APPLICATIONS OF SAMPLE CONTROLLED THERMAL ANALYSIS (SCTA) TO KINETIC ANALYSIS AND SYNTHESIS OF MATERIALS

L.A PÉREZ-MAQUEDA, J.M. CRIADO, P.E. SÁNCHEZ-JIMÉNEZ, M.J. DIÁNEZ

Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-C.S.I.C., Américo Vespucio 49,41092 Sevilla (Spain)

ABSTRACT: The advantages of the Sample Controlled Thermal Analysis (SCTA) for both the kinetic analysis of solid state reactions and the synthesis of materials are reviewed. This method implies an intelligent control of the temperature by the solid state reaction under study in such a way that the reaction rate as a function of the time fits a profile previously defined by the user. It has been shown that SCTA has important advantages for discriminating the kinetic model of solid state reactions as compared with conventional rising temperature methods. Moreover, the advantages of SCTA methods for synthesizing materials with controlled texture and structure are analyzed.

INTRODUCTION

Smart temperature methods for studying chemical reactions imply controlling the temperature in such a way that the reaction itself follows a trend predefined by the user. The most widely used smart temperature control method is the Sample Controlled Thermal Analysis (SCTA), independently developed by Rouquerol [1-2] and the Paulik brothers [3], although the last authors named the method Quasi-isothermal Quasi-isobaric Thermal Analysis as shown in the review of J. Simon [4]. This method involves controlling the temperature in such a way that the reaction rate is maintained constant all over the process. SCTA has been used by several authors for the synthesis of different materials, such as catalysts and sorbents with controlled porosity [5-23], structural ceramics [24-27] or electroceramics [28-31] and for binder burnout [32-34]. Besides it has many applications in analytical chemistry [35-38]. CRTA has been also extensively applied to the kinetic analysis of solid state reactions [39-62]. The scope of this work is to summarize the advantages of SCTA methods for performing the kinetic analysis of solid state reactions and for the synthesis of materials.

THE SCTA METHOD

The graphic representation proposed by Reading [63, 64], shown in Fig. 1, is very useful for remarking the advantages of SCTA with regards to conventional methods from the point of view of the experimental condition control. Fig. 1 represents the evolution of the temperature, mass change and partial pressure of the evolved gases as a function of the time for different experimental conditions. In general, the lower the reaction rate, the lower is the chance of appreciable temperature or pressure gradients within the sample bed. Therefore, Constant Rate Thermal Analysis (CRTA) provides an advantage in terms of maintaining constant the product gas pressure and the reaction rate at a strictly constant value. Thus, SCTA method reduces the pressure and temperature gradients within the sample and, therefore, minimizes the influence of heat and mass transfer phenomena on the forward reaction, leading to meaningful kinetic parameters necessary for an adequate kinetic analysis. On the other hand, the isothermal and conventional rising temperature methods would lead to significant changes in the reaction rate and in the product gas pressure, which 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 proper control that SCTA methods exert on both the atmosphere surrounding the sample and the real temperature of the sample bed explains that it has been frequently observed that the activation energies calculated by this method, for either reversible [45, 65-78] or irreversible [79] thermal decomposition of solids, are 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.

Fig. 2 illustrates, by way of example, a simple and universal SCTA device developed by us [80, 81] that could be used with any thermoanalytical instrument (TAI). It is constituted by a conventional PID temperature programmer, which has the thermocouple connected to the input socket, for setting preselected isothermal or rising temperature conditions. A second programmer is used for controlling the profile of the TAI output signal as a function of the time. The control of the reaction rate is achieved by connecting the control relay of the TAI programmer to the digital input of the temperature programmer. SCTA control is performed by selecting from the menu of the digital input that allows one to move the temperature program from a preset heating rate when the TAI control relay is closed to a preset cooling rate when the TAI control relay is open. In other words, the temperature increases if the output signal supplied by the TAI is higher than the programmed setpoint and decreases if it is lower than the setpoint. This device has been successfully attached to different analytical devices for SCTA control. Fig. 3 shows, by way of example [80], the change of weight and temperature as a function of the time obtained for the thermal decomposition of PVC under SCTA control at a previously selected constant decomposition rate rate C = $1.2.10^{-3}\%.\ s^{-1}$. In this case the output corresponding to the total change of weight supplied by the electrobalance was used as input of the TAI signal programmer on the device outlined in Fig. 2. It can be observed that the plot of the reacted fraction as a function of the time fits a straight line with a slope equal to the previously selected constant decomposition rate.

