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Influence of precipitation conditions of magnesium hydroxide on its thermal decomposition in the preparation of active MgO

V.R. Choudhary[1], S.G. Pataskar, M.Y. Pandit and V.G. Gunjikar

Chemical Engineering Division, National Chemical Laboratory, Pune 411008 (India)

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Abstract

Thermal decomposition of magnesium hydroxide, prepared by its precipitation from a magnesium salt solution with ammonium hydroxide using different salts and different conditions (concentration of Mg salt, mode of mixing of the Mg salt and ammonium hydroxide solution, pH and temperature of precipitation, and the ageing period of the precipitate) has been investigated by TG, DTG and DTA techniques in the temperature range 30–600 °C. The thermal analysis showed that the preparation conditions of magnesium hydroxide have a strong influence on its thermal decomposition to active magnesium oxide. An exothermic DTA peak was observed in the decomposition for only a few of the magnesium hydroxide samples.

INTRODUCTION

Active MgO can be prepared by thermal decomposition of magnesium hydroxide [1,2]. The kinetics and mechanism of the thermal decomposition of precipitated $Mg(OH)_2$ and natural brucite to MgO have been thoroughly investigated earlier [2–17]. However, the influence of the preparation conditions of the precipitated $Mg(OH)_2$ (which is the common precursor for active MgO, used as a catalyst or catalyst component) on its thermal decomposition has not been investigated so far. In our recent studies [18], we have observed that the surface area, basicity and base strength distribution of MgO obtained from precipitated $Mg(OH)_2$ are strongly influenced by its preparation conditions, namely the magnesium salts and precipitation agents used, their modes of mixing and the precipitation conditions, i.e. concentration, pH, temperature and ageing period of the precipitate. It is, therefore, very interesting to study the influence of the various preparation conditions of $Mg(OH)_2$ on its thermal decomposition using TG, DTG and DTA. The present investigation was undertaken for this purpose.

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[1] Author to whom correspondence should be addressed.

EXPERIMENTAL

Preparation of $Mg(OH)_2$ samples

A number of samples of magnesium hydroxide were prepared by precipitating it from an aqueous magnesium salt solution with an aqueous ammonium hydroxide solution (28%), varying the magnesium salt ($Mg(NO)_2$, $MgCl_2$, $MgSO_4$ and $Mg(CH_3COO)_2$), the precipitating conditions (concentration of Mg salt, 0.1–2.0 mol. l^{-1}; temperature, 5–60 ° C; pH 9.0–11.3; mode of mixing: (A) ammonium hydroxide solution added slowly with stirring to magnesium salt solution, (B) magnesium salt solution added slowly with stirring to ammonium hydroxide solution, and (C) mixing the solution of magnesium salt and ammonium hydroxide by adding both solutions simultaneously while stirring) and the ageing period (0.5–288 h). After ageing the precipitated $Mg(OH)_2$, it was washed thoroughly with

TABLE 1

Preparation (precipitation and ageing) conditions of magnesium hydroxide samples

$Mg(OH)_2$ sample code	Precipitation conditions					
	Mg salt used	Conc. of Mg salt (mol l^{-1})	Mode of mixing [a]	Temperature (° C)	pH	Ageing period (h)
MH(S-1)	Mg nitrate	1.0	A	30	10.2	6
MH(S-2)	Mg chloride	1.0	A	30	10.2	6
MH(S-3)	Mg sulphate	1.0	A	30	10.2	6
MH(S-4)	Mg acetate	1.0	A	30	10.2	6
MH(C-1)	Mg nitrate	0.1	A	30	10.2	6
MH(C-2)	Mg nitrate	0.5	A	30	10.2	6
MH(C-3)	Mg nitrate	1.0	A	30	10.2	6
MH(C-4)	Mg nitrate	2.0	A	30	10.2	6
MH(T-1)	Mg nitrate	2.0	A	5	10.2	6
MH(T-2)	Mg nitrate	2.0	A	30	10.2	6
MH(T-3)	Mg nitrate	2.0	A	60	10.2	6
MH(pH-1)	Mg nitrate	2.0	A	30	9.0	6
MH(pH-2)	Mg nitrate	2.0	A	30	10.0	6
MH(pH-3)	Mg nitrate	2.0	A	30	11.3	6
MH(Ad-1)	Mg nitrate	2.0	A	30	10.2	6
MH(Ad-2)	Mg nitrate	2.0	B	30	10.2	6
MH(Ad-3)	Mg nitrate	2.0	C	30	10.2	6
MH(Ag-1)	Mg nitrate	2.0	A	30	10.2	6
MH(Ag-2)	Mg nitrate	2.0	A	30	10.2	48
MH(Ag-3)	Mg nitrate	2.0	A	30	10.2	192
MH(Ag-4)	Mg nitrate	2.0	A	30	10.2	480

