

# PHYSICO-CHEMICAL PROPERTIES OF SYNTHETIC HYDROTALCITES IN RELATION TO COMPOSITION

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**Abstract**—Hydrotalcite solid solutions were prepared by coprecipitation followed by hydrothermal treatment between 150° and 250°C. Based on the structural formula  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}[(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}]^{x-}$ , pure solid solutions were formed in the range  $\text{Al}/(\text{Al} + \text{Mg}) = 0.2$  to 0.33, where  $m = (1 - 3x/2)$ . Maximum crystallite size was achieved by hydrothermal treatment between 180° and 200°C, with  $x = 0.337$  to 0.429. Crystal strain was also minimized at these values of  $x$ . The adsorption capacity for Naphthol Yellow S increased as  $x$  increased and reached a maximum ( $1.56 \times 10^{-6}$  moles/m<sup>2</sup>) when  $x = 0.287$ , a value eight times larger than that of  $\text{Mg}(\text{OH})_2$ . A weak endothermic DTA peak at about 350°C is probably due to the loss of structural water in the main layer of the structure. On calcination between 400° and 700°C, only periclase was detected, probably containing Al in solid solution. Hydration of the calcined product resulted in the reconstruction of the original hydrotalcite structure.

**Key Words**—Crystal strain, Hydrotalcite, Solid solution, Synthesis, Thermal stability.

## INTRODUCTION

Synthetic hydrotalcite  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$  is utilized as an antacid, an anti-peptin, a Ziegler-Natta type catalyst support, and an adsorbent for acid and anionic substances. Recently, it has also been used in combination with a polyolefin as a nontoxic and non-smokey flame retardant. The composition and physical properties of solid solutions of hydrotalcite, however, are not well established. Two minerals have the above formula: hexagonal manasseite, with  $a = 3.1 \text{ \AA}$  and  $c = 15.3 \text{ \AA}$ , and rhombohedral hydrotalcite, with  $a = 3.1 \text{ \AA}$  and  $c = 23.1 \text{ \AA}$  (Frondel, 1941). These are respectively the 2- and 3-layer polytypes of the same basic structure. Syntheses by coprecipitation were reported by Feitknecht (1942), Gastuche *et al.* (1967), and Miyata *et al.* (1971). The products showed hydrotalcite-like structures and were of variable composition expressed by the formula  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}[(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}]^{x-}$ , where  $x$  varied from about 0.1 to 0.34 and  $m = 1 - 3x/2$ . The unit layer of the hydrotalcite structure consists of a basic layer that is positively charged by substitution of Al for Mg, and a negatively charged interlayer containing carbonate and water molecules (Allmann, 1968). The carbonate ion in the interlayer can be exchanged with other anions, and the thickness of the layer is determined by the ionic radius of the anion. The dehydrated material shows a molecular sieving property, and calcination yields highly active MgO (Kobo *et al.*, 1967; Miyata *et al.*, 1971; Miyata, 1975).

Roy *et al.* (1953) prepared hydrotalcite phases hydrothermally. In the present study, a more complex method was used, consisting of coprecipitation followed by hydrothermal treatment to facilitate crystallization, thus giving more precise information on the structure and physicochemical properties of the products. The samples and their calcined products were studied by X-ray powder diffraction, chemical analysis,

thermal analysis, adsorption of Naphthol Yellow S, electron microscopy, and BET surface area measurements. The results give information on the precise structural formula and the thermal stability of the interlayer water.

## EXPERIMENTAL

### Preparation of sample

Aqueous solutions of  $\text{MgCl}_2$  and  $\text{AlCl}_3$  ( $\text{Mg}^{2+} + \text{Al}^{3+} = 1 \text{ M}$ ),  $\text{NaOH}$  (2 M), and  $\text{Na}_2\text{CO}_3$  (0.2 M) were continuously added to a 2-liter reactor at total flow rate 40 ml/min,  $\text{CO}_3^{2-}/\text{Al}^{3+} = 0.70$ , temperature  $40 \pm 1^\circ\text{C}$ , and  $\text{pH} = 10 \pm 0.2$ . The mixture was thoroughly stirred during the reaction. The precipitate was filtered, and the  $\text{Cl}^-$  in the precipitate exchanged with  $\text{CO}_3^{2-}$  by adding 0.1 mole of  $\text{Na}_2\text{CO}_3$  per liter, corresponding to  $\text{CO}_3^{2-}/\text{Al}^{3+} = 0.5$ . The precipitate was washed with water and dried at 80°C for 20 hr. The dried sample (100 g) was suspended in 700 ml of deionized water and placed in a 1-liter autoclave. Following a hydrothermal treatment, the sample was filtered, washed with water, and dried at 80°C for 20 hr.

