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New incremental isoconversional method for kinetic analysis of solid thermal decomposition

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Abstract A simple and precise incremental isoconversional integral method based on Li-Tang (LT) method is proposed for kinetic analysis of solid thermal decomposition, in order to evaluate the activation energy as a function of conversion degree. The new method overcomes the limitation of LT method in which the calculated activation energy is influenced by the lower limit of integration. By applying the new method to kinetic analysis of both the simulated nonisothermal case and experimental case of strontium carbonate thermal decomposition, it is shown that the dependence of activation energy on conversion degree evaluated by the new method is consistent with those obtained by Friedman (FR) method and the modified Vyazovkin method. As the new method is free from approximating the temperature integral and not sensitive to the noise of the kinetic data, it is believed to be more convenient in nonisothermal kinetic analysis of solid decompositions.

Keywords Isoconversional method · Solid thermal decomposition · Activation energy · Nonisothermal kinetic analysis

Introduction

Thermal analysis techniques (TG/DTG, DTA, and DSC) are often used for determination of the degradation processes that take place in the progressive heating of solid materials. Evaluation of the kinetic triplet (activation energy, pre-exponential factor, and conversion function) of each degradation step is one important target of kinetic investigations. Many kinetic analysis methods have been developed, among which isoconversional methods have been widely used [1–5], because they can evaluate the activation energy without the prior knowledge of conversion function. Isoconversional methods are recommended by many investigators [6, 7]. By using isoconversional methods, the evaluated activation energy of a process is often a function of the conversion degree, which provides important information about reaction mechanisms [8–10]. Owing to their advantages, many isoconversional methods have been proposed to calculate activation energies of thermally activated reactions.

Isoconversional methods start from the classical kinetic equation of solid-state reaction,

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{1}$$

where α is the conversion degree, t is the time, $A(\mathrm{min}^{-1})$ is the pre-exponential factor, E(kJ/mol) is the activation energy, R is the gas constant, and T(K) is the absolute temperature. The function $f(\alpha)$ is the so-called "conversion function" which relates to the reaction mechanism. For the linear heating rate program, $\beta = dT(t)/dt$, it leads to

$$\beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

Integrating Eq. 2 gives,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT = \frac{AE}{\beta R}p(x) \tag{3}$$

where $p(x)$ is the famous temperature integral, which has no analytical solution [11]. In the classic integral

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isoconversional methods, such as Ozawa–Flynn–Wall method (OFW) [12, 13], the approximations of $p(x)$ [14–16] should be adopted and thus systematic errors in calculating the activation energy are introduced [17].

In order to avoid approximating the temperature integral, Li and Tang [18–20] proposed an isoconversional method for the analysis of thermoanalytical data. Their method takes the logarithm and integration of the both sides of Eqs. 1 or 2,

$$\int_0^{\alpha}\left(\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\mathrm{d}\alpha=\int_0^{\alpha}\left(\ln\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\mathrm{d}\alpha=-\frac{E}{R}\int_0^{\alpha}\frac{\mathrm{d}\alpha}{T}+G(\alpha) \tag{4}$$

where

$$G(\alpha)=\alpha\ln A+\int_0^{\alpha}[\ln f(\alpha)]\mathrm{d}\alpha \tag{5}$$

As $G(\alpha)$ is constant for a given α for several heating programs, a plot of $\int_0^{\alpha}\mathrm{In}\,(\mathrm{d}\alpha/\mathrm{d}t)\mathrm{d}\alpha$ against $\int_0^{\alpha}(1/T)\mathrm{d}\alpha$ will be a straight line and the value of the activation energy E_{α} can be obtained from the slope of the line.

Same as Friedman (FR) method [21], Li-Tang (LT) method avoids the systematic errors introduced by the temperature integral approximations in the calculation of activation energy. Moreover, this method is more tolerant of data noises in calculating activation energy than FR method, because the data sets of $\int_0^{\alpha}\mathrm{In}\,(\mathrm{d}\alpha/\mathrm{d}t)\mathrm{d}\alpha\sim\int_0^{\alpha}(1/T)\mathrm{d}\alpha$ of LT method are less sensitive to raw data noises by integration than those of ln $(\mathrm{d}\alpha/\mathrm{d}t)\sim 1/T$ of FR method.

Budrugeac et al. [22] pointed out that it is difficult to determine the initiation point of solid reaction when using LT method and thus recommended an improved version of Eq. 4 with a nonzero lower limit of α for integration,

$$\int_{\alpha_1}^{\alpha}\left(\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\mathrm{d}\alpha=-\frac{E}{R}\int_{\alpha_1}^{\alpha}\frac{\mathrm{d}\alpha}{T}+G(\alpha) \tag{6}$$

where the lower limit of integral is $\alpha_1>0$, and

$$G(\alpha)=(\alpha-\alpha_1)\ln A+\int_{\alpha_1}^{\alpha}[\ln f(\alpha)]\mathrm{d}\alpha \tag{7}$$

However, it is shown that the activation energy obtained by this improved method depends on the lower limit of integration, α_1, and the activation energy with $\alpha<\alpha_1$ is missed [22]. Thus, Budrugeac et al. considered that LT method is not suitable to find the dependence of $E=E(\alpha)$ [22].

