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Thermal decomposition of basic zinc carbonate in nitrogen atmosphere

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Abstract

Dynamic kinetic analyses were performed on basic zinc carbonate using TG and DTA measurements in N_2. The thermal behavior and the kinetics of decomposition were studied. The effect of procedural variables on the kinetics was investigated. In this work, the procedural variables included heating rate and sample size. To estimate the activation energy of decomposition, the Friedman isoconversional method was applied. The activation energy (E_a) was calculated as a function of conversion (a).

Keywords: Basic zinc carbonate; Decomposition kinetics

1. Introduction

Zinc oxide (ZnO) is a white powder with exceptional and unique properties. In recent years, it has received a considerable amount of attention because of many applications it has found in shock resistance, sound insulation, photosensitization, fluorescence, gas sensitization, and catalysis [1–4]. Synthesis of zinc oxide is often achieved by thermal decomposition of the precursor of basic zinc carbonate obtained via chemical reaction. The behavior of the basic zinc carbonate under heating is of great value for the industrial applications.

Extensive work has been carried out on the non-isothermal decomposition kinetics of solid system. Multiple techniques were reported in literatures for determining the reaction mechanism and deducing kinetic parameters [5–11]. Contrary to the homogeneous reaction, the kinetics of solid decomposition will vary with many factors such as the change of reaction condition, crystal form and particle size. It is mainly owing to the influence of heat transfer and mass transfer on the phase boundaries [12]. Thermal analysis of basic zinc carbonate has been studied [13], its decomposition reaction as suggested by Eq. (1).

$$Zn_3CO_3(OH)_4 \rightarrow 3ZnO + CO_2 \uparrow + 2H_2O \uparrow \quad (1)$$

In the present work, the objective is to determine basic zinc carbonate decomposition kinetics in nitrogen atmosphere and to evaluate whether kinetic parameters are influenced by the procedural variables used in the kinetic study.

2. Experimental

The synthesis of basic zinc carbonate is described elsewhere [14]. The precipitate was filtered, washed with deionized water and dried at 100 °C to steady weight. The product was submitted to thermal analysis. All the experiments were performed on Mettler Toledo simultaneous thermal analyzer (TGA/SDTA851e) with system interface device and a computer workstation. All the samples were placed in aluminum crucibles. Three series of experiments were performed using sample sizes of 5 ± 0.4, 15 ± 0.4 and 30 ± 0.4 mg. All the experiments were conducted under nitrogen as the purge gas. The flow rate of the gas was 50 ml/min. The range of temperature studied was from 50 to 400 °C, at the heating rates of 10, 20, 30 and 40 °C/min.

3. Theory

The commonly used equation in the non-isothermal decomposition kinetics is presented as [15]

$$\frac{da}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(a)] \quad (2)$$

where a is the fraction decomposed at time t, da/dt the rate of the reaction, A the pre-exponential factor, E_a the apparent

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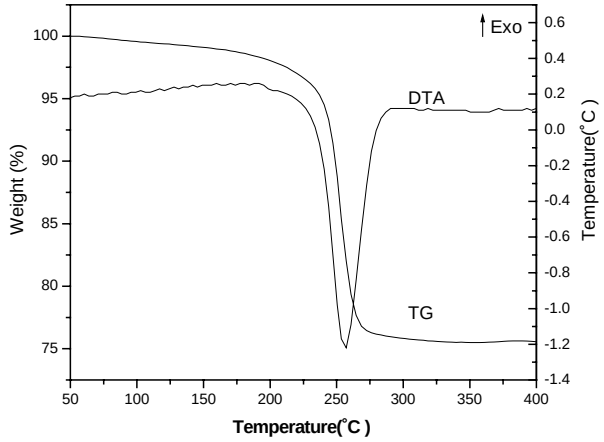

Fig. 1. Typical TG-DTA plot for basic zinc carbonate.

