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Isoconversional method in CRTA

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Abstract

This paper applies the advantage of isoconversional method to the new experimental arrangement of controlled rate thermal analysis (CRTA). The CRTA technique leads to a more effective control of heat and mass transfer phenomena such that much greater sensitivity can be achieved. © 1997 Elsevier Science B.V.

Keywords: Thermal analysis; Controlled rate thermal analysis; Heat transfer; Mass transfer

1. Introduction

Different isoconversional relationships have been published by several authors [1–3] for estimating the kinetic parameters by linear heating thermal analysis. In these methods an approximately linear relationship between heating rate and temperature, at the same degree of conversion, is used. Kissinger [4] found that this held at the maximum rate of conversion but Akahira [5] demonstrated later that it was valid at a given conversion. The wide applicability of these methods that are based on several experiments have been proved in the last years.

The great importance of the methods based on several experiments is that the kinetic law whose mathematical form is very difficult to calculate unambiguously can be ignored completely. Moreover, with this isoconversional methods we are able to test the values of kinetic parameters and see whether they stay constant over the whole conversion.

Another important success of these methods is when competitive and independent reaction proceed concurrently in a system, the nature of the reaction may be revealed by either increasing or decreasing the heating rates [1].

The aim of this paper is to apply the advantages of isoconversional procedures to new experimental methods, i.e. the controlled rate thermal analysis (CRTA), developed in France by Rouquerol [6]. The basis of this new technique is that the temperature of the sample is controlled in such a way that the reaction rate is maintained constant (or controlled) throughout the process. It has been shown in previous paper [7,8] that this method allows better discrimination between the kinetic models of solid state reactions than conventional linear heating thermal analysis. Moreover, CRTA has been employed with success in the synthesis of materials with controlled texture and structure [9,10].

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2. Theoretical

2.1. Kinetic analysis of CRTA curves

It is well known that the rate of a solid state reaction is given by the general expression.

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E/RT) \tag{1}$$

Table 1 summarises the mathematical expressions of the $f(\alpha)$ functions for different kinetic models. If thermoanalytical curves are obtained at constant decomposition rates $C = d\alpha/dt$ then for the CRTA approach and from Eq. (1) we get

$$C = Af(\alpha)\exp(-E/RT) \tag{2}$$

taking logarithms we can write:

$$\ln C = \ln(Af(\alpha)) - \frac{E}{RT} \tag{3}$$

Table 1
Analytical expressions for the $f(\alpha)$ and $g(\alpha)$ functions in solid state reactions

Symbol	$f(\alpha)$	$g(\alpha)$
F1	$(1-\alpha)$	$-\ln(1-\alpha)$
R1	1	α
R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
A2	$2[-\ln(1-\alpha)]^{1/2}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/2}$
A3	$3[-\ln(1-\alpha)]^{2/3}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/3}$
D1	$\alpha/2$	α^2
D2	$\frac{-1}{\ln(1-\alpha)}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{-1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$
D4	$\frac{3}{2[(1-\alpha)^{-1/3}-1]}$	$(1-\frac{2\alpha}{3})-(1-\alpha)^{2/3}$

2.2. Kinetic evaluation from several experiments (isoconversional method)

Lack of knowledge of the analytical form of $f(\alpha)$ can be obtained quite easily because of a number of CRTA experiments with differing decomposition rates C we can write for the same extent of reaction α

$$\ln C = -\frac{E}{RT} + \text{constant} \tag{4}$$

The plot of ln C vs. $1/T$, for a given value of α, gives the activation energy E. Thus we have a method of high reliability for determining E which does not depend on a knowledge of the analytical form of $f(\alpha)$. On the other hand an agreement between values of E calculated from several experiments at different rates of decomposition C which does not depend on a knowledge of the $f(\alpha)$ functions with those obtained from the kinetic analysis of a single TG curve, largely depending on the kinetic law obeyed by the reaction [11], is largely achieved when the proper kinetic model has been chosen for carrying out the calculation. Thus a comparison of the kinetic parameters determined by both methods is a very good way of determining the reaction mechanism of solid-state reactions.

3. Experimental

Calcium carbonate D'Hemio was used. The experiments were performed in a Mettler Thermoanalyzer under a vacuum of approximately 2×10^{-5} mbar. All experiments were carried out at different rate of decomposition C ranging from 10^{-5} to 5×10^{-4}.

