*Thermochimica Acta*, 232 (1994) 95–110
Elsevier Science B.V., Amsterdam
*SSDI* 0040-6031(93)01373-B

# Influence of preparation conditions of basic magnesium carbonate on its thermal analysis

V.R. Choudhary *, S.G. Pataskar, V.G. Gunjikar and G.B. Zope
*Chemical Engineering Division, National Chemical Laboratory, Pune-411 008 (India)*

(Received 12 April 1993; accepted 18 May 1993)

## Abstract

Thermal analysis (TG, DTG, DTA) of a number of basic magnesium carbonate samples, prepared by precipitation using different magnesium salts (magnesium nitrate, sulphate, chloride, and acetate) and precipitating agents (viz. sodium carbonate and bicarbonate and potassium carbonate and bicarbonate) at different concentrations of magnesium salt (0.005–2.0 M), temperatures (0–100°C) and pH 9–11 using different modes of mixing in the precipitation and also by ageing the precipitate for different periods (0.5–96 h) has been carried out in the temperature range 30–600°C. The thermal decomposition and surface area of the resulting MgO are found to be strongly influenced by the preparation conditions of basic magnesium carbonate.

## INTRODUCTION

Magnesium oxide with promoters such as alkali metal oxides [1–8] and rare earth oxides [9–12] is an active catalyst for the oxidative coupling of methane to ethane and ethylene, which is considered a process of great practical importance for converting natural gas into petro-chemicals/petroleum products. In earlier studies we have observed that highly active and selective MgO catalysts (with different promoters) for this reaction could be prepared by the thermal decomposition of basic magnesium carbonate impregnated with the promoter precursors [7,8,11,12]. Since basic magnesium carbonate can be prepared by its precipitation and ageing of the precipitate under different conditions, it is interesting to study the influence of the preparation conditions of basic magnesium carbonate on its thermal analysis and the surface properties of the resulting magnesium oxide.

Thermal analysis of basic magnesium carbonate of general formula $x\text{MgCO}_3 \cdot y\text{Mg(OH)}_2 \cdot z\text{H}_2\text{O}$ has been thoroughly investigated earlier

---

* Corresponding author.

[13–17]. However, no detailed investigation of the influence of precipitation and ageing conditions on the thermal decomposition behaviour of basic magnesium carbonate has been reported so far. The present investigation was, therefore, undertaken to study the influence of various precipitation and aging conditions of basic magnesium carbonate, prepared using different magnesium salts and precipitating agents and also following different modes of mixing in its precipitation, on its thermal analysis by TG, DTG and DTA.

## EXPERIMENTAL

### *Preparation of basic magnesium carbonate*

A number of magnesium carbonate samples have been prepared by systematically varying one preparation condition at a time while keeping all the other conditions the same, as given in Table 1. After the precipitation and ageing of basic magnesium carbonate, it was thoroughly washed with deionised water until free from the ions formed in the precipitation, filtered and dried under vacuum at 100°C for 8 h. All the samples were powdered and heated in an air oven at 100°C for 1 h and stored in a desiccator.

In the preparation of the magnesium carbonate samples, analytical reagent grade chemicals were used. The preparation conditions varied were as follows.

(i) Magnesium salt: magnesium nitrate, magnesium sulphate, magnesium acetate and magnesium chloride were used.

(ii) Precipitating agent: sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate were employed.

(iii) *Precipitation and ageing conditions*: concentrations of magnesium salt used were 0.005, 0.5, 1.0 and 2.0 M; concentrations of the precipitating agent were equimolar to the magnesium salt solution used; temperatures used were 0, 30, 50 and 100°C; the pH was 9, 10.1, 10.6 or 10.9; the ageing period was 0.5, 8, 24 or 96 h; four modes of mixing of magnesium salt and precipitating agent solutions were employed: A, precipitating agent solution to magnesium salt solution; B, magnesium salt solution to precipitating agent solution; C, slow addition of both the solutions; D, simultaneous fast addition of both the solutions.

### *Thermal analysis*

The thermal analysis data (TG, DTG, DTA) for the magnesium carbonate samples prepared under different conditions (Table 1) were obtained using an automatic NZ STA 409 simultaneous thermal analysis apparatus, under the following experimental conditions: particle size, 250–300 mesh; sample size, 30 mg; reference compound, $\alpha$-alumina; sample holder, platinum crucible; temperature range, 30–600°C; linear heating rate, 10°C min$^{-1}$; atmosphere, static air.

TABLE 1

Preparation (precipitation and ageing) conditions of basic magnesium carbonate samples

| Sample code | Mg-salt used | Conc. of Mg-salt-mol $l^{-1}$ | Precipitating agent | Mode of mixing [a] | Temp./°C | pH | Ageing period/h |
|---|---|---|---|---|---|---|---|
| S-1 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| S-2 | Sulphate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| S-3 | Acetate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| S-4 | Chloride | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| PA-1 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| PA-2 | Nitrate | 1.0 | $K_2CO_3$ | A | 30 | 9.0 | 0.5 |
| PA-3 | Nitrate | 1.0 | $NaHCO_3$ | A | 30 | 9.0 | 0.5 |
| PA-4 | Nitrate | 1.0 | $KHCO_3$ | A | 30 | 9.0 | 0.5 |
| AD-1 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| AD-2 | Nitrate | 1.0 | $Na_2CO_3$ | B | 30 | 9.0 | 0.5 |
| AD-2 | Nitrate | 1.0 | $Na_2CO_3$ | C | 30 | 9.0 | 0.5 |
| AD-4 | Nitrate | 1.0 | $Na_2CO_3$ | D | 30 | 9.0 | 0.5 |
| C-1 | Nitrate | 0.005 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| C-2 | Nitrate | 0.5 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| C-3 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| C-4 | Nitrate | 2.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| T-1 | Nitrate | 1.0 | $Na_2CO_3$ | A | 0 | 9.0 | 0.5 |
| T-2 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| T-3 | Nitrate | 1.0 | $Na_2CO_3$ | A | 50 | 9.0 | 0.5 |
| T-4 | Nitrate | 1.0 | $Na_2CO_3$ | A | 100 | 9.0 | 0.5 |
| PH-1 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| PH-2 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 10.1 | 0.5 |
| PH-3 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 10.6 | 0.5 |
| PH-4 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 10.9 | 0.5 |
| Ag-1 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 0.5 |
| Ag-2 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 8 |
| Ag-3 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 24 |
| Ag-4 | Nitrate | 1.0 | $Na_2CO_3$ | A | 30 | 9.0 | 96 |

[a] A, Precipitating agent solution to Mg-salt solution; B, Mg-salt solution to precipitating agent solution; C, slow addition of both the solutions; D, simultaneous fast addition of both the solutions.