[a] Mode of mixing: A, addition of ammonia solution to Mg salt solution while stirring; B, addition of Mg salt to ammonia solution while stirring; and C, mixing both solutions simultaneously while stirring.

deionised water until free of cations and anions, and filtered and dried at 80 °C in a vacuum oven for 12 h. The dried mass was then crushed to 120–150 mesh particles.

The preparation conditions of the different $Mg(OH)_2$ samples, along with their sample codes, are given in Table 1. In order to study the influence of a particular variable of the preparation, the magnesium hydroxide samples (Table 1) were prepared simultaneously by varying systematically one of the conditions at a time while keeping all the other conditions the same.

In the preparation of the magnesium hydroxide samples, analytical reagent grade chemicals were used.

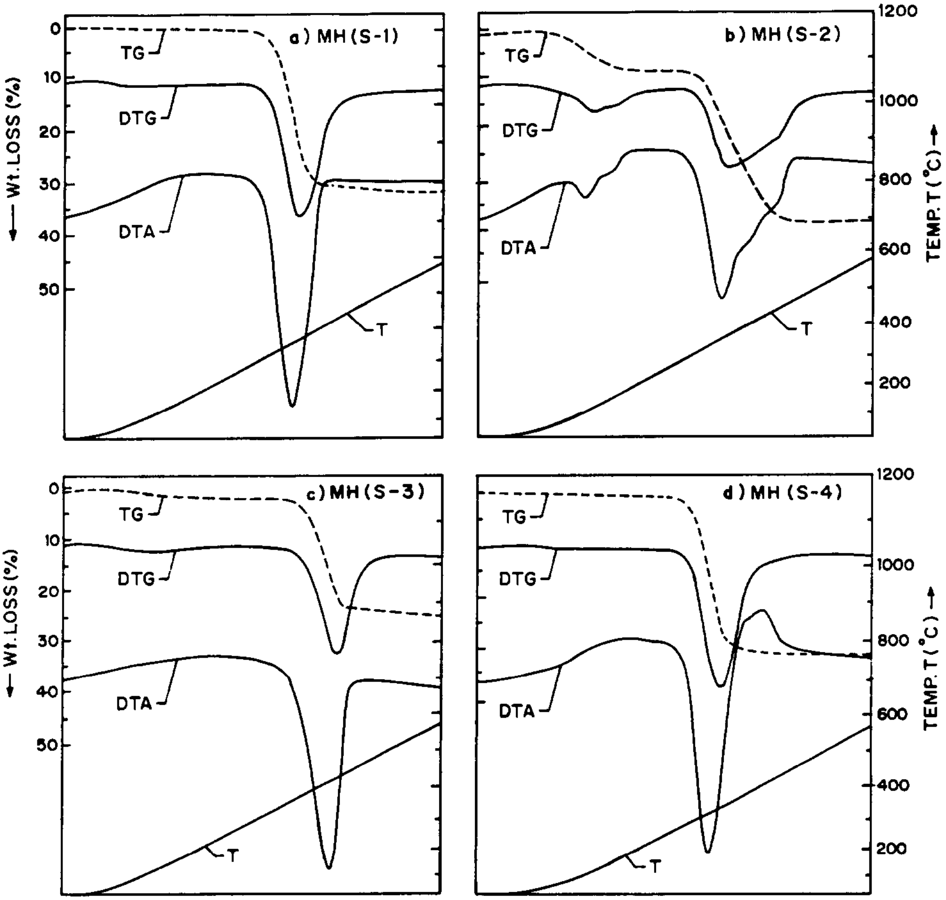

Fig. 1. TG, DTG and DTA curves for magnesium hydroxide prepared from different magnesium salts: (a) magnesium nitrate, (b) magnesium chloride, (c) magnesium sulphate and (d) magnesium acetate.

