THERMAL DECOMPOSITION OF BASIC MAGNESIUM CARBONATE IN THE PREPARATION OF ACTIVE MgO CATALYST

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DEDICATED

TO

MY LOVING

PARENTS & BROTHERS

CERTIFICATE

I certify that the thesis presented by Mr. Ganesh B. Zope represents his original work which was carried out by him at Chemical Engineering Division, National Chemical Laboratory, Pune, under my guidance and supervision during the period June 1993 to December 1995. I further certify that the foregoing statements made by him in regard to his thesis are correct.

Place Pune
Date 5/5/1997

Signature of Research Guide
(Dr. V.R. Choudhary)

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CONTENTS

SUMMARY AND CONCLUSIONS

CHAPTER-1 : Influence of preparation conditions of basic magnesium carbonate on its thermal analysis

CHAPTER-2 : Surface properties of magnesium oxide obtained from basic magnesium carbonate Influence of preparation conditions of magnesium carbonate

SUMMARY AND CONCLUSIONS

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Magnesium oxide with promoters like 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 as process of great practical importance for converting natural gas into petrochemicals/petroleum products. Highly active/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 surface properties of the resulting magnesium oxide. This investigation was undertaken with the following objectives.

- To study the influence of preparation conditions of basic magnesium carbonate on its thermal analysis
- To investigate the influence of preparation conditions of magnesium carbonate on surface properties of magnesium oxide obtained from basic magnesium carbonate

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

Thermal analysis (TG / DTG / DTA) of a number of basic magnesium carbonate samples, prepared by precipitation using different magnesium salts (viz. magnesium nitrate, sulfate, chloride, and acetate) and precipitating agents (viz. sodium carbonate and bicarbonate and potassium carbonate and bicarbonate) at different concentrations of Mg-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 at different periods (0.5-96h) has been carried out in the temperature range of 30° - 600°C. The thermal decomposition and surface area of resulting MgO are found to be strongly influenced by the preparation conditions of basic magnesium carbonate.

Influence of preparation conditions of magnesium carbonate on surface properties of magnesium oxide obtained from basic magnesium carbonate.

Surface area, total basicity and base strength distribution (weak, strong and intermediate strength basic sites) of magnesium oxide obtained from basic magnesium carbonate (by its decomposition at 600°C) prepared by precipitation using different magnesium salts, precipitating agents and precipitating conditions (viz. concentration of magnesium salt, pH, temperature, mode of mixing and ageing period) have been thoroughly investigated. The total basicity and base strength distribution of the different magnesium oxide samples have been determined by step-wise thermal desorption of carbon dioxide from 30°C to 980°C. The chemical composition of basic magnesium carbonate and the surface properties and carbon dioxide content of magnesium oxide are found to be strongly influenced by the above mentioned preparation conditions of basic magnesium carbonate.

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CHAPTER-1

INFLUENCE OF PREPARATION CONDITIONS OF BASIC MAGNESIUM CARBONATE ON ITS THERMAL ANALYSIS

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INFLUENCE OF PREPARATION CONDITIONS OF BASIC MAGNESIUM CARBONATE ON ITS THERMAL ANALYSIS

1.1 INTRODUCTION

Magnesium oxide with promoters like 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 petrochemicals/petroleum products. In the earlier studies we have observed that highly active/ 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 surface properties of the resulting magnesium oxide.

Thermal analysis of basic magnesium carbonate of general formula : $xMgCO_3 . yMg(OH)_2 . zH_2O$ has been thoroughly investigated earlier (13-17). However, no detailed investigation of the influence of precipitation and ageing conditions on the thermal decomposition behavior of basic magnesium carbonate has been reported so far. The present investigation was, therefore, undertaken to study the influence of various precipitation and ageing 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.

1.2 EXPERIMENTAL

1.2.1 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 deionized 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 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

ii) Precipitating agent : Sodium carbonate, Potassium carbonate and Sodium bicarbonate, and Potassium bicarbonate

iii) Precipitation and Ageing conditions :

Concentration of Magnesium salt : 0.005, 0.5,1.0 and 2.0 M

Concentration of the precipitating agent : equimolar to the magnesium salt solution used.

Temperature (°C) : 0, 30, 50 and 100

pH : 9, 10.1, 10.6 and 10.9

Mode of mixing of magnesium salt and precipitating agent solutions :

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.

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-3	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	8.0
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 solution

E. Ageing period : 0.5, 8, 24 and 96 h.

1.2.2 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 NETSCH STA 409 model simultaneous thermal analysis apparatus, under following experimental conditions : particle size, 250-300 mesh; sample size, 30 mg; reference compound, α-alumina; sample holder, platinum crucible; temperature range, 30^o-600^oC; linear heating rate, $10^oC\ min^{-1}$ and atmosphere, static air.

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

1.3 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^oC are given in Tables 2-8. Thermal decomposition of hydromagnesite $4MgCO_3$. $Mg(OH)_2$. $4H_2O$ is expected to proceed via dehydration (removal of water of crystallization) at lower temperature ($< 250^oC$), dehydroxylation (i.e. decomposition of magnesium hydroxide to MgO) at intermediate temperatures (about 250^o - 350^oC) and decarbonation (i.e. decomposition of magnesium

