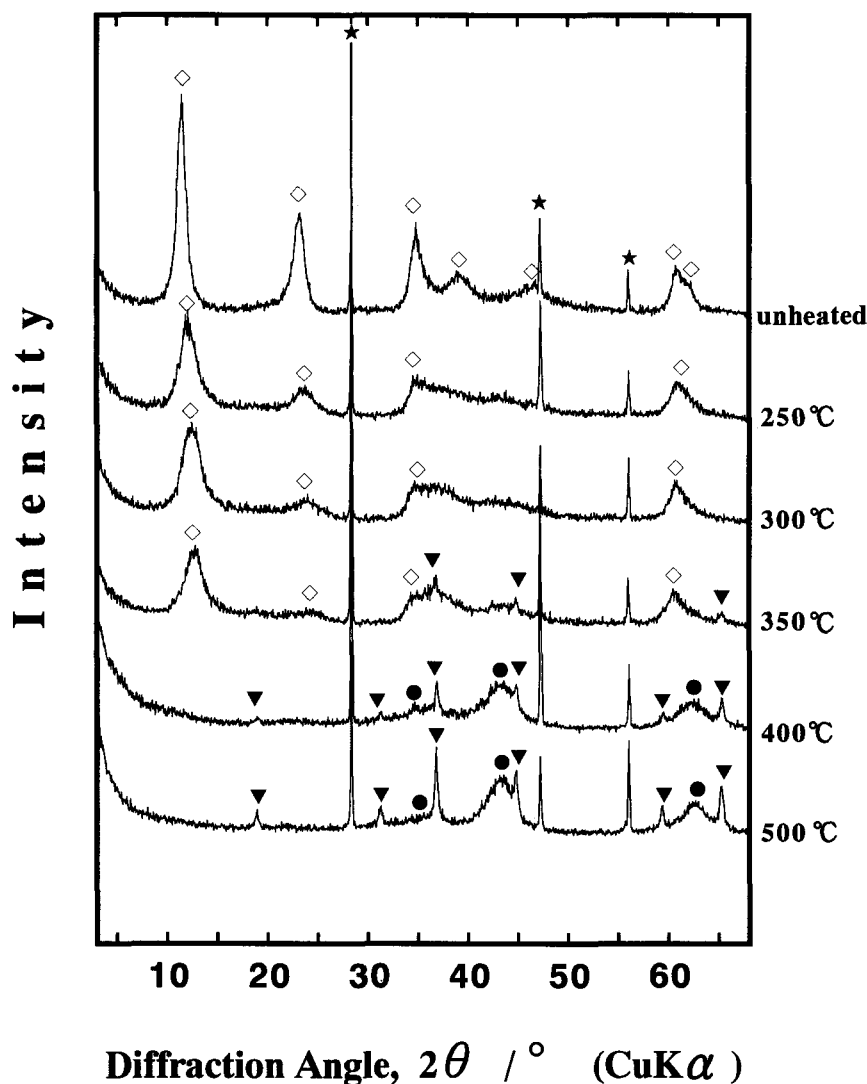
Figure 8. XRD patterns of the Mg-Al-CO$_3$ HTlc reconstructed from pimelate intercalate, calcined in nitrogen at various temperatures. (★) internal standard (Si), (◇) HTlc, (●) MgO and (▼) spinel, MgAl$_2$O$_4$.

For the reconstructed Mg-Al-CO$_3$ HTlcs that yielded spinel at 400 °C, it has been found that they have 2 distinctive peculiarities: they contained only 55–70% of carbonate anions calculated with the ideal formula, and the crystallites of their starting HTlcs, dicarboxylate intercalates, were tightly aggregated. Based on these 2 facts, we speculate that nuclei of spinel form between edges of crystallites during calcination of starting HTlcs whose crystallites coagulated tightly. In general, Al ions' occupation of cation sites in double hydroxide layers is likely to be as far apart as possible because of mutual repulsion (Brindley and Kikkawa 1979). Therefore, Al ions are surrounded by Mg ions and never occupy cation sites adjacent to each other. However, Al octahrdra on edges of different crystallites can be next to and close to each other (Figure 9).

Thus, an oxide that contains neighboring Al octahedra could form when HTlcs whose crystallites tightly coagulated were calcined. Such oxides could be nuclei of spinel, because spinel formation requires neighboring Al octahedra. The following fact supports our explanation that nuclei of spinel form between crystallite edges: formation of spinel at low temperature did not occur when platelets of starting HTlcs did not aggregate tightly. Those nuclei, however, may be intrinsically unstable due to mutual repulsion of neighboring Al octahedra, until the nuclei grow and become spinel. The fact that spinel formation at low temperature was inhibited by grinding implies this unstableness. We consider that this fact is due to mechanical destruction of the nuclei of spinel, just like deformation of the crystal structure of kaolinite by grinding (Kodama et

Table 2. Carbonate contents and thermal decomposition phases of reconstructed Mg-Al-CO₃ HTlcs.

