Decomposition kinetics of alkaline earth carbonates by integral approximation method

(Cinética de decomposição de carbonatos de terra alcalina pelo método de aproximação integral)

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Abstract

The decomposition kinetics of four synthetic alkaline earth metal carbonates ($MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$) was studied under non-isothermal conditions from thermo-gravimetric measurements as compared to. The integral approximation method of Coats and Redfern was used to determine the kinetic parameters for the decomposition processes. The decomposition reactions followed mostly first order kinetics and the activation energy of the decomposition reactions increased with the increase in the molecular mass of the carbonates. The change in enthalpy for the decomposition processes was also calculated and compared with the activation energies for the decomposition processes. The activation energy of the decomposition process for all the carbonates was higher than the enthalpy of the reaction excepting $SrCO_3$
Keywords: decomposition, alkaline earth carbonates, non-isothermal kinetics, thermogravimetry.

Resumo

A cinética de decomposição de quatro carbonatos sintéticos de metais de terra alcalina ($MgCO_3$, $CaCO_3$, $SrCO_3$ e $BaCO_3$) foi estudada sob condições não isotérmicas por meio de medidas de termogravimétricas e feita sua comparação. O método de aproximação integral de Coats e Redfern foi usado para determinar os parâmetros cinéticos dos processos de decomposição. As reações de decomposição seguiram principalmente cinética de primeira ordem e a energia de ativação para as reações de decomposição aumentou com o aumento da massa molecular dos carbonatos. A variação na entalpia para os processos de decomposição foi também calculada e comparada com as energias de ativação. A energia de ativação dos processos de decomposição de todos os carbonatos foi maior que a entalpia da reação excepto para $SrCO_3$.
Palavras-chave: decomposição, carbonatos de terra alcalina, cinética não isotérmica, termogravimetria.

INTRODUCTION

Alkaline earth metal carbonates are widely used as starting materials for the synthesis of electronic ceramics and their decomposition behaviour has been attracting the attention of scientists since a long time ago. Some of the important findings in this area are given below.

Criado et al [1] studied the influence of the mechanical treatment on the structure and thermal stability of alkaline earth carbonates and proposed a model to account for the changes observed in the activation energy and enthalpy of the thermal decomposition of alkaline earth carbonates as a function of grinding. Arvanitidis et al [2] investigated the kinetics of decomposition of calcium, strontium and barium carbonates by thermogravimetric and differential thermal analyses during linear heating. The theoretical treatment was based on fundamental heat balance equations.

The activation energy of the decomposition of $CaCO_3$ obtained by this method was in good agreement with the result obtained by thermogravimetric analysis carried out simultaneously. L'vov [3] analyzed available literature data on the kinetics of the thermal decomposition of alkaline earth carbonates. The author compared the most reliable data with the kinetic parameters calculated for three conceivable paths of the process and showed that the mechanism involving intermediate hydroxide formation was the most probable one. Ninan et al[4] carried out thermo-gravimetric studies on two varieties of calcium carbonate viz., analytical reagent grade and in situ generated from calcium oxalate monohydrate. The authors observed that the kinetic parameters were marginally higher for the in situ generated calcium carbonate and they explained it by the presence of more micro-pores in the in situ generated calcium carbonate. The authors described the decomposition

mechanism as phase boundary reaction with cylindrical symmetry. Sanders et al [5] performed dynamic kinetic analyses on $CaCO_3$ decomposition using simultaneous TG and DSC measurements in both wet and dry flowing argon. They discussed the differences in the results in terms of the property measured and the possible influence of the atmosphere on the structural nature of the solid product, CaO. The DSC and TG studies yielded different results in subsequent kinetic analyses using a wide range of numerical methods. The presence of moisture in the atmosphere produced slightly lower values of the Arrhenius parameters with less variation during the course of the reaction. L'vov and Ugolkov [6] studied the kinetics of free-surface decomposition of magnesium, strontium and barium carbonates analyzed thermogravimetrically by the third-law method. They observed that the data of activation energy and enthalpy of decomposition are in a good agreement with the mechanism of congruent dissociative evaporation of carbonates with the simultaneous condensation of low-volatility oxides.

