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STUDY OF THE THERMAL BEHAVIOUR OF HYDROXIDE MIXTURES AIMED AT THE PREPARATION OF Mg-Al SPINELS

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The thermal behaviour of hydroxide mixtures aimed at Mg-Al spinel preparation is reported. The mixtures of hydroxides were prepared by precipitation reaction from Mg and Al nitrate solutions, stoichiometric to the spinel formation. Hydroxide mixtures with different phase distributions were investigated, prepared by varying the precipitation procedure. The results were related to the thermal behaviour of mechanical mixtures of separately precipitated hydroxides. The spinel formation was identified performing XRD analysis on powder samples heated at different temperatures. The coprecipitated mixtures are completely decomposed to spinel at 400°C. The presence of the Mg–Al mixed hydroxide phase in the mixture is of primary concern to get spinel at low temperatures.

Introduction

Methods of $MgAl_2O_4$ preparation, based upon thermal decomposition of precursors, have been proposed in past years by many authors [1–6]. In this paper the thermal behaviour of Mg–Al coprecipitated hydroxides mixtures aimed at spinel synthesis is investigated, in comparison to that of mechanical mixtures of different hydroxides, either single or double. Thermal analysis of likely mixtures are reported in literature by Bratton [1] and Yamaguchi *et al.* [5]. The mechanical mixtures were studied in order to clarify the effect on the spinel synthesis of the presence of mixed hydroxide and the importance of the mixing degree of the components, already shown in the literature [7, 8].

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Experimental

Preparation of coprecipitated hydroxide mixtures

The Mg–Al hydroxide mixtures were prepared by coprecipitation [6], adding drop by drop solutions of Mg and Al nitrates, stoichiometric to the spinel formation, to a stirred NH_4OH solution at $pH = 10$ and 60°. Further hydroxide mixtures were prepared by two-step precipitation [6], that is adding first the Mg nitrate solution to the NH_4OH solution, and then the Al nitrate in molar ratio Mg/Al 1:2. The precipitates were aged for two hours, filtered under vacuum, washed, dried at 105° and milled for 30 min in a vibratory ball mill. Carlo Erba RPE-ACS reagents were used.

Preparation of mechanical mixtures of hydroxides

Given the composition of the coprecipitated hydroxide mixtures [6], as set out below, mechanical mixtures of Mg–Al mixed hydroxide phase and $Al(OH)_3$ in stoichiometric amount to the spinel formation, were prepared in reproducing the coprecipitated mixture. Mechanical mixtures without the mixed hydroxide phase, that is mixtures of $Mg(OH)_2$ and $Al(OH)_3$, were also prepared, again with an Mg/Al molar ratio of 1:2. All the mechanical mixtures were obtained by mixing the components in a vibratory ball mill for two hours.

Each component of the mixtures was synthesized by precipitation from nitrates in the same conditions of the coprecipitated mixtures. In particular, precipitations were performed from: Mg nitrate; Al nitrate; solution of Mg and Al nitrates with Mg/Al molar ratio 2:1. The last precipitation was performed in order to get the mixed hydroxide phase [9–12].

Characterization

The following techniques were used to characterize the powders obtained:

a) X-ray diffractometry, performed using a Ni filtered CuK_α radiation ($\lambda = 0.1542$ nm) (Siemens mod. D500);

b) elemental chemical analysis: Mg and Al were determined by atomic absorption spectrophotometry (Philips mod. PU 2500), while C, H and N were determined using an elemental analyzer (Carlo Erba Strumentazione mod. 1106);

c) simultaneous thermogravimetric (TG) and differential thermal analysis (DTA), under the following conditions: static air, heating rate

10 deg/min, sample weight about 20 mg, reference sample Al_2O_3, sensitivity 40 μV (Stanton mod. 781).

Results and discussion

Coprecipitated mixtures

As previously reported [6], the XRD pattern of the precipitate showed the presence of three crystalline phases: α–$Al(OH)_3$ (gibbsite), β–$Al(OH)_3$ (bayerite) and the Mg–Al mixed hydroxide with molar ratio 2:1 [1, 9–12].

The chemical analyses gave the following results:

	Mg	Al	H	N	C
%wt	10.65	23.35	3.76	–	1.15

The presence of C in the powder can be explained by the high anion exchange capacity [13, 14] of the hydroxide ions present within the interlayer sheet of the Mg–Al mixed hydroxide layered structure [15, 16]. For this reason, the mixed hydroxide easily reacts with the CO_2 dissolved in the precipitation solution and in the washing water, transforming the mixed hydroxide into hydroxycarbonate [17–21].

