

STRUCTURE AND PHASE CHANGES IN THERMALLY TREATED MIXED HYDROXIDES OF Mg AND Al-EFFECT OF COMPACTION

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ABSTRACT

Mechanically mixed (I) and coprecipitated (II), hydroxides of magnesium and aluminium were investigated in both powder and compact forms in the temperature range 200-1000 °C using DTG, DTA and X-ray techniques.

Upon thermal treatment of the mechanically mixed hydroxide, the solid material gives rise to products which at first become poorly crystalline and then gradually pass into the crystalline state indicating a mixture of MgO, θ , δ and α -alumina together with a new spinel. This new spinel is stable in the temperature range 400-800 °C—three of its distinct d -spacings are at 4.87, 3.86 and 3.74 Å.

Coprecipitated hydroxides (II) proved to constitute a new species—probably a hydrated spinel. The spinel $MgAl_2O_4$ commences to form at a temperature as low as 200 °C.

Compaction with either 10 or 30 tons $in.^{-2}$ decreases the crystallinity of products from (I) dehydrated ≤ 500 °C, whereas it favours crystallization for the products from II. Above ~ 500 °C, compaction has no appreciable effect on crystallization.

INTRODUCTION

Mixed oxides, especially binary systems, have been employed successfully in many industrial catalytic processes^{1,2}. Recently, Linnett and Rahman³, have focussed attention on a type of such systems in which both metal ions play a part in the geometry of the crystals. These systems are spinels with the formula $M_x''M_{3-x}O_4$. Binary systems in which Al and Mg form the trivalent and divalent metal ions, respectively, have lately attracted some attention^{4,7}. Some surface properties and structural changes accompanying the calcination of the mixed hydroxide system were investigated⁴. However, in view of the oxide/oxide interaction

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in the mixture at suitably varying temperatures, the effect of compaction becomes an essential pre-requisite to understand further studies on certain surface properties. The present work represents a study on the effect of compaction prior to thermal treatment of the aluminium–magnesium hydroxide mixture on the phase and structural changes upon dehydration, by means of XRD, DTG and DTA.

EXPERIMENTAL

2.1. Materials

Aluminium hydroxide was prepared by the slow addition of 1.2 M ammonia solution to an equal volume of 0.4 M aluminium nitrate (BDH) solution. The final pH of the medium was 8.15. Magnesium hydroxide was also prepared by slowly running 2 M ammonia solution into an equal volume of 1 M magnesium nitrate (BDH) solution. Both precipitates were thoroughly washed with 1% ammonia solution and dried at 110 °C to constant weight. The water content of the prepared $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ is 34.54 and 30.88%, respectively.

The parent hydroxides are mechanically mixed in 1:1 mole ratio in suspension form. The pH of the medium was 8.75. The mixed precipitate (I) was then filtered and dried to constant weight at 110 °C. Its chemical analysis corresponds to the formula $\text{MgO} \cdot 1.05 \text{Al}_2\text{O}_3 \cdot 3.53 \text{H}_2\text{O}$.

Coprecipitated mixed hydroxides of aluminium and magnesium were formed by precipitating a mixed solution of equal volumes of 0.2 M magnesium nitrate and 0.4 M aluminium nitrate with 1.6 M ammonia solution. The pH of the supernatant liquid was 10. The precipitate (II) was thoroughly washed with 1% ammonia solution till NO_3^- free, filtered and dried at 110 °C to constant weight. Chemical analysis of this preparation corresponds to the formula $\text{MgO} \cdot 0.99 \text{Al}_2\text{O}_3 \cdot 4.5 \text{H}_2\text{O}$.

Samples of the mixed hydroxides I and II were compacted in the form of pellets under pressures of 10 and 30 tons in.^{-2} and are designated $\text{MC}_{\text{I-10}}$, $\text{MC}_{\text{I-30}}$, $\text{MC}_{\text{II-10}}$ and $\text{MC}_{\text{II-30}}$.

