

KINETIC STUDY OF THERMAL DECOMPOSITION OF DOLOMITE BY CONTROLLED TRANSFORMATION RATE THERMAL ANALYSIS (CRTA) AND TG

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The mechanism of the thermal decomposition of dolomite was studied. It was shown that a comparison of the kinetic data obtained from the kinetic analysis of a single TG trace and a single curve recorded using the constant rate thermal analysis (CRTA) method allows discrimination of the actual kinetic model obeyed by the reaction and also determination of its corresponding kinetic parameters.

Introduction

Methods that allow the course of a thermal decomposition reaction to be followed by monitoring the sample temperature in such a way that the reaction rate remains constant throughout the process have been developed by Rouquerol [1] and Paulik [2]. The former called this technique 'constant decomposition rate thermal analysis', while Paulik used the term 'quasi-isothermal thermogravimetry (QTG)'. Following the recent advice of the Nomenclature Committee of the International Confederation on Thermal Analysis, we use the name 'controlled transformation rate thermal analysis (CRTA)', which in our opinion gives a better description of the method. CRTA can be defined as a general thermoanalytical method where by a physical or chemical property x of a substance is modified following a predetermined program $x=f(t)$ under the appropriate action of temperature [1].

The above method has been widely used [3-6] to characterize processes of thermal degradation of solids, and it has been reported that QTG [7] or

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CRTA [8] allows a higher resolution power than that of the conventional TG procedure as concerns the discrimination of overlapping reactions.

However, publications relating to the use of CRTA in kinetic studies are scarce. Paulik *et al.* recently concluded [9] that QTG does not permit kinetic analysis of the thermal decomposition of solids because the temperature is not a previously known function of time and therefore the reacted fraction, α , cannot be expressed as a simultaneous function of these two variables. However, it may be argued against this reasoning that, provided that the decomposition rate is constant over the α range (i.e. $C = d\alpha/dt$), the constant C permits the expression of α as a function of time, while the Arrhenius law defines its dependence with respect to temperature. Accordingly, the reacted fraction can be represented as a function of both temperature and time.

On the basis of the above considerations, the following expression was derived earlier [10, 11] for the kinetic analysis of thermogravimetric traces obtained at constant decomposition rate C :

$$\ln(1/f(\alpha)) = \ln(A/C) - E/RT \quad (1)$$

where E is the activation energy, A is the preexponential factor of Arrhenius and $f(\alpha)$ is a function depending on the reaction mechanism (Table 1).

Equation (1) was successfully applied [12] to the thermal decomposition of alkaline-earth carbonates. In the present work, we apply both CRTA and conventional TG techniques to study the mechanism of thermal decomposition of dolomite under high vacuum.

Experimental

A sample of dolomite, $\text{CaMg}(\text{CO}_3)_2$, supplied by S. A. E. de Productos Dolomíticos, Santander (Spain), was used. The analysis of the sample gave the following results (in brackets the theoretical composition):

$$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3 = 0.63\%$$

$$\text{CaO} = 30.20\% (30.49\%)$$

$$\text{MgO} = 21.05\% (21.80\%)$$

$$\text{loss on ignition} = 46.44\% (47.72\%)$$

residue not soluble in HCl = 0.60%.

Table 1 Algebraic expressions for $f(\alpha)$, and $g(\alpha)$ functions for the most common mechanism operating in solid state reactions

Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
Unimolecular decay law	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
Avrami-Erofeev equation	Am	$m(1-\alpha)[- \ln(1-\alpha)]^{1-1/m}$	$[- \ln(1-\alpha)]^{1/m}$
Two dimensional diffusion	D2	$1/- \ln(1-\alpha)$	$(1-\alpha) \cdot \ln(1-\alpha) + \alpha$
Three dimensional diffusion(Jander equation)	D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$
Three dimensional diffusion(Ginstlein-Brounshtein equation)	D4	$\frac{3}{2[(1-\alpha)^{1/3}-1]}$	$(1-2\alpha/3) - (1-\alpha)^{2/3}$

The experimental system has been described elsewhere [12]. The CRTA diagram of dolomite was recorded at a sample weight of 19.5 mg, a constant CO₂ residual pressure of $4 \cdot 10^{-5}$ mbar and a constant specific decomposition rate of $3.7 \cdot 10^{-3} \text{ min}^{-1}$.

The TG diagram of dolomite was obtained by using an initial weight of 1.10 mg and a heating rate of 0.5 deg·min. The pressure, recorded continuously throughout the experiment, never exceeded $2 \cdot 10^{-6}$ mbar, which is the best vacuum available in our experimental system.

The experimental conditions employed in both CRTA and TG experiments allow the influence of mass or heat transfer phenomena to be avoided, as shown previously [12].

The kinetic analysis of the CRTA trace was carried out by plotting the left-hand side of Eq. (1) against reciprocal temperature. Therefore, the activation energy and the preexponential Arrhenius factor can be calculated from the slope and the intercept of the plot, respectively.

The kinetic analysis of the TG diagram was carried out by the Coats and Redfern method [13]:

$$\ln g(\alpha) - 2 \ln T = \ln (AR/E\beta) - E/RT \quad (2)$$

where β is the heating rate and $g(\alpha)$, $[g(\alpha) = \int d\alpha/f(\alpha)]$ is a function depending on the reaction mechanism (Table 1).

A plot of the left-hand side of Eq. (2) against $1/T$ should be a straight line from whose slope and intercept the kinetic parameters of the reaction can be obtained.

