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Gas concentration programming – a new approach to sample controlled thermal analysis

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Abstract

Sample controlled thermal analysis (SCTA) is the generic name used to describe a family of techniques where the heating rate is not pre-determined as in conventional thermal analysis, but altered as some function of a property of the sample (i.e. mass loss, rate of gas evolution, etc.). We demonstrate here a new form of SCTA, where the reaction rate for gas–solid reactions can be controlled by programming the concentration of the reactive gas whilst keeping the temperature constant. © 1998 Elsevier Science B.V.

Keywords: Sample controlled thermal analysis; Copper oxide; Gas concentration programming

1. Introduction

In a number of industrially important areas thermal analysis is used to study gas–solid reactions. For example, in heterogeneous catalysis, various thermal techniques such as temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) are widely used. In conventional (linear heating) thermal analysis, the results are complicated not only by the temperature gradients throughout the sample but also by the changing concentration of the reactive gas-phase component(s). Previous workers have demonstrated that SCTA[1] techniques, such as constant rate thermal analysis (CRTA) [1] where the heating rate is continuously altered so as to keep the reaction rate constant, can provide enhanced resolution between adjacent thermal events and improved kinetic data [2–4]. In this paper, we will show that it is possible to perform experiments analogous to both, conventional temperature programming and SCTA by programming the gas-phase composition under isothermal conditions[2].

A general expression for the rate of a solid–gas reaction, ignoring any diffusion contribution, is

$$\mathrm{d}\alpha/\mathrm{d}t = A\mathrm{e}^{-E_\mathrm{a}/RT}f(c) \qquad (1)$$

where the variables A and E_a can be regarded as temperature coefficients, and the function of

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[1] The proposal for the term ‘sample controlled thermal analysis’ first arose in discussions between the authors, Drs. J. Rouquerol and M. Reading at the ESTAC 6 (Grado, 1994) and TMG (Leeds, 1996) conferences and was endorsed at the workshop on SCTA methods, held at the 11th ICTAC, Philadelphia, 1996.

[2] The concept of ‘concentration programming’ SCTA was first described by the authors at the Constant Rate session, ESTAC 6, (Grado, 1994).

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concentration, which is dependent on the reaction, can be represented generally as:

$$f(c) = c^n \tag{2}$$

where the variable n usually assumes values in the range 0–2. It can be seen that, in the case of temperature programmed experiments, whether conventional or some form of SCTA, the overall shape of the TA curve is determined primarily by the exponential term in Eq. (1). However, if the experiment is carried out isothermally, the curve shape will be governed by the concentration term defined in Eq. (2). The first important consequence of this is that a change in temperature will exert a greater influence than variations in concentration of a gas-phase reactant. The effect of this is that peaks found in conventional thermal analysis (i.e. linear increase in temperature) generally will be sharper than those found in the analogous case, where the concentration of a gas-phase reactant increases linearly. However, if the concentration is altered such that it produces a constant reaction rate, the reaction will proceed under near equilibrium conditions of both temperature and concentration and, hence, produce measurements which have a greater fundamental significance.

2. Experimental

The basic apparatus used has been described in detail elsewhere [5]. The major components comprise a small, water-cooled furnace (Stanton Redcroft), the temperature of which is continuously altered via a temperature controller (818P, Eurotherm), using SCTA software developed by the authors. The reaction rate is monitored by measuring the evolution of water using a hygrometer (SGE), the output of which is fed back to the computer via a 16-bit ADC (Comark). Normally, a single mass-flow controller (Brookes) is used to set the flow of carrier gas through the furnace and EGA detector. For the gas-phase concentration experiments, however, a second mass-flow controller was added in parallel. One controller was operated with pure helium and the other with a 5% hydrogen in helium mixture, and their outputs were combined before passing into the furnace. The software was adapted so that, via two DACs (Comark), the mass-flow controllers could be made to produce any blend of hydrogen in helium between 0 and 5% whilst keeping the total flow rate constant (at 20 $\mathrm{cm^3\ min^{-1}}$).

To demonstrate the techniques, the reduction of copper (II) oxide (Aldrich, AnalaR grade) was used as a model system. Copper oxide is reduced by hydrogen to produce copper metal with the formation of water:

$$\mathrm{CuO + H_2 \rightarrow Cu + H_2O}$$

All experiments were performed using a ceramic crucible and a sample mass of 2.5 mg.