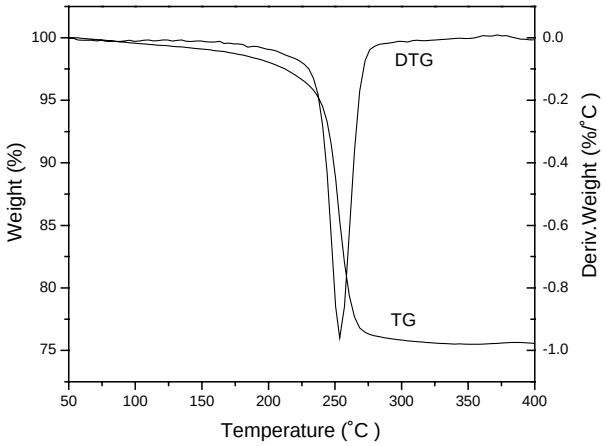

Fig. 2. Typical TG-DTG plot for basic zinc carbonate.

activation energy, and $f(a)$ is an expression describing the kinetic model. Possible kinetic models and $f(a)$ expressions are listed in literature [16].

The purpose of kinetic analysis in thermal analysis is to obtain conclusions about the mechanism of a reaction or to extract reference values of certain parameters, such as activation energy.

The apparent activation energy of the decomposition process in non-isothermal conditions can be calculated by isoconversional method. The isoconversional method avoids the use of explicit kinetic models. Isoconversional method of Friedman is applied on TG data. It starts from Eq. (2) and follows that:

$$\ln\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right) = -\frac{E_\mathrm{a}}{RT} + \ln[Af(a)] \tag{3}$$

The slope of $\ln(\mathrm{d}a/\mathrm{d}t)$ vs. $1/T$ for the same value of a gives the value of apparent energy. The apparent activation energy can be calculated for various values of a and in this way it is possible to verify an invariance of E_a with respect to a.

4. Results and discussion

Figs. 1 and 2 represent TG-DTG-DTA plots of basic zinc carbonate, for an experiment carried out at 10 °C/min with a sample size of 5 mg in nitrogen. The TGA trace confirm that the decomposition process starts at about 220 °C and reaches a constant weight loss of 24%, corresponding to zinc oxide.

The experiments were carried out with different heating rates and sample sizes in order to determine the effect of changing the experimental variables on the kinetics. Tables 1 and 2 summarize some general characteristics for the curves with 5 and 30 mg sample sizes, respectively. Figs. 3–5 show the effect of heating rates and sample sizes on TG and DTA curves. It is evident that the apparent temperatures of reaction become higher with increasing heating rate and sample size. The amplitude of the DTA peak decreases with decreasing heating rate.

Table 1
Selected values for the TG-DTG-DTA of 5 mg samples of basic zinc carbonate heated in N_2

Heating rate (°C/min)	Sample size (mg)	DTG, T_{max} (°C)	DTA, T_{max} (°C)
10	5.3442	255.54	258.08
20	5.0494	262.61	266.31
30	4.9241	267.78	271.52
40	4.9124	270.37	274.07

Table 2
Selected values for the TG-DTG-DTA of 30 mg samples of basic zinc carbonate heated in N_2

Heating rate (°C/min)	Sample size (mg)	DTG, T_{max} (°C)	DTA, T_{max} (°C)
10	30.1576	265.40	269.30
20	30.1083	265.72	272.20
30	29.7034	268.42	276.58
40	29.6945	273.66	283.87

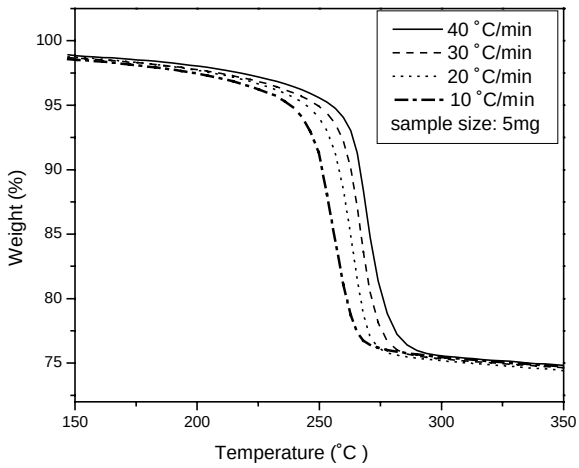

Fig. 3. The TG plots employed for studying the effect of heating rate on basic zinc carbonate.