### Chemical analysis

Mg and Al were determined by chelatometric titration after dissolution in dilute HCl (Ueno, 1961). Carbonate was determined by a neutralization-titration method following the evolution of  $\text{CO}_2$ .

### X-ray powder diffraction

The X-ray powder diffraction pattern of each sample was recorded on a Philips X-ray diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation at 40 kV and 20 mA and a scanning rate of  $1/4^\circ 2\theta/\text{min}$ . A true half-maximum breadth ( $\beta$ ) was obtained from the equation  $B = b + \beta$ , where  $B$  is the half maximum breadth and  $b$  is an instrument breadth determined by using pure silicon.

Table 1. Effects of hydrothermal treatment time on the crystallite size ( $\epsilon$ ) and strain ( $\eta = \Delta d/d$ ) in the  $\{001\}$  direction.<sup>1</sup>

Temperature (°C)	40	150	150	150	150
Time (hr)	0	5	10	24	48
$\epsilon$ (Å)	112	526	654	800	909
$\eta$ ( $\times 10^{-3}$ )	2.18	3.15	2.73	3.29	3.26

<sup>1</sup> Al/(Mg + Al) = 0.250.

$K\alpha_1$  peaks were resolved by the Jones method (1938). The crystallite size ( $\epsilon$ ) and strain ( $\eta = \Delta d/d$ ) were calculated from the equation of Williamson and Hall (1953):

$$\beta_{(hkl)} = \lambda/\epsilon_{(hkl)} \cdot \cos \theta_{(hkl)} + 2\eta_{(hkl)} \cdot \tan \theta_{(hkl)},$$

where  $\lambda$  is the wavelength of the radiation.

#### Thermal analysis

The differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) diagrams were recorded on a Rigaku Denki DG-CIH unit using a heating rate of 5°C/min.

#### Surface area

Specific surface areas were measured by the BET method using  $N_2$  at liquid nitrogen temperature.

#### Adsorption of Naphthol Yellow S (NYS)

About 1 g of sample was added to 100 ml of an aqueous solution of NYS (500 ppm) in a 300-ml flask and stirred overnight at 30°C. The mixture was then filtered, and 5 ml of the filtrate was diluted with deionized water to 250 ml. The amount of NYS adsorbed was estimated by measuring the difference in absorption at 430 nm using a Hitachi model 101 spectrophotometer.

#### Electron microscopy

Transmission electron micrographs of the samples suspended in ethyl alcohol and dispersed ultrasonically for 5 min were taken with a Nihon Denshi JEM-T7S electron microscope at a magnification of 30,000 times and an accelerating voltage of 60 kV.

## RESULTS AND DISCUSSION

#### Effects of hydrothermal treatment on the crystallite size and strain

The crystallite size and strain of the compound with  $x = 0.250$  after hydrothermal treatment at 150°C for

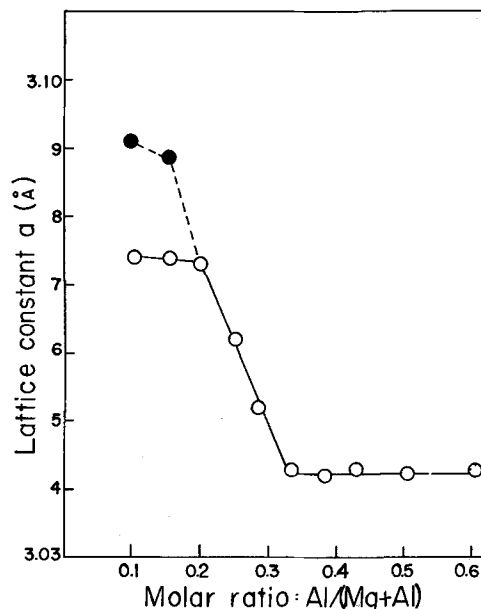


Figure 1. The relation between the ratio Al/(Mg + Al) and lattice parameter  $a$ . O and ● denote  $CO_3^{2-}/Al^{3+}$  ratios of 0.70 and 0.50, respectively.

different times are given in Table 1. The crystallite size increased markedly in the first 10 hr. Crystallite strain was almost independent of the treatment time. Table 2 shows effects of the treatment temperature for samples treated for 24 hr. The crystallite size increased up to 180°C but decreased above 200°C. Strain became larger at the higher temperatures and reached a maximum at 250°C. Maximum crystallite size was achieved at 180°–200°C with  $x = 0.250$  to 0.429. Strain was minimum at 150°C with  $x = 0.337$  to 0.429. The sample having  $x = 0.337$  had a larger crystallite size and smaller strain than that having  $x = 0.250$  after the same hydrothermal treatment (150°C, 24 hr).

