Thermochimica Acta, 223 (1993) 121–128
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition kinetics of natural Turkish limestones under non-isothermal conditions

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(Received 18 December 1992; accepted 22 January 1993)

Abstract

The kinetic parameters for the thermal decomposition of 20 natural Turkish limestones, including the activation energy, pre-exponential factor and mechanism, were determined from their non-isothermal TG data. Thermogravimetric measurements were made in pure N_2 and in a mixture of 15% CO_2 and 85% dry air, at a constant heating rate of 10 K min^{-1}. A computer program written in BASIC was used to evaluate the kinetic parameters of the decomposition reactions from experimental TG data. Five different calculation methods were employed in the kinetic analysis of the TG curves of the samples; this analysis also incorporated 14 different model equations reported in the literature concerning solid state rate-controlling mechanisms. It was observed that the values of the kinetic parameters showed differences depending on the method of calculation, the gaseous atmosphere and the sample properties.

INTRODUCTION

Thermoanalytical methods are often used to study the kinetics and mechanism of solid state decomposition reactions. Dynamic thermogravimetry has been widely applied in the study of various solid state processes [1]. The shape of the thermogravimetric curves is a function of the reaction kinetics and, hence, the information obtained from these curves is useful in evaluating the kinetic parameters.

Several computational methods for obtaining kinetic information from non-isothermal TG curves have been presented in the literature [2–9]. Flynn and Wall [10] have grouped these methods into five classes: integral methods; differential methods; difference differential methods; methods applicable to initial rates; and non-linear or cyclic heating rate methods. Despite this classification, most of the methods are based on the equations

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

$$k = A\exp(-E/RT) \tag{2}$$

$$T = T_0 + bt \tag{3}$$

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where α is the degree of conversion, t is the time (s), k the reaction rate constant (s^{-1}), $f(\alpha)$ a function depending on the reaction mechanism, A the pre-exponential factor (s^{-1}), E the apparent activation energy (kJ mol^{-1}), R the gas constant (kJ mol^{-1} K^{-1}), T the absolute temperature (K), b the linear heating rate (K s^{-1}) and T_0 the initial reaction temperature (K).

The reaction rate constant k depends on the absolute temperature according to the Arrhenius equation, eqn. (2). A combination of the above equations yields the general non-isothermal kinetic equation

$$\frac{d\alpha/dT}{f(\alpha)} = (A/b)\exp(-E/RT) \tag{4}$$

In this investigation, non-isothermal thermogravimetry was used to study the thermal decomposition kinetics of 20 natural Turkish limestones. Computational techniques were used to obtain the kinetic parameters from experimental non-isothermal TG data.

EXPERIMENTAL

A Shimadzu thermal analyser (TG 41) was used to obtain non-isothermal TG curves of the samples. Samples were heated from room temperature to 1223 K at a constant heating rate of 10 K min^{-1}. In the measurements,

TABLE 1

Chemical analyses (%) of the limestone samples

Sample code	CaO	MgO	Fe_2O_3	SiO_2	Al_2O_3
L 01	55.23	–	0.28	0.21	0.59
L 02	54.98	–	0.13	0.14	0.50
L 03	54.09	–	0.40	0.58	0.55
L 04	54.03	0.26	0.12	0.11	0.60
L 05	53.65	–	0.26	2.12	0.42
L 06	53.39	0.26	0.38	1.35	0.54
L 07	52.48	1.27	0.57	2.05	0.39
L 08	52.17	1.05	0.08	0.61	0.21
L 09	51.90	2.50	0.34	0.94	0.66
L 10	50.60	1.53	0.75	3.10	2.20
L 11	49.21	0.79	0.47	6.49	1.21
L 12	43.13	1.78	0.16	8.64	4.60
L 13	37.45	4.65	3.54	12.64	6.70
L 14	54.05	0.52	0.25	0.40	1.14
L 15	47.91	1.82	0.44	6.80	2.58
L 16	53.56	0.26	0.08	0.35	1.27
L 17	54.48	0.26	0.02	0.22	0.54
L 18	54.29	–	0.04	0.02	1.02
L 19	54.08	0.76	0.10	0.02	1.20
L 20	49.91	2.70	0.46	3.66	2.04

