

New Approach to the Investigation of Mechanisms and Apparent Activation Energies for the Reduction of Metal Oxides Using Constant Reaction Rate Temperature-Programmed Reduction

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A new system has been developed for the study of both bulk and surface metal oxides by temperature programmed reduction (TPR) under both conventional linear heating and constant rate thermal analysis (CRTA) conditions. It is shown that constant rate temperature-programmed reduction (CR-TPR) is capable of producing higher resolution of overlapping events, provides more insight into reduction mechanisms, and allows easier quantification of reduction processes than conventional TPR. The CR-TPR curves for both bulk and supported copper oxides confirmed that reduction followed a nucleation or autocatalytic mechanism. Bulk nickel oxide was found to reduce via a similar mechanism. Advantages of the CR-TPR “rate-jump” technique to determine reaction energetics are illustrated by investigation of the apparent activation energy (E_a) of CuO reduction, and the results are compared with those obtained under linear heating conditions. Both approaches yield reasonable values of E_a under the appropriate experimental conditions employed. However, the CR-TPR “rate-jump” technique allows variations in E_a to be measured as a function of the extent of reduction, revealing changes in the reaction mechanism or kinetics. Our results suggest it is possible to estimate the apparent activation energy of both the nucleation and growth stages involved in reduction. The validity of the “rate-jump” technique employed is confirmed using the thermal decomposition of CaCO_3 , a widely investigated process. The TPR system uses a hygrometer cell to monitor the production of H_2O as the sample is reduced. The sample temperature is controlled by a computer in such a way that the production of H_2O , i.e., the rate of reduction, can be maintained at a constant preselected value for CR-TPR experiments. Important instrumental features include a fast response furnace, direct temperature measurement, a sensitive specific detector, and control and data analysis software developed specifically for this work.

1. Introduction

1.1 Conventional Temperature Programmed Reduction.

Temperature-programmed reduction (TPR) is a thermal analysis method that is used for the qualitative study of metal oxides. In particular, it has been widely applied in the study of catalyst systems and their preparation procedures.¹ Typically, the sample is subjected to a predetermined linear heating rate and sample reduction is followed by employing a katharometer to monitor the uptake of H_2 from a reducing gas mixture. The resulting TPR profile contains information on the nature of the reducible species present in the sample. Unfortunately, the use of linear heating rates in thermal analysis techniques results in nonuniform reaction conditions throughout the sample leading to relatively poor resolution and kinetic data.^{2,3} TPR studies are further complicated by the fact that variations in sample mass, heating rate, or gas flow rate lead to different H_2 consumption rates. Such changes in the concentration of H_2 during sample reduction can lead to large distortions in the profiles obtained.^{4,5} For these reasons, TPR profiles are known to be remarkably dependent on the experimental conditions employed, which can affect both the shape and resolution of reduction steps as well as peak temperatures.^{1,2,4–7} A typical example of this is illustrated in Figure 1, which shows reduction profiles for V_2O_5 obtained using different heating rates under a 5% H_2 in He atmosphere.

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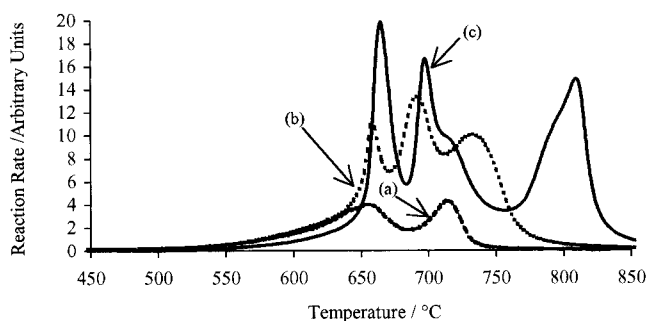


Figure 1. TPR profile of V_2O_5 in a 5% H_2 in He atmosphere using a sample weight of 3.0 ± 0.3 mg at linear heating rates of (a) 3, (b) 10, and (c) $20\text{ }^\circ\text{C min}^{-1}$.

1.2. Advantages of Constant Rate Thermal Analysis in TPR. One solution to these problems is to apply the technique of constant rate thermal analysis (CRTA) to TPR studies. Advantages of CRTA, in which the rate of reaction is regulated to maintain a constant rate of reactant consumption or product formation by controlling the temperature appropriately, have been reported particularly for the study of thermal decomposition processes.^{3,8} Compared to conventional linear heating rate techniques, CRTA reduces both temperature and pressure gradients across the sample bed and allows the concentration of reactant and product gases to be maintained at a constant level throughout the whole process. CRTA can thereby enhance resolution and provide better conditions for kinetic studies.^{2,3,8}

In addition, CRTA data can be used to distinguish between reaction mechanisms and, in particular, to identify nucleation/autocatalytic processes. The existence of a significant nucleation step is revealed in CRTA experiments by an initial temperature "overshoot" that is needed to initiate a reaction. This is followed by a period where there is a fall in the temperature as the nuclei grow and the reaction interface expands, before the temperature rises again as the expanding regions of product overlap and the reaction interface decreases. In the reduction of oxides, autocatalysis can occur in which adsorption of molecular hydrogen on the metal may give rise to chemisorbed hydrogen atoms, which further facilitate the reduction of adjacent oxide particles, a process which produces a similar temperature profile to that described above.

1.3. Activation Energy in Solid-State Reactions. The concept of activation energy in reactions involving solids is somewhat different from the usual meaning of the term as applied to homogeneous systems. In solid-state reactions, the rate-controlling factors may not be simply chemical in origin but may involve geometrical considerations, e.g., the nature and size of the interface, the extent of lattice imperfections, which can serve as the source of nuclei, or diffusion of either reactants to the reaction interface or of products from it. For these reasons, the term activation energy is referred to in this context as the "apparent" activation energy.

