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Synthesis and properties of Mg–Zn–Al–SO$_4$ hydrotalcite-like compounds

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Sulphate-based magnesium–zinc–aluminium synthetic hydrotalcite-like compounds have been prepared by coprecipitation with a sodium hydroxide solution. The corresponding metal solutions were coprecipitated at pH 10, aged in the mother liquor, washed several times and dried at 40 °C. Whatever the ratio of metal ions in the initial metal sulphate solutions, hydrotalcite compounds were formed during coprecipitation. The temperature of preparation and ageing time did not effect the final crystal structure. By comparing the properties of the Mg–Al layered compounds, it seems that when the zinc content increases, the thermal stability of the hydrotalcite-like compounds decreases.

1. Introduction

The hydrotalcite-like compounds are composed of a positively charged layer of di- and trivalent metal hydroxides, this charge being compensated by interstitial anions and water [1, 2], hence the compensation is not stoichiometric [3, 4]. The basic structure of the layered compound is magnesium hydroxide (brucite) in which the divalent cation occupies the octahedral position; the positive charge is created by the substitution of the divalent cation by a trivalent cation. Water molecules and anions are intercalated and are located between the layers, and so maintain the electroneutrality of the crystal. The general formula of the solid solution is $\mathrm{M(II)}_{1-x}\ \mathrm{M(III)}_x\ (\mathrm{OH})_2\mathrm{A}^{n-}_{x/n}\cdot m\mathrm{H}_2\mathrm{O}$ where $\mathrm{M(II)} = \mathrm{Mg}^{2+}$, Zn^{2+}, $\mathrm{Ni}^{2+}, \ldots$, $\mathrm{M(III)} = \mathrm{Al}^{3+}$, $\mathrm{Fe}^{3+}, \ldots$, $A^{n-} = \mathrm{OH}^-$, $\mathrm{Cl}^-\mathrm{NO}_3^-$, $\mathrm{SO}_4^{2-}, \ldots$, and $0.2 < x < 0.33$ [5, 6]. In certain cases, x can be higher than 0.33 in the Zn–Al system [7]. The above formula could be extended to include a monovalent cation in the octahedral position [8]. The natural occurrence of two divalent metals in the same layer has been reported [9], and was investigated for the preparation of industrial catalysts such as Cu/ZnO/Al$_2$O$_3$ [10].

In the present study, multi-metallic magnesium–zinc–aluminium layered hydrotalcite-like compounds were synthesized by coprecipitation. The influence of metal ratio, precipitation temperature and zinc content on the crystal structure and properties are reported.

2. Experimental procedure

2.1. Preparation

The solid solutions were prepared at constant temperature by the coprecipitation method using different ratios Zn/Mg and (Mg + Zn)/Al. 50 ml of each aqueous solution (magnesium, zinc and aluminium sulphates) were added drop-wise by pumps into 100 ml distilled water, with constant stirring. The rate of addition was 75 ml h^{-1}, and the pH was kept constant at 10 by hand addition of 3N NaOH. The coprecipitation and ageing temperature was varied from room temperature up to 75 °C. The coprecipitates were aged in their mother liquor at the synthesis temperature for 1 h, then filtered and washed with 2 l tepid distilled water, and finally dried at 40 °C for 24 h.

2.2. Characterization

The zinc, magnesium and aluminium contents in each solid solution were determined by X-ray fluorescence (XRF) with Jeol 300 spectrometer, after fusing 0.5 g sample in 5 g dilithium tetraborate using a beam-bed sampler Nt 2000 Tokyo Kogaku around 1200 °C. Water and sulphate contents were determined by thermogravimetry (TG–DTA analysis) using 5–6 mg sample with a Rigaku Unit at a heating rate of 15 °C min^{-1}.

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku RU300 using CuK_α radiation, with a nickel filter to determine the crystallographic parameters of the obtained phases.

A transmission electron microscope (TEM) Philips 300 connected to an energy dispersive spectrometer (EDS) was used to observe the morphology of crystals and to perform a chemical analysis for these particles. The powders were sonicated in pure alcohol and then deposited on a copper grid.