100 mg samples of particle size $<250\ \mu m$ were used. The experiments were carried out in gaseous atmospheres of pure N_2 and in a mixture consisting of 15% CO_2 and 85% dry air. The total flow rate of the gases ($40\ cm^3\ min^{-1}$) was maintained constant. The decomposition TG curves of the samples were recorded using a chart speed of $2.5\ mm\ min^{-1}$. In order to determine the chemical composition of the samples (Table 1), ASTM standard methods [11] were followed.

COMPUTATIONAL PROCEDURE APPLIED TO OBTAIN KINETIC PARAMETERS

The kinetic parameters were calculated using five different computational methods: method I, Coats–Redfern [4]; method II, Freeman–Carroll [7]; method III, Horowitz–Metzger [3]; method IV, Dharwadkar–Karkhanavala [8]; and method V, Doyle [2] modified by Zsako [9].

The most appropriate kinetic mechanisms $f(\alpha)$ describing the decomposition reactions were determined using methods I, III, IV and V; only method II was used to determine the value of n, the reaction order, for the function $f(\alpha) = (1 - \alpha)^n$. The values of E and A were then calculated using each of the above methods.

The equations of $f(\alpha)$ and $g(\alpha) = \int d\alpha / f(\alpha)$ for the most common mechanisms describing solid-state decomposition reactions are given in Table 2. These equations were considered as $f(\alpha)$ functions in the present work. In order to determine the $f(\alpha)$ function that best represents the decomposition mechanism, only the functions yielding the highest correlation coefficient r for methods I, III and IV, and the lowest standard deviation for method IV, were accepted. The most appropriate n values were determined as those giving the highest correlation coefficient for method II. The computation of the Arrhenius parameters (E and A) was carried out after the stated conditions for $f(\alpha)$ and n values had been satisfied.

A computer program written in BASIC which enables regression analysis, was used to determine the kinetic parameters from the non-isothermal TG data of the samples. The selection of the $f(\alpha)$ functions and n values, and also the computation of the Arrhenius parameters were incorporated into the program. The constant heating rate, the initial and final sample weights, the initial and final reaction temperatures, and the α–T data derived from the TG curves were used as input data for the computer program.

RESULTS AND DISCUSSION

Tables 3 and 4 summarize the kinetic parameters for the thermal decomposition reactions of 20 natural limestones in N_2 and (CO_2 + dry air) atmospheres, respectively. It can be seen that the kinetic parameters are strongly affected by the gaseous atmosphere. Some of the variations in the

TABLE 2

Model equations used in the kinetic analysis [12–16]

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

values can be attributed to the method of calculation and to the sample properties.

The results presented in Table 3 for the thermal decomposition of the limestones in N_2 atmosphere indicate that the variation of the $f(\alpha)$ functions depending on the sample properties is the same when methods I and V are used. Different results are obtained with methods III and IV which are compatible with each other. Thus, the best models determined by methods I and V are $f(\alpha) = (1-\alpha)^n$ ($n = 1/3$, 0) and $f(\alpha) = 2(1-\alpha)^{1/2}$, and those by methods III and IV are $f(\alpha) = (1-\alpha)^n$ ($n = 1/3$, 1/2) and $f(\alpha) = 2(1-\alpha)^{1/2}$.

TABLE 3

Kinetic parameters for the thermal decomposition of limestones in N_2 atmosphere for the different calculation methods

