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Thermal decomposition of Mg-Al hydroxides coprecipitated in the presence of oxalate ions [1]

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Abstract

The thermal decomposition of Mg-Al hydroxides coprecipitated from nitrate solutions in the presence of oxalate ions has been studied. Samples were prepared with Mg/Al atomic ratios of 2:1 and 1:2. The coprecipitation products were always characterized by the presence of an Mg-Al mixed hydroxide containing oxalate ions in the interlayer sheet.

Decomposition of the separately precipitated mixed phase passes through formation of the corresponding carbonated phase before reaching MgO and $MgAl_2O_4$. The mechanism of spinel formation from thermal decomposition of hydroxide mixtures is strongly influenced by the presence of oxalate ions in the mixed phase.

INTRODUCTION

The thermal behaviour of hydroxide mixtures, precursors to $MgAl_2O_4$ spinel synthesis, and the mechanism of spinel formation from their thermal decomposition have been described in our recent papers [1,2]. These mixtures were prepared by coprecipitation from nitrate solutions with an Mg/Al molar ratio of 1:2 [3]. The coprecipitates were made up of three Al hydroxides (gibbsite, bayerite and pseudoboehmite) and a carbonated Mg-Al mixed hydroxide with an Mg/Al molar ratio of 2:1; this carbonation is attributable to the material's layered structure, on which positively charged brucite-like layers alternate with balancing hydroxyl ion sheets [4-6]. The interlayer sheet hydroxyl ions are thus easily exchanged with other anions [7-9] and are very readily replaced by carbonate ions [10-13] from atmospheric CO_2 dissolved in the aqueous solution.

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The aim of this study was to check the correctness of the mechanism proposed for spinel formation from the thermal decomposition of coprecipitated Mg–Al hydroxide mixtures, postulated for carbonated mixtures [2], when the carbonate ions of the mixed phase are replaced by other anions. For this purpose, coprecipitations from Mg and Al nitrate solutions with Mg/Al ratios of 1:2 and 2:1 were performed in the presence of oxalate ions, and the thermal behaviour of the products of these coprecipitations was investigated. The need to clearly differentiate the X-ray diffraction patterns from those of the carbonated samples led us to choose intercalating oxalates, which are larger than carbonate ions, because the relevant literature shows that the larger the intercalated anion diameter, the larger is the crystallographic distance between two adjacent layers [14–19].

EXPERIMENTAL

Materials

A 75 ml volume of an aqueous solution of Mg and Al nitrates with Mg/Al atomic ratio of either 1:2 or 2:1 was added drop by drop to 225 ml of a stirred aqueous solution of oxalic acid at 60°C. The number of moles of oxalic acid was equal to the total moles of dissolved nitrate. A 30% NH_4OH solution was then added drop by drop until a pH value of 9.5 was reached. The precipitate was allowed to age for 2 h at the same temperature under moderate stirring. Its pH was kept constant by adding ammonia. It was then filtered off and washed, air-dried at 105°C, and milled to break down the major agglomerates as described for carbonated hydroxides in [3]. Figure 1 sets out the precipitation procedure.

Characterization

The powders were characterized by the following techniques. Elemental chemical analysis: Mg and Al were determined by atomic absorption spectrophotometry (Philips model PU 2500); C, H and N were determined with an elemental analyser (Carlo Erba Strumentazione model 1106). Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) (Stanton model 781) under the following conditions: static air, heating rate 10°C $\min^{-1}$, sample weight about 20 mg, reference sample Al_2O_3, sensitivity 40 μV. X-ray diffraction analysis (XRD) using Ni filtered Cu Kα radiation ($\lambda = 0.1542$ nm) (Siemens model D500).

In-depth investigation of the thermal behaviour of the coprecipitation products was obtained by XRD analysis of samples heated to the temperatures corresponding to the completion of the main DTA effects, using the Stanton thermoanalyser to heat the powders at the same rate.