TG DTG and DTA

The data of the thermal analysis (TG, DTG and DTA) of the $Mg(OH)_2$ samples were obtained using an automatic Netzsch 409 model (Netzsch Geratebau GmbH) simultaneous thermal analysis apparatus under the following conditions: sample holder, platinum; sample size, 30 mg; reference compound, α alumina; atmosphere, static air; temperature range, 30–600 ° C; and heating rate, 10 ° C min^{-1}.

RESULTS AND DISCUSSION

The TG, DTG and DTA curves for the magnesium hydroxide samples (Table 1) prepared under different conditions are presented in Figs. 1–6.

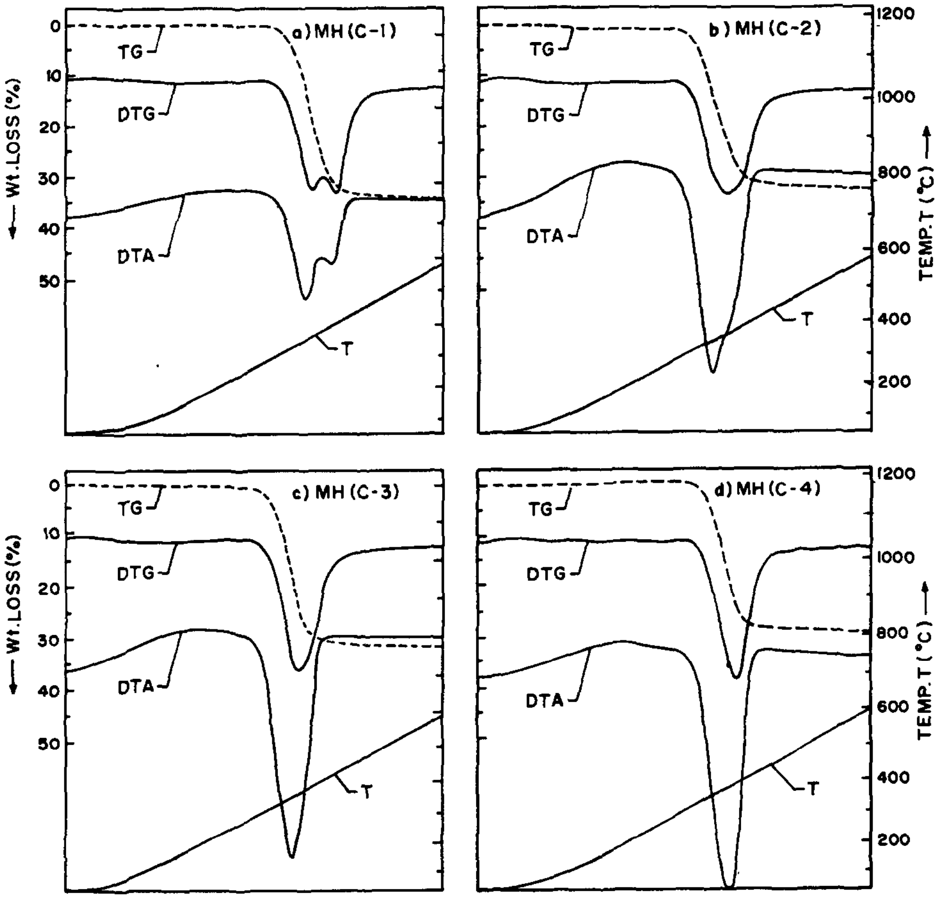

Fig. 2. TG, DTG and DTA curves for magnesium hydroxide precipitated at different concentrations of magnesium nitrate: (a) 0.1 mol l^{-1}, (b) 0.5 mol l^{-1}, (c) 1.0 mol l^{-1} and (d) 2.0 mol l^{-1}.

