

The thermal decomposition of magnesite in nitrogen

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Abstract

Numerical predictor–corrector analysis of non-isothermal TG curves with heating rates of 3, 10 and 30 °C min⁻¹ were made for different models for the decomposition of magnesite in nitrogen. A contracting volume (R3) model was found to give the best fit, and the values of the kinetic parameters were refined by non-linear least-squares methods using a minicomputer. Respective values of the activation energy of 170, 174 and 174 kJ mol⁻¹, and of the pre-exponential constant of 4.2×10^{11} , 6.7×10^{11} and 7.8×10^{11} min⁻¹, were found for heating rates of 3, 10 and 30 °C min⁻¹. The R3 model was also found to fit best the isothermal measurements of the decomposition of two particle sizes of magnesite in nitrogen over the temperature range 500–650 °C. The reaction rates were fitted to the Arrhenius equation, and gave values of 161 kJ mol⁻¹ for the activation energy and 2.9×10^8 min⁻¹ for the pre-exponential constant. The good agreement between the results from the two experimental methods confirms that sensible values of the activation energies can be obtained from non-isothermal TG measurements.

INTRODUCTION

The factors affecting the wide spread of values of the kinetic parameters derived from non-isothermal TG curves are well known [1] and arise from experimental conditions and methods of mathematical analysis. Sensible parameters can be obtained by careful experimental technique and the use of numerical predictor–corrector methods [2], which are being increasingly applied to the analysis of TG curves [3–6]. This paper demonstrates that values of the activation energy determined by non-isothermal analyses are similar to those derived from isothermal experiments.

Magnesite was chosen for study as a simple model for the decomposition of carbonates in the retorting and combustion stages of oil shale processing. The kinetics of the thermal decomposition of magnesite have been studied over the temperature range 540–600 °C in vacuo [7], and have been shown to follow the F contracting core model.

EXPERIMENTAL

Powdered material was used from a mineralogical specimen of magnesite obtained from Bulong, Western Australia. A Stanton–Redcroft TG761

thermobalance was used for both the isothermal-style and the non-isothermal measurements. For isothermal work, the sample was rapidly heated at $70^{\circ}\text{C min}^{-1}$ then held at the experimental temperature until the reaction was completed, while recording the mass and temperature as a function of time. For convenience, at some of the slower reaction rates, the final mass loss was determined by heating the sample to higher temperatures. Although this method is not strictly isothermal, only the data taken at the equilibrium temperature were used for kinetic analysis. Non-isothermal measurements were made at nominal heating rates of 3, 10 and $30^{\circ}\text{C min}^{-1}$. The data were collected and processed using an IBM-XT minicomputer with a Metrobyte Dash-8 interface card and software written in this laboratory.

The experiments used 2 mg of < 75 or $250\text{--}425\ \mu\text{m}$ sized material which was thinly spread over the base of the platinum pan. A flow rate of $20\ \text{cm}^3\ \text{min}^{-1}$ of dry nitrogen was normally used. The effect of altering flow rate was also investigated, but no changes were observed, indicating that the evolved carbon dioxide was rapidly removed by the nitrogen flow.

RESULTS

Non-isothermal kinetics

The experimental TG curves were transformed to fractional mass loss α and compared with numeric predictor–corrector solutions of the differential equation generated for values of the pre-exponential constant A , the heating rate H and the activation energy E :

$$\frac{d\alpha}{dT} = \frac{A}{H} g(\alpha) \exp(-E/RT)$$

For the R3 contracting core model

$$g(\alpha) = 3(1 - \alpha)^{2/3}$$

Comparison of the calculated and transformed experimental curves was made graphically on a VDU. Since a range of values of A and E gave reasonable agreement for the TG curves, a comparison of the DTG curves narrowed the range of parameters. The final values of A and E are given in Table 1 and were determined by a non-linear least-squares method adapted from the book Numerical Recipes [8]. The time taken on a 4.77 MHz

TABLE 1

Variation of kinetic parameters for magnesite decomposition with heating rate for the R3 model

Pre-exponential constant A (min^{-1})	Activation energy E (kJ mol^{-1})	Heating rate H ($^{\circ}\text{C min}^{-1}$)
4.2×10^{11}	170	3
6.7×10^{11}	174	10
7.8×10^{11}	174	30

