KINETIC STUDIES IN SOLID STATE REACTIONS BY SMART TEMPERATURE METHODS AND ADVANCED ANALYSIS PROCEDURES

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ABSTRACT

A comparative study of both conventional rising temperature and smart temperature control methods, like Constant Rate Thermal Analysis (CRTA), is carried out after analysing a set of solid state reactions using both methods. It is shown that CRTA avoids the influence of heat and mass transfer phenomena for a wide range of sample sizes leading to reliable kinetic parameters. On the other hand,conventional rising temperature methods yield α-T plots dependent on experimental conditions, even when using samples sizes smaller than 2 mg. Moreover, it is shown that the discrimination of overlapping processes is dramatically improved by using smart temperature control methods instead of conventional heating procedures. An advanced method for performing the kinetic analysis of complex processes from a single CRTA experiment is proposed.

INTRODUCTION

Smart temperature methods for studying chemical reactions imply controlling the temperature in such a way that the reaction itself follows a trend previously designed by the user. The most widely used smart temperature control method is the Constant (or Controlled) Rate Thermal Analysis (CRTA), independently developed by Rouquerol [1, 2] and the Paulik brothers [3]. This method involves controlling the temperature in such a way that the reaction rate is maintained constant all over the process. CRTA has been used by several authors for the synthesis of different materials, such as catalysts and sorbents with controlled porosity [4-24], structural ceramics [25-28] or electroceramics [29-32] and for binder burnout [33-35]. Besides it has many applications in analytical chemistry [36-39]. CRTA has been also extensively applied to the kinetic analysis of solid state reactions [40-61], after Criado et al. [62, 63] showed

the advantages of this method as compared to conventional rising temperature ones for discriminating among the different kinetic models. It was demonstrated that, while conventional rising temperature α-*T(t)* plots always present a sigmoidal shape independently of the reaction mechanism, the shape of the CRTA curves is strongly dependent on the reaction mechanism. Thus, the curves corresponding to "n order" models are convex with regards to the *T* axis, while those following diffusion kinetic equations present an inflection point and, finally, curves obeying an Avrami-Erofeev kinetic model show a minimum in temperature for certain value of α. Thus, CRTA experiments corresponding to reactions following this latter mechanism start with a rise in temperature until reaching the preset value of the reaction rate. This step is immediately followed by a temperature fall until reaching a determined value of the reacted fraction that depends on the *n* coefficient of the Avrami-Erofeev equation; then the temperature rises again until the reaction is over.

On the other hand, it has been claimed [61, 64] that CRTA has higher resolution power than conventional non-isothermal methods for discriminating mutually independent overlapping reactions . This behavior can be understood as a consequence of the high level of control provided by CRTA, i.e. the reaction rate is measured with a great accuracy (since it is constant), the uncertainty about the sample temperature is reduced by imposing a low reaction rate that minimize the temperature gradients while the surrounding atmosphere is also well controlled because of the reduction of the pressure gradients. In other words, CRTA provides almost automatically the experimental conditions required for meaningful and reliable kinetic experiments. Three different examples are presented, which illustrate the ability of CRTA for avoiding the influence of heat and mass transfer phenomena leading to reliable kinetic data and for discriminating overlapping processes in complex reactions (blended materials).

EXPERIMENTAL PART

The following materials were used: $PbCO_3$ supplied by Merck, PVC fine powder (with average M_n = 47000 and average M_w = 80.000) supplied by Aldrich and a sample of PVC

blended with a 33% of DINCH (1,2cyclohexane dicarbocylic acid, diisononyl ester) as plasticizer.

For thermal analysis experiments, a homemade system that allows working under a vacuum better than $2 \cdot 10^{-6}$ mbar or under a controlled flow of any inert or reactive permanent gas and in the temperature range from room temperature to 1250 K has been attached to a CI Electronic electrobalance.

