COMMENT

Comment on the use of temperature-programmed desorption of H_2 as a tool to determine metal surface area of Cu catalysts

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Introduction

It has recently been suggested that the use of hydrogen desorption spectra would provide an accurate an non-invasive method for the determination of copper areas in oxide supported copper catalysts [1]. It is further argued that modelling of these hydrogen desorption spectra using available single crystal data [2] would allow evaluation of the morphology of the copper surface. This letter is written to express our reservations about the method, particularly with respect to measuring copper metal areas and copper morphology on copper/zinc oxide/alumina catalysts.

Experimental

Two catalysts are reported: they are copper/zinc oxide/alumina catalysts of composition $CuO/ZnO/Al_2O_3$, 49% w/w, 33% w/w, 18% w/w (catalyst A), and 55% w/w, 35% w/w, 10% w/w (catalyst B). Both were prepared by co-precipitation from their mixed nitrate solution using sodium carbonate, followed by filtration, washing, drying and calcination [3]. Their total surface areas measured in situ by nitrogen adsorption at 77 K were 64.7 $m^2\ g^{-1}$ (catalyst A) and 67.2 $m^2\ g^{-1}$ (catalyst B). The copper metal areas measured after reduction were 16.9 $m^2\ g^{-1}$ and 35.4 $m^2 g^{-1}$ (A and B respectively) by N_2O reactive frontal chromatography [4]. The apparatus used in this experiment has been described in detail previously [5].

The reduction was carried out carefully in a flowing hydrogen/helium mixture (10% H_2 in He, 25 $cm^3\ min^{-1}$, 295 K) raising the temperature from over

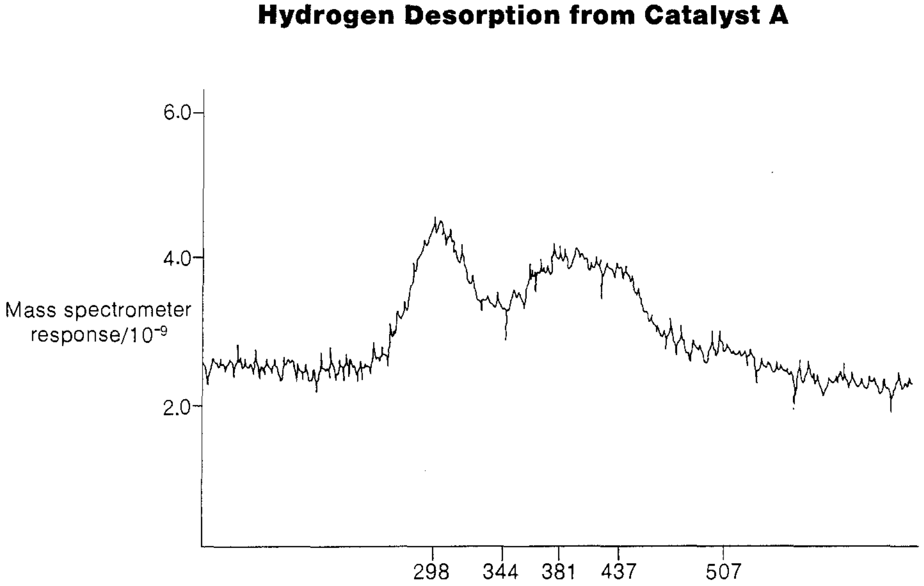

Fig. 1.

the catalyst ($\approx$ 1 g, 0.3–0.45 mm dia) from at ambient to 453 K at 1 K min^{-1}. The temperature was then held at 453 K under the flowing H_2/He mixture for 16 h fully to reduce the catalyst. The temperature of 453 K was chosen since it was the value at which the rate of reduction of the copper component of the catalyst maximised in temperature-programmed reduction [5].

Having reduced the catalyst, the temperature was then lowered to 77 K under the hydrogen/helium stream. The flow as then switched to helium and the gas phase hydrogen was swept out ($\approx$ 15 min), after which the temperature was raised in the flowing helium from 77 to 553 K, following hydrogen on the mass spectrometer, so producing the hydrogen desorption spectra (figs. 1, 2).

