

Non-isothermal decomposition kinetics of magnesite

(Decomposição não isotérmica de magnesita)

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Abstract

Kinetics of thermal decomposition of Indian magnesite was studied by thermo-gravimetric analysis under non-isothermal condition. Coats and Redfern Integral approximation method was used to determine the kinetic parameters. Using the kinetic parameters different kinetic functions were analyzed with the experimental data to ascertain the decomposition mechanism of magnesium carbonate and it was observed that the decomposition reaction followed a contracting sphere kinetic mechanism.

Keywords: magnesite, decomposition kinetics, thermogravimetry, kinetic function

Resumo

A cinética de decomposição térmica de magnesita indiana foi estudada por análise termogravimétrica sob condição não-isotérmica. O método da aproximação da integral de Coats e Redfern foi usado para determinar os parâmetros cinéticos. Usando estes parâmetros, foram analisadas diferentes funções cinéticas com os dados experimentais para avaliar o mecanismo de decomposição do carbonato de magnésio e foi observado que a reação de decomposição segue o mecanismo cinético de contração de esfera.

Palavras-chave: magnesita, cinética de decomposição, termogravimetria, função cinética.

INTRODUCTION

The mineral magnesite essentially consists of magnesium carbonate crystals belonging to the trigonal system, similar to quartzite. When magnesium carbonate is heated it undergoes decomposition, which is an important class of solid-state reaction. The decomposition reaction of carbonates in general is a rich field of investigation from the reaction kinetics point of view. A thorough understanding of the decomposition kinetics can be useful in elucidating the reaction mechanism, which is significantly important in controlling the course of the reaction, quality of the product and optimization of the process parameters. Many workers have carried out studies on the decomposition kinetics of carbonates [1-8] with respect to parameters like crystallinity, surface area, impurities present, particle size, and compaction of the starting materials. It was reported that [6] the isothermal kinetic data of magnesite samples fit the "contracting sphere model", which describes the reaction as a phase-boundary process. However, not much mechanistic information is available on the decomposition process of natural magnesite under non-isothermal dynamic condition.

In the present investigation decomposition kinetics of magnesite sample of Indian origin (Almora) was studied. Mineralogically it is ultra-basic rock and formed by replacement of dolomite and limestone as masses and is observed to be associated with calcite and dolomite and

contained coarse, elongated grains of magnesite. Findings of the present investigation can be related to the magnesite samples of similar geology.

EXPERIMENTAL

A magnesite sample of Indian origin (Almora) was used for the present investigation. The sample was used in the

Table I - Physico-chemical characteristics of magnesite sample.

[Table I - Características físico-químicas da amostra de magnesita.]

Chemical Constituent	% Composition
SiO ₂	1.82
Al ₂ O ₃	0.28
Fe ₂ O ₃	1.12
TiO ₂	0.02
CaO	0.92
MgO	45.42
LOI at 800 °C	50.24
Physical Properties	
Av. Particle Size	14.44 μm
Sp. Surface Area	0.3741 sqm/gm

powder form. The surface area, average particle size and chemical composition of the sample were determined and the results are given in Table I. The kinetic study of the decomposition process was carried out by thermogravimetry. A thermo-balance was used for the non-isothermal study of the kinetic parameters from a dynamic thermo-gravimetric study, with a heating rate of 10 °C/min. The sample was taken in the form of loose powder.

RESULTS AND DISCUSSION

Compared to conventional isothermal studies, non-isothermal methods for determining kinetic parameters have several advantages. A single sample and fewer data are required and the kinetics can be calculated over an entire temperature range in a continuous manner. But a particular disadvantage of the non-isothermal data method, compared to the isothermal one, is the uncertainty over the reaction mechanism.

Again conventional methods [9-11] used for the kinetic analysis results in ambiguity under linear heating conditions, especially if the studied reaction follows a diffusion-controlled kinetic law. In the present work, the kinetic parameters were first calculated using a model free approach of Coats and Redfern [12] from DTG data (Fig. 1) in the following way.

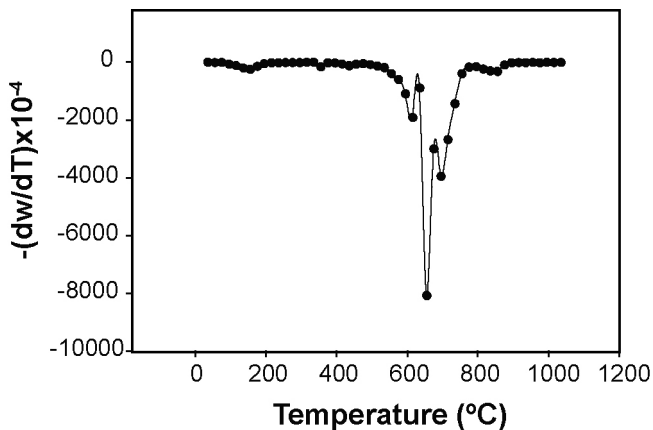


Figure 1: DTGA plot of the magnesite sample.
[Figura 1: Gráfico da diferencial da análise termogravimétrica da amostra de magnesita.]