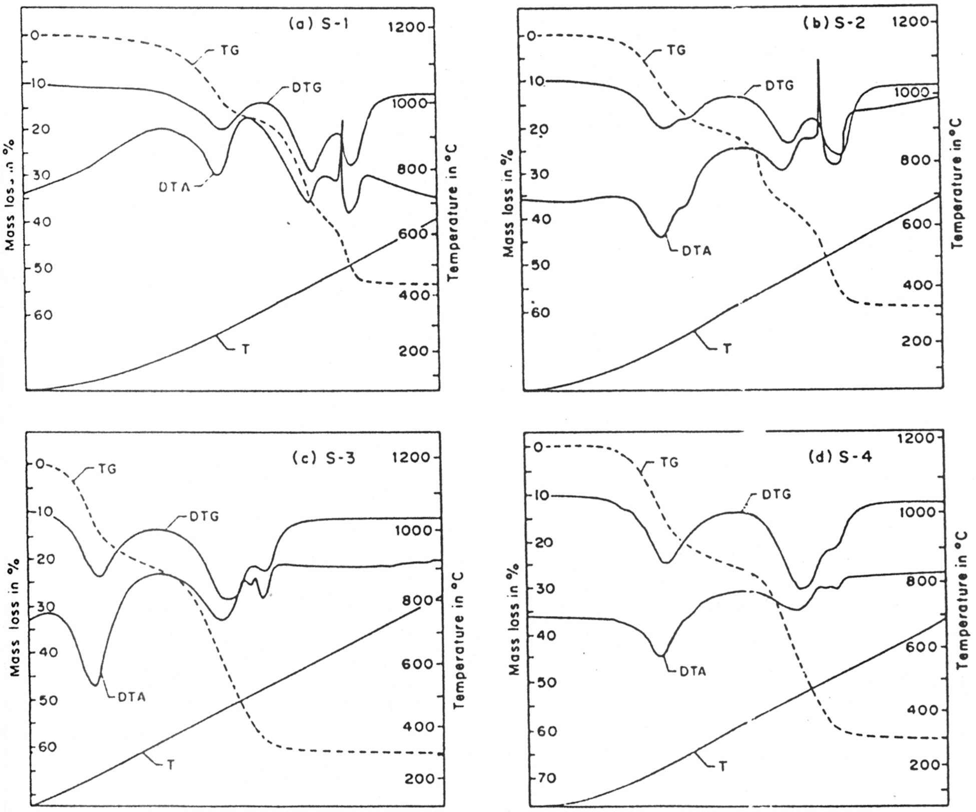

Fig. 1. TG, DTG and DTA curves for magnesium carbonate samples (S-1–S-4) prepared using different magnesium salts: (a) S-1, magnesium nitrate; (b) S-2, magnesium sulphate; (c) S-3, magnesium acetate; and (d) S-4, magnesium chloride.

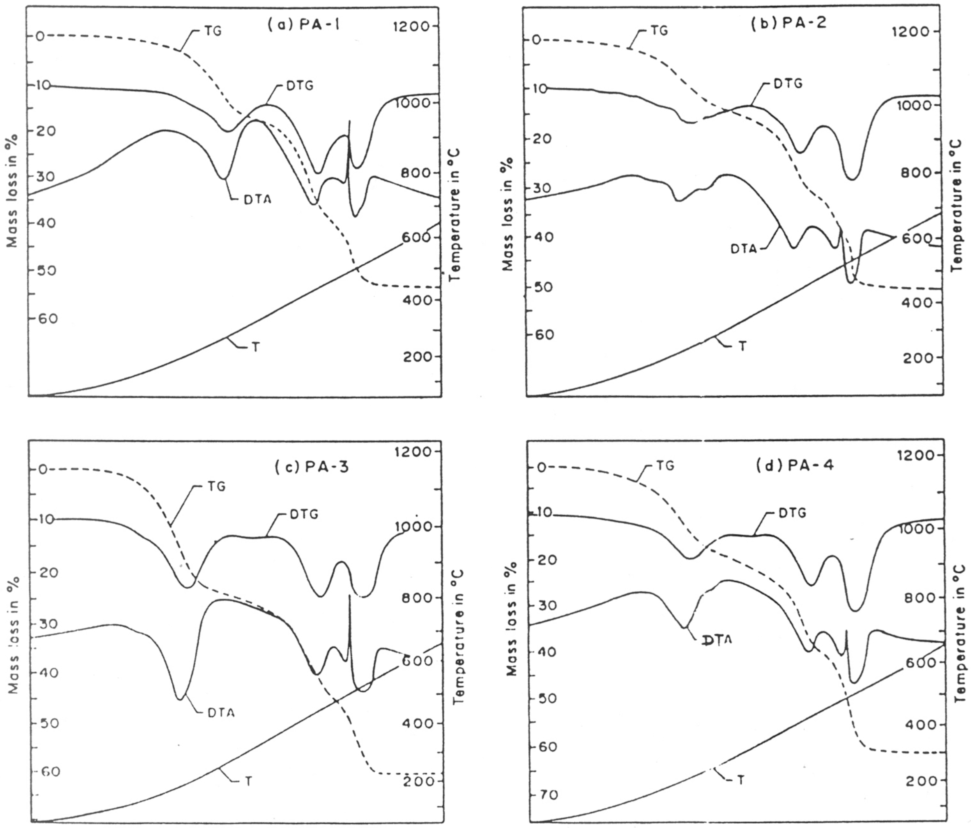

Fig. 2. TG, DTG and DTA curves for magnesium carbonate samples (PA-1–PA-4) precipitated with different precipitating agents: (a) PA-1, Na_2CO_3; (b) PA-2, K_2CO_3; (c) PA-3, $NaHCO_3$; (d) PA-4, $KHCO_3$.