The specific surface area of MgO, obtained in the decomposition of the different basic magnesium carbonate samples at 600°C in static air for 8 h, was determined by a single point Brunauer–Emmett–Teller (BET) method by measuring the adsorption of nitrogen at liquid nitrogen temperature and at a nitrogen concentration of 30 mol% (balance helium) using a Monosorb Surface Area Analyser (Quanta Chrome Corpn. USA) based on a dynamic adsorption/desorption technique.

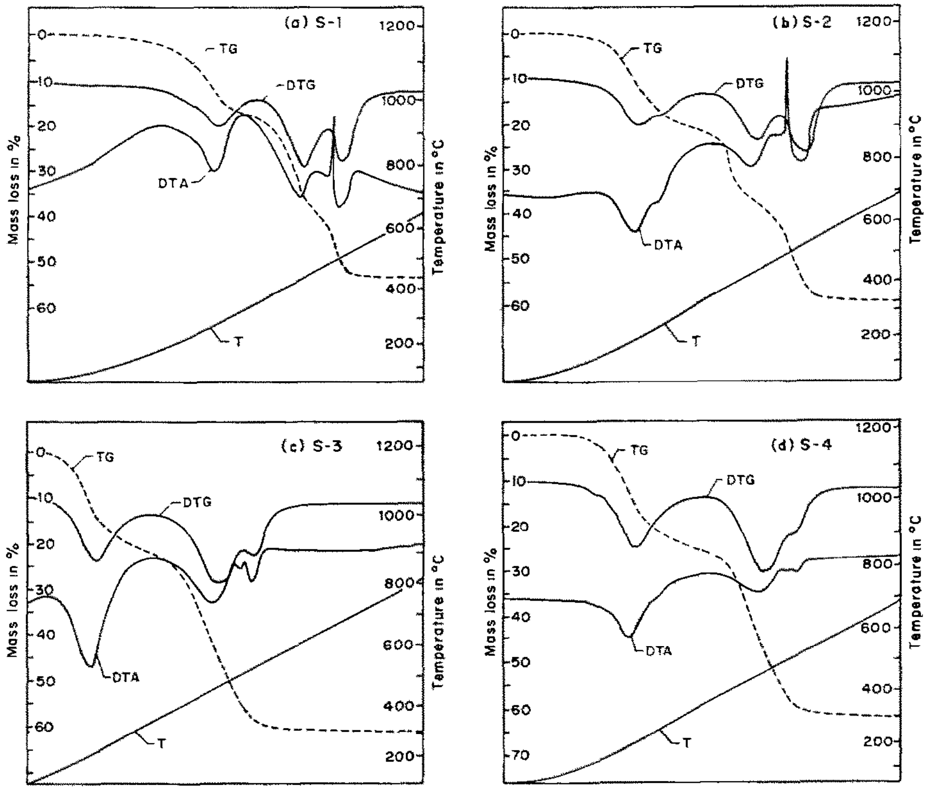

Fig. 1. TG, DTG and DTA curves for magnesium carbonate samples (S-1–S-4) prepared using different magnesium salts: (a) S-1, magnesium nitrate; (b) S-2, magnesium sulphate; (c) S-3, magnesium acetate; and (d) S-4, magnesium chloride.

## RESULTS AND DISCUSSION

The TG, DTG and DTA curves for the magnesium carbonate samples prepared under different conditions (Table 1) are presented in Figs. 1–7. The thermal analysis data obtained from the TG, DTG and DTA of the magnesium carbonate samples and the surface area of the MgO obtained in the thermal decomposition of the samples at 600°C are given in Tables 2–8. Thermal decomposition of hydromagnesite $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ is expected to proceed via dehydration (removal of water of crystallisation) at lower temperature (<250°C), dehydroxylation (i.e. decomposition of magnesium hydroxide to MgO) at intermediate temperatures (about 250–350°C) and decarbonation (i.e. decomposition of magnesium carbonate to MgO) at higher temperatures (>350°C) with a theoretical mass loss of 15.4, 3.8 and 37.6%, respectively (total theoretical mass loss = 56.8%).

$$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O \rightarrow 5MgO + 5H_2O(g) + 5CO_2(g)$$