ADVANTAGES OF SCTA

Discrimination of the kinetic model

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

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

where α is the reacted fraction, *t* is the time, *d*α/*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*(α) is a function representing the kinetic model.

Eq. (1) must be accomplished for whatever thermal pathway is followed for achieving a particular point of the triplet (dα/dt)-α-T. If the α-T (or t) plot is obtained at a constant decomposition rate (*C* = *d*α/*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. It was previously shown from a theoretical analysis [62] that only the f(α) function that really describes the kinetic model obeyed by the reaction fulfil Eqn. (2), contrarily to what occurs in rising temperature experiments[82-93]. In this latter case, a number of different kinetic models can fit simultaneously a given α-T plots, making impossible to discriminate the kinetic model from a single experiment recorded under a linear heating program. In order to illustrate this behaviour it has been shown in Fig. 4 that a unique TG curve can be calculated by assuming different kinetic models: F1, A2 and A3, while these models can be unambiguously discriminated by CRTA as shown on the right side of Fig. 4 that represents the curves calculated from Eq. 1 for the models F1, A2 and A3 by assuming the same kinetic parameters used in Fig. 4.6 and a constant reaction rate, C = 5.10^{-6} s^{-1}.

This analysis leads to the conclusion that SCTA method is a more reliable approach than conventional non-isothermal methods both for discriminating the real kinetic model obeyed by solid state reactions and for obtaining correct values of their activation energies.

The experimental results included in Fig. 5 for the thermal dehydroclorination of PVC supports the above conclusion. Thus, the SCTA α-T plot obtained from Fig. 3 is compared with a conventional thermogravimetric curve (TG) obtained for the thermal decomposition of PVC under a heating rate of $3{,}3.10^{-2}$ $K.s^{-1}$. It is observed that the SCTA experiment allows discriminating the two steps evolved in the dehydroclorination of PVC, while conventional TG cannot. Moreover, the shape of the α-T plot clearly shows that the first step of the dehydroclorination takes place through an Avrami-Erofeev kinetic model. It has been shown [62,94] that in such a case the α-T plot starts with a rise of temperature until reaching the preset value of the reaction rate that is immediately followed by a decreasing of the temperature until reaching a given value, α_m, of the reacted fraction (that depends on the value of the coefficient n of the Avrami-Erofeev equation), and the temperature rises again once the corresponding α_m value is attained. Thus, a glance to the shape of the SCTA curve would be enough for envisioning the kinetic model of a solid state reaction contrarily what occurs with the TG curves have always led to sigmoidal shaped α-T plot, independently of the reaction mechanism obeyed by the reaction.

Synthesis of materials with controlled texture and structure

The SCTA methods allow a precise control of the reaction rate, what implies a direct or indirect control of the partial pressure of the gases generated or consumed in the reaction and the associated heat evolution rate. This temperature control allows both minimizing the heat and mass transfer phenomena and performing a very precise control of the atmosphere surrounding the samples.These features have been exploited for developing materials with controlled porosity and structure for being used either as adsorbents or catalysts [5,9,21-23, 95-100].