4. Results and discussion

Fig. 1 shows a series of CRTA curves at different rates of decomposition C for the thermal decomposition of $CaCO_3$. The isoconversional lines obtained in plotting ln C vs. the reciprocal of the temperature in Fig. 2, at the same degree of conversion α, are all parallel straight lines yielding the same activation energy E as Table 2 shows.

We can see that the calcium carbonate is a case where the activation energy calculated by means of

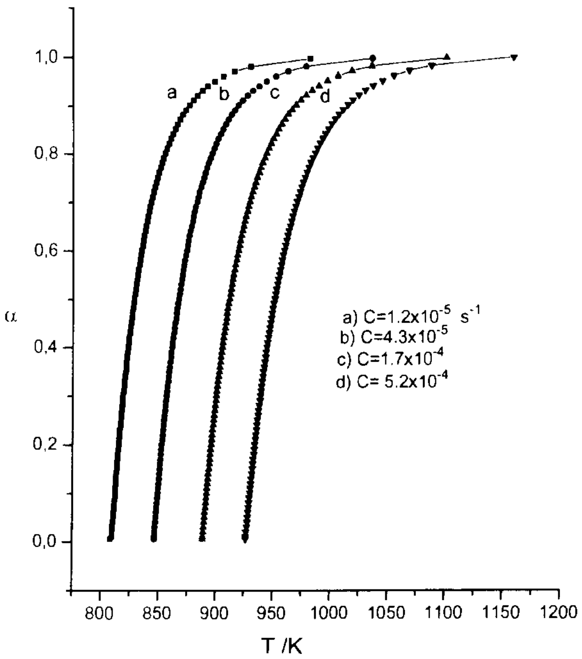

Fig. 1. CRTA curves for the thermal decomposition of calcite obtained at different rate of decomposition C.

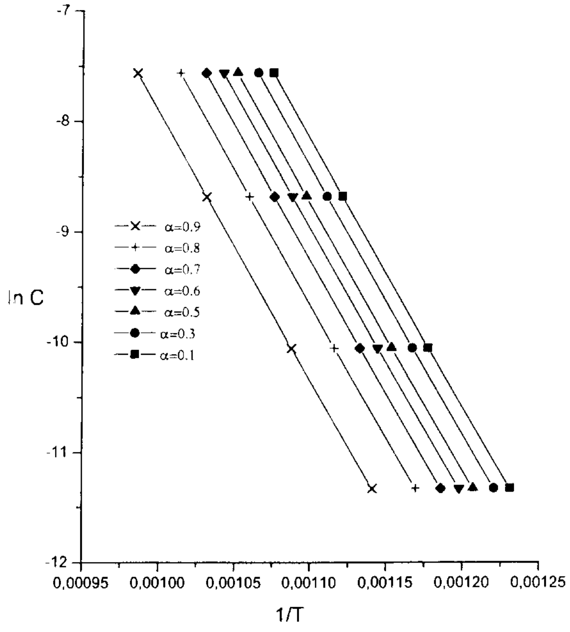

Fig. 2. Isoconversional method in CRTA (Eq. (4)).

Table 2
Activation energy for the thermal decomposition of calcite obtained by means of Eq. (4).

Values of α	E(KJ/mol)
0.1	201.6
0.3	201.7
0.5	201.7
0.6	201.7
0.7	201.8
0.8	201.8
0.9	201.9

Eq. (4) is independent of the rate of decomposition C and the degree of conversion α. Here a distinction must be made between CRTA and the conventional methods (TG, DTG, DTA, DSC etc.). In a recent work [12] we have shown that for the calcium carbonate the scatter of E values is very high when conventional method is employed because the experimental factors (heating rates, sample size etc.) affect significantly the course of this reaction. Consequently, we have concluded that the isoconversional method is not adequate for the study of samples which are path dependent when conventional technique is used.

The above results show that by using CRTA technique instead of conventional ones a much greater sensitivity can be achieved. The activation energy calculated from CRTA data are independent of the decomposition rate C selected over all the range investigated. This fact points out that the kinetic parameters obtained do not seem to be influenced by heat and/or mass transfer phenomena which is in agreement with previous work [13] which states that CRTA technique leads to a more effective control of these phenomena than conventional ones. This enhance the importance of choosing a method based on comparing CRTA data from several experiments.

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