The small mass loss (5–7%) and the corresponding DTG and DTA

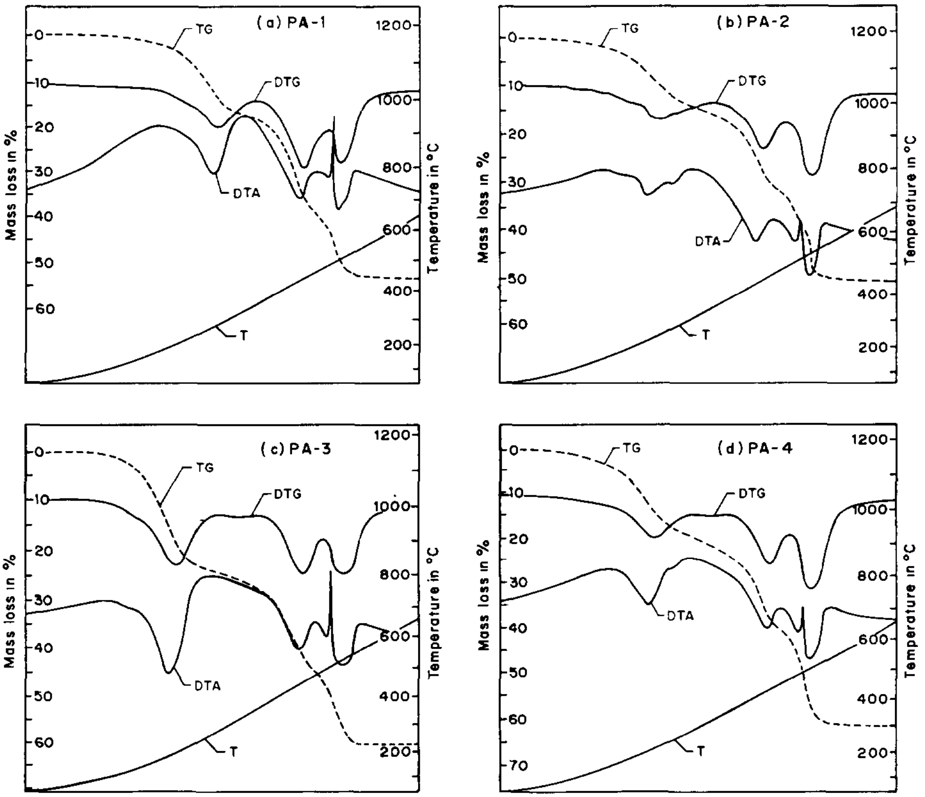

Fig. 2. TG, DTG and DTA curves for magnesium carbonate samples (PA-1–PA-4) precipitated with different precipitating agents: (a) PA-1, $Na_2CO_3$; (b) PA-2, $K_2CO_3$; (c) PA-3, $NaHCO_3$; (d) PA-4, $KHCO_3$.

(endothermic) peaks at 97°C and 90°C, respectively for sample T-3 (see Table 6 and Fig. 5) is expected to be due to desorption of physically adsorbed water. However, the DTG and DTA (endothermic) peaks in the temperature range 100–300°C, corresponding to mass loss of 12–28% are due to either dehydration or dehydroxylation, or both. The small mass loss (<5%) and the corresponding DTG and DTA (endothermic) peaks in the temperature range 246–286°C for samples C-2 and C-4 (see Table 5 and Fig. 4) are mostly due to dehydroxylation, whereas the DTG and DTA (endothermic) peaks at the higher temperatures (i.e. above 375°C) and the corresponding mass losses are due to decarbonation.

A small exothermic DTA peak (without a corresponding DTG peak) has been observed at 480–510°C for all the samples except Ad-3, C-1, C-4 and PH-3. This exothermic peak is followed by a prominent DTG peak (at the higher temperature) and the corresponding endothermic DTG peak. This observation contrasts with that of Sawada et al. [17] who observed a sudden mass loss in TG due to rapid evolution of $CO_2$ at the same temperature at

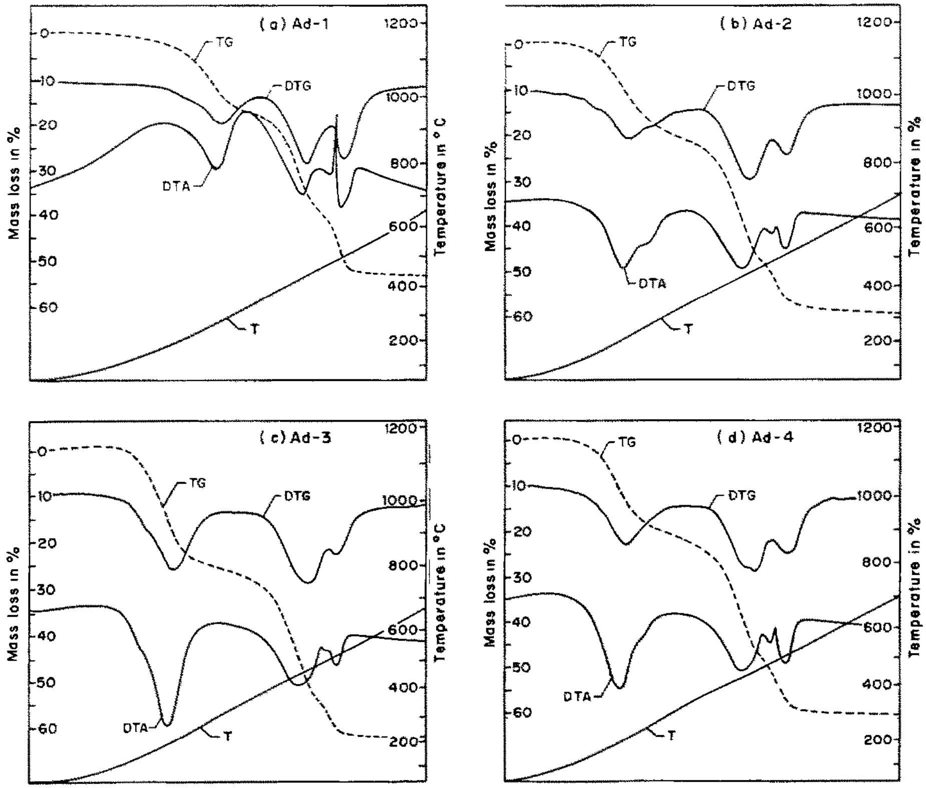

Fig. 3. TG, DTG and DTA curves for magnesium carbonate samples (Ad-1–Ad-4) prepared by employing different modes of mixing: (a) Ad-1, alkali solution to magnesium salt solution; (b) Ad-2, magnesium salt solution to alkali solution; (c) Ad-3, slow addition of both solutions; (d) Ad-4, simultaneous fast addition of both solutions.

which the exothermic peak was observed. The observed exothermic phenomenon may be the result of crystallisation of amorphous $MgCO_3$ [13, 16–20] and/or the disorder → order reaction (metastable oxide → crystalline oxide) in the oxide lattice [21].

