

AN INVESTIGATION OF THE DECOMPOSITION MECHANISM OF CALCIUM CARBONATE

Received – Priljeno: 2016-09-06

Accepted – Prihvaćeno: 2016-12-06

Original Scientific Paper – Izvorni znanstveni rad

This paper focuses on investigating the decomposition mechanism of calcium carbonate. The non-isothermal thermal decompositions of calcium carbonate under vacuum and flowing nitrogen atmosphere have been studied by thermogravimetric analysis. With the application of the advanced nonlinear isoconversional method, the determined activation energy for each condition is dependent on the extent of reaction. Based on the dependences, a process involving two consecutive decomposition steps has been simulated. The simulation results match the experimental results of flowing nitrogen atmosphere. Results indicate that the decomposition of calcium carbonate undergoes the process of the formation of the intermediate and metastable product.

Key words: calcium carbonate, thermal decomposition, advanced nonlinear isoconversional method, activation energy, mechanism

INTRODUCTION

The thermal decomposition of calcium carbonate has important implications in extra-

consecutive metallurgy. The decomposition process is generally represented as the simplistic stoichiometry, $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. However, the decomposition process is not as simple as the equation, Rodriguez-Navarro et al. [1] have detected the metastable CaO^* through the microscope examination, and Zhao et al. [2] have investigated the intermed-

iates by the quantum chemical computing. In the thermal kinetic analysis of this solid-state reaction, large investigations have been done, they have shown that different experimental conditions and methods for analyzing kinetic data lead to different kinetic descriptions [3]. The traditional kinetic analysis based on a constant kinetic parameter may offer inadequate description about the intermediate and metastable product in the multi-step process. In contrast with the constant activation energy, the dependence of activation energy on the extent of reaction, derived by the isoconversional method under non-isothermal condition, has the advantage of indicating the multi-step character of the process. Some researches [4, 5] based on the isoconversional method have been reported with different experimental conditions, however, to further investigate the complex decomposition mechanism caused by the in-

termediate and metastable product, there is still much work to do.

In this work, two dependencies of the activation energy on the extent of reaction for non-isothermal decomposition of CaCO_3 under vacuum and flowing nitrogen atmosphere have been derived by the advanced nonlinear isoconversional method respectively. Based on the kinetic information from the two dependencies, this paper has simulated a process that involves two consecutive decomposition steps, with the purpose to demonstrate the complexity of the decomposition mechanism caused by the intermediate and metastable product.

THEORY

Kinetic analyses of solid-state reactions under non-isothermal conditions are usually based on the following kinetic equation:

$$\frac{d\alpha}{dT} = k(T) f(\alpha) = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where T is the temperature, k is the rate constant expressed by Arrhenius equation, β is the heating rate, α is the extent of reaction, $f(\alpha)$ is a function that represents the reaction model, A is the frequency factor, E is the activation energy, R is the gas constant.

Equation 1 can be rearranged and integrated to obtain

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{A}{\beta} I(E, T) \quad (2)$$

where $g(\alpha)$ is the integral form of the reaction model, $I(E, T)$ is an approximation of the exponential integral, the 3th degree Senum-Yang approximation [6] is adopted here, as

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$$I(E, T) = T \cdot \exp(-u) \cdot \left(\frac{u^2 + 10u + 18}{u^3 + 12u^2 + 36u + 24} \right) \quad (3)$$

where $u = E/RT$.

According to an assumption that the reaction model is independent of the heating rate, an advanced nonlinear isoconversional method [7] has been developed, which replace the regular integration from 0 to T_α (equation 2) used in original isoconversional method [8] with integration over small segment ($\Delta\alpha$). For a set of n experiments carried out at different heating rates β_i ($i = 1, \dots, n$), this method can be represented as

$$\Omega(E_\alpha) = \min \left| \sum_{i=1}^n \sum_{j \neq i}^n \frac{\beta_j J(E_\alpha, T_{\alpha, j})}{\beta_i J(E_\alpha, T_{\alpha, i})} \right| \quad (4)$$

where,

$$J(E_\alpha, T_\alpha) \equiv \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT = I(E_\alpha, T_\alpha) - I(E_\alpha, T_{\alpha-\Delta\alpha})$$

and α varies from $2\Delta\alpha$ to $1 - \Delta\alpha$ with a step $\Delta\alpha = (m + 1)^{-1}$, where m is the number of the equidistant values of α chosen for the analysis. Substituting experimental values of β_i and $T_{\alpha, i}$ into equation 4, the E_α value can be found by minimizing this function.