1.4. Measurement of Activation Energy Using the CRTA "Rate Jump" Method. The basic CRTA approach can be adapted to give the "rate-jump" method, which allows the measurement of a model-free activation energy for the reaction while still minimizing temperature and pressure gradients.⁸⁻¹¹ This is achieved by causing the reaction rate to alternate between two preselected values while monitoring the changes in sample temperature required to ensure the desired rates are obtained. Provided the reaction is allowed to reach equilibrium at the two successive rates, the corresponding sample temperature measurements can then be used to calculate an apparent activation energy of the reaction. By making a number of "rate-jump" measurements throughout the reaction, any variation in activation energy throughout the process is readily observed.^{2,8,9,12} Conventional methods used for the calculation of activation energy under linear heating TPR conditions involve measuring the temperature of maximum reduction, i.e., the peak temperature, as a function of heating rate.^{1,13} This approach involves a number of experiments and assumes that the kinetic model is unaffected by the heating rates in the range employed.

1.5. Previous Applications of CRTA. The number and diversity of thermal analysis techniques in which the heating regime is modified, in some manner, by the rate at which the sample reacts is ever increasing.^{2,3,14-17} In the present work, we focus on one of these techniques, i.e., constant rate thermal analysis (CRTA). Although originally developed for applications under vacuum conditions,¹⁸ CRTA has also been applied by several workers under flowing gases to study thermal decomposition reactions.^{3,14,19} A detailed review of the technique was given by Rouquerol⁸ in 1989 who pointed out the similar nature of CRTA to the technique of "quasi-isothermal and quasi-isobaric" thermal analysis developed by F. and J. Paulik,²⁰ which, in essence, relies on the same basic principle, i.e., control of the rate of reaction. In a previous paper,³ we have demonstrated the usefulness of CRTA as an analytical tool for the study of decomposition reactions. The application of CRTA to temperature-programmed oxidation (TPO) studies has also been documented.¹⁴ To the best of our knowledge, the only previous reports of TPR performed under CRTA conditions were by

Stacey¹⁹ and ourselves,¹⁷ who both briefly mention the technique. The use of the CRTA "rate-jump" method to provide kinetic information on the reduction of metal oxides has not been reported.

1.6. Experimental Considerations in CRTA-TPR. Conventional TPR has proved to be a valuable technique for the qualitative comparison of materials. However, the temperature gradients throughout the system can cause the sample temperature to differ from that of the thermocouple that is used to estimate its temperature. This occurs in part because of the differing heat capacities of the thermocouple, the sample holder, and the sample. Thus, assuming a uniform supply of thermal energy, it is not uncommon to have errors of several degrees. The situation is further complicated by the differing emissivities of these components and the difficulty in obtaining a completely uniform hot zone in the furnace. In CRTA methods, time is allowed for the system to reach a pseudothermal equilibrium and so the measured temperature reflects the sample temperature more accurately. In the present study, the sample holder is placed directly on a plate-type thermocouple, thus ensuring better temperature measurement in both linear heating and CRTA experiments than is given by systems where the thermocouple and sample pan are not in direct contact. The use of a hygrometer to detect H₂O production rather than H₂ uptake allows direct monitoring of the reduction process as a function of temperature. The hygrometer response is directly proportional to the reduction rate, and the highly sensitive nature of this detector permits the use of small samples, which helps to further reduce the effects of residual temperature or pressure gradients, H₂ concentration changes, and any possible influences of water vapor on the profiles obtained.^{1,4-7,13}

2. Theoretical Background to the Measurement of E_a for CuO Reduction

2.1. Linear Heating Conditions. Hurst et al.¹ proposed a method for the calculation of activation energy from TPR measurements. Equation 1 was used to express the rate of reaction between a gas (H₂) and a solid (S) at constant temperature (T).

$$\text{rate} = A[\text{H}_2]^p[\text{S}]^q \exp(-E_a/RT) \quad (1)$$

where [S] represents the concentration of metal oxide, A is the preexponential factor, and E_a is the apparent activation energy. Using this equation, it was shown that for a reduction process that is first order with respect to H₂ concentration (i.e., $p = 1$) and assumed to be first order in metal oxide concentration (i.e., $q = 1$), the variation of the temperature of maximum reduction rate (T_m) with linear heating rate (β) may be expressed as

$$2 \ln T_m - \ln \beta + \ln [\text{H}_2]_m = E_a/RT_m + \text{constant} \quad (2)$$

where $[\text{H}_2]_m$ is the hydrogen concentration at T_m .¹ The reduction of CuO has been reported to be first order with respect to H₂ concentration,¹ and hence, a plot of the left-hand side of eq 2 versus $1/T_m$ should give a straight line with slope E_a/R . The pre-exponential factor (A) from the Arrhenius equation is included in the constant part of eq 2.

An alternative method proposed by Wimmers et al.¹³ is based on the following form of the general kinetic equation for solid-state reactions

$$d\alpha/dt = A f(\alpha) \exp(-E_a/RT) \quad (3)$$

where α is the fraction of sample reacted at time t and $f(\alpha)$ is

a function depending on the reaction mechanism. It was proposed that the activation energy for reduction of a metal oxide under linear heating conditions can be determined without knowledge of the specific reduction mechanism using the following equation:

$$\ln(\beta/T_m^2) = -E_a/RT_m + \ln(AR/E_a) + C \quad (4)$$

When $\ln(\beta/T_m^2)$ is plotted versus $1/T_m$ a straight line is expected with a slope of $-E_a/R$. The authors¹³ noted that eq 4 is generally applicable for the determination of activation energy from conventional TPR measurements. This method assumes that any changes in the reduction model ($f(\alpha)$) and the extent of reduction (α) at T_m , caused by the changes in heating rate employed, are negligible.