The data in the figures and tables indicate that the thermal decomposition of magnesium carbonate and the surface area of the resulting MgO are greatly influenced by the history of the preparation of magnesium carbonate. The influence of the preparation variables of magnesium carbonate on its thermal decomposition is discussed below.

### *Influence of magnesium salts*

A comparison of the TG, DTG and DTA curves (Fig. 1) and the thermal analysis data (Table 2) for the magnesium carbonate samples (S-1–S-4) prepared using different magnesium salts, shows that the type of magnesium salt used in the preparation of magnesium carbonate has a strong

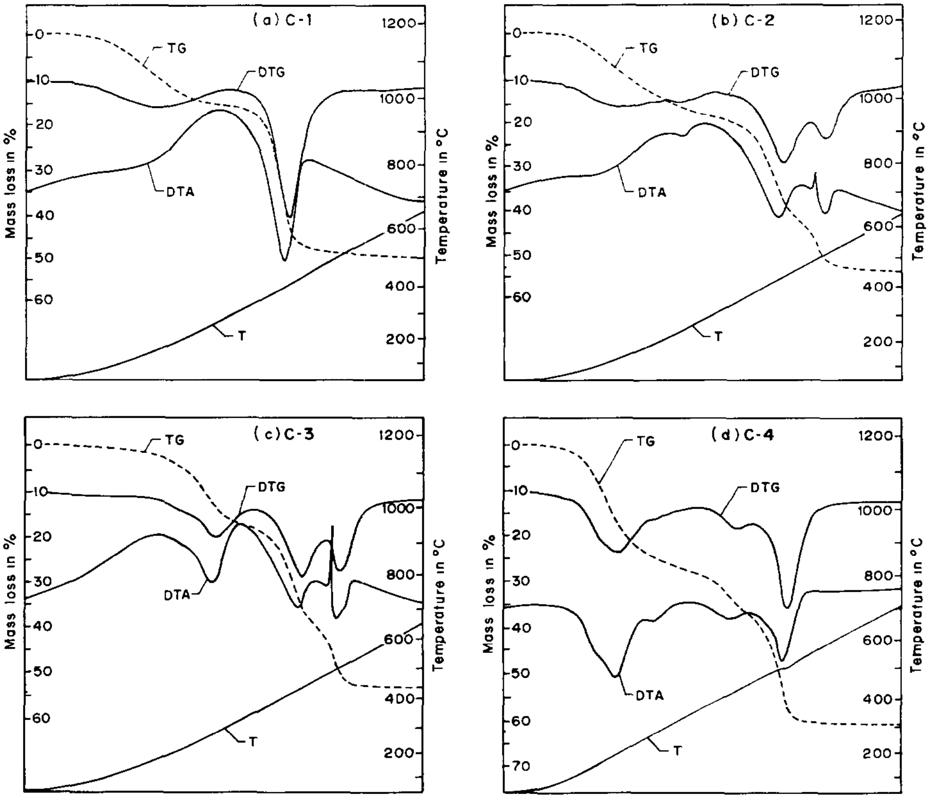

Fig. 4. TG, DTG and DTA curves for magnesium carbonate samples (C-1–C-4) prepared with different concentrations of magnesium nitrate solution: (a) C-1, 0.005 M; (b) C-2, 0.5 M; (c) C-3, 1.0 M; (d) C-4, 2 M.

influence on its thermal decomposition and also on the surface area of the MgO obtained in the decomposition. The exothermic peak is observed only for samples S-1 and S-2. The decarbonation reaction for all the samples occurs in a number of steps as shown by the different peaks and humps. The mass loss observed for the decomposition of sample S-1 is somewhat lower than that of the other samples. Furthermore there is a variation in the surface area of MgO obtained from the samples S-1–S-4. All these observations reveal that the anions ($NO_3^-$, $SO_4^{2-}$, $CH_3COO^-$ and $Cl^-$) present during the precipitation of magnesium carbonate strongly affect its properties, leading to different thermal behaviour.

### *Influence of precipitating agents*

The TG, DTG, DTA curves for the decomposition of basic magnesium carbonate precipitated using the precipitating agents $Na_2CO_3$, $K_2CO_3$, $NaHCO_3$ and $KHCO_3$ are shown in Fig. 2. The data on thermal analysis of the samples and surface area of the resulting MgO are given in Table 3.

