Thermochimica Acta, 170 (1990) 7–11
Elsevier Science Publishers B.V., Amsterdam

EFFECTS OF IMPURITIES IN THE KINETICS OF CALCITE DECOMPOSITION

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(Received 5 February 1990)

ABSTRACT

The effects of impurities on the observed kinetic parameters of calcium carbonate decomposition were studied. The kinetic parameters observed were found to be strongly affected by small amounts of impurities; however, the kinetic model is not affected. Therefore the activation energy for calcite containing at least 98.2% of calcium carbonate is 110.5 kJ mol^{-1} and for calcite with 99.5% of calcium carbonate it is 193.8 kJ mol^{-1}. The kinetic model in both cases is a superficial reaction in cylindrical geometry.

INTRODUCTION

The kinetics of calcium carbonate decomposition has been widely studied in the literature because calcium oxide is being used more and more to avoid the emissions of sulphur and nitrogen compounds.

Several contributions [1–4] suggest that the value of the activation energy is near 209 kJ mol^{-1}. However, lower values of the activation energy were sometimes found, and they explain the wide dispersion of the available data in relation to the influence of physical processes, namely inter- and intraparticle diffusion, heat transfer resistance, sintering etc.

In previous work [5] we studied the influence of macrokinetic parameters on the value of the activation energy of calcite over the wide range of experimental conditions used in the TGA studies. The conclusion was that the influence of macrokinetic parameters is low within this range. The E value for calcite was around 109 kJ mol^{-1}, much lower than the value previously proposed [1–4].

The aim of this work is to show that differences in measured activation energies are due to the influence of impurities instead of physical processes when the TGA analysis is carried out. We show this by comparing the results obtained in the previous work with those for calcite of high purity.

The kinetic analysis was carried out by using the method of Romero et al. [6].

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EXPERIMENTAL

Calcite containing 99.5% of calcium carbonate was used.

The decomposition behaviour of solid samples of mass 10 ± 0.15 mg, randomly distributed in the sample pan, was observed using a Dupont model 951 thermogravimetric analyser. Nitrogen with a flow rate of 2 cm^3 s^{-1} was used as a purge gas. Decomposition experiments were carried out at five different heating rates: 0.5, 1, 2, 5 and 10 K min^{-1}.

Other experimental details have been described previously [7].

RESULTS AND DISCUSSION

Experimental α–T data from calcite (99.5% calcium carbonate) decomposition are shown in Fig. 1. With an analysis at constant temperature [6], α–t data were obtained from α–T curves for each temperature. The α–t points must satisfy the following equation:

$$g(\alpha) = K_n t \tag{1}$$

where

$$K_n = \frac{\int_{T_0}^{T} A \exp(-E/RT)\,\mathrm{d}T}{(T - T_0)} \tag{2}$$

Figure 2 shows eqn. (1) applied to high purity calcite decomposition. The $g(\alpha)$ used corresponds to a cylindrical phase boundary reaction. Other models used, listed in previous papers, do not fit the data with accuracy.

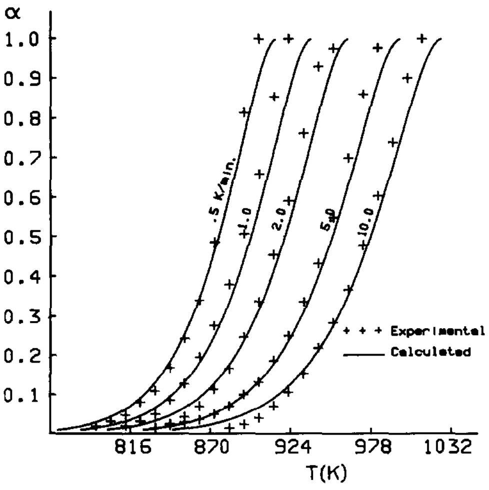

Fig. 1. Experimental and calculated α–T data.

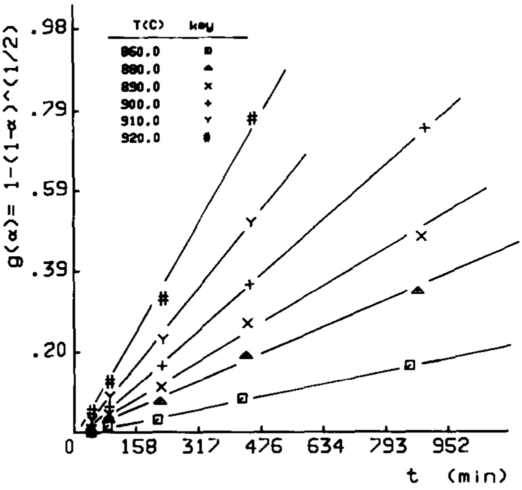

Fig. 2. Analysis at constant temperature.

