Journal of Thermal Analysis and Calorimetry, Vol 56 (1999) 733-737

SAMPLE CONTROLLED THERMAL ANALYSIS
Temperature programmed reduction of bulk and supported copper oxide

P. A. Barnes[*], *M. J. Tiernan*[**] *and G. M. B. Parkes*

Centre for Applied Catalysis, Materials Research Division, University of Huddersfield
Queensgate, Huddersfield, HD1 3DH, UK

Abstract

The reduction of bulk and supported copper oxide was investigated using Constant Rate Temperature Programmed Reduction (CR-TPR) and conventional linear heating rate TPR. Linear heating profiles indicated that the reduction of supported samples was more facile than that of the bulk oxide. CRTA results revealed that both supported and bulk oxide samples were reduced via a mechanism involving a nucleation step and/or auto-catalysis. The increased reducibility of the supported samples is attributed to a higher dispersion which provides a larger reactive surface area and a high concentration of defects at which reduction is initiated.

Keywords: catalysis, constant rate thermal analysis (CRTA), copper oxide, temperature programmed reduction (TPR)

Introduction

Characterisation of catalyst systems often involves the use of conventional thermal analysis techniques which employ linear heating rates to investigate various properties of the catalyst as a function of temperature. Methods such as temperature programmed reduction (TPR) and temperature programmed desorption (TPD) have proved to be extremely valuable catalyst characterisation tools [1, 2]. For example, the inherent simplicity and high sensitivity of conventional linear heating TPR make it a very important analytical method for investigating catalyst reducibility.

Unfortunately, the use of linear heating rates in thermal analysis techniques results in non-uniform reaction conditions throughout the sample leading to relatively poor resolution and kinetic data [3–5]. Further difficulties arise in TPR because variations in sample mass, heating rate or gas flow rate lead to different H_2 consumption rates. 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 processes as well as peak temperatures [1, 3, 4–6]. Kinetic interpretation

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[*] Author to whom all correspondence should be addressed

[**] Current address: School of Chemical Sciences, Dublin City University, Dublin 9 Ireland

1418-2874/99/ $ 5.00

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of linear heating profiles is also limited because of the need to make assumptions about the mechanism of reduction and the associated kinetic model [3, 7].

In order to provide more suitable conditions for kinetic analysis of TPR profiles we have recently described an apparatus capable of performing reduction under Constant Rate Thermal Analysis (CRTA) conditions as well as conventional linear heating rates [8]. The advantages of CRTA, where the reaction can be forced to proceed at a low and constant rate, are well documented particularly for the study of decomposition reactions [9–11]. CRTA provides superior control of mass and thermal transfer effects allowing the activation energy of reaction to be determined while the shape of the temperature profile obtained provides an insight into the reaction mechanism [8, 12].

The reducibility of supported copper catalysts has been widely investigated using conventional TPR because of important industrial and environmental applications such as methanol synthesis or the selective catalytic reduction (SCR) of nitrogen oxides [1, 13–15]. In the present study, both CRTA and linear heating rate methods are used to investigate the reduction of various copper catalysts. The results presented illustrate the information which can be obtained by employing Sample Controlled Thermal Analysis (SCTA) techniques such as CRTA for the study of catalyst systems.

Experimental

Supported copper oxide samples were prepared by a wet impregnation technique using aqueous solutions of copper acetate (Aldrich). The powdered support materials employed were γ-Al_2O_3 (Alfa Chemicals), amorphous SiO_2 (Crossfield Chemicals) and a pure siliceous form of MCM-41 prepared according to the procedure described in [16] using sodium silicate as the source of silicon. After impregnation of the support, excess water was removed by rotary evaporation and the sample was dried at 100°C for 8 h. Calcination was then performed in static air at 400°C for 30 min in a muffle furnace. Unsupported bulk copper oxide was obtained by calcination of copper acetate under the same conditions. All samples were sieved to 180 μm prior to reduction experiments. X-ray diffraction (XRD) spectra, obtained using CuK_α (λ=1.5418 Å) radiation, indicated that oxidised copper was present as a mixture of CuO and Cu_2O phases in approximately the same ratio in both the bulk and supported samples.

The CRTA apparatus, which uses a hygrometer to detect H_2O production during reduction, has been described previously [8]. For all experiments the reduction atmosphere consisted of 5% hydrogen in helium at a flow rate of 50 cm^3 min^{-1}. Linear heating experiments employed a heating rate of 5°C min^{-1} and a sample mass of 10 mg. CRTA runs were performed using maximum heating and cooling rates of 5°C min^{-1} and −10°C min^{-1}, respectively, in order to maintain a pre-selected target reduction rate which varied from $7\cdot10^{-4}$ mg H_2O min^{-1} to $7\cdot10^{-3}$ mg H_2O min^{-1} for the different samples.

Results and discussion

The temperature of maximum reduction rate (T_m) in linear heating TPR experiments is often used to compare the reducibility of supported and unsupported metal oxides [14, 17]. Table 1 shows T_m values obtained for both supported and unsupported copper oxide samples in the current study. It is seen that supported CuO reduced at a lower temperature than the bulk oxide irrespective of the type of support material employed. The lower peak temperatures for the supported samples agree with previous findings that supported CuO reduces more easily than bulk CuO [1, 13]. This has been attributed to an increased dispersion of the supported oxide providing a larger reactive surface area and, therefore, a higher concentration of defects at which reduction can start [13]. This dispersion effect also explains the increase in reducibility observed for the 5 mass% Cu/Al_2O_3 sample compared with the higher loading 10 mass% Cu/Al_2O_3 sample.

