



Reaction pathway and kinetics of CdO nanoparticles prepared from CdCO₃ precursor using thermal decomposition method

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Abstract: The non-isothermal kinetics of CdO nanoparticles prepared from CdCO₃ precursor using thermal decomposition method was investigated. A model-fitting Malek approach and a model-free advanced isoconversional method of Vyazovkin were applied to the analysis of the DSC and TGA data. The results showed that CdO nanoparticles prepared from CdCO₃ followed an autocatalytic reaction. Sestak–Berggren model could favorably describe the studied reaction process. Moreover, the apparent activation energy of CdCO₃ decomposition was calculated to be (119.19±9.97) kJ/mol and the explicit rate equation form of CdCO₃ decomposition was established.

Key words: CdCO₃; CdO nanoparticle; kinetic modeling; thermal decomposition; advanced isoconversional method

1 Introduction

Recently, nanoparticles have become the focus of modern materials science because of their potential technological importance and unique physical properties [1]. Metal oxide nanoparticles have some unique physical and chemical properties which make them superior to conventional metal oxide in many applications [2]. CdO is an important n-type semiconductor with a direct band gap of 2.5 eV and an indirect band gap of 1.98 eV. Consequently, it has promising applications in catalysts, sensors, nonlinear materials, solar cells, and other optoelectronic devices [3,4].

In our previous work, a facile technique for the CdO nanoparticles preparation from the anodic materials of the spent Ni–Cd batteries by thermal decomposition method was presented [5]. Practically, the proposed method has advantages such as easy to control and no need of costly reactants. But it suffers from conceptual principles. Some of the most important restrictions are ambiguity of the mechanism during the thermal decomposition and appropriate identification of reaction

route. In solid state reactions, appropriate kinetic equations, rate limiting steps and calculation of kinetic parameters could supply a deeper conception into the possible mechanisms of transformation [6].

The mechanism and kinetics of carbonates of thermal decomposition to produce particles in micron or larger scale were studied previously according to the isothermal conditions [7–13]. Nevertheless, to the best of our knowledge, non-isothermal kinetics modeling of CdO nanoparticles preparation from carbonates (in particular, CdCO₃ precursor) by thermal decomposition method has not been investigated yet.

It is necessary to note that strictly isothermal experiments are not possible, because there is always a finite non-isothermal heat-up time. The most disadvantages of isothermal trials are limited temperature ranges. At lower temperatures, it may be very difficult to obtain complete conversion over a reasonable time period. While at higher temperatures, the heat-up time becomes comparable to the characteristic time of process, which means that a significant extent of conversion is obtained before the isothermal regime sets in. The problem of non-zero conversion is easy to avoid in constant heating rate trials by starting heating from the

temperature that is below the temperature at which a process becomes detectable [14].

In this work, the non-isothermal kinetics of process was investigated using DSC and TGA with a model-fitting Malek approach and a model-free advanced isoconversional method of Vyazovkin. Then, the results were compared with isothermal conditions [9–13]. Our current contribution will provide the comprehensive data to better understand the mechanism of CdCO_3 decomposition.

2 Experimental

The raw material, i.e., CdCO_3 , was taken from the anodic material of spent Ni–Cd batteries [5]. To study the kinetics of CdCO_3 decomposition, the precursor (7 ± 0.5) mg was studied through DSC–TGA (STA409PG) at four heating rates of 5, 10, 15 and 20 °C/min in the temperature range of 25–600 °C in air. For each sample and heating rate, three repetitive TGA curves were obtained in order to assure the reproducibility of the results.

The crystalline structure, morphology and size of CdO nanoparticles were characterized by XRD (Philips, X'pert-MPD system using $\text{Cu K}\alpha$) and HRSEM (Hitachi S-4160), respectively. IR spectra were recorded in the wave length range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} , using Bruker tensor 27 FTIR spectrometer with RT-DIATGS detector and KBr pellet technique. The histogram of nanoparticle size distribution was estimated from the HRSEM images by randomly measuring the diameters of at least 650 particles.