#### Degree of aluminum replacement for magnesium

Miyata *et al.* (1971) assumed that Al could replace Mg in the range  $x = 0.1$ –0.34. This assumption was based on a linear relation between the ratio Al/(Mg + Al) and the thickness of the unit layer [ $d(003)$ , for a 3-layer polytype]. However, the change in the thickness of unit layer is caused not only by dimensional changes in the main layer,  $[Mg_{1-x}Al_x(OH)_2]^{x+}$ , but also by such changes in the interlayer,  $[(CO_3)_{x/2} \cdot mH_2O]^{x-}$ .

Table 2. Effects of hydrothermal treatment temperature on the crystallite size ( $\eta$ ) and strain ( $\eta$ ) in the  $\{001\}$  direction.<sup>1</sup>

Temperature (°C)	40	150	170	180	200	250
Time (hr)	0	24	24	24	24	24
$\epsilon$ (Å)	134	870	1282	1616	1653	820
$\eta$ ( $\times 10^{-4}$ )	6.82	2.27	7.12	5.91	6.59	87.1

<sup>1</sup> Al/(Mg + Al) = 0.337.

The change in the thickness of the main layer should be directly related to a change in the lattice parameter,  $a$ . If  $\text{Al}^{3+}$  substitutes for  $\text{Mg}^{2+}$ , the lattice parameter  $a$  should change linearly with the ratio  $\text{Al}/(\text{Mg} + \text{Al})$ . Figure 1 shows that such a linear relation holds in the range of  $x = 0.201\text{--}0.337$ . When  $x = 0.201$ , hydromagnesite formed easily. When a sample with  $x = 0.201$  was prepared at  $\text{CO}_3^{2-}/\text{Al}^{3+} = 0.5$ , a linear relation was found between  $x = 0.156$  and  $x = 0.337$ . A slight difference in slope between a range of  $x = 0.156\text{--}0.201$  and that of  $x = 0.201\text{--}0.337$  suggests a slight difference in structure. From the intercept at  $x = 0$ , a value of  $3.141 \text{ \AA}$  is obtained, very close to that of  $\text{Mg}(\text{OH})_2$ .

Other products formed included boehmite ( $\alpha\text{-AlOOH}$ ) for  $x > 0.337$ , hydromagnesite ( $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) for  $0.105 < x < 0.201$ , and a mixture of hydromagnesite and  $\text{Mg}(\text{OH})_2$  for  $x < 0.105$ .

#### Relation of $\text{Al}/(\text{Mg} + \text{Al})$ and $\text{CO}_3^{2-}/2\text{Al}^{3+}$

Table 3 gives  $\text{CO}_3^{2-}/\text{Al}^{3+}$  ratios and other data for various samples in which solid solutions were formed. When  $x \leq 0.2$ , the ratio of  $\text{CO}_3^{2-}/2\text{Al}^{3+}$  is high, due to formation of hydromagnesite. In contrast, the ratio is less than 1 for the sample with  $x = 0.337$  because of formation of boehmite. When  $0.250 < x < 0.337$ , the ratio of  $\text{CO}_3^{2-}/2\text{Al}^{3+}$  is nearly unity. The ratio was closest to unity for sample s-6, where  $\text{Al}/(\text{Mg} + \text{Al})$  is 0.337.

#### Electron microscopy

Electron micrographic examination of sample s-4 showed that after hydrothermal treatment at  $150^\circ\text{C}$  for 24 hr, most of the crystals are spherulitic aggregates of thin crystals. Many of the grains in samples s-6 and s-8 are hexagonal-like aggregates of thick crystals, suggesting that in addition to rhombohedral

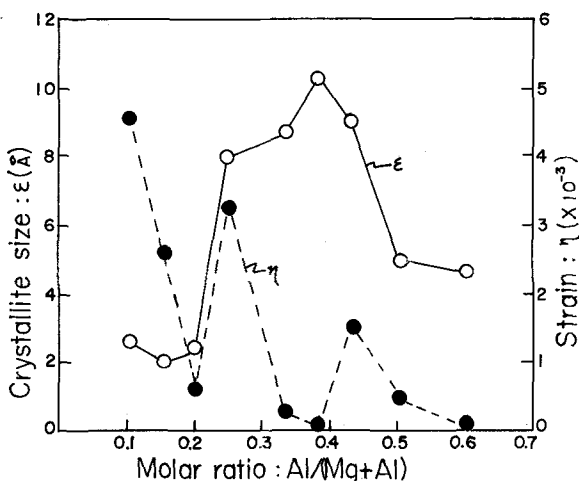


Figure 2. The relation between the ratio  $\text{Al}/(\text{Mg} + \text{Al})$ , crystallite size ( $\epsilon$ ), and crystal strain ( $\eta$ ).

hydrotalcite, the formation of hexagonal manasseite becomes appreciable as the proportion of Al increases.