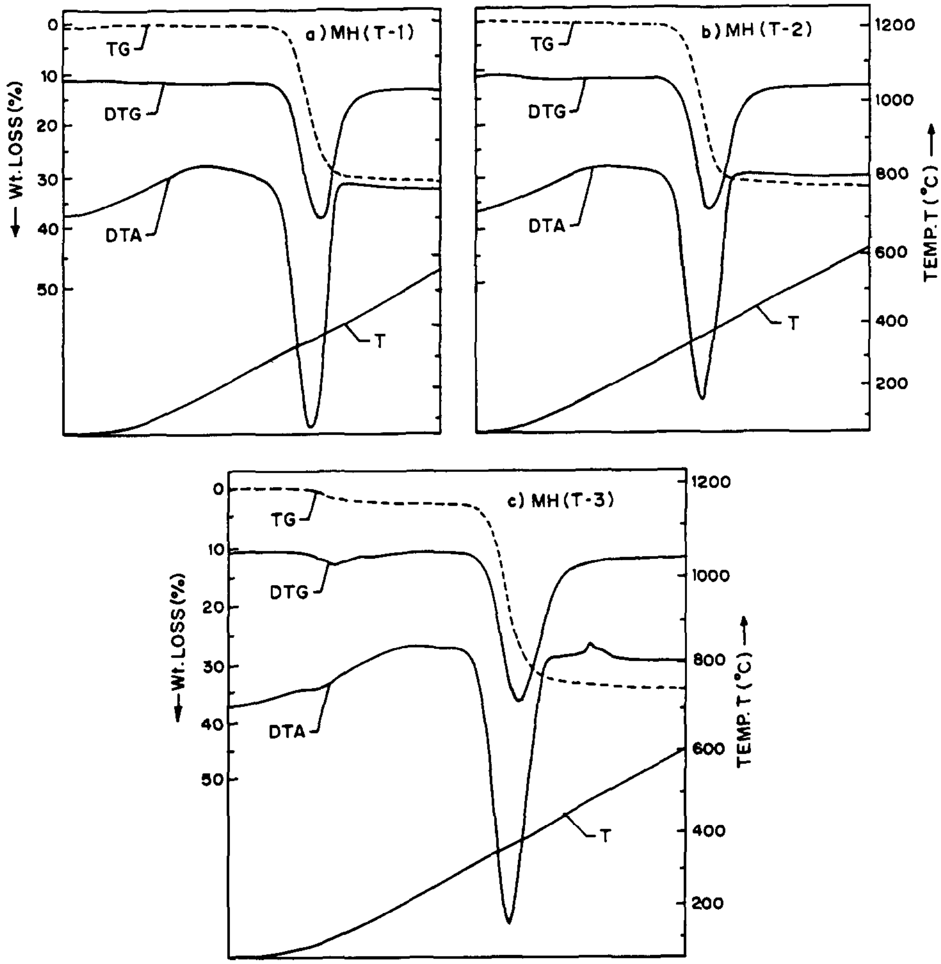

Fig. 3. TG, DTG and DTA curves for magnesium hydroxide precipitated at different temperatures: (a) 5 ° C, (b) 30 ° C and (c) 60 ° C.

The thermal analysis data obtained from the TG, DTG and DTA of the $Mg(OH)_2$ samples and also the surface properties (surface area and basicity) of the MgO obtained in the thermal decomposition of the samples at 600 ° C, are given in Table 2. The weight loss and the corresponding DTG and endothermic DTA peak observed in the lower temperature region (below 200 ° C) for some of the samples are due to a desorption of physically adsorbed water; whereas those in the higher temperature region (240–550 ° C) are due to the dehydroxylation of magnesium hydroxide according to the well-known decomposition reaction