Equations 2 and 4 are essentially the same (since $-\ln(\beta/T_m^2) = 2 \ln T_m - \ln \beta$), except that eq 2 takes into account the possible effects of the change in $[H_2]_m$ as a function of heating rate. In the present work, both equations are employed to indicate any effects of H_2 concentration changes during linear heating experiments on the E_a measured. The method derived by Wimmers et al.¹³ in eq 4 has the advantage that it is not necessary to assume first-order kinetics with respect to the metal oxide and knowledge of the order in H_2 is also unnecessary. Gas–solid reactions such as reductions are typified by complex kinetics that cannot be described by a single n th order expression over the entire reaction.^{1,13}

2.2. CRTA “Rate-Jump” Method. Kinetic analysis of “rate-jump” experiments in solid-state reactions is based on the general kinetic eq 3 above.

E_a at each jump is calculated using

$$E_a = RT_1 \frac{T_2}{T_1 - T_2} \ln((d\infty/dt)_1/(d\infty/dt)_2)$$

$$\text{or } E_a = RT_1 \frac{T_2}{T_1 - T_2} \ln(C_1/C_2) \quad (5)$$

where T_1 and T_2 are the temperature measurements corresponding to the two preset target reaction rates C_1 and C_2 .¹⁰ No knowledge of the reduction model is required. For this method to be successful, the time taken to execute each rate jump should be as small as possible in comparison to the total duration of the reduction process since it is assumed that the changes in α and $f(\alpha)$ at each rate jump are negligible. This arises because the rate of solid-state processes, such as reduction, is controlled by the interfacial area between reactant and product and the object in the “rate-jump” method is to measure the temperatures required for two specified rates for a negligible change in interfacial area. For this reason, the magnitude of the rate jumps is kept as small as possible which also serves to minimize changes in reactant and/or product concentrations. Furthermore, by using a large number of rate jumps, which can be achieved with low reaction rates and/or high sample masses, it is possible to explore the reduction process in detail.

3. Experimental Section

3.1. Equipment. The apparatus has been previously described and used to study decomposition reactions under both linear heating and a variety of sample-controlled heating techniques including CRTA.³ The essence of the system is that it involves computer control of the sample temperature to regulate the reaction rate via a feedback loop. The sample furnace and hygrometer detector cell are interfaced via a Comark Compuface

(16 channel, 16 bit) analog-to-digital convertor (ADC) and a Eurotherm 818P temperature programmer using a 486DX PC computer. The software, developed by the authors, controls the temperature programmer, acquires the data, and processes the results. The program was written in ANSI C using a C++ compiler (Borland) and provides the option to perform either linear heating or various SCTA experiments including CRTA.

The ceramic sample holder is placed on a plate-type thermocouple (type R) in a water-cooled furnace (Stanton Redcroft model 761, swept volume $<7.5 \text{ cm}^3$). This allows both accurate temperature measurement and the fast furnace response, including cooling regimes, required for CRTA experiments. An accurate constant flow of reducing gas over the sample is maintained using an electronic Bronkhorst Hi-Tec mass-flow controller. Gases evolved from the sample are analyzed using an electrolytic hygrometer detector cell (Mark 2) supplied by Salford Electrical Instruments that is capable of a full-scale response of 10 ppm at a flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$. In this application, it is used on the least sensitive settings to avoid overloading the detector. The response is flow rate dependent and a calibration factor is used to correct for the actual flow rate used and convert the output directly into the rate of evolution of water expressed in milligrams per minute. The hygrometer is mounted immediately above the furnace and is connected by 10 cm of 3 mm o.d. stainless steel tubing to minimize the swept volume and time delay between H_2O production and detection. The connecting tubing is held at 120°C to eliminate the risk of condensation and adsorption effects. For decomposition experiments on CaCO_3 , used to investigate the validity of “rate-jump” activation energy measurements, a katharometer was used to detect the CO_2 evolved.

3.2. Materials. CuO (99.9999%, Aldrich) and “green” NiO (99.99%, Aldrich) were used. An equal mass mixture of the two oxides was made by grinding the two components together and sieving through a $180 \mu\text{m}$ mesh.

A supported $\text{Cu}/\text{Al}_2\text{O}_3$ sample, containing a nominal concentration of 10 wt % Cu, was prepared by a wet impregnation technique using an aqueous solution of cupric acetate (Aldrich). The $\gamma\text{-Al}_2\text{O}_3$ (Alfa Chemicals) used was preheated at 800°C in air for 15 min. After impregnation and removal of excess H_2O by rotary evaporation, the sample was dried at 100°C for 8 h. Calcination was then achieved in air at 400°C for 30 min. The sample was ground and sieved to less than $180 \mu\text{m}$ prior to reduction. X-ray diffraction (XRD) data, obtained using $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation, indicated that copper was present as CuO in the calcined sample with the main CuO peak evident at a 2θ angle of 35.5° . Analysis of the line breadth indicated a mean particle diameter of 14 nm.

CaCO_3 (Analar grade) was supplied by BDH and used as received.

