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INFLUENCE OF PARTICLE SIZE DISTRIBUTION OF A SAMPLE ON THE KINETIC PARAMETERS DETERMINED BY THERMOGRAVIMETRIC CURVES

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ABSTRACT

The influence of particle size distribution in a sample on the kinetic parameters determined by using TG and DTG curves was examined mathematically. TG and DTG curves for the reactions following the rate equations of the contracting cube (mode I), Jander (mode II), or Avrami (mode III) models were calculated by assuming that the radii of the particles in the sample were in the normal distribution with standard deviation s and by settling parameters such as activation energy E_a and pre-exponential factor A arbitrarily. The rate analyses of the calculated curves were carried out by the methods of Coats–Redfern (method I) and Achar et al. (method II). The E_a and A values obtained by either method were found to deviate negatively from the given values as the s values increased; the deviation was a little larger by method II than by method I. For the reactions of modes I and II, the E_a and A values obtained by both methods were close to the given values and were independent of the s values. For the mode III reaction, both methods gave E_a and A values which deviated substantially from the given values though good, linear Arrehnius-plots were delineated as the s values increased. It is not preferable to induce the kinetic parameters from the rate analysis of reactions such as mode III without taking the particle size distribution into consideration.

INTRODUCTION

Several methods of kinetic analysis employing thermoanalytical curves, such as TG or DTG, have so far been developed [1]. All of these methods are based on rate equations of the following form [2].

$$d\alpha/dT = (A/\beta)\exp(-E_a/RT)f(\alpha)$$

where α represents the conversion; T, the temperature; A, the pre-exponential factor; β, the heating rate; E_a, the activation energy; and R, the gas constant. The function $f(\alpha)$ is given in an appropriate form depending on the

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reaction modes; it is, in most cases, derived by considering only a single particle in a sample [3]. Samples provided for thermal analysis usually consist of particles of various sizes. Therefore, the different particle size distribution in a sample may influence the kinetic parameters determined by employing thermoanalytical curves. However, no investigation has yet been carried out with regard to such an influence.

In the present study, the TG–DTG curves of thermal reactions which follow the contracting cube equation (mode I) [4], Jander's equation (mode II) [5], and Avrami's equation ($n = 3$; mode III) [6] were drawn by calculations taking the particle size distribution into account. Kinetic parameters were induced from the TG–DTG curves calculated by applying the methods of Coats and Redfern [7] and of Achar et al. [8]. The influence of the particle size distribution exerted upon the kinetic parameters was then examined.

CALCULATION

TG–DTG curves

In order to simplify the calculations, it was assumed that the particles in a sample are spherical and their size (radius) distribution can be described by a normal distribution with an average radius r and a standard deviation s. The distribution curves were divided into 31 slices which were parallel to the vertical axis and had a breadth equivalent to each other on the abscissa. Then, when a reaction occurred at a temperature T, the conversion $\alpha(T)$ of the sample was given as

$$\alpha(T) = \sum_{m=1}^{31} Q_m(T)(\mathrm{d}V/V)_m$$

Here, $Q_m(T)$ and $(\mathrm{d}V/V)_m$ denote the conversion and the volume fraction of the m-th slice, respectively [9]. Calculations of $Q_m(T)$ values were carried out according to the following equations: when $s(T) < \bar{r}_m$

$$Q_m(T) = 1 - [1 - s(T)/\bar{r}_m]^3 \text{ for the reaction of mode I}$$

$$Q_m(T) = 1 - \{1 - [s(T)/\bar{r}_m]^{1/2}\}^3 \text{ for the reaction of mode II}$$

$$Q_m(T) = 1 - \exp\{-[s(T)/\bar{r}_m]^3\} \text{ for the reaction of mode III}$$

when $s(T) \geqslant \bar{r}_m$

$$Q_m(T) = 1$$

In the above equations, $s(T) = \int_0^T k\,\mathrm{d}T$ and $\bar{r}_m$ is the average radius of particles in the m-th slice.

The $s(T)$ values were computed according to the following equation

$$s(T) = \sum \mathrm{d}_n(T) = \sum(-AE_a/\beta T)\exp(-u)/u^2[(-1)^n(n+1)!u^n] \quad u = RT$$

The computation was continued until the $d_n(T)$ values became less than 10^{-7} of the $\Sigma d_n(T)$ values. The $(dV/V)_m$ values were calculated by

$$(dV/V)_m = P_m\bar{r}_m^3/\sum P_m\bar{r}_m^3$$

where P_m denotes the fraction of particles present in the m-th slice, which was taken from a numerical table. The reaction rate, $d\alpha/dT$, at temperature T is calculated by

$$d\alpha/dT = [\alpha(T+1) - \alpha(T)]/2 + [\alpha(T) - \alpha(T-1)]/2$$

In order to draw the TG and DTG curves by calculation, the following parameters were incorporated: $E_a = 83.7$ kJ mol^{-1}, $A = 1 \times 10^7$ mm min^{-1}, $r = 1 \times 10^{-3}$ mm, $\beta = 1$ or 10 K min^{-1}, and $s = 0$, 0.1, 0.2, or 0.3×10^{-3} mm.

