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THE EFFECT OF RAW MATERIAL TYPE ON THE CHARACTERISTICS OF Mg-Al DOUBLE HYDROXIDES SYNTHESIZED BY HYDROTHERMAL METHOD

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ABSTRACT

Mg-Al double hydroxide was synthesized by refluxing water suspensions of three mixtures of suitable aluminium and magnesium compounds. When the mixture tested was: gamma alumina and magnesia, a unique double hydroxide was formed, it had a layer structure with a c' spacing of 7.36 Å which is shorter than any value given in literature. Some of its diffraction peaks were broaden and shifted. It is suggested that in this particular mixture some AlO^-_2 anions are formed at the interface of the double hydroxide, which expell the interlayer CO_3^{-2} anions as CO_2.

INTRODUCTION

Natural or synthetic magnesium aluminium hydroxides have formula and structure which fits the natural group of double hydroxides known as the pyroaurite-sjogrenite group. It comprises composition of the type: $R^{+2}_{1-x}R^{+3}_x(OH)_2\ {}^{+x}R^{-n}_{x/n}\cdot yH_2O$, where R^{+2} and R^{+3} are divalent and trivalent cations respectively, and R^{-n} is the anion. The structure consists of brucite-like octahedral layers with x net positive charge, per unit formula, balanced by an equal negative charge from interlayer anions. Water molecules occupy the remaining interlayer space (1). In the pyroaurite subgroup the layers are stacked in rombohedral symmetry of three layers per unit cell, while in the sjogrenite subgroup the stacking is hexagonal of two layers per unite cell. The interlayer anions are exchangable and may be replaced by an anion exchange process. The dominant anion in natural double hydroxides is CO_3^{-2}, the structural position of which in the interlayer spacing was described by Taylor (2). The value of the interlayer spacing of the Mg-Al double hydroxides depends on the character of its interlayer anions and the proportion of $Al^{+3}/Mg^{+2}+Al^{+3}$ in the brucite-like layers, being smaller for Al rich double hydroxides. When the interlayer anion is CO_3^{-2} or OH^- the values are between 7.6–7.8 Å. The unit-cell parameter a also decreases when the proportion of $Al^{+3}/Mg^{+2}+Al^{+3}$ increases, its value generally is 3.04–3.08 Å.

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Feitknecht and Greber in 1942 (3) were the first to synthesize magnesium-aluminium hydroxide, by precipitation with NaOH, from a solution containing both $MgCl_2$ and $AlCl_3$. The product was of rombohedral symmetry. Since then similar syntheses were described, all of which were based on precipitation from solutions of magnesium and aluminium salts, followed by washing out the remaining free ions. Few years ago a new method of synthesis, based on hydrothermal treatment, was described by Mascolo and Marino (4), the synthesis was carried out by heating water suspension of magnesium oxide and alumina gel in closed containers. The double hydroxide obtained by this method was of rombohedral symmetry. Its CO_2 content was less than 1%, relative to about 7% in hydrotalcite a natural magnesium aluminium hydroxide. The product of the hydrothermal treatment may also contain some brucite – $Mg(OH)_2$, gibbsite – $Al(OH)_3$, and boehemite – $AlO(OH)$, depending on the heating temperature and on Mg/Al molar ratio of the initial suspension (5).

Magnesium and aluminium coprecipitates are widelly used as raw materials for the spinel – $MgAl_2O_4$ preparation (6). The hydrothermal method attracted attention as a possible alternative for this aim. In this paper some of the results of this method of synthesis are described.

EXPERIMENTAL

Products preparation: Mixtures of Al and Mg compounds were refluxed in water for pre determined time, and up to 12 days. Since the intention was to prepare raw material for the spinel production the Al/Mg molar ratio of 2:1 was used (instead of 0.2–0.33, which is sufficient for double hydroxides). After the reflux the suspension was filtered and dried at 110°C, and stored in a dessicator containing silica gel. Three different sets of experiments were carried on, with the following mixtures:

I Moderately-reactive magnesia, of iodine No. 33 (Merck 5868), with aluminium hydroxide gel (poor crystalized gibbsite – Merck 1088);

II Magnesium hydroxide (Merck 5870), with the above mentioned aluminium hydroxide gel;

III The above-mentioned magnesia with aluminium oxide (Merck 1077), which was identified to be gamma alumina.

Products examination: Powder XRD patterns were obtained with CuK_α radiation. For obtaining accurate crystallographic interplanar spacing measurements, the samples were mixed with KBr or $Pb(NO_3)_2$ as internal standards.

Infra-red radiation absorption spectra were obtained using the KBr pellet technique, in which vacuum pressing of 2.5 mg of sample material in 250 mg of KBr was utilized.

D.T.A examinations were carried out with 50–100 mg samples at a heating rate of 10°C/min in ambient atmosphere.

The CO_2 content determinations were done by using a calcimeter.

