Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 829-833

KINETICS OF THERMAL DECOMPOSITION OF DOLOMITE

M. Olszak-Humienik and J. Możejko

Department of Chemical Engineering and Physical Chemistry, Technical University of Szczecin, Al. Piastów 42, Szczecin, Poland

Abstract

The thermal decomposition reactions of calcitic dolomite were investigated. Simultaneous TG/DTG/DTA were applied under non-isothermal conditions. From the recorded curves, the activation energies, pre-exponential factors and thermodynamic parameters of activation were calculated for the two thermal decomposition steps.

Keywords: dolomite, kinetics, thermal decomposition

Introduction

The calcination of dolomite is of considerable technological importance. Dolomite occurs widely scattered in nature and is an important material for the metallurgical (as a flux), pharmaceutical, paper and fertilizer industries. The calcination reaction is reversible and occurs at an interface; the rate of CO_2 release is sensitive to the prevailing pressure of this product in the vicinity of the reaction interface [1]. Both apparent kinetic parameters and reactivity are influenced by the prevailing CO_2 pressure.

Dolomite is a double carbonate of Ca and Mg. Its theoretical composition is 21.86% MgO, 30.41% CaO and 47.73% CO_2. It crystallizes in the rhombohedral unit cell, in space group R3, with a=6.0 Å, β=47.5° and Z=1.

The atomic positions in the dolomite and calcite structures are identical. The *M* atoms and CO_3 groups are arranged in layers which run parallel to the basal plane of the hexagonal unit cell. Each metal atom is thereby surrounded by six oxygen atoms from the adjacent CO_3 layers. The layer-type structure of dolomite is responsible for the strong anisotropy of the physical properties, including the thermal expansion [2].

The thermal dissociation of dolomite at low pressures proceeds in a single stage between 900 and 950 K, according to the scheme

$$CaMg(CO_3)_2 \leftrightarrow CaO + MgO + 2CO_2$$

When the pressure of CO_2 is higher than 24 Torr, the reaction at about 960 K is

$$CaMg(CO_3)_2 \leftrightarrow CaCO_3 + MgO + CO_2$$

1418-2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

As the pressure of CO_2 is increased to 760 Torr, the reaction temperature rises to 1170 K [1].

The differential thermal analysis of carbonate minerals has been extensively reported in the literature [1–4]. The activation energies calculated by Britton, Gregg and Windsor [2] for the thermal decomposition of dolomite in vacuum ranged from 206.5 to 232.4 kJ mol^{-1} for different samples, while that calculated by Criado and Ortega [1] from the TG and CRTA (controlled transformation rate thermal analysis) diagrams was 146.3 kJ mol^{-1} for first-order kinetics (F1).

The aim of this paper is to study the thermal behaviour of calcitic dolomite in which the molar ratio $MgCO_3$:$CaCO_3$ is about 40:60, in air under non-isothermal conditions, to calculate the kinetic parameters for the best kinetic models, and to compare the results with the energy of excitation calculated via quantum mechanical methods and literature data.

Experimental

The thermal decomposition of the dolomite was studied under non-isothermal conditions in air atmosphere. The raw dolomite used in the investigation was from the Zelatowa mine (Poland), and contained 16.13% MgO, 33.66% CaO, 2.86% R_2O_3 and 2.54% mass SiO_2 with a particle size of ≤0.25 mm. The dolomite contains calcium carbonate in excess over magnesite. The impurities in the dolomite cause the colour of the sample and of the residue.

Simultaneous recordings of thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermoanalytical (DTA) curves were made on a Derivatograph-C (Hungarian Optical Works).

The thermoanalytical diagrams of the dolomite were recorded at a sample mass of 50 mg in the temperature range from 20 to 1000°C, at a heating rate of 5°C min^{-1} in a static air atmosphere. Five experiments were carried out under the same conditions. The reproducibility was good.

Results and discussion

TG, DTG and DTA curves obtained for the investigated calcitic dolomite are shown in Fig. 1. It can be seen that the thermal decomposition of the dolomite under the applied experimental conditions is complex. It occurred in two overlapping endothermic steps in the temperature range 545–859°C, with distinct maximum rates at 793 and 828°C. The mass losses in these two steps are associated with the liberation of CO_2 from magnesium carbonate (first) and calcium carbonate bonded in the dolomitic lattice and calcium carbonate of the calcite type (second complex endo peak). Separation of the processes of liberation of CO_2 from the different forms of calcium carbonate was impossible under the given experimental conditions.

The kinetic analysis of the thermal decomposition of dolomite was performed via the TG and DTG curves.

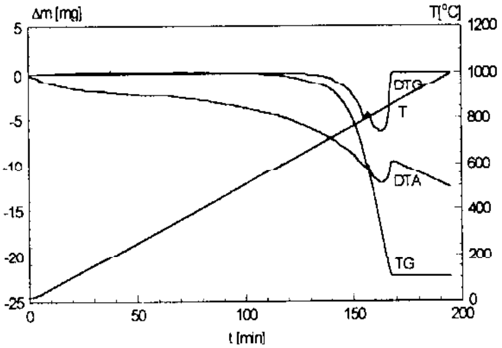

Fig. 1 Thermoanalytical curves of thermal decomposition of dolomite

It is known that the quantitative evaluation of TG curves is difficult if two or more transformation processes overlap [6]. The DTG curve affords a possibility to find the inflection point in the TG curve, to separate the overlapping mass changes and to define their probable extent.