Sample code	Coats–Redfern			Freeman–Carroll			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}	n	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}	$f(\alpha)$
L 01	166.95	4.20	$(1-\alpha)^{1/3}$	150.76	16.02	−0.02	201.82	6.84	$(1-\alpha)^{1/3}$	235.35	8.46	$(1-\alpha)^{1/3}$	167.40	8.15	$(1-\alpha)^{1/3}$
L 02	176.26	4.42	$(1-\alpha)^{1/3}$	218.01	11.45	0.73	225.37	7.98	$2(1-\alpha)^{1/2}$	269.30	10.09	$2(1-\alpha)^{1/2}$	175.77	8.58	$(1-\alpha)^{1/3}$
L 03	180.79	4.51	$(1-\alpha)^{1/3}$	204.64	13.02	0.63	219.17	7.60	$(1-\alpha)^{1/3}$	245.48	8.86	$(1-\alpha)^{1/3}$	179.96	8.75	$(1-\alpha)^{1/3}$
L 04	190.51	4.68	$(1-\alpha)^{1/3}$	144.13	18.15	0.05	240.14	8.49	$2(1-\alpha)^{1/2}$	256.21	9.25	$2(1-\alpha)^{1/2}$	192.51	9.26	$(1-\alpha)^{1/3}$
L 05	182.21	4.55	$(1-\alpha)^{1/3}$	135.99	19.16	−0.21	232.80	8.28	$(1-\alpha)^{1/2}$	263.83	9.77	$(1-\alpha)^{1/2}$	188.33	9.19	$(1-\alpha)^{1/3}$
L 06	190.78	4.76	$(1-\alpha)^{1/3}$	123.58	18.03	−0.21	236.52	8.63	$(1-\alpha)^{1/2}$	260.72	9.80	$(1-\alpha)^{1/2}$	192.51	9.42	$(1-\alpha)^{1/3}$
L 07	187.30	4.66	$(1-\alpha)^{1/3}$	178.35	14.25	0.36	225.31	7.92	$(1-\alpha)^{1/3}$	252.21	9.21	$(1-\alpha)^{1/3}$	188.33	9.15	$(1-\alpha)^{1/3}$
L 08	189.57	4.69	$(1-\alpha)^{1/3}$	234.38	11.77	0.82	240.84	8.55	$2(1-\alpha)^{1/2}$	256.80	9.31	$2(1-\alpha)^{1/2}$	188.33	9.11	$(1-\alpha)^{1/3}$
L 09	196.61	4.89	$(1-\alpha)^{1/3}$	163.62	15.18	0.05	231.66	8.30	$(1-\alpha)^{1/3}$	244.32	8.91	$(1-\alpha)^{1/3}$	196.69	9.62	$(1-\alpha)^{1/3}$
L 10	173.69	4.33	$(1-\alpha)^{1/3}$	231.51	11.05	0.88	222.38	7.71	$(1-\alpha)^{1/2}$	249.29	9.00	$(1-\alpha)^{1/2}$	175.77	8.50	$(1-\alpha)^{1/3}$
L 11	193.59	4.66	$2(1-\alpha)^{1/2}$	228.99	10.38	1.00	228.27	8.06	$2(1-\alpha)^{1/2}$	241.09	8.67	$2(1-\alpha)^{1/2}$	192.51	9.35	$2(1-\alpha)^{1/2}$
L 12	132.98	3.36	$(1-\alpha)^{0}=1$	100.96	22.50	−0.46	181.48	5.81	$(1-\alpha)^{1/3}$	217.09	7.53	$(1-\alpha)^{1/3}$	133.92	6.37	$(1-\alpha)^{0}=1$
L 13	141.34	3.53	$(1-\alpha)^{0}=1$	122.48	17.63	−0.18	188.33	6.11	$(1-\alpha)^{1/3}$	207.98	7.05	$(1-\alpha)^{1/3}$	142.29	6.72	$(1-\alpha)^{0}=1$
L 14	186.76	4.62	$(1-\alpha)^{1/3}$	194.19	13.20	0.45	236.75	8.40	$2(1-\alpha)^{1/2}$	272.98	10.12	$2(1-\alpha)^{1/2}$	188.33	9.11	$(1-\alpha)^{1/3}$
L 15	139.07	3.50	$(1-\alpha)^{0}=1$	125.19	21.75	−0.09	194.29	6.30	$(1-\alpha)^{1/3}$	235.58	8.26	$(1-\alpha)^{1/3}$	138.11	6.56	$(1-\alpha)^{0}=1$
L 16	188.52	4.66	$(1-\alpha)^{1/3}$	123.94	20.84	−0.31	237.86	8.43	$(1-\alpha)^{1/2}$	255.46	9.27	$(1-\alpha)^{1/2}$	188.33	9.09	$(1-\alpha)^{1/3}$
L 17	192.15	4.73	$(1-\alpha)^{1/3}$	212.77	11.63	0.60	240.34	8.57	$(1-\alpha)^{1/2}$	260.06	9.51	$(1-\alpha)^{1/2}$	192.51	9.28	$(1-\alpha)^{1/3}$
L 18	198.12	4.75	$2(1-\alpha)^{1/2}$	173.19	14.13	0.43	234.78	8.31	$2(1-\alpha)^{1/2}$	267.33	9.85	$2(1-\alpha)^{1/2}$	200.88	9.42	$2(1-\alpha)^{1/2}$
L 19	191.98	4.74	$(1-\alpha)^{1/3}$	168.40	14.56	0.12	240.16	8.60	$(1-\alpha)^{1/2}$	253.74	9.25	$(1-\alpha)^{1/2}$	192.51	9.31	$(1-\alpha)^{1/3}$
L 20	178.74	4.42	$(1-\alpha)^{1/3}$	190.79	12.42	0.07	224.67	7.82	$(1-\alpha)^{1/2}$	248.50	8.96	$(1-\alpha)^{1/2}$	179.96	8.65	$(1-\alpha)^{1/3}$