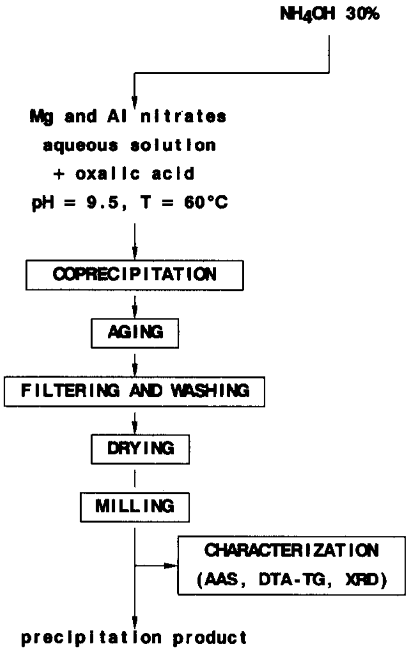

Fig. 1. Flowsheet of the coprecipitation process.

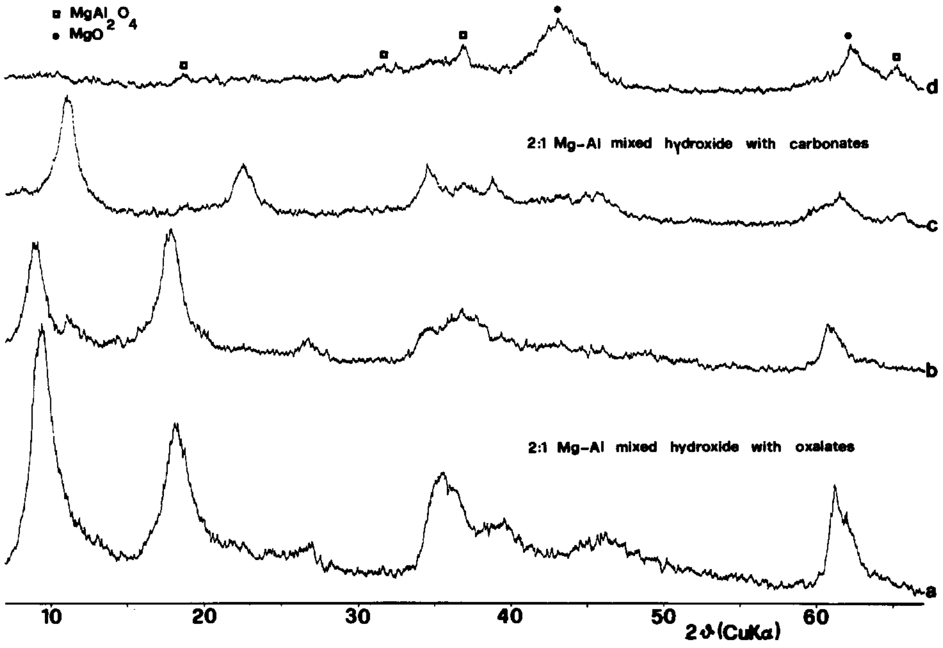

Fig. 2. XRD patterns of the coprecipitate with Mg/Al ratio 2:1, heated at: 100°C (curve a); 340°C (curve b); 380°C (curve c); 450°C (curve d).

RESULTS AND DISCUSSION

Coprecipitation with Mg / Al atomic ratio 2 : 1

Chemical analyses gave 20.28 wt% Mg, 10.93 wt% Al, 3.08 wt% H, 5.84 wt% C, 0 wt% N.

The XRD pattern of the precipitate (Fig. 2, curve a) shows the presence of only one crystalline phase, with a layered hexagonal structure, similar to those of the Mg–Al mixed hydroxide with an Mg/Al ratio of 2 : 1 [20] and of the corresponding carbonated form [2], but with a shifting of the peaks: the (003) line is shifted to 9.2° in 2θ, corresponding to $d = 0.96$ nm, as expected from the increased distance between two adjacent layers attributable to the interlayer oxalate ions in comparison with the carbonated phase ($d = 0.78$ nm).

The DTA and TG curves are shown in Fig. 3. The total experimental weight loss, determined from the TG curve, was 45%, whereas the loss calculated excluding the water lost at temperatures lower than 100°C was 44.1%. The following precipitate composition $Mg_4Al_2C_2O_4(OH)_{12} \cdot 1.5H_2O$ was deduced. Its theoretical and experimental weight losses are the same.