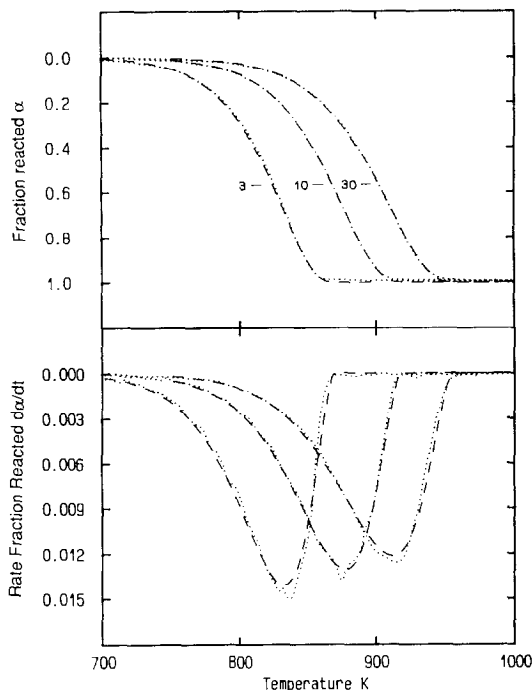


Fig. 1. Observed (dotted line) and calculated (broken line) TG and DTG curves for the decomposition of $< 75 \mu\text{m}$ magnesite in nitrogen.

IBM-XT with an 8087 co-processor to refine the values of A and E for a fit of 80 points was of the order of 5 min. Figure 1 shows the excellent agreement between calculated (broken lines) and transformed (dotted lines) experimental TG and DTG curves for the three heating rates.

Isothermal kinetics

The isothermal mass values were transformed to give the fraction of reacted magnesite, α , using the initial and final mass losses. Rate constants were calculated for various types of reaction mechanism using expressions tabulated in ref. 1. Several models gave straight-line fits over a limited range of α , but only the R3 contracting core model covered the full range of α values over the experimental temperature range, and the results for this model are shown in Fig. 2.

$$ktr^{-3} = 1 - (1 - \alpha)^{1/3}$$

The rate constants for this model are shown in Table 2. The rate constants were fitted to the Arrhenius equation

$$k = A \exp(-E/RT)$$

The Arrhenius plots for the two sizes of magnesite particle are shown in Fig.

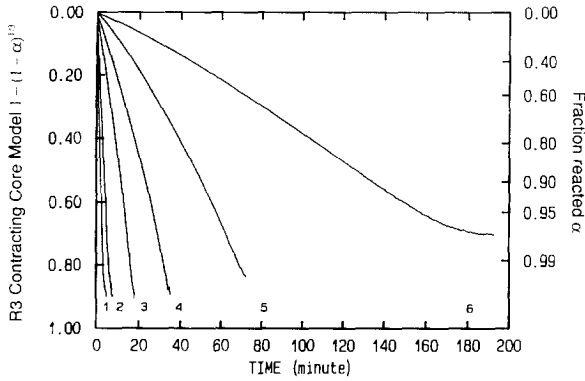


Fig. 2. R3 model for isothermal decomposition of $< 75 \mu\text{m}$ magnesite in nitrogen at 653°C (curve 1), 622°C (curve 2), 592°C (curve 3), 561°C (curve 4), 531°C (curve 5) and 503°C (curve 6).

TABLE 2

Isothermal rate constants for magnesite decomposition for the R3 model

Size (μm)	Temp ($^\circ\text{C}$)	k (s^{-1})	α range
< 75	503	7.0×10^{-5}	0.15–0.94
< 75	531	1.9×10^{-4}	0.15–0.94
< 75	561	4.0×10^{-4}	0.15–0.94
< 75	592	7.7×10^{-4}	0.15–0.94
< 75	622	2.2×10^{-3}	0.25–0.94
< 75	653	3.9×10^{-3}	0.50–0.94
250–425	505	1.1×10^{-4}	0.15–0.72
250–425	536	3.1×10^{-4}	0.15–0.88
250–425	566	6.4×10^{-4}	0.15–0.88
250–425	596	1.7×10^{-3}	0.28–0.94
250–425	626	3.8×10^{-3}	0.50–0.94
250–425	657	8.6×10^{-3}	0.78–0.94