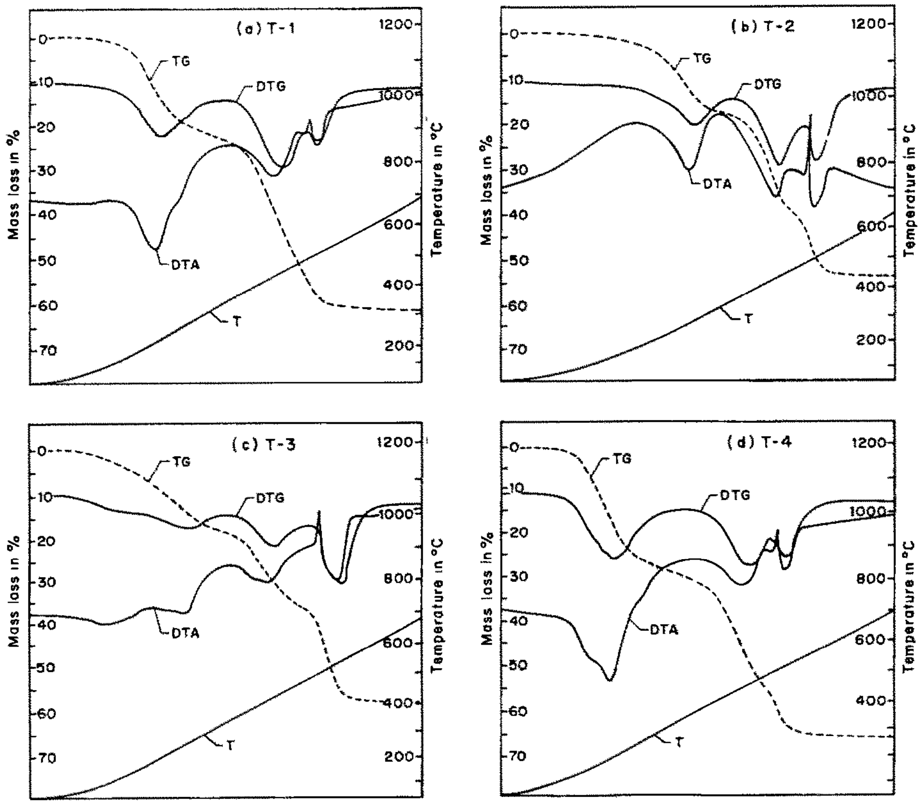

Fig. 5. TG, DTG and DTA curves for magnesium carbonate samples (T-1–T-4) precipitated at different temperatures: (a) T-1, 0°C; (b) T-2, 30°C; (c) T-3, 50°C; (d) T-4, 100°C.

From the comparision of thermal curves in Fig. 2 and data in Table 3, it is observed that the decomposition of samples PA-1–PA-4 occurs in three stages with a sharp exothermic peak around 485–505°C. The DTA/DTG peak temperatures differ from sample to sample depending upon the precipitating agents used. Total mass loss for the samples is in the order PA-3 > PA-4 > PA-1 ≈ PA-2, and surface area of the resulting MgO is in the order PA-3 > PA-1 ≫ PA-2 > PA-4.

All these observations reveal that thermal decomposition behaviour of $MgCO_3$ sample and surface area of resulting MgO depend strongly on the precipitating agent used in the precipitation of magnesium carbonate.

### *Influence of mode of mixing in precipitation*

A comparison of TG, DTG and DTA curves (Fig. 3) and data (Table 4) for magnesium carbonate samples precipitated using different modes of mixing of magnesium salt and sodium carbonate solution indicates that the

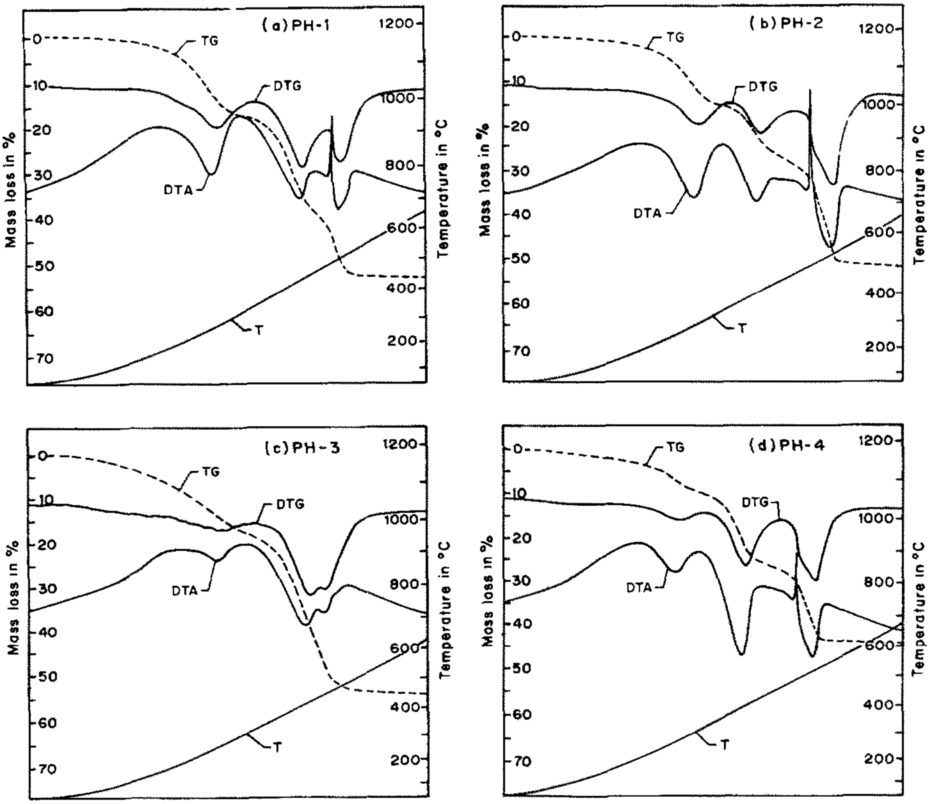

Fig. 6. TG, DTG and DTA curves for magnesium carbonate samples (PH-1–PH-4) precipitated at different pH values: (a) PH-1, pH 9.0; (b) PH-2, pH 10.1: (c) PH-3, pH 10.6; (d) PH-4, pH 10.9.

mode of mixing has a very significant effect on the thermal decomposition and the surface area of the solid product. It is interesting to note that intensity of the exothermic peak varies with a change in the mode of mixing. The different thermal behaviour (in the decomposition) and surface area (of the resulting MgO) arise from the fact that the nucleation and growth of the $MgCO_3$ crystals occur at different concentrations and pH values when the precipitation takes place under different mixing procedures resulting in $MgCO_3$ crystals with different properties.