$$Mg(OH)_2 \rightarrow MgO + H_2O\uparrow$$

involving a simple crystallographic transformation of the hexagonal hydrox-

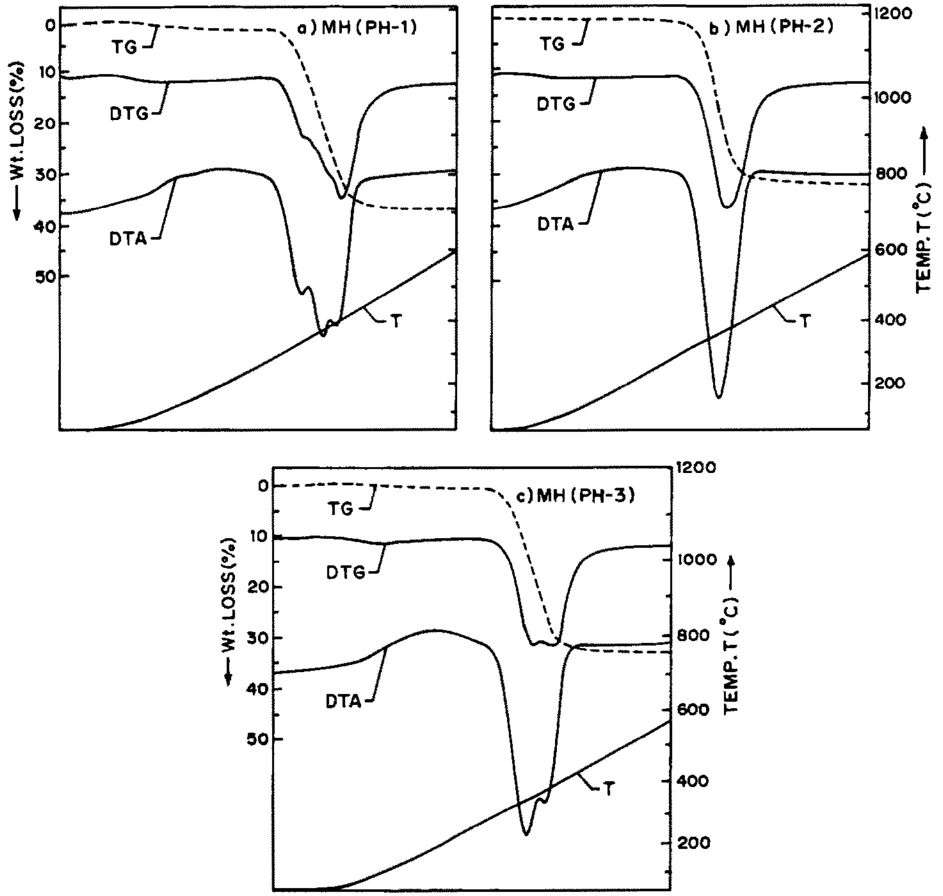

Fig. 4. TG, DTG and DTA curves for magnesium hydroxide precipitated at different pH values: (a) 9.0, (b) 10.2 and (c) 11.3.

ide lattice to the cubic oxide lattice, with a theoretical weight loss of 31.0%. However the small exothermic DTA peak observed for the samples MH(S – 4) at 409 °C, MH(P – 3) at 475 °C and MH(Ad – 3) at 429 °C (Figs. 1, 3 and 5) is due to recrystallisation (delayed crystallisation) of the products in the final stage of the above endothermic decomposition reaction. Earlier, Rao and Pitzer [4] observed that magnesium hydroxide first shows a very large endothermic reaction peak at around 500 °C, immediately followed by a small exothermic reaction peak at around 560 °C. In the present case, the exothermic peak was observed only for the above three samples at temperatures (Table 2) much lower than that reported earlier.

The data in the figures and tables indicate that the thermal decomposition of magnesium hydroxide and the surface properties of the resulting MgO are very much influenced by the history of the preparation of