Table 1 Temperature of maximum reduction rate (T_m) for various copper oxide samples

Sample*	Cu content/mass%	T_m/°C
Bulk oxide	–	283
Cu/Al_2O_3	5	184
Cu/Al_2O_3	10	204
Cu/SiO_2	10	222
Cu/Si-MCM-41	10	223

* All samples were oxidized at 400°C in a static air atmosphere prior to TPR

Figure 1 shows the extent of reaction *vs.* temperature (α *vs.* T) profiles for the reduction of a Cu/Si-MCM-41 sample under linear heating (curve a) and CR-TPR conditions (curve b). Comparison of the two different profiles reveals that reduction occurs at a considerably lower temperature in CR-TPR experiments than for the corresponding linear heating experiment. The 'u-shaped' α *vs.* T curve obtained under CR-TPR conditions is characteristic of a nucleation and/or auto-catalytic reduction mechanism.

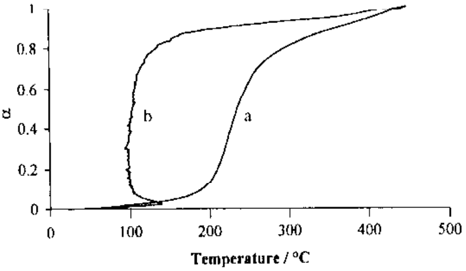

Fig. 1 α *vs.* temperature profile for the reduction of an MCM-41 supported copper oxide sample under a – linear heating and b – CR-TPR conditions

Figure 2 shows α *vs.* *T* profiles for the reduction of a sample of a Cu/SiO$_2$ sample under linear heating (curve a) and CR-TPR conditions (curve b). Again, it is evident that the majority of the reduction occurs at a much lower temperature for the CR-TPR experiment. The shape of α *vs.* *T* curve for the latter experiment is also consistent with a nucleation/auto-catalytic reduction mechanism.

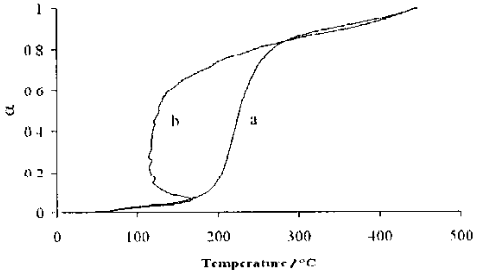

Fig. 2 α *vs.* temperature profile for the reduction of a SiO$_2$ supported copper oxide sample under a – linear heating and b – CR-TPR conditions

Due to the different experimental conditions employed in conventional TPR and CR-TPR, there are difficulties in making a direct comparison of the temperatures at which the reduction occurs. As described above, for linear heating experiments the temperature at which the reaction reaches its maximum rate is often selected. This peak maximum occurs at the temperature at which the greatest number of copper ions are reduced and thus (very) approximately corresponds to the plateau observed in CRTA where the majority of the reduction process occurs. However, in CRTA as the rate is theoretically constant for the entire reaction this plateau does not, therefore, correspond to a single temperature, although the temperature range is often narrow. It is possible to compare the temperatures at a single value of α, e.g. α=0.5 which usually corresponds to the peak maximum in linear heating experiments. However, we feel it is sometimes more informative to plot the 'temperature differential', i.e. the difference between the linear heating and CRTA temperatures ($T_{\text{linear}}-T_{\text{CRTA}}$) for a given value of α, as a function of α.

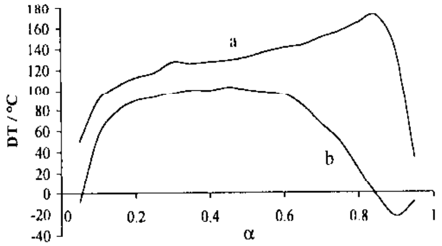

Fig. 3 'Differential temperature' profiles ($T_{\text{linear heating}}-T_{\text{CRTA}}$) for the reduction of a – MCM-41 supported copper oxide and b – SiO$_2$ supported copper oxide plotted as a function of α

Figure 3 shows 'differential temperature' for the profiles two sets of reduction experiments shown in Figs 1 and 2. The figure clearly illustrates the effect the support has on the entire reduction process as well as further emphasising the considerable temperature difference between the two types of reduction experiment. Comparison of the two 'differential temperature' profiles shows that the Cu/Si-MCM-41 sample is reduced at a lower temperature than the Cu/SiO_2 sample throughout the whole process, the effect being especially marked after α=0.6. Further studies would be necessary to provide a detailed explanation for this observation, but one possibility is that the oxide is more evenly dispersed on the Si-MCM-41 support.

Conclusions

Results are presented which demonstrate the application of CR-TPR to the study of supported copper catalysts. The reduction mechanism for copper oxide was found to be described by a nucleation and/or autocatalytic mechanism for both supported and unsupported materials. However, supported copper oxide reduced at lower temperatures than the bulk unsupported material in linear heating rate experiments which is attributable to an increased reactive surface area. The use of 'temperature differential' plots, which compare the temperatures of matching linear heating and CRTA experiments, provide an added insight into metal – support interactions.

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