3 Theoretical

Generally, the rate of degradation reaction can be described in terms of two functions, i.e., $k(T)$ and $f(\alpha)$, thus,

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \quad (1)$$

where α is the degree of conversion, t is the reaction time, T is the thermal dynamic temperature, β is the heating rate, $k(T)$ is the rate constant, and $f(\alpha)$ is the type of reaction or function of reaction mechanism. In TGA analysis, the degree of conversion can be defined as the ratio of actual mass loss to the total mass loss corresponding to the decomposition process [15,16]:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (2)$$

where m_0 , m and m_f are the initial, actual and final masses of the sample, respectively. The dependence of the reaction rate constant on temperature can be described by Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where A is the pre-exponential factor, R is the mole gas constant (8.314 J/(mol·K)), and E_a is the apparent activation energy. A relatively complete thermal analysis kinetics method proposed by MALEK [17] was chosen to analyze the non-isothermal experiment data. The Malek method contains two functions, $y(\alpha)$ and $z(\alpha)$, to find the appropriate kinetic model that best describes the conversion function of the studied process. They are as follows [17,18]:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \exp(u) = \beta \left(\frac{d\alpha}{dT}\right) \exp(u) \quad (4)$$

$$z(\alpha) = P(u) \left(\frac{d\alpha}{dt}\right) \frac{T}{\beta} = P(u) \left(\frac{d\alpha}{dT}\right) T \quad (5)$$

where $u = E_a/(RT)$ and $P(u)$ is the expression of the temperature integral, which can be well approximated by the fourth rational expression as shown in Eq. (6) [17,18–21]:

$$P(u) = \frac{u^3 + 18u^2 + 88u + 96}{u^4 + 20u^3 + 120u^2 + 240u + 120} \quad (6)$$

Function $y(\alpha)$ is proportional to function $f(\alpha)$, being characteristic for a given kinetic model. The shapes and maxima of both $y(\alpha)$ and $z(\alpha)$ functions, normalized within (0, 1) interval, provide valuable information for determining the most appropriate kinetic model to describe the process studied.

According to the Malek method, E_a must be determined independently using other methods. To estimate the activation energy, various methods have been proposed. These methods can be generally categorized as isoconversional and model-fitting methods [15,16,22–27].

In addition, there are more complex “model-free” methods, such as the nonlinear isoconversional method by VYAZOVKIN and WIGHT [28] and VYAZOVKIN [29], solutions of which can only be obtained using computer algorithms. Due to great calculation accuracy and versatile applicability for various heating programs [15,16,18,20], the advanced isoconversional method developed by VYAZOVKIN, that is, the VYAZOVKIN method, was adopted to analyze the non-isothermal reaction. Specifically, the Vyazovkin method is applicable to a non-isothermal kinetic process with a series of linear heating, which can be written as [14–16,18,20]:

$$\Phi(E_a) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_a, T_{\alpha,i}) \beta_j}{I(E_a, T_{\alpha,j}) \beta_i} \quad (7)$$

$$I(E_a, T_{\alpha,i}) = \int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}} \exp\left(-\frac{E_a}{RT_{\alpha}}\right) dT \quad (8)$$

where β_i and β_j represent different heating rates, T_α and $T_{\alpha-\Delta\alpha}$ are the reaction temperatures corresponding to α and $\Delta\alpha$, respectively. Minimizing Eq. (7) for each α with a certain conversion increment (usually $\Delta\alpha=0.05$) results in the correction of E_a with α . The detailed descriptions of how to use the Vyazovkin method to treat calorimetric data can be acquired elsewhere [15,16].