#### Crystallite size and strain

Figure 2 shows variations of crystallite size ( $\epsilon$ ) and strain ( $\eta$ ) in the direction of  $\{001\}$  for samples of varying  $\text{Al}/(\text{Mg} + \text{Al})$  ratios after hydrothermal treatment at  $150^\circ\text{C}$  for 24 hr. The crystallite size increased with the increase of Al at  $x = 0.385$  and decreased at  $x > 0.385$ . The strain generally decreased with the increase of Al content, except at  $x = 0.250$ . In the range  $0.250 < x < 0.383$ , the crystallite size increased and the strain decreased with an increase of Al. The maximum crystallite size and minimum strain were observed at  $x = 0.337\text{--}0.383$ .

Table 3. Carbonate contents, BET results, lattice parameters, and products at various  $\text{Al}/(\text{Mg} + \text{Al})$  ratios.

Sample no.	Ratio $\text{Al}/(\text{Mg} + \text{Al})$	Ratio $\text{CO}_3^{2-}/2\text{Al}^{3+}$	BET $\text{m}^2/\text{g}$	Lattice parameter		Products <sup>1</sup>
				$a$ (Å)	$c$ (Å)	
s-1	0.105	3.66 (2.51) <sup>2</sup>	71	3.091 (3.091) <sup>2</sup>	23.78	HT, HM, B
s-2	0.156	1.90 (1.39) <sup>2</sup>	50	3.074 (3.089) <sup>2</sup>	23.76	HT, HM
s-3	0.201	1.48	45	3.073	23.69	HT, HM
s-4	0.250	1.07	24	3.062	23.34	HT
s-5	0.287	1.04	19	3.052	23.08	HT
s-6	0.337	0.988	15	3.043	22.70	HT
s-7	0.383	0.706	18	3.042	22.67	HT, A
s-8	0.429	0.646	28	4.043	22.67	HT, A
s-9	0.504	0.425	68	3.042	22.68	HT, A
s-10	0.604	0.309	85	3.043	22.69	HT, A

<sup>1</sup> HT, HM, A, and B denote hydrotalcite, hydromagnesite, boehmite ( $\alpha\text{-AlOOH}$ ), and  $\text{Mg}(\text{OH})_2$ .

<sup>2</sup> Parentheses denote that the preparation condition was  $\text{CO}_3^{2-}/\text{Al}^{3+} = 0.5$  and that the precipitate formed was not ion-exchanged with  $\text{Na}_2\text{CO}_3$  solution.

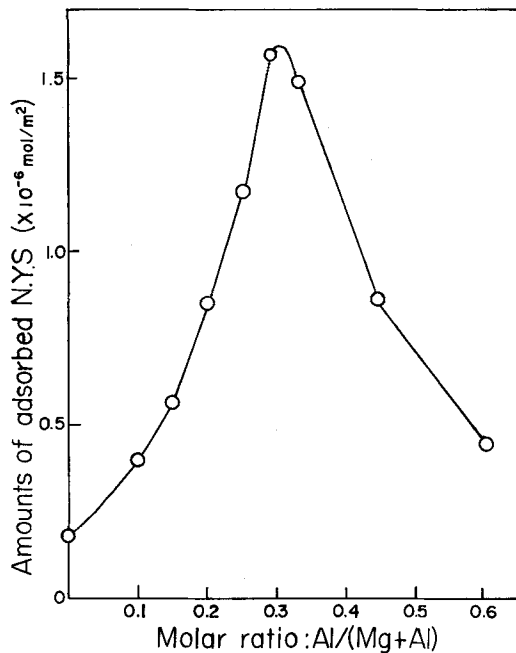


Figure 3. Naphthol Yellow S adsorption on hydrotalcites at various ratios of Al/(Mg + Al).

#### Derivation of structural formulae

Chemical analyses of samples s-11 and s-12, hydrothermally treated at 200°C for 24 hr, are given in Table 4. The Al/(Mg + Al) ratios of these samples are in the solid solution range. The first stage decreases on the TGA diagrams ( $-W_1$ ) and the amounts of physically adsorbed water (assumed from the losses on drying at 105°C for 3 hr) are also given in Table 4. The amount of interlayer water was determined by subtracting the amount of physically adsorbed water from the ( $-W_1$ ) value. The amount of structural water was obtained by subtracting the ( $-W_1$ ) value from the total amount of water. The structural formulae are summarized in Table 5. The amount of interlayer water is about  $5H_2O$  for

Table 4. Chemical analysis and thermal gravimetric analysis.