EXPERIMENTAL

In this work, the chemical reagent of CaCO_3 with high purity was supplied by Sigma-Aldrich, Inc. (Lot Number MKBL0094V), average particle size of sample was $40 \mu\text{m}$. The thermogravimetric analysis (TGA) experiments were carried out using a Setaram SETSYS Evolution. The temperature range was from ambient to 1600°C , with heating rate from $0,1$ to 100 K/min . The thermocouple was placed directly under the sample. The thermal history was determined by the analyzer controller after a standard calibration procedure under the proper conditions. The weighting capacity was 50 mg with a sensitivity of $0,1 \mu\text{g}$. Samples of CaCO_3 ($2,0 \pm 0,1 \text{ mg}$) were placed in open platinum crucible (5 mm by 8 mm) and heated under vacuum (10^{-5} mbar) and flowing nitrogen (30 ml/min) atmosphere. The instrument was programmed to heat the sample from room temperature to 1200 K at constant heating rates of $7,5$, 10 , and 15 K/min .

RESULTS AND DISCUSSIONS

Data from the TGA experiments are shown in Figure 1. $\alpha - T$ curves of two conditions of the vacuum and the flowing nitrogen atmosphere are distinguished by dot lines and solid lines, and the different heating rates are indicated. Note that the TGA results obtained at nitrogen atmosphere exhibit a shift of the decomposition reaction to higher temperatures.

For each condition, the non-isothermal data were analyzed by the advanced nonlinear isoconversional method [7], in which $\Delta\alpha = 0,1$. The obtained dependences of E_α on α are shown in Figure 2. For both condi-

tions, the E_α values change with α , they may indicate that the thermal decomposition of calcium carbonate is a tangled interplay of different single species-dependent steps, and these steps have their own different activation energies [9]. For each condition, the E_α dependence shows the decreasing trend. Linearly fit each set of the E_α values by the least-squares method, and extend to $\alpha = 0$ and $\alpha = 1$, which are regarded as defining the general value range. In vacuum, the E_α values change in a general range of $285 \sim 220 \text{ kJ/mol}$, while in the flowing nitrogen atmosphere, the E_α values change in a general range of $210 \sim 185 \text{ kJ/mol}$. The two sets E_α values here reported are accord with those most commonly reported in the literature [10].

Some authors [11] have reported a higher activation energy value of the calcium carbonate decomposition under vacuum conditions, here, by the isoconversional method, the determined E_α values in vacuum are higher than in flowing nitrogen atmosphere. It is commonly known that the vacuum conditions increase the proba-

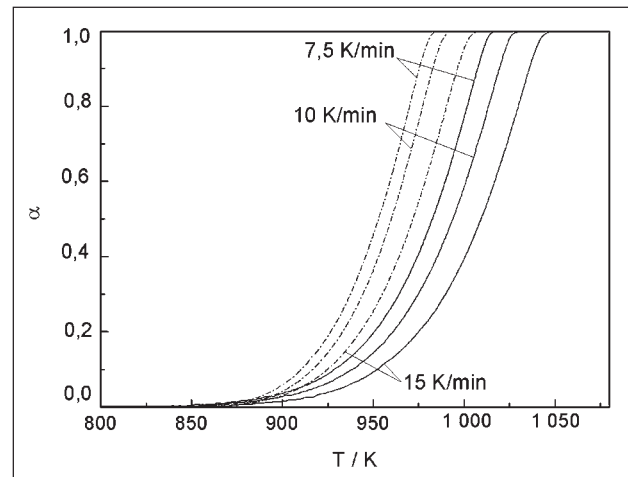


Figure 1 $\alpha - T$ curves for the thermal decomposition of calcium carbonate under vacuum (dotted lines) and flowing nitrogen atmosphere (solid lines) at different heating rates.