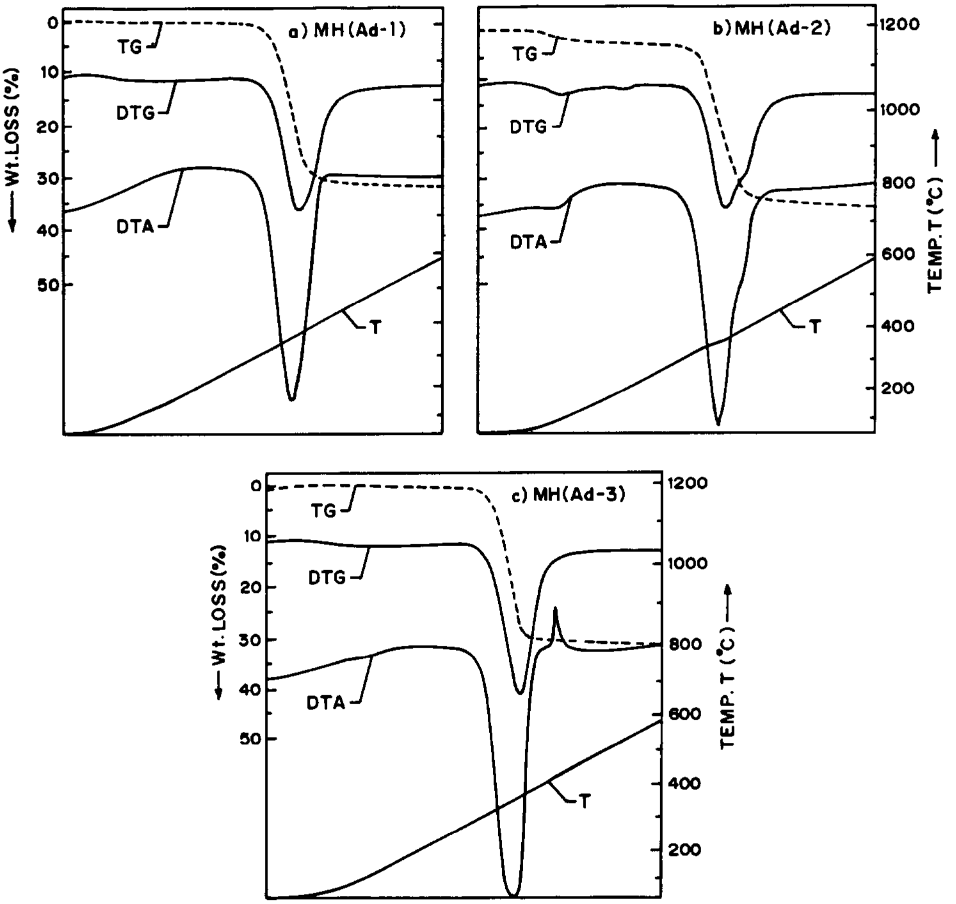

Fig. 5. TG, DTG and DTA curves for magnesium hydroxide precipitated by different modes of mixing the solutions of magnesium nitrate and ammonium hydroxide: (a) A, (b) B and (c) C (see text).

magnesium hydroxide. The influence of the preparation variables of magnesium hydroxide on its thermal decomposition is discussed below.

Influence of magnesium salts

A comparision of the TG, DTG and DTA curves (Fig. 1) and the thermal analysis data (Table 2) for the magnesium hydroxide samples MH(S – 1), MH(S – 2), MH(S – 3) and MH(S – 4) prepared using different magnesium salts, namely, magnesium nitrate, magnesium chloride, magnesium sulphate and magnesium acetate respectively, shows that the type of magnesium salt used in the preparation of magnesium hydroxide has a strong influence on its thermal decomposition and also on the surface area and basicity of the MgO obtained in the decomposition. Also the

TABLE 2

Data on thermal analysis of $Mg(OH)_2$ samples and surface properties of MgO obtained from $Mg(OH)_2$ by its calcination at 600 °C

Sample code	Thermal analysis data								Surface properties of MgO	
	DTG peak temp (°C)		DTA peak temp (°C)			Weight loss (%)			Surface area (m^2 g^{-1})	Basicity (mmol g^{-1})
	I [a]	II [b]	I(endo) [a]	II(endo) [b]	III(exo) [c]	I [a]	II [b]	Total		
MH(S-1)	–	361	–	351	–	–	31.0 (286–456 °C)	31.0	72.1	0.30
MH(S-2)	132	366	125	350	–	8.0	29.3 (291–501 °C)	37.3	20.8	0.18
MH(S-3)	111	418	105	408	–	2.3	22.0 (318–526 °C)	24.3	146.8	0.46
MH(S-4)	–	329	–	313	409	–	30.6 (246–476 °C)	30.6	39.7	0.43
MH(C-1)	–	355 392	–	345 387	–	–	33.3 (in two steps) (285–506 °C)	33.3	63.5	0.21
MH(C-2)	–	361	–	340	–	–	31.0 (263–506 °C)	31.0	51.0	0.21
MH(C-3)	–	361	–	351	–	–	31.0 (286–456 °C)	31.0	72.1	0.31
MH(C-4)	–	378	–	361	–	–	28.3 (291–481 °C)	28.3	59.4	0.33
MH(T-1)	–	360	–	356	–	–	29.6 (296–501 °C)	29.6	66.0	0.35
MH(T-2)	–	361	–	351	–	–	31.6 (286–456 °C)	31.6	72.1	0.30
MH(T-3)	97	365	84	355	475	3.0	30.6 (in two steps) (280–460 °C)	33.6	53.3	0.19

							(286–456 ° C)			
MH(T-3)	97	365	84	355	475	3.0	30.6 (in two steps) (280–460 ° C)	33.6	53.3	0.19
MH(pH-1)	92	361 366 393	78	334 356 387	–	2.0	33.6 (in three steps) (286–522 ° C)	35.6	34.0	0.10
MH(pH-2)	–	361	–	351	–	–	31.0 (286–456 ° C)	31.0	72.1	0.29
MH(pH-3)	91	345 372	77	334 366	–	1.3	32.0 (in two steps) (274–536 ° C)	33.3	40.3	0.30
MH(Ad-1)	–	361	–	351	–	–	31.0 (286–456 ° C)	31.0	72.1	0.29
MH(Ad-2)	93	356 393 (hump)	85	345 387 (hump)	–	3.3	30.6 (291–516 ° C)	33.9	51.8	0.19
MH(Ad-3)	91	361	84	350	429	1.0	29.6 (284–491 ° C)	30.6	92.0	0.31
MH(Ag-1)	–	361	–	351	–	–	31.0 (286–456 ° C)	31.0	72.1	0.29
MH(Ag-2)	–	323	–	312	–	–	32.3 (240–516 ° C)	32.1	41.6	0.21
MH(Ag-3)	–	373	–	361	–	–	30.0 (296–491 ° C)	30.0	80.6	0.58
MH(Ag-4)	–	361	–	350	–	–	28.6 (280–465 ° C)	28.6	76.6	0.31