Dehydration products of I and II in both powder (MP_{I} and MP_{II}) and compact forms were obtained by thermal decomposition in nitrogen atmosphere at temperatures ranging between 200–1000 °C for 5 h. In case of compacted samples, compaction was effected prior to heat treatment. The temperature of dehydration is indicated between parenthesis next to the sample symbol; thus, e.g., sample $\text{MC}_{\text{II-30}}$ (200) indicates coprecipitated mixed hydroxides (II) compacted under 30 tons in.^{-2} and heated at 200 °C for 5 h.

2.2. Apparatus and technique

Thermogravimetric analysis was carried out with the aid of an automatic recording thermobalance, at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, manufactured by Gebrüder Netzsch, ABT, Prüfgeräte, selb, Bayern, G.F.R.

Differential thermal analysis was carried out using high temperature α -alumina as inert standard and a program temperature controller "Ether" transitrol type 994/2 was used to permit a linear rate of heating, being 10 deg min^{-1} together with a Cambridge Recorder Model "B" for recording the temperature difference.

X-ray diffraction patterns were obtained by means of a General Electric X-ray Diffraction Unit, Model XRD-6, using Ni-filtered Cu radiation. The d -distances were calculated and compared with their relative intensities with recently published patterns⁸ and also with the data in the ASTM cards⁹.

RESULTS AND DISCUSSION

3.1. Differential thermogravimetric analysis (DTG)

Thermogravimetric analyses of aluminium and magnesium hydroxides represented in the differential form in Fig. 1 (curves a and b) show a sharp band in each, centered at 280 and 360 °C which are associated with their decomposition to the corresponding oxide namely Al_2O_3 and MgO , respectively. At temperatures below 220 °C some loosely bound water is evolved.

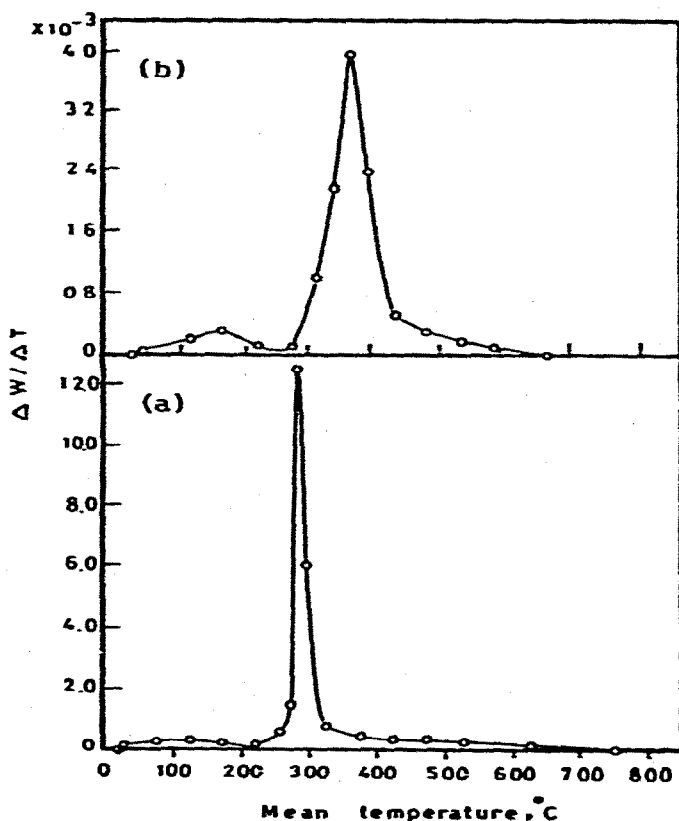


Fig. 1. Differential thermogravimetric analysis (DTG) for (a) $\text{Al}(\text{OH})_3$; (b) $\text{Mg}(\text{OH})_2$.

The DTG for the mechanically mixed preparation (I) in both powder and compact forms, reveals the existence of three different regions (Fig. 2); a low temperature region occurring below 180 °C which is responsible for the release of