The thermal behaviour of the precipitate is illustrated by the DTA curve (Fig. 3). There are several endothermic effects: one at 165°C, another weak one at 315°C, two peaks with maxima at 375 and 430°C respectively, and a small final peak at 500°C. Examination of the corresponding TG curve enables the weight loss to be divided into stages, approximately evaluating their percentages: the first is continuous up to 250°C; excluding the free

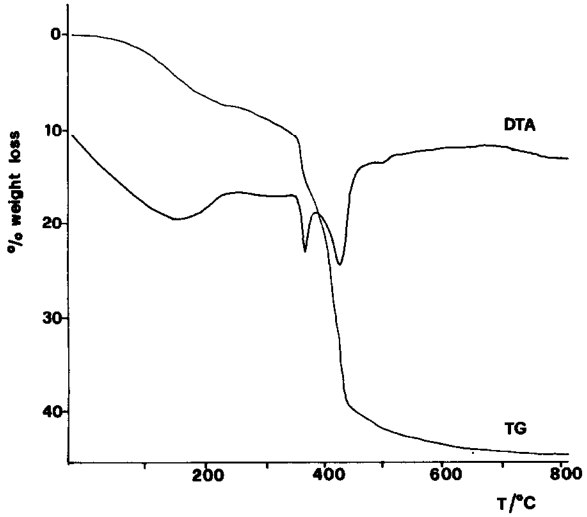

Fig. 3. DTA and TG curves of the coprecipitate with Mg/Al atomic ratio 2:1.

water, the weight loss from 100 to 250°C corresponds to 5.7%; from 250 to 350°C there is a slow weight loss stage, corresponding to 2.7%, followed by two very rapid steps up to 375 and 430°C respectively, with weight losses of 6.3% and 23.7%. The last, 5.7%, stage is marked by a decreasing rate, and weight loss is completed at about 750°C.

The thermal analysis results were correlated with those of the XRD analysis. Up to 340°C (Fig. 2, curve b), no meaningful variations of the XRD patterns were detected, apart from a slight shifting of the (003) peak towards lower angles; at 340°C, small peaks of a new phase were present; at 380°C (Fig. 2, curve c), i.e. completion of the DTA peak, these peaks were well defined and ascribable to the presence of the carbonated form of the Mg–Al 2:1 mixed hydroxide [2]; at 450°C (Fig. 2, curve d), the mixed phase peaks were no longer present, and the reflections of MgO and $MgAl_2O_4$ were detectable.

Because the XRD pattern of the thermal analysis residue shows the presence of MgO and $MgAl_2O_4$, the number of moles lost during each TG step for one mole of produced spinel was evaluated from the percentage weight loss, given that one mole of precipitate leads to the formation of $1MgAl_2O_4$ and 3MgO. It was therefore calculated that, apart from the loss of 0.5 molecule of free water, the first stage corresponds to the loss of $1.5H_2O$, attributable to loss of interlayer water according to the literature [13,19,21]; the second, up to 350°C, corresponds to the loss of $0.67H_2O$, ascribable to the beginning of the brucite-like dehydroxylation, which is very slow in this temperature range. The weight loss from 350 to 375°C is equivalent to 1CO; this is in agreement with the XRD analysis results, which showed the decomposition of the oxalate-containing mixed hydroxide into the corresponding carbonated phase. The two last stages cannot be distinguished; however the total weight loss above 375°C corresponds to $5.3H_2O$ and $1CO_2$, i.e. final decomposition of the mixed phase.

The following thermal decomposition mechanism can thus be proposed: after losing the interlayer water and a part of the hydroxyl ions of the mixed phase, there is intermediate formation of the carbonated form of the mixed hydroxide, with final decomposition to MgO and $MgAl_2O_4$ starting at 450°C.

The interlayer water is lost at a lower temperature and with a weaker DTA effect with respect to the carbonated form [2]; this results from the weaker electrostatic attraction between the layers because they are further apart. The data for carbonated mixed hydroxide [2] indicated that dehydroxylation of the brucite-like layers between 250 and 350°C probably starts from the hydroxyl ions bonded to the Al sites, because Al hydroxides, but not brucite, are already decomposed at this temperature. Decomposition of the oxalate ions into carbonate, characterized by the DTA peak at 375°C, occurs at the temperature of transition from the slow to the rapid mixed-phase dehydroxylation, so that the corresponding TG step, which is a