Kinetic analysis

The kinetic analyses were performed by applying the methods of Coats and Redfern and of Achar et al.; these methods employ the following relations, respectively

$$\ln\left[\int f(\alpha)d\alpha/T^2\right] = \ln(AR/\beta E_a)(1 - 2RT/E_a) - E_a/RT$$

and

$$\ln[(d\alpha/dT)/f(\alpha)] = \ln(A/\beta) - E_a/RT$$

When it is certain that the reaction progresses in such a manner as indicated by the reaction mode I, II, or III, the plots of the values given by the left-hand side of the above equations against $1/T$ will give straight lines, from which E_a and A values can be determined. The least-squares method was applied for the determination of E_a and A values.

All computations were carried out by use of a Hitachi ACOS 600 computer according to the programs coded in FORTRAN.

RESULTS AND DISCUSSION

The calculated TG and DTG curves for the samples with different s values are shown in Fig. 1. As seen in Fig. 1, changes in the s values cause a slight change in the TG curves, while rather appreciable changes occur in the DTG curves. As the s values increase, the peak height of DTG curves decreases and the peak and the final temperatures of the peak shift to a higher temperature region; the most remarkable change on the DTG curves is seen for the reaction of mode III.

The results of the kinetic analyses are given in Table 1. These analyses were carried out on the TG and DTG curves delineated by taking a heating rate of 1 K min^{-1}. As the s values increase, both the E_a and A values thus

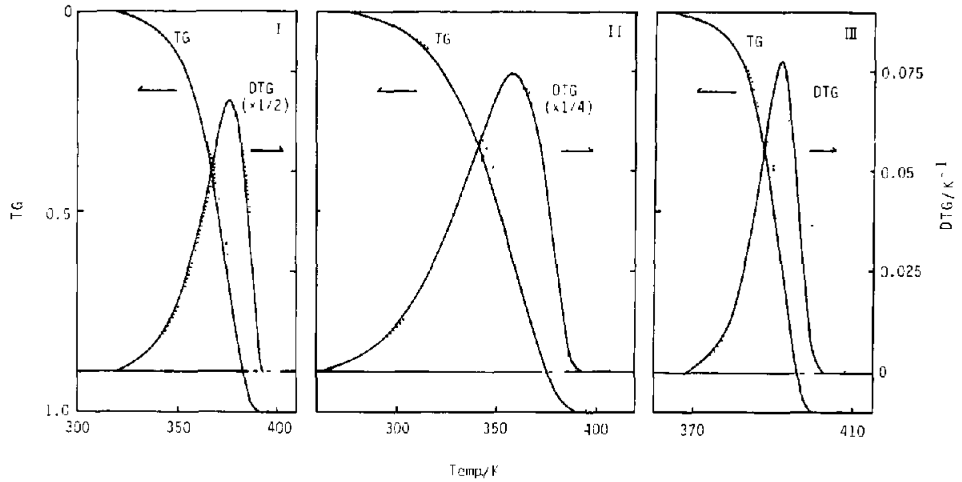

Fig. 1. Influence of the change in s values on the calculated TG–DTG curves. (———) $s=0$; (------) $s=0.3$. Reaction modes: I, contracting cube equation (mode I); II, Jander's equation (mode II); III Avrami's equation (mode III). Settled parameters: $E_a=83.68$ kJ mol^{-1}; $A=1\times10^7$ mm min^{-1}; $r=1\times10^{-3}$ mm; heating rate $=1$ K min^{-1}.

obtained tend to be smaller than those settled beforehand. The above trend is common for either method of analysis, i.e., the methods of Coats and Redfern and Achar et al. In addition, the uncertainties associated with the E_a and A values increase with increasing s value. These uncertainties, however, are as small as those often seen in actual kinetic analyses. The method of Achar et al. gives E_a and A values with a rather larger deviation

