ELSEVIER

Thermochimica Acta 367–368 (2001) 285–295

thermochimica acta

www.elsevier.com/locate/tca

Isolation and identification of the intermediate and final products in the thermal decomposition of dolomite in an atmosphere of carbon dioxide

M. Samtani, D. Dollimore[†], F.W. Wilburn, K. Alexander[*]

Department of Chemistry and College of Pharmacy, The University of Toledo, 2801 W Bancroft St.,
Toledo, OH 43606 3390, USA

Received 19 October 1999; accepted 20 July 2000

Abstract

Extensive studies have been done on the behavior of dolomite when subjected to a rising temperature program. In this study a literature survey was prepared related to the thermal decomposition of dolomite and the probable mechanisms proposed by various workers for the above reaction. Dolomite undergoes a two-stage decomposition in one atmosphere of carbon dioxide; while the same decomposition proceeds via a single step at lower partial pressures of carbon dioxide. The intermediate and final products for the two-stage decomposition of dolomite were isolated and identified using thermogravimetry and X-ray powder diffraction. On each of the isolated samples scanning electron microscopy was carried out. The intermediate products were found to be dolomite, calcite and periclase, while the final products were calcium oxide and periclase. Using these results a mechanism of thermal decomposition for dolomite is proposed.

Keywords: Dolomite; Calcite; Periclase; TG–DTG; DTA; X-ray powder diffraction; SEM

1. Introduction

Dolomite finds wide application both industrially and pharmaceutically. Dolomite is used as a calcium and magnesium supplement in the pharmaceutical industry. The $MgCO_3$ part of the dolomitic structure functions as a source of Mg to microorganisms and is therefore used as an additive for fertilizers. For the same reason it is also used as an additive in fodder and food. Industrially dolomite is widely used in the mineral wool, ceramic, insulation, construction, glass, polishing powder, glaze and chemical industries [1]. The process and degree of dolomitization are important in petroleum geology [1]. Dolomite is also of mineralogical significance. Thus, dolomite finds wide application and the thermal decomposition of dolomite has been the subject of study by many authors.

At low partial pressures (below 200 Torr inside and/or around the sample) [2], dolomite decomposes via a single step mechanism represented by

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \quad (1)$$

At higher partial pressures the decomposition occurs via a two-stage mechanism, which is depicted as follows [3]:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \quad (2)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

---

[*] Corresponding author.
E-mail address: kalexan@utnet.utoledo.edu (K. Alexander).
[†] Deceased.

PII: S0040-6031(00)00662-6

Even though most published literature says that the first step is not sensitive to carbon dioxide pressure and the second one is, the work done by Bandi and Krapf [2] proves that both endotherms are sensitive to carbon dioxide pressure but in opposite ways. Thus, as the partial pressure of carbon dioxide is reduced, the two curves that appear in the decomposition of dolomite will approach each other and then fuse into one single step. The effect of partial pressure on the second step is enormous as compared to the first step. For this reason it is often quoted in the literature that the first step in the decomposition of dolomite is not sensitive to carbon dioxide pressure.

Many researchers have attempted to describe the mechanism of the above reaction. There is still some speculation concerning the intermediate products formed after the first stage decomposition of dolomite. The following mechanisms have been proposed for the first stage thermal decomposition:

1. Formation of magnesite–calcite solid solution [4] which is depicted as

$$\mathrm{CaMg(CO_3)_2 \rightarrow CaCO_3 \cdot (1-}n\mathrm{)MgCO_3 + }n\mathrm{MgO + }n\mathrm{CO_2} \tag{4}$$

where n increases from 0 to 1 with time.

2. According to Dollimore et al. [5] "a more correct representation of the decomposition" is the primary dissociation into individual carbonates, followed by immediate decomposition to magnesite

$$\mathrm{CaMg(CO_3)_2 \rightarrow CaCO_3 + MgCO_3} \tag{5}$$

$$\mathrm{MgCO_3 \rightarrow MgO + CO_2} \tag{6}$$

3. Britton et al. [6] proposed that the initial reaction was

$$\mathrm{CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2} \tag{7}$$

followed by rapid recombination of CaO with ambient CO_2 to form $CaCO_3$.

4. It has also been suggested that in the initial step both CaO and MgO are formed. The CaO formed undergoes an exchange reaction with unreacted dolomite and thus the reaction can be represented as [7]

$$\mathrm{CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2} \tag{8}$$

$$\mathrm{CaO + CaMg(CO_3)_2 \rightarrow MgO + 2CO_2 + 2CaO} \tag{9}$$

There is a lot of speculation regarding the mechanism of the decomposition of dolomite. Our study was specially designed to isolate and identify the intermediate and final products of the thermal decomposition of dolomite. Using these results an attempt was made to suggest a probable mechanism of the thermal decomposition of dolomite.

2. Material and methods

2.1. Materials

The material studied was "James White River Dolomite" supplied by FMC Corp/PD, Newark, DE 19711. This sample was ground using a ceramic ball mill equipped with a General Electric AC motor. The sample was ground for a period of 3 h. US standard testing sieves were used for size classification. The following set of US standard sieves was used for size classification, namely the 20, 40, 60, 80 100, 120, 140, 170, 200, 230, 250, 300 and 325-mesh sieves. A Rotap Sieve Shaker was used to hasten the size classification process. The period of operation for this equipment was one and a half hours. The fraction retained on the 200-mesh sieve was used for further study.