RESULTS AND DISCUSSION

The X.R.D patterns of double hydroxides obtained from the above mentioned three mixtures, after 266, 289, and 236 hours of reflux, respectively, are shown schematically in Fig. 1. The double hydroxides obtained from mixtures I and II show sharp diffraction peaks and it is possible to identify weak peaks in the neighbourhood of strong peaks. The unit cell parameter a was calculated from the exact position of 1120 reflection peak near 1.52 A and the c parameter from the exact position of the peak near 3.78 Å which its index is 0006 when rombohedral symmetry is assumed or 0004 when hexagonal symmetry is assumed. From the results obtained the positions of the other peaks was calculated and compared to the experimental positions, once for rombohedral, and once for hexagonal indexing. The results of both mixtures fit the rombohedral symmetry. The unit cell parameters, a and c, and the interlayer spacing c' are respectively 3.044, 22.74, and 7.58 Å for mixture I, and 3.05, 22.62, 7.54 Å for mixture II. The results obtained, and the presence of some boehemite which accompained the double hydroxides, are in accordance with those obtained by Mascolo *et al.* (5) for similar Al/Mg molar ratio and heating temperature.

In mixture III the results are some what different. Some of the diffraction peaks are broader and shifted from their regular positions. The methods used in the former cases to define the symmetry did not give satisfactory results in this case. The comparison between calculated and experimental peak positions did not show any conclusive preference for either rombohedral or hexagonal indexing. As a matter of fact, in both possibilities the correlations were worse than those found for the rombohedral indexing in the products of mixtures I and II. Therefore in Fig. 1 the diffraction peaks of the double hydroxide of mixture III, are marked by both possible index systems. Another difference is in the value obtained for the interlayer spacing c', which is 7.36 Å. This value is lower than any value reported in literature. The value of the unit cell parameter a is 3.05 Å which is similar to the results obtained from the other two mixtures.

The low interlayer spacing value in mixture III product was obtained after a long reflux time of 236 hours. At short reflux period this value is similar to those obtained from the other mixtures (Table 1). A decrease in the c spacing was observed when the reflux period was between 70 and 120 hours, when the spacing was suddenly found to collapse (Fig. 2). The process at that time was accompained by considerable loss of CO_2. The unit cell parameter a is practically unaffected by the reflux time.

In Fig. 3 representative I.R. absorption spectra, of mixture III products, are shown. At the range of 4000–1200 cm^{-1}, which is not shown, the spectra are similar to those of hydrotalcite and synthetic Mg-Al hydroxide, as described by Ross and Kodama (7). At the range below 600 cm^{-1}, two bands near 400 and 450 cm^{-1} indicate Al rich double hydroxide. By comparison with the spectra given by Brindley and Kikkawa (1), it can be concluded that the proportion of $Al^{+3}/Mg^{+2}+Al^{+3}$ in the brucite like layers exeeded 0.3, and practically there are no changes in the composition of these layers during the

TABLE 1
Influence of reflux time on interlayer space c' and unit cell parameter a of the double hydroxide and CO_2 content in the products.

Reflux time mixture III (hours)	$d_{(0006)}$ or (0004) (Å)	c' (Å)	$d_{(11\bar{2}0)}$ (Å)	a (Å)	CO_2%
4	3.80	7.60			3.0
8	3.80	7.60	1.526	3.052	3.9
12	3.81	7.62	1.523	3.046	3.6
25	3.80	7.60	1.523	3.046	3.4
46	3.79	7.58	1.525	3.050	3.4
72	3.78	7.56	1.525	3.050	2.6
121	3.71	7.42	1.524	3.048	2.0
148	3.70	7.40	1.525	3.050	2.2
168	3.70	7.40	1.525	3.050	1.8
236	3.68	7.36	1.525	3.050	1.2
mixture I, 266 hours	3.79	7.58	1.522	3.044	5.1
mixture II, 289 hours	3.77	7.54	1.525	3.050	3.6

reflux period. After the collapse, some new weak bands were observed in the spectra, like the one at 430 cm^{-1}. Their intensities were too weak for conclusive assignment.

The collapse event is also accompanied by some changes in the D.T.A curves. The well defined endothermic peak at 275°C is splitted when reflux time exceeded 120 hours (Fig. 4). Such changes did not occur with the other two mixtures. The splitting is probably connected to the loss of CO_2. Such splitting has been found when D.T.A curves of Mg-Al double hydroxide with high and low CO_2 content, were compared (8).

It is suggested that in the particular case of mixture III, AlO^-_2 ions are formed on the surface of the double hydroxide layers, which exchange for CO_3^{-2} ions and expell them as CO_2 according to the equation:

$$\gamma\text{-}Al_2O_3 + CO_3^{-2}\,(\text{interlayer}) \rightarrow 2AlO^-_2\,(\text{interlayer}) + CO_2\,(g)$$

Other possibilities like exchange of OH^- (from the water) for CO_3^{-2} will not result in decreasing of c' below 7.5-7.6 Å (9-11).

CONCLUSIONS

When Al-Mg double hydroxide is obtained by refluxing magnesia and gamma alumina AlO^-_2 anions are formed between the layers. This phenomenon results in decreasing of c down to 7.36 Å, which is less than any former reported value in the literature.