The rate of decomposition of raw magnesite is given by

$$-dw/dt = kw \quad (A)$$

Incorporating into this equation $k = Ae^{-\frac{E}{RT}}$ and heating rate $h = dT/dt$ and rearranging we get,

$$\frac{1}{w} \frac{dw}{dT} = \frac{A}{h} e^{-\frac{E}{RT}} \quad (B)$$

The rate equation may also be expressed in terms of fractional conversion X and reaction order n as follows:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} - dx/dt = k(1-\alpha)^n \quad (C)$$

Incorporating expressions of heating rate h and rate constant k into (C), rearranging and integrating the following equation is obtained.

$$\int_0^x \frac{dx}{(1-\alpha)^n} = \frac{A}{h} \int_0^T e^{-\frac{E}{RT}} dT \quad (D)$$

Several approximate solutions of the above equation in literature are available. The equations given by Coats & Redfern are the most commonly used and are as follows:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{hE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{for } n=1 \quad (E)$$

$$\ln\left[-\ln\left\{\frac{1-(1-x)^n}{(1-n)T^2}\right\}\right] = \ln\left[\frac{AR}{hE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{for } n \neq 1 \quad (F)$$

Therefore, a plot of $\ln\left\{\frac{\ln(1-\alpha)}{T^2}\right\}$ vs. $1/T$ for $n=1.0$ and $\ln\left[-\ln\left\{1-(1-\alpha)^{1-n}\right\}/(1-n)T^2\right]$ vs. $1/T$ for $n \neq 1$ gives the value of E from the slope and value of A from the intercept.

Using different 'n' values equations (E) and (F) were plotted as discussed above. From these plots that 'n' value, which resulted in the best correlation coefficient and the minimum standard error was selected. In the present investigation it was observed to be 1.5. (Table II). The activation energy as determined from the slope and the intercept of the plot using $n=1.5$ was found to be 143.37 kJ/mol and $7.4 \times 10^7 \text{ s}^{-1}$ respectively (Table III).

Table II - Values of the correlation coefficient and standard error for different n values.

[Tabela II - Valores de coeficiente de correlação e erro padrão para diferentes valores de n.]

n	CC	SE
0.5	0.9323	0.9964
0.75	0.9243	1.2686
1.0	0.9093	1.0574
1.25	0.9388	1.1231
1.5	0.9846	0.2422
1.75	0.9240	1.0229
2.0	0.9385	1.6310

Table III - Values of the kinetic parameters.

[Tabela III - Valores dos parâmetros cinéticos.]

Employed Equation	Activation Energy (KJ Mol ⁻¹)	Pre-exponential Factor (s ⁻¹)
Coats and Redfern [12]	145.56	7.4×10^7
Jerez et al [13]	131.37	7.09×10^7

To determine the kinetic function of the decomposition reaction the method proposed by Jerez et al. [13] was used. The rate of a reaction of a thermal decomposition of solids can be expressed by the following general equation:

$$\frac{d\alpha}{dt} = A.e^{-\frac{E}{RT}} f(\alpha) \quad (G)$$

where $f(\alpha)$ is a function which depends on the actual reaction mechanism. When the temperature of the sample is increased at a constant rate,

$$\beta = \frac{dT}{dt}$$

we can write

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (H)$$

By differentiating the logarithmic form of equation (H) with respect to $d(\ln(1-\alpha))$ we obtain:

$$\frac{d(\ln(d\alpha/dT))}{d(\ln(1-\alpha))} = -\frac{E}{R} \frac{d(1/T)}{d(\ln(1-\alpha))} + \frac{d(\ln f(\alpha))}{d(\ln(1-\alpha))} \quad (I)$$

or,

$$\frac{\Delta(\ln(d\alpha/dT))}{\Delta(\ln(1-\alpha))} = -\frac{E}{R} \frac{\Delta(1/T)}{\Delta(\ln(1-\alpha))} + \frac{\Delta(\ln f(\alpha))}{\Delta(\ln(1-\alpha))} \quad (J)$$

or,

$$\frac{\Delta(\ln(d\alpha/dT)) - \Delta(\ln f(\alpha))}{\Delta(\ln(1-\alpha))} = -\frac{E}{R} \frac{\Delta(1/T)}{\Delta(\ln(1-\alpha))} \quad (K)$$

and, thus, the plots of the left-hand side of equation (11) against $\Delta(1/T) / \Delta(\ln(1-\alpha))$ should be a straight line with a slope of $-E/R$, irrespective of the $f(\alpha)$ employed. However, we can select $f(\alpha)$ that best fit the actual mechanism of the studied reaction by means of the intercept value, which, in an ideal agreement with equation (K) should be zero (Table V).