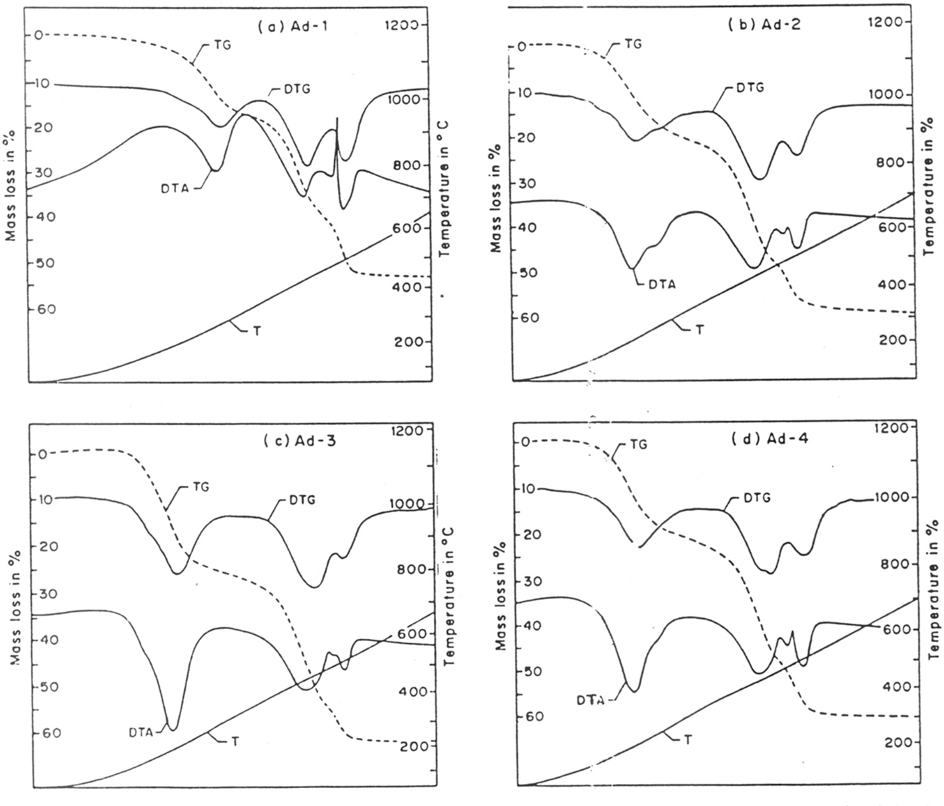

Fig. 3. TG, DTG and DTA curves for magnesium carbonate samples (Ad-1–Ad-4) prepared by employing different modes of mixing: (a) Ad-1, alkali solution to magnesium salt solution; (b) Ad-2, magnesium salt solution to alkali solution; (c) Ad-3, slow addition of both solutions; (d) Ad-4, simultaneous fast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

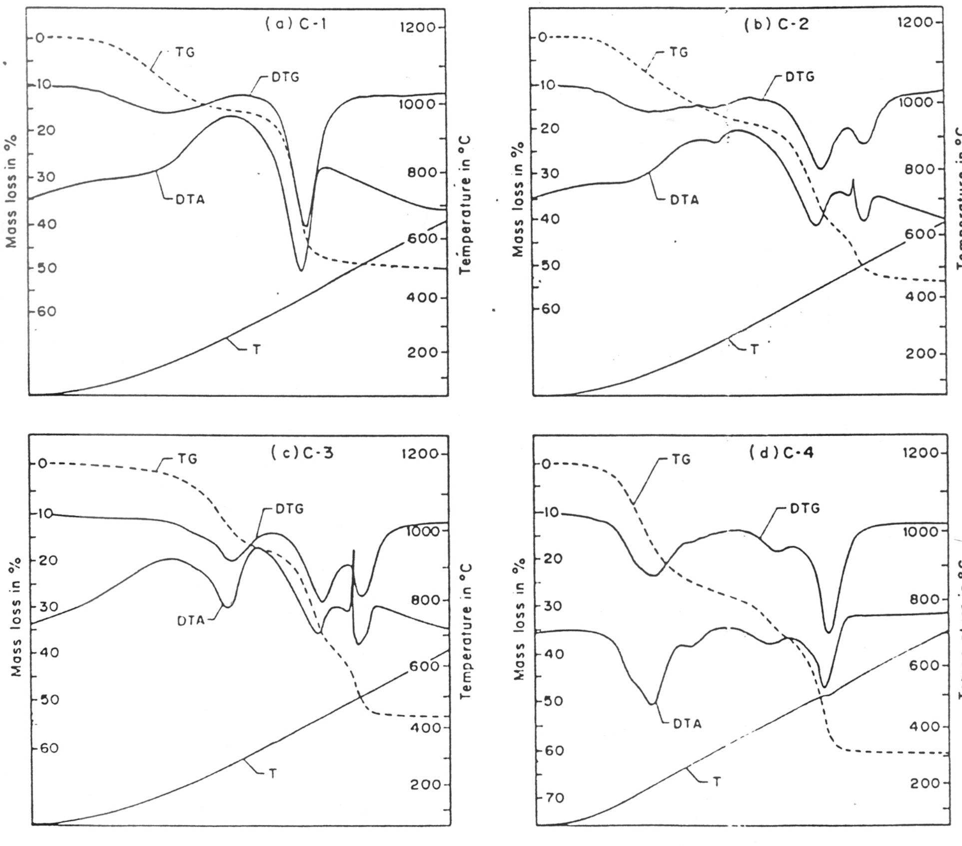

Fig. 4. TG, DTG and DTA curves for magnesium carbonate samples (C-1–C-4) prepared with different concentrations of magnesium nitrate solution: (a) C-1, 0.005 M; (b) C-2, 0.5 M; (c) C-3, 1.0 M; (d) C-4, 2 M.

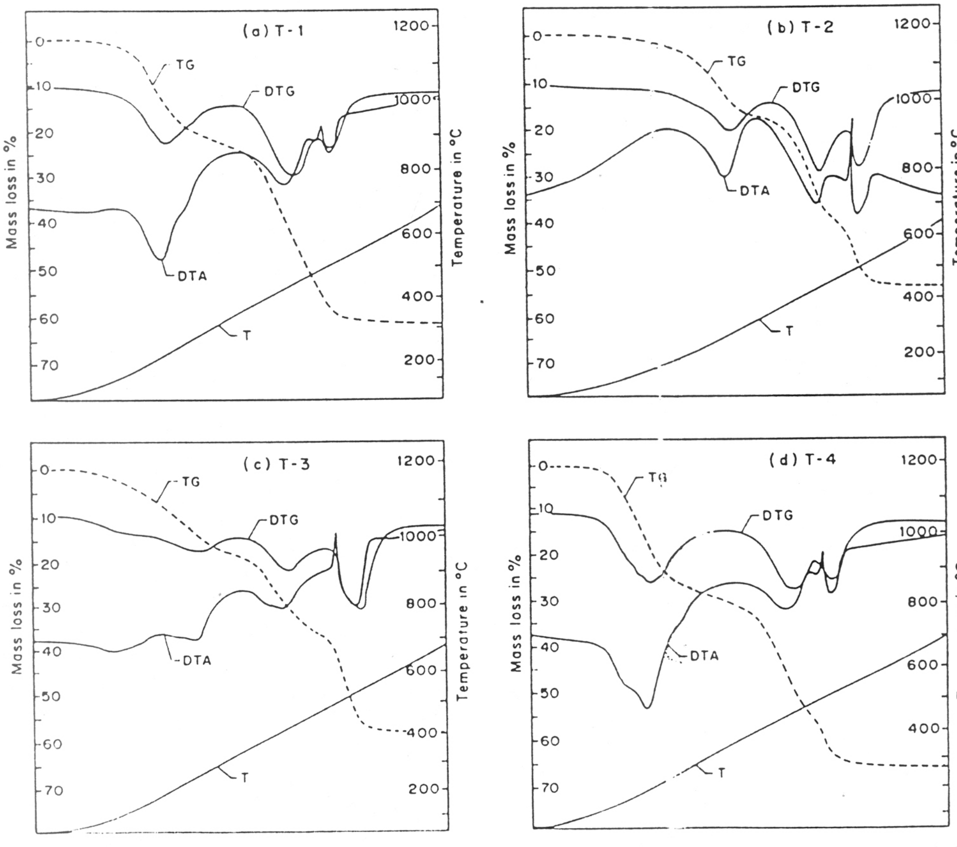

Fig. 5. TG, DTG and DTA curves for magnesium carbonate samples (T-1–T-4) precipitated at different temperatures: (a) T-1, 0°C; (b) T-2, 30°C; (c) T-3, 50°C; (d) T-4, 100°C.