Compared with isothermal experiments, non-isothermal experiments are more convenient to carry out because it is not necessary to perform a sudden temperature jump of the sample at the beginning. Moreover compared isothermal kinetics non-isothermal kinetics requires fewer data for evaluating and analyzing the kinetic parameters

In the present investigation the decomposition kinetics of alkaline earth carbonates was investigated using Coat and Redfern [7] integral approximation method. Kinetic parameters were compared among the carbonates. The enthalpy change of the decomposition reactions during decomposition was also computed and compared with the activation energy.

EXPERIMENTAL

The kinetics of thermal decomposition of four synthetic alkaline earth metal carbonates ($MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$) of G.R. grade supplied by E.Merck (Mumbai,
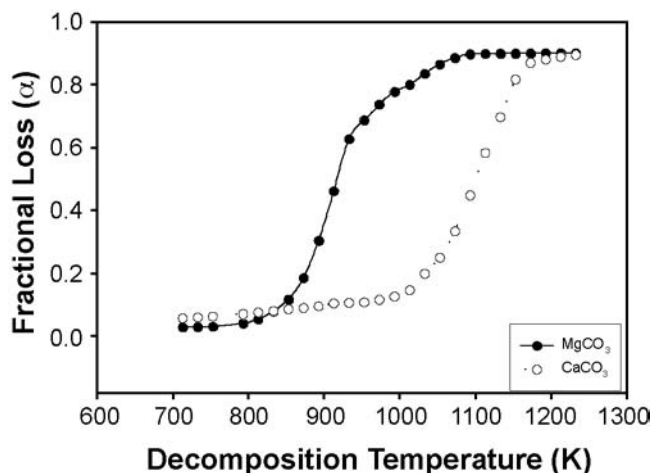

Figure 1: Variation of fractional loss with temperature in the decomposition range of $MgCO_3$ and $CaCO_3$.
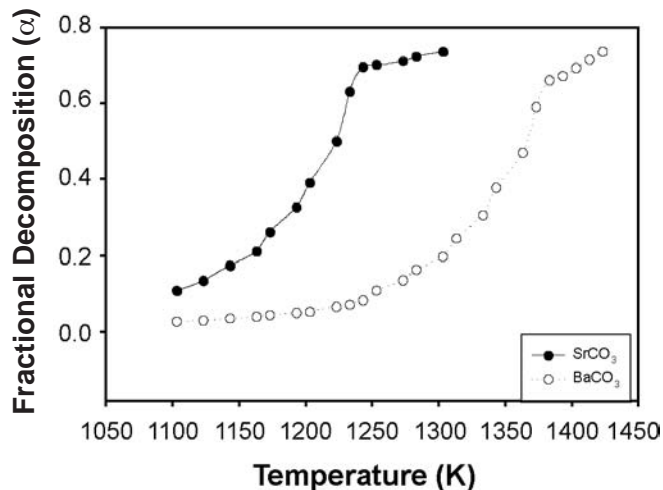*[Figura 1: Variação da perda fracional com a temperatura na faixa de decomposição de $MgCO_3$ e $CaCO_3$.]*

Figure 2: Variation of fractional decomposition with temperature in the decomposition range of $SrCO_3$ and $BaCO_3$.
[Figura 2: Variação da decomposição fracional com a temperatura na faixa de decomposição de $SrCO_3$ e $BaCO_3$.]

India) was studied under non-isothermal condition by thermogravimetry. To make these materials moisture free they were first heated to 200 ºC in an atmosphere of carbon dioxide. The samples were cooled to room temperature and allowed to stand overnight under carbon dioxide atmosphere.

TG-DTA measurements of the samples were carried out in air using a Netzsch (Germany) simultaneous thermal analyzer (STA-409) in air. Nitrogen was used as initial purge gas and scans were carried out at four different heating rates of 2.5, 5, 7.5 and 10 K/min. The fractional losses due to the decomposition reactions of the samples in the decomposition ranges have been shown in Figs. 1 and 2.

RESULTS AND DISCUSSION

Most workers consider that the movement of an interface between the two solid phases controls the rate of reaction and that the rate equation can be expressed in the form:

$$\frac{d\alpha}{dt} = k\,(1-\alpha)^n \qquad\qquad (A)$$

k is the rate constant, n the order of reaction, and α the fraction of the carbonates decomposed at time t.