TABLE 4

Kinetic parameters for the thermal decomposition of limestones in CO_2 + dry air atmosphere for the different calculation methods

Sample code	Coats–Redfern			Freeman–Carroll			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}	n	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}	$f(\alpha)$
L 01	471.61	10.46	$(1-\alpha)$	436.80	5.62	0.96	509.67	20.49	$(1-\alpha)$	401.06	15.56	$(1-\alpha)$	472.91	21.98	$(1-\alpha)$
L 02	480.44	10.61	$(1-\alpha)$	438.71	6.03	0.99	521.87	20.92	$(1-\alpha)$	378.21	14.43	$(1-\alpha)$	481.28	22.30	$(1-\alpha)$
L 03	548.19	11.97	$(1-\alpha)$	315.56	7.07	0.36	580.82	23.75	$(1-\alpha)$	384.72	14.85	$(1-\alpha)$	548.24	25.31	$(1-\alpha)$
L 04	493.35	10.80	$(1-\alpha)$	512.54	4.49	1.27	527.35	21.36	$(1-\alpha)$	397.24	15.29	$(1-\alpha)$	493.83	22.71	$(1-\alpha)$
L 05	431.43	9.69	$(1-\alpha)$	449.54	4.76	1.62	461.01	18.58	$(1-\alpha)$	354.97	13.69	$(1-\alpha)$	431.06	20.18	$(1-\alpha)$
L 06	503.22	11.08	$(1-\alpha)$	413.12	6.04	0.96	544.63	22.05	$(1-\alpha)$	409.13	15.91	$(1-\alpha)$	506.39	23.47	$(1-\alpha)$
L 07	457.41	10.20	$(1-\alpha)$	465.54	4.71	1.28	490.87	19.85	$(1-\alpha)$	355.88	13.66	$(1-\alpha)$	460.35	21.47	$(1-\alpha)$
L 08	454.70	10.09	$(1-\alpha)$	397.77	6.06	0.95	491.51	19.63	$(1-\alpha)$	386.85	14.89	$(1-\alpha)$	456.17	21.16	$(1-\alpha)$
L 09	478.14	10.53	$(1-\alpha)$	368.61	6.22	0.76	512.28	20.54	$(1-\alpha)$	390.44	15.03	$(1-\alpha)$	481.28	22.21	$(1-\alpha)$
L 10	416.98	9.29	$(1-\alpha)$	399.74	5.84	1.12	451.74	17.81	$(1-\alpha)$	375.78	14.37	$(1-\alpha)$	418.50	19.37	$(1-\alpha)$
L 11	421.52	9.46	$(1-\alpha)$	382.23	5.86	1.34	453.92	18.14	$(1-\alpha)$	329.12	12.42	$(1-\alpha)$	422.69	19.74	$(1-\alpha)$
L 12	360.46	8.22	$(1-\alpha)$	445.38	4.68	1.87	388.36	15.25	$(1-\alpha)$	256.96	9.15	$(1-\alpha)$	359.91	16.89	$(1-\alpha)$
L 13	333.37	7.58	$(1-\alpha)$	337.85	5.61	1.22	439.66	17.63	$(1-\alpha)^2$	342.45	13.14	$(1-\alpha)^2$	334.80	15.56	$(1-\alpha)$
L 14	498.23	10.85	$(1-\alpha)$	379.67	6.40	0.74	533.37	21.25	$(1-\alpha)$	387.55	14.72	$(1-\alpha)$	498.02	22.79	$(1-\alpha)$
L 15	390.62	8.78	$(1-\alpha)$	466.03	4.62	1.40	424.96	16.75	$(1-\alpha)$	345.60	13.12	$(1-\alpha)$	389.20	18.10	$(1-\alpha)$
L 16	495.62	10.80	$(1-\alpha)$	343.71	6.76	0.68	530.31	21.17	$(1-\alpha)$	394.85	15.09	$(1-\alpha)$	498.02	22.80	$(1-\alpha)$
L 17	480.59	10.57	$(1-\alpha)$	399.61	6.15	0.95	519.02	20.73	$(1-\alpha)$	433.54	16.88	$(1-\alpha)$	485.46	22.39	$(1-\alpha)$
L 18	502.59	10.97	$(1-\alpha)$	310.05	6.88	0.46	534.23	21.49	$(1-\alpha)$	426.63	16.64	$(1-\alpha)$	506.39	23.23	$(1-\alpha)$
L 19	434.29	9.60	$(1-\alpha)^{2/3}$	379.04	6.61	0.66	541.46	21.92	$(1-\alpha)$	388.60	15.00	$(1-\alpha)$	435.24	20.04	$(1-\alpha)^{2/3}$
L 20	483.88	10.78	$(1-\alpha)^2$	492.62	4.25	2.58	518.53	20.89	$(1-\alpha)^2$	429.65	16.86	$(1-\alpha)^2$	485.46	22.71	$(1-\alpha)^2$