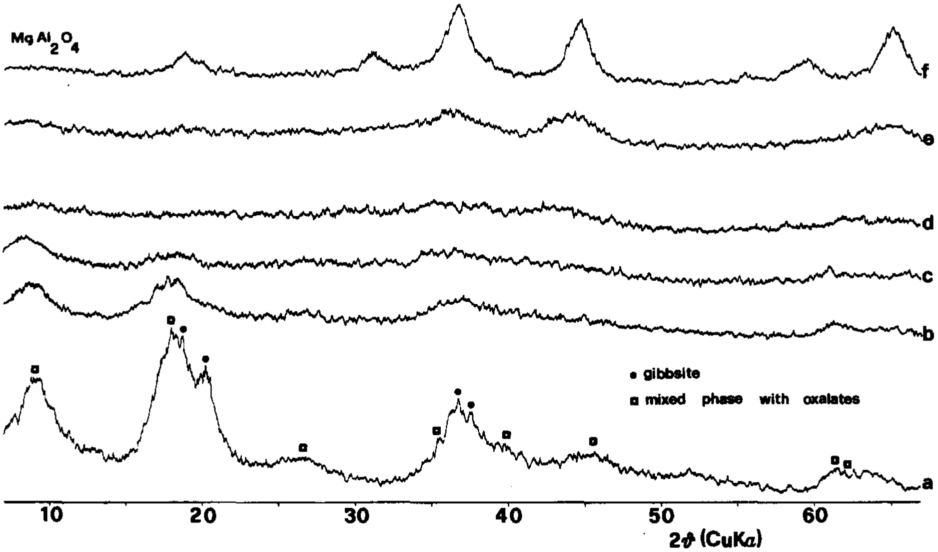

Fig. 4. XRD patterns of the coprecipitate with Mg/Al ratio 1:2, heated at: 100°C (curve a); 280°C (curve b); 380°C (curve c); 480°C (curve d); 600°C (curve e); 950°C (curve f).

summation of the slow water loss and the very fast CO loss processes, virtually involves the fast process only and is equivalent to the loss of 1CO. The DTA peak at 430°C is related to the final decomposition of the mixed phase; this temperature is higher than that of the corresponding peak of the related carbonated phase.

Coprecipitation with Mg/Al atomic ratio 1:2

It has been proved that precipitations from different salts lead to products with different compositions, morphologies and microstructures [3]. In the same way, the presence of oxalate ions in solution affects the characteristics of the precipitate from nitrates. The XRD pattern of the powder coprecipitated in the presence of oxalate ions from nitrate solution with an Mg/Al ratio of 1:2 (Fig. 4, curve a), in fact, shows a lower crystallinity and a different composition; the phases identified are the Mg–Al mixed phase described above, with interstitial oxalates, and α-$Al(OH)_3$ (gibbsite). Bayerite and pseudoboehmite are not detectable.

Chemical analyses gave 9.91 wt% Mg, 22.13 wt% Al, 3.55 wt% H, 3.42 wt% C, and no N.

Figure 5 shows the DTA and TG curves. From the TG curve, the total weight loss is 44.2% (39.4% excluding the weakly-bonded water, lost at temperatures lower than 100°C). These results and those for coprecipitation with Mg/Al 2:1 give the powder composition $Mg_4Al_2C_2O_4(OH)_{12} \cdot 1.5H_2O + 6Al(OH)_3$. The theoretical and experimental weight losses are again the same.

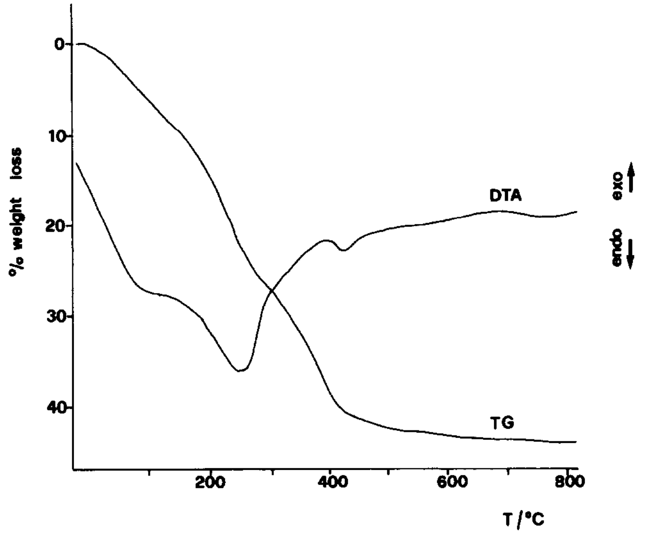

Fig. 5. DTA and TG curves of the coprecipitate with Mg/Al atomic ratio 1:2.