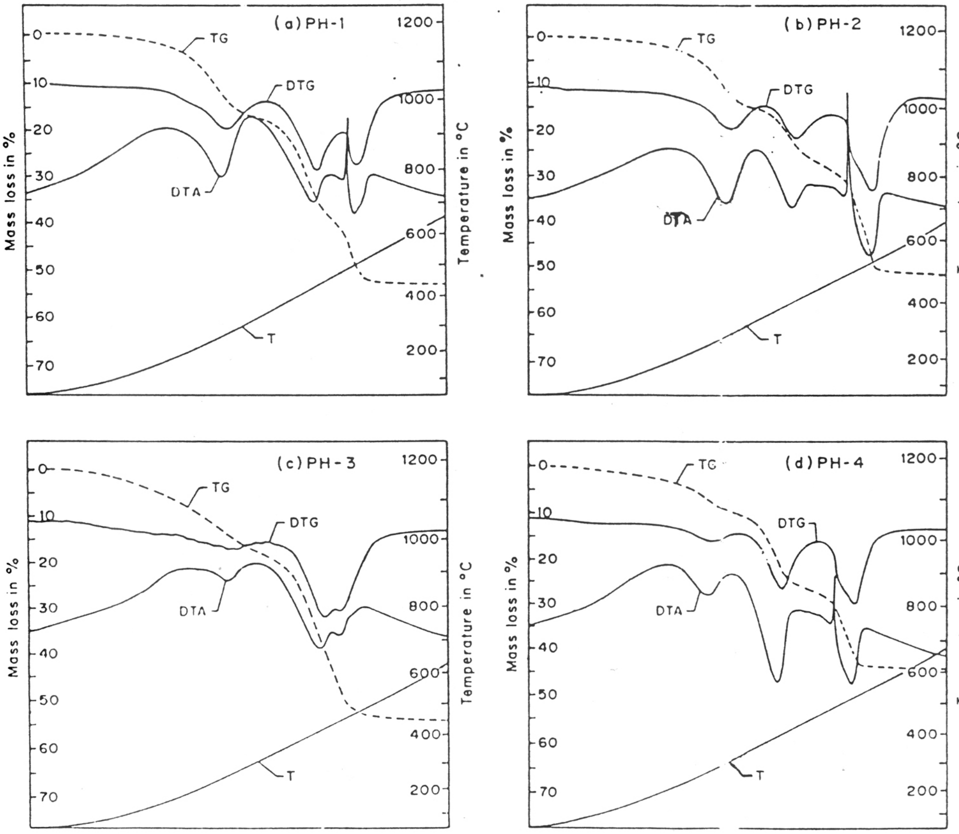

Fig. 6. TG, DTG and DTA curves for magnesium carbonate samples (PH-1–PH-4) precipitated at different pH values: (a) PH-1, pH 9.0; (b) PH-2, pH 10.1: (c) PH-3, pH 10.6; (d) PH-4, pH 10.9.

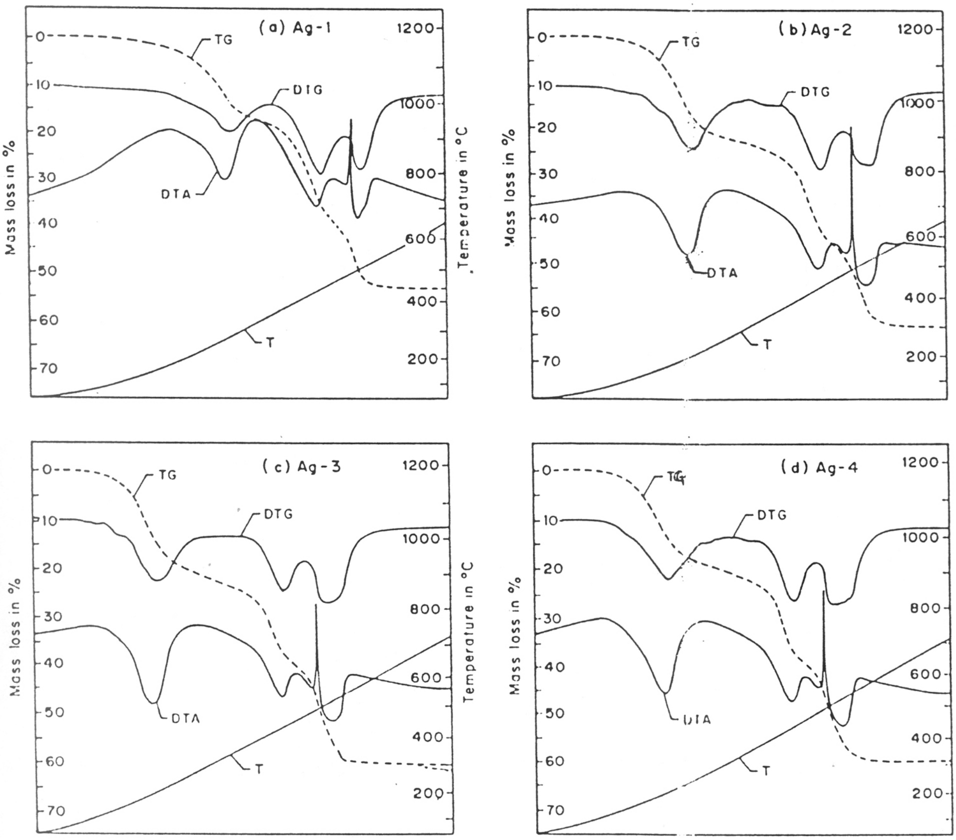

Fig. 7. TG, DTG and DTA curves for magnesium carbonate samples (Ag-1–Ag-4) aged for different periods: (a) Ag-1, 0.5 h; (b) Ag-2, 8.0 h; (c) Ag-3, 24 h; (d) Ag-4, 96 h.