2.2. Equipment

The SDT 2960, simultaneous TGA–DTA, TA instrument with Universal Analysis for Windows 95/NT Ver. 2.3 C was used to examine the thermal decomposition of dolomite. An electronic flow meter from J&W Scientific, model ADM 1000 was used to regulate the flow of purge gas through the sample. In order to decompose and isolate sufficient quantities of half-burnt and dead burnt dolomite a tube furnace was used. The temperature control was monitored in this equipment using a CN 9000A series miniature Autotune temperature controller. A flow rate of 100 ml/min of the purge gas (CO_2) was maintained in all the tube furnace experiments. Samples were cooled in an atmosphere of nitrogen and sealed in conical stoppered flasks in an atmosphere of nitrogen.

To identify the components of the original sample, half-burnt and dead burnt dolomite, X-ray diffraction (XRD) experiments were performed on a SCINTAG XDS2000 diffractometer with Cu Kα, $\lambda = 1.5406$ Å and solid state Ge detector cooled by liquid nitrogen. The experimental conditions were as follows: 45 kV, 40 mA, divergent beam slits 2 and 4 mm, receiving slits 1 and 0.2 mm, $2\theta = 5-70°$, continuous scan with scan rate 2°/min and step size of 0.03° for intensity integration. The measurements were taken at room temperature, in air and at the normal pressure. The data was processed using SCINTAG software DMS2000, Ver. 3.43 on Microva3100 with Tektronix 4207 for graphical display. The $k\alpha_2$ data was stripped from the raw intensity, background subtracted and the data smoothed using "fast fourier filtering". The JCPDS Vol. 47 database loaded within the computer was used for the identifications of the components.

Scanning electron micrographs of all the isolated fractions were obtained. The scanning electron microscope (SEM) studies were performed on the JOEL JSM-6100 microscope, wherein the surface of the sample was coated with a thin, electric gold conductive film, the excitation voltage used was 10 kV and the magnification used was 500×. Only for the original dolomite sample the magnification used was 1000× and the excitation voltage was set at 2 kV (Fig. 3).

2.3. Procedure

The original dolomite sample (from the 200-mesh sieve) was first examined using thermogravimetry (TG), XRD and SEM. The following three samples were isolated using the tube furnace and were identified using TG, XRD and SEM.

Sample A: the original dolomite sample was heated in the tube furnace at a temperature of 725°C for 2 h. Sample B: the original dolomite sample was heated in the tube furnace at a temperature of 725°C for 5 h. Sample C: the original dolomite sample was heated in the tube furnace at a temperature of 920°C for 5 h. The samples were heated in the tube furnace in an atmosphere of carbon dioxide and were cooled in an atmosphere of nitrogen. The rationale for choosing the temperatures is discussed in the following section. For the sake of convenience these samples will be referred to as sample A, B and C in the above-mentioned order.

Thermogravimetric analysis, XRDs and SEMs were done on the original and isolated samples. In all these TG experiments the sample was heated at the rate of 10°C/min and the flow rate for the purge gas (CO_2) used was 50 ml/min.

An additional run in nitrogen atmosphere was performed on sample C. Only for this sample run was the heating chamber purged with nitrogen (200 ml/min) for 1 h before the run to remove all traces of CO_2 and moisture from the heating chamber. To ensure a complete nitrogen atmosphere the flow during the experiment was also maintained at the higher value of 200 ml/min.

3. Results and discussion

3.1. Original dolomite sample

The TG plot (% weight vs. temperature) for the thermal decomposition of dolomite, in an atmosphere of carbon dioxide, showed a two-stage process (Fig. 1). This is in agreement with the literature [2]. The onset temperature of the first step was found to be 725°C. Thus, in order to obtain half-burnt dolomite the temperature of the tube furnace was set at 725°C (sample A and B). Similarly the second step of the decomposition started at 920°C, so the temperature used for isolating dead burnt dolomite in the tube furnace was set at 920°C (sample C).

To confirm the purity of the sample an XRD study was done on the sample, which indicated that the sample was indeed pure dolomite (Fig. 2). The first step in the thermal decomposition shows an initial slow reaction, which then proceeds at a faster rate at higher temperatures. The SEMs done on the sample indicated the reason for this. The magnification used was 1000× (Fig. 3), which showed that the sample has fine fluffy dolomite particles sticking to the dolomite crystals. This fluffy matter decomposes earlier as compared to the crystals and this causes an initial slow reaction followed by the increase in the reaction rate when the crystals begin to decompose.

3.2. Sample A

The TG curve (Fig. 1) shows a two-stage decomposition in an atmosphere of carbon dioxide and the two stages occur at the same temperature as observed in the original sample. This indicates that sample A still contains traces of the original dolomite sample.

