

Kinetic analysis of non-isothermal calcination TG curves of natural Turkish dolomites

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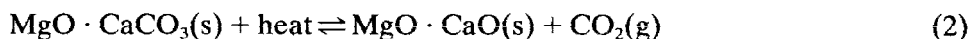
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Abstract

Calcination kinetics of six dolomite samples originating from different parts of Turkey were investigated by using the non-isothermal thermogravimetry technique. Calcination TG curves of samples were obtained under two different atmospheres of (1) pure nitrogen and (2) a mixture consisting of 15 vol.% CO₂ and 85 vol.% dry air, by using a constant heating rate of 10 K min⁻¹. Kinetic analysis of the curves was achieved by applying four different methods of calculation; also, 14 different model equations of possible solid-state rate controlling mechanisms were considered. Arrhenius parameters *E* and *A* and the model function *f*(α) that best describes the reaction mechanism were evaluated for the decomposition reactions of both MgCO₃ and CaCO₃ components of samples. A computer program in BASIC which enables regression analysis to be carried out was used to obtain kinetic results from experimental non-isothermal TG data. It was observed that besides differences in the chemical composition of samples, gaseous atmosphere and the method of calculation influenced the results obtained.

INTRODUCTION

According to the heating curves recorded between 293 and 1273 K the thermal decomposition of dolomite occurs in two main steps; the first mass loss corresponds to the decomposition of MgCO₃ (eqn. (1)) and the second step is attributed to the decomposition of CaCO₃ (eqn. (2)) [1]



In recent years thermoanalytical methods have been widely used to study the kinetics of various solid state decomposition reactions. Kinetic studies can be carried out with a simple and rapid experimental procedure by using the non-isothermal thermogravimetry technique [2]. Several computation

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methods have been presented in the literature which utilize non-isothermal TG data to obtain kinetic information [3–10].

Generally the rate of mass loss for a decomposition reaction is described by the equation

$$d\alpha/dt = kf(\alpha) \quad (3)$$

where α is the degree of conversion, t is the time, k is the reaction rate constant and $f(\alpha)$ is the conversion function which depends on the reaction mechanism. The temperature T dependence of the reaction rate constant can be given by the Arrhenius equation

$$k = A \exp(-E/RT) \quad (4)$$

$$T = T_0 + bt \quad (5)$$

where A and E are the pre-exponential factor and apparent activation energy, respectively, R is the gas constant and b is the linear heating rate. By combining the above expressions the general non-isothermal kinetic equation

$$[(d\alpha/dT)/f(\alpha)] = (A/b) \exp(-E/RT) \quad (6)$$

is obtained. Most of the existing methods used to evaluate non-isothermal kinetic parameters are based on this general equation (eqn. (6)).

In the present work, kinetic analysis of the calcination TG curves of six natural Turkish dolomites was achieved by using computational techniques. The non-isothermal thermogravimetry technique was employed to obtain the calcination TG curves of the samples.

EXPERIMENTAL

Thermogravimetric experiments of samples were performed by using a Shimadzu TG 41 thermal analyser. The initial mass and particle size of samples used in the measurements were about 100 mg and $<250 \mu\text{m}$, respectively. The experiments were carried out from room temperature to 1223 K with a programmed heating rate of 10 K min^{-1} . Pure N_2 and a mixture consisting of 15 vol.% CO_2 and 85 vol.% dry air were used as gaseous atmospheres. The flow rate of gases was maintained at a constant rate of $40 \text{ cm}^3 \text{ min}^{-1}$ throughout the measurements. Calcination TG curves were traced by using a chart speed of 2.5 mm min^{-1} .

In order to determine the chemical composition of dolomite samples ASTM standards [11] were followed and the results are presented in Table 1.

TABLE 1

Chemical analysis in % of the dolomite samples

Sample code	CaO	MgO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃
D 01	36.02	14.66	0.60	2.67	1.40
D 02	32.50	16.87	0.17	4.97	0.97
D 03	31.85	19.21	0.36	1.16	0.36
D 04	31.52	19.87	0.12	0.64	0.26
D 05	20.30	22.60	0.25	13.30	1.90
D 06	30.04	19.22	0.32	—	1.23

RESULTS AND DISCUSSION

Four different computational methods which are given below were used to evaluate the kinetic results from the calcination TG curves: (1) Method I, Coats–Redfern [5]; (2) Method II, Horowitz–Metzger [4]; (3) Method III, Dharwadkar–Karkhanavala [9] and (4) Method IV, Doyle [3] modified by Zsakó [10].