		Sample no.		
		s-11	s-12	s-13
$Al_2O_3$	(Wt. %)	16.3	18.6	21.9
$MgO$	(Wt. %)	38.6	36.5	34.3
$CO_2$	(Wt. %)	7.51	8.34	8.40
$H_2O$	(Wt. %)	37.6	36.5	43.8
Physisorbed				
$H_2O$	(Wt. %) <sup>1</sup>	0.70	0.60	0.86
$-W_1$	(Wt. %) <sup>2</sup>	4.9	13.8	12.9

<sup>1</sup> Weight decrease during heating at 105°C for 3 hr.

<sup>2</sup> Weight decrease at the first step of thermal gravimetric analysis.

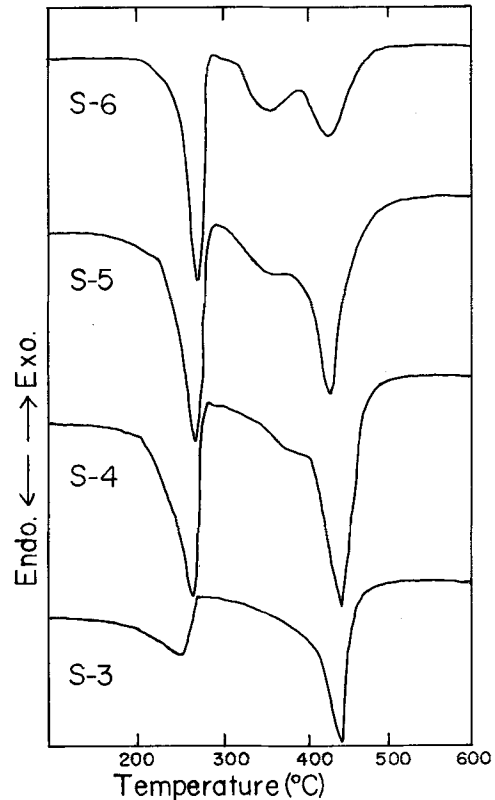


Figure 4. DTA curves for hydrotalcites treated hydrothermally at 150°C for 24 hr.

sample s-11 whose ratio of Mg to Al is similar to that of the natural hydrotalcite. The structural formula of synthetic hydrotalcite prepared at room temperature was determined by Miyata *et al.* (1971) by the same method to be  $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ , which has one molecule of  $H_2O$  less than in s-11. Frondel (1941) reported that natural hydrotalcite also has the same formula. On the other hand, Taylor (1973) reported that the general formula may be written as  $[Mg_{1-x}Al_x(OH)_2][CO_3]_{x/2}(H_2O)_{1-3x/2-\Delta}]$  where  $\Delta$  is  $< 0.125$ . The interlayer water for s-11 and s-12 correspond to  $\Delta = 0$ . Accordingly, the interlayer spaces of s-11 and s-12 are almost close packed with  $CO_3^{2-}$  and  $H_2O$ .

#### Chemisorption of Naphthol Yellow S (NYS)

The amounts of Naphthol Yellow S adsorbed at 30°C on samples hydrothermally treated at 150°C for 24 hr are plotted against Al/(Mg + Al) in Figure 3. The amount increased with the Al/(Mg + Al) ratio to a maximum of about  $x = 0.287-0.337$ , which is regarded as the upper limit for the solid solution. Above  $x = 0.337$ , the amount of adsorption decreased. The maximum amount of  $1.56 \times 10^{-6}$  mole/m<sup>2</sup> for the sample with  $x = 0.287$  is 8 times larger than the amount chemisorbed

Table 5. Structural formula for samples s-11 and s-12.

Sample no.	Structural formula
s-11	$[\text{Mg}_{0.750}\text{Al}_{0.250}(\text{OH})_{1.97}] [(\text{CO}_3)_{0.134}(\text{H}_2\text{O})_{0.618}]$ OR $[\text{Mg}_{5.99}\text{Al}_2(\text{OH})_{15.78}] [(\text{CO}_3)_{1.07} \cdot 4.94\text{H}_2\text{O}]$
s-12	$[\text{Mg}_{0.713}\text{Al}_{0.287}(\text{OH})_{1.99}] [(\text{CO}_3)_{0.149}(\text{H}_2\text{O})_{0.577}]$ OR $[\text{Mg}_{4.97}\text{Al}_2(\text{OH})_{13.85}] [(\text{CO}_3)_{1.04} \cdot 4.02\text{H}_2\text{O}]$

on  $\text{Mg}(\text{OH})_2$  prepared from  $\text{MgCl}_2$  and  $\text{Ca}(\text{OH})_2$  at pH 9.2 and 30°C; it corresponds about one molecule of NYS per 100 Å<sup>2</sup>.