The DTA curve (Fig. 5) displays an endothermic effect at 100°C due to loss of weakly bonded water, plus a large endothermic peak with its maximum at 250°C and a smaller one at 425°C. The corresponding TG curve, excluding the loss of weakly bonded water, can be divided approximately into three stages: the first of 18.3% up to 250°C, the second characterized by a constant weight loss rate of 16.7% up to 420°C, and the third of 4.4%, with a decreasing rate up to about 700°C, at which the weight loss is completed.

To see whether the spinel formation mechanism for carbonated mixtures in [2] was equally true for mixtures containing oxalates, XRD analysis of samples heated to the DTA effect completion temperatures was carried out. The XRD pattern at 280°C (Fig. 4, curve b) (completion of the first DTA peak) did not show the α-Al(OH)$_3$ peaks, or signs of its decomposition products; the reflections are similar to those of the main mixed phase peaks, yet the broad reflection at 37° in 2θ seems to indicate a different attribution. The structural variation exhibited by carbonated mixtures [2], with formation of an intermediate, cubic phase, was not shown in this case. Even though the sample was poorly crystalline, a tentative, approximate indexing of its broad peaks showed that the phase detected was probably hexagonal rather than cubic. The situation was the same at 380°C (Fig. 4, curve c). On completion of the last DTA effect, 480°C (Fig. 4, curve d), the XRD pattern was completely amorphous; the first spinel reflections were detectable at 600°C (Fig. 4, curve e).

Once again the number of moles lost during each TG stage was evaluated using a similar procedure; according to the XRD of the powder heated to 950°C (Fig. 4, curve f), which shows the presence of spinel only,

$4MgAl_2O_4$ were formed by decomposition; with reference to the formation of four spinel molecules after the loss of two molecules of weakly bonded water, the first stage is thus equivalent to the loss of $9.5H_2O$, the second to $7H_2O$ and 1CO, and the last to $1CO_2$.

The thermal behaviour can be described as follows. After the free water loss, the first DTA effect is approximately related to interlayer water loss and to $Al(OH)_3$ decomposition. However, the water loss processes do not correspond precisely to the related TG stages. In the light of the Mg/Al 2:1 results, it seems probable that the oxalate ions decompose at the same temperatures, i.e. at the end of the second weight loss stage, although there is no DTA peak corresponding to this decomposition. Moreover, the endothermic peak for the mixed phase at 430°C is sharply decreased, in a way similar to that displayed by the carbonated mixtures [2].

These results clearly show that oxalate ions strongly affect the mechanism of spinel formation. The absence of endothermic peaks at 375 and 430°C, in particular, points to an exothermic reaction between the mixed phase without interlayer water and the Al hydroxide decomposition products. However, the product of this reaction is not cubic as for carbonated mixtures. Spinel formation is thus hindered until the decomposition temperature of oxalate ions is reached, after which it occurs from the non-cubic, probably hexagonal, phase resulting in amorphous spinel. Spinel reflections can only be discerned by XRD analysis at a temperature of at least 600°C.

CONCLUSIONS

By comparison with the related carbonated system, the presence of oxalate ions in the Mg–Al mixed hydroxide interlayer sheet strongly affects its thermal decomposition. This occurs at higher temperatures after passing through the intermediate formation of the carbonated phase.

As far as the stoichiometric system is concerned, the spinel formation temperature increases slightly up to about 450°C. Its mechanism is modified by the presence of oxalate ions: spinel is probably still produced through a reaction between the mixed phase and the Al hydroxide decomposition products, although this does not lead to a cubic transition phase; the hexagonal structure is probably maintained up to the oxalate decomposition temperature. In summary, an increase in spinel formation temperature was found, and its crystallization occurred at higher temperatures.

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