According to the general non-isothermal kinetic equation (eqn. (6)) a plot of $\ln[(d\alpha/dT)/f(\alpha)]$ versus $1/T$ should give a straight line if the appropriate $f(\alpha)$ function is selected. Arrhenius parameters (E and A) can be obtained from the slope and intercept, respectively after the selection of $f(\alpha)$ function is satisfied. In this study, 14 different kinetic models were tested to determine the most appropriate mechanism describing the calcination reactions. Table 2 lists these models with their corresponding $f(\alpha)$ and $[g(\alpha) = \int d\alpha/f(\alpha)]$ expressions.

The determination of the non-isothermal kinetic parameters for the decomposition reactions (eqns. (1) and (2)) were carried out by using a BASIC computer program. The experimental data such as constant heating rate, initial and final sample masses, initial and final reaction temperatures and α – T data derived from TG curves were used as input parameters for the computer programme.

The $f(\alpha)$ functions which provide a reasonably good fitting to the experimental data were chosen as those which give the highest correlation coefficient for methods I, II and III and give the lowest standard deviation for method IV.

Tables 3 and 4 summarize the calculated kinetic parameters for the first step decomposition (eqn. (1)) reactions carried out in N₂ and dry air + CO₂ atmospheres, respectively.

Similarly, the kinetic parameters determined for the second step decomposition (eqn. (2)) in N₂ and dry air + CO₂ atmospheres are shown in Tables 5 and 6, respectively.

TABLE 2 Model equations used in the kinetic analysis [12–14]

Model	Mechanism	Differential function $f(\alpha)$	Integral function $g(\alpha) = \int d\alpha / f(\alpha)$
(1) First-order eqn. ($n = 1$)	Chemical reaction	$(1 - \alpha)$	$-\ln(1 - \alpha)$
(2) Zero-order eqn. ($n = 0$)	Chemical reaction	1	α
(3) One-third order eqn. ($n = 1/3$)	Chemical reaction	$(1 - \alpha)^{1/3}$	$(3/2)[1 - (1 - \alpha)^{2/3}]$
(4) One-half order eqn. ($n = 1/2$)	Chemical reaction	$(1 - \alpha)^{1/2}$	$2[1 - (1 - \alpha)^{1/2}]$
(5) Two-thirds order eqn. ($n = 2/3$)	Chemical reaction	$(1 - \alpha)^{2/3}$	$3[1 - (1 - \alpha)^{1/3}]$
(6) Second-order eqn. ($n = 2$)	Chemical reaction	$(1 - \alpha)^2$	$-[1 - (1 - \alpha)^{-1}]$
(7) Phase boundary controlled reaction	Contracting geometry (cylindrical symmetry) (R2)	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
(8) Phase boundary controlled reaction	Contracting geometry (spherical symmetry) (R3)	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
(9) Avrami–Erofeev eqn.	Random nucleation and growth of nuclei ($n = 2$) (A2)	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
(10) Avrami–Erofeev eqn.	Random nucleation and growth of nuclei ($n = 3$) (A3)	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
(11) Avrami–Erofeev eqn.	Random nucleation and growth of nuclei ($n = 4$) (A4)	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
(12) Valensi–Barrer eqn.	Two-dimensional diffusion (D2)	$(- \ln(1 - \alpha))^{-1}$	$\alpha + (1 - \alpha) \ln(1 - \alpha)$
(13) Jander eqn.	Three-dimensional diffusion (spherical symmetry) (D3)	$(3/2)(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
(14) Grinstling–Brounshtein eqn.	Three-dimensional diffusion (cylindrical symmetry) (D4)	$(3/2)[(1 - \alpha)^{-1/3} - 1]^{-1}$	$[1 - (2/3)\alpha] - (1 - \alpha)^{2/3}$

TABLE 3 Kinetic parameters for the first step thermal decomposition of dolomites in N₂ atmosphere

Sample code	Coats-Redfern		Horowitz-Metzger		Dharwadkar-Karkhanavala		Doyle-Modified by Zsako	
	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$
D 01	139.65	3.53 (1 - α) ⁰ = 1	172.73	6.16 (1 - α) ⁰ = 1	194.74	7.32 (1 - α) ⁰ = 1	142.29	6.83 (1 - α) ⁰ = 1
D 02	252.55	6.28 (1 - α) ⁰ = 1	285.34	12.02 (1 - α) ⁰ = 1	252.93	10.35 (1 - α) ⁰ = 1	259.47	13.03 (1 - α) ⁰ = 1
D 03	171.29	4.35 (1 - α) ⁰ = 1	202.40	7.88 (1 - α) ⁰ = 1	223.30	8.98 (1 - α) ⁰ = 1	184.14	9.16 (1 - α) ⁰ = 1
D 04	316.42	7.99 (1 - α) ²	338.67	15.21 (1 - α) ²	245.96	10.31 (1 - α) ²	322.25	16.77 (1 - α) ²
D 05	127.45	3.17 D2	77.92	1.24 (1 - α) ⁰ = 1	116.74	3.43 (1 - α) ⁰ = 1	133.92	6.27 D2
D 06	214.69	5.37 (1 - α) ⁰ = 1	251.22	10.20 (1 - α) ⁰ = 1	260.85	10.69 (1 - α) ⁰ = 1	221.81	11.03 (1 - α) ⁰ = 1