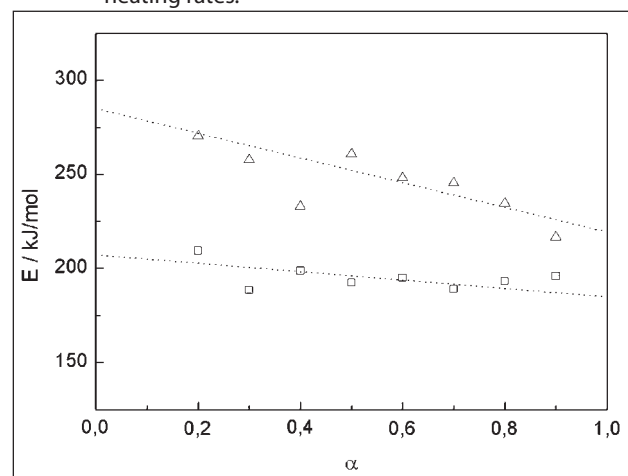
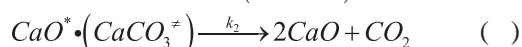
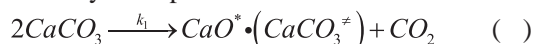


Figure 2 Dependences of the E_α on α of vacuum (open triangles) and flowing nitrogen (open squares) determined by the advanced nonlinear isoconversional method. The dashed lines represent the linear regression results.

bility of the formation of metastable CaO^* to be observed may account for the higher activation energy value. Moreover, it has been observed that the change of the pressure influences the coverage of metastable CaO^* on the reaction surface [12, 13]. Therefore, in view of the actual experimental conditions that the vacuum degree is decreasing, in addition, with the increase of the temperature and the accumulation of the product gas the actual pressure is increasing, it may be inferred that the metastable CaO^* has contributed to the decreasing E_a values.

Furthermore, through the quantum chemical computing, the intermediate has been proved to exist before the decomposition [2]. Assuming the coexistence of the intermediate and the metastable CaO^* , the decomposition process may be expressed as follow:



where, the superscript “ \ddagger ” and “*” respectively denote the intermediate and the metastable phase. Referring to [14], the kinetic analysis of this sequence of successive reactions for non-isothermal linear heating with the rate β is performed with the corresponding kinetic equations:

$$\frac{d\alpha_1}{dT} = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right) (1 - \alpha_1) \quad (5)$$

$$\frac{d\alpha_2}{dT} = \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right) (\alpha_1 - \alpha_2) \quad (6)$$

where α_1 and α_2 are the values of the conversion degree for reaction and , respectively, the overall degree of conversion, α , is given by: $\alpha = (\alpha_1 + \alpha_2)/2$. In this work, the E_1 and E_2 values are assigned with the upper limit and lower limit of the two derived E_a dependences, which are $E_1 = 285$ kJ/mol and $E_2 = 185$ kJ/mol. By the method mentioned in [15], the value of A_1 is derived from the data of vacuum and the value of A_2 is derived from the data of flowing nitrogen, which are $A_1 = 8\,901,5 \times 10^9$ 1/s and $A_2 = 9\,889,6 \times 10^3$ 1/s. The numeric method for solving this equations system is given in [14], here the temperature range is comprised by T_α ($0,1 \leq \alpha \leq 0,9$) from the data of vacuum, by which the $\alpha_1 - T$, $\alpha_2 - T$, and $\alpha - T$ dependences derived are shown in Figure 3.