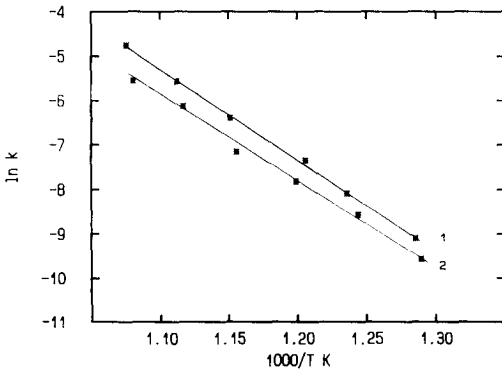


Fig. 3. Arrhenius plots for the isothermal decomposition of $250\text{--}425 \mu\text{m}$ magnesite (curve 1) and $< 75 \mu\text{m}$ magnesite (curve 2) in nitrogen.

TABLE 3

Effect of particle size on isothermal kinetic parameters for magnesite decomposition for the R3 model

Size (μm)	A (min^{-1})	E (kJ mol^{-1})
< 75	2.9×10^8	161
250–425	1.3×10^9	168

3, and the values of the pre-exponential constants, A , and activation energies, E , obtained are shown in Table 3.

DISCUSSION

The R3 contracting core model gives satisfactory fits for the non-isothermal TG and DTG curves, and the range of the values of A and E given in Table 1 does not alter greatly over the heating rates of 4, 10 and $30^\circ\text{C min}^{-1}$. The respective values for the decomposition of the $< 75 \mu\text{m}$ magnesite are about $7.0 \times 10^{11} \text{ min}^{-1}$ and 172 kJ mol^{-1} . The same model fits the isothermal results over the smaller temperature range $500\text{--}650^\circ\text{C}$ and gives values of 3.0×10^8 for A and 161 kJ mol^{-1} for E for the $< 75 \mu\text{m}$ magnesite. The expression for the R3 model shows an r^3 dependence for A , but the value 4 for the ratio of the pre-exponential values for the two sizes of magnesite particle is less than the value of 64 calculated for the two sizes.

The values of the activation energy for the decomposition of magnesite in nitrogen, 161 and 174 kJ mol^{-1} , obtained from the isothermal and non-isothermal measurements are in good agreement. They may be compared with the figure of 149 kJ mol^{-1} obtained previously [7] for the isothermal decomposition of 0.5 g of magnesite (size 1.7–2.0 mm) in vacuo with rates measured for an α value of 0.3. Close agreement has been reported for a few decompositions [9–11], but the agreement for reversible reactions has not been so satisfactory [12]. However, the pre-exponential factor obtained from the non-isothermal measurements is some three orders of magnitude greater than that from the isothermal model, which may be due to the experimental temperature range of 250°C compared with 150°C for the isothermal method.

It is apparent that the process controlling the decomposition of magnesite can be fitted using a simple model, which covers almost the complete range of α . This model might seem to be an oversimplification, since some form of reversible reaction might be expected between the escaping carbon dioxide and the outer core of magnesium oxide. Such a mechanism has been suggested for the related decomposition of calcium carbonate, and it has been reported that decomposition of recarbonated material occurs at a faster rate [7]. The good fit over the complete range of α suggests that the predominant rate process at the reaction interface, and that rapid release of

carbon dioxide through the magnesium oxide layer occurs for small particle sizes.

CONCLUSIONS

This work has demonstrated that, provided small sample sizes are used to allow rapid removal of gaseous products, suitable mathematical analysis of non-isothermal measurements can lead to activation energies which are in good agreement with the more usually accepted isothermal values. It has also shown that rapid calculation of kinetic parameters is now feasible with minicomputers using suitable software. The time factor for the evaluation of least-squares parameters is no longer prohibitive and makes identification of a likely reaction mechanism possible from analysis of a single TG measurement.

The values for the activation energies, 161 and 174 kJ mol⁻¹, obtained by isothermal and non-isothermal techniques for the R3 contracting core model for the decomposition of magnesite in nitrogen are only slightly higher than the previous value of 149 kJ mol⁻¹ [7].

Despite the apparent success of the R3 model over the full range of α , more evidence is required to confirm the model. Future isothermal and non-isothermal work on the decomposition of magnesite in carbon dioxide/nitrogen atmospheres may elucidate the problem.

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