4 Results and discussion

4.1 Synthesis of CdO nanoparticles

Figure 1(a) shows the XRD pattern of CdCO_3 precursor. As shown, all diffraction peaks were consistent with CdCO_3 (QCPDS card No. 00–042–1342). Figure 1(b) shows typical XRD pattern of CdO nanoparticles prepared at the heating rate of 10 °C/min. Accordingly, the precursor was completely decomposed at about 500 °C into single phase of the pure crystallite CdO (QCPDS card No. 00–005–0640). This result was confirmed by TGA–DSC observation. Figures 2(a) and (b) show the FT-IR spectra of precursor CdCO_3 and CdO nanoparticles prepared at the heating rate of 10 °C/min, respectively. The peaks (Fig. 2(a)) of around 1380, 860, and 719 cm^{-1} are the characteristic vibration bands of

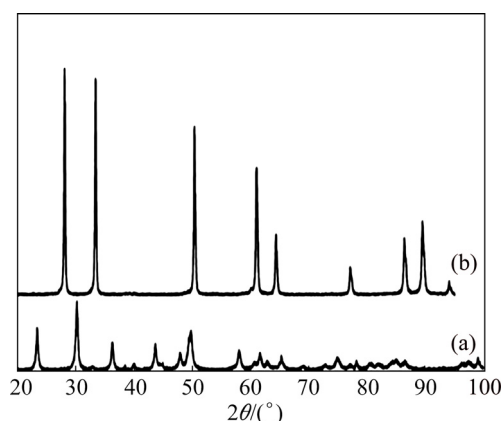


Fig. 1 XRD patterns of precursor CdCO_3 (a) and CdO nanoparticles prepared at heating rate of 10 °C/min (b)

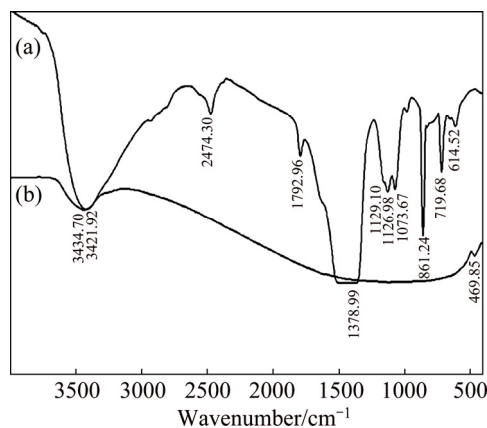


Fig. 2 FTIR spectra of precursor CdCO_3 (a) and CdO nanoparticles (b)

CO_3^{2-} [30,31]. The absorption bands at 614 and 1129 cm^{-1} are attributed to sulfate groups (SO_4^{2-}) [2,30]. In Fig. 2(b), the peak at around 470 cm^{-1} is assigned to Cd—O of CdO, confirming the formation of pure CdO nanoparticles [30,31]. And, the peak at 3400 cm^{-1} corresponds to the OH— stretching [2,31].

Figure 3(a) shows HRSEM image of CdCO_3 precursor and Fig. 3(b) shows the typical image of CdO nanoparticles prepared at the heating rate of 10 °C/min. Accordingly, single CdO particles exhibit a strong tendency to form nanoparticle agglomerates. The solid-state reconstruction of nanoparticles into aggregates is a usual phenomenon showing a tendency of nanoparticulate systems to restrain unsaturated surface forces via surface recombination [32]. EDX analysis of CdO nanoparticles (Fig. 3(c)) confirms the high purity of the products. The size distribution histogram of the CdO nanoparticles (Fig. 3(d)) reveals that the size of CdO particles varies from 8 to 108 nm.

4.2 Non-isothermal decomposition of CaCO_3 precursor

The TGA–DSC curves of non-isothermal degradation of the CaCO_3 precursor for four different heating rates (5, 10, 15, and 20 °C/min) are shown in Fig. 4. Accordingly, mass loss of about 26% found between 311 and 462 °C (endothermic peak) was related to the decomposition of CdCO_3 into CdO and CO_2 [31]. Moreover, with increasing the heating rate, the TGA curve and peak of DSC curve shifted to a higher temperature, and the final mass loss presented a decreasing trend.

From Fig. 4, with increasing the heating rate, the reaction area was shifted to a higher temperature range. Moreover, onset reaction temperatures, peak temperatures, and end temperatures were enhanced with increasing heating rate (Table 1).

The conversional curves (α – T) for non-isothermal decomposition of CdCO_3 are indicated in Fig. 5. These conversional curves exhibit the sigmoidal profile, and with increasing heating rate, the curves shift toward the higher temperature. In other words, the higher the heating rate, the higher the temperature for the reaction to reach the identical α .