DTA and TG curves are reported in Fig. 1. The DTA curve shows, in addition to a first effect at about 70° ascribable to the loss of free water, two endothermic peaks, a small one and a large one with maxima respectively at

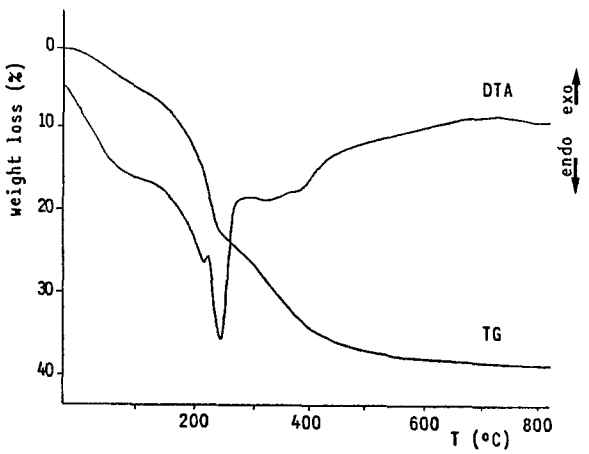

Fig. 1 DTA and TG curves of the coprecipitated hydroxide mixtures

about 230 and 260°, two endothermic effects at about 330 and 390° can be seen. On the other hand, the TG curve, after the loss of free water which ends at about 100°, can be divided into three more steps; the first one, which ends at about 260°, is the result of the overlapping of three other different effects. The second one, up to about 410°, is characterized by a constant weight loss rate, while the third one shows a decreasing weight loss rate and is nearly completed at about 680°.

In order to explain these weight losses, the results of XRD analysis must be taken into consideration. An XRD pattern of the powder heated to 400° shows very broad $MgAl_2O_4$ reflections; at increasing temperature, the spinel crystallizes; the residue of thermal analysis, heated up to 950°, consists only of $MgAl_2O_4$. Starting from this point, it was possible to evaluate the number of spinel units from the final anhydrous weight of the sample; then, the different weight losses of each TG step were found to be equivalent respectively to 0.625, 2.3 and 1.5 molecules of H_2O for 1 unit of spinel, and the last step to 0.25 CO_2 for 1 unit of spinel. The global weight loss was 38.8%, while it was 35.7% if the free water was not considered.

From these results, the composition of the precipitate was initially hypothesized as the following:

$$Mg_4Al_2CO_3(OH)_{12}\cdot 2H_2O + 6Al(OH)_3 \quad (1)$$

The corresponding theoretical loss however, which is 38.2%, does not fit well with the experimental value. Moreover, the results of chemical analyses show some differences from this composition.

In order to ascertain the composition of the mixture, the aforesaid precipitation from Al nitrate was considered. An XRD pattern of this precipitate showed the presence of a certain amount of pseudo-boehmite, a weakly-crystalline gel with boehmite-like reflections [22], besides those of gibbsite and bayerite. The corresponding DTA and TG curves are reported in Fig. 2: apart from an initial endothermic peak at about 80°, due to the free water loss, one peak in the DTA curve at about 260° is noticeable. After the free water loss, the TG curve can be divided into two weight loss steps: the first, up to 260°, corresponds to the loss of 1.4 H_2O for 1 unit of alumina, and the second, nearly ended at 700°, corresponds to 1 H_2O. The experimental weight loss was 30%. These results clearly show that the composition of the precipitate was approximately $1.4Al(OH)_3 + 0.6AlOOH$. In fact, the two steps correspond respectively to the decomposition of $1.4Al(OH)_3$ to AlOOH and to the dehydration of 2AlOOH.

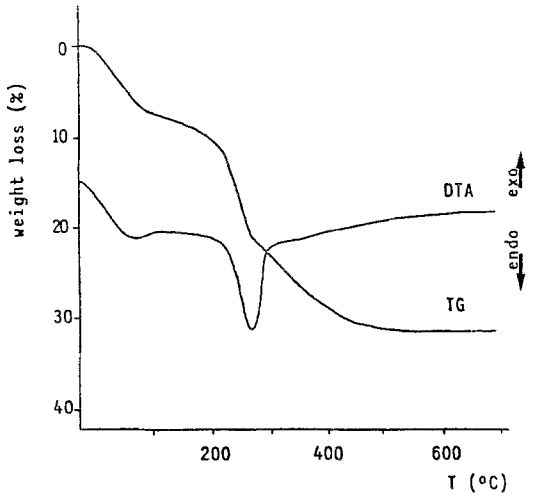

Fig. 2 DTA and TG curves of the product of the precipitation

Coming back again to the coprecipitated mixture, the presence of the same percentage of AlOOH was hypothesized. From chemical analysis data, with this hypothesis, the following composition was deduced:

$$Mg_4Al_2CO_3(OH)_{12}\cdot 2H_2O + 4.3Al(OH)_3 + 1.7AlOOH \qquad (2)$$

The theoretical weight loss for this mixture is 36.0%, which fits with the experimental one. Thus, referring to the formation of $4MgAl_2O_3$ to which this mixture leads, other than the about 2.5 molecules of free water, the different steps of the TG curve can be attributed as follows: the first one to the loss of 9.2 molecules of H_2O, corresponding to the loss of the mixed hydroxide interlayer water and to the dehydration of the Al hydroxides; the second and the third respectively to the loss of 6 H_2O and 1 CO_2 coming from the decomposition of the mixed Mg–Al hydroxycarbonate phase.

These results are in agreement with those obtained by the authors for the separately precipitated mixed hydroxide [23]. In fact, in that case it was ascertained that the 2:1 Mg–Al mixed hydroxide, precipitated in the same conditions, contains two molecules of water within the interlayer sheet. Moreover, the thermal analysis of the mixed hydroxide in comparison with that of Al hydroxides showed that the interlayer water loss occurs at the same temperature range in which the $Al(OH)_3$ decomposition starts.

Mixtures prepared by two-step precipitation

The product of the two-step precipitation has a different phase composition, with respect to the coprecipitated powders: the XRD pattern, in fact, showed the presence of $Mg(OH)_2$ peaks; besides those of the double hydroxide, gibbsite and bayerite; this was explained by the fact that the separately precipitated $Mg(OH)_2$ is poorly reactive and it is not able to completely transform itself into the mixed hydroxide [6]. Furthermore, weak reflections of pseudo-boehmite were present.

The chemical analyses gave the following results:

	Mg	Al	H	N	C
%wt	10.95	24.38	3.51	–	1.2

DTA and TG curves are shown in Fig. 3. Apart from free water loss, the DTA curve shows three endothermic peaks at 210°, 270° and 385°; a comparison with the coprecipitated mixture shows a slight shifting of the first peak towards lower temperatures and the presence of the peak at 385°, marked in this case.

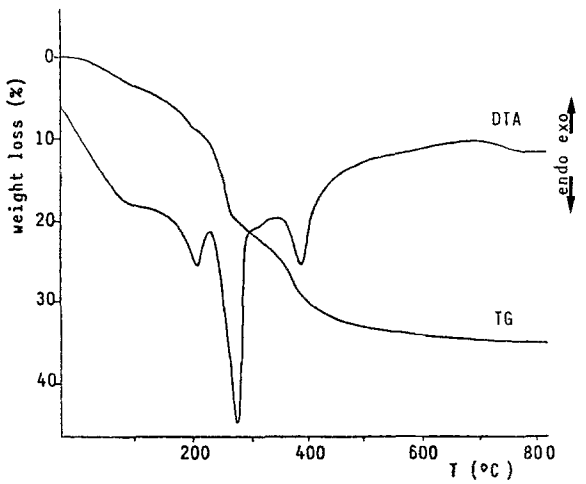

Fig. 3 DTA and TG curves of the product of the two-step precipitation

From the TG curve, the total experimental weight loss was 35.2%, while it was 33.3% of the anhydrous weight. In this case the XRD pattern of the powder heated to 400° showed the presence of peaks of MgO, Al_2O_3 and $MgAl_2O_4$; at 950° an increase of the spinel peaks intensity was evident, with

a simultaneous decrease of the periclase and alumina peaks; this demonstrates the occurrence of a solid state reaction between MgO and Al_2O_3 at increasing temperatures. In order to calculate the weight losses of the different TG steps, the same procedure was used as for the coprecipitated mixture. According to the chemical analyses, the residue of the thermal analysis, even if not completely combined into spinel, can be considered a mixture of spinel and MgO plus Al_2O_3 in molar ratio 1:1. As in the previous case, for each TG step, the losses were referred to 4 units of spinel. After the loss of about 1 molecule of free water, the first step, up to about 200°, corresponds to the loss of 2.8 H_2O; the second, up to 260°, and the third, up to about 360°, are equivalent to the loss of 5.3 and 3 H_2O, respectively; the following step, which ends at about 420°, corresponds to the loss of 2.8 H_2O, and it is an overlapping of two steps; finally, up to about 650°, 0.8 CO_2 were lost.