Table 1 shows the kinetic parameters obtained from analysis at constant temperature for all used models. The best correlation coefficient is that for the model used in Fig. 1. This allows us to conclude that the kinetic model which describes the decomposition of calcite is that with $g(\alpha) = 1 - (1 - \alpha)^{1/2}$.

From an analysis at constant conversion [6], the temperature values for a preset conversion and different heating rates were used to obtain the temperature influence, i.e. to obtain the kinetic parameters. The relationship between temperature, heating rate and kinetic parameters at a preset conversion is given by

$$\frac{\beta}{RT^2} = \frac{A/E}{g(\alpha)}\exp(-E/RT) \tag{3}$$

Using a linear expression of eqn. (3) it is possible to obtain the kinetic parameters. Figure 3 shows the experimental data fitted by the logarithmic

TABLE 1

Kinetic parameters from analysis at constant temperature

Model	E (kJ mol^{-1})	A (min^{-1})	r
F1	304.6	2.8×10^{16}	0.9954
F2	165.4	8.2×10^{7}	0.9834
F3	108.1	2.0×10^{4}	0.9586
R1	176.9	2.6×10^{8}	0.9973
R2	197.3	1.9×10^{9}	0.9997
R3	231.4	3.7×10^{11}	0.9985
D1	321.1	9.3×10^{16}	0.9951
D2	377.1	1.5×10^{20}	0.9956
D3	404.3	1.7×10^{21}	0.9959

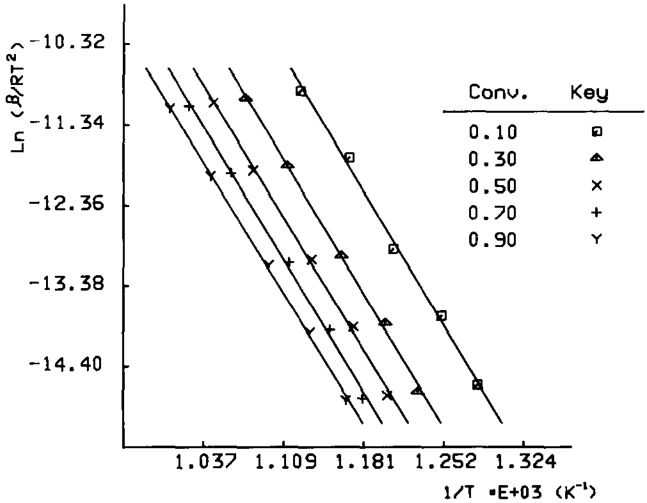

Fig. 3. Analysis at constant conversion.

form of eqn. (3). Parallel straight lines are obtained for the entire conversion range.

Table 2 shows the E and A values for each preset conversion. These values are very close to those obtained in the constant temperature analysis when the model used was $g(\alpha) = 1 - (1 - \alpha)^{1/2}$.

The result of the kinetic analysis for calcite containing 99.5% of calcium carbonate is the following kinetic equation:

$$\frac{d\alpha}{dt} = 1.9 \times 10^9 \exp\left(-\frac{193\,827}{RT}\right)(1-\alpha)^{1/2} \qquad (4)$$

The result for calcite containing 100% ± 1.8% of calcium carbonate was the following equation:

$$\frac{d\alpha}{dt} = 1.3 \times 10^6 \exp\left(-\frac{110\,477}{RT}\right)(1-\alpha)^{1/2} \qquad (5)$$

Clearly, the presence of impurities is a cause of variations in the kinetic parameters obtained. The impurities could function as catalysts owing to

TABLE 2

Analysis at constant conversion

α	E (kJ mol^{-1})	A (min^{-1})
0.1	196.0	7.4×10^{11}
0.3	195.6	8.2×10^{10}
0.5	192.9	1.8×10^{10}
0.7	193.7	8.9×10^{9}
0.9	191.0	3.0×10^{9}

their influence in the crystalline structure. A microscopic analysis of solid structures is necessary to confirm such a hypothesis.

In conclusion, differences in the obtained activation energy for a given compounds could be due to the influence of solid impurities and/or physical processes.

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