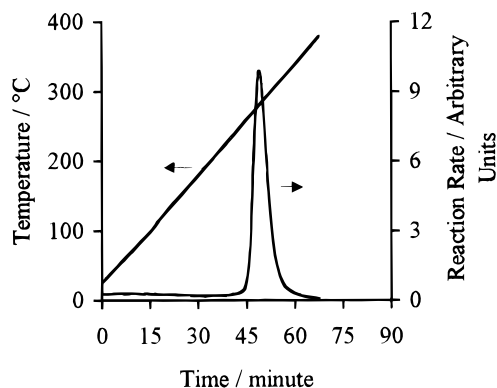
3.3. TPR Conditions. For all reduction experiments, the reduction atmosphere consisted of 5% hydrogen in helium at a flow rate of $52 \text{ cm}^3 \text{ min}^{-1}$.

3.3.1. Linear Heating Conditions. Apart from experiments performed at various heating rates for the calculation of the activation energy of CuO reduction, all conventional TPR experiments used a linear heating rate of $5^\circ \text{C min}^{-1}$. For the reduction of individual bulk metal oxides, a sample weight of $1.5 \pm 0.1 \text{ mg}$ was employed. The reduction of the mixture of both oxides was carried out using a sample mass of $3.0 \pm 0.1 \text{ mg}$ to maintain a constant mass of each oxide and thereby allow direct comparisons to be made. For supported $\text{CuO}/\text{Al}_2\text{O}_3$, a sample mass of $11.5 \pm 0.1 \text{ mg}$ was used. To measure the apparent activation energy of bulk CuO reduction, a series of

TABLE 1: Experimental Conditions Employed for CRTA "Rate-Jump" Experiments for the Reduction of CuO

run	sample mass (mg)	C_1^a (mg H ₂ O min ⁻¹)	C_2^b (mg H ₂ O min ⁻¹)	O^c (%)	R^d (mg H ₂ O min ⁻¹ mg ⁻¹)	no. of rate jumps
a	40.0	1.04×10^{-2}	1.26×10^{-2}	0.2	0.26×10^{-3}	78
b	20.0	1.04×10^{-2}	1.26×10^{-2}	4.3	0.52×10^{-3}	31
c	10.3	8.10×10^{-3}	1.04×10^{-2}	8.8	0.79×10^{-3}	21
d	4.7	5.85×10^{-3}	8.10×10^{-3}	15.0	1.24×10^{-3}	10

^a C_1 = lower water evolution rate target. ^b C_2 = higher water evolution rate target. ^c O = percentage of the total reduction process which occurred in the initial "overshoot" of the target reduction rates in each run. ^d R = rate of water evolution per unit mass of sample.

**Figure 2.** TPR profile of CuO under linear heating rate conditions.

linear heating experiments was performed using 1.5 mg of CuO at heating rates of 2, 5, 10 and 20 °C min⁻¹. Equations 2 and 4 were then used to yield values for the apparent activation energy of the reduction.

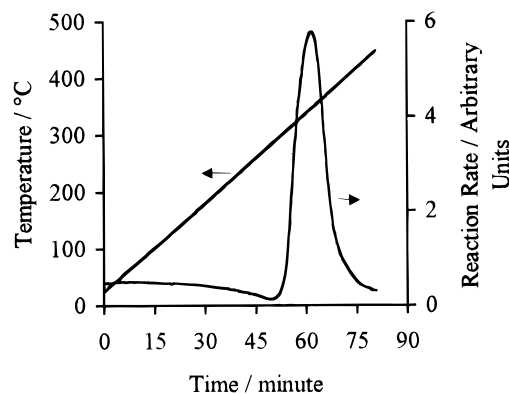
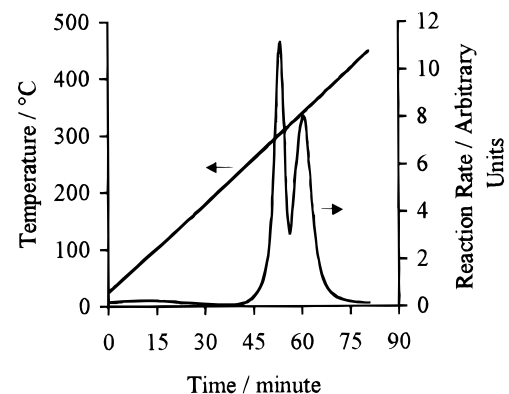
3.3.2. CRTA Conditions. CRTA runs were performed using maximum heating and cooling rates of 5 and 10 °C min⁻¹, respectively. The heating rate was varied between these limits in order to maintain a constant target water evolution rate (i.e., reduction rate) of ca. 1×10^{-3} mg min⁻¹. A sample mass of 1.5 ± 0.1 mg of each bulk oxide was employed. A CRTA experiment was also performed using 3.2 ± 0.1 mg of the CuO/NiO mixture. For the supported CuO/Al₂O₃ sample, a sample mass of 12.5 ± 0.1 mg was employed.

For the measurement of E_a , CRTA "rate-jump" experiments were performed on CuO as outlined in Table 1. Maximum heating and cooling rates of 5 and 10 °C min⁻¹, respectively, were again used in order to alternate between the target water evolution rates, C_1 and C_2 . Equation 5 was used to calculate the activation energy for each jump.

3.4. Decomposition of CaCO₃. To demonstrate the validity of the "rate-jump" method, the activation energy for the decomposition of CaCO₃ (in He at 25 cm³ min⁻¹) was investigated. Maximum heating and cooling rates of 5 and 10 °C min⁻¹, respectively, were used in order to maintain target carbon dioxide evolution rates of 5.1×10^{-2} (C_1) and 6.5×10^{-2} (C_2) throughout 10 rate jumps with 15.8 ± 0.1 mg of sample.