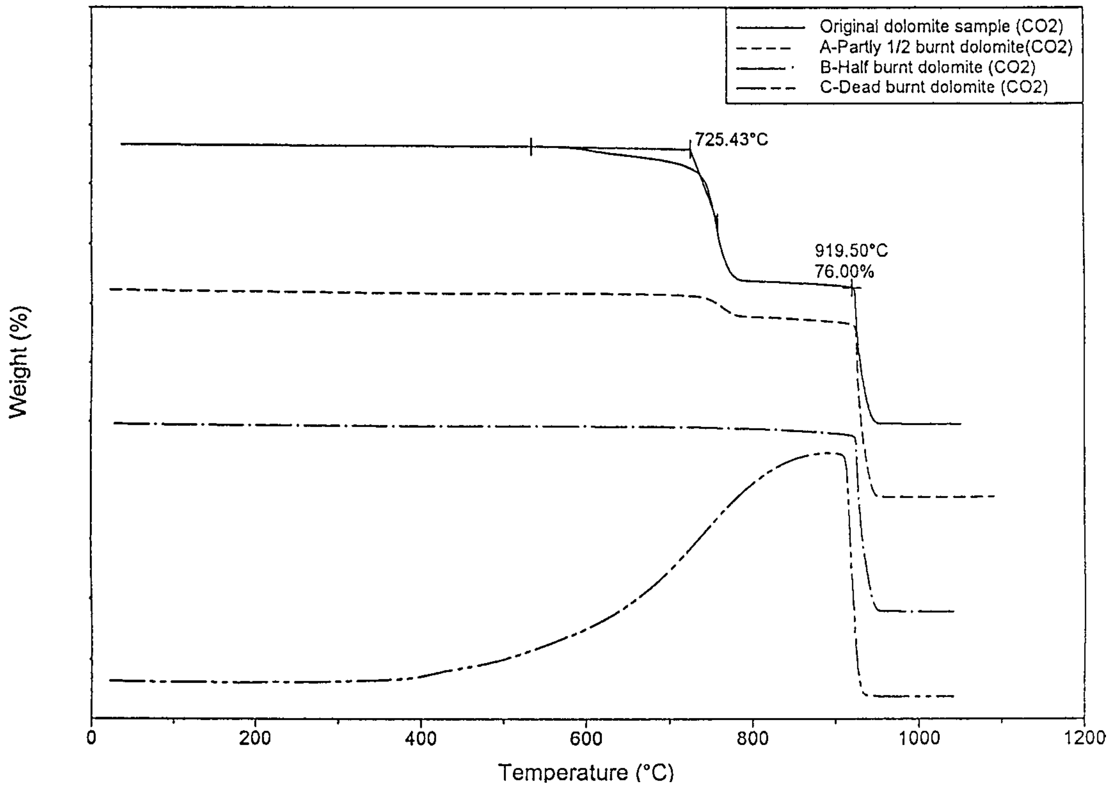

Fig. 1. TG plot for thermal decomposition of the original dolomite sample, sample A, sample B and sample C at a heating rate of 10°C/min. The purge gas used in all these runs was carbon dioxide and is indicated in brackets. Flow rate used was 50 ml/min. The plot indicates the onset temperature of the first and second step in the thermal decomposition of the original dolomite sample. To estimate the percent loss for the Y-axis 1 cm = 9.905% loss.

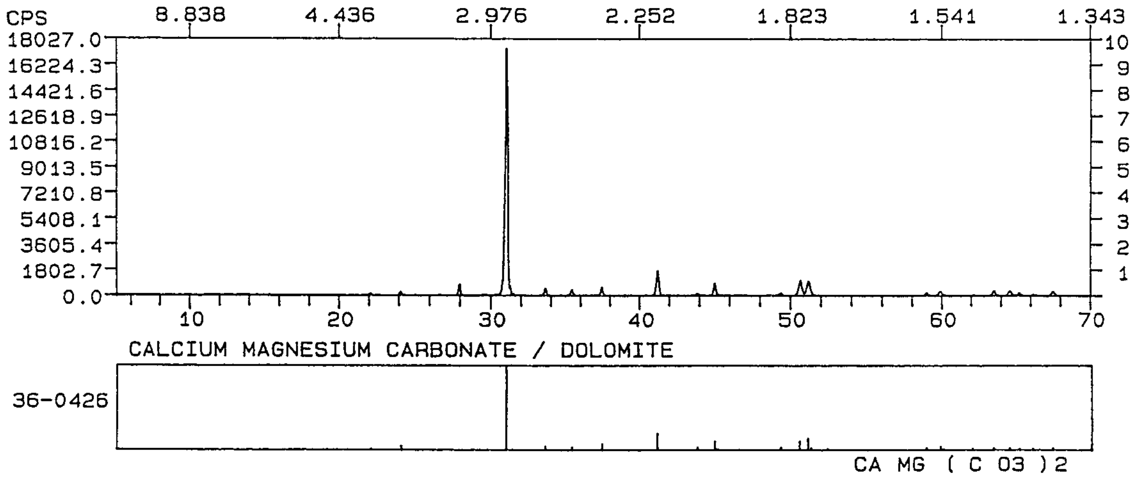

Fig. 2. X-ray diffraction pattern for the original dolomite sample. The purity of the original sample was confirmed using the JCPDS (Vol. 43) database, which indicates presence of single component, i.e. dolomite.