Results and discussion

Both the CRTA and TG curves obtained for dolomite are included in Fig. 1. Table 2 shows the results obtained from the kinetic analysis of the CRTA and TG curves in Fig. 1 by means of Eqs (1) and (2), respectively, after considering the $f(\alpha)$ and $g(\alpha)$ functions of the mechanism of thermal decomposition of solids common in the literature (Table 2).

We can see that the analysis of the TG curve of dolomite gives a very good linear correlation coefficient, whatever the kinetic law assumed in the calculation of the kinetic parameters. This means that it not possible to discriminate the actual reaction mechanism from the kinetic analysis of a single TG curve, in agreement with previous statements [14]. As regards the kinetic analysis of the CRTA curve of dolomite, Table 1 shows that good cor-

relation coefficient are obtained only by introducing the $f(\alpha)$ function corresponding to n -order kinetic laws (R2, R3 and F1). This fact can easily be understood if it is borne in mind [12] that the analysis of a single CRTA curve has the limitation that reactions following n_1 -order kinetics ($n_1 \neq 0$) with an activation energy E_1 necessarily fit any kinetic law of n_2 order giving an activation energy $E = (n_1/n_2)E$ and therefore does not supply enough information for the calculation of n when it is different from zero.

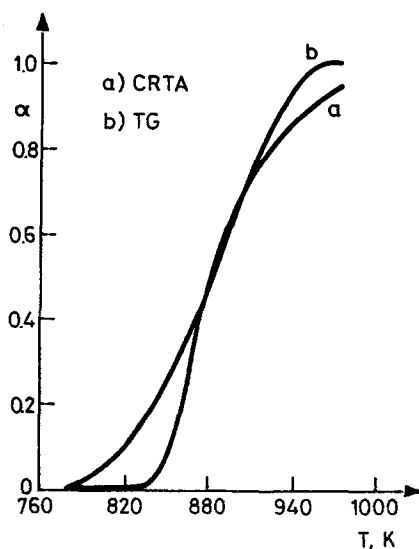
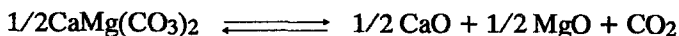


Fig. 1 a) CRTA and b) TG curves for the thermal decomposition of CaCO_3

However, we earlier concluded [11, 12] that a comparison of the values of the activation energy and the preexponential factor of Arrhenius obtained from CRTA and TG curves affords an excellent procedure for determination of the actual reaction mechanism. Table 2 shows that both a good correlation coefficient and good agreement between the kinetic parameters calculated from the TG and CRTA diagrams of dolomite is obtained only if we assume that the reaction follows first-order kinetics (F_1). Moreover, the activation energy ($E = 146.3 \text{ kJ/mol}$) is very close to the enthalpy of the reaction:



$$\Delta H = 151.3 \text{ kJ/mol}$$

which we calculated from the enthalpy of formation of dolomite from its solid components, calcite and magnesite, reported by Halla [15], and from the corresponding decomposition enthalpies of MgCO_3 and CaCO_3 [16].

Table 2 Kinetic parameters of the thermal decomposition of dolomite calculated from TG and CRTA (in brackets) curves by assuming various reaction mechanism

Mechanism	$E/\text{kJ}\cdot\text{mol}^{-1}$	A/min^{-1}	Correlation coefficient
R2	120.4(71.1)	$1.3\times 10^6(8.4\times 10)$	-0.9924(-0.9994)
R3	129.6(94.5)	$1.6\times 10^5(2.4\times 10^3)$	-0.9953(-0.9994)
F1	149.6(146.3)	$5.6\times 10^6(1.3\times 10^6)$	-0.9989(-0.9994)
A2	135.0(130.8)	$7.7\times 10(1.4\times 10^3)$	-0.9985(-0.9105)
A3	120.4(119.5)	$1.4\times 10^{-50}(6.3\times 10^{-1})$	-0.9980(-0.7205)
D1	206.9(96.10)	$5.7\times 10^9(1.5\times 10^3)$	-0.9819(-0.8851)
D2	236.2(152.9)	$2.1\times 10^{11}(2.3\times 10^6)$	-0.9894(-0.9464)
D3	273.8(225.7)	$1.2\times 10^{13}(1.4\times 10^{10})$	-0.9959(-0.9761)
D4	248.3(178.1)	$3.4\times 10^{20}(1.8\times 10^7)$	-0.9921(-0.9610)

The symbols of SHARP et al. [20] have been used

It is noteworthy that the work of Britton, Gregg and Windsor [17] is, to our knowledge, the only report in the literature concerning kinetic study of the thermal decomposition of dolomite in vacuum. The activation energies calculated by these authors for four different samples (ranging from 206.5 to 232.4 kJ/mol) are higher than the one reported in the present paper. This disagreement may be explained if we take into account that Britton *et al.* [17] obtained their thermogravimetric data by using a sample weight of 400 mg and a starting vacuum of 0.01 mbar. We have demonstrated [18] that, under the experimental conditions used in [17], the reaction is modified by mass and heat transfer phenomena; these were avoided in the present paper.

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Zusammenfassung — Es wurde der Mechanismus der thermischen Zersetzung von Dolomit untersucht. Es wurde gezeigt, daß ein Vergleich der kinetischen Angaben aus einer kinetischen Analyse eines einfachen TG-Durchlaufes und einer mittels CRTA einmal registrierten Kurve die Unterscheidung desjenigen kinetischen Modelles ermöglicht, dem die Reaktion gerade unterliegt und außerdem die Bestimmung der zugehörigen kinetischen Parameter ermöglicht.