From the plot of equation (K) with different kinetic functions as listed in Table IV, it was observed that the value of the intercept was the minimum for contracting sphere mechanism. The activation energy, as determined from the slope of the plot, was found to be 131.37 kJ/mol, which is slightly lower than the value obtained using the model free approach. The reaction under state is therefore also interface controlled with progressively contracting volume of the starting reactant particles like that isothermal condition. From the identified mechanism it is apparent that rapid growth rate at the product phase (MgO) and progressive removal of the stable product layer (MgO) from the reactant layer ($MgCO_3$) during the decomposition of magnesite takes place. From the mechanism it is clear that the mass transfer through the static interface between un-decomposed carbonates and formed oxides is the rate controlling process for magnesite.

Table IV - Classification of kinetic models for reaction mechanism [11].

[Tabela IV - Classificação de modelos cinéticos para mecanismo de reação [11].]

Kinetic classification	$f(\alpha) = (1/k)(d\alpha/dt)$
(1) Sigmoidal α -t curves	
Avrami-Erofeev (A2)	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$
Avrami-Erofeev (A3)	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$
Avrami-Erofeev (A4)	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$
Prout-Tompkins (B1)	$\alpha(1-\alpha)$
(2) Acceleratory α -t curves	
Power law (P1)	$n\alpha^{(n-1)/n}$
Exponential Law (E1)	α
(3) Deceleratory α -t curves	
(3.1) Based on Geometrical Models	
Contracting area (R2)	$2(1-\alpha)^{1/2}$
Contracting volume (R3)	$2(1-\alpha)^{1/3}$
(3.2) Based on diffusion mechanism	
One-dimensional (D1)	α^{-1}
Two dimensional (D2)	$[- \ln(1-\alpha)]^{-1}$
Three Dimensional (D3)	$2/3(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
(3.3) Based on "order" of reaction	
First-order (F1)	$(1-\alpha)$
Second-order (F2)	$(1-\alpha)^2$
Third-order (F3)	$1/2(1-\alpha)^3$

Table V - Intercept and standard error values for different kinetic functions.

[Tabela V - Valores de interceptos e de erro padrão para diferentes funções cinéticas.]

Kinetic Function	Standard Error	Intercept
Exponential Law (E1)	0.9717	0.637
Avrami-Erofeev (A2)	0.9683	0.094
Avrami-Erofeev (A3)	0.9795	0.171
Avrami-Erofeev (A4)	0.9895	0.192
Prout-Thompkin(B1)	0.9270	0.588
Contracting Area (R2)	0.9420	0.465
Contracting Volume (R3)	0.9995	0.071
One Dimensional(D1)	0.9246	0.378
Two-Dimensional (D2)	0.9495	0.519
Three Dimensional(D3)	0.9733	0.108
1 st -Order(F1)	0.9818	0.432
2 nd Order(F2)	0.9799	0.098
3 rd Order(F3)	0.9610	0.276

After the mechanism was established, the pre-exponential factor was determined following the process described by Jerez et al [13].

$$\ln\left(\frac{d\alpha/dT}{f(\alpha)}\right) = \ln \frac{A}{\beta} - \frac{E}{RT} \quad (L)$$

The value of the pre-exponential factor was observed to be $7.09 \times 10^7 \text{ sec}^{-1}$, which is in close agreement with the value determined using Coats and Redfern [12] equation.

SUMMARY AND CONCLUSION

Kinetics of thermal decomposition of Indian magnesite was studied under non-isothermal condition using thermogravimetry. Coats and Redfern integral approximation method was first used to determine the activation energy (145.56 kJ/mol) and the pre-exponential factor ($7.4 \times 10^7 \text{ s}^{-1}$) of the reactions. The kinetic function of the decomposition reaction was determined by the intercept method described by Jerez *et al* and followed contracting volume of the spherical reactant particles. The activation energy and the pre-exponential factor determined by the intercept method were found to be in agreement with the values determined by Coats and Redfern method.

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