TABLE 2

Thermal analysis data for magnesium carbonate prepared using different magnesium salts

Sample code	Mg-salt	Peak temp/^{o}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	22.3	60.3	60.6
		250 (hump)	256	--		
		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		

TABLE 3

Thermal analysis data for magnesium carbonate precipitated using different precipitating agents

Sample code	Precipitating agent	Peak temp/°C DTA	Peak temp/°C DTG	Mass loss corresponding to DTG peak/%	Total mass loss /%	Surface area of resulting MgO/m^2.g^{-1}
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		

TABLE 4

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

Sample code	Mode 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/^{o}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	97	05.7	55.6	72.0
		250	256	12.3		
		402	418	17.0		
		495 (exo)	--	--		
		531	541	20.0		
T-4	100	181	187	29.0	64.7	53.9
		439	444	25.0		
		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		

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 %).

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

The small mass loss (5 - 7 %) and the corresponding DTG and DTA (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 which the exothermic peak was observed. The observed exothermic phenomenon may be the result of crystallization 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.

1.3.1 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 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 to 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 behavior.

1.3.2 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.

From the comparison of thermal curves in Fig. 2 and data Table 3, it is observed that the decomposition of samples PA-1 to 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 behavior of $MgCO_3$ sample and surface area of resulting MgO depend strongly on the precipitating agent used in the precipitation of magnesium carbonate.

1.3.3 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 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 the intensity of the exothermic peak varies with a change in the mode of mixing. The different thermal behavior (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.

1.3.4 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 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.

1.3.5 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 curves. A small endothermic peak around 90°C in sample T-3 is due to desorption of physically adsorbed 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.

1.3.6 Influence of 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 to 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 higher pH values (10.6 and 10.9) are very low (7.5 and 7.8 $m^2.g^{-1}$, respectively).

1.3.7 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 .

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

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CHAPTER-2

SURFACE PROPERTIES OF MAGNESIUM OXIDE OBTAINED FROM BASIC MAGNESIUM CARBONATE : INFLUENCE OF PREPARATION CONDITIONS OF MAGNESIUM CARBONATE

CHAPTER-2

SURFACE PROPERTIES OF MAGNESIUM OXIDE OBTAINED FROM BASIC MAGNESIUM CARBONATE : INFLUENCE OF PREPARATION CONDITIONS OF MAGNESIUM CARBONATE

2.1 INTRODUCTION

A number of magnesium oxide catalysts promoted with alkali metals (1 - 9); rare earth metals (10 - 14); lead (15,16); metal chloride (17,18); sodium and manganese (19); etc. have been used for oxidative coupling of methane (OCM) to ethane and ethylene; which is a process of great commercial importance for the future.

Highly active magnesium oxide for OCM reaction can be prepared by thermal decomposition of basic magnesium carbonate (general formula : $xMgCO_3 . yMg(OH)_2 . zH_2O$) under controlled conditions (20). On its decomposition, magnesium carbonate prepared by precipitation using different magnesium salts and precipitating agents, and also at different precipitating conditions (viz. magnesium salt concentration, mode of mixing of magnesium salt and precipitating agents, temperature, pH and ageing period of the precipitate) is expected to yield magnesium oxide of different surface properties. The influence of these preparation conditions on thermal decomposition of magnesium carbonate has been thoroughly investigated (21). However, the effect of these preparation conditions on the surface properties of magnesium oxide (obtained from magnesium carbonate), such as surface area and surface basicity, which is very important for the catalytic activity and selectivity of magnesium oxide catalysts has not yet been thoroughly investigated.

Because of the increased use of magnesium oxide catalysts, it would be interesting to carry out the above investigations The present investigation was, therefore, undertaken in order to study the surface properties of magnesium oxide, obtained from magnesium carbonate (by its decomposition at 600°C) prepared under different precipitating and ageing conditions. The basicity /base strength distribution of magnesium oxide, is determined by step-wise thermal desorption of carbon dioxide.

2.2 EXPERIMENTAL

Magnesium carbonate was prepared by precipitating it from an aqueous magnesium salt solution by varying the magnesium salt precipitating agent, precipitating conditions and ageing period. The variables considered for the preparation of magnesium carbonate were magnesium salt (magnesium nitrate, chloride, sulfate and acetate), . precipitating agents (sodium carbonate, potassium carbonate, sodium and potassium bicarbonate :and ammonium carbonate), concentration of magnesium nitrate solution : 0.05 - 2.0 M), mode of mixing : [(i) precipitating agent solution added to magnesium salt solution, (ii) magnesium salt solution added to precipitating agent solution, (iii) slow addition of both the solutions in a stirred vessel, (iv) fast addition of both the solutions in a stirred vessel], temperature (0° - 65°C), pH (9 - 11) and ageing period (0.5 to 96 h.). A number of magnesium carbonate samples were prepared by systematically varying one of the preparation conditions at a time, while keeping all the other conditions constant. The preparation conditions of the different magnesium carbonate samples are given in Tables 1 - 7.

After ageing the precipitated magnesium carbonate, it was washed thoroughly with deionized water until free from cations, filtered and dried at 60°C in an air oven under vacuum for 8 h. The dried mass was crushed to 30 - 40 mesh size particles.

Samples of magnesium oxide were prepared by thermal decomposition of he magnesium carbonate samples in a muffle furnace at 600°C under static air for 6 h. The final calcination temperature was attained at a heating rate about 10°C min^{-1} The magnesium oxide samples were stored in a desiccator

TABLE 1

Surface properties of magnesium oxide obtained by decomposition of basic magnesium carbonate (at 600°C for 6h) prepared by precipitation using different magnesium salts.

