



SAMPLE CONTROLLED THERMAL ANALYSIS AND KINETICS

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The SCTA methods for the kinetic analysis of solid-state reactions have been reviewed. It has been shown that these methods present two important advantages with regards to the more conventional rising temperature experiments. Firstly, they have a higher resolution power for discriminating among the reaction kinetic models and, secondly, SCTA is a powerful tool for minimizing the influence of the experimental conditions on the forward reaction.

Keywords: controlled rate thermal analysis, kinetics, sample controlled thermal analysis, stepwise isothermal analysis

Introduction

The rising temperature experiments have become very popular as indicated by several thousands of citations in the last ten years, many of them in this journal [1–12], according to the ISI Web of Science data base. Very often the kinetic parameters of the solid-state reactions have been determined from the kinetic analysis of a single α - T plot obtained under a linear heating program. This procedure has been widely criticized, firstly, because it rests on the assumption of a single step reaction [13] and, secondly, because even in such a case the kinetic parameters obtained are strongly dependent on the choice of reaction model [13]. In fact, Criado and Morales demonstrated in former papers [14, 15] that the $\ln(\alpha)$ functions of the different kinetic models proposed for describing solid-state reactions are linearly correlated among themselves, what means that a single TG curve must be necessarily fitted by every selected kinetic model. Figure 1 shows that a unique TG curve can be calculated by assuming different reaction models and kinetic parameters, supporting the Criado and Morales conclusion [14, 15].

The isoconversional methods that allow determining the activation energy as a function of the conversion without previous assumptions regarding to the reaction kinetic model, have been often proposed for discriminating between single-step and multiple-step reactions [13, 16, 17]. In fact, a dependence of the activation energy on the extent of the reaction has been reported for a number of solid-state reactions [13, 16, 17]. Vyazovkin [13, 16] has suggested that in most of the cases the activation energy variation is caused by the fact that the overall rate measured by a thermal analysis method is a

function of the rates of several simultaneously occurring single step reactions, each of which has its own energy barrier. Galwey [18] has recently reviewed the topic and has proposed up to five different reasons for explaining the variation of the apparent activation energy with the temperature, one of them being the influence of heat and mass transfer phenomena on the reaction rate, which would lead to an apparent (and false) dependence of the activation energy on the reacted fraction.

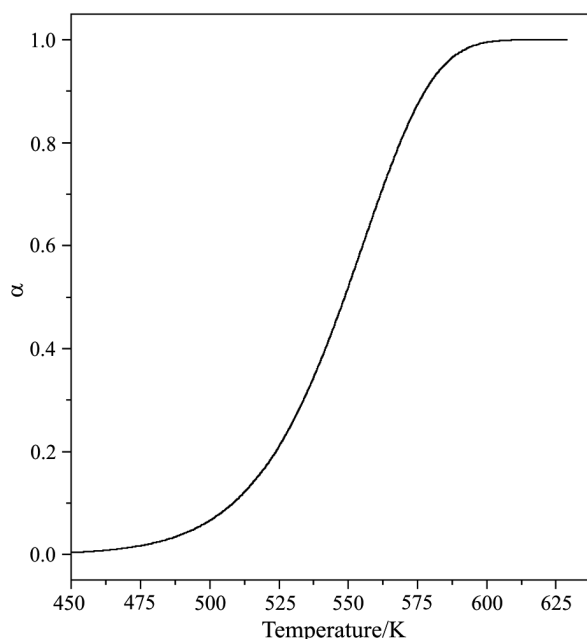


Fig. 1 A single TG curve at a heating rate of 1 K min^{-1} for three different models: F1: $E_a=172.3 \text{ kJ mol}^{-1}$ and $A=2.30 \cdot 10^{13} \text{ s}^{-1}$; A2: $E_a=118.1 \text{ kJ mol}^{-1}$ and $A=1.24 \cdot 10^8 \text{ s}^{-1}$; A3: $E_a=100.0 \text{ kJ mol}^{-1}$ and $A=1.66 \cdot 10^6 \text{ s}^{-1}$

