

## DISCRIMINATION BETWEEN SYNTHETIC Mg–Al DOUBLE HYDROXIDES AND RELATED CARBONATE PHASES

G. MASCOLO and O. MARINO

*Istituto di Chimica Applicata, Facoltà d'Ingegneria dell'Università di Napoli, Naples (Italy)*

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### ABSTRACT

Pure mixed Mg–Al double hydroxides were utilized for the preparation of the corresponding Mg–Al hydroxycarbonates. Three different modes of carbonation were adopted: CO<sub>2</sub> was bubbled through Mg–Al double hydroxides or these compounds underwent exchange with NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> in aqueous solution. The resulting carbonated phases were investigated by X-ray, DTA, TG, and analysed chemically, and the results compared with those of mixed Mg–Al double hydroxides.

### INTRODUCTION

The synthesis of pure Mg–Al double hydroxides was reported in a previous paper [1]. These compounds can be considered as Mg(OH)<sub>2</sub>–Al(OH)<sub>3</sub> solid solutions having the following formula: [Mg<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup> [x OH(0.81 – x)H<sub>2</sub>O]<sup>x-</sup>, with 0.23 ≤ x ≤ 0.33. They were indexed on the basis of a rhombohedral lattice; the *c* values for the compounds at the ends of the range are 22.6 and 23.4 Å for the Al-rich and Al-poor compounds, respectively.

These compounds have the same basic structure as hydrotalcite [2] and synthetic materials [3] described elsewhere as Mg–Al hydroxycarbonates, which consist of positively-charged brucite-like layers, and an interlayer balancing sheet containing carbonate ions and water molecules.

As the Mg–Al double hydroxides showed a pronounced capacity for anionic exchange [1], due to exchangeable OH<sup>-</sup> in the interlayer sheet, it is interesting to study exchange with CO<sub>3</sub><sup>2-</sup> anions. This has a dual purpose, firstly to prepare Mg–Al hydroxycarbonates from Mg–Al double hydroxides, and secondly to discriminate between them, since there is some debate in the literature on this subject at present [4–6].

### EXPERIMENTAL

Pure Mg–Al double hydroxides (DH) were prepared according to a previous paper [1], except that the temperature adopted was 50°C. Three different methods were employed in the carbonation of the DH samples; in the first place, CO<sub>2</sub> gas was bubbled through suspensions of pure DH in dis-

tilled water at room temperature for 24 h. The other experiments involved anionic exchange: in the first case a 0.1 M aqueous solution of  $\text{NaHCO}_3$  was passed over a solid bed of the DH sample, while in the second a 0.1 M aqueous solution of  $\text{Na}_2\text{CO}_3$  was utilized for the exchange. The solids were then dried over silica gel and characterized.

$\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  were determined using atomic absorption spectroscopy (Perkin-Elmer 300 s) by dissolving the solid in dilute nitric acid.  $\text{H}_2\text{O}$  was determined as the difference between ignition loss and  $\text{CO}_2$  content, the latter being determined by a calcimeter. The evolution of  $\text{CO}_2$  from the solid was also determined after heating the sample at different temperatures. Thermogravimetric analyses (TG) were carried out on 50-mg samples at a heating rate of  $6^\circ\text{C min}^{-1}$ , using a Stanton Massflow. A Du Pont 900 thermal analyzer was used for DTA employing the following conditions: heating rate  $10^\circ\text{C min}^{-1}$ , a 20-mg sample, reference sample  $\alpha\text{-Al}_2\text{O}_3$ , and  $\Delta T$  sensitivity of  $0.02\text{ mV in}^{-1}$ .

The reaction products were characterized using by X-ray powder diffraction analysis using  $\text{CuK}\alpha$  radiation and a Guinier de Wolff camera.  $\text{Pb}(\text{NO}_3)_2$  was used as a reference.