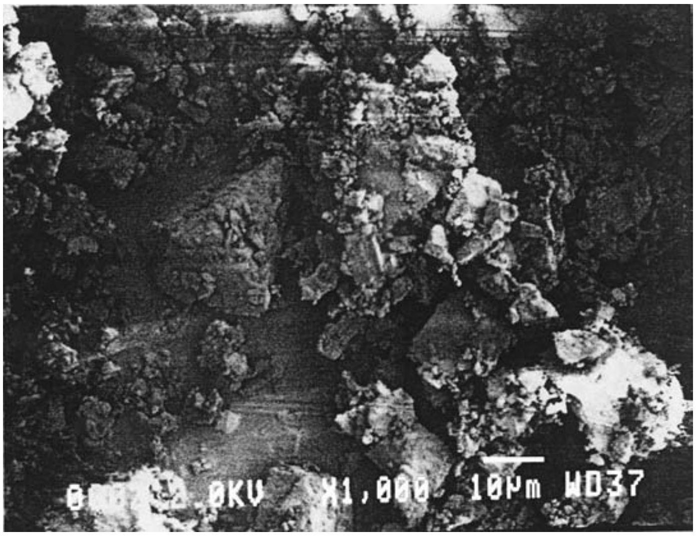

Fig. 3. SEM of the original sample using a magnification of 1000× and excitation voltage of 2 kV.

The XRD (Fig. 4) pattern is more useful in confirming the identity of this sample. The database search results clearly indicate the presence of magnesium oxide, calcium carbonate and dolomite. This composition would also explain the TG behavior of the sample. The initial decomposition stage is due to the $Mg(CO)_3$ from the dolomite. Since this sample has been heat-treated it has partially decomposed to half-burnt dolomite ($MgO{\cdot}CaCO_3$). The calcium carbonate from both, the half-burnt dolomite and the unreacted original sample produce the second stage decomposition on the TG plot.

The SEM (Fig. 5) was done at 500× magnification. The important thing noted was that although the original sample was nearly of uniform particle size, sample A showed the presence of fines. This is probably due to the evolution of CO_2 from the sample, which causes the intact grains of dolomite to break apart, thus producing the fine particles.

3.3. Sample B

The TG curve (Fig. 1) in an atmosphere of carbon dioxide shows a single stage decomposition, indicating that the sample has been fully converted to half-burnt dolomite. The single stage decomposition is that of calcite and this is confirmed by the XRD (Fig. 6). The other component of half-burnt dolomite MgO, does not have any effect on the TG curve, but is detected in the XRD pattern. Again the SEM (Fig. 7) shows the presence of fines indicating that the larger particles break down when CO_2 is evolved. The results obtained for sample A and sample B give some idea as to what the mechanism of the reaction could be for the first stage decomposition of dolomite. The half-burnt dolomite shows the presence of calcium only in the form of calcite. The presence of Ca only as calcite after the first stage decomposition of dolomite has been observed by Wilsdorf and Haul [8] and is confirmed in our present study.

3.4. Sample C

Two thermogravimetric runs were performed on this sample. The TG run in CO_2 atmosphere (Fig. 1) shows a rise in sample weight due to the conversion of calcium oxide to calcium carbonate. Due to the apparent weight gain the presence of other components in the sample was obscured and therefore the run in nitrogen was necessitated. Before performing the run in nitrogen atmosphere the sample was purged in nitrogen in the heating chamber for 1 h, to remove all traces of CO_2 and moisture from the heating chamber. To maintain a complete nitrogen atmosphere the flow rate was set at a higher value of 200 ml/min. The TG