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The scope of the present work is to show that sample controlled thermal analysis (SCTA) methods would be a powerful tool for a better insight in the reaction kinetics and for minimizing the influence of heat and mass transfer phenomena on the forward solid-state reactions. The two SCTA methods more commonly used for kinetic analysis have been the constant rate thermal analysis (CRTA), formerly developed by Rouquerol [19, 20] and Paulik brothers [21, 22] and the stepwise isothermal analysis (SIA) developed by Sørensen [23, 24]. CRTA implies to control the reaction temperature in such a way that the reaction rate is maintained constant all over the process. SIA method imposes to the sample a preset heating rate until the reaction rate exceeds a preset upper limit, C , at this point the increase of temperature stops and the reaction proceeds isothermally until the rates becomes smaller than a preset lower limit, $C-\delta$, when the heating is resumed again. In general, it seems to be accepted [25] that SIA approaches to CRTA provided that the upper and lower limits are close enough (i.e. $\delta \approx 0$) as shown in Fig. 2.

Theory

General equations

The reaction rate of a solid-state reaction can be expressed by the general constitutive equation

$$\frac{d\alpha}{dt} = A \exp(-E_a / RT) f(\alpha) \quad (1)$$

where α is the conversion at the time t , A is the pre-exponential factor of Arrhenius, E_a is the activation energy, T is the absolute temperature and $f(\alpha)$ is a function depending on the kinetic model.

If the α - T plot is obtained at a constant decomposition rate ($C = d\alpha/dt$), Eq. (1) can be rearranged, after taking logarithms, in the form

$$-\ln f(\alpha) = \ln \frac{A}{C} - \frac{E_a}{RT} \quad (2)$$

The plot of the left hand side of Eq. (2) as a function of $1/T$ lead to a straight line where the slope leads to the activation energy and the intercept to the pre-exponential factor of Arrhenius, provided that the proper $f(\alpha)$ function were selected, except if the kinetic model were represented by the function $f(\alpha) = (1-\alpha)^n$ (i.e. R2, R3 and F1 models, frequently referred as 'n-order' reactions). In such a case, Eq. (2) becomes:

$$-\ln(1-\alpha) = \ln \frac{A}{nC} - \frac{E_a}{RT} \quad (3)$$

and E_a and n cannot be simultaneously determined from a single experiment [26, 27]. This limitation

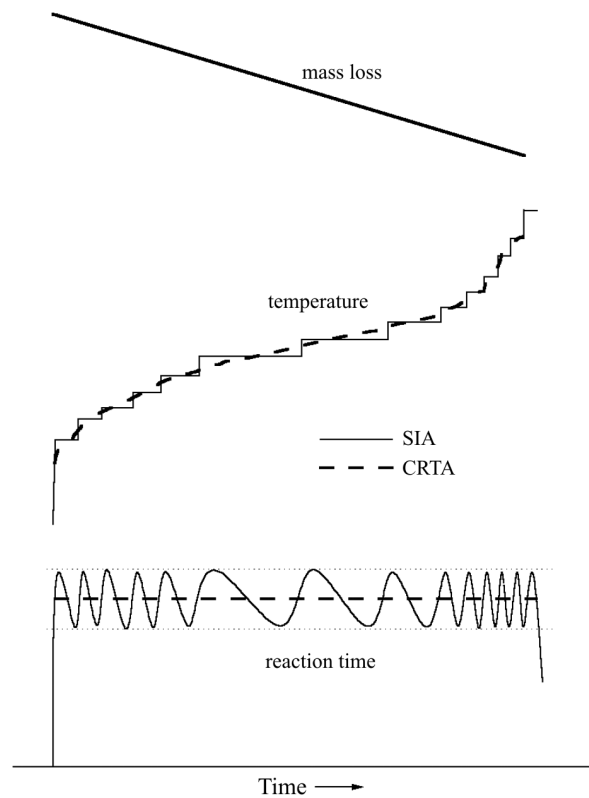


Fig. 2 Comparison of SIA and CRTA curves

could be overcome by the cyclic reaction rate or rate jump method proposed by Rouquerol [28–30].