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[a] DTG/DTA peak I and weight loss correspond to the desorption of physically adsorbed water.

[b] DTG/DTA peak II and weight loss correspond to the dehydroxylation of magnesium hydroxide to MgO.

[c] DTA peak III (which is exothermic) corresponds to recrystallisation of MgO.

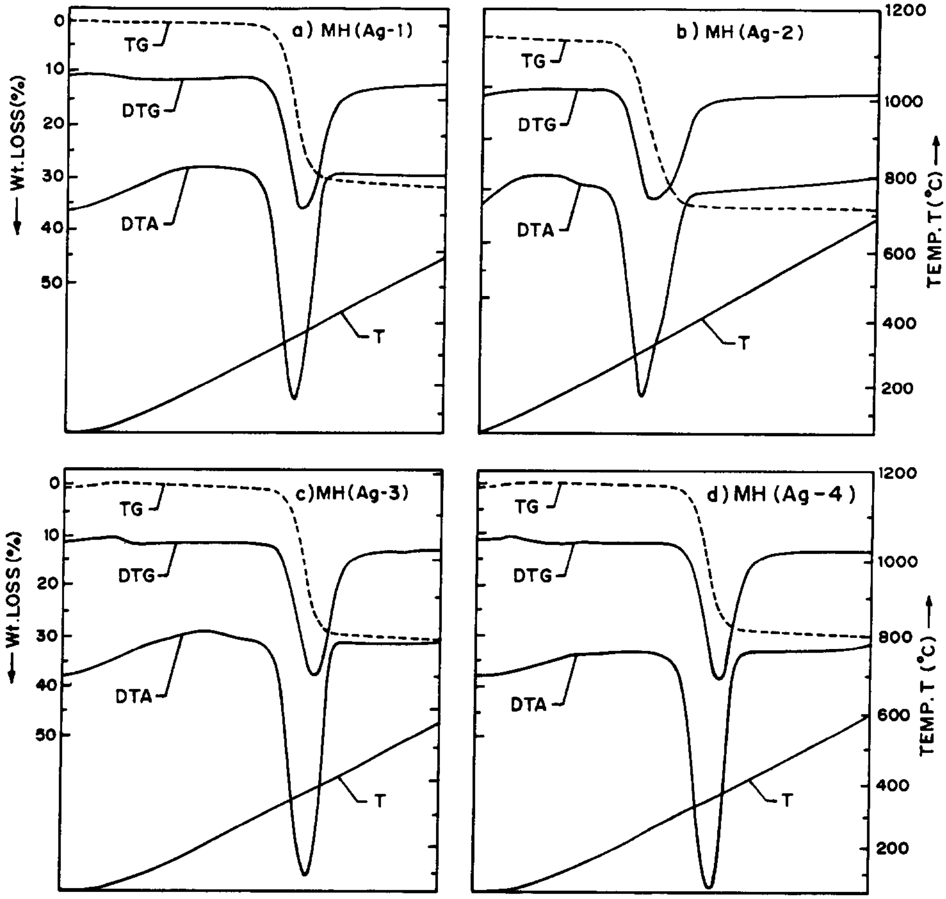

Fig. 6. TG, DTG and DTA curves for magnesium hydroxide prepared by ageing the precipitate for different periods: (a) 6 h, (b) 48 h, (c) 192 h and (d) 480 h.

exothermic peak due to delayed recrystallisation of the product is only observed for the sample prepared using magnesium acetate, MH(S – 4). The temperature of the start and completion of the dehydroxylation reaction is very different for the samples prepared using the different Mg salts; it is higher for sample MH(S – 3) and lower for sample MH(S – 4). The DTG/DTA peak temperatures are also consistent with the above.