While the hygrometer response gives absolute values for the concentration of water vapour, its response is dependent on the flow rate. The results presented below are recorded in arbitrary units (a.u.) which serve to show the different rates of reaction. In evolved gas analysis (EGA), it should be noted that the reaction rate is directly proportional to the magnitude of the signal, thus a peak maximum corresponds to the fastest rate of reaction.

Our implementation of the 'temperature programmed' CRTA technique has three principle parameters which can be set by the user. These are a target reaction rate, a heating rate and a cooling rate. A three-term PID control algorithm is used to maintain the desired reaction rate by altering the heating rate as required between these upper and lower values. The 'concentration programmed' CRTA technique is similar except that it is the concentration of the reactant gas that is altered to maintain the desired reaction rate under isothermal conditions.

3. Results and discussion

Fig. 1 shows the conventional temperature programmed reduction of 2.5 mg of copper oxide using a 5°C $\mathrm{min^{-1}}$ heating rate to 400°C and a fixed 5% blend of hydrogen in helium. A single peak centred on 290°C is evident with a maximum height of $\approx$18 a.u.

Fig. 2 shows the equivalent 'concentration programmed' experiment, holding at 225°C and linearly programming the blend of hydrogen in helium at a rate of 10% $\mathrm{h^{-1}}$ from 0 to 5%. The plateau at the end, caused by the limit of 5% hydrogen being reached, can be viewed as being analogous to holding at a fixed temperature at the end of a conventional TPR run. It can be seen that the hydrogen concentration profile is

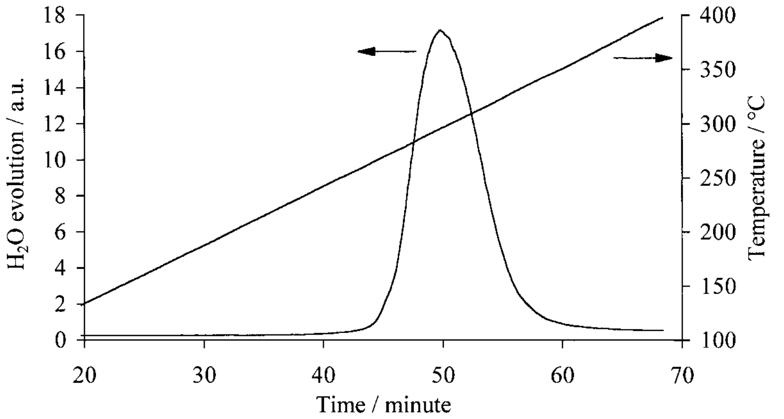

Fig. 1. Reduction of 2.5 mg of copper(II) oxide in a 5% hydrogen in helium atmosphere under linear heating conditions of 5°C min^{-1}.

similar to that of the temperature in Fig. 1 and that the peak is somewhat broader than the temperature programmed equivalent.

Fig. 3 shows the reduction using the constant rate SCTA technique with a heating rate which was allowed to vary between +3 and −20°C min^{-1} and a target rate of 0.25 a.u. (approximately equivalent to 1.4% of the maximum reaction rate achieved during the linear temperature programmed experiment). It can be seen that there is an initial overshoot of the evolved water and the temperature has to fall by ≈80°C before the reaction rate attains its set target. A fast cooling rate was necessary to ensure that this overshoot, which has been attributed to the autocatalytic nature of the reduction [6,7], was sufficiently brief to allow the majority of the reduction to proceed under constant rate conditions.

The concentration programmed equivalent of the Constant rate SCTA experiment is illustrated in Fig. 4. The temperature is again held isothermally at 225°C, but the rate of change of concentration of the hydrogen gas was controlled as necessary (within limits set at +2 to −2% h^{-1}) to maintain a target rate of water evolution of 0.25 a.u. The essential similarity of the evolved water profiles in both the temperature and concentration programming experiments is apparent, as is the correspondence of the hydrogen concentration profile to that of the temperature (Fig. 3).