4. Results and Discussion

4.1. Comparison of CRTA and Linear Heating Techniques. Figures 2–4 illustrate the TPR results obtained under linear heating conditions of 5 °C min⁻¹. Figure 2 shows the hygrometer profile produced for the reduction of CuO. A single peak is seen over a temperature range of 245–335 °C with a maximum at 280 °C. The maximum rate of H₂O production was ca. 3.3×10^{-2} mg min⁻¹. Previous TPR studies of

**Figure 3.** TPR profile of NiO under linear heating rate conditions.**Figure 4.** TPR profile of an equal mass mixture of CuO and NiO under linear heating rate conditions.

unsupported CuO have reported a wide variety of peak temperatures including 187,²² 320,²³ and 333 °C²⁴ when using a katharometer to monitor H₂ uptake under linear heating conditions. Comparison of peak temperatures is difficult because of different experimental and pretreatment conditions employed by the various workers.¹ Boyce et al.²³ showed that the temperature at which the maximum rate of copper reduction occurred varied considerably with the experimental conditions such as heating rate and sample size, even when there was no major depletion of H₂. It was also found that different samples of CuO exhibited different reduction characteristics.²³

A similar reduction profile was obtained for the CuO/Al₂O₃ sample under linear heating conditions with a single peak covering a temperature range of 155–265 °C and peak maximum at 205 °C. The lower peak temperature for the supported sample agrees with previous findings that supported CuO reduces more easily than bulk CuO.¹

Figure 3 shows the profile obtained for NiO. As expected, a single peak is observed over a temperature range of 300–420 °C with a maximum at 346 °C. The maximum rate of H₂O production is 2×10^{-2} mg min⁻¹. Mile et al.²⁵ studied the TPR of NiO using a 5% H₂/N₂ reducing gas mixture, a heating rate of 12 °C min⁻¹, and a sample size of 60 mg. A peak temperature of 400 °C for unsupported NiO was reported. Again, comparison with the present study is difficult because of the different experimental conditions employed. The higher peak temperature they reported may be due to the higher heating rate and/or larger sample mass used. Differences in the purity of the oxide employed may also have contributed; they also reported the presence of a small peak, attributable to traces of black Ni₂O₃, in some of their profiles.

The profile obtained for the reduction of the equal mass mixture of the two oxides is shown in Figure 4. Two strongly

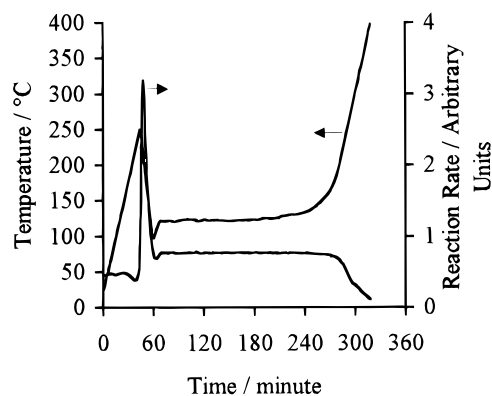


Figure 5. TPR profile of CuO under CRTA conditions.

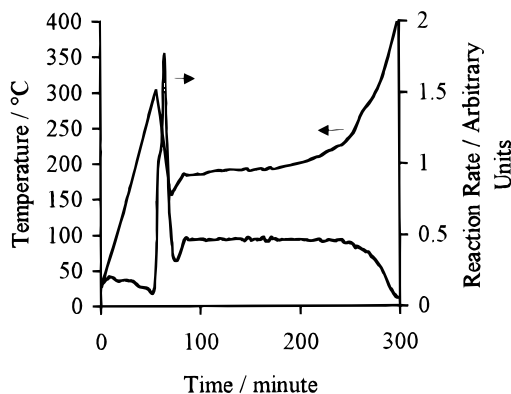


Figure 6. TPR profile of NiO under CRTA conditions.

overlapping peaks are seen covering a temperature range of 245–410 °C with maxima at 303 and 341 °C for the CuO and NiO, respectively. The increase in peak temperature for CuO compared with 280 °C in Figure 2 appears to be due to overlap of the two reduction peaks. Doping with NiO has been previously reported to lower the reduction temperature of pure CuO in TPR experiments due to modification of the CuO lattice by the dopant producing extra nucleation sites.²⁴ However, such a phenomenon would not be expected in the present study when using a physical, rather than chemical, mixture of the two oxides.

Figure 5 shows the reduction of CuO under CRTA conditions. The temperature trace shows how the computer system controls the sample temperature in attempting to maintain a constant rate of reaction. It can be seen that apart from the initial “overshoot” of the target reaction rate, the rate of H₂O production is maintained at a constant level (corresponding to a reduction rate of ca. 1×10^{-3} mg of H₂O min⁻¹) over the majority of the reduction process. The reduction proceeds at a constant rate over a temperature range of 120–160 °C. This shows that the reduction of CuO can be achieved at a much lower temperature than that indicated in Figure 2 under conventional linear heating conditions. It should be noted that the transient overheating or “overshoot” at the initial stage of the reduction does not arise from poor temperature control but indicates that the reduction process involves either a nucleation reaction mechanism²¹ or autocatalysis.³ This “overshoot” effect is not found in systems that do not exhibit a significant nucleation stage.^{3,20} The results illustrate the ability of CRTA experiments to reveal kinetic and mechanistic information that is not apparent from conventional TPR curves (Figure 2) and are discussed in greater detail below.