## RESULTS AND DISCUSSION

Four Mg–Al double hydroxides, free of  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$ , were synthesized at  $50^\circ\text{C}$ . The compositions, expressed as the molar ratio  $X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Al})$ , were 0.67, 0.69, 0.71 and 0.73.

Three specimens were obtained for each DH sample, one by each of the three different carbonation methods employed; these showed no significant differences on characterization. On the other hand, no significant variation was observed between the X-ray powder pattern of DH and that of the corresponding carbonated sample (DHC), making discrimination by X-ray powder analysis impossible.

Thermal data, however, offer one possible means of discriminating between the DH and the corresponding DHC phases. Figure 1 shows the DTA curves of the DH samples (a) and the corresponding DHC phases (b). The low temperature peak due to the water molecules of the interlayer sheet in the DH samples [1] has quite disappeared in the corresponding DHC curves. On the other hand, an increase in the area of the second peak is observed for the carbonated samples. The latter peak coincides with the loss of the interlayer OH groups as water from the DH samples.

Figure 2 shows the TG curves obtained for the DH sample ( $X_{\text{Mg}} = 0.71$ , a) and the corresponding DHC sample (b). A difference in total weight loss of about 1% has been found both in this case and for all other DHC and corresponding DH samples. The first loss of weight by the DH sample in Fig. 2 coincides perfectly with the loss of the water molecules of the interlayer sheet [1]. This weight loss shifts to a higher temperature for the DHC sample and a  $\Delta W$  can be observed, corresponding with the temperature at which all the interlayer water was evolved from the DH sample. This sample shows a second drop, corresponding to loss of the interlayer OH anion: the evolution

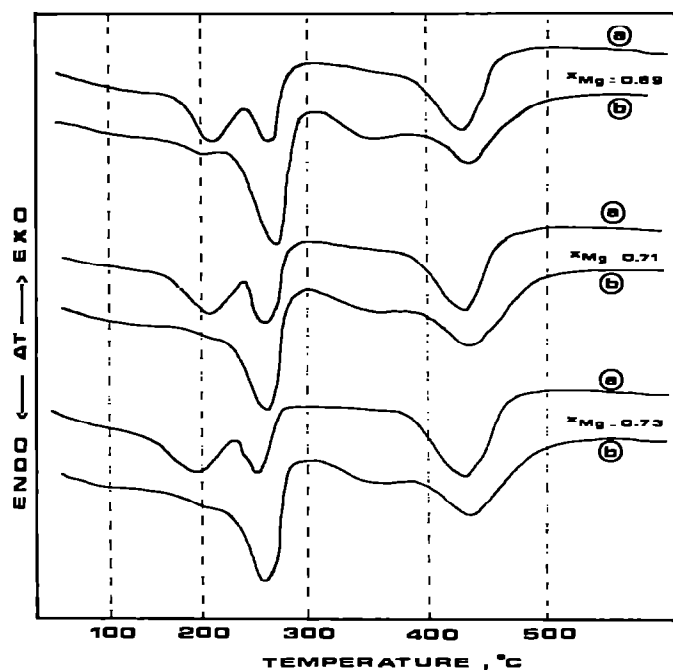


Fig. 1. DTA curves of Mg-Al double hydroxides (a) and the corresponding hydroxycarbonates (b).