Analysis of the temperatures and gas concentrations involved in the two CRTA experiments shows that

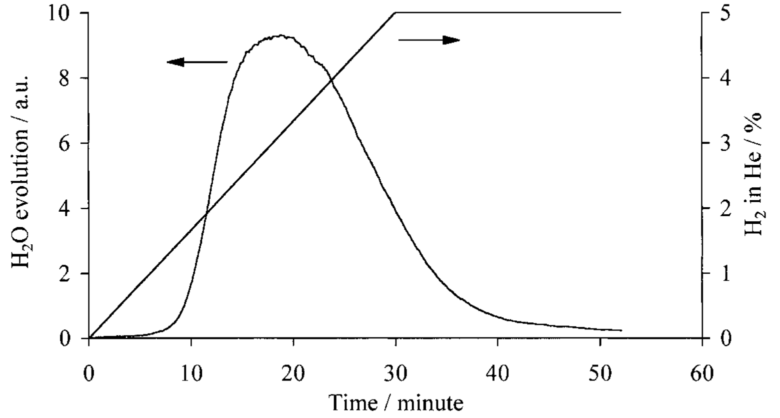

Fig. 2. Reduction of 2.5 mg of copper(II) oxide under isothermal conditions of 225°C using a linear programmed blend of hydrogen in helium of 10% h^{-1}.

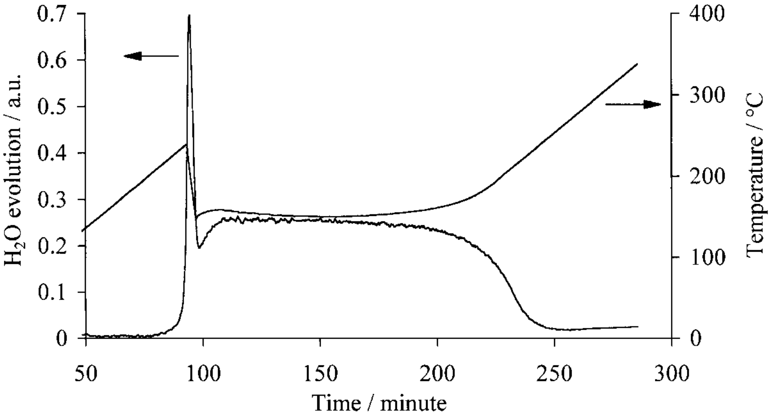

Fig. 3. CRTA reduction of 2.5 mg of copper(II) oxide in a 5% hydrogen in helium atmosphere with a target reaction rate of 0.25 a.u. and heating rates between +3 and −20°C min^{-1}.

a change in either parameter significantly affects the results. In the first CRTA experiment under 5% hydrogen in helium, an average temperature of ca. 170°C was required to maintain a constant reaction rate. In contrast, the 'gas concentration' CRTA experiment was performed at 225°C and required an average hydrogen concentration of 1.5% to maintain the same rate of reaction. Thus, for these experiments a change in temperature of ca. 11% is equivalent to a change in hydrogen concentration of ca. 70%, which is consistent with the mathematical form of Eq. (1) where the temperature dependence of the rate is exponential whilst that of the concentration is not.

4. Conclusions

We have demonstrated that the concept of SCTA can be extended to control of the rate of a process using the concentration of a reactant gas. A major potential advantage of control of the gas-phase composition is found in the study of some types of oxidation reactions, which can be sufficiently exothermic to undergo thermal runaway. In these systems, it should be easier to effect SCTA control by reducing the partial pressure of the oxidising gas rather than by lowering the sample temperature as this eliminates problems of the thermal mass of the sample and furnace and heat-transfer effects.

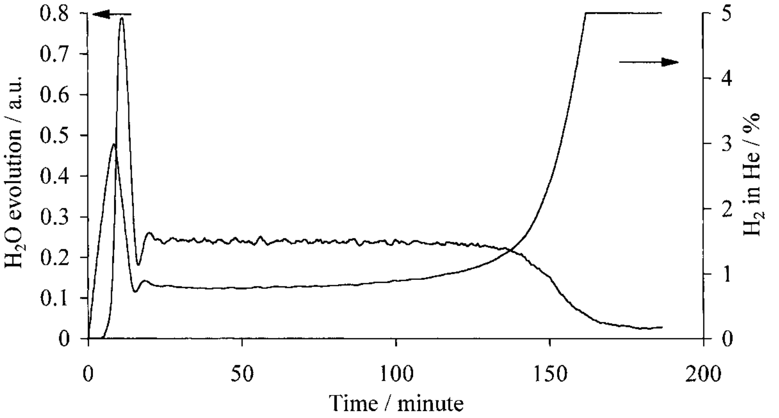

Fig. 4. CRTA reduction of 2.5 mg of copper(II) oxide under isothermal conditions of 225°C with a target reaction rate of 0.25 a.u. and programmed blend of hydrogen in helium between +2 and −2% h^{-1}.

In this note, we have only shown results for the gas concentration equivalents of linear heating and CRTA. However, other SCTA techniques [5,8] can also be effected by this approach.

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