*Influence of the concentration of magnesium salt*

The DTG and DTA curves (Fig. 4) show that decarbonation of sample C-1 prepared at low magnesium salt concentration (0.1 mol $l^{-1}$), occurs in two steps, whereas for samples prepared at higher concentrations (0.5–2 mol $l^{-1}$) decarbonation occurs in more than two steps. It may be noted that the exothermic peak is absent in samples prepared from the lowest and

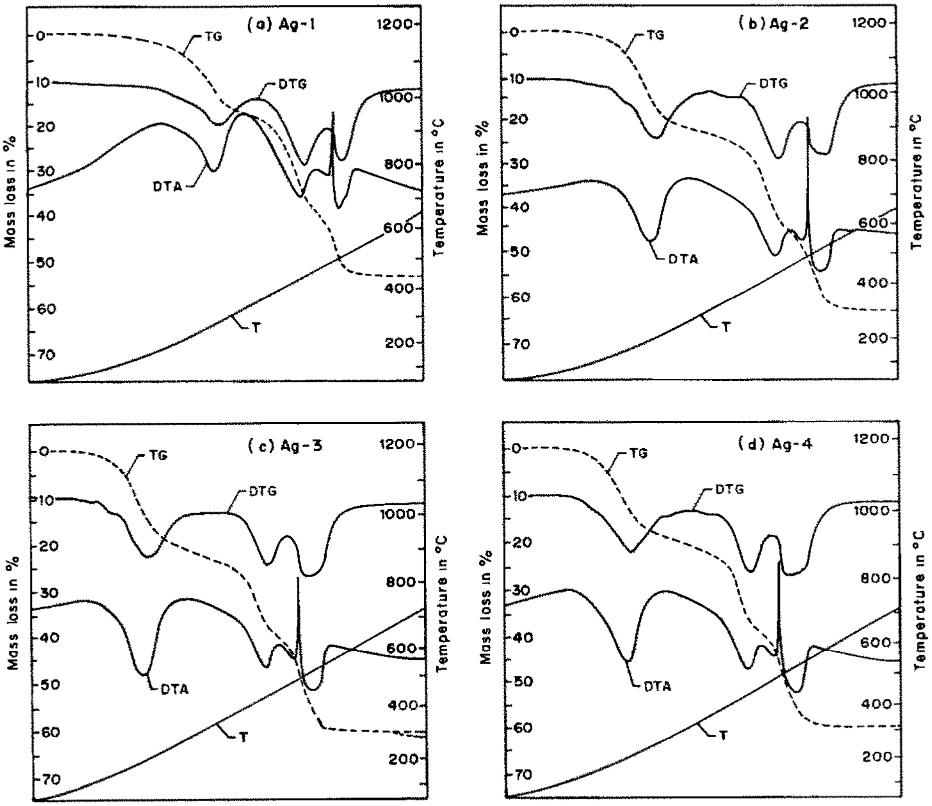

Fig. 7. TG, DTG and DTA curves for magnesium carbonate samples (Ag-1–Ag-4) aged for different periods: (a) Ag-1, 0.5 h; (b) Ag-2, 8.0 h; (c) Ag-3, 24 h; (d) Ag-4, 96 h.

highest concentrations of magnesium salt (C-1 and C-4). A small DTG and DTA peak in the lower temperature region (118°C) for sample C-2 is due to desorption of physically adsorbed water. Total mass loss in $MgCO_3$ samples is in the order C-4 > C-3 > C-2 > C-1 and the surface area of the resulting MgO is in the order C-1 ≫ C-3 > C-2 ≥ C-4.

These facts and the thermal analysis data (Table 5) indicate that thermal decomposition is affected strongly by the change in concentration of the magnesium salt used in the precipitation of magnesium carbonate. The surface area of the resulting MgO is also affected strongly, particularly at the very low magnesium salt concentrations.

### *Influence of precipitation temperature*

A comparison of TG, DTG and DTA curves (Fig. 5) and thermal analysis data (Table 6) reveals that the mode of thermal decomposition of magnesium carbonate changes with the change in the precipitation temperature from 0 to 100°C as seen from the shape of DTG and DTA

TABLE 2

Thermal analysis data for magnesium carbonate prepared using different magnesium salts

| Sample code | Mg-salt | Peak temp./°C | | Mass loss corresponding to DTA peak/% | Total mass loss/% | Surface area of resulting MgO/ $m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
| | | DTA | DTG | | | |
| S-1 | Nitrate | 262 | 274 | 18.7 | 53.7 | 46.6 |
| | | 424 | 439 | 24.0 | | |
| | | 491 (exo) | – | – | | |
| | | 496 | 501 | 11.0 | | |
| S-2 | Sulfate | 199 | 210 | 23.3 | 60.3 | 60.6 |
| | | 250 (hump) | 256 (hump) | – | | |
| | | 428 | 444 | 20.3 | | |
| | | 505 (exo) | – | – | | |
| | | 521 | 531 | 16.7 | | |
| S-3 | Acetate | 199 | 210 | 23.0 | 61.8 | 52.8 |
| | | 448 | 457 | 32.6 | | |
| | | 500 (exo) | – | – | | |
| | | 520 | 525 | 06.2 | | |
| S-4 | Chloride | 193 | 204 | 25.7 | 63.1 | 47.7 |
| | | 439 | 454 | 33.7 | | |
| | | 495 (exo) | – | – | | |
| | | 515 | 510 | 03.7 | | |

curves. A small endothermic peak around 90°C in sample T-3 is due to desorption of physically absorbed water. The DTG and DTA peak temperatures are different for all the $MgCO_3$ samples (T-1–T-4). Total mass loss in the decomposition is in the order T-4 > T-1 > T-3 > T-2 and the surface area of MgO obtained from the samples is in the order T-3 > T-4 > T-2 ≫ T-1.

### *Influence of the pH of precipitation*

The results (Fig. 6 and Table 7) show that the pH of the precipitation has a very strong influence on the thermal decomposition of magnesium carbonate and also on surface area of the resulting MgO. All $MgCO_3$ samples (PH-1–PH-4) decompose in multiple steps with an exothermic peak around 491°C, (the exothermic peak is absent for the PH-3 sample, i.e. for magnesium carbonate precipitated at pH 10.6). The surface areas of the resulting MgO precipitated at the higher pH values (10.6 and 10.9) are very low (7.5 and 7.8 $m^2 g^{-1}$, respectively).