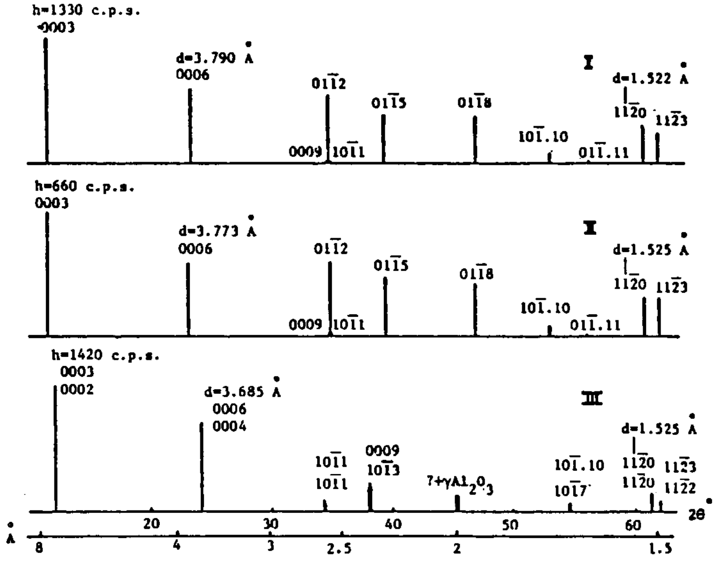

Fig. 1: X.R.D patterns of double hydroxides obtained as reflux product from tested mixtures. Peaks of other compounds are omitted. Peaks of mixture III indicated in both possible index systems.

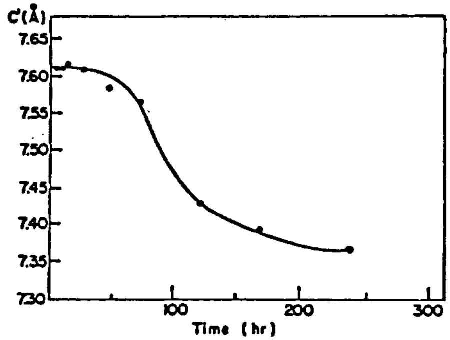

Fig. 2: Variation of interlayer space of magnesium-aluminium hydroxide during refluxing, mixture III.

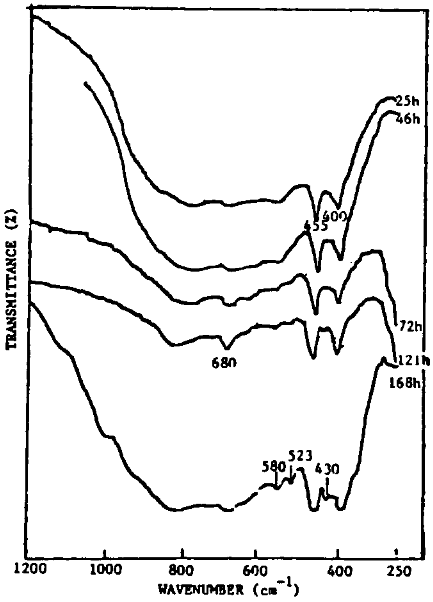

Fig.3: I.R. spectra after different refluxing times, mixture III.

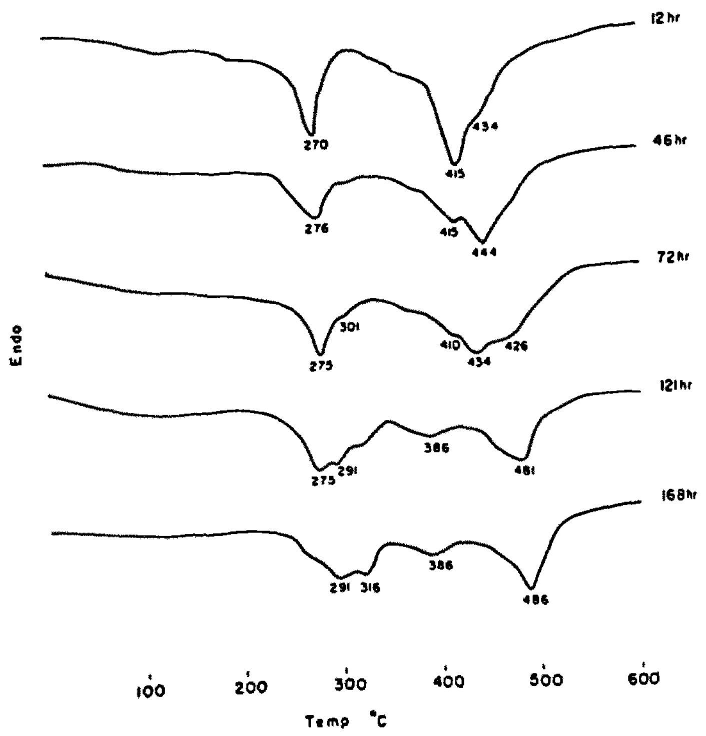

Fig. 4: D.T.A curves of reflux products obtained from gamma alumina and magnesia (mixture III).

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