#### Effects on the dehydration temperature and the amount of interlayer water

DTA and TGA data for samples hydrothermally treated at 150°C for 24 hr are shown in Figure 5. The weight decrease ( $-W_1$ ) is attributed to loss of the interlayer water. Both starting and peak temperatures for loss of interlayer rose with an increase in Al and reached a maximum for  $x = 0.337$ – $0.383$  at 170°C and 280°C, respectively. The interlayer water can be represented by the general formula described previously to be  $1 - 3x/2$ , and hence, will decrease with an increase in  $x$ , the lower limit for the formation of the solid solution. This relation is satisfied at  $x = 0.201$ – $0.337$  where no byproducts except for the solid solution were formed.

#### Assignment of the second endothermic peak in the DTA curve

On the DTA curve of natural hydrotalcite, a small second endothermic peak begins at about 300°C and reaches a maximum at about 350°C. Beck (1950) suggested that this second endotherm is due to loss of structural water bound with Al in the main layer. However, the peak has a small shoulder beginning at 400°C and can hardly be distinguished from the third peak.

The peak height of the second endothermic peak increases with Al content. The second endothermic peak is therefore attributed to the loss of structural water bound with Al or to the evolution of  $\text{CO}_2$ . Further, chemical analyses on outgassed samples s-6 ( $x = 0.337$ ) at 300°C, 400°C, and 500°C (Figure 4) showed that the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  contents did not change after outgassing at 300°C. When the sample was outgassed at 400°C, a temperature just above the second endothermic peak, the OH content decreased to 68% of the original amount, while the content of  $\text{CO}_2$  remained unchanged. After outgassing at 500°C, a temperature slightly above the third DTA peak, the amounts of  $\text{CO}_2$  and OH decreased to 23% and 5% of their original values, respectively. Therefore, the second endothermic peak is probably caused by the dehydration of a part of the OH. The third peak may be due to both dehydration of the remaining OH and removal of  $\text{CO}_2$ .

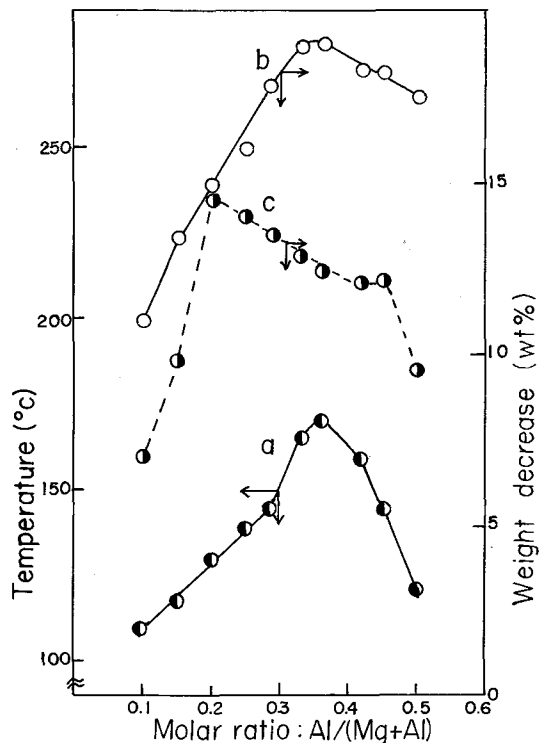


Figure 5. The relation of starting (a) and peak (b) temperature of dehydration of interlayer water and weight loss (c) at various ratios of Al/(Mg + Al).

#### Calcined hydrotalcite solid solution

It is of interest to know the form in which the Al occurs after thermal decomposition of the hydrotalcite structure. A sample with  $x = 0.287$ , hydrothermally treated at 200°C for 24 hr, was calcined at 300°–1000°C in air for 2 hr. After calcination at 300°C, both hydrotalcite and  $\text{MgO}$  were detected by X-ray diffraction, but after calcination at 400°–800°C only  $\text{MgO}$  could be detected. At 900°C  $\text{MgO}$ ,  $\text{MgAl}_2\text{O}_4$ , and a trace of  $\gamma\text{-Al}_2\text{O}_3$  were detected.