Disperse medium before drying of starting HTlc	Starting HTlc	Grinding before reconstruction	Carbonate content in reconstructed Mg-Al-CO₃ HTlc (wt%)	Phase after heating to 400 °C
Water				
	Mg-Al-CO₃ Htlc	yes	12.7	Mg-Al double oxide
		no	12.7	Mg-Al double oxide
	oxalate intercalate	yes	12.6	Mg-Al double oxide
		no	12.7	Mg-Al double oxide
	malonate intercalate	yes	10.6	Mg-Al double oxide
		no	7.0	spinel + Mg-Al double oxide
	glutalate intercalate	yes	11.3	Mg-Al double oxide
		no	8.9	spinel + Mg-Al double oxide
	pimelate intercalate	yes	11.2	Mg-Al double oxide
		no	8.5	spinel + Mg-Al double oxide
Ethanol				
	pimelate intercalate	yes	11.4	Mg-Al double oxide
		no	11.2	Mg-Al double oxide

al. 1989; Kristóf et al. 1993). Furthermore, size of the nuclei would be very small, because neighboring Al octahedra occurs only at small area of broken crystallite edges. Therefore, growth of the nuclei is necessary to become crystalline spinel that can be detected by XRD. We discuss the growth of the nuclei later.

It is unlikely that oxides having neighboring Al octahedra (nuclei of spinel) reconstruct to HTlc, because Al oxides do not rehydrate to Al hydroxides only by exposure to aqueous solutions. When calcined HTlc containing the nuclei is exposed to an Na_2CO_3 aqueous solution, calcined material except the nuclei can reconstruct to Mg-Al-CO₃ HTlc, because all the calcined material except the nuclei is Mg-Al double oxide, as indicated by XRD. However, the HTlc reconstructed from the part (all the calcined material except the nuclei) contains less Al than before reconstruction by the amount of Al in the nuclei. Therefore, the carbonate content in those reconstructed HTlc decreases, since carbonate content in Mg-Al-CO₃ HTlcs is proportional to amount of Al. This speculation can sufficiently explain our observation of 55–70% of calculated carbonate content in reconstruction of HTlcs which formed spinel at 400 °C. Moreover, the speculation is supported by a reverse case: carbonate contents of Mg-Al-CO₃ HTlcs reconstructed from starting HTlcs whose crystallites loosely flocculate approach those calculated with the ideal formula.

EDS analysis did not reveal nuclei of such spinel, but it is difficult to detect the spectrum only from neighboring crystallite edges because crystallites overlap each other. Moreover, we consider that size of nuclei of spinel is too small to detect by EDS.

When nuclei of spinel form at crystallite edges at about 400 °C, the whole crystallites simultaneously convert to oxide, and then migration of cations (Mg and Al ions) might be completed. Therefore, the nuclei

cannot grow very much at that temperature because the migration is needed for growth of nuclei of spinel. It is easy to imagine that higher temperature gives rise to migration of cations. Indeed, Figure 3 shows that spinel forms at 900 °C. However, there is another way to give rise to the migration. Calcined HTlcs can reconstructed to HTlcs by exposure to aqueous solutions. When the reconstructed HTlcs are calcined again at 400 °C, the reconstructed HTlcs convert to oxide, and then migration of Mg and Al ions occurs. We believe that this migration brings on growth of nuclei of spinel, and that this is mechanism of spinel formation from the reconstructed HTlcs at low temperature of 400 °C. Thus, we conclude that formation of spinel at low temperature from reconstructed Mg-Al-CO₃ HTlcs is a consequence of the reaction that occurs between edges of different crystallites.

In summary, our speculation does not require a breakage preferentially exposing Al cations, but formation of nuclei resulting from neighboring Al octahedra between crystallite edges during calcination of the starting HTlcs. We believe that the nuclei can grow and become spinel during subsequent calcination of the reconstructed HTlcs, even if the number of the nuclei per unit surface area of crystallite edges is very small after calcination of the starting HTlcs. Fortunately, the starting HTlcs had large specific surface areas because of small crystallite size. Therefore, the number of the nuclei per unit weight of samples become large due to the large surface areas. Thus, we conclude that spinel formation from the reconstructed HTlcs at low temperature was observed clearly in the present study.