In this article, an incremental version of LT method, which is independent of the lower limit of integration, is proposed and verified by numerical and experimental examples. The values of activation energy calculated by the new method are compared with those obtained by some other isoconversional methods, such as LT method and its improved version by Budrugeac et al., OFW method, FR method, and the modified Vyazovkin method (AIC) [23].

The incremental version of LT method

In the deviation of LT method or the procedure improved by Budrugeac et al., E and A should be independent of the conversion degree. Otherwise, the integration from 0 or α_1 to current α in this method will lead to systematic errors. However, the systematic error can be minimized if Eq. 1 is integrated over a very small interval of conversion degree, $\Delta\alpha$, since the activation energy can be regarded as constant within a very small segment. Thus, Eq. 3 can be switched to

$$\int_{\alpha-\Delta\alpha}^{\alpha}\left(\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\mathrm{d}\alpha=-\frac{E}{R}\int_{\alpha-\Delta\alpha}^{\alpha}\frac{\mathrm{d}\alpha}{T}+G(\alpha) \tag{8}$$

where

$$G(\alpha)=\Delta\alpha\ln A+\int_{\alpha-\Delta\alpha}^{\alpha}[\ln f(\alpha)]\mathrm{d}\alpha \tag{9}$$

in which, α varies from $3\Delta\alpha/2$ to $1-\Delta\alpha/2$ with a step $\Delta\alpha=1/(m+1)$, where m is the number of the equidistant values of α. The plot of the left side of Eq. 8 against the integration of the reciprocal of temperature should be a linear and E_{α} can be obtained from the slope of the regression line.

Obviously, the above incremental isoconversional method avoids the problem of LT method of that the calculated activation energy is dependent on the lower limit of integration. This new method is expected to give more consistent results with those from FR method (for noise-free data) or modified Vyazovkin method.

Applications

This section will verify the advantage of the new incremental isoconversional method by numerical and experimental examples.

Numerical example

Unlike the experimental data of solid reactions, the simulated data are not affected by noises and, therefore, are most suitable to testify the newly proposed method. In order to evaluate the performance of the new method, FR and AIC methods are also used to analyze the simulated data and the results are compared. FR method is chosen because it is directly based on the kinetic equation (Eq. 1) and thus gives reliable activation energy values for the simulated data without noise. Similarly, AIC method is chosen because it is believed to be an accurate integral isoconversional method though it is complex to perform [23]. Note the same way to testify the quality of an isoconversional method appeared in many other articles [23–28].

In this study, a process that involves two parallel reactions, which lead to a variation in the effective activation energy, is simulated. The overall kinetic equation of this process is described as:

$$\frac{d\alpha}{dT}=\frac{A_1}{\beta}\exp\left(-\frac{E_1}{RT}\right)(1-\alpha)^2+\frac{A_2}{\beta}\exp\left(-\frac{E_2}{RT}\right)(1-\alpha) \qquad (10)$$

where $E_1 = 80$ kJ/mol, $A_1 = 10^8\text{min}^{-1}$, $E_2 = 160$ kJ/mol, $A_2 = 10^{16}\text{min}^{-1}$ and the four linear heating rates, $\beta_{1\text{–}4} = 1, 2, 4, 8$ K/min. Note similar equation forms as Eq. 10 are used in the aforementioned articles [23–28], just with different Arrhenius parameters or model functions.

The dependence of the apparent activation energy as a function of the conversion degree obtained by aforementioned isoconversional methods is displayed in Fig. 1, which indicates that:

(1) The E_α dependence calculated by the new method is practically identical to that estimated by FR method and AIC method, i.e., $E_{\text{new}} \approx E_{\text{AIC}} \approx E_{\text{FR}}$;

(2) The E_α dependence estimated by LT method (Eq. 3) and the version improved by Budrugeac et al. (Eq. 5) deviates noticeably from the dependence estimated by FR method;

(3) As noted by Budrugeac et al. [22], the activation energy values obtained by LT method depend on the lower limit of the integral α_1. With the increases of the lower limit of α_1, the information of E_α for $\alpha < \alpha_1$ will be lost.

From the simulated data it is shown that the new method gives reliable activation energy for the case of that E varies with the degree of conversion. And it can be concluded the new method is much better than the regular LT method and the method improved by Budrugeac.

Experimental example

The thermal decomposition of strontium carbonate ($SrCO_3$), which is used as the experimental example, was carried out in a 50 mL/min flow of N_2 at 0.5, 5, 7.5 K/min from room temperature (300 K) to 1000 K on a Shimadzu DTG-60H Simultaneous TGA/DTA Analyzer. The $SrCO_3$ sample (purity of >99.99%) was supplied by Tianjin Guangfu Fine Chemical Research Institute. Sample was first dried for 2 h under 450 Celsius degree and then weighted 23.8–24.3 mg for experiments. The actual values of heating rates were calculated from the recorded sample temperature against time.