The reduction of NiO under CRTA conditions is shown in Figure 6. The profile obtained is broadly similar to that of CuO in Figure 5. Again, there is a brief initial “overshoot”, indicating

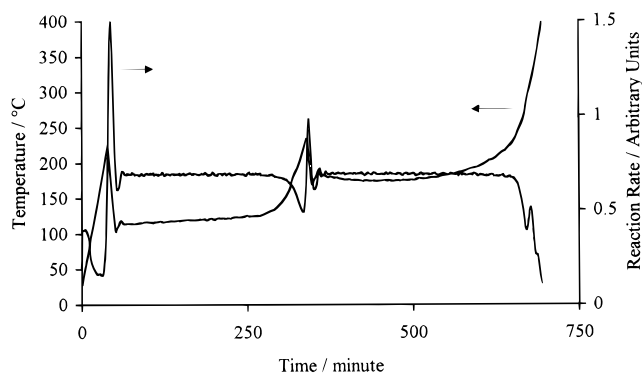


Figure 7. TPR profile of an equal mass mixture of CuO and NiO under CRTA conditions.

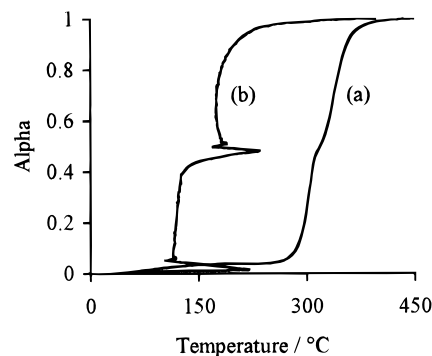


Figure 8. Extent of reaction (α) versus temperature plot for the TPR of an equal mass mixture of CuO and NiO under (a) linear heating and (b) CRTA conditions.

a nucleation or autocatalytic reduction mechanism, which is followed by a long period where the rate is maintained at a constant level. During this stage, the temperature covers a range of between 180 and 230 °C, again much lower than would appear to be possible from the linear heating profile (Figure 3).

Figure 7 shows the reduction of the equal mass mixture of CuO and NiO under CRTA conditions. The overall profile mirrors those for the individual oxides with CuO reduction proceeding at a constant rate over a temperature range of 110–150 °C, while NiO is reduced at a constant rate between 170 and 230 °C.

The greater resolution of the two reduction processes obtained under constant rate conditions becomes more apparent when the α (extent of reaction) versus temperature profile for the linear heating experiment (Figure 8a) is compared to that for the CRTA experiment (Figure 8b). This form of presentation is extremely valuable for quantitative comparison of the effects of the two TPR methods.

The unusual shape of the alpha (α) versus temperature profile in Figure 8b can be explained as follows. As mentioned above, a transitional overheating in the initial stages of a CRTA curve has been previously attributed to a significant nucleation stage.^{3,20} Both CuO and NiO have been reported to exhibit sigmoidal reduction isotherms characteristic of a nucleation or autocatalytic reduction mechanism.^{1,26,27} In terms of the reduction of metal oxides, the nucleation step involves the initial removal of oxygen atoms from the lattice. Once the concentration of vacancies reaches a critical value, they are then annihilated by lattice rearrangement with the formation of metal nuclei. The nuclei then grow and, as they expand, the area of the sample–product interface, i.e., the interface between the metal oxide and the metal nuclei, increases causing the reduction process to accelerate. In addition, the reaction interface increases

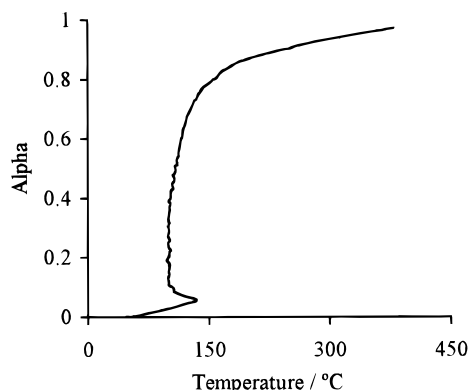


Figure 9. Extent of reaction (α) versus temperature plot for the TPR of a CuO/Al₂O₃ sample under CRTA conditions.

due to the appearance of new nuclei. In a CRTA experiment, this means that, as reduction proceeds, the temperature must drop in order to maintain a constant rate of reaction as the reaction interface increases. In some cases, e.g. NiO,¹ the metal nuclei formed are thought to dissociate and activate dihydrogen molecules leading to autocatalysis. As the reduction proceeds, the expanding metal nuclei continue to grow and eventually merge. This merging causes the area of the sample–product interface to decrease, and the temperature has to rise again to prevent deceleration of the reaction. It is this rise, fall, and then rise again of the temperature that causes the α versus temperature profile to curve back on itself during both reduction processes in Figure 8b.

As mentioned above, isothermal studies have also indicated the existence of a nucleation/autocatalytic mechanism for the reduction of CuO. For example, Pease and Taylor²⁶ noted that CuO reduction occurs most readily at the copper–copper oxide interface with the rate of water production being proportional to the interface area, which increases after formation of the first metal nuclei. A similar conclusion was reached by Hayden et al.²⁸ who measured the rate of H₂O production from an adsorbed monolayer of oxygen on a Cu{110} single crystal surface exposed to a supersonic molecular beam of hydrogen molecules under ultrahigh vacuum conditions. At a constant molecular beam energy and surface temperature, the rate of reaction was found to be slow at the start, increase rapidly, and then gradually decrease. This behavior was explained by a model in which H atoms (formed by dissociation of H₂ on the surface) could only react with oxygen atoms at the edges of oxygen islands.²⁹ Thus, one of the important factors in the reaction rate was the size of the interface between the clean and oxygen-covered copper surface.