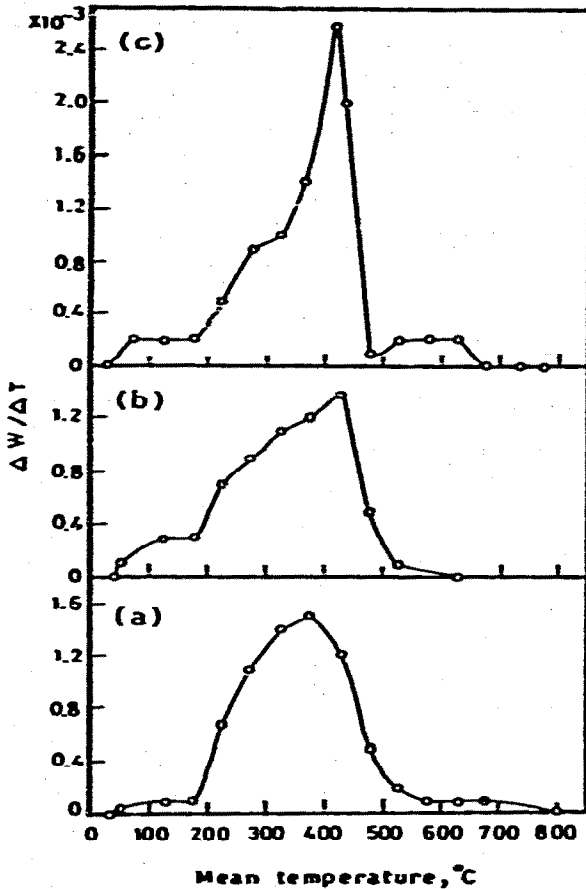


Fig. 2. Differential thermogravimetric analysis (DTG) for mechanically mixed preparation I. (a) MP_1 ; (b) MC_{1-10} ; (c) MC_{1-30} .

weakly bound water, an intermediate temperature region covering the range 180 to ~ 500 °C, where variable structural changes seem to take place with the evolution of most of the water content, and a high temperature region above 500 °C and varying in extent, but is mainly due to the evolution of the remaining traces of water. The dehydration of this mixed hydroxide begins at a relatively lower temperature (~ 180 °C) than the separate constituent hydroxides. No separate distinct effects of each component are clearly observed, but compaction below a pressure of 10 tons in.^{-2} seems to cause the individual hydroxides to manifest themselves and a wide shoulder is observed at 180–380 °C followed by a maximum at 420 °C (Fig. 2(b)). Increase in compaction to 30 tons in.^{-2} appears to distinguish further the individual effects of the decomposition of each hydroxide.

Coprecipitated preparation II does not show an initial slow rate process in its DTG curve (Fig. 3(a)) but instead a rapid evolution of water vapour takes place and continues to higher temperatures—up to 570 °C. This broad peak shows a plateau over the temperature range 170–380 °C.

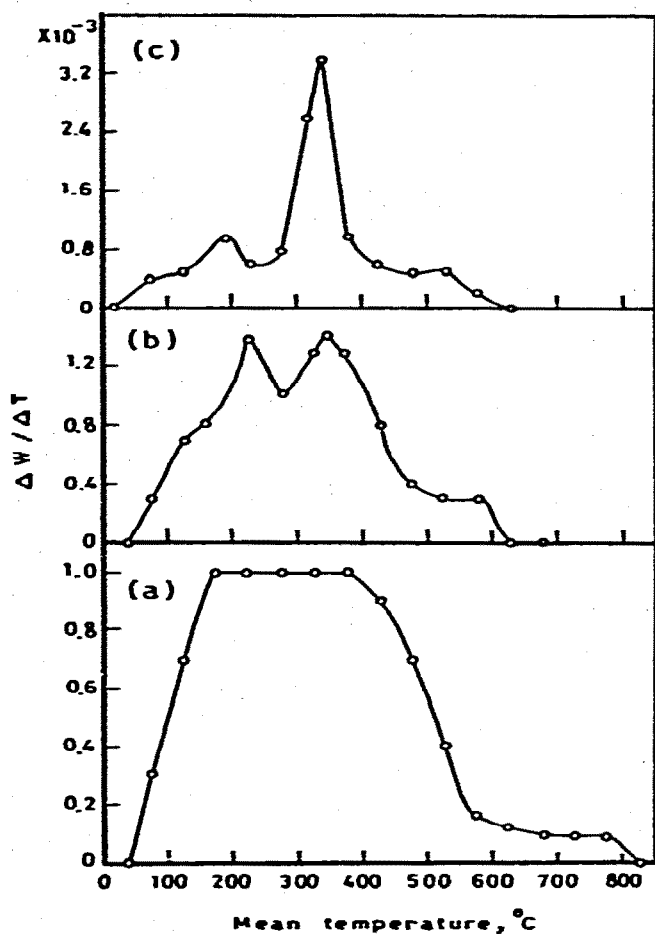


Fig. 3. Differential thermogravimetric analysis (DTG) for coprecipitated preparation II. (a) MP_{II} ; (b) MC_{II-10} ; (c) MC_{II-30} .