TABLE 1

E_a and A values determined from the calculated TG–DTG curves [a]

s [b]	Method [c]	Reaction					
		Mode I		Mode II		Mode III	
		E_a	log A	E_a	log A	E_a	log A
0	CR	83.7±0.1	7.0±0.0	83.9±0.1	7.0±0.0	83.5±0.0	7.0±0.0
	AR	83.5±0.1	7.2±0.0	83.8±0.0	7.0±0.0	83.2±0.0	7.0±0.0
0.1	CR	83.0±0.1	6.9±0.0	83.6±0.2	6.9±0.0	80.8±0.2	6.6±0.1
	AR	82.7±0.4	7.1±0.1	83.1±0.2	6.9±0.0	74.3±0.9	5.7±0.1
0.2	CR	82.6±0.3	6.8±0.1	82.5±0.3	6.7±0.1	74.7±0.5	5.7±0.2
	AR	80.3±0.9	6.8±0.1	81.6±0.7	6.6±0.1	62.3±2.1	4.1±0.3
0.3	CR	81.6±0.4	6.6±0.1	81.6±0.5	6.5±0.1	70.5±0.5	5.1±0.3
	AR	78.2±1.5	6.4±0.2	79.9±0.9	6.3±0.1	53.7±1.9	2.9±0.3

[a] Activation energy E_a (kJ mol^{-1}) and pre-exponential factor A (mm min^{-1}) were calculated using the data: $0.2<\alpha<0.8$.

[b] Standard deviation in the normal distribution.

[c] CR, method of Coats and Redfern; AR, method of Achar et al. Settled parameters: $E_a=83.68$ kJ mol^{-1}; log A (mm min^{-1}) $=7.00$; heating rate $=1$ K min^{-1}; others, see the text.

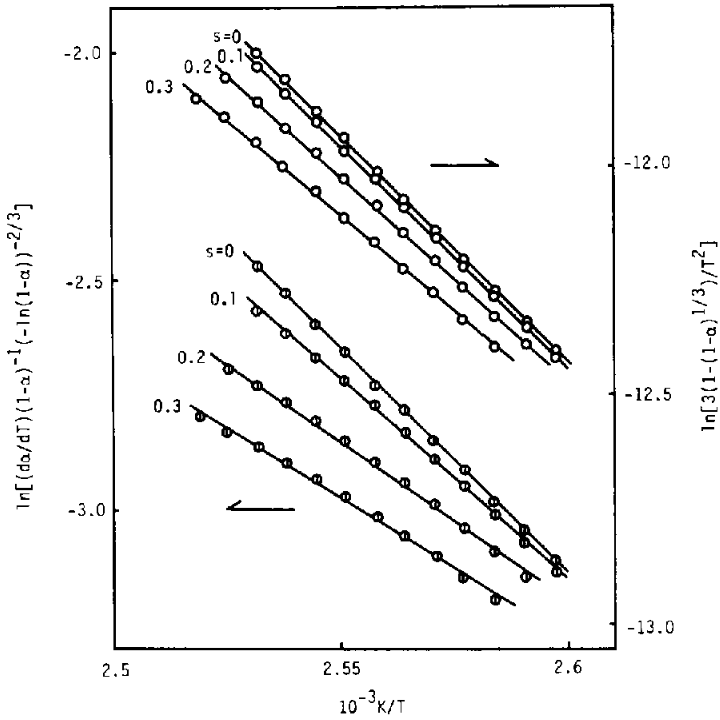

Fig. 2. Kinetic analysis on the calculated TG–DTG curves for Avrami's equation. (○) Coats and Redfern method; (◑) Achar method. Settled parameters: see Fig. 1.

from the settled parameters and with a larger uncertainty than by the method by Coats and Redfern. This difference in the results of the rate analyses can be interpreted by taking into acocunt that the equation of Achar et al. includes two weight-dependent terms, f(α) and dα/dT, and hence it suffers dually from the effect arising from the different particle size distribution. A similar trend is also observed in the kinetic analysis of the TG and DTG curves delineated by taking a heating rate of 10 K min^{-1}.

For the reactions of modes I and II, the influence due to the different particle size distribution is negligible. As is seen in Table 1, the deviation of the kinetic data from the settled parameters is quite small and the uncertainties are also small. One can analyze these reactions without seriously considering the particle size distribution. On the contrary, as for the reaction of mode III, the E_a and A values obtained deviated largely from the settled parameters when the s values exceeded 0.2, although a good linearity in the rate plots was observed (Fig. 2). That is, a good linear relation in the rate plots does not warrant a precise derivation of the E_a and A values. It is not preferable to analyze the reactions which follow Avrami's equation (mode III) without taking the particle size distribution into account.

Besides the influence due to the particle size distribution, the thermal conductivity of the sample may also bring about a certain effect on the actual TG and DTG curves. Inspection on such an effect is beyond the scope of the present investigation.

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