The thermal decomposition of $PbCO_3$ was studied under both conventional linear heating rate and CRTA conditions in vacuum. Samples were outgassed at room temperature until reaching the best vacuum available (4.10^{-5} mbar). For linear heating rate experiments sample sizes smaller than 5 mg were used. CRTA experiments were carried out using the Rouquerol approach [65]. It consists on monitoring the furnace temperature in such a way that the pumping rate and the residual pressure in the close vicinity of the sample is maintained constant all over the process. The CRTA diagrams were recorded using a constant CO_2 residual pressure of 4.10^{-5} mbar and a constant decomposition rate of about $1.6.10^{-3}$ min^{-1}. A starting sample size of 20 mg was used. In addition, a cyclic CRTA experiment was performed using a sample size of 100 mg. In such case two decomposition rates were set at $1.6.10^{-3}$ min^{-1} and $1.9.10^{-3}$ min^{-1} and they were maintained constant during alternative periods of 1 hour. These conditions allow performing about 15 cycles during the decomposition of the $PbCO_3$.

For PVC and PVC blend, experiments were performed under 100 ml min^{-1} nitrogen flow using both linear heating rate and CRTA experiments. For the CRTA experiments, the temperature was controlled in such a way that the mass change as a function of time fits a predefined linear function. A detailed description of this temperature control system can be found in a previous reference [66].

THEORETICAL PART

The reaction rate of a solid state reaction can be represented by the following equation:

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

where α is the reacted fraction, t is the time, $d\alpha/dt$ is the reaction rate, T is the temperature, A is the preexponential factor of Arrhenius, E is the activation energy, R is the gas constant and $f(\alpha)$ is a function representing the kinetic model.

Eq. (1) must be accomplished whatever would be the thermal pathway followed for achieving a particular point of the triplet $(d\alpha/dt)$-α-T. If the α-T (or t) plot is obtained at a constant decomposition rate $(C = d\alpha/dt)$, Eq. (1) can be rearranged, after taking logarithms, in the form:

$$-lnf(\alpha) = ln\frac{A}{C} - \frac{E}{RT} \qquad (2).$$

The plot of the left hand side of Eq. (2) as a function of $1/T$ leads to a straight line, where the slope leads to the activation energy and the intercept to the pre-exponential factor of the Arrhenius expression of the process, provided that the proper $f(\alpha)$ function is selected, except if the kinetic model is 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:

$$-ln(1 - \alpha) = ln\frac{A}{nC} - \frac{E}{nRT} \qquad (3)$$

E an n cannot be simultaneously determined from a single experiment unless one of these two parameters is known from other source. The method of *Cyclic Reaction Rate* also named *Rate Jump method* proposed by Rouquerol [67] would allow overcoming this limitation. This method imposes periodical jumps between two pre-set decomposition rates and 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 jump, at which the reaction rate and the temperature have moved to C_2 and T_2, respectively. Taking into account that the two states of the sample to be compared have practically the same reacted fraction, one gets

$$E = \frac{RT_1T_2}{(T_2 - T_1)} \, ln\frac{C_2}{C_1} \qquad (4).$$

Equation (4) permits to obtain the activation energy of the process without any assumption regarding 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).

RESULTS AND DISCUSSION

CRTA and control of the heat and mass transfer phenomena

The study of the thermal decomposition of lead carbonate illustrates the advantages of CRTA for minimizing the influence of mass and/or heat transfer phenomena on the forward reaction in order to get reliable kinetic information. The study of this reaction from rising temperature thermogravimetric experiments recorded under high vacuum has shown that it is not possible to obtain TG curves independent of the starting sample mass, not even for sample sizes smaller than 2 mg and heating rates as low as 0.5 K min^{-1}, as illustrated in Fig. 1. These results clearly demonstrate that it is not possible to derive reliable kinetic data of the thermal decomposition of this carbonate from conventional TG, even under high vacuum, which is expected to minimize the influence of the CO_2 self-generated in the thermal decomposition.