The dependence of activation energy on the conversion degree obtained by aforementioned isoconversional methods is shown in Figs. 2 and 3. From Fig. 2, it can be seen that the activation energy decreases with the increases of conversion degree of the reaction. The results obtained by the new method and AIC method are consistent, while those obtained by FR method seem less consistent because of the effect of experimental noises. Taking the values calculated by the Modified Vyazovkin method as benchmark, the standard deviation of E values determined by new method is 4.14 while the value calculated by FR

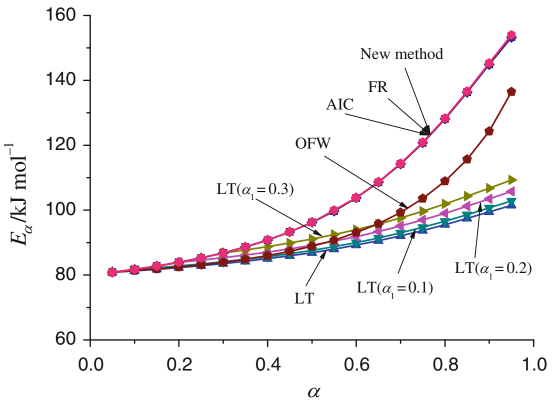

Fig. 1 E_α dependencies evaluated for the simulated process by Li-Tang method with different lower limit of the integral, α_1, as well as by OFW, AIC, FR, and the new method

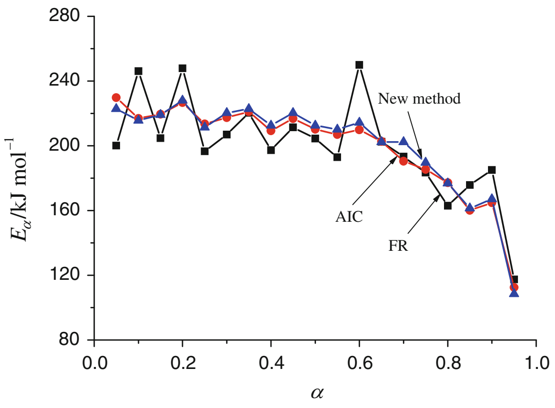

Fig. 2 E_α dependencies evaluated for the decomposition of $SrCO_3$ by the new method, FR method, and AIC method

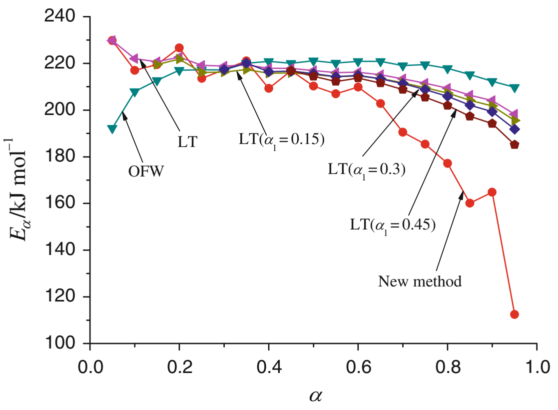

Fig. 3 E_α dependencies evaluated for the $SrCO_3$ decomposition by the new method and Li-Tang method with different lower limit of the integral, α_1, as well as by OFW method

method reaches 17.79. Moreover, from Fig. 3 it can be seen that:

Ozawa–Flynn–Wall method gives much lower values near the onset ($\alpha < 0.15$) of the reaction, and then rather stable values for $\alpha > 0.15$.

Li-Tang method method gives consistent values in the beginning of the process but also leads to rather stable values for $\alpha > 0.15$. As expected, the E_α dependence obtained by the procedure improved by Budrugeac et al. depends on the lower limit α_1 in Eq. 6.

The values of the activation energy obtained by OFW, LT method, and the procedure improved by Budrugeac et al. differ considerably to the results obtained by those methods independent of the situation where E varies with α (Fig. 2).

From Figs. 2 and 3 it is known that the new approach proposed in this study has distinct advantage over some integral isoconversional methods (OFW, LT, etc.). Furthermore, it can be concluded that the new approach is capable of providing valid values of activation energy even if E varies strongly with the conversion degree.

Conclusions

An incremental isoconversional method has been developed based on LT method without any additional assumption. The incremental version not only avoids the integration of the rate equation and lowers the noise effect which is encountered in FR method, but also eradicates the limitation of LT method that the activation energy calculated by which depends on lower limit of the integration. Moreover, the procedure is very simple and can give consistent activation energy values with those obtained by FR and the modified Vyazovkin method. It is believed the new method could play its own role in kinetic analysis of solid reactions.

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