The universal SCTA control device outlined in Fig. 2 has been used for controlling both the reaction rate and the partial pressure during the thermal decomposition under vacuum of precursors of catalysts and ferroelectric materials. The output signal of the pirani or penning was used as TAI input control signal at the time that the decomposition rate was monitored through a proper control of the pumping rate of the vacuum system. Thus, both the partial pressure of the gases generated in the reaction and the thermal decomposition rate were simultaneously controlled. The results obtained by using the described SCTA vacuum system for the synthesis of α- Fe_2O_3 (hematite) from the thermal decomposition under vacuum of α-FeO(OH) (goethite) samples with acicular shaped particles [19,20] are reported as way of example. Slit pore channels oriented along the c-lattice axis (the long axis of the particle) were formed at very low water vapour pressures as shown in Fig. 6. Isolated round pores were progressively formed as far as the water vapour pressure was increased at the time that its size was increasing as a function of the pressure as Fig. 6 shows. A diminution of the water vapour pressure during the thermal decomposition of goethite strongly promoted the increase of the specific surface of the hematite obtained as final product. A similar behaviour was reported for the textural properties of the γ-Fe_2O_3 (maghemite) obtained by controlling both the rate and the water vapour pressure during the thermal decomposition of the γ-FeOOH (lepidocrocite) precursor by means of the SCRT method [18]. Very recently, SCTA has been used for enhancing the long-term CO2 capture of CaO at Ca-looping conditions. Thus it has been shown that CaOregenerability at conditions close tothe Calcium-looping (CaL) process is improved by means of a relativelyshort-timed preheating treatment and carried out at a relativelylow temperature, which is based on SCTA in an air/CO2 atmosphere [100]

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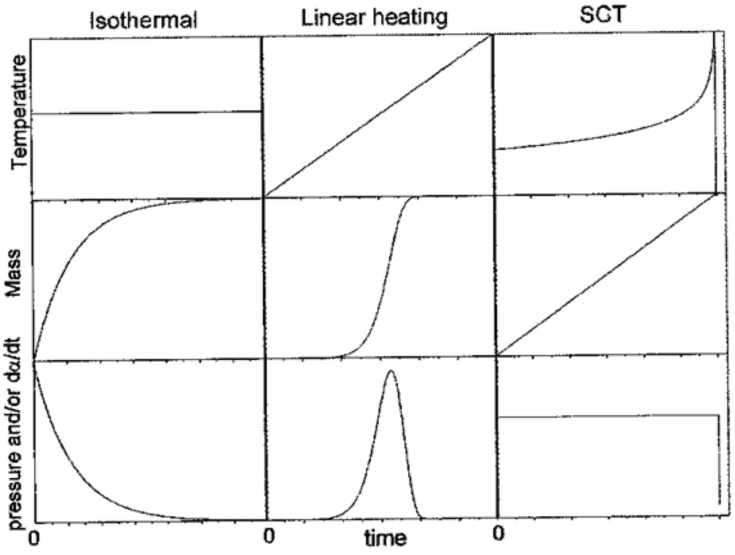
Figure 1.



Isothermal
Linear heating
SCT
Temperature
Mass
pressure and/or dα/dt
0
0
time
0

Figure 2.

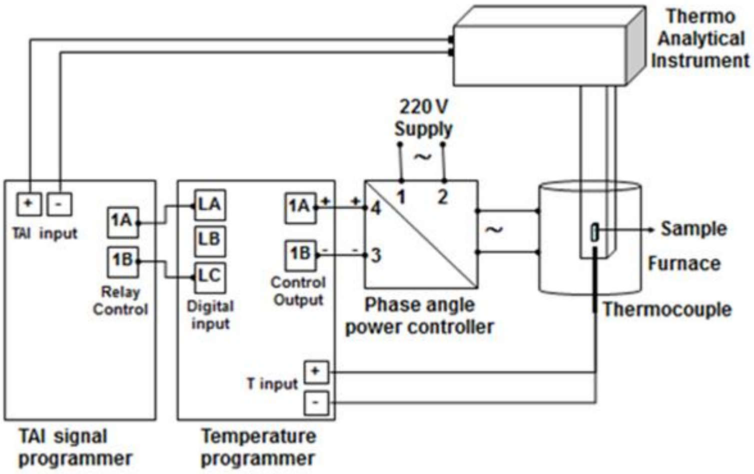

Thermo
Analytical
Instrument
220 V
Supply
~
+
-
TAI input
1A
1B
Relay
Control
LA
LB
LC
Digital
input
1A
1B
Control
Output
+
-
4
3
1
2
~
Phase angle
power controller
Sample
Furnace
Thermocouple
T input
+
-
TAI signal
programmer
Temperature
programmer

Figure 3.