Figure 2 shows the α-*T* CRTA curve obtained at constant decomposition rate, i.e. *C* = 1.6.10^{-3} min^{-1}, for a starting sample size of 20 mg. The concave shape of the plot suggests that the thermal decomposition of $PbCO_3$ obeys an "n order" reaction and, therefore, as stated in the theoretical section, it is not possible to determine simultaneously the activation energy and the exponent *n*. However, the value of *E*/*n* can be obtained from the slope of the plot of the left hand side of Eq. (3) versus 1/*T* as indicated in the theoretical section, yielding a value of *E*/*n*= 122 kJ mol^{-1}. An additional cyclic CRTA experiment has been carried out under the experimental conditions described in the experimental section, for calculating the activation energy. Fig. 3 shows a detail of a tooth taken from the cyclic CRTA curve. The activation energy determined from this cycle is *E* = 121 kJ mol^{-1}, while very similar values were obtained for each of the 15 cycles recorded from α = 0.05 up to α = 0.95, leading to an average value of E = 120 ± 10 kJ mol^{-1}. The comparison of this *E* value with the *E*/*n* value, obtained for the CRTA curve in Fig. 2, shows that the thermal decomposition of $PbCO_3$ fits a F1 kinetic model, i.e. *n*=1. It is noteworthy to remark that the α-*T* points taken from the traces of the cyclic CRTA curve at which the decomposition rate is equal to 1.6. 10^{-3} min^{-1} matches the CRTA of Fig. 2 recorded at the same constant decomposition rate, as shown in Fig. 2 with the superimposed points. This behavior clearly demonstrates that the α-*T* plots here obtained by the CRTA method are quite independent of the starting sample mass, unlike those obtained under rising temperature experiments, as it was previously shown in Fig. 1.

Advanced kinetics procedure for complex reactions

The kinetics of the thermal dehydrochlorination of polyvinyl chloride (PVC) was carried out in a previous paper [56]. In such work, it was concluded that the reaction takes place in two independent steps that were separated using and advanced kinetic analysis procedure, which involves the simultaneous analysis of a set of TG curves

obtained at different heating rates. It was shown [56] that the first step fits an Avrami-Erofeev kinetic model, followed by a second overlapping step that obeys a diffusion kinetic model. The microscopic observations support that the reaction follows an Avrami-Erofeev kinetic model (formation and growth of nuclei) and that part of the HCl formed in the dehydrochlorination reaction is trapped into bubbles and later released as the temperature increases. This latter process accounts for the second diffusion step.

The use of CRTA simplifies the kinetic analysis by improving the resolution of overlapping processes. This method provides a much better discrimination power of the solid state reaction kinetic models than conventional linear heating or isothermal experiments, because the shape of the CRTA α-T curve is dependent on the kinetic model followed by the process, unlike curves recorded under linear heating rate conditions, that always have a sigmoidal shape [61-63].

Figure 4 shows the α-T plot obtained at a constant decomposition rate, i.e. $C = 6.10^{-3}$ min^{-1}, for the thermal dehydrochlorination of PVC. Two overlapping steps are clearly observed in this figure. At the initial part, temperature sharply rises, until reaching the preset value of the reaction rate. At this point temperature immediately drops, until reaching a certain conversion value, followed by a new temperature rise. Thus, the curve falls back on itself upon achieving the preset constant rate. This shape is characteristic of a nucleation and growth of nuclei mechanism [61-63]. The shape of the second part of the curve is more difficult to discriminate because of the overlapping, but it seems to have a sigmoidal shape characteristic of diffusion processes [61-63].