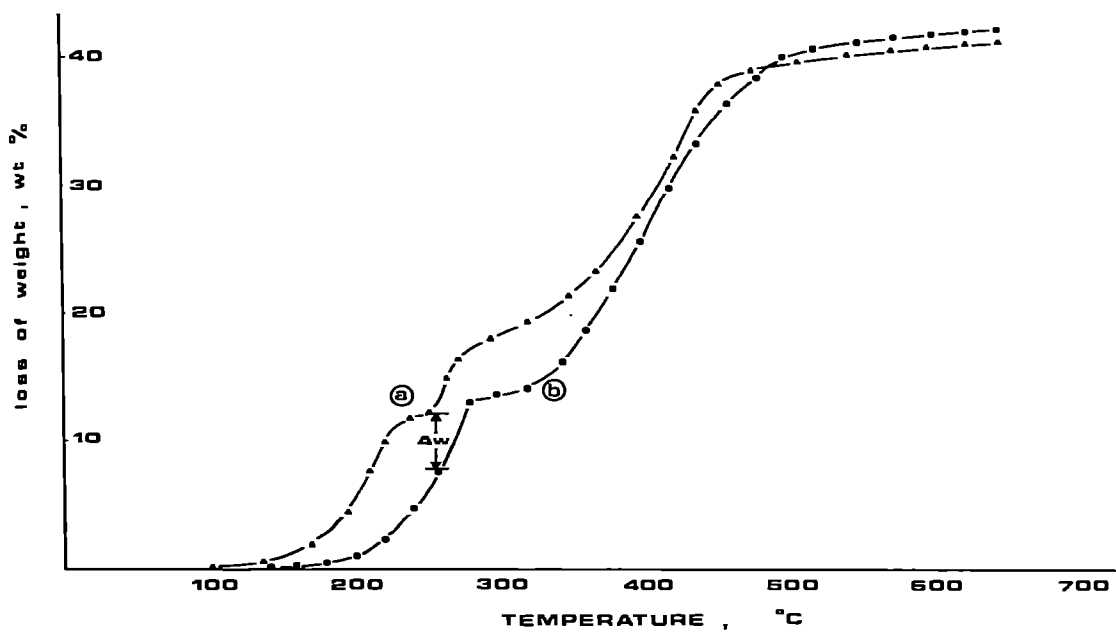


Fig. 2. TG curves for Mg-Al double hydroxide (a) and the corresponding carbonated phase (b), with composition  $X_{Mg} = 0.71$ .

of  $\text{CO}_2$  from the DHC sample possibly corresponds to the  $\Delta W$  temperature (curve b in Fig. 2), since the latter is comparable with the temperature maximum  $\text{CO}_2$  evolution from the DHC sample (Fig. 3). Some of the difference is related to dynamic and static determination, respectively.

Since no variation in the X-ray powder patterns has been observed between the DH and the corresponding DHC samples, this implies that number of moles of oxygen in the interlayer sheet must be equal for both samples. The chemical formula for the DH phase is [1]  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+} \cdot [x \text{ OH}(0.81 - x)\text{H}_2\text{O}]^{x-}$ , with  $0.23 \leq x \leq 0.33$ . The following substitutions may be hypothesized on carbonation:  $\text{CO}_2$  for  $2 \text{ H}_2\text{O}$ ;  $\text{HCO}_3^-$  for  $\text{OH}^- + 2 \text{ H}_2\text{O}$  and  $\text{CO}_3^{2-}$  for  $2 \text{ OH}^- + \text{H}_2\text{O}$ .

The substitution of  $\text{CO}_2$  for  $2 \text{ H}_2\text{O}$  involves a total difference in weight loss of about 2% between the DHC and the corresponding DH samples, which is in disagreement with the observed value of about 1% for all the samples. The substitution of  $\text{HCO}_3^-$  for  $\text{OH}^- + 2 \text{ H}_2\text{O}$  involves no interlayer water for the DHC samples with  $X_{\text{Mg}} > 0.73$  and is again in disagreement with TGA data. The more reliable substitution is  $\text{CO}_3^{2-}$  for  $2 \text{ OH}^- + \text{H}_2\text{O}$ , which agrees with the  $\Delta W$  given in Fig. 2, related to the different loss of interlayer water between the DHC and the corresponding DH phases.

Assuming the substitution  $\text{CO}_3^{2-} = 2 \text{ OH}^- + \text{H}_2\text{O}$ , the following formula can be assigned to the DHC samples:  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+} \cdot [x/2 \text{ CO}_3 \cdot (0.81 - 3/2 x)\text{H}_2\text{O}]^{x-}$ , with  $0.23 \leq x \leq 0.33$ . The chemical compositions of the DHC samples were calculated on this basis and compared with those found experimentally. Very good agreement may be observed from the data shown in Table 1. It must be pointed out that no alkali was found in specimens carbonated with aqueous solutions containing  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ ; hence no cation exchange was observed to take place.