4.3 Calculation of activation energy (E_a)

The dependence of E_a on α for the decomposition of CdCO_3 is presented in Fig. 6. According to Refs. [33,34], if E_a values were independent of α , the decomposition process was dominated by a single reaction step. Moreover, if the difference between the maximum and minimum values of E_a (i.e., 19.93 kJ/mol) was less than 20%–30% of the average E_a (i.e., 119.86 kJ/mol), the activation energy was independent of α [15,16].

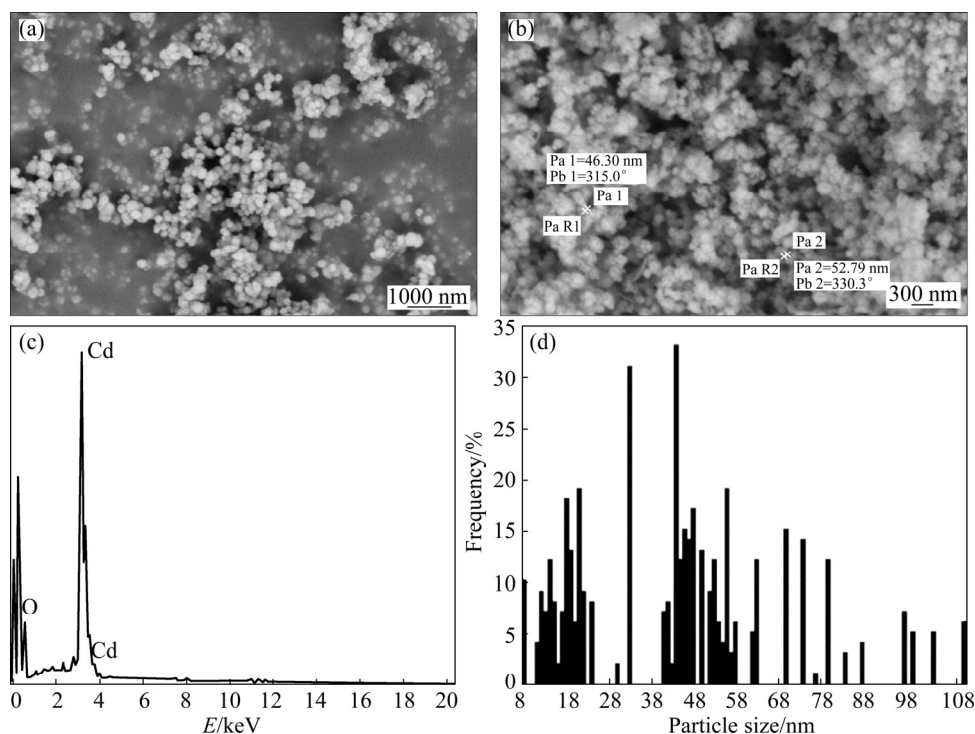


Fig. 3 HRSEM image of CdCO₃ precursor (a) and typical image of CdO nanoparticles prepared at heating rate of 10 °C/min (b), EDS pattern of CdO nanoparticles (c) and histogram of CdO nanoparticle size distribution (d)

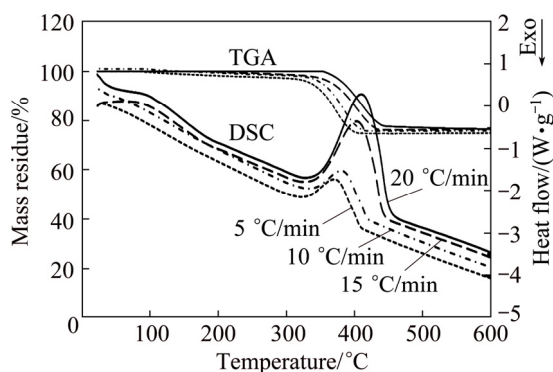


Fig. 4 TGA–DSC curves for thermal decomposition of precursor CdCO₃ at heating rates of 5, 10, 15 and 20 °C/min in air

Table 1 Typical parameters of thermal decomposition of CdCO₃ precursor

Heating rate/(°C·min ⁻¹)	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{peak}}/^{\circ}\text{C}$	$T_{\text{end}}/^{\circ}\text{C}$
5	311	373	412
10	318	381	421
15	321	403	454
20	322	412	462

Therefore, from Fig. 6, it is obvious that CdCO₃ decomposition is a single-step process. Based on the Vyazovkin method, E_a showed an almost stable behavior with the average of $E_a = (119.19 \pm 9.97)$ kJ/mol which falls within the expected range of literature, i.e., 96–135 kJ/mol [9–13].