From the $\alpha(T)$ dependences, various kinetic equations for the individual steps of the thermal decomposition of dolomite were estimated by assuming various reaction mechanisms [9].

Values of the kinetic parameters were deduced by fitting the conversion degree of the decomposition for each step to the Coats and Redfern equation [10]:

$$\ln(g(\alpha)) - 2\ln T = \ln\frac{AR}{E\beta}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \tag{1}$$

where α is the transformation degree, $g(\alpha)$ is a function depending on the reaction mechanism, T is the absolute temperature, R is the gas constant, β is the linear heating rate, E is the apparent activation energy, and A is the pre-exponential factor.

The best models for particular steps were selected in the following way. The algorithm of the theoretical TG curve from the kinetic equations was fed into the computer. From this algorithm, the various function pairs and their derived curves corresponding to the TG and DTG curves of the overlapping partial reactions were simulated. The single members of the TG and DTG curve pairs were then shifted in phase to overlap. These theoretical curves were compared with the experimental TG and DTG curves.

Table 1

Stage	E/ kJ mol^{-1}	A/ min^{-1}	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol–1 K^{-1}	ΔG^*/ kJ mol–1	r
D1 model	219	$1.52\cdot10^{09}$	210	–122	344	0.9440
F1 model	390	$3.98\cdot10^{17}$	381	39	339	0.9603

It was found that the first stage of the decomposition was governed by a one-dimensional diffusion D1 model:

$$g(\alpha) = \alpha^2$$

and the second step by a random nucleation F1 model:

$$g(\alpha) = -\ln(1 - \alpha)$$

The values of the kinetic and thermodynamic parameters for particular stages are given in Table 1.

The thermodynamic parameters of the activated complexes were calculated from the Eyring equation [9]. The apparent energy of activation calculated from the Arrhenius equation for the first stage was E=219 kJ mol^{-1}, while that for the second stage was E=390 kJ mol^{-1}. The free energy activation was 344 kJ mol^{-1} and 339 kJ mol^{-1}, respectively.

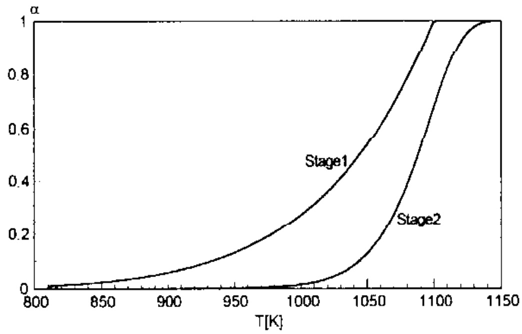

Fig. 2 Variation of conversion degree with temperature for different stages of decomposition of dolomite

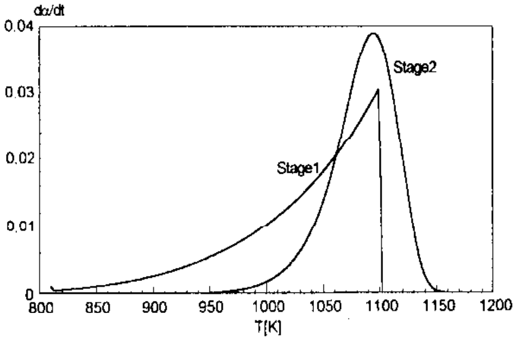

Fig. 3 Variation of reaction rates with temperature for different stages of decomposition of dolomite

From the derived kinetic equations, the dependences of the conversion degree (Fig. 2) and the reaction rates on temperature (Fig. 3) were calculated. Our results are in agreement with previous findings [1].

The excitation energy calculated from the electron spectrum for crystalline dolomite by means of the computer program HYPERChem was 224 kJ mol^{-1}. This value is very close to the activation energy for the first step of decomposition calculated from kinetic analysis of the experimental TG curves of the investigated dolomite. The excitation energy for magnesite is 195 kJ mol^{-1} and that for calcite is 389 kJ mol^{-1}.

References

1 Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Oxford 1980.
2 G. Bayer, Z. Kristallogr., 133 (1971) 85.
3 J. M. Criado and A. Ortega, J. Thermal Anal., 37 (1991) 2369.
4 H. T. S. Britton, S. J. Gregg and G. W. Winsor, Trans. Faraday Soc., 48 (1952) 53.
5 K. V. G. K. Gokhale and T. C. Rao, J. Thermal Anal., 2 (1970) 83.
6 A. Bolewski, Mineralogia szczegółowa, Warszawa 1982, Wyd. Geologiczne.
7 D. N. Todor, Thermal analysis of minerals, ABACUS Press Tunbridge Wells, 1976.
8 F. Paulik and M. Arnold, J. Thermal Anal., 36 (1990) 2313.
9 J. Straszko, M. Olszak-Humienik and J. Możejko, Inz. Chem. i Proc., 1 (1995) 45.
10 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.