A comparison of the low temperature region in both I and II implies that the initial components of each are different. Though both contain aluminium and magnesium hydroxides as starting materials and as identified by XRD, it seems that in preparation II an amorphous compound is formed, probably a form of a hydrated spinel, which is easily dehydrated at low temperatures. The formation of hydrated spinels under similar conditions was previously reported with other oxide systems⁴.

Compaction with 10 and 30 tons $in.^{-2}$ is found to favour the dehydration of the individual components to some extent, to take place abruptly with no over-

lap and this results in a more specific location of the dehydration temperature which is found to decrease slightly upon compaction (Figs. 3 (b) and (c)).

3.2. Differential thermal analysis

DTA curves of aluminium and magnesium hydroxides display one endothermic peak each, centered at 320 and 410 °C, respectively, which are at their characteristic temperature conversion range to the corresponding oxide¹⁰. A small exothermic effect covering the range 480–580 °C is also observed in the DTA of aluminium hydroxide resulting from the conversions to the various modifications of alumina¹¹.

Mixed preparation (I) displays two endothermic peaks at 330 and 410 °C (Fig. 4(a)), which reflect the characteristic features of the individual components, namely aluminium and magnesium hydroxides.

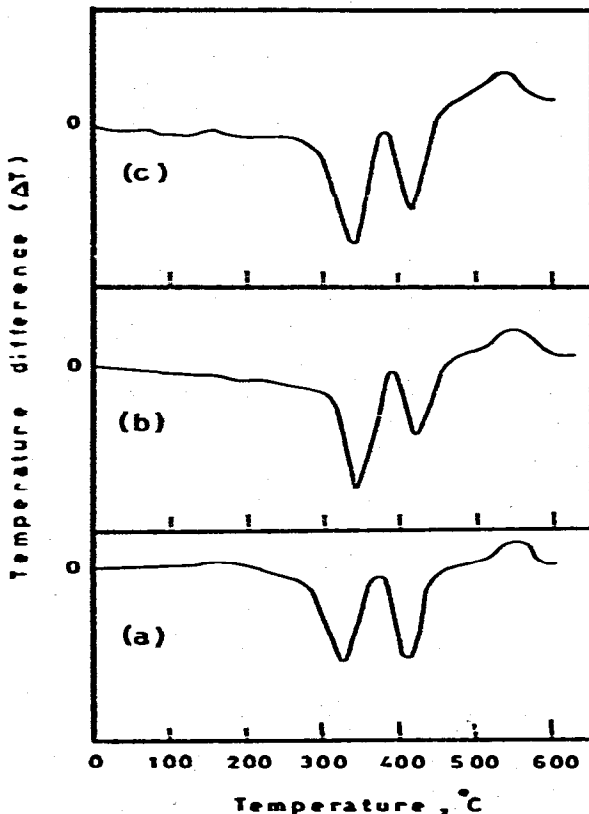


Fig. 4. Differential thermal analysis for mixed preparation I. (a) MP_I ; (b) MC_{1-10} ; (c) MC_{1-30} .

Compaction affects only the height of the endothermic peak at 415 °C, which may result if in such a compaction process the aluminium hydroxide surrounds the magnesium hydroxide to form a shielding effect (Figs. 4(b) and (c)).