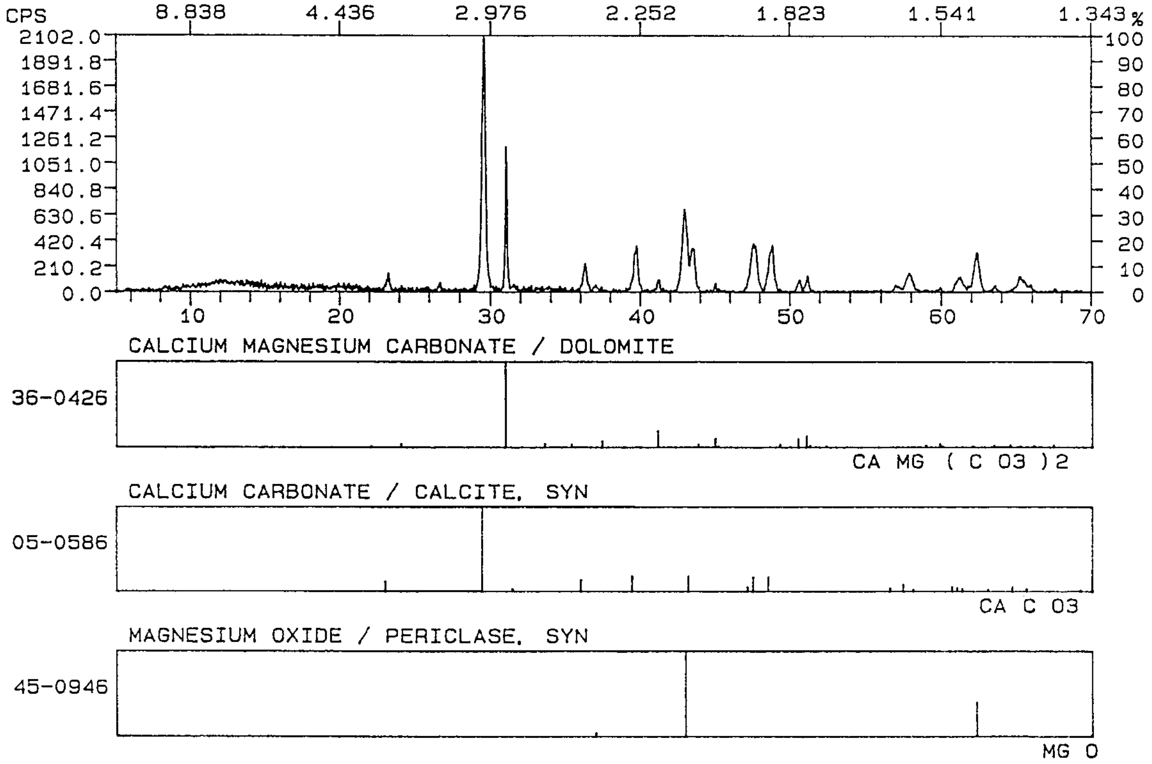

Fig. 4. X-ray diffraction pattern for sample A. The JCPDS database search match result indicates presence of magnesium oxide, calcium carbonate and dolomite.

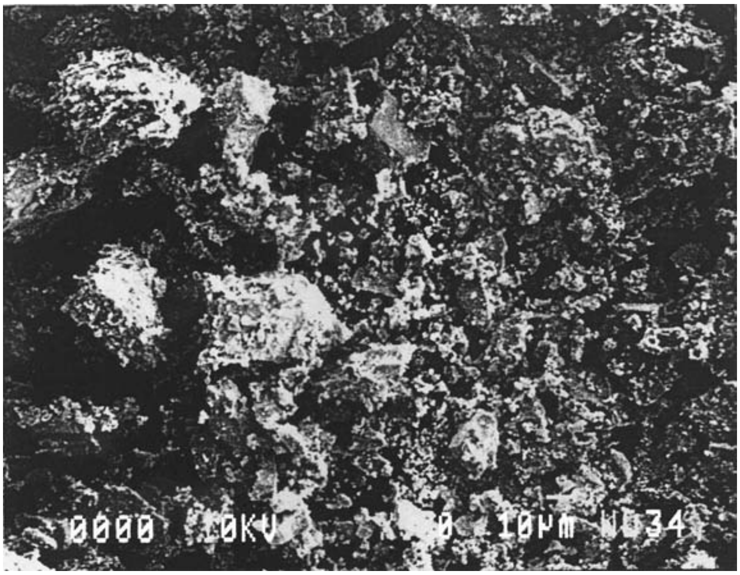

Fig. 5. SEM of sample A using a magnification of 500× and excitation voltage of 10 kV.

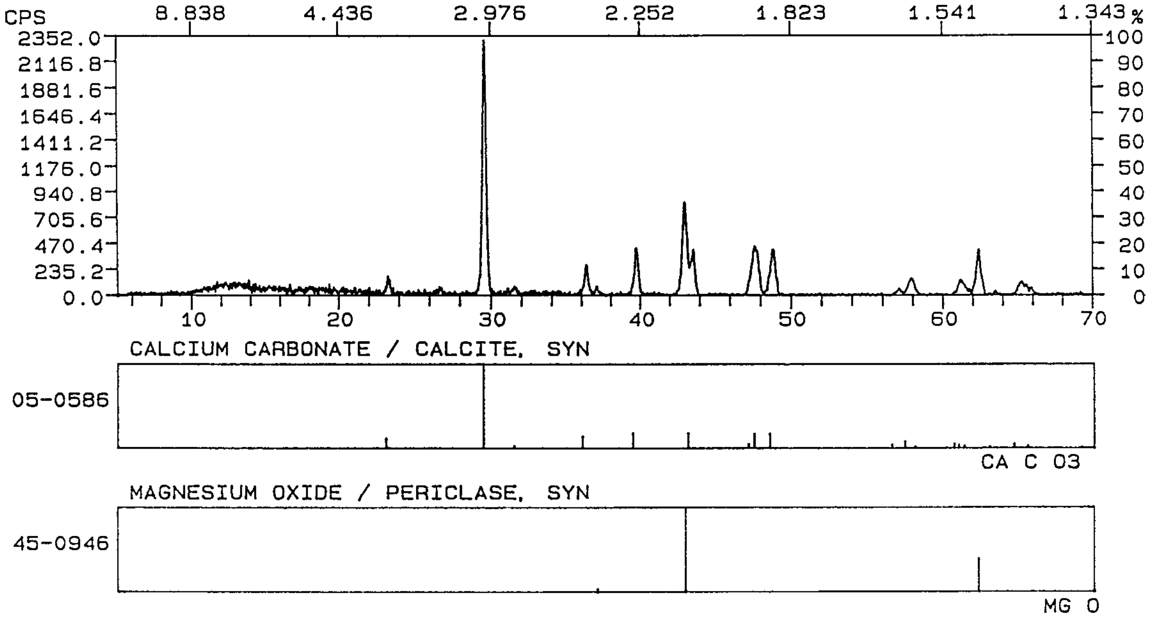

Fig. 6. X-ray diffraction pattern for sample B. The JCPDS database search match result indicates the presence of both calcium carbonate and magnesium oxide.

curve for this sample shows two stages of weight loss (Fig. 8).