A complete kinetic analysis of this complex reaction requires deconvoluting the overall curve into its individual processes and determining their kinetic parameters, i.e. activation energies, preexponential factors and kinetic models. No solution is found if the deconvolution of the overlapping curves is attempted by assuming two parallel competitive reactions, in agreement with the conclusion of Sánchez-Jiménez et al. [56], where two independent reactions are considered. Thus, the deconvolution has been carried out by resolving the following system of differential equations:

$$C = \frac{d\alpha}{dt} = l_1 A_1 \exp\left(-\frac{E_1}{RT}\right) f_1(\alpha_1) + l_2 A_2 \exp\left(-\frac{E_2}{RT}\right) f_2(\alpha_2) \tag{5}$$

$$l_1 + l_2 = 1 \tag{6}$$

$$l_1 \alpha_1 + l_2 \alpha_2 = \alpha \tag{7},$$

where the subscripts 1 and 2 correspond to the first and second process, respectively, l_1 and l_2 being the contribution fraction of each process. It has been shown in a previous paper [68] that the $f(\alpha)$ functions of all the different kinetic models proposed in literature can be represented by the following modified Sestak-Berggren equation,

i.e. $f(\alpha) = c\,\alpha^m(1-\alpha)^n$. This empirical approximation also accounts for deviations from the ideal kinetic models due to inhomogenities in shape and particle size distribution. Thus, the modified Sestak-Berggren equation has been used for $f_1(\alpha_1)$ and $f_2(\alpha_2)$ in Eq. (5).

All the kinetic parameters are determined by comparing the experimental curve with the theoretical one obtained from Eqns. (5), (6) and (7) using iterative optimization.

Considering the CRTA shape analysis discussed before, the experimental curve was fitted assuming Avrami-Erofeev and tridimensional diffusion mechanisms for the beginning and the end of the reaction, respectively, while the resulting kinetic parameters were used as starting values for the optimization process. The iterative optimization procedure yielded the following kinetic parameters: $l_1 = 0{,}66$, $E_1 = 113$ kJ/mol, $c_1 A_1 = 5{,}8.10^{10}$ min^{-1}, $n_1 = 1{,}17$, $m_1 = 0{,}68$; $l_2 = 0{,}34$, , $E_2 = 202$ kJ/mol, $c_2 A_2 = 1{,}1.10^{17}$ min^{-1}, $n_2 = 1.37$ and $m_2 = -1.89$. These values are in very good agreement with those previously reported [69] for the same sample from the simultaneous kinetic analysis of a set of TG diagrams obtained under different heating rates. Moreover, the theoretical curve constructed with these parameters matches quite well the experimental curve, as shown in Fig. 4.

The values of n_1 and m_1 agree with the values expected for an A_2 Avrami-Erofeev kinetic model, while the values obtained for n_2 and m_2 agree with the values expected for a tridimensional diffusion controlled reactions as shown in previous references [56, 69]. In summary, the results here reported show that CRTA method considerably simplifies the kinetic analysis of complex processes.

Applications of the resolution power of CRTA methods in Analytical Chemistry

Elastomers often contain an appreciable amount of oil as a plasticizer. Hammer [70] has shown that in many cases, accurate determination of oil and polymer content is difficult because oil vaporization and elastomer thermal decomposition overlap. CRTA method is a powerful tool for overcoming this problem.

The higher resolution power of CRTA with regards to conventional rising temperature methods is of great interest for increasing the efficiency of thermogravimetry as an analytical tool. It has been shown in a recent paper [37] that CRTA allows to perform compositional analysis of multicomponent polymeric materials by means of thermogravimetric experiments. Fig. 5 shows the conventional linear heating rate and CRTA curves obtained for PVC blended with DINCH plasticizer (1,2cyclohexane dicarbocylic acid diisononyl ester). It can be observed that the CRTA curve leads to a complete separation of both the evaporation of the plasticizer and the thermal decomposition of the polymer. This is not achieved in the curve recorded under linear heating rate conditions where both processes totally overlap. Besides, the shape of α-T plot corresponding to the dehydroclorination of PVC, as shown in Fig. 4, is observed in the second step of the CRTA curve of Fig. 5, after the plasticizer is released. Thus, it can

be concluded that CRTA constitutes a powerful tool for determining the percentage of plasticizers contained in blended polymers, avoiding the use of chromatographic techniques that are rather cumbersome and time consuming [71, 72].

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Captions of figures

Fig. 1. Curves obtained under high vacuum at a linear heating rate of 0.5 K min^{-1} for 4.5 mg (a) and 1.9 mg (b) of PbCO$_3$.