Coprecipitated preparation II displays only one endothermic peak commencing with a steep shoulder and centered at 320 °C (Fig. 5(a)). Two processes are

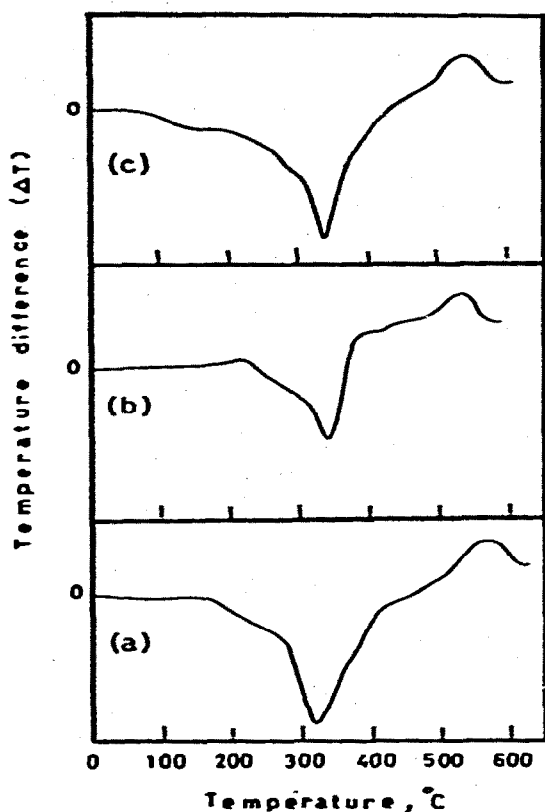


Fig. 5. Differential thermal analysis for coprecipitated preparation II. (a) MP_{II} ; (b) MC_{II-10} ; (c) $^{*}C_{II-30}$.

believed to take place consecutively, one responsible for the shoulder and the other for the peak at 320 °C. From XRD, the starting material shows lines characteristic for both aluminium and magnesium hydroxides with those of the former hydroxide more pronounced. This signifies that upon coprecipitation the aluminium hydroxide formed a shield around the magnesium hydroxide. This might be due to the adsorption of aluminium hydroxide on the surface of magnesium hydroxide. As a result of this adsorption, there is an indication of some interaction between both hydroxides to yield a new compound (cf. section 3.3) which might be tentatively called a hydrated spinel. Also the complete disappearance of the endotherm at 415 °C characteristic of the $Mg(OH)_2$ - MgO transformation, is in agreement with the XRD results which prove the presence of the spinel $MgAl_2O_4$ at a temperature as low as 200 °C. It is, therefore, reasonable to assume that the observed endothermic effects arise from the dehydration of the hydrated spinel and the spinel $MgAl_2O_4$, together with the decomposition of the remaining gibbsite.

Compaction does not influence the general trend of the DTA curves obtained (Fig. 5(b) and (c)).

3.3. X-ray analysis

X-ray diffraction patterns determined for the individual component hydroxides and represented in the form of the Debyogram of Fig. 6 identifies aluminium hydroxide to be composed essentially of bayerite and traces of boehmite¹¹ whereas magnesium hydroxide occurs as brucite⁹.