All these results indicate the following composition for this hydroxide mixture:

$$0.8Mg_4Al_2CO_3(OH)_{12}\cdot 2H_2O + 0.8Mg(OH)_2 + 3.4Al(OH)_3 + 3AlOOH \quad (3)$$

The theoretical weight loss corresponding to this composition is 33.3%, which is equal to the experimental one. Thus, the different TG steps can be explained as follows: during the first step the loss of the interlayer water (1.6 H_2O) occurs and the dehydration of the Al hydroxides (1.2 H_2O) starts; the latter is completed during the second step (5.3 H_2O), with a total experimental loss of 6.5 H_2O. Then, the two following steps correspond to the dehydration of the mixed hydroxide and of $Mg(OH)_2$, partially overlapped. The final step is equivalent to the loss of 0.8 CO_2 from the mixed phase.

A different ratio between $Al(OH)_3$ and AlOOH with respect to the coprecipitated mixture must be emphasized. This is not surprising, if the different precipitation mechanism is taken into consideration: in fact, during coprecipitation Mg and Al combine in the ratio 2:1 to give the mixed hydroxide phase; the amount of Al, in excess with respect to Mg, precipitates as Al hydroxides, keeping the same ratio between $Al(OH)_3$ and AlOOH as in the separate precipitation from Al nitrate; on the other hand, in the two-step precipitation $Mg(OH)_2$ is formed at first; when Al nitrate is added to the solution, Al hydroxides are precipitated., and the formation of the mixed hydroxide occurs only during ageing, by means of the reaction between $Mg(OH)_2$ and very probably $Al(OH)_3$, explaining the increase of AlOOH in the mixture, with respect to $Al(OH)_3$.

Mechanical mixtures

Mixture of $Mg(OH)_2$ and $Al(OH)_3$

Figure 4 shows the DTA and TG curves. The DTA curve shows two endothermic peaks at temperatures of 275 and 380°. The TG curve exhibits, in correspondence to the DTA peaks, two different dehydration steps, each one made up of two other steps. The experimental weight loss was 30.4%. Once again this is understandable if a composition of $Mg(OH)_2 + 1.4Al(OH)_3 + 0.6AlOOH$ is considered, the theoretical weight loss of this mixture being 30.1%. The first TG step, which is related to the dehydration of the Al hydroxides, gives a loss of 2.1 H_2O, and partially overlaps the $Mg(OH)_2$ dehydration step, which in fact gives a loss of 1.3 H_2O.

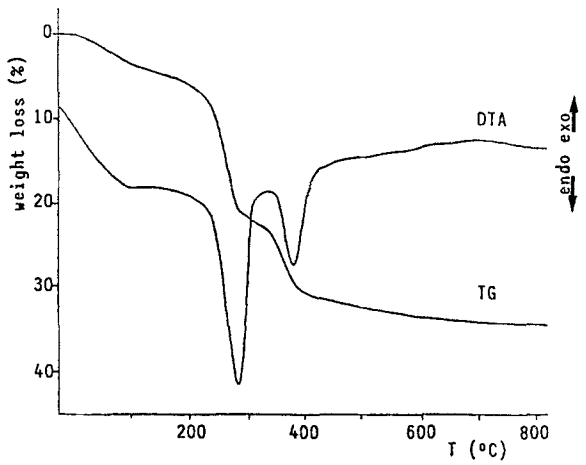

Fig. 4 DTA and TG curves of the mechanical mixture of $Mg(OH)_2$ and $Al(OH)_3$

These results confirm that the two different hydroxides dehydrates independently one from the other; therefore the spinel synthesis does not occur at low temperatures: the Al_2O_3 and MgO formed are only able to react at higher temperatures. This observation was confirmed by XRD analysis. In fact, an XRD pattern of the powder heated to 300° showed $Mg(OH)_2$ and η–Al_2O_3 peaks, while that of the powder heated to 430° showed the presence of MgO and still that of the alumina; the XRD pattern of the powder heated to 950° revealed in addition the presence of the spinel peaks, demonstrating that an incomplete solid state reaction occurred between the two oxides formed.

Considering also the results obtained for the mixture prepared in the two-step precipitation, it is evident that the presence of $Mg(OH)_2$ in the mixture hinders the formation of the spinel at low temperatures.