CRTA jump method

This method imposes periodical jumps between two presets decomposition rates. The rate-jump method compares the state of the sample immediately before the rate jump, at which the reaction rate is C_1 and the temperature is T_1 , with the state immediately after the rate jump, at which the reaction rate and the temperature have moved to C_2 and T_2 , respectively. By assuming that the two states of the sample to be compared have almost the same reacted fraction, one gets

$$E = \frac{RT_1 T_2}{(T_2 - T_1)} \ln \frac{C_2}{C_1} \quad (4)$$

Equation (4) permits to obtain the activation energy of the process without any assumption regarding to the kinetic law obeyed by the reaction. The value of the 'reaction order' n can be determined from Eq. (3) once the activation energy has been determined from Eq. (4).

Reduced rate master plots

The first derivative of Eq. (2) can be rearranged in the form

$$T^2 \frac{d\alpha}{dT} = - \frac{E_a f(\alpha)}{Rf'(\alpha)} \quad (5)$$

The ‘reduced rates’ [31] can be calculated by taking as reference point the absolute temperature and rate at which $\alpha=0.5$ leading to the following expression

$$\left(\frac{T}{T_{0.5}} \right)^2 \frac{d\alpha / dT}{(d\alpha / dT)_{0.5}} = \frac{f'(0.5) f(\alpha)}{f(0.5) f'(\alpha)} \quad (6)$$

The left hand side of Eq. (6) is named ‘reduced rate’. This equation indicates that the plot of the ‘reduced rate’ vs. α depends neither on the kinetic parameters nor on the reaction rate, but only on the kinetic model. The master plots calculated from Eq. (6) for the kinetic models more commonly used for describing solid-state reactions are shown in Fig. 3. It can be observed the full overlapping of the ‘ n -order’ reaction master curves in contrast with the good discrimination of all the other kinetic models as indicated in a previous paper [32] in which the shapes of the SCTA curves were discussed. The superiority of SCTA methods for discriminating the kinetic model of solid-state reactions is clearly shown in Fig. 4 that represents the curves calculated for the models F1, A2 and A3 by assuming the same kinetic parameters used in Fig. 1 and a constant reaction rate $C=5 \cdot 10^{-6} \text{ s}^{-1}$. It is clearly dem-

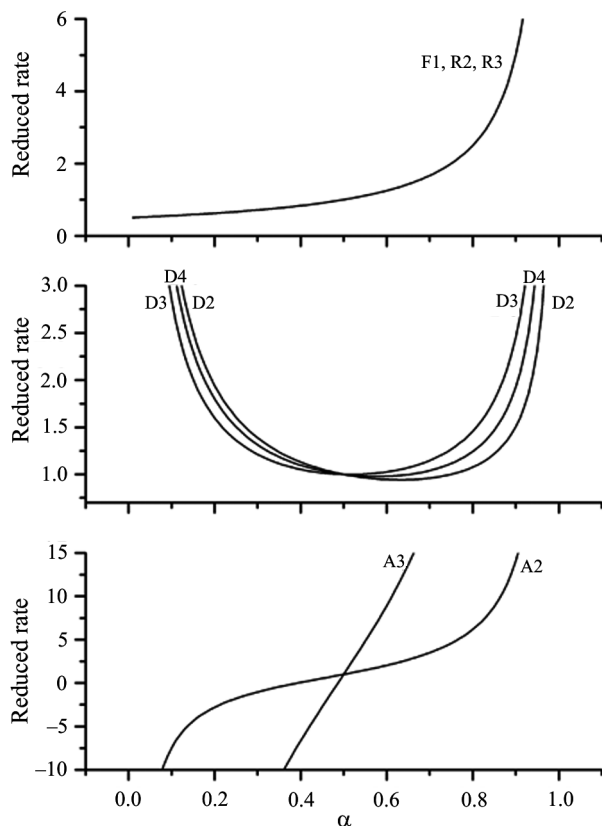


Fig. 3 Reduced rate master plots

onstrated that this kinetic models can be unambiguously discriminated by CRTA, which is not possible from conventional rising temperature α - T plots.