In thermogravimetric (TG) studies, this can be equated to w/w_F, where, w is the weight loss at time t and w_F the total weight loss. By incorporating the expressions of heating rate h and the rate constant K in the above equation, rearranging and integrating it, the following equation can be written ($K = A\,e^{-E/RT}$ and the heating rate $h = dT/dt$):

$$\int_0^X \frac{dX}{(1-X)} = \frac{A}{h}\int_0^T e^{-E/RT}\,dT \qquad\qquad (B)$$

Out of several approximate solutions of the above equations which do not take into account any mechanism,

the solution given by Coats and Redfern appears to be less free from error [8] and hence it was first tried in the experiment to find out the kinetic parameters. The equation may be written in the form:

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2\,(1-n)}\right]=\log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT} \qquad (C)$$

α is the fraction of the sample decomposed at time t, n the order of the reaction, T the temperature (K), A the pre-exponential factor, R the gas constant, and a the conversion factor to transfer from a time scale to a temperature scale, i.e., a = dT/dt.

Equation (C) holds true for all values of n =1; in which case the equation becomes:

$$\log_{10}\left[-\log_{10}\frac{(1-\alpha)}{T^2}\right]=\log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT} \qquad (D)$$

If it is assumed that the expression $\log_{10}\dfrac{AR}{aE}\left[1-\dfrac{2RT}{E}\right]$ remains constant over the temperature range of the decomposition, then a plot of either

(a) $\log_{10}\left[\dfrac{1-(1-\alpha)^{1-n}}{T^2\,(1-n)}\right]$ as a function of 1/T for n ≠ 1

or

(b) $\log_{10}\left[-\log_{10}\dfrac{(1-\alpha)}{T^2}\right]$ as a function of 1/T for n=1

should result in a straight line, of slope –E/2.303R

For different values of n the plots were carried out using Curve Expert software and from the correlation co-efficient and standard error of the linear plots the values of n, activation energy and the pre-exponential factors were determined. The results are shown in Tables I-V. A close scrutiny of the tables suggested that the activation energy for the decomposition reaction was the lowest in the case

Table II - Variation in standard error and correlation coefficient for $CaCO_3$ with different values of n (for Coat-Redfern Model).
[Table II - Variação do erro padrão e do coeficiente de correlação para $CaCO_3$ com diferentes valores de n (para o modelo de Redfern-Coat).]

n	SE	CC
0.2	3.4710	0.6043
0.4	0.9332	0.7796
0.5	3.0859	0.6343
0.8	2.5986	0.6933
0.9	2.3400	0.6724
1.0	**1.8716**	**0.9055**
1.1	1.9159	0.7863
1.2	1.9039	0.8113
1.3	1.8956	0.8266
1.4	1.9533	0.8298
1.5	2.1023	0.8199
1.8	3.0174	0.7378
2.0	3.8538	0.6694

Table I - Variation in standard error and correlation coefficient for $MgCO_3$ with different values of n (for Redfern-Coat model).
[Table I - Variação do erro padrão e do coeficiente de correlação para $MgCO_3$ com diferentes valores de n (para o modelo de Redfern-Coat).]

n	SE	CC
0.6	3.4984	0.6572
0.8	2.8606	0.7044
0.9	2.4542	0.7295
1.0	**0.5245**	**0.9875**
1.1	1.1567	0.9296
1.2	0.5746	0.9841
1.25	0.7215	0.9846
1.27	0.611	0.9835
1.3	0.8159	0.9720
1.5	2.755	0.801
2.0	8.1365	0.466

Table III - Variation in standard error and correlation coefficient for $SrCO_3$ with different values of n (for Coat-Redfern Model).
[Table III - Variação do erro padrão e do coeficiente de correlação para $SrCO_3$ com diferentes valores de n (para o modelo de Redfern-Coat).]

n	SE	CC
0.6	1.1951	0.8359
0.8	1.4952	0.8360
0.99	0.9558	0.8505
1.0	**0.4358**	**0.9934**
1.1	0.8639	0.9391
1.5	0.9128	0.9505
1.55	0.9933	0.9433
1.6	1.4380	0.8984
1.75	1.438	0.8984
2.0	2.141	0.8206
3.0	5.3617	0.5487

of $MgCO_3$ decomposition, whereas, it increased steadily with then increase in the molecular mass of the carbonates and became maximum for the decomposition of $BaCO_3$. All the decomposition reactions followed first order reaction kinetics.

Enthalpy values of the samples were calculated from the standard enthalpy changes using Kirchoff's law corresponding to the reaction temperature. Since the decomposition occurred over a wide temperature range, the reaction temperature was taken as the temperature for the mid point of the decomposition.