CONCLUSION

Crystallite aggregation of dicarboxylate intercalates of HTlc depended on the dispersing medium before
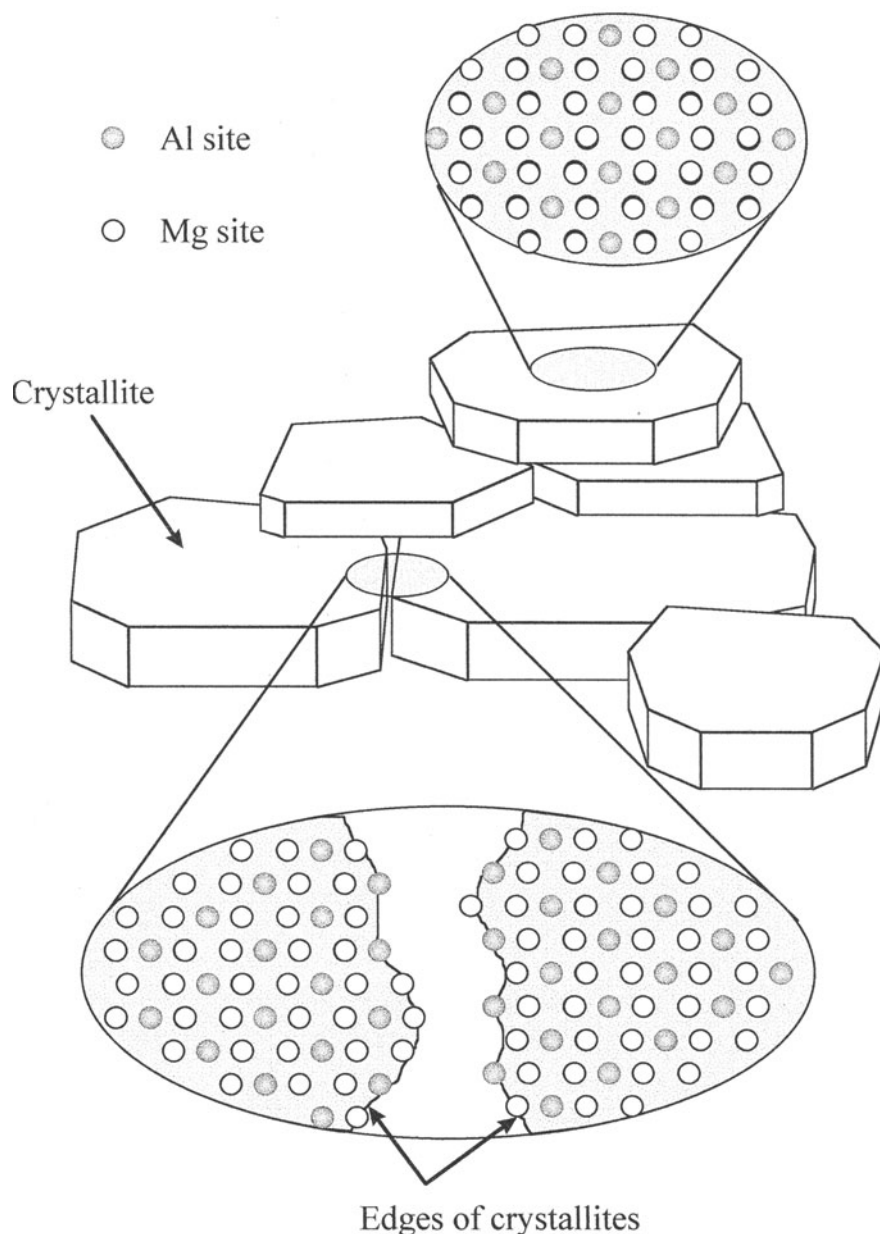
Figure 9.   Suggested mechanism of spinel nucleus formation between edges of crystallites. Dotted areas are magnified, and distributions of Mg and Al cations in octahedral sheets are shown. Potential spinel nuclei can be formed between proximate Al octahedra on edges of adjacent crystallites.

drying. When the dispersing medium was ethanol, the crystallites flocculated loosely. The Mg-Al-CO$_3$ HTlcs reconstructed from the dicarboxylate intercalates yielded spinel at 900 °C, the same temperature at which virgin Mg-Al-CO$_3$ HTlc yields spinel. In contrast, when the dispersing medium was water, crystallites of dicarboxylate intercalates other than oxalate intercalate coagulated tightly. The Mg-Al-CO$_3$ HTlcs reconstructed from these dicarboxylate intercalates yielded spinel at 400 °C. This was a very low tem-

perature, compared with Mg-Al-CO$_3$ HTlcs that have been reported to yield spinel only at 900 °C. The present study suggests that formation of spinel at low temperature is a reaction between edges of crystallites. This reaction was not observed with oxalate and carbonate intercalates, because their crystallites do not aggregate tightly. Furthermore, grinding procedure inhibited the reaction. These evidences suggest that reconstruction of HTlcs is a more complicated reaction than was previously thought.

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