The lattice parameter  $a$  and crystallite size  $\epsilon$  for  $\text{MgO}$

Table 6. Chemical analysis for calcined  $\text{Mg}_{0.865}\text{Al}_{0.335}\text{Al}_{0.335}(\text{OH})_{1.95}(\text{CO}_3)_{0.149}(\text{H}_2\text{O})_{0.523} \cdot 1$

	Calcination temperature (°C)		
	300	400	500
Weight decrease (%)	12.4	23.8	38.7
Weight from TGA (%)	12.9	22.4	34.1
$\text{Al}_2\text{O}_3$ (%)	25.2	27.5	37.0
$\text{MgO}$ (%)	39.4	43.0	57.9
$\text{CO}_2$ (%)	9.70	10.6	3.31
$\text{H}_2\text{O}$ (%)	25.7	18.9	1.8
Molar ratio: $\text{CO}_2/(\text{Mg} + \text{Al})$	0.149	0.150	0.034
Molar ratio: $\text{OH}/(\text{Mg} + \text{Al})$	1.94	1.31	0.090

<sup>1</sup> 300°–500°C, 1hr, in air.

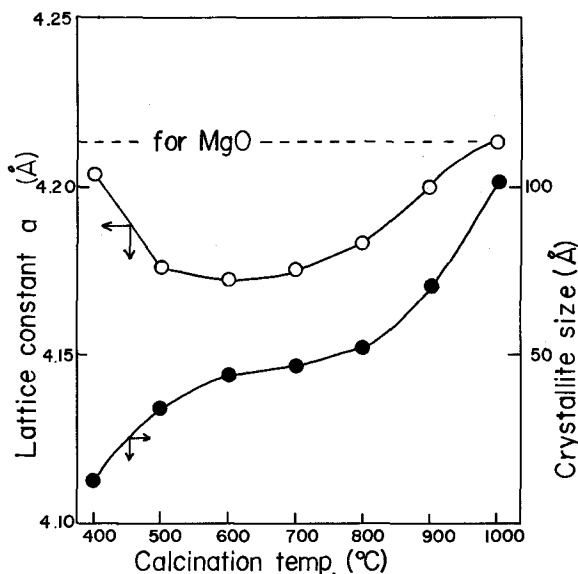


Figure 6. The relation between lattice parameter  $a$  (O), crystallite size (●), and calcination temperature for hydrotalcite  $[\text{Al}/(\text{Mg} + \text{Al})]$  calcined for 1 hr in air.

are plotted against calcination temperature in Figure 6. The value  $a$  was obtained by extrapolation of the lattice parameter calculated from the (200), (220), and (222) reflections to  $\Theta = 90^\circ$ . The value of  $\epsilon$  was calculated from the half height breadth of the (200) reflection. The  $a$  value of the samples calcined at  $500^\circ\text{--}700^\circ\text{C}$  showed a nearly constant value of  $4.174 \text{ \AA}$ , which is smaller than that  $4.214 \text{ \AA}$  for pure MgO (JCPDS, 1967) by  $0.039 \text{ \AA}$ . The  $a$  value increased with a rise of calcination temperature above  $800^\circ\text{C}$  and finally reached the value for pure MgO at  $1000^\circ\text{C}$ . Consequently, Al substitutes in MgO at  $500\text{--}700^\circ\text{C}$ .

The crystallite size was smaller than  $50 \text{ \AA}$  when the sample was calcined below  $800^\circ\text{C}$ . This value was much smaller than that for MgO obtained from pure  $\text{Mg}(\text{OH})_2$ . On calcination above  $800^\circ\text{C}$ , the crystallite size rapidly increased. The changes of the crystallite size and lattice parameter  $a$  have the same tendency. Consequently, Al substituting in MgO acts to inhibit crystal growth. If Al-containing MgO is reacted with water, it should first form hydrotalcite. Hydrotalcite calcined at  $400\text{--}800^\circ\text{C}$  with  $x = 0.287$  was hydrated at  $80^\circ\text{C}$  for 24 hr, and the products were examined by X-ray powder diffraction. According to Table 7, hydrotalcite was the only hydrated product detected in samples calcined at  $400\text{--}700^\circ\text{C}$ . The lattice parameter  $a$  is the same as that of the original sample. The samples calcined at  $800^\circ\text{C}$  also formed only hydrotalcite

Table 7. Hydrated product and lattice parameter for samples hydrated at  $80^\circ\text{C}$  for 24 hr after hydrotalcite with  $x = 0.287$  was calcined at  $400\text{--}800^\circ\text{C}$  in air.