For most solids, the constant pressure heat capacity (Cp) as a function of temperature is expressed by a formula of the type:

Table IV - Variation in standard error and correlation coefficient for $BaCO_3$ with different values of n (for Coat-Redfern Model).
[Table IV - Variação do erro padrão e do coeficiente de correlação para BaCO$_3$ com diferentes valores de n (para o modelo de Redfern-Coat).]

n	SE	CC
0.8	1.3129	0.7157
0.9	1.4519	0.7393
0.98	1.7031	0.7438
0.99	1.0708	0.7387
1.0	**0.2901**	**0.9968**
1.11	1.0232	0.8857
1.2	0.9977	0.9021
1.3	0.9609	0.9158
1.4	0.9413	0.9242
1.5	0.9562	0.9267
1.52	0.9643	0.9265
1.55	0.9798	0.9256
1.6	1.0147	0.9229
1.75	1.1821	0.9065
2.0	1.6136	0.8589

$$Cp = a + bx10^{-3}T + cx10^5 T^{-2} \qquad (E)$$

a, b and c are constants and T is the absolute temperature.

The heat capacity estimation was carried out following Kubaschewski and Unal method [9]. This model expresses the heat capacity of a substance as the sum of the contributions from the ionic groups, which make up the compound. Using $CaCO_3$ as an example, $Cp[CaCO_3, 298] = \Xi_{Ca} + \Xi_{CO_3}^{2-}$, where Ξ represents the particular contribution of an ionic group. The values of a, b and c are given by Kubaschewski and Unal [8]:

$$a = \frac{[T_d x10^{-3}(\Sigma\Xi + 1.2524n) - 0.298nx10^5 T_d^{-2} - 2.16n]}{T_d x\,10^{-3} - 0.298} \qquad (F)$$

$$b = \frac{6,125n\,x\,10^5 nT_d^{-2} - \Sigma\Xi}{T_d x\,10^{-3} - 0.298} \qquad (G)$$

$$c = -n \qquad (H)$$

T_d is the midpoint of the decomposition range, i.e $\alpha = 0.50$ and n is the number of atoms per molecule. Using these equations heat capacities were measured for all the carbonates as a function of temperature.

It can be seen that, within the experimental error, good agreement was obtained between the observed activation energy and the calculated value for ΔH for the alkaline earth metal carbonates (Table V). The similarity in the activation energy and enthalpy of decomposition suggested that the reaction rate is governed by the rate of heat transfer to the reaction zone.

The activation energy for all carbonates was higher than the enthalpy of reaction excepting for $SrCO_3$. This suggested that the decomposition of $SrCO_3$ is more irreversible compared to the other carbonates.

From this apparent agreement it can be concluded that the reverse reaction, i.e., the recombination of oxide and carbon dioxide to form carbonates, must involve zero energy of activation.

Table V - Kinetic parameters from Coat-Redfern equation for the bivalent-metal carbonates.
[Table V - Parâmetros cinéticos da equação de Coat-Redfern para carbonatos de metais divalentes.]

Compound	Decomposition range (K)	Order of reaction	Activation energy (C-R) KJ/mol	Pre-exponential factor (A)	Enthalpy of reaction* (KJ/mol)
$MgCO_3$	783-1023	1.0	140.16	2.0×10^6	128.25
$CaCO_3$	673-1233	1.0	190.46	3.4×10^7	177.25 (1023 K)
$SrCO_3$	1083-1273	1.0	238.32	7.3×10^7	254.37 (1203 K)
$BaCO_3$	1203-1428	1.0	292.98	1.4×10^8	267.78 (1303 K)

CONCLUSIONS

The kinetics of thermal decomposition of four alkaline earth carbonates was studied from thermogravimetry under non-isothermal conditions using Coat and Redfern's integral approximation method. The decomposition reactions followed first order reaction kinetics. The activation energy of the decomposition reactions increased with the increase in the molecular mass of the carbonates. The enthalpy changes for these decomposition reactions were also calculated using heat capacity values determined by the process described by Kubalchewski and Unal. The activation energy for all the carbonates studied was higher than the enthalpy of reaction excepted for $SrCO_3$, thus it suggesting that the decomposition of $SrCO_3$ is more irreversible compared to the other carbonates.

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