Fig. 2. CRTA curve of PbCO$_3$ obtained under high vacuum at a constant decomposition rate C = 1.6.10^{-3} min^{-1}. The superimposed black points have been taken from the part of the cyclic CRTA experiment that is running at C = 1.6.10^{-3} min^{-1}.

Fig. 3. A tooth in a cyclic CRTA for PbCO$_3$, showing the evolution of temperature and mass loss. Values of T_1 and T_2 corresponding to the C_1 and C_2 reaction rates have been marked in the figure.

Fig. 4. CRTA curve resulting from the thermal dehydroclorination of PVC sample at a constant reaction rate of 6.10^{-3} min^{-1}. Experimental curve is represented by points while the theoretical reconstructed one is represented by a line.

Fig. 5 Experimental mass loss against temperature recorded under flowing nitrogen atmosphere at a constant reaction rate of 3.10^{-3} min^{-1} for a blend PVC-DINCH (solid line). The linear heating rate experiment recorded at 1 K min^{-1} has been included for comparison (dotted line).
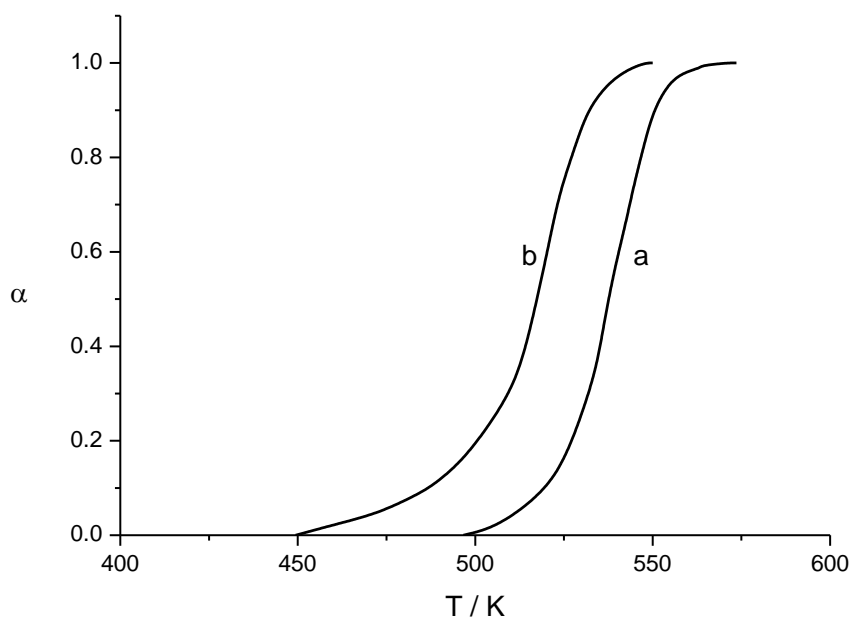
Figure 1.