It can be seen from Figure 3 that the simulated $\alpha - T$ result of a process involving two consecutive decomposition steps with the kinetic parameters derived from the non-isothermal data by the advanced nonlinear isoconversional method matches the experimental result of flowing nitrogen within the specified temperature range for each heating rate. And, the derived activation energy (285 kJ/mol) for the first step to form the intermediate and metastable product agrees with the reported highest energy barrier (283,31 kJ/mol) to overcome to form an intermediate in this reaction by the quantum chemical calculation [2]. It can be concluded that the decomposi-

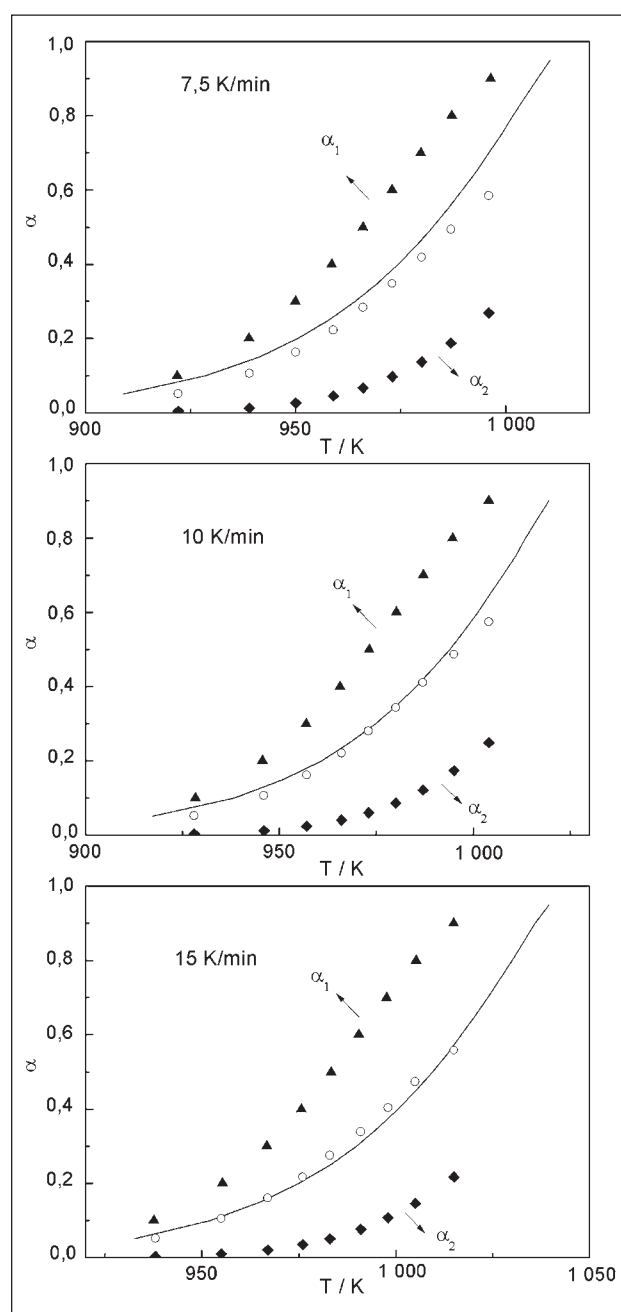


Figure 3 The two-step simulation result for each heating rate determined by Equations 5 and 6: α_1 for step I (solid triangles), α_2 for step II (solid diamonds), and α for the overall process (open circles). The solid line represents the experimental result under flowing nitrogen atmosphere.

tion of calcium carbonate undergoes the process of the formation of the intermediate and metastable product.

CONCLUSIONS

The mechanism of the thermal decomposition of calcium carbonate was investigated from the thermogravimetric analyses under the non-isothermal conditions of vacuum and flowing nitrogen atmosphere. With the application of the advanced nonlinear isoconversional method on the kinetic data of each condition, the determined activation energy is dependent on the extent of reaction, which indicates the multi-step char-

acter of the decomposition. Based on the determined dependences, the kinetics of the decomposition process is described as undergoing two successive decomposition steps. The proposed mechanism manifests the formation of the intermediate and metastable product in the decomposition process.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No.51634004) and the Educational Department of Liaoning Province (No. L2015552).

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Note: The responsible translator for English language is X.T. Yin - University of Science and Technology Liaoning, China