Magnesium salts	Composition of basic magnesium carbonate	Surface area ($m^2\,g^{-1}$)	CO_2 content ($mmol\,g^{-1}$)	Basic sites ($mmol\,g^{-1}$)		Distribution of basic sites (%)		
				Total	Strong	Weak sites	Intermediate strength sites	Strong sites
$Mg(NO_3)_2$	$MgCO_3 \,.\, 0.36\ Mg(OH)_2 \,.\, 0.73\ H_2O$	46.6	0.01	0.65	0.35	29.2	16.9	53.8
$Mg(COOCH_3)_2$	$MgCO_3 \,.\, 0.2\ Mg(OH)_2 \,.\, 1.72\ H_2O$	52.7	0.09	1.26	0.37	35.7	34.9	29.4
$MgSO_4$	$MgCO_3 \,.\, 0.37\ Mg(OH)_2 \,.\, 1.78\ H_2O$	60.5	0.1	0.84	0.29	34.5	30.5	35.0
$MgCl_2$	$MgCO_3 \,.\, 0.24\ Mg(OH)_2 \,.\, 2.12\ H_2O$	47.7	0.09	0.85	0.28	38.8	28.2	33.0

Preparation conditions : concentration of magnesium salt solution (1.0 M), mode of addition : precipitating agent solution added to magnesium salts solution, precipitating agent : sodium carbonate solution (1.0 M), temperature : 30°C ; pH : 9.0 ; ageing period : 0.3h.

TABLE 2

Surface properties of magnesium oxide obtained by decomposition of basic magnesium carbonate (at 600°C for 6h) prepared by precipitation with different precipitating agents.

Precipitating agent	Composition of basic magnesium carbonate	Surface area ($m^2 g^{-1}$)	CO_2 content (mmol g^{-1})	Basic sites (mmol g^{-1})		Distribution of basic sites (%)		
				Total	Strong	Weak sites	Intermediate strength sites	Strong sites
Na_2CO_3	$MgCO_3$. 0.36 $Mg(OH)_2$. 0.73 H_2O	46.6	0.01	0.65	0.35	29.2	16.9	53.8
K_2CO_3	$MgCO_3$ .1.46 $Mg(OH)_2$. 2.39 H_2O	14.3	0.89	0.41	0.25	6.6	14.5	78.9
$NaHCO_3$	$MgCO_3$. 1.53 $Mg(OH)_2$. 6.72 H_2O	68.1	0.15	0.61	0.18	36.1	32.8	31.1
$KHCO_3$	$MgCO_3$. 1.62 $Mg(OH)_2$. 5.02 H_2O	11.8	0.86	0.33	0.15	29.5	26.7	43.6
Ammonium carbonate		50.6	0.08	0.58	0.23	39.6	20.69	39.6

Preparation conditions : mode of addition : precipitating agent solution to magnesium nitrate solution ; temperature : 30°C ; pH : 9.0 ; ageing period : 0.5 h ; concentration : equimolar concentration of magnesium nitrate solution and precipitating agent solution.

TABLE 3

Surface properties of magnesium oxide obtained by decomposition of basic magnesium carbonate (at 600°C for 6h) prepared by precipitation from magnesium nitrate solution of different concentrations.

Concentration of magnesium nitrate (mol dm^{-3})	Composition of basic magnesium carbonate	Surface area ($m^2\ g^{-1}$)	CO_2 content (mmol g^{-1})	Basic sites (mmol g^{-1})		Distribution of basic sites (%)		
				Total	Strong	Weak sites	Intermediate strength sites	Strong sites
0.005	$MgCO_3$. 2.47 $Mg(OH)_2$. 2.66 H_2O	113.6	0.07	0.59	0.098	59.4	23.8	16.8
0.5	$MgCO_3$ . .0.69 $Mg(OH)_2$. 1.19 H_2O	40.9	0.48	0.64	0.31	26.5	25.0	48.5
1.0	$MgCO_3$. 0.36 $Mg(OH)_2$. 0.72 H_2O	46.6	0.01	0.65	0.35	29.2	16.9	53.9
2.0	$MgCO_3$. 0.47 $Mg(OH)_2$. 2.48 H_2O	39.5	0.2	0.49	0.16	34.8	32.6	32.6

Preparation conditions : precipitating agent : sodium carbonate solution, mode of addition : precipitating agent added to magnesium nitrate solution ; temperature : 30°C ; ageing period : 0.5 h ; pH : 9.0.

TABLE 4

Surface properties of magnesium oxide obtained by decomposition of basic magnesium carbonate prepared (at 600°C for 6h) by precipitation at different temperatures.

Temperature of precipitation (°C)	Composition of basic magnesium carbonate	Surface area ($m^2\ g^{-1}$)	CO_2 content ($mmol\ g^{-1}$)	Basic sites ($mmol\ g^{-1}$)		Distribution of basic sites (%)		
				Total	Strong	Weak sites	Intermediate strength sites	Strong sites
0	$MgCO_3$. 0.31 $Mg(OH)_2$. 2.01 H_2O	18.8	0.06	1.18	0.55	27.9	25.4	46.6
30	$MgCO_3$ . .0.36 $Mg(OH)_2$. 0.72 H_2O	46.6	0.01	0.65	0.35	29.2	16.9	53.8
50	$MgCO_3$. 0.48 $Mg(OH)_2$. 1.24 H_2O	72.0	0.06	0.33	0.003	75.7	24.2	0.9
100	$MgCO_3$. 0.26 $Mg(OH)_2$. 2.06 H_2O	53.8	0.07	0.49	0.16	38.8	28.6	32.6

Preparation conditions : concentration of magnesium salt solution : magnesium nitrate solution (1.0 M), precipitating agent : sodium carbonate solution (1.0 M), mode of addition : sodium carbonate solution to magnesium nitrate solution ; pH : 9.0 ; ageing period : 0.3h ; temperature : 30°C .

TABLE 5

Surface properties of magnesium oxide obtained by decomposition of basic magnesium carbonate (at 600°C for 6h) by precipitation with different pH values.

pH of precipitation	Composition of basic magnesium carbonate	Surface area ($m^2 g^{-1}$)	CO_2 content ($mmol\ g^{-1}$)	Basic sites ($mmol\ g^{-1}$)		Distribution of basic sites (%)		
				Total	Strong	Weak sites	Intermediate strength sites	Strong sites
9.0	$MgCO_3 . 0.36\ Mg(OH)_2 . 0.73\ H_2O$	46.6	0.01	0.65	0.35	29.2	16.9	53.9
10.1	$MgCO_3 .0.48\ Mg(OH)_2 . 0.43\ H_2O$	63.4	0.13	0.50	0.14	48.0	24.0	28.0
10.7	$MgCO_3 . 1.57\ Mg(OH)_2 . 2.69\ H_2O$	111.8	0.10	0.55	0.03	54.5	40.1	5.4
10.9	$MgCO_3 . 1.84\ Mg(OH)_2 . 0.55\ H_2O$	82.4	0.10	0.42	0.09	40.5	38.1	21.4

Preparation conditions : mode of addition : sodium carbonate added to magnesium nitrate solution (equimolar concentration) ; temperature : 30°C ; ageing period : 0.5 h.