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Figure 2

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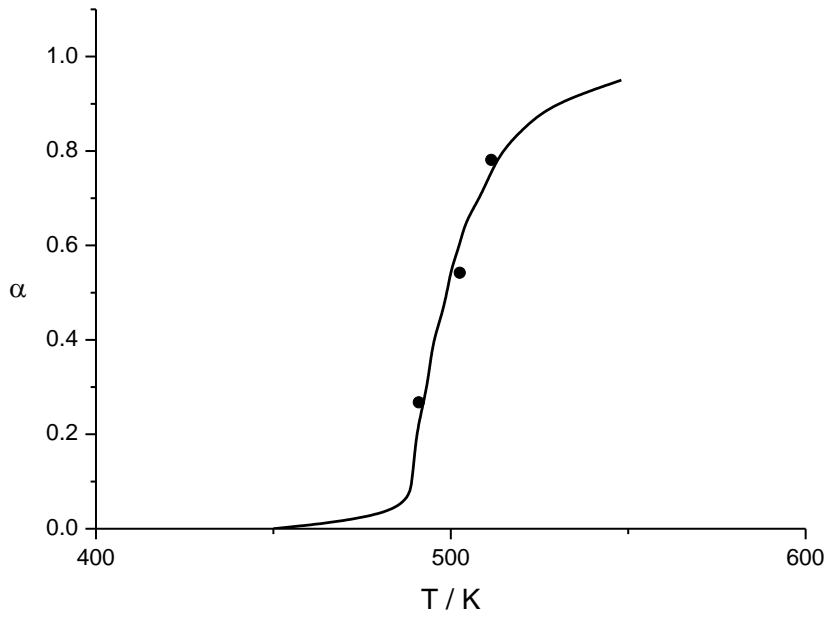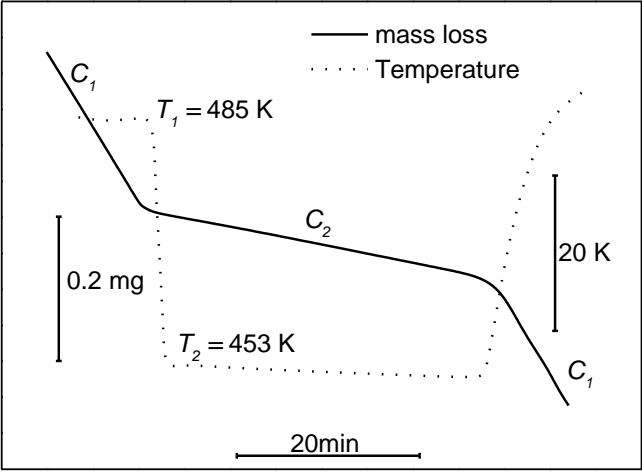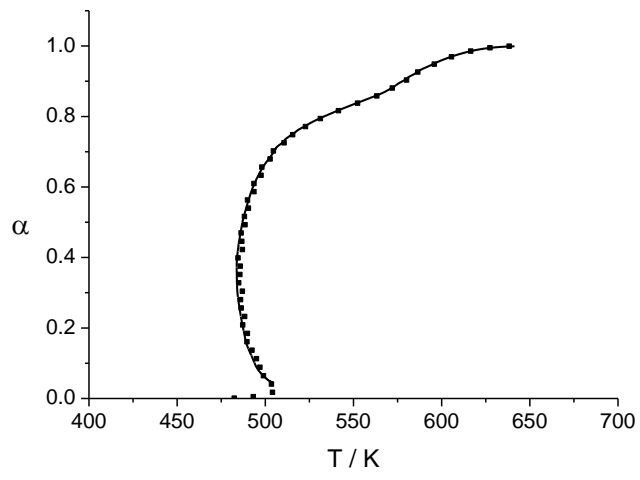54
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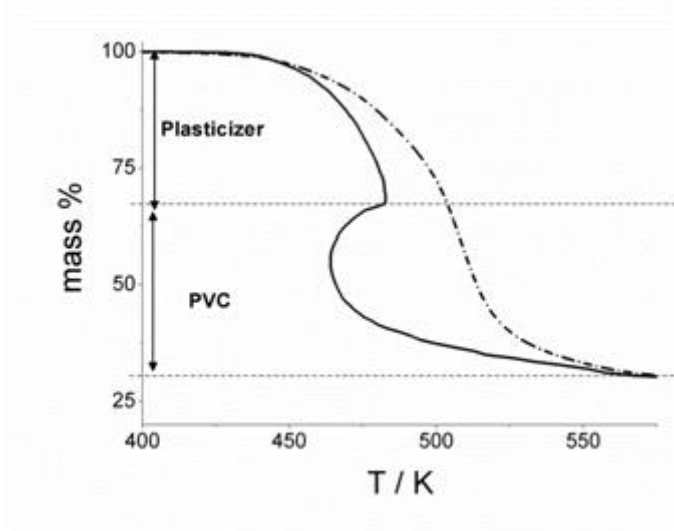63
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Figure 3

Figure 4

Figure 5

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