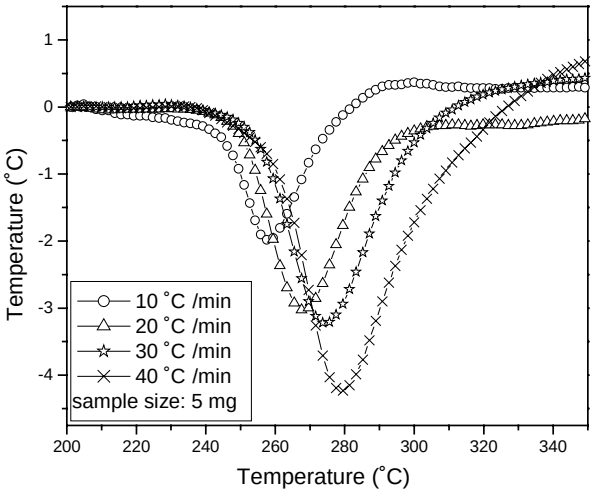

Fig. 4. The DTA plots employed for studying the effect of heating rate on basic zinc carbonate.

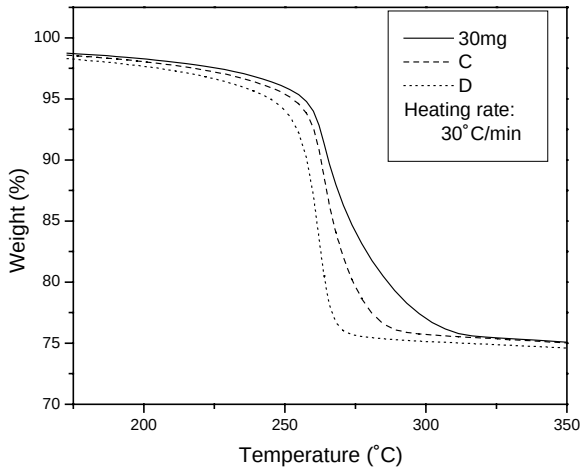

Fig. 5. The TG plots employed for studying the effect of sample size on basic zinc carbonate.

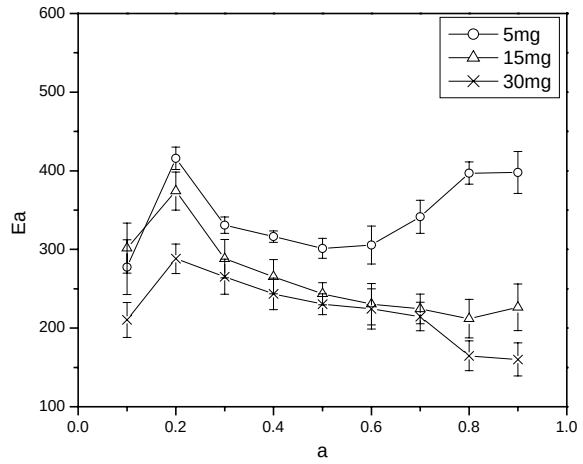

Fig. 6. A plot of E_a as a function of a for the decomposition of the sample in N_2.

The kinetic analysis of isoconversional method has the advantage of alleviating the need to select a specific kinetic model and hence any dependence on this choice. Based on Friedman method, the values of E_a derived from the TG measurement are showed in Fig. 6. It contains the variation of E_a for a from 0.1 to 0.9. The activation energy obtained with sample sizes of 5 ± 0.4, 15 ± 0.4 and 30 ± 0.4 mg are 319.17 ± 22.75, 241.86 ± 21.06 and 238.66 ± 19.86 kJ/mol, respectively. The larger sample size has lower value of E_a. Sanders and Gallagher regard it is because of the influence of thermal transport on the rate of reaction [17].

5. Conclusions

1. Basic zinc carbonate decomposes via a single stage process in an atmosphere of nitrogen. The decomposition process starts at about 220 °C and reaches weight loss of 24%.
2. The procedural variables can affect the shape of the DTA curves. An increase in the heating rate causes an increase in the peak temperature, and an increase in the peak height.
3. An increase in sample size causes an increase in the reaction temperature, and a decrease in the value of E_a. The energy of activation with 5, 15 and 30 mg are 319.17 ± 22.75, 241.86 ± 21.06 and 238.66 ± 19.86 kJ/mol, respectively.

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