The comparison of the experimental reduced rate plots of the thermal decomposition of CaCO_3 and $\text{Ni}(\text{NO}_3)_2$ under high vacuum with the corresponding theoretical master plots included in Fig. 5 clearly shown that the thermal decomposition of calcium carbonate [33–35] and anhydrous nickel nitrate [36] fit an ‘ n -order’ and an Avrami–Erofeev kinetic model with an Avrami–Erofeev exponent $n \approx 2$, respectively [37].

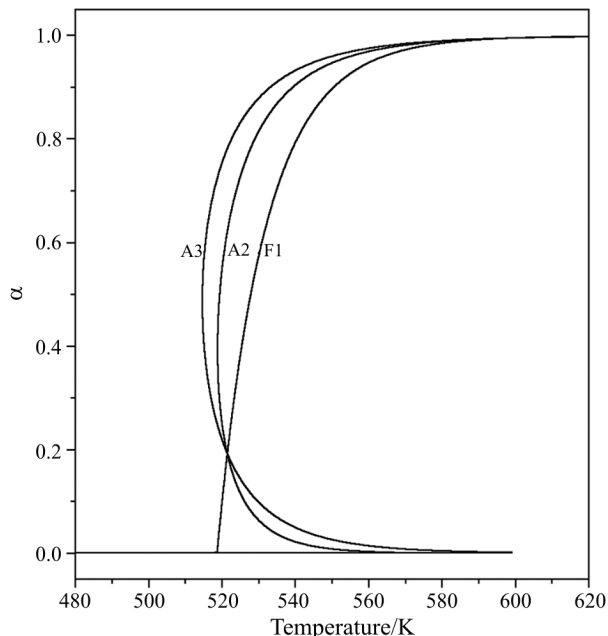


Fig. 4 Discrimination between the three kinetic models (F1, A2, A3) of Fig. 1 by means of the CRTA method ($C=5 \cdot 10^{-6} \text{ s}^{-1}$)

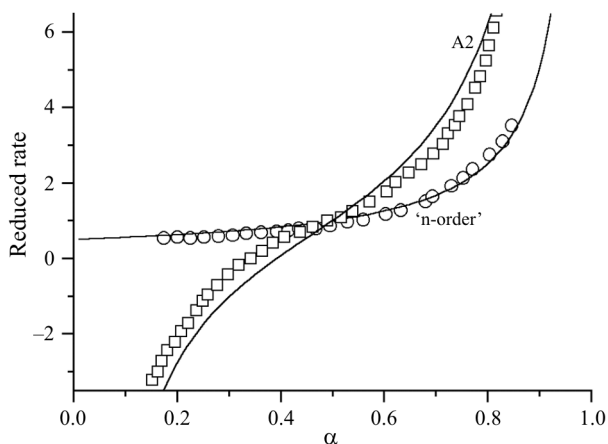
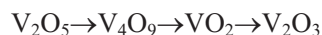


Fig. 5 A comparison of the experimental reduced rate plots of the thermal decomposition of \circ – CaCO_3 and \square – nickel nitrate with the master plots corresponding to ‘ n -order’ and A2 kinetic model, respectively