TABLE 5

Variation intervals of calculated Arrhenius parameters

Method	N_2		Dry air + CO_2	
	E/kJ mol^{-1}	log A/s^{-1}	E/kJ mol^{-1}	log A/s^{-1}
I	133–198	3.36–4.89	333–548	7.58–11.97
II	101–234	10.38–22.50	310–512	4.25–7.07
III	182–241	5.81–8.63	388–581	15.25–23.75
IV	208–273	7.05–10.12	257–434	9.15–16.88
V	134–201	6.37–9.62	335–548	15.56–25.31

The results in Table 4 show that almost all the decomposition reactions in CO_2 + dry air atmosphere provide the best fit when the kinetic model $f(\alpha) = (1 - \alpha)$ is used. However, the n values determined using method II show differences that depend on the sample properties and the atmosphere employed, as seen from Tables 3 and 4.

Table 5 lists the variation intervals of the calculated Arrhenius parameters, based on the five calculation methods, for the decomposition reactions of the samples in the two different atmospheres. It is evident that the parameters are markedly influenced by the CO_2 concentration in the furnace atmosphere. The calculated activation energy values E increased with increasing concentration of the decomposition product (CO_2). This change is attributed to the reversible nature of the decomposition reactions.

The increase in E is balanced by a corresponding increase in A due to the "kinetic compensation" behaviour when methods I, III, IV and V are used; conversely, a decrease in the A values occurs when method II is used. The kinetic compensation effect for the thermal decomposition of $CaCO_3$ has been investigated by several researchers [17–20]. They observed that the variaton in E is accompanied by a corresponding change in A according to the linear equation $\log A = aE + b$. This observation is in agreement with the results obtained in this study.

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