TABLE 6

Surface properties of magnesium oxide obtained by decomposition of basic magnesium carbonate (at 600°C for 6h) prepared by precipitation following different modes of addition of magnesium nitrate solution and sodium carbonate solution.

Mode of addition	Composition of basic magnesium carbonate	Surface area ($m^2 g^{-1}$)	CO_2 content ($mmol\ g^{-1}$)	Basic sites ($mmol\ g^{-1}$)		Distribution of basic sites (%)		
				Total	Strong	Weak sites	Intermediate strength sites	Strong sites
A1	$MgCO_3 . 0.36\ Mg(OH)_2 . 0.73\ H_2O$	46.6	0.01	0.65	0.35	29.2	16.9	53.8
A2	$MgCO_3 . 0.46\ Mg(OH)_2 . 1.81\ H_2O$	42.8	0.31	0.39	0..01	53.8	43.6	2.6
A3	$MgCO_3 . 0.20\ Mg(OH)_2 . 2.56\ H_2O$	30.9	0.12	0.52	0.16	40.4	28.8	30.8
A4	$MgCO_3 . 0.77\ Mg(OH)_2 . 3.28\ H_2O$	68.6	0.07	0.45	0.09	46.7	33.3	20.0

Preparation conditions of magnesium nitrate and sodium carbonate solution (1.0 M), temperature : 30°C ; pH : 9.0 ; ageing period : 0.5h ; mode of addition : A1 : precipitating agent solution to magnesium nitrate solution ; A2 : magnesium salt solution added to precipitating agent solution ; A3 : slow simultaneous addition of both the solutions in stirred vessel ; A4 : fast simultaneous addition of both the solutions in stirred vessel.

TABLE 7

Surface properties of magnesium oxide obtained by decomposition of basic magnesium carbonate (at 600°C for 6h) prepared by ageing precipitate at different periods.

Ageing periods (h)	Surface area (m^2 g^{-1})	CO_2 content (mmol g^{-1})	Basic sites (mmol g^{-1})		Distribution of basic sites (%)		
			Total	Strong	Weak sites	Intermediate strength sites	Strong sites
0.5	46.6	0.01	0.65	0.35	29.2	16.9	53.8
8.0	71.1	0.08	0.53	0.23	24.5	32.1	43.4
24.0	98.3	0.06	0.53	0.24	22.6	32.1	45.3
96.0	85.3	0.11	0.48	0.15	37.5	31.2	31.3

Preparation conditions : magnesium salt used : magnesium nitrate solution (1.0 M) ; precipitating agent : sodium carbonate solution (1.0 M), mode of addition of precipitating agent solution to magnesium nitrate solution ; temperature : 30°C ; pH : 9.0.

The surface area of magnesium oxide samples was determined by the single point BET method by measuring the adsorption of nitrogen at liquid nitrogen temperature and at nitrogen concentration of 30 mol% (balance helium) using a Monosorb Surface Area Analyzer (Quanta Chrome Corp. U.S.A.) based on dynamic adsorption/desorption technique.

The surface basicity (i.e. total number of basic sites) and base strength distribution, (i.e. weak, intermediate strength, strong basic sites) on the magnesium oxide samples were determined by the step-wise thermal desorption (STD) of carbon dioxide with evolved gas analysis (22). The STD of carbon dioxide was carried out by desorbing the carbons dioxide chemisorbed at 50°C on the magnesium oxide (250 - 300 mg sample packed in quartz cell) in a flow of helium (20 cm^3 . min^{-1}) by heating it from 50° - 980°C in three successive temperature steps (50° - 250°C, 250° - 500°C, 500° - 980°C). When the maximum temperature of the respective step was attained, it was maintained for a period of 30 min. to desorb the carbon dioxide reversibly adsorbed on the magnesium oxide at that temperature. The amount of carbon dioxide desorbed in each step was determined gravimetrically by absorbing it completely in an aqueous barium hydroxide solution. The chemisorption of carbon dioxide at 50°C and 500°C (i.e. the number of total and strong basic sites, respectively) was determined from the carbon dioxide desorbed when the temperature was increased from 50° to 980°C, and 500° to 980°C respectively. The detailed procedure for measuring the base strength distribution by the STD of carbon dioxide has been described previously (22). The basicity data reported in this chapter are presented after subtraction from the STD data. The carbon dioxide content of the magnesium oxide was determined by measuring quantitatively the carbon dioxide evolved when the magnesium oxide (after its pretreatment at 600°C in the flow of helium for 1 h) was heated from room temperature to 980°C in a flow of helium for 1 h. In this chapter, the chemisorption of carbon dioxide is considered as the amount adsorbed retained by the presaturated magnesium oxide after it was swept with pure helium for a period of 30 min.

2.3 RESULTS AND DISCUSSION

Data on the surface area, surface basicity and distribution of basic sites on the magnesium oxide samples obtained from magnesium carbonate prepared by precipitation using different magnesium salts, precipitating agents and magnesium salt concentrations, at different temperatures and pH, following different modes of mixing the solution of magnesium salt and precipitating agent, ageing the precipitate at different periods and decomposing the resulting magnesium carbonate (at 600°C for 6h under static air) are presented in Tables 1- 7. It may be noted that the magnesium carbonate samples were prepared by varying systematically one variable at a time while keeping all the other precipitation parameters constant. The composition of basic magnesium carbonate samples, obtained at the different precipitation conditions (Tables 1 - 7), was estimated from the knowledge of total weight loss and amount of carbon dioxide evolved in their complete decomposition (at 1000°C).

The surface basicity and base strength distribution (i.e. weak, intermediate strength and strong basic sites) on the magnesium oxide samples have been determined by the STD of carbon dioxide chemisorbed at 50°C from 50° to 980°C in three successive temperature steps (viz. 50°- 250°C, 250°C-500°C and 500°C-980°C). The total basic sites on magnesium oxide samples were measured in terms of the carbon dioxide chemisorbed at 50°C (i.e. the amount of CO_2 desorbed from 50° to 980°C). The weak, intermediate strength and strong basic sites were measured in terms of the carbon dioxide desorbed when the temperature of STD is increased from 50° to 250°C, 250° to 500°C and 500° to 980°C respectively. In the STD, the amount of carbon dioxide evolved above 980°C was found to be insignificant. The carbon dioxide content of magnesium oxide (i.e. the amount of CO_2 retained after decomposition at 600°C) was subtracted from the carbon dioxide desorbed from 500° to 980°C for calculating, the total and strong basic sites. The observed high carbon dioxide content of magnesium oxide is caused by an incomplete decomposition of basic magnesium carbonate or chemisorption of carbon dioxide (formed in the decomposition) on the strong basic sites (i.e. low co-ordinate surface O^{2-}) of the magnesium oxide, or both.