Applications of SCTA

The analysis of Fig. 4 shows that in the case of the reactions following the Avrami–Erofeev mechanism the process starts with a rise in temperature until reaching the selected constant reaction rate, C . This step is immediately followed by a temperature fall until reaching a certain value of the reacted fraction at which the temperature rises again. The part of the α – T profile on which the curve back on itself would correspond to the acceleratory period in which the total surface area of the growing nuclei would increase leading to an acceleration of the reaction that would be offset by a diminution of the temperature [38]. This feature makes CRTA a powerful tool for studying solid-state reactions whose rate is controlled by the formation and growing of nuclei. The application of CRTA methods to the kinetic analysis of solid-state reactions has clearly shown that these processes very often follow Avrami–Erofeev mechanisms in spite that they are frequently analysed from rising temperature experiments by assuming ‘ n -order’ reactions. Figures 6 and 7 include some examples of reactions for which the use of the SCTA method allows to conclude that they obey Avrami–Erofeev kinetic models. It must be remarked that the results reported by Fresenko *et al.* [39] for the reduction of V_2O_5 under flow of hydrogen clearly shows that it takes place through the three following steps:



every one fitting an Avrami–Erofeev kinetic model (Fig. 6).

On the other hand, it is noteworthy to point out that the shape of SIA curves does not coincides with the corresponding ones to CRTA in the case of reactions following an Avrami–Erofeev kinetic law, as shown in Fig. 7. In this case, SIA control forces the reaction to take place at a constant temperature almost all over the α range. This behaviour can be understood

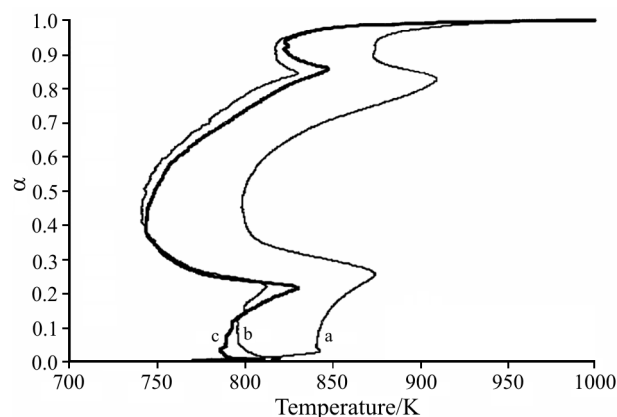


Fig. 6 Reduction of V_2O_5 using CRTA technique: a – 10 mg, b – 15 mg, c – 20 mg [39]

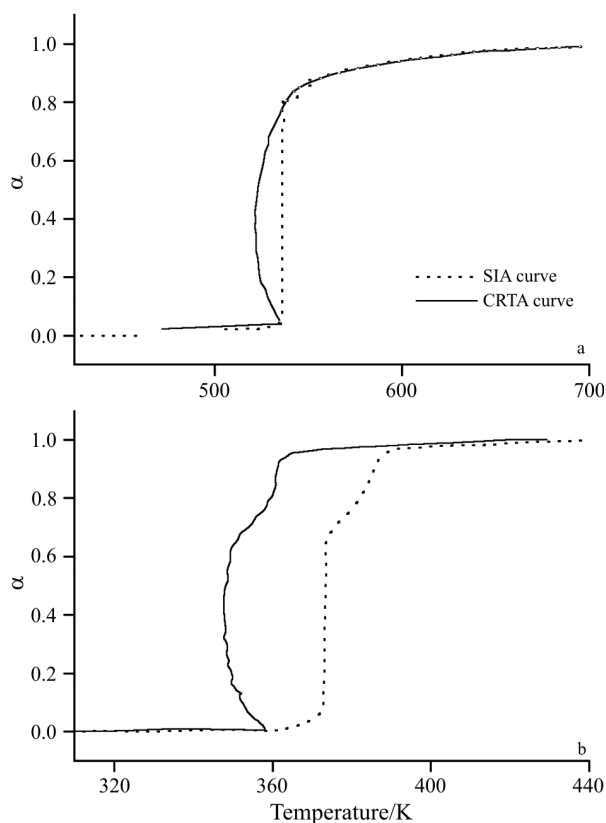


Fig. 7 SIA and CRTA curves recorded for a – the decomposition of anhydrous nickel nitrate [40], and b – dehydration of calcium sulphate dihydrate [41]