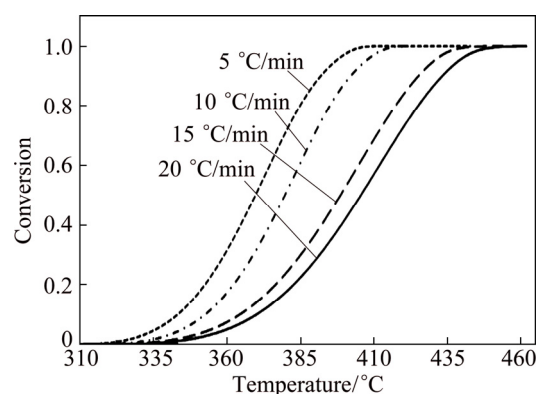


Fig. 5 Conversion–temperature curves for thermal decomposition of CdCO₃ precursor at heating rates of 5, 10, 15 and 20 °C/min in air

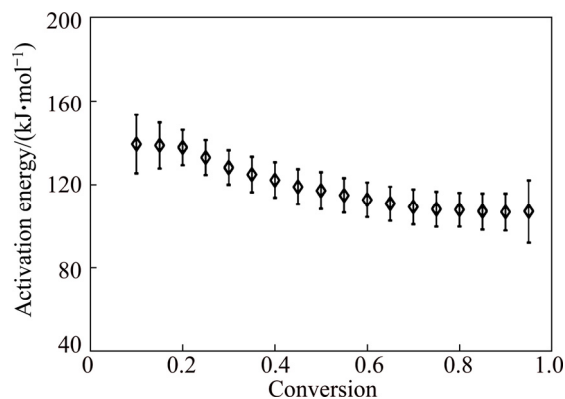


Fig. 6 Dependence of activation energy (E_a) on conversion (α) for thermal decomposition of CdCO₃ precursor

Furthermore, the variation of E_a for $\alpha < 0.10$ and $\alpha > 0.90$ was not of the major concern, because the parameters were affected hardly by the startup of the experiment and by minor errors in baseline determination, respectively [14]. It should be mentioned that, the dependence of E_a on α was a source of additional kinetic information of process [35–37]. The results indicated that the dependence of E_a on α helped not only to reveal the complexity of reduction processes, but also to identify its kinetic scheme. Therefore, at following, the suitable kinetics model for describing CdO nanoparticles processing from spent Ni–Cd batteries using thermal decomposition method was determined.

4.4 Determination of most probable reaction mechanism function

Figure 7 shows the relationship between the reaction rate and conversion of decomposition of CdCO_3 . Accordingly, the reaction rate ($\beta da/dT$) increased with the increase of the heating rate. Furthermore, the peak reaction rate appeared in the conversion (α_p) range of 0.598–0.609. Hence, the model-free kinetic method was suitable for the experiment.

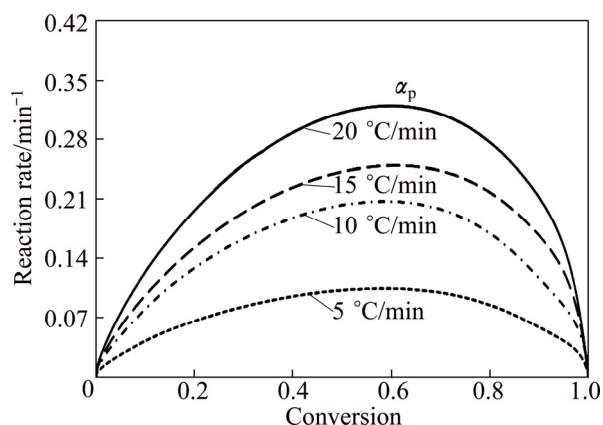


Fig. 7 Reaction rate ($\beta da/dT$) as function of conversion (α) for thermal decomposition of CdCO_3 precursor at heating rates of 5, 10, 15, and 20 °C/min in air