Criado et al.^{15,21} have illustrated the usefulness of CRTA in determining the kinetics of solid-state decomposition reactions from an analysis of the shape of the α versus temperature profile. From this work, the shapes of the profiles for each process shown in Figure 8b appear characteristic of a formation and growth of nuclei/autocatalytic kinetic model.²¹

The α versus temperature curve obtained for the reduction of CuO/Al₂O₃ is shown in Figure 9 and is again characteristic of a nucleation or autocatalytic reduction mechanism. Supported CuO has been previously reported to show a sigmoidal reduction isotherm characteristic of this type of reduction mechanism.^{1,27} Determination of the reduction mechanism of metal oxides using linear heating TPR has also been attempted based on the analysis of TPR patterns measured at several heating rates.¹³ This approach requires several experiments to yield similar information that would be obtained from a single CRTA curve. In

TABLE 2: Variation of T_m with Linear Heating Rate (β) for CuO Reduction

β (°C min ⁻¹)	T_m (°C)
2	245
5	280
10	297
20	340

addition, comparison of parts a and b of Figures 8a and 8b clearly shows the enhanced resolution obtainable using CRTA.

4.2. Measurement of E_a for CuO Reduction. **4.2.1. Linear Heating Conditions.** The variation of T_m for CuO reduction with β is shown in Table 2. A plot of $2 \ln T_m - \ln \beta + \ln [H_2]_m$ versus $1/T_m$ was found to be a straight line described by the equation $Y = 6677.3X - 10.2$ (correlation coefficient = 1.000). Using eq 2, the apparent activation energy for CuO reduction by H₂ was therefore calculated to be 55.5 kJ mol⁻¹. Similarly, a plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ was also found to be a straight line ($Y = -6576.9X + 0.9$ (correlation coefficient = 1.000), which, from eq 4, produces a value for E_a of 54.7 kJ mol⁻¹. The correlation between the values obtained using eqs 2 and 4 indicates that changes in H₂ concentration during reduction are negligible even at a heating rate of 20 °C min⁻¹ when the maximum rate of H₂O evolution was as high as ca. 6.76×10^{-2} mg min⁻¹. An apparent activation energy of ca. 55 kJ mol⁻¹ is in reasonable agreement with previous literature values determined using eq 2. Gentry et al.²⁴ reported an activation energy of 67 ± 10 kJ mol⁻¹ using a reducing mixture of 10% H₂ in N₂, while Boyce et al.²³ reported values of between 67 and 82 kJ mol⁻¹ using 6% H₂ in N₂. The activation energy of 52 kJ mol⁻¹, found by Hayden et al.²⁸ in an experiment which measured the rate of production of H₂O from the reaction of a supersonic molecular beam of H₂ at fixed energy with an oxygen-covered Cu{110} surface at temperatures between 377 and 527 °C, also agrees well with our result.

4.2.2. CRTA “Rate-Jump” Method. The activation energy of CuO reduction was also investigated by the CRTA “rate-jump” method. In selecting the values for the reaction rates, two different considerations apply. First, the underlying “constant” rate (i.e., the lower level) is chosen to provide enough time to achieve a reasonable number of “rate jumps”, typically 20–30, during the experiment. The upper reaction rate has to be sufficiently different from the lower rate to ensure the corresponding change in temperature can be measured accurately. However, it is important that the difference in the two rates is not so great as to risk a change in mechanism or a significant alteration in the extent of the nature of the reaction interface.

The validity of the CRTA “rate-jump” method employed was first confirmed using the decomposition of CaCO₃ as a model reaction. The activation energy appeared to remain constant throughout the decomposition with an average value of 205 ± 15 kJ mol⁻¹. Activation energies for this reaction have been reviewed in detail by Reading et al.^{11,30} who noted that, although there is a wide variation in reported values, measurements made under appropriate experimental conditions and using “sensible” methods to calculate E_a yielded values of between 190 and 227 kJ mol⁻¹. Such values were believed to be in reasonable agreement with the reported value for the enthalpy of formation of CaCO₃ of about 177 kJ mol⁻¹.¹¹

A typical “rate-jump” experiment for CuO reduction is shown in Figure 10. Again there is a brief initial “overshoot”, followed by a longer period where the reaction rate swings between the two preset target levels of 1.04×10^{-2} (C₁) and 1.26×10^{-2} (C₂) mg H₂O min⁻¹. These rates were selected in accordance with the criteria mentioned above. For each of the 31 rate jumps,

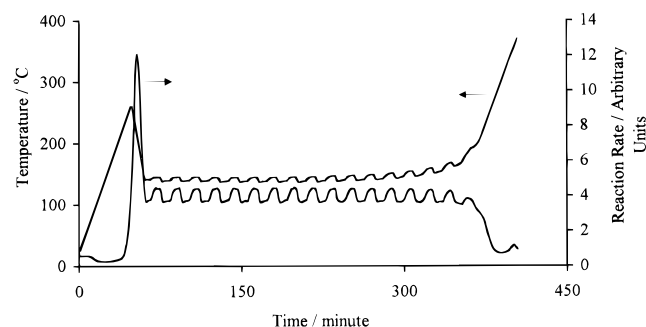


Figure 10. TPR profile of CuO under CRTA "rate-jump" conditions.