bearing in mind that once the preset reaction rate is reached and the acceleratory period starts, the temperature drops in order to compensate the abrupt increase of the reaction rate. CRTA permits to control the temperature in such a way that, if required, the α – T curve back on itself while SIA cannot and, as a consequence, the temperature remains constant while the measured reaction rate increases above the upper preset limit, which practically occurs almost all over the α range. The comparison of the CRTA and SIA curves obtained for the thermal decomposition of anhydrous nickel nitrate [40] and the thermal dehydration of copper sulphate dehydrate [41], respectively, supports the above conclusion as Fig. 7 shows. The CRTA curves in this figure falls back on itself upon achieving the preset constant rate while the SIA curve becomes an isotherm at the temperature T attained at the moment at which the preset upper limit was reached.

Advantages of SCTA for minimizing the influence of heat and mass transfer phenomena on the forward reaction

SCTA methods have important advantages for controlling the heat and mass transfer phenomena with re-

gards to conventional non-isothermal and even isothermal methods. The graphic representation proposed by Reading [41, 42], shown in Fig. 8, is very useful for remarking the advantages of SCTA with regards to conventional methods from the point of view of the experimental condition control. Figure 8 represents the evolution of the temperature, mass change and partial pressure of the evolved gases as a function of the time. In general, the lower the reaction rate, the lower is the chance of appreciable temperature or pressure gradients in the sample bed. The advantage of constant rate thermal analysis (CRTA) in terms of maintaining constant the product gas pressure and the reaction rate at a strictly constant value becomes clear from Fig. 8. Thus, SCTA method allows to minimize the pressure and temperature gradients within the sample and, therefore, to minimize or even avoiding the influence of heat and mass transfer phenomena on the forward reaction, leading to meaningful kinetic parameters from an adequate kinetic analysis. On the other hand, the isothermal and conventional rising temperature methods (Fig. 8) would lead to significant changes in the reaction rate and in the product gas pressure, that generally cannot be controlled by the user and could modify the shape of the α - T plots leading to a meaningless interpretation of the reaction mechanism. The good control that SCTA methods exert on both the atmosphere surrounding the sample and the real temperature of the sample bed explains that it were frequently observed that the activation energies calculated for either reversible [44–58] or irreversible [59] reactions of thermal decomposition of solids were independent of the sample size in a wide range of starting sample mass, while a similar behaviour was not observed when rising temperature experiments were concerned. Thus, Criado *et al.* [33] reported that the activation energy for the thermal decomposition of calcium

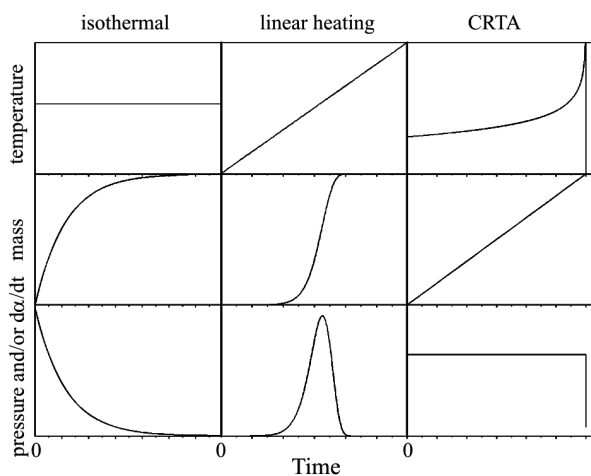


Fig. 8 Trend of temperature, mass and pressure (and/or $d\alpha/dt$) during a thermal decomposition reaction for different methods [43]

carbonate, as determined under a high dynamic vacuum from SCTA experiments, was independent of the starting sample mass in the investigated range, i.e. from 0.5 to 50 mg. However, the activation energy obtained for this compound under high vacuum from conventional linear heating TG diagrams is strongly depending on the experimental conditions and it is necessary to decrease the sample mass below 2 mg and to use a heating rate lower than 1 K min^{-1} in order to obtain kinetic parameters independent of the selected experimental conditions. These results are consistent with those later on reported by Reading *et al.* [48] for the same reaction.