The normalized function curves of $y(\alpha)$ and $z(\alpha)$ were respectively constructed from Eqs. (4) and (5) for thermal decomposition of CdCO_3 and shown in Fig. 8. As shown, the $y(\alpha)$ curves exhibited peak values in the conversion (α_M) range of 0.228–0.237, and the $z(\alpha)$ curves showed a practically isoconversional peak value conversion, α_p^∞ , within 0.653–0.659.

Table 2 shows the characteristic peak conversion values, i.e., α_p , α_M and α_p^∞ , for the thermal decomposition of CdCO_3 . These findings demonstrated that the effect of the heating rates on the whole reaction kinetics could be omitted by applying the Malek method to the non-isothermal kinetics data of CdCO_3

degradation. Furthermore, the peak value of $y(\alpha)$ appeared while α was much larger than 0, implying that the reaction is auto-catalyzed [38]. Besides, the larger value of α_M indicated increasing the autocatalytic tendency of the decomposition process [39].

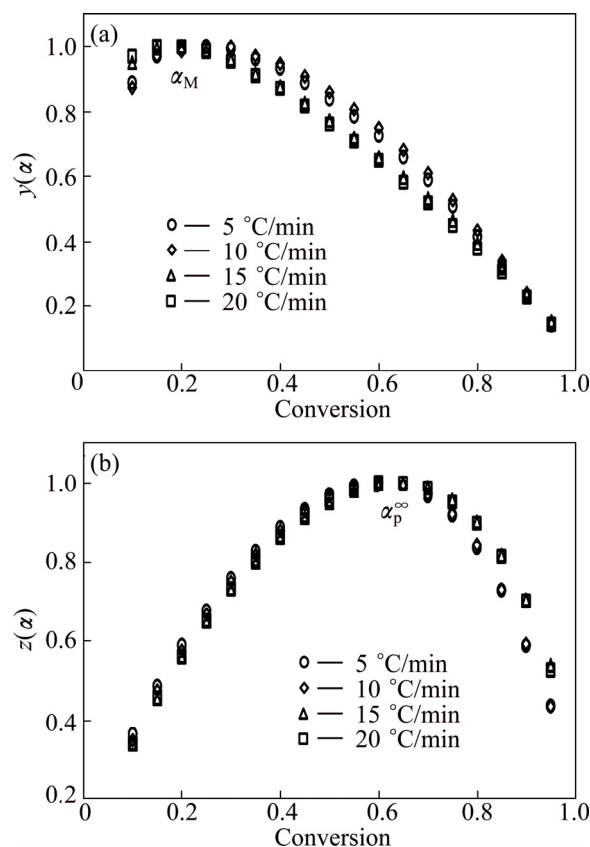


Fig. 8 Plots of normalized $y(\alpha)$ (a) and $z(\alpha)$ (b) against conversion (α) for thermal decomposition of CdCO_3 precursor at heating rates of 5, 10, 15 and 20 °C/min in air

Table 2 Characteristic peak conversion values, i.e., α_p , α_M and α_p^∞ , for thermal decomposition of CdCO_3 precursor

Heating rate/ (°C·min ⁻¹)	α_p	Mean of α_p	α_M	Mean of α_M	α_p^∞	Mean of α_p^∞
5	0.598	0.603	0.237	0.233	0.653	0.656
10	0.601		0.234		0.656	
15	0.603		0.231		0.657	
20	0.609		0.228		0.659	