A Jasco J-0017 infrared spectrometer (IR) was used to obtain more information about the orientation of the sulphate anion in the interlayer space. The sample was prepared in KBr pellets.

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TABLE I Chemical analysis results and lattice parameters of the coprecipitates

Sample	Zn/Mg		(Zn + Mg)/Al		$A^{2-}/2Al^{3+}$	Unit cell parameter	
	Theo.	Exp.	Theo.	Exp.		a(nm)	c(nm)
1	0	0	1	1.16	0.51	0.300	3.060
2	0	0	2	1.99	0.78	0.303	2.978
3	0	0	3	3.01	0.9	0.305	2.540
4	0.087	0.072	1	1.12	0.58	0.300	2.760
5	0.087	0.079	2	2.09	0.83	0.303	2.687
6	0.087	0.081	3	3.10	1.05	0.304	2.617
7	0.2	0.18	3	2.94	0.99	0.304	2.565
8	0.5	0.43	3	2.74	0.97	0.305	2.600
9	1	0.83	3	2.63	1.38	0.306	2.625
10	4	3.41	3	2.22	1.06	0.306	2.651
11	6	5.27	3	1.98	1.29	0.307	2.570
12	10	10.2	3	2.00	1.16	0.307	2.650
13	1	0.83	1	1.85	0.78	0.305	3.120

Theo., theoretical; Exp., experimental; A^{2-}, SO_4^{2-} and CO_3^{2-}.

The heat treatment of the samples was performed in air for 2 h in the temperature range 200–1000 °C in a thermolyne 10 500 furnace.

3. Results and discussion

3.1. Chemical analysis

Table I shows the results obtained with powders having various Zn/Mg and (Mg + Zn)/Al ratios. The theoretical Zn/Mg and (Mg + Zn)/Al ratios are based on the weights of chemicals used and the experimental ratios are calculated from the chemical analysis. In the case of the magnesium–aluminium solid solutions, the experimental values are near the theoretical values except when Mg/Al = 1. This difference may be due to the incomplete coprecipitation of the cations.

In the magnesium–zinc–aluminium system containing a small amount of zinc, the experimental ratios are slightly higher than the theoretical values. However, if the theoretical (Mg + Zn)/Al ratios are higher than 3, the experimental ratios are always smaller than the theoretical ratios. These results are not in agreement with other studies in which the synthesized solid solutions have similar composition to the starting solutions [11, 12], but are similar to Brindley and Kikkawa's [13] results which interpreted the lower experimental values compared to the theoretical ratios in the case of Mg–Al hydroxy-carbonates as a smaller preference for aluminium ions in the crystalline products than in the coexisting solutions.

When the ratio of Zn/Mg is higher than 0.5, the experimental values of Zn/Mg and (Mg + Zn)/Al ratios are lower than the theoretical ones. If the theoretical (Mg + Zn)/Al ratio is equal to 3, and varying the theoretical Zn/Mg ratio, as noticed before, the experimental Zn/Mg ratio is lower than in the starting solutions. Of course, this affected the experimental (Mg + Zn)/Al ratio. The XRF results did not show a large variation for the aluminium content between the experimental and theoretical values. A lower percentage of zinc was incorporated in the structure as the zinc content increases compared to magnesium, which indicates a lower reactivity of zinc ions during the coprecipitation.

In hydrotalcite-like compounds, the substitution of divalent ions of the brucite-like layers by aluminium ions creates a positive charge. To maintain the electroneutrality, the intercalated anion (A^{n-}) has the opposite charge, so that the ratio of A^{n-}/nAl is equal to unity. All the samples contained trace amounts of CO_3^{2-} arising from air contamination during synthesis. Its presence was evinced by IR spectroscopy. As shown in Table I, the ratio of $(SO_4^{2-} + CO_3^{2-})/2Al^{3+}$ is generally higher than 1, which suggests that the excess of anions are adsorbed on the positive surface [6]. The presence of another aluminium phase such as $Al(OH)_3$ could explain a ratio smaller than 1. In this latter case, Miyata [4] suggested that the ratio of Mg/Al is in excess of the limit of substitution of divalent ion by aluminium ion.