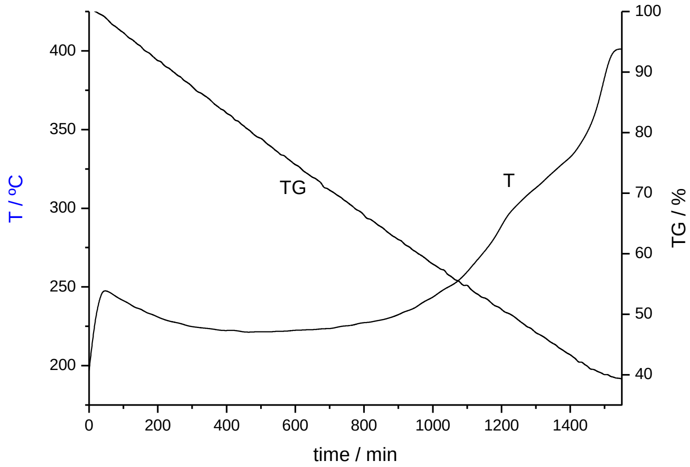

T / °C
400
350
300
250
200
TG
T
100
90
80
70
60
50
40
TG / %
0
200
400
600
800
1000
1200
1400
time / min

Figure 4.

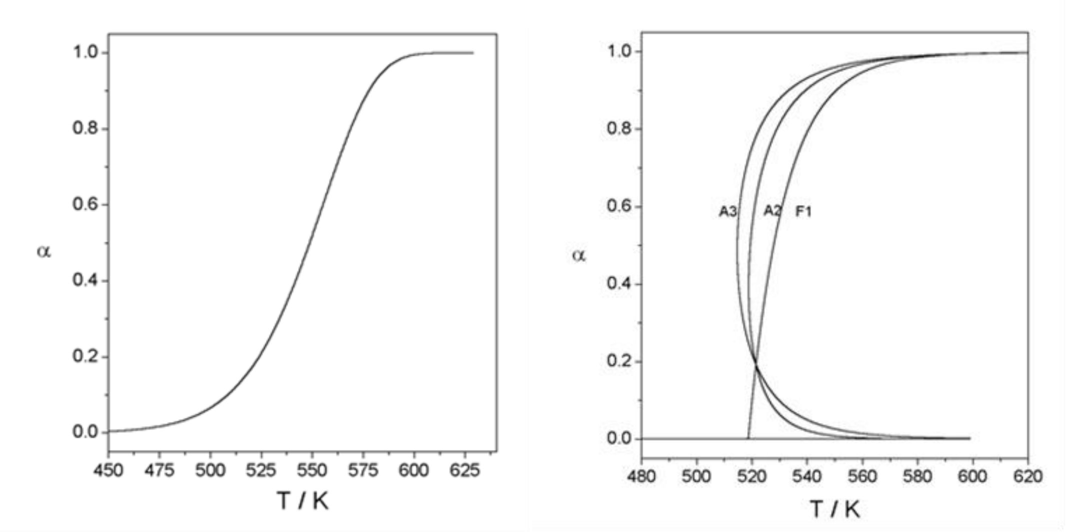

1.0
0.8
0.6
0.4
0.2
0.0
α
450
475
500
525
550
575
600
625
T / K
1.0
0.8
0.6
0.4
0.2
0.0
α
A3
A2
F1
480
500
520
540
560
580
600
620
T / K

Figure 5.