The XRD pattern (Fig. 9) clearly indicates that this sample contains both calcium oxide and magnesium oxide. The whole sample turns moist, even though it was stored in a nitrogen atmosphere. Calcium oxide is very sensitive to moisture and is a very reactive species. It probably undergoes carbonation and hydroxylation

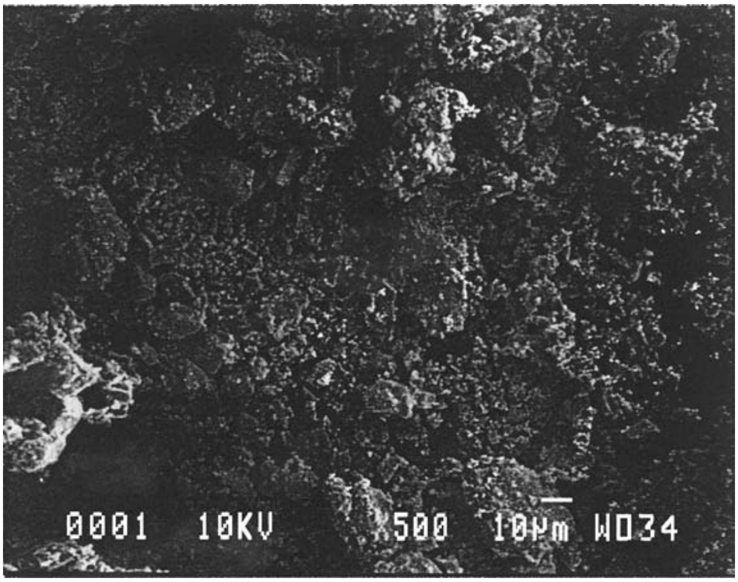

Fig. 7. SEM of sample B using a magnification of 500× and excitation voltage of 10 kV.

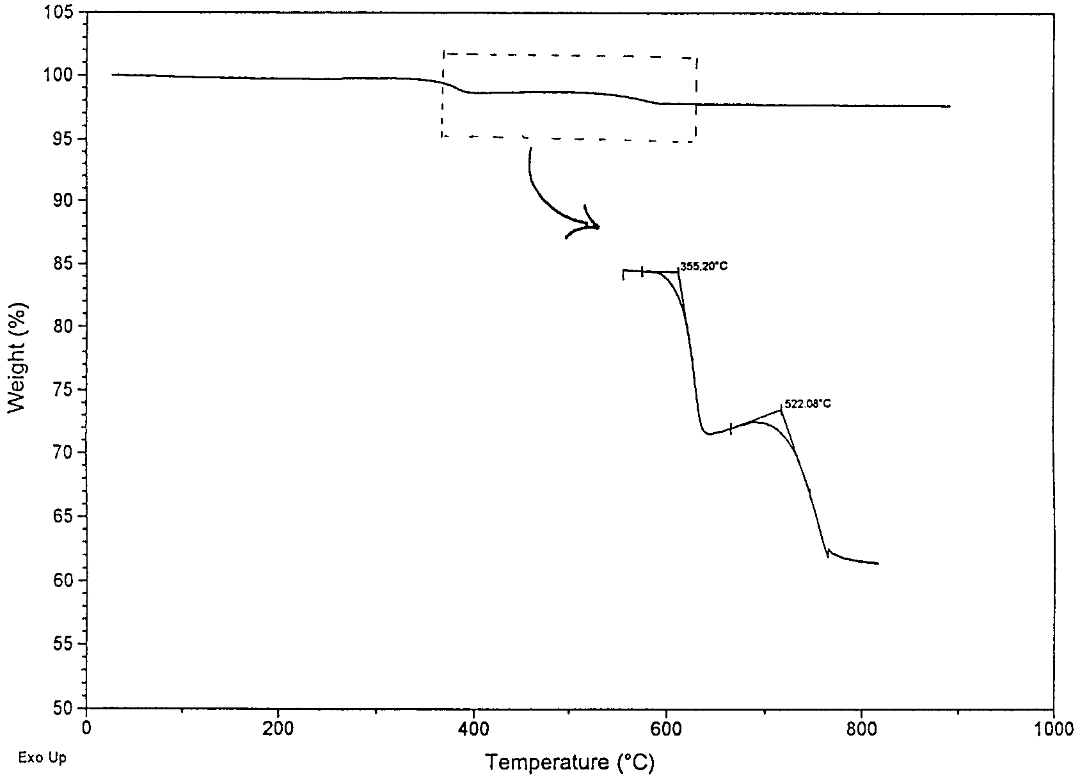

Fig. 8. TG plot for sample C in an atmosphere of nitrogen (flow rate 200 ml/min) at a heating rate of 10°C/min. The region enclosed in the dotted box has been magnified to indicate presence of two impurities formed in the sample during storage.

upon combining with carbon dioxide and moisture respectively from air. These reactions produce calcium hydroxide and calcium carbonate and this is the reason that the sample shows two minor weight loss processes when heated in an atmosphere of nitrogen. The first weight loss occurs at 355°C, which is in the right region for the decomposition of calcium hydroxide [9]. The second weight loss occurs at 522°C and is supposedly due to calcium carbonate. The temperature at which this decomposition is observed seems to be low for calcium carbonate. The reasons for this can be attributed to either of the following:

1. The decomposition of calcium carbonate in an atmosphere of nitrogen depends on sample size [10]. The smaller the sample size the lower the temperature of decomposition. This sample has only traces of calcium carbonate and this could be one of the reasons for the lowering of the decomposition temperature.
2. The other reason could be that calcium carbonate is formed from the calcium oxide portion of the dead burnt dolomite. The temperature of decomposition could be lowered because of the way in which the calcium carbonate is formed. The study done by the above workers [10] was done on AR calcium carbonate, which has pure calcium carbonate and hence can have a different decomposition temperature as compared to the calcium carbonate formed from the calcium oxide portion of dead burnt dolomite.

It is not to be expected that the peaks are due to magnesium hydroxide or magnesium carbonate because magnesium oxide is not as reactive as calcium oxide. Hence, it would not readily combine with atmospheric moisture or CO_2 to form magnesium hydroxide or magnesium carbonate.

The XRD pattern clearly indicates the presence of both calcium oxide and magnesium oxide confirming

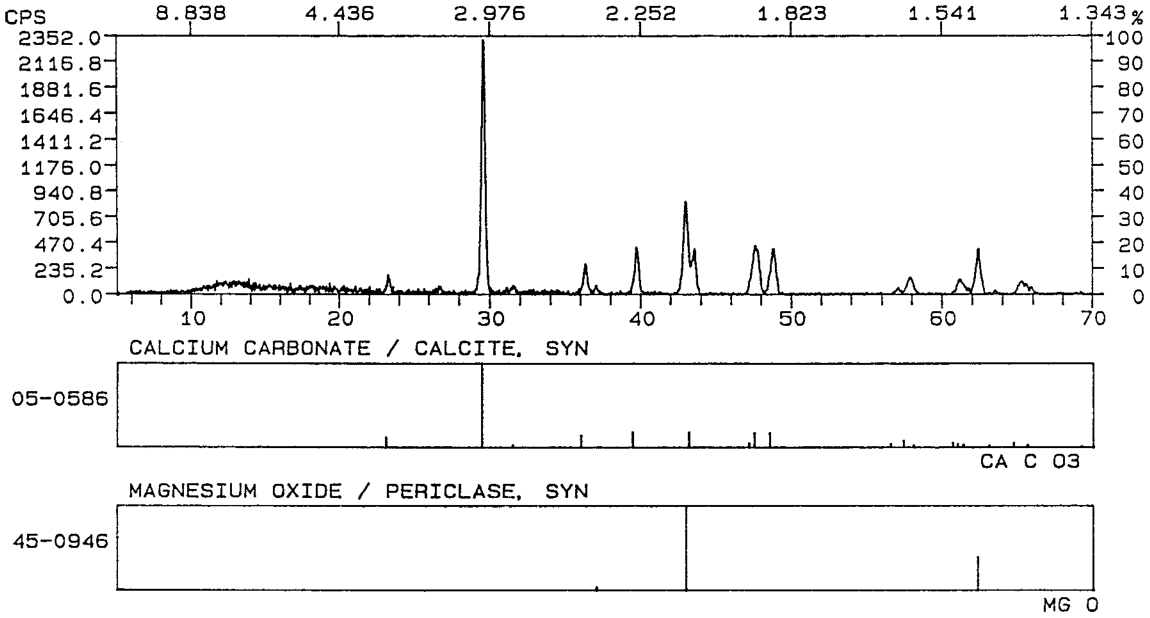

Fig. 9. X-ray diffraction pattern for sample C. The JCPDS database search match result indicates presence of both calcium oxide and magnesium oxide.

that the complete decomposition of dolomite to dead burnt dolomite did take place, but it does not indicate the presence of either calcium carbonate or calcium hydroxide. Compared to XRD, TG is a more sensitive technique and is able to detect these minor impurities.

The SEM (Fig. 10) shows a maximum amount of fines compared to all the other samples. This is expected because this sample has undergone complete decomposition resulting in the break down of larger grains to small fines.

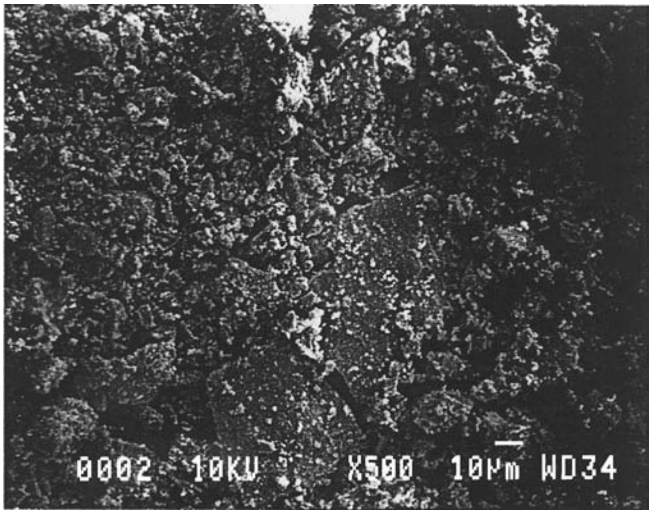

Fig. 10. SEM of the sample C using a magnification of 500× and excitation voltage of 10 kV.