3.2. Microscope observations

The examination of the morphology of the sample showed the presence of platy particles 70 nm in size which formed aggregates (Fig. 1a). A high magnification of such particles showed that the platy crystals (10 nm in size) are connected to each other (Fig. 1b). Quantitative EDS analysis of the product gives different values for zinc, magnesium and aluminium, depending on the particles or the aggregates which were analysed. These data show that the powders are heterogeneous in composition.

3.3. X-ray powder diffraction

The XRD patterns of samples having an (Mg + Zn)/Al ratio up to 2 showed sharp and symmetrical peaks and other broad and asymmetric peaks characteristic of hydrotalcite-like compounds. For (Mg + Zn)/Al < 2, the patterns showed broad symmetric and asymmetric peaks with relatively high d_{003} value of 1.020–1.065 nm. The X-ray pattern can

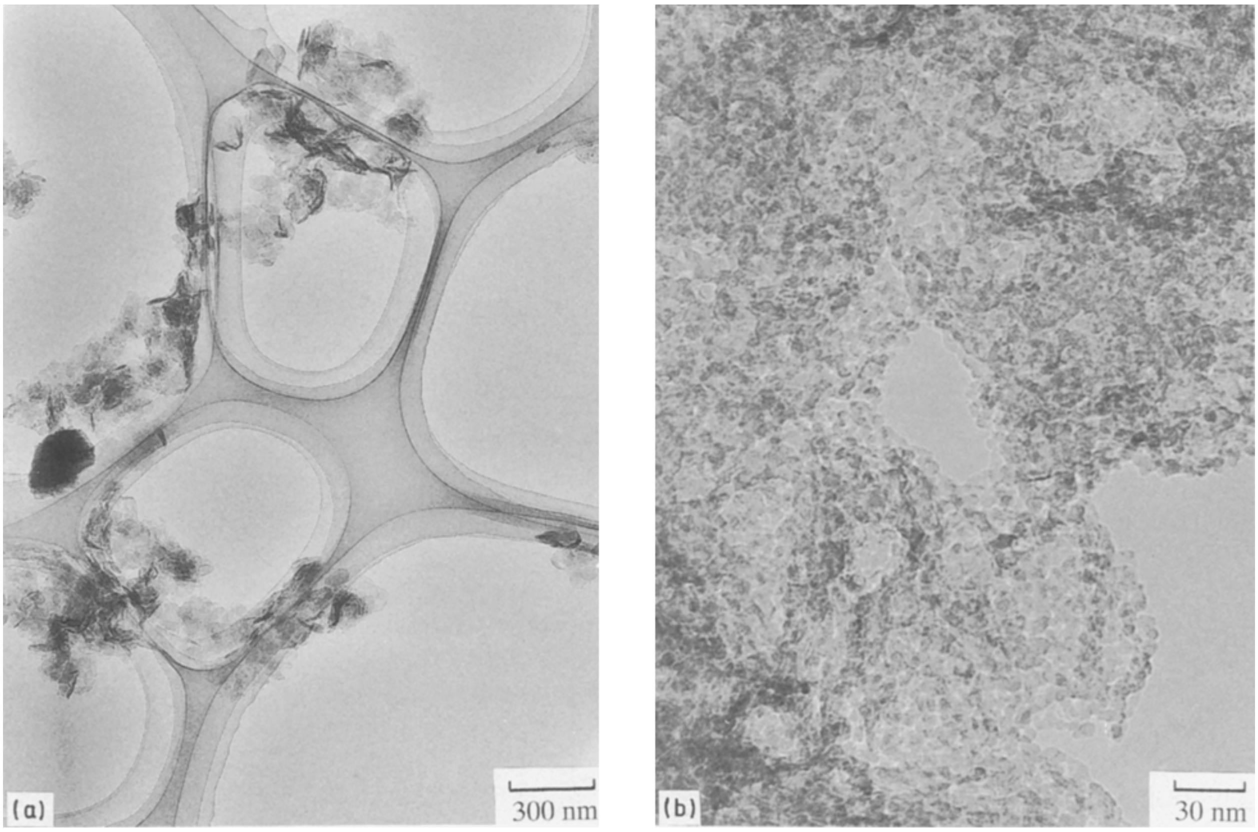

Figure 1 Transmission electron micrographs of Sample 4.

be interpreted in rhombohedral symmetry with *a* and *c* unit cell parameters, where *c* corresponds to three times the thickness of one brucite-type layer (Table II).