TABLE 4 Kinetic parameters for the first step thermal decomposition of dolomites in CO₂ + dry air atmosphere

Sample code	Coats-Redfern		Horowitz-Metzger		Dharwadkar-Karkhanavala		Doyle-Modified by Zsako	
	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$	$E/$ kJ mol ⁻¹	$\log(A/)$ s ⁻¹) $f(\alpha)$
D 01	276.48	7.07 (1 - α) ²	302.64	13.51 (1 - α) ²	237.47	10.02 (1 - α) ²	284.58	14.87 (1 - α) ²
D 02	347.04	8.71 (1 - α) ²	353.32	16.38 (1 - α) ²	269.20	11.85 (1 - α) ²	380.84	19.86 (1 - α) ²
D 03	327.61	8.23 (1 - α) ⁰ = 1	361.07	16.51 (1 - α) ⁰ = 1	323.93	14.54 (1 - α) ⁰ = 1	334.80	17.38 (1 - α) ⁰ = 1
D 04	408.54	14.25 (1 - α) ²	423.36	24.04 (1 - α) ²	285.62	16.68 (1 - α) ²	435.24	26.95 (1 - α) ²
D 05	99.41	2.81 (1 - α) ²	119.09	3.66 (1 - α) ²	194.89	7.87 (1 - α) ²	117.18	6.24 (1 - α) ²
D 06	435.03	10.68 (1 - α) ²	446.41	20.84 (1 - α) ²	272.39	11.70 (1 - α) ²	477.09	24.67 (1 - α) ²

TABLE 5 Kinetic parameters for the second step thermal decomposition of dolomites in N₂ atmosphere

Sample code	Coats-Redfern		Horowitz-Metzger		Dharwadkar-Karkhanavala		Doyle-Modified by Zsako	
	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹
D 01	122.59	3.12	145.49	4.08	110.40	2.34	125.55	5.98
D 02	156.32	4.00	172.86	5.62	130.40	3.49	159.03	7.83
D 03	276.63	6.55	304.75	11.83	220.13	7.76	276.21	13.20
D 04	254.54	6.10	281.55	10.87	213.30	7.55	255.29	12.28
D 05	197.35	4.60	219.40	7.97	130.40	3.52	196.69	8.92
D 06	361.52	8.10	202.36	6.96	143.00	4.04	364.10	16.76

TABLE 6 Kinetic parameters for the second step thermal decomposition of dolomites in CO₂ + dry air atmosphere

Sample code	Coats-Redfern		Horowitz-Metzger		Dharwadkar-Karkhanavala		Doyle-Modified by Zsako	
	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹	$E/$ kJ mol ⁻¹	$\log(A/ f(\alpha))$ s ⁻¹
D 01	137.55	3.43	163.62	4.78	116.82	2.52	138.11	6.50
D 02	283.51	6.49	311.56	11.85	236.80	8.33	284.58	13.13
D 03	278.47	6.45	307.18	11.66	216.77	7.39	280.40	13.08
D 04	295.75	6.80	321.93	12.39	230.48	8.07	297.14	13.83
D 05	236.88	5.99	253.87	9.46	155.58	4.66	242.73	12.32
D 06	309.70	7.10	338.73	13.10	231.60	8.06	313.88	14.62

The kinetic results obtained for the first step thermal decomposition of samples (Tables 3 and 4) indicate that there are marked variations in the value of Arrhenius parameters (E and A) depending on sample properties, gaseous atmosphere and the method of calculation. However the selected kinetic models [$f(\alpha)$] are only strongly affected by calcination gaseous atmosphere. Although the $f(\alpha) = (1 - \alpha)^0 = 1$ and $f(\alpha) = (1 - \alpha)^2$ model equations were selected most often for the first step decomposition reactions of samples in N_2 and dry air + CO_2 atmospheres, respectively; other equations which are $(1 - \alpha)^2$, $[-\ln(1 - \alpha)]^{-1}$ for N_2 and $(1 - \alpha)^0 = 1$ for dry air + CO_2 atmospheres were indicated as well. These slight variations can be attributed to the sample properties and the method of calculation.