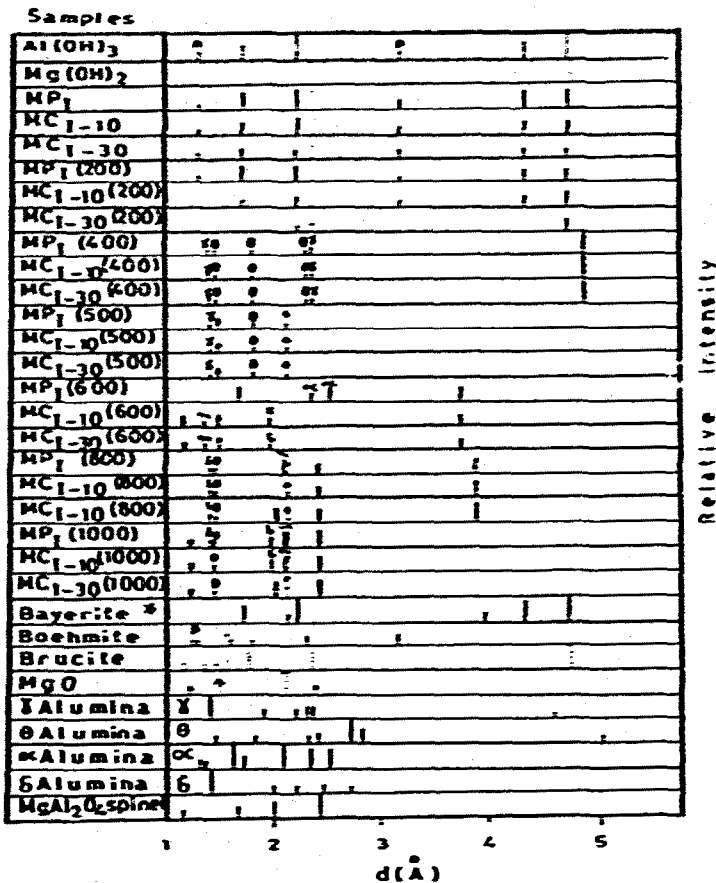


Fig. 6. Debyogram: the well-defined X-ray d -spacings and relative intensities of $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ mechanically mixed preparation I and its thermal dehydration products. Ξ , New lines; *, refer to refs. 8, 9 and 11.

The mechanically mixed preparation I, in both powder and compact forms, shows clearly the characteristic diffraction lines of the two hydroxide components, bayerite with traces of boehmite and brucite. Compaction affects the crystallinity of the samples in general, and using 30 tons in.^{-2} compaction causes a decrease in the intensity of the peaks characterising the samples. Upon the isothermal heating of the mechanically mixed sample to 200 °C, the powder sample retained the same crystal structure as the original powder sample. But upon compaction the crystallinity of the dehydrated samples decreases markedly. Not only did the intensities of various peaks diminish but also about 50% of them disappeared

when compaction was achieved under 30 tons in^{-2} . It is believed that compaction destroys the crystal lattice which is also facilitated by heating and causes an overlap of the different X-ray reflections.

Heating at 400 °C would certainly decompose brucite into its oxide and should likewise affect bayerite to give one or more of the modifications of alumina. From XRD (Fig. 6) the peaks obtained denoted the existence of a mixture of γ - and β -alumina together with a band having a d -spacing of 4.87 Å. No peaks were observed which would characterise the magnesium present either as magnesium oxide or as magnesium aluminate (spinel). It is, therefore, reasonable to assume that the 4.87 Å d -spacing indicates a new spinel between magnesium and aluminium formed under the above conditions of preparation and at a temperature which is very sensitive to both bayerite and brucite transformation.

The solid state remains invariant by heating to 500 °C but the crystallinity is decreased. Two definite peaks characteristic of MgO appeared which did not exist in the 400 °C samples. In the meantime the new line previously observed at 4.87 Å for samples heated at 400 °C disappeared at 500 °C. Compaction had almost a negligible effect upon the crystal structure of samples obtained at 400 and 500 °C.

The closely related lattice structure of γ -alumina to that of spinel MgAl_2O_4 ⁸ is expected to facilitate the formation of the latter which took place on raising the temperature to 600 °C. At this temperature some of the alumina is transformed to the α -form together with the formation of magnesium aluminate. Compaction seems to influence the arrangement of the different structural species in such a way as to mask the MgAl_2O_4 and most of the α -bands exposing peaks characteristic of MgO, δ - and α -alumina. A peak occurring at 3.74 Å was also observed which is not included among those of the well-established peaks for alumina or magnesium spinels. Such a peak might be correlated with that formed at 400 °C which gave a peak at 4.87 Å; each peak being a result of reflection from a specific crystal face.

Heating the solid above 600 °C, namely at 800 and 1000 °C, stabilizes the crystal structure of the solid material and more defined X-ray patterns are obtained at these two temperatures. The XRD patterns of the samples heated at 800 °C also showed a new peak centered at 3.86 Å which disappeared at 1000 °C. It is thus believed that a new spinel is formed which is stable in the temperature range 400–800 °C, three of its distinct d -spacings are 5.87, 3.74 and 3.86 Å. It is interesting to note that the d -spacing at 3.74 Å was previously reported to exist in the system magnesium–aluminium hydroxide mixtures under different experimental conditions.

It is generally observed in the present investigation that the temperature at which aluminium hydroxide transforms to the different alumina modifications is much lower than for a pure species¹¹ of $\text{Al}(\text{OH})_3$. The presence of a magnesium hydroxide–oxide system seems to facilitate such transformations (causing them to take place at lower temperatures).