According to the shape of $y(\alpha)$ and characteristic values of $y(\alpha)$ and $z(\alpha)$, it can be concluded that the truncated Sestak–Berggren model or the two-parameter Sestak–Berggren model [17,38,39] or extended Prout–Tompkins model (the regular Prout–Tompkins model, i.e., $f(\alpha)=a(1-\alpha)$), SB (m , n), was suitable for kinetic modeling of CdCO_3 degradation. Moreover, from Table 2, it can be observed that $0 < \alpha_M < \alpha_p^\infty$ and $\alpha_p^\infty \neq 0.632$,

which strongly indicated that the truncated SB (m, n) [39] was suitable. SESTAK and BERGGREN [39] proposed an empirical model for $f(\alpha)$:

$$f(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^s \quad (9)$$

According to the Sestak–Berggren model, the combination of m, n , and s can be represented a number of different reaction models. It was generally applied in truncated form ($s=0$ in Eq. (9)). The truncated Sestak–Berggren model was an example of an autocatalytic model. According to the truncated SB (m, n) model and Eq. (3), Eq. (1) can be transformed into the following form [39]:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) \alpha^m (1-\alpha)^n \quad (10)$$

where m and n are the reaction orders, and other parameters have the same meaning as the above equations. The ratio of m to n , i.e., p , equals $\alpha_M/(1-\alpha_M)$ according to MALEK [17]. Thus, Eq. (10) can be transformed into the following form:

$$\ln\left[\left(\beta \frac{d\alpha}{dT}\right) \exp\left(\frac{E_a}{RT}\right)\right] = \ln A + n \ln[\alpha^p (1-\alpha)] \quad (11)$$

The kinetic parameter n can be derived from the slope of $\ln(\beta d\alpha/dT) \exp[E_a/(RT)]$ versus $\ln[\alpha^p (1-\alpha)]$ for $0.2 < \alpha \leq 0.95$ [38], the intercept is $\ln A$, and $m=pn$. These data perform good linearity (Fig. 9). The values of m, n , and $\ln A$ could be calculated from the intercept and slope of these fit straight lines, which are listed in Table 3. These kinetic parameters vary slightly with heating rates, with deviation less than 10% of their average values. In addition, the higher value of the kinetic parameter n ($n>1$) indicated the increasing complexity and the decreasing autocatalytic tendency of the degradation process [39].

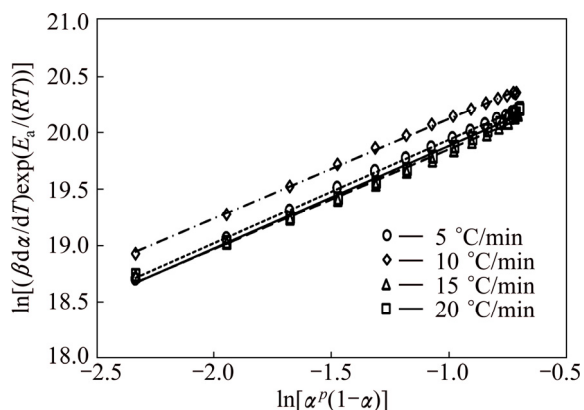


Fig. 9 Plots of $\ln[(\beta d\alpha/dT) \exp(E_a/(RT))]$ vs $\ln[\alpha^p (1-\alpha)]$ for different heating rates for thermal decomposition of CdCO_3 precursor for $0.2 < \alpha \leq 0.95$ at heating rates of 5, 10, 15 and 20 °C/min in air

Table 3 Calculated kinetic parameters m, n and $\ln A$ for SB (m, n) model for thermal decomposition of precursor CdCO_3

Heating rate/ (°C·min ⁻¹)	m	Mean of m	n	Mean of n	$\ln A$	Mean of $\ln A$	R^2
5	0.284		0.915		20.849		0.9996
10	0.269	0.272	0.882	0.897	21.150	20.902	0.9985
15	0.265		0.883		20.733		0.9949
20	0.268		0.907		20.877		0.9942

Therefore, the thermal decomposition of CdCO_3 was a process with high autocatalytic tendency.

The sensitivity of SB model to the process features, such as the effect of heating rate, has been evidenced by the variation of the kinetic exponents. This clearly shows the flexibility of the SB empirical function in describing several shapes of the $d\alpha/dT$ against α curve satisfying the condition $\alpha_M \neq 0$. However, some limitations of the model due to its purely empirical character are to be accounted. Unfortunately, it is extremely difficult or even impossible to give a physical meaning to the kinetic exponent's m and n of the SB model [39]. Thus, no theoretical models based on physico-geometric assumptions of the reaction interface movements were found to describe our experimental data, probably as a consequence of the complexity of the process under study. Nevertheless, these limitations are not critical considering the comparative nature of the kinetic study performed here.