It is clear from the results presented in Tables 5 and 6 that gaseous atmosphere, method of calculation and sample properties influenced the kinetic parameter values obtained for the second step decomposition reactions of samples. For the reactions which were carried out in N_2 atmosphere the variation of the best fitting expressions [$f(\alpha)$] depending on sample properties was found to be the same when methods I and IV used; the $f(\alpha)$ functions determined with methods II and III also showed the same variation for all samples except D 06 (Table 5). The model equations of $f(\alpha) = (1 - \alpha)^n$ ($n = 0.5, 0$); $f(\alpha) = [-\ln(1 - \alpha)]^{-1}$ and $f(\alpha) = (3/2)[(1 - \alpha)^{-1/3} - 1]^{-1}$ were determined as best fitting expressions.

The results given in Table 6 indicate that the mechanisms of the reactions carried out in dry air + CO_2 atmosphere can be described by three different kinetic equations of $(1 - \alpha)^0 = 1$, $[-\ln(1 - \alpha)]^{-1}$ and $(1 - \alpha)^2$ depending on sample properties.

If we compare the calculated Arrhenius parameter values of both first and second step decomposition reactions of samples in two different atmospheres (Tables 3–6) it can be concluded that parameters are affected by the partial pressure of the gaseous product of reactions. Generally there is an increase in E values with increasing partial pressure of CO_2 in furnace atmosphere. This increase is due to the reversible nature of the reactions. An increment in the value of E is balanced by a corresponding increase in A . This linear relationship between E and A (the kinetic compensation effect) has been pointed out in the literature by several researchers [15–18]. The results reported in this work are in agreement with this effect.

REFERENCES

- 1 T. Takats and M. Boros, Silikattechnik, 14 (1963) 3.
- 2 W.W. Wendlandt, Thermal Analysis, 3rd edn., John Wiley, New York, 1986, pp. 57–83.
- 3 C.D. Doyle, Nature, 207 (1965) 290.
- 4 H.H. Horowitz and G. Metzger, A new analysis of thermogravimetric traces, Anal. Chem., 35 (1963) 1464–1468.

- 5 A.W. Coats and J.P. Redfern, Kinetic parameters from thermogravimetric data, *Nature*, 201 (1964) 68.
- 6 B.N.N. Archer, G.W. Brindley and J.H. Sharp, *Proc. Int. Clay Conf.*, 1 (1966) 67.
- 7 J.H. Sharp and S.A. Wentworth, Kinetic analysis of thermogravimetric data, *Anal. Chem.*, 41 (1969) 2060–2062.
- 8 E.S. Freeman and B. Carroll, The application of thermo-analytical techniques to reaction kinetics: the thermo-gravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate, *J. Phys. Chem.*, 62 (1958) 394–397.
- 9 S.R. Dharwadkar and M.D. Karkhanavala, Calculation of activation energy of decomposition reactions from thermogravimetric analysis, in R.F. Schwenker, Jr. and P.D. Garn (Eds.), *Thermal Analysis, Vol. II*, Academic Press, New York, 1969, pp. 1049–1059.
- 10 J. Zsako, *J. Therm. Anal.*, 8 (1975) 593.
- 11 Annual Book of ASTM Standards, Part 13, 1977, Method C-25-72.
- 12 T.P. Bagchi and P.K. Sen, Combined differential and integral method for analysis of non-isothermal kinetic data, *Thermochim. Acta*, 51 (1981) 175–189.
- 13 J.M. Criado, A. Ortega and F. Gotor, Correlation between the shape of controlled-rate thermal analysis curves and the kinetics of solid-state reactions, *Thermochim. Acta*, 157 (1990) 171–179.
- 14 O. Carp and E. Segal, BASIC program to discriminate among mechanisms of solid–gas decomposition, *Thermochim. Acta*, 185 (1991) 111–127.
- 15 P.K. Gallagher and D.W. Johnson, Jr., Kinetics of the thermal decomposition of CaCO_3 in CO_2 and some observations on the kinetic compensation effect, *Thermochim. Acta*, 14 (1976) 255–261.
- 16 J. Zsako and H.E. Arz, Kinetic analysis of thermogravimetric data VII. Thermal decomposition of calcium carbonate, *J. Therm. Anal.*, 6 (1974) 651–656.
- 17 P.D. Garn, An examination of the kinetic compensation effect, *J. Therm. Anal.*, 7 (1975) 475–478.
- 18 A.E. Mericboyu, S. Küçükbayrak and B. Durus, Evaluation of kinetic parameters of natural Turkish limestones from their thermogravimetric curves using a computer program, *J. Therm. Anal.*, 39 (1993) 707–714.