3.5. Mechanism for the first stage decomposition

Hashimoto et al. [11] in their work concluded that Mechanism 1, as previously described in this research, which involves the formation of the magnesite–calcite solid solution, was the actual mechanism of thermal decomposition of dolomite. In this study we have not found anything that can support or reject this mechanism. However, Mc Intosh et al. [3] in their work wrote that although this mechanism seems very "attractive" and can possibly explain nearly all features of the thermal decomposition of dolomite, it falls short in one respect. According to them this mechanism cannot explain the dependence of the thermal decomposition of dolomite on the partial pressure of CO_2, which is so characteristic of dolomite.

Mechanisms 3 and 4, as previously described in this paper, suggest the decomposition of dolomite to calcium oxide in the first step itself. This does not seem to be the case, because in neither sample A nor B was calcium oxide detected. If dolomite were to decompose to individual oxides the weight loss associated with this mechanism would mathematically be 48% [3]. It is evident from Fig. 1 that after the first stage decomposition the weight loss is only around 25%. It was also noted in the next sample that if the sample contains calcium oxide and if a TG experiment is performed on such a sample in an atmosphere of carbon dioxide, it should show a gain in weight because of the conversation of the calcium oxide to calcium carbonate. After the first stage decomposition, the original dolomite sample shows no weight gain. This indicates that after the first stage of thermal decomposition the calcium exists completely as calcium carbonate and the magnesium exists completely as magnesium oxide. The presence of calcium oxide at this stage seems unlikely.

After considering all the above possibilities, Mechanism 4 seems to be the mechanism that could be responsible for the typical thermal behavior of dolomite. Mc Intosh et al. [3] also concluded that this is the possible mechanism for the thermal decomposition of dolomite. The only probable reason why magnesium carbonate was not detected in both sample B and C is that when dolomite breaks down into individual carbonates the magnesium carbonate is in a highly unstable state. It decomposes immediately and this is what makes isolation of magnesium carbonate in half-burnt dolomite so difficult.

3.6. Mechanism for the second stage decomposition

The run for dead burnt dolomite in CO_2 shows that the calcium oxide can be re-carbonated to form calcium carbonate. Thus, the second stage decomposition of the reaction is a reversible process and can be depicted as follows:

$$CaCO_3 \rightleftarrows CaO + CO_2 \tag{10}$$

The extent of this reversibility depends on the temperature.

4. Conclusion

1. The first stage decomposition occurs by a formation of individual carbonates, with the magnesium carbonate being in an unstable state which decomposes immediately. This is the reason it was not detected in half-burnt dolomite (sample B). The reaction mechanism can then be depicted as follows:

   $$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgCO_3 \tag{11}$$

   $$MgCO_3 \rightarrow MgO + CO_2 \tag{12}$$

   Since magnesium carbonate is difficult to isolate the net reaction can be written as

   $$nCaMg(CO_3)_2 \rightarrow (1-n)CaCO_3 + (1-n)MgO + (1-n)CO_2 \tag{13}$$

   where n goes from 1 to 0 with time. This has been depicted in the above manner because sample A showed the presence of both dolomite and half-burnt dolomite.
2. The second stage decomposition of dolomite involves the dissociation of calcite and this is a reversible process which can be depicted as

   $$CaCO_3 \rightleftarrows CaO + CO_2 \tag{14}$$
3. The calcium oxide portion of the dead burnt dolomite is a highly reactive species. It forms calcium hydroxide, which shows a 1% weight loss on the TG curve in an atmosphere of nitrogen. This experiment also indicated the presence of

another impurity, which produced a second weight loss. The exact identity of this impurity could not be determined with certainty and it was speculated that it was calcium carbonate. Both these impurities did not appear on the XRD pattern because they are present in very small quantities. The TG being a more sensitive equipment could detect these impurities.

References

[1] K.V. Nair, Masters Thesis, University of Toledo, OH, August 1994, p.1.

[2] W.R. Bandi, G. Krapf, Thermochim. Acta 14 (1976) 221.

[3] R.M. Mc Intosh, J.H. Sharp, F.W. Wilburn, Thermochim. Acta 165 (1990) 281.

[4] D. Beruto, A.W. Searcy, J. Chem. Soc., Faraday Trans. I 70 (1974) 2145.

[5] D. Dollimore, J.G. Dunn, Y.F. Lee, B.M. Penrod, Thermochim. Acta 237 (1994) 125.

[6] H.T.S. Britton, S.J. Gregg, G.W. Winsor, Trans. Faraday Soc. 48 (1952) 63.

[7] J.A. Hedvall, Geol. Foeren. Toerh. Stockholm 47 (1925) 73.

[8] H.G.F. Wilsdorf, R.A.W. Haul, Nature 167 (1951) 945.

[9] D. Chen, Ph.D. Thesis, University of Toledo, OH, 1994, p. 196.

[10] R.M. Mc Intosh, J.H. Sharp, F.W. Wilburn, D.M. Tinsley, Therm. Anal. 37 (1991) 2003.

[11] H. Hashimoto, E. Komaki, F. Hayashi, U. Ueatsu, Solid State Chem. 33 (1980) 181.