The dehydroxylation reaction for sample MH(S – 2) occurs in a number of steps as shown by the humps in the DTG/DTA peak (Fig. 1), whereas for the other samples it occurs in a single step. The weight loss observed for the dehydroxylation of sample MH(S – 3) is lower than that for the other samples. Furthermore, there is a large variation in the surface area and basicity of the MgO obtained by decomposition of the different samples. All these observations reveal that the anions (NO_3^-, SO_4^{2-}, CH_3COO^- and Cl^-) present during the precipitation strongly affect the properties of the $Mg(OH)_2$ crystals formed, leading to the different thermal behaviour of the magnesium hydroxide samples.

Influence of the concentration of magnesium salts

The DTG/DTA curves (Fig. 2) show that the dehydroxylation of sample MH(C – 1), prepared at a low concentration of Mg salt (0.1 mol l^{-1}), occurs in two steps, whereas for samples prepared at higher concentrations (0.5–2.0 mol l^{-1}), the dehydroxylation occurs in a single step, although the shapes of the individual DTG/DTA curves are different. These facts and the thermal analysis data (Table 2) indicate that the thermal decomposition is affected to an appreciable extent by the change in concentration of the magnesium salt used in the precipitation of the magnesium hydroxide. The surface properties of the resulting MgO are also affected significantly by the change in the magnesium salt concentration.

Influence of precipitation temperature

A comparison of the DTG/DTA curves (Fig. 3) and thermal analysis data (Table 2) reveals that the thermal decomposition of magnesium hydroxide is influenced to only a small extent by the change in the precipitation temperature from 5 to 60 ° C, except that an exothermic process indicated by a small DTA peak at 475 ° C was only observed for the sample precipitated at high temperature, i.e. at 60 ° C. The surface area and basicity of the MgO obtained from the samples precipitated at 60 ° C were much lower.

Influence of the pH of precipitation

The results (Fig. 4 and Table 2) show that the pH of the precipitation has a very strong influence on the thermal decomposition of magnesium hydroxide and also on the surface area and basicity of the solid products (MgO).

The magnesium hydroxide precipitated at pH 10.2 is dehydroxylated in a single step, as indicated by a single narrow DTG/DTA peak. In contrast, the dehydroxylation of magnesium hydroxide precipitated at lower or higher pH, i.e. at pH 9.0 or 11.3, takes place in more than one step, as indicated by the multiple DTG/DTA peaks (Fig. 4). Furthermore, the temperature required for the complete dehydroxylation of magnesium hydroxide precipitated at pH 10.2 is lower (456 ° C) than that required when it is precipitated at pH 9.0 or 11.3 (about 530 ° C).

Influence of mode of mixing in precipitation

A comparison of the DTG/DTA curves (Fig. 5) and the data (Table 2) for the $Mg(OH)_2$ samples precipitated using different modes of mixing of the magnesium salt and ammonium hydroxide solutions indicates that the mode of mixing has a very significant effect on the thermal decomposition of the solid product. It is interesting to note that a small but sharp exothermic DTA peak (429 ° C) is only observed for the $Mg(OH)_2$ precipitated by simultaneously mixing the solution of magnesium salt and ammonium hydroxide. The different thermal behaviours and surface properties of the solid product arise from the fact that the nucleation and growth of the $Mg(OH)_2$ crystals occur at different concentrations and pH values when the precipitation takes place under the three different mixing procedures, resulting in $Mg(OH)_2$ crystals with different properties.

Influence of ageing period of precipitate

The DTG/DTA curves (Fig. 6) and data (Table 2) reveal that the ageing period of the precipitated $Mg(OH)_2$ has a significant effect on its thermal decomposition and also on the surface properties of the solid products. The influence, which is quite complex, may be attributed to crystal growth and change in the crystal properties of the $Mg(OH)_2$ during the process of ageing.

CONCLUSIONS

The dehydroxylation of precipitated $Mg(OH)_2$ in its thermal decomposition is strongly influenced by its preparation conditions, i.e. the Mg salt used and the precipitation conditions (concentration of magnesium salt, pH, temperature, the mode of mixing of magnesium salt and ammonium hydroxide, and the ageing period of the precipitate). The influences of the magnesium salt and of the pH of the precipitation are dominant. The exothermic DTA peak attributed to the recrystallisation of the solid products was observed for only a few samples of precipitated magnesium hydroxide.

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