TABLE 3

Thermal analysis data for mangesium carbonate precipitated using different precipitating agents

| Sample code | Precipitating agent | Peak temp./°C | | Mass loss corresponding to DTG peak/% | Total mass loss/% | Surface area of resulting MgO/ $m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
| | | DTA | DTG | | | |
| PA-1 | $Na_2CO_3$ | 262 | 273 | 18.7 | 53.7 | 46.6 |
| | | 424 | 439 | 24.0 | | |
| | | 491 (exo) | – | – | | |
| | | 496 | 501 | 11.0 | | |
| PA-2 | $K_2CO_3$ | 210 | 264 | 16.5 | 53.5 | 14.3 |
| | | 418 | 433 | 19.0 | | |
| | | 505 (exo) | – | – | | |
| | | 525 | 520 | 18.0 | | |
| PA-3 | $NaHCO_3$ | 187 | 193 | 26.2 | 65.5 | 68.1 |
| | | 439 | 449 | 23.7 | | |
| | | 495 (exo) | – | – | | |
| | | 520 | 519 | 15.7 | | |
| PA-4 | $KHCO_3$ | 198 | 210 | 20.3 | 60.9 | 11.8 |
| | | 423 | 431 | 21.6 | | |
| | | 485 (exo) | – | – | | |
| | | 505 | 505 | 19.0 | | |

### *Influence of ageing period of precipitate*

The DTG and DTA curves (Fig. 7) and data given in Table 8 reveal that the ageing period of the precipitated $MgCO_3$ has a significant effect on its thermal decomposition and also, in the surface area of the resulting solid product. The influence, which is quite complex, may be attributed to crystal growth and change in the crystal properties of the $MgCO_3$ during the process of ageing.

## CONCLUSIONS

The thermal decomposition of precipitated magnesium carbonate and the surface area of the resulting solid product MgO are strongly influenced by the preparation conditions (magnesium salt and precipitating agent used and the precipitation conditions (concentration of magnesium salt, pH, temperature, mode of mixing of magnesium salt and precipitating agents, and ageing period of the precipitate) of basic magnesium carbonate. The

TABLE 4

Thermal analysis data for magnesium carbonate prepared using different modes of mixing

| Sample code | Mode of of addition | Peak temp./°C |  | Mass loss corresponding to DTG peak/% | Total mass loss/% | Surface area of resulting MgO/ $m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
|  |  | DTA | DTG |  |  |  |
| Ad-1 | Alkali to salt | 262 | 274 | 18.7 | 53.7 | 46.6 |
|  |  | 424 | 439 | 24.0 |  |  |
|  |  | 491 (exo) | – | – |  |  |
|  |  | 496 | 501 | 11.0 |  |  |
| Ad-2 | Salt to alkali | 207 | 218 | 22.3 | 58.9 | 42.8 |
|  |  | 430 | 440 | 28.3 |  |  |
|  |  | 482 (exo) | – | – |  |  |
|  |  | 532 | 502 | 08.3 |  |  |
| Ad-3 | Slow addition | 195 | 201 | 27.3 | 65.6 | 31.0 |
|  |  | 440 | 462 | 31.3 |  |  |
|  |  | 513 | 513 | 07.0 |  |  |
| Ad-4 | Simultaneous fast addition | 195 | 213 | 23.3 | 61.9 | 68.6 |
|  |  | 456 | 441 | 28.3 |  |  |
|  |  | 487 (exo) | – | – |  |  |
|  |  | 512 | 507 | 10.3 |  |  |

TABLE 5

Thermal analysis data for magnesium carbonate precipitated using different concentrations of magnesium nitrate solution

| Sample code | Concentration of magnesium nitrate solution mol $l^{-1}$ | Peak temp./°C |  | Mass loss corresponding to DTG peak/% | Total mass loss/% | Surface area of resulting MgO/ $m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
|  |  | DTA | DTG |  |  |  |
| C-1 | 0.005 | 158 | 164 | 15.7 | 49.4 | 113.6 |
|  |  | 384 | 398 | 33.7 |  |  |
| C-2 | 0.5 | 112 | 118 | 14.7 | 53.0 | 41.0 |
|  |  | 251 | 246 | 04.0 |  |  |
|  |  | 418 | 429 | 25.0 |  |  |
|  |  | 491 (exo) | – | – |  |  |
|  |  | 506 | 506 | 09.3 |  |  |
| C-3 | 1.0 | 262 | 274 | 18.7 | 53.7 | 46.6 |
|  |  | 424 | 439 | 24.0 |  |  |
|  |  | 491 (exo) | – | – |  |  |
|  |  | 496 | 501 | 11.0 |  |  |
| C-4 | 2.0 | 195 | 189 | 24.7 | 62.7 | 39.5 |
|  |  | 275 | 286 | 04.7 |  |  |
|  |  | 420 | 430 | 10.3 |  |  |
|  |  | 502 | 512 | 23.0 |  |  |

TABLE 6

Thermal analysis data for magnesium carbonate precipitated at different temperatures

| Sample code | Precipitation temp./°C | Peak temp./°C | | Mass loss corresponding to DTG peak/% | Total mass loss/% | Surface area of resulting MgO/ $m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
| | | DTA | DTG | | | |
| T-1 | 0 | 205 | 216 | 23.0 | 62.0 | 18.8 |
| | | 434 | 454 | 31.0 | | |
| | | 500 (exo) | – | – | | |
| | | 508 | 511 | 08.0 | | |
| T-2 | 30 | 262 | 274 | 18.7 | 53.7 | 46.6 |
| | | 424 | 439 | 24.0 | | |
| | | 491 (exo) | – | – | | |
| | | 496 | 501 | 11.0 | | |
| T-3 | 50 | 90.0 | 97 | 05.7 | 55.6 | 72.0 |
| | | 250 | 256 | 12.3 | | |
| | | 402 | 418 | 17.6 | | |
| | | 495 (exo) | – | – | | |
| | | 531 | 541 | 20.0 | | |
| T-4 | 100 | 181 | 187 | 29.0 | 64.7 | 53.9 |
| | | 439 | 444 | 25.00 | | |
| | | 495 (exo) | – | – | | |
| | | 511 | 516 | 10.7 | | |