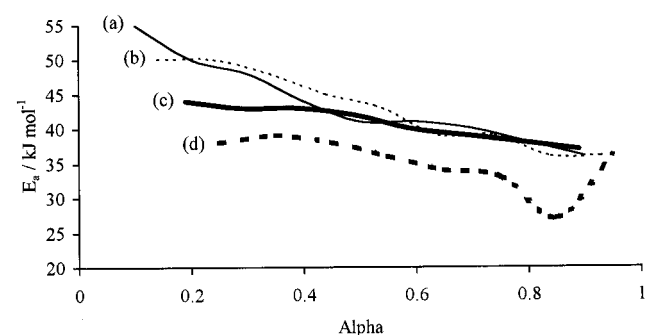


Figure 11. Apparent activation energy (E_a) for CuO reduction as a function of the extent of reduction (α), measured from CRTA "rate-jump" experiments.

a value for E_a was obtained using eq 5 thereby allowing any variation in E_a with extent of reduction (α) to be determined. Obviously, the rate of H_2 consumption is not constant throughout the reduction process in Figure 10 due to the small changes in rate at each jump. However, as discussed above, changes in H_2 concentration during reduction under linear heating conditions, when the maximum rate of H_2O evolution varied from $6.76 \times 10^{-2} \text{ mg min}^{-1}$ at $20^\circ \text{C min}^{-1}$ to $1.65 \times 10^{-2} \text{ mg min}^{-1}$ at $2^\circ \text{C min}^{-1}$, did not affect the measured activation energy. Therefore, it would seem reasonable that the small change in H_2 concentration at each rate jump can be considered to be negligible under the conditions used for the rate jump experiments (see Table 1).

Laureiro et al.¹² studied the variation of E_a with extent of reaction using the CRTA "rate-jump" method to investigate the dehydration kinetics of Wyoming montmorillonite. It was found that the apparent activation energy increased during the course of the dehydration process indicating increasing difficulty in the progress of the reaction. The authors noted that this behavior was not exceptional and as such the measurement of mean values of kinetic parameters using conventional thermal methods must be questioned.¹² Other studies^{9,11} have also reported the use of the "rate-jump" method to investigate variations in E_a in thermal decomposition reactions.

Figure 11 illustrates the variation of E_a as a function of α (after the initial "overshoot") for the various rate-jump experiments performed on CuO reduction. Two trends are apparent. First, there is a decrease in the initial apparent activation energies measured for runs a–d from 55 to 35 kJ mol^{-1} . This trend is accompanied by a marked increase in the percentage of reaction occurring in the "overshoot" stage from 0.2% to 15% (Table 1, column "O"). This observation can be explained in the terms of a nucleation and growth model of reduction in which the activation energy required during nucleation is higher than that needed in the growth stage. Thus, when a large percentage of the reaction occurs in the "overshoot" (nucleation) part of the CRTA curve, the reduction will have progressed further into

the acceleratory growth stage before the rate jumps, and the activation energy measurements, begin. In this case, the measured value of E_a reflects the *growth* stage rather than the *nucleation* stage. The initial differences in E_a , found over the 6-fold range of reaction rates used (Table 1, column "R"), decrease as the reaction proceeds with the values converging once the initial influence of nucleation diminishes.

We believe that the activation energy measurement of 55 kJ mol^{-1} made under linear heating experiments is similar to that obtained for the initial value for run a because the T_m value is mainly determined by the reduction rates on the low-temperature side of the TPR peak¹³ where the effect of nucleation will predominate.

The second trend seen in Figure 11, namely the decrease in the activation energy over of course of the reduction, possibly arises due to autocatalytic effects as described in the Introduction. Voge and Atkins²⁷ reported similar findings for the decrease in the activation energy of the isothermal reduction of supported CuO. A similar decrease in the activation energy was also reported by Hayden et al. in their molecular beam experiment.²⁸ While no conclusive explanation was given, they suggested that lateral interactions between adsorbed oxygen atoms or adsorbate-induced surface reconstructions might influence the barrier height.

The E_a values determined in the last few rate jumps in each experiment were deemed unreliable because the reaction rate did not quite reach the set target levels as the reduction neared completion. Thus, Figure 11 only shows E_a values as a function of α until ca. 90% of the reduction is complete. The discrepancy between curves a–c and curve d in Figure 11 may indicate that the small number of rate jumps in the latter experiment did not satisfy the assumption that α remain constant in each jump.¹¹

The CRTA "rate-jump" method possesses the same advantages as ordinary CRTA experiments. The uniform reaction conditions allow more reliable kinetic data to be obtained than under conventional linear heating conditions.^{8–10} The correlation between the E_a measurements from "rate-jump" and linear heating experiments in the present study would appear to indicate that linear heating experiments can provide an acceptable measurement of an "overall" value of E_a , at least under the experimental conditions employed. Reading et al.³⁰ reported that rising temperature experiments also yielded reasonable results for the activation energy of CaCO_3 decomposition provided reasonable care was taken with the experimental conditions and calculation methods used. In the present study, it can be seen that, because the "rate-jump" method employed measures the variation of E_a with extent of reaction, it gives a greater insight into the reduction process. It also casts doubt on the validity of measuring a single activation energy for many solid–gas reactions. Further work is necessary to fully explore the potential of the "rate-jump" technique in providing important information that may be correlated with the mechanism of reactions.

5. Conclusions

The use of CRTA for the study of the reduction of metal oxides has been shown to have several advantages over conventional linear heating TPR. Reduction under CRTA conditions provides a greater insight into the nature of the reduction mechanism, improves resolution of overlapping processes, and reveals that reduction can be achieved at considerably lower temperatures than indicated in linear heating experiments. The CRTA curves for the reduction of CuO and NiO clearly confirmed that both reactions followed a nucleation/

autocatalytic mechanism. A supported CuO sample was found to be reduced by a similar mechanism. The CRTA "rate-jump" method allowed the measurement of the apparent activation energy of CuO reduction without any prior knowledge of the specific reduction model. E_a was measured as a function of the extent of reaction by employing a number of rate-jumps that thereby provided further insight into the nature of the reduction model by allowing separate values to be obtained for the nucleation and growth stages of the process. It is believed that the experimental apparatus developed in this work has considerable potential for application in the study of supported catalyst systems and in corrosion studies where the properties of surface oxide films are of great importance.

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