In the Mg–Al system, the *a* parameter decreases when the aluminium content increases in the solid solution. This behaviour is due to the smaller size of the aluminium ion compared with the magnesium ion. However, the *c* parameter increases, which is in contradiction with the results of Brindley and Kikkawa [13]. The difference observed between our results and the latter is probably due to the intercalated water which affected the orientation of the sulphate ion in the interlamellar space [14]. A small addition of zinc did not affect the cell parameters described above. When further zinc was added, the *a* parameter increased from 0.300 nm to 0.305 nm for (Mg + Zn)/Al = 1, and from 0.304 nm to 0.307 nm for the ratio equal to 3. The same behaviour is observed for the *c* parameter, which increases with Zn/Mg ratio. The increase in *a* when zinc is added, is probably due to the substitution of magnesium by zinc which creates difficulties for aluminium dissolution. These difficulties in the substitution of magnesium and zinc by aluminium result in a less positive charge in the brucite-like layer. As a consequence, a weak interaction between the anions in the interlamellar space and the brucite layers can partially explain the increase of the *c* parameter.

For few samples, the X-ray pattern showed the presence of two phases with different *c* parameters indicating the coexistence of hydrated layers with high distance d_{003} about 1.20 nm, and non-hydrated layers with $d_{003} = 0.86$ nm. Brindley and Kikkawa [15] suggested the presence of an interstratified compound with sulphate anions in the Mg–Al system, but in our case we could not detect the presence of the combined layer spacing (2.06 nm).

TABLE II Observed and calculated X-ray diffraction pattern for Sample 9

d_{obs} (nm)	I/I_0	d_{calc} (nm)	*hkl*
0.875	100	0.8750	003
0.4383	45	0.4375	006
0.2612	27	0.2602	102
0.2329	18	0.2369	105
0.1948	12	0.1968	108
0.1533	26	0.1533	110

3.4. TG and DTA analysis

According to TG analysis in Fig. 2, the samples showed the presence of the first weight loss step around 60–200 °C corresponding to the loss of interlayer water and the physically adsorbed water. In the range 300–500 °C, the loss of hydroxyl ions and CO_3^{2-} is observed. The third step is assigned to the decomposition of the sulphate ion at a relatively high temperature between 800 and 1000 °C. The first two weight losses are well known in the case of hydrotalcite-like compounds [16].

The DTA curves (Fig. 2) indicate the existence of endothermal peaks for each step of weight loss. The loss of physically adsorbed water is accompanied by an endothermal peak around 70 °C for the samples. The peak between 150 and 180 °C corresponds to the loss of intercalated water. This peak is shifted to lower temperature in the Mg–Zn–Al system compared to the Mg–Al system. The decomposition of the brucite layers corresponds to the endothermal peak in the range 300–500 °C. The position depends on the zinc content: when it increases, the peak shifts to lower temperature. This suggested that the zinc ion decreases the forces between anions and brucite layers in agreement with the results of X-ray diffraction studies.

Attempts were made to calculate the interlayer water content and to correlate it to the interlayer distance, but the physically adsorbed water in some cases was difficult to determine precisely.

The third peak in DTA is at 930–970 °C. Its position is lower in the Mg–Zn–Al system than in the Mg–Al system (970 °C). The SO_4^{2-} anion is decomposed to SO_3, and the structure of the product is totally changed to metallic oxide and spinel form.

3.5. Influence of preparation temperature

For some samples the synthesis and ageing temperature were varied from room temperature to 40, 60 and 75 °C. The chemical analysis showed that for a temperature in the range 70–75 °C the difference between theoretical and experimental ratios of Zn/Mg and (Mg + Zn)/Al is negligible, indicating that the metallic ions are more reactive in the solid solutions at 70–75 °C than at room temperature. However, the ratio SO_4/2Al is always different from 1 with a small variation at high temperature compared to room temperature.