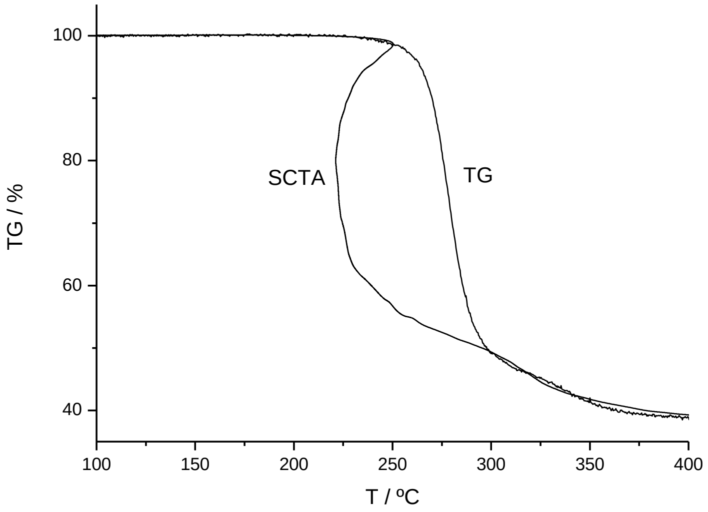
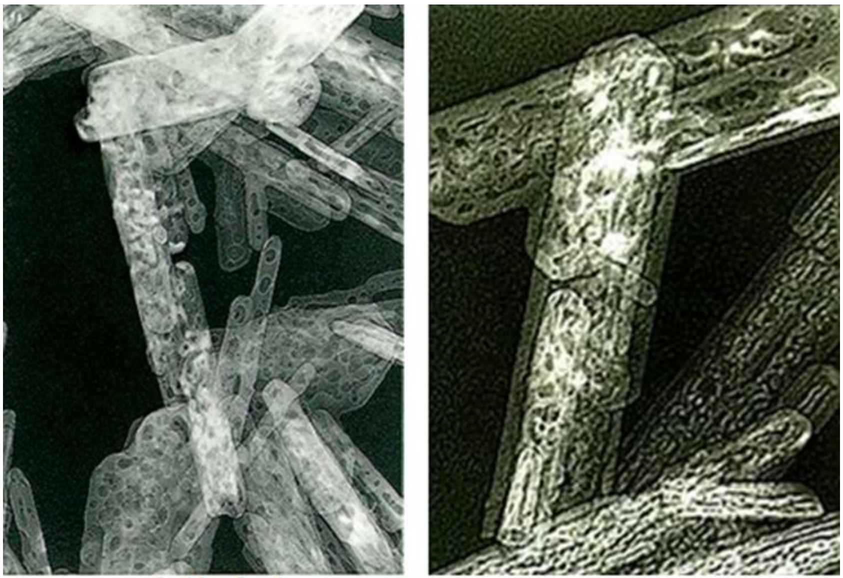


Figure 6.



S: 44 m2 g-1

S=102 m2 g-1

Captions of figures.

Figure 1.Trend of temperature, mass and pressure (and/or dα/dt) during a thermal decomposition reaction for different methods.

Figure 2. Scheme of the universal SCTA device to be used for controlling the reaction temperature of any thermoanalytical device.

Figure 3. SCTA plot obtained for the dehydroclorination of PVC at a constant decomposition rate C =5.10^{-4} s^{-1} ($5{,}0.10^{-4}$ mg.s^{-1})

Figure 4. A single TG curve at a heating rate of 1 ºC/min for three different models: F1: Ea= 172.3 kJ mol^{-1} and A = 2.30 10^{13} s^{-1}; A2: Ea= 118.1 kJ mol^{-1} and A = 1.24 10^{8} s^{-1}; A3: Ea= 100.0 kJ mol^{-1} and A = 1.66 10^{6} s^{-1} (left). Discrimination between the three kinetic models (F1, A2, A3) of Fig. 4.6 by means of the SCTA method (right).

Figure 5. A comparison of the α-T plot obtained from the SCTA experimental data included in Figure 3 with a TG recorded for the dehydroclorination of PVC at a heating rate $\beta = 3{,}3.10^{-2}$ K.s^{-1}

Figure 6. TEM micrographs corresponding to hematite sample prepared by thermal decomposition of goethite under SCTA conditions: P= $5.5x10^{-5}$ mbar andC = $1{,}6.10^{-5}$ s^{-1} (left) and P=8.3 mbar and C= $1{,}2.10^{-5}$ s^{-1}.