Vyazovkin [13] has recently applied isoconversional methods for determining the relationship between the activation energy for the thermal decomposition of CaCO_3 and the reacted fraction from TG diagrams obtained under a linear heating rate and a partial pressure of CO_2 close to 0.5 mbar and he has concluded that the activation energy decreases by increases α as shown in Fig. 9. However, the study of the same reaction under high vacuum ($2 \cdot 10^{-6}$ mbar) carried out by Koga *et al.* [57] by using CRTA jump methods indicates that the activation energy determined from every tooth of Fig. 10 remains constant all over the α range at a value $E=223 \pm 8.7 \text{ kJ mol}^{-1}$. These results suggest that the dependence of the activation energy on α found by Vyazovkin [13] is rather apparent than real and it is probably caused by the influence of mass transfer on the forward reaction provided that the thermal decomposition of CaCO_3 is reversible and the partial pressure of CO_2 used is close to the equilibrium pressure at the temperature range investigated. Thus, it can be concluded that the obser-

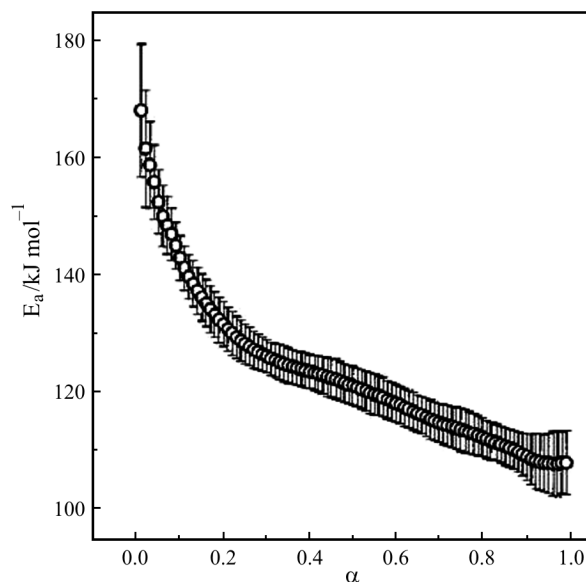


Fig. 9 Dependence of the activation energy on extent of CaCO_3 conversion determined using the isoconversional method from TG experiments [13]

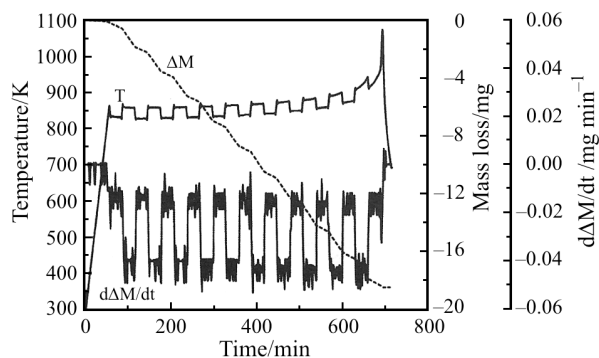


Fig. 10 Cyclic CRTA for the thermal decomposition of calcium carbonate powders at a vacuum of $2 \cdot 10^{-6}$ mbar [57]

variation of dependence between E and α from the application of isoconversional methods to rising temperature experiments is not enough for concluding that the reaction is taking place through several simultaneously occurring single step reactions, each of which has its own energy barrier as has been frequently assumed in literature. It would be necessarily required to check that the kinetic results obtained are not influenced by heat and mass transfer phenomena. SCTA methods would be a powerful tool for this purpose.

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