The rise of temperature does not influence the nature of the phase formed. The hydrotalcite is the most important phase obtained with various d_{003}, depending on the hydration state. The same kind of results were obtained by Doesburg *et al.* [17] in the Cu–Zn–Al system where hydroxide layers were formed by coprecipitation of metal carbonate solutions at different temperatures.

3.6. Infrared spectroscopy

The infrared spectra were recorded for all the samples in the 4000–400 cm^{-1} range. The changes in the interlayer orientation and arrangement of sulphate ions can be characterized by the molecular vibration of anion bands [12, 14]. This technique is used to obtain further information about the behaviour of the sulphate anions in the interlamellar space of our products. The infrared data did not show an important variation in the bands with zinc addition except for the band characteristics of the carbonate ion (Fig. 3). In the 3500–3200 cm^{-1} region, the spectra show a broad band due to the OH stretching with a maximum at 3300 cm^{-1} evincing that the samples contain hydrogen bonds. An absorption band at 1600–1580 cm^{-1} indicates the presence of molecular water. The ν_3 (stretching) mode for the sulphate ion is at 1100 cm^{-1} showing that the ν_3 band does not effectively split. In addition, the SO_4^{2-} group retains the (43 *m*) symmetry. Thus, we can conclude that sulphate ions are not directly coordinated to the metallic ions. Furthermore, the small differences between the observed vibration and those of the free anion, $\nu_3 = 1105\ cm^{-1}$, indicate that the perturbation produced inside the interlameller space is rather symmetric. This confirms that there is no change in the symmetry group of the sulphate anion. Depending on the sample, the other bands characteristic of the sulphate anion at 620 and 450 cm^{-1}, cannot be detected.

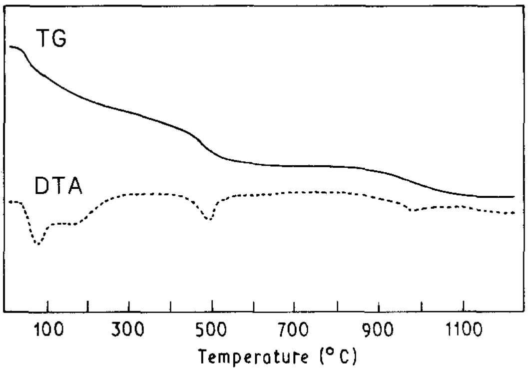

Figure 2 DTA and TG curves of sulphate hydrotalcite of Sample 4.

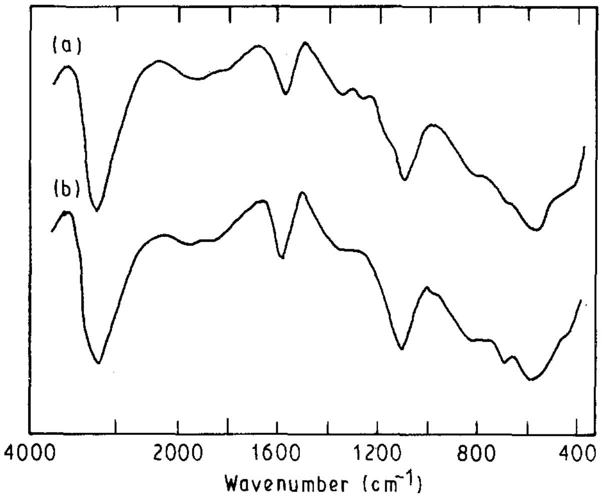

Figure 3 Infrared absorption spectra of sulphate hydrotalcite at (Mg + Zn)/Al = 3 and different Zn/Mg ratios: (a) 0.2, (b) 10.

On studying the Mg–Al system with the SO_4 ion, Miyata and Okada [6] observed a clear split of ν_3 and ν_4 bands of sulphate modes, but in our case we did not record this split and our results are in good agreement with those of Hernandez-Moreno *et al.* [12] and Danilov *et al.* [18].