Preparation II is found to consist of $Mg(OH)_2$ and gibbsite with traces of nordstrandite (Fig. 7); both being different forms of aluminium hydroxide. Gibbsite, a product of bayerite and previously reported by others¹² to be easily formed in presence of an alkali, especially K_2O and Na_2O , seems to be also easily formed in the presence of the weak alkali, $Mg(OH)_2$. However, the absence of gibbsite from preparation I formed from the same starting materials as those of preparation II, seems to arise from the bearing of the method of preparation on such structural details, where in coprecipitation the Mg ions are in intimate contact with the Al ions, close enough to affect the lattice structure. Further effects are also manifested by the formation of traces of nordstrandite which is normally formed in the presence of a chelating agent.

The most intense line in the XRD of this preparation is that characteristic of $Mg(OH)_2$. There is also a small band at a d -spacing of 8.67 Å which increases in intensity upon compaction and which does not belong to any definite structural species. The formation of hydrated spinels was previously reported¹³ but did not constitute this 8.67 Å d -spacing and an intense peak at a d -spacing of 7.56 Å was reported.

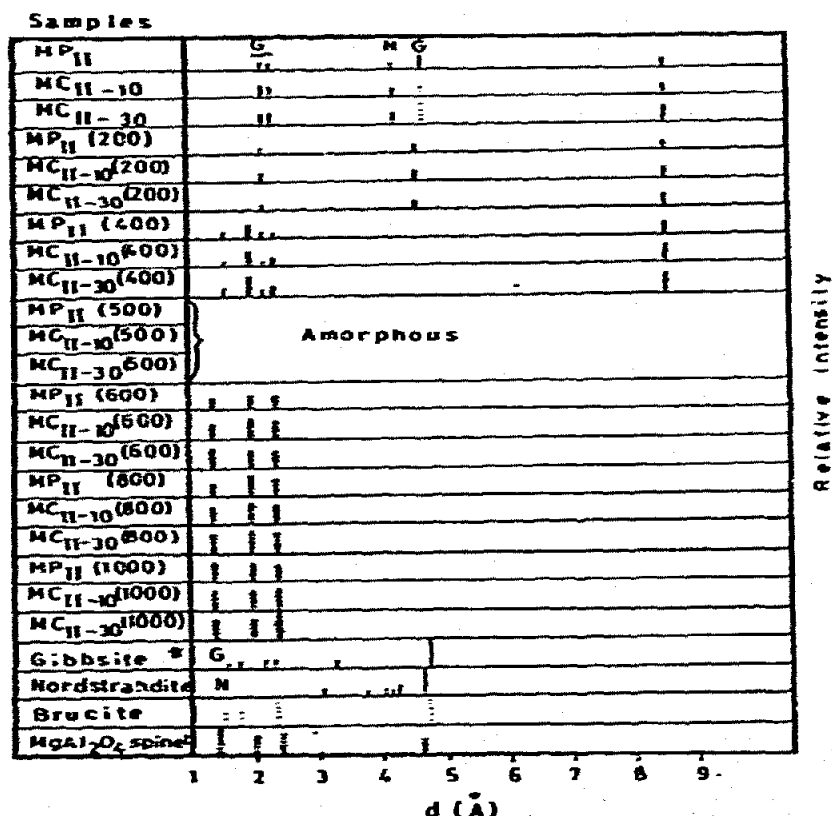


Fig. 7. Debyeogram: The well defined X-ray d -spacings and relative intensities of coprecipitated preparation II and its thermal decomposition products. \ddagger , New lines; *, refer to refs. 8, 9 and 11.

Heating at 200 °C produces MgAl₂O₄ with gibbsite while the new line at 8.67 Å still exists. Raising the temperature to 400 °C does not affect the nature of the constituents but the powder form becomes poorly crystalline, Compaction of the samples prior to heating at 200 or 400 °C increases the crystallinity of the samples and the new line at 8.67 Å becomes well established.

The temperature of 500 °C seems to be a transition temperature where both the powder and compact samples lose most of their crystalline structure and only small broad bands appear which upon further heating to higher temperatures become more specific and intense to indicate the presence of magnesium aluminate only as observed by samples produced at 600 °C and higher temperatures. Compaction seems to aid in the alignment of the crystallites and a better XRD pattern is produced.

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