Furthermore, the kinetic exponent's m and n are parameters that define relative contribution of acceleratory and deceleratory part of the crystallization process. These parameters are rather empirical constant, and too much physical significance should not be attached to their numerical values [40].

By substituting the calculated kinetic parameters (n, m and $\ln A$ in Table 3 along with previously calculated E_a) into Eq. (10), the explicit rate equation for the decomposition reaction of CdCO_3 was obtained as Eq. (12):

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = 1.196 \times 10^9 \exp\left(-\frac{119190}{RT}\right) \alpha^{0.272} (1-\alpha)^{0.897}, \quad \alpha \in [0.10, 0.95] \quad (12)$$

To check the predictability of the explicit kinetics model (Eq. (12)), the predicted rate curves for different heating rates were calculated (Fig. 10). As shown in Fig. 10, there was a good agreement between the experimentally obtained $\beta d\alpha/dT-T$ curves and numerically calculated rate curves, using the corresponding kinetic triplets, hence, the truncated SB (m, n) model was suitable for predicting decomposition rate of CdCO_3 .

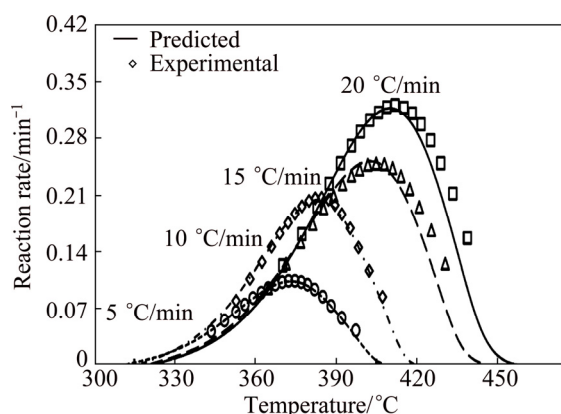


Fig. 10 Comparison of experimental reaction rate and that predicted from SB (m, n) model (Eq. (12)) vs temperature for thermal decomposition of CdCO_3 precursor at heating rates of 5, 10, 15 and 20 $^{\circ}\text{C}/\text{min}$ in air

5 Conclusions

1) The non-isothermal kinetics of process was studied using DSC and TGA with a model-fitting Malek approach and a model-free advanced isoconventional method of Vyazovkin.

2) The decomposition of CdCO_3 precursor was a single step process.

3) In the conversion (α) range of 0.10–0.95, E_a presented an almost stable behavior with the average value of $E_a = (119.19 \pm 9.97) \text{ kJ/mol}$.

4) The thermal decomposition of CdCO_3 precursor was a process with the high autocatalytic tendency.

5) There was a good agreement between the experimentally obtained $\beta da/dT-T$ curves and numerically calculated rate curves, using the corresponding kinetic triplets; hence, the truncated SB (m, n) model was suitable for predicting decomposition rate of CdCO_3 precursor.

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用热分解法从 CdCO_3 前驱体制备 CdO 纳米颗粒的反应路径和反应动力学

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摘 要: 研究用热分解法从 CdCO_3 前驱体制备 CdO 纳米颗粒的非等温动力学。采用 Malek 模型模拟法和改进的非模型等转化率 Vyazovkin 法对所得 DSC 和 TDA 数据进行分析。结果表明, 从 CdCO_3 制备 CdO 纳米颗粒的反应属于自动催化反应。Sestak–Berggren 模型能很好地描述该反应过程。另外, 计算得到 CdCO_3 热分解反应的表观活化能为 $(119.19 \pm 9.97) \text{ kJ/mol}$, 并建立了该热分解反应的反应速率方程。

关键词: CdCO_3 ; CdO 纳米颗粒; 动力学建模; 热分解; 改进等转化率法

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