The difficulty in the synthesis of carbonate-free products is shown by infrared spectroscopy. All the spectra of our products possessed an absorption band at 1360–1340 cm^{-1} corresponding the ν_3 mode. Its intensity is variable from one sample to another, but generally is weaker than the band of SO_4 anions.

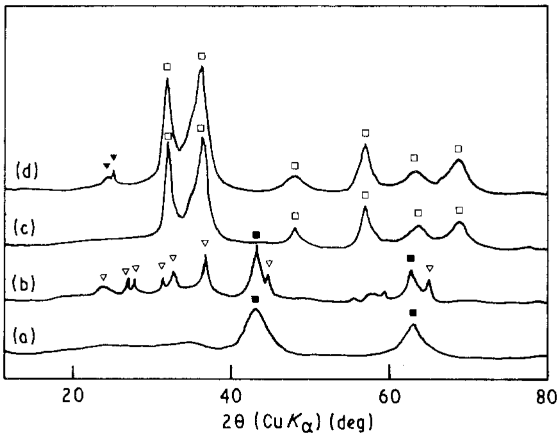

Figure 4 X-ray powder patterns of sulphate hydrotalcite at (Mg + Zn)/Al = 3 and different Zn/Mg ratios calcined at 500 °C. Zn/Mg: (a) 0, (b) 0.087, (c) 1, and (d) 10. (■) MgO, (□) ZnO, (▼) (Mg, Zn)SO_4, (▽) unknown phase.

3.7. Thermal behaviour at high temperature

At low temperature around 100–200 °C, the loss of interlayer water leads to a decrease in the interlayer distance d_{003}. This dehydration of the sample is easier on the addition of zinc to the solid solution. At 350 °C, the hydrotalcite containing a small amount of zinc is still stable. However, in the case of a large amount of zinc, we also observed the presence of zinc oxide. With the ratios Zn/Mg = 6 and (Mg + Zn)/Al = 3, the destruction of hydrotalcite occurs at 350 °C, and only the formation of zinc oxide was observed.

At 500 °C, the structure of hydrotalcite is destroyed in all the samples, and the metallic oxide is formed. Magnesium oxide is formed at very low Zn/Mg ratios; and zinc oxide and magnesium sulphate ($MgSO_4$) are formed at relatively high Zn/Mg ratios (Fig. 4). In the range 500–750 °C, we obtained the metal oxide (ZnO, MgO), the magnesium sulphate and the magnesium–zinc sulphate (Zn, Mg)SO_4 with spinel form to a small extent. At high temperature around 1000 °C, the sulphate phase is transformed to magnesium oxide and spinel at low Zn/Mg ratio; the zinc and magnesium oxides appeared together with the spinel phase around Zn/Mg = 0.5–2. The magnesium phase disappears, when the Zn/Mg ratio is high, and only zinc oxide and spinel phases are observed.

In the Mg–Al system, the hydrotalcite is stable at temperatures higher than 300 °C, but the presence of zinc accelerates the decomposition of the structure and decreases the thermal stability of the metal hydroxide layers. These remarks are in good agreement with the results obtained by DTA analysis.

According to the results reported above, the thermal decomposition is achieved by the following steps: around 100–300 °C the dehydration of the hydrotalcite occurs, complete dehydroxylation and formation of MgO and/or ZnO with substitution by aluminium occurs at 300–500 °C; at 500–800 °C $MgSO_4$ and (Zn, Mg)SO_4 are decomposed into oxides and the interaction between aluminium and MgO forms a spinel phase.

4. Conclusions

1. The formation of hydrotalcite-like compounds in the magnesium–zinc–aluminium sulphate system is possible, whatever the Zn/Mg and (Mg + Zn)/Al ratios. This is not possible in the zinc–copper–aluminium carbonate system.
2. The increase in the preparation temperature of the hydrotalcite improves the reactivity of the metal cations during the coprecipitation.
3. The presence of the zinc cation in the solid solution decreases the thermal stability of the hydrotalcite at relatively high temperatures, compared to the Mg–Al system.

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