Mixture of Mg–Al mixed hydroxide and $Al(OH)_3$

In this case the DTA curve (Fig. 5) shows three endothermic peaks, with maxima at 220°, 275° and 375°; the third peak has an area nearly equivalent to that of the two-step precipitation product, which is to say rather larger than the one of the corresponding effect of the coprecipitated powder and much smaller than that of the mechanical mixture of single hydroxides. The experimental weight loss was 36.4%: this fits quite well with the theoretical weight loss of the mixture with the composition (2) reported for the coprecipitate. It is possible to divide the weight loss into different steps, related to the production of 4 spinel units: after the loss of about 3 H_2O up to 100°, the first two steps, up to 265°, correspond to the loss of 3.5 and 5.8 H_2O, respectively, equivalent to the theoretical loss of 9.3 H_2O due to the loss of the mixed hydroxide interlayer water and the dehydration of the Al hydroxides; the following step, completed at 365°, is equivalent to a loss of 5.2 H_2O; the final step can be attributed to 1 more molecule of water and to 1 CO_2.

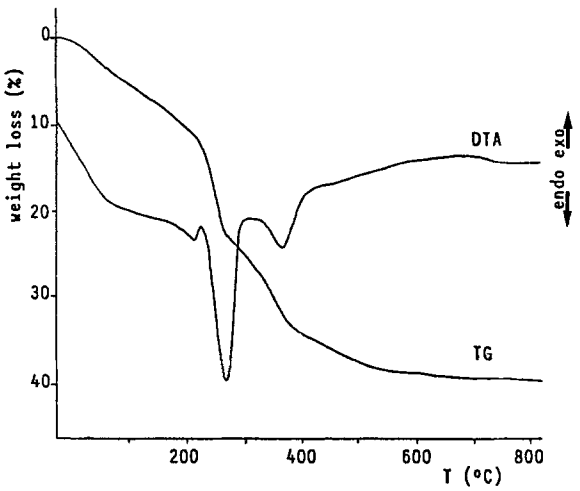

Fig 5 DTA and TG curves of the mechanical mixture of Mg-Al mixed hydroxide and $Al(OH)_3$

An XRD pattern of the powder heated to 400° shows the peaks of MgO and η–alumina, besides that of $MgAl_2O_4$; at 950° the same phases are

present, but in different ratios, showing that a solid state reaction to form $MgAl_2O_4$ has occurred.

According to these results, the presence of the Mg–Al mixed hydroxide phase is of primary concern to get the spinel formation at low temperatures; the less intimate mixing degree however does not allow the complete reaction, and MgO and alumina are present at 400°, the temperature at which the coprecipitated mixture shows only spinel. The endothermic peak at 375° is the result of the decomposition to MgO of the mixed hydroxide part which was not able to react with alumina to form spinel. The last step of the TG curve is further evidence for this observation.

Conclusions

The thermal decomposition of coprecipitated hydroxide mixtures leads to $MgAl_2O_4$ formation at a temperature as low as 400°. If the precipitation procedure is such as to produce mixtures containing $Mg(OH)_2$, the complete formation of the spinel does not occur at low temperatures, because the $Mg(OH)_2$ present in the mixture separately decomposes to MgO; Mg should be present in the mixture only as mixed hydroxide to achieve the spinel formation at 400°.

Once again the influence of the mixing degree of the components was stressed: whilst an intimate mixture like the coprecipitated one is able to completely form the spinel at low temperature, a mechanical mixture of the same components leads also to the formation of MgO and alumina; it rather points to the fact that, as shown in another paper [23], the formation of the spinel passes through a reaction step, which is influenced by the mixing degree of the reactants.

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Zusammenfassung – Im Hinblick auf die Präparation von Mg–Al Spinell wird das thermische Verhalten von Hydroxid-Mischungen beschrieben. Letztere wurden durch Fällung von Mg- und Al–Nitratlösungen im stöchiometrischen Verhältnis der Spinellbildung hergestellt. Durch Variation des Fällungsvorgangs wurden Hydroxid-Mischungen unterschiedlicher Phasenzusammensetzung erzeugt. Die Resultate werden mit dem thermischen Verhalten von mechanischen Mischungen separat gefällter Hydroxide verglichen. Die Identifizierung der Spinellbildung erfolgte durch Röntgendiffraktion an pulverförmigen, auf verschiedene Temperaturen aufgeheizten Proben. Die durch simultane Fällung erhaltenen Mischungen wurden bei 400°C vollständig zu Spinell zersetzt. Um bei tiefer Temperatur Spinell zu erhalten, kommt dem Vorhandensein der Mg–Al–Mischhydroxidphase in der Mischung vorrangige Bedeutung zu.