The following hypotheses can be put forward to justify the substitution

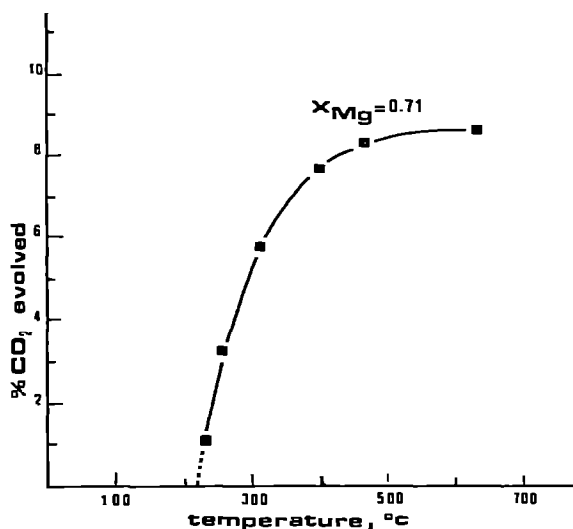


Fig. 3. Evolution of  $\text{CO}_2$  from Mg-Al hydroxycarbonate with  $X_{\text{Mg}} = 0.71$  heated to various temperatures.

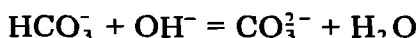
TABLE 1

Found and calculated (in parentheses) chemical analyses of Mg—Al hydroxycarbonates (% by weight) \*

$X_{Mg}$	MgO	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	CO <sub>2</sub>	Ignition loss
0.67	(36.12)	(22.50)	(31.65)	(9.71)	(41.36)
	36.02	22.78	32.00	9.04	41.04
0.69	(37.26)	(21.17)	(32.42)	(9.13)	(41.56)
	37.13	20.87	32.79	9.01	41.80
0.71	(38.39)	(19.84)	(33.19)	(8.56)	(41.75)
	38.65	19.55	33.13	8.67	41.80
0.73	(39.53)	(18.50)	(33.97)	(7.98)	(41.95)
	40.28	28.52	32.94	8.33	41.17

\* The chemical analyses were carried out on samples dried on silica gel.

of CO<sub>3</sub><sup>2-</sup> for 2 OH<sup>-</sup> + H<sub>2</sub>O during the carbonation of the DH samples by CO<sub>2</sub> gas. Diffusion of CO<sub>2</sub> in the interlayer sheet of the DH samples gives, firstly, substitution of CO<sub>2</sub> for 2 H<sub>2</sub>O, followed by redistribution in accordance with the substitution of CO<sub>3</sub><sup>2-</sup> for 2 OH<sup>-</sup> + H<sub>2</sub>O mentioned above. Another possibility is related to the equilibria of CO<sub>2</sub> in alkaline solution



and the higher selectivity of the DH sample for the CO<sub>3</sub><sup>2-</sup> anion during the exchange.

## CONCLUSIONS

Mixed Mg—Al double hydroxides [Mg<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>[x OH(0.81 - x)-H<sub>2</sub>O]<sup>x-</sup>, with 0.23 ≤ x ≤ 0.33 give the corresponding carbonated phases [Mg<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>[x/2 CO<sub>3</sub>(0.81 - 3/2 x)H<sub>2</sub>O]<sup>x-</sup> with the substitution of CO<sub>3</sub><sup>2-</sup> for 2 OH<sup>-</sup> + H<sub>2</sub>O. No variation in the characteristics of carbonated phases with method of carbonation has been observed.

X-ray analysis showed no variation between Mg—Al double hydroxides and the related carbonated phase. Discrimination between these compounds can be obtained by thermal or chemical analysis.

## ACKNOWLEDGEMENT

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