TABLE 7

Thermal analysis data for magnesium carbonate precipitated at different pH values

| Sample code | pH of precipitation | Peak temp./°C | | Mass loss corresponding to DTG peak/% | Total mass loss/% | Surface area of resulting MgO/ $m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
| | | DTA | DTG | | | |
| PH-1 | 9.0 | 262 | 274 | 18.7 | 53.7 | 46.6 |
| | | 424 | 439 | 24.0 | | |
| | | 491 (exo) | – | – | | |
| | | 496 | 501 | 11.0 | | |
| PH-2 | 10.1 | 274 | 285 | 15.5 | 50.3 | 65.4 |
| | | 393 | 401 | 12.2 | | |
| | | 491 (exo) | – | – | | |
| | | 534 | 527 | 22.6 | | |
| PH-3 | 10.6 | 261 | 274 | 18.0 | 53.7 | 7.5 |
| | | 398 | 408 | 26.0 | | |
| | | 436 | 445 | 9.7 | | |
| PH-4 | 10.9 | 263 | 271 | 9.3 | 43.3 | 7.8 |
| | | 377 | 387 | 16.7 | | |
| | | 486 (exo) | – | – | | |
| | | 506 | 516 | 17.3 | | |

TABLE 8

Thermal analysis data for magnesium carbonate aged for different periods

| Sample code | Ageing period/h | Peak temp./°C | | Mass loss corresponding to DTG peak/% | Total mass loss/% | Surface area of resulting MgO/ $m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
| | | DTA | DTG | | | |
| Ag-1 | 0.5 | 262 | 273 | 18.7 | 53.7 | 46.6 |
| | | 424 | 439 | 24.0 | | |
| | | 491 (exo) | – | – | | |
| | | 496 | 501 | 11.0 | | |
| Ag-2 | 8.0 | 204 | 210 | 23.3 | 62.1 | 71.1 |
| | | 439 | 439 | 28.2 | | |
| | | 495 (exo) | – | – | | |
| | | 550 | 530 | 10.6 | | |
| Ag-3 | 24 | 198 | 198 | 23.7 | 62.4 | 98.3 |
| | | 428 | 434 | 20.0 | | |
| | | 495 (exo) | – | – | | |
| | | 515 | 520 | 18.7 | | |
| Ag-4 | 96 | 198 | 204 | 21.6 | 61.6 | 85.0 |
| | | 423 | 434 | 21.6 | | |
| | | 485 (exo) | – | – | | |
| | | 525 | 526 | 18.3 | | |

exothermic DTA peak, attributed to the recrystallisation of solid product, is not found for all the $MgCO_3$ samples.

## REFERENCES

1 T. Ito and J.H. Lunsford, Nature, 314 (1985) 721.
2 T. Ito, J.H. Wang, C.H. Lin and J.H. Lunsford, J. Am. Chem. Soc., 107 (1985) 5062.
3 J.B. Kimble and J.H. Kolts, Chemtech (1987) 501.
4 T. Moriyama, N. Takasaki, E. Iwamatsu and K. Aika, Chem. Lett., (1986) 1165.
5 V.R. Choudhary, D.B. Akolekar and A.M. Rajput, in B.D. Kulkarni, R.A. Mashelkar and M.M. Sharma (Eds.), Recent Trends in Chemical Reaction Engineering, Vol. 1, Wiley Eastern, Delhi, 1987, p. 80.
6 E. Iwamatsu, T. Moriyama, N. Takasaki and K. Aika, J. Catal., 113 (1988) 25.
7 V.R. Choudhary, M.Y. Pandit, V.H. Rane and S.T. Chaudhari, Paper presented at 1st Indo-French Symp. on Catalysis by Oxides and Zeolites, Pune, India, 5–7 Dec. 1989, paper 19.
8 V.R. Choudhary, S.G. Pataskar, M.Y. Pandit and V.G. Gunjikar, Thermochim. Acta, 180 (1991) 69.
9 V.R. Choudhary, S.T. Chaudhari, V.H. Rane and A.M. Rajput, J. Chem. Soc. Chem. Commun., (1989) 555, 1526.
10 V.R. Choudhary, S.T. Choudhary, V.H. Rane and A.M. Rajput, Res. Ind., 34 (1989) 258.

11 V.H. Rane, Preparation, Characterization and Evaluation of Basic Solid Catalysts for Direct Conversion of Methane to Higher Hydrocarbons, Ph.D. Thesis, University of Poona, July 1992.
12 S.T. Chaudhari, Oxidative Conversion of Methane to Ethylene, Ph.D. Thesis, University of Bombay, Aug. 1992.
13 R.M. Dell and S.W. Weller, Trans. Faraday Soc., 55 (1959) 2203.
14 G. Raade, Am. Mineral., 55 (1970) 1457.
15 W. Holand and K. Heide, Thermochim. Acta, 15 (1976) 287.
16 Y. Sawada, J. Yamaguchi, O. Sakarai, K. Uematsu, N. Mizutani and M. Kato, Thermochim. Acta, 32 (1979) 277.
17 Y. Sawada, J. Yamaguchi, O. Sakarai, K. Uematsu, N. Mizutani and M. Kato, J. Inorg. Nucl. Chem., 40 (1978) 979.
18 Y. Sawada, J. Yamaguchi, O. Sakurai, K. Uematsu, N. Mizutani and M. Kato, Thermochim. Acta, 33 (1979) 127.
19 Y. Sawada, K. Uematsu, N. Mizutani and M. Kato, Thermochim. Acta, 27 (1978) 45.
20 Y. Sawada, J. Yamaguchi, O. Sakurai, K. Uematsu, N. Mizutani and M. Kato, Thermochim. Acta, 34 (1979) 333.
21 C.N.R. Rao, S.R. Yoganarasimhan and M.P. Lewis, Can J. Chem., 38 (1960) 2359.