The total and strong basicity data given in Tables 1-7 were obtained by subtracting the carbon dioxide content from the strong basic sites (i.e. CO_2 desorbed from 500° to 980°C) , and hence may be considered as the lower limit of the basicity of the magnesium oxide. The upper limit of the basicity could be obtained by adding the carbon dioxide content to the reported total and strong basicity data; in this case, the base strength distribution will also be changed (i.e. the percentage of strong basic sites will be more). Unfortunately, the exact amount of carbon dioxide chemisorption on the magnesium oxide could not be obtained because of the difficulty in determining the fraction of carbon dioxide content as chemisorbed carbon dioxide or bulk carbonate phase.

It may be noted that the strength of basic sites is expressed in terms of the temperature at which carbon dioxide is chemisorbed on them. The sites involved in the chemisorption of carbon dioxide at higher temperatures are stronger basic sites and vice-versa.

The presence of basic sites on magnesium oxide is attributed to its surface O^{2-} (23). Magnesium oxide has a highly defective surface structure showing steps, kinks, corners, etc. which provide O^{2-} sites of low co-ordination (24). These low coordinated O^{2-} sites (O^{2-} on faces, O^{2-} on edges and O^{2-} on corners) are expected to be responsible for the basic sites of different strengths. The lower the co-ordination number of the O^{2-} site, higher the strength of basic sites.

The results (Tables 1 to 7) indicate that the surface properties of magnesium oxide are influenced markedly by the preparation conditions of basic magnesium carbonate. In our earlier studies (25), we have also observed strong influence of preparation conditions of magnesium hydroxide on the surface properties of magnesium oxide obtained from magnesium hydroxide. The influence of preparation conditions of basic magnesium carbonate on its composition and also on the surface properties of magnesium oxide obtained from it by thermal decomposition at 600°C are briefly described below.

2.3.1 Effect of Magnesium Salt

The results in Table 1 suggest that when different magnesium salts are used in the precipitation of basic magnesium carbonate, both the composition of the basic magnesium carbonate and the surface properties and carbon dioxide of he magnesium oxide obtained from their decomposition are change. This is because of the presence of different anions (NO_3^-, SO_4^{2-}, Cl^- and CH_3COO^-) during the precipitation. Also trace amounts of anions occluded in the structure of magnesium carbonate can affect its thermal decomposition properties (21) and consequently the surface properties of the resulting magnesium oxide.

2.3.2 Effect of Precipitating Agents

A comparison of the results in Table 2 reveals that both the composition of basic magnesium carbonate and the properties of magnesium oxide are drastically changed owing to a change in the precipitating agent. These changes are also caused by the presence of different cations (Na^+, K^+ or NH_4^+) and anions (CO_3^{2-} or HCO_3^-) during the precipitation. The presence of trace amounts of cations, particularly Na^+ and K^+, is expected to affect the basicity /base strength distribution of MgO.

2.3.3 Effect of Concentration of Magnesium Salt

The results in Table 3 show that the composition of basic magnesium carbonate and the surface properties and carbon dioxide content of magnesium oxide are influenced to an appreciable extent by a change in the concentration of magnesium nitrate used in the precipitation of basic magnesium carbonate. This is because of the presence of Mg^{2+} and NO_3^- ions at different concentrations during the precipitation. The influence of concentration is however quite complex.

2.3.4 Effect of Precipitation Temperature

The precipitation temperature also shows a strong influence on the composition of basic magnesium carbonate and the properties of magnesium oxide (Table 4). When the precipitation temperature is increased, the surface area of magnesium oxide passes through a maximum whereas the carbon dioxide content and both the total and strong basicity of magnesium oxide pass through a minimum. The observed influence of precipitation temperature is mostly caused by a change in the rate of nucleation and/or crystal growth during the precipitation because of a change in the temperature.

2.3.5 Effect of pH

The results of Table-5 show a very strong influence of pH of the precipitation on the composition of basic magnesium carbonate and the properties of the magnesium oxide. When the pH is increased, the concentration of magnesium hydroxide relation to magnesium carbonate is increase, the surface area of magnesium oxide and its carbon dioxide content pass through a maximum and the strong basicity passes through a minimum. A very strong influence of pH on the surface area and surface basicity/basicity distribution of magnesium oxide obtained from magnesium hydroxide was also observed earlier (25, 26). The pH is expected to have a strong influence on the rate of nucleation and crystal growth (27).

2.3.6 Effect of Method of Mixing in Precipitation

The method of mixing of magnesium salt solution and sodium carbonate solution in the precipitation of basic magnesium carbonate also has a very significant effect on the composition of basic magnesium carbonate and on the carbon dioxide content, surface area and basicity/base strength distribution of magnesium oxide (Table 6). When the precipitation is carried out by the four different methods of mixing, the nucleation and growth of basic magnesium carbonate crystals occur at different concentrations and pH, producing basic magnesium carbonate of different compositions and consequently magnesium oxide with different carbon dioxide contents and surface properties.

2.3.7 Effect of Ageing

The results in Table 7 show a complex influence of ageing of the precipitated basic magnesium carbonate on the surface properties of magnesium oxide. During the process of ageing, crystal growth and change in crystal morphology of basic magnesium carbonate are expected to occur and these may be responsible for the observed effect.

2.4 CONCLUSIONS

The surface properties (viz. surface area and total basicity/base strength distribution) and carbon dioxide content of magnesium oxide obtained from basic magnesium carbonate depend strongly upon the magnesium salt and precipitating agent used for precipitation of basic magnesium carbonate, the precipitation conditions (i.e. concentration of magnesium salt, pH, temperature, and mode of mixing of the salt solution and the precipitating agent) used and the ageing period of the precipitated basic magnesium carbonate.

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LIST OF PUBLICATIONS

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I) Influence of preparation conditions of basic magnesium carbonate on its thermal analysis
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