Calcination temperature ( $^\circ\text{C}$ )	Hydrated product	Lattice parameter $a$ ( $\text{\AA}$ )
Untreated	Hydrotalcite	3.052
400	Hydrotalcite	3.052
500	Hydrotalcite	3.052
600	Hydrotalcite	3.053
700	Hydrotalcite	3.053
800	Hydrotalcite	3.065

but their lattice parameters are larger than that of the original sample. According to Figure 1, the molar ratio of this product is  $x = 0.235$ . On the other hand,  $\text{Al}_2\text{O}_3$  does not react with water under the above-mentioned conditions. Therefore, the results suggest that Al enters product MgO when hydrotalcite is calcined between  $400$  and  $700^\circ\text{C}$ .

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**Резюме**—Твердые растворы гидроталькита приготавливались соосаждением с последующей гидротермальной обработкой при температурах между 150° и 250°C. Чистые твердые растворы, основанные на структурной формуле  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}[(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}]^{x-}$ , образовывались в диапазоне  $\text{Al}/(\text{Al} + \text{Mg}) = 0,2$  до 0,33, где  $m = (1 - 3x/2)$ . Максимальный размер кристаллита был достигнут гидротермальной обработкой при температуре между 180° и 200°C, с  $x = 0,337$  до 0,429. Кристаллическая напряженность также была минимальной при этих значениях  $x$ . Адсорбционная способность для Нафтола желтого S увеличивалась с увеличением  $x$  и достигала максимума ( $1,56 \times 10^{-6}$  мол/м<sup>2</sup>) при  $x = 0,287$ , что в восемь раз выше значения для  $\text{Mg}(\text{OH})_2$ . Слабый эндотермический ДТА пик при температуре 350°C возможно обусловлен потерей структурной воды в главном слое структуры. При кальцинировании между 400° и 700°C был обнаружен только периклаз, возможно содержащий Al в твердом растворе. Гидротация кальцинированного продукта приводит к восстановлению первоначальной гидроталькитной структуры. [N. R.]

**Resümee**—Hydrotalkit-Mischkristalle wurden durch Fällung und anschließende hydrothermale Behandlung bei Temperaturen zwischen 150° und 250°C erzeugt. Gemäß der Strukturformel  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}[(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}]^{x-}$  werden reine Mischkristalle im Bereich  $\text{Al}/(\text{Al} + \text{Mg}) = 0,2$  bis 0,33 gebildet, wobei  $m = (1 - 3x/2)$  ist. Die maximale Kristallitgröße wurde durch eine hydrothermale Behandlung zwischen 180° und 200°C erreicht mit  $x$ -Werten von 0,337 bis 0,429. Die Kristalldeformation war bei diesen  $x$ -Werten minimal. Das Adsorptionsvermögen für Naphthol Gelb S nahm mit zunehmendem  $x$  zu und erreichte bei  $x = 0,287$  ein Maximum von  $1,56 \times 10^{-6}$  Mol/m<sup>2</sup>. Dieser Wert ist achtmal höher als der von  $\text{Mg}(\text{OH})_2$ . Ein schwacher endothermer DTA Peak bei ungefähr 350°C ist wahrscheinlich auf den Verlust von Kristallwasser zurückzuführen, das sich in den Hauptschichten der Struktur befindet. Bei der Kalzinierung zwischen 400° und 700°C wurde nur Periklas gefunden, der wahrscheinlich Al in fester Lösung enthält. Die Hydratisierung des kalzinierten Produktes führte wieder zu der ursprünglichen Hydrotalkitstruktur. [U. W.]

**Résumé**—Des solutions solides d'hydrotalcite ont été préparées par coprécipitation suivie d'un traitement hydrothermique entre 150° et 250°C. En se basant sur la formule de structure  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}[(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}]^{x-}$ , des solutions solides pures ont été formées sur l'étendue  $\text{Al}/(\text{Al} + \text{Mg}) = 0,2$  à 0,33, où  $m = (1 - 3x/2)$ . La taille maximum de cristallite a été atteinte par traitement hydrothermique entre 180° et 200°C, avec  $x = 0,337$  à 0,429. L'effort cristallin était aussi minimisé pour ces valeurs de  $x$ . La capacité d'adsorption pour le Naphthol Yellow S a augmenté proportionnellement à la croissance de  $x$  et a atteint un maximum ( $1,56 \times 10^{-6}$  moles/m<sup>2</sup>) quand  $x = 0,287$ , une valeur huit fois plus grande que celle de  $\text{Mg}(\text{OH})_2$ . Un faible sommet endothermique DTA à approximativement 350°C est probablement dû à la perte d'eau structurale dans la couche principale de la structure. Lors de la calcination entre 400° et 700°C, on n'a détecté que du périclase, contenant sans doute du Al en solution solide. L'hydratation du produit calciné a donné lieu à la reconstruction de la structure d'hydrotalcite d'origine. [D. J.]