Discussion

The hydrogen desorption spectrum from catalyst A is shown in fig. 1 and from catalyst B in fig. 2. Four distinct peak maxima are seen in fig. 1 at 298, 381 and 437 K and at 507 K. The peak at 298 K is the same as that obtained for hydrogen desorption from polycrystalline copper [6] and so can be attributed to desorption from the copper component of the catalyst. Indeed the peak maximum temperature is the same as that reported by Muhler et al. for hydrogen desorption from alumina supported copper catalysts [1].

The four higher temperature peaks at 298, 381, 437 and 507 K have similar peak maximum temperatures to those obtained for hydrogen desorption from

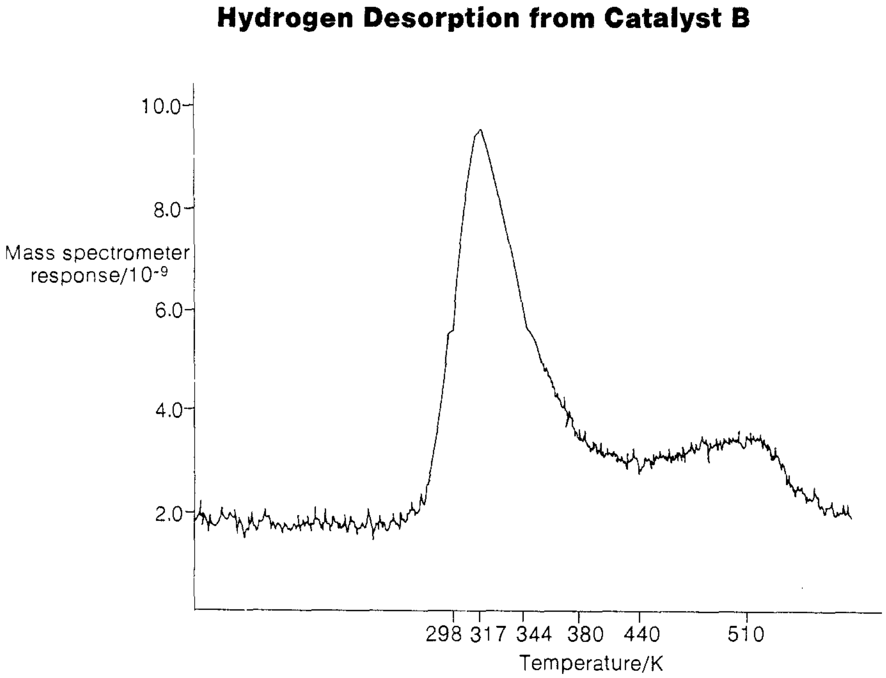

Fig. 2.

zinc oxide alone [7] and so these are attributed to that component of the catalyst.

The hydrogen desorption spectrum from catalyst B shows only two peak maximum temperatures – at 317 and 540 K. The larger lower temperature peak is ascribed to the copper component of the catalyst while the higher ill-defined peak is designated as deriving from the zinc oxide.

Several points should be made on the basis of these spectra. The first is that interference between the hydrogen desorbing from the tail of the copper peak and from the leading edge of the zinc oxide peak means that it is probably invalid simply to draw a line between minima at each side of the hydrogen peak as a rising baseline from which to integrate the area of the hydrogen desorption peak. Some form of peak deconvolution is required, the most accurate form of which is probably dropping a vertical from the minimum in the tail of the copper hydrogen peak (at 344 K, see fig. 1) to the original baseline extended horizontally. While this may be reasonably accurate for catalyst A, because of the long, flat minimum between the copper and zinc oxide hydrogen peaks of catalyst B (fig. 2) such an integration is fraught with uncertainty and likely to be less accurate than the N_2O reactive frontal chromatographic method which exhibits a sharp cutoff [5].

The second point of note is in respect of the hydrogen atom/copper atom ratio estimated from the initial desorption peaks. For catalyst A the ratio is 0.2

and for catalyst B it is 0.44. For catalyst A the hydrogen atom coverage was measured by dropping a vertical at 344 K and measuring the peak area up to this temperature. For catalyst B, the first peak was simply triangulated and the area between 259 and 423 K on the baseline and the peak maximum was measured. These appeared the most accurate method of integrating these peaks. The fact that the H : Cu ratio is not constant and for catalyst A is only 0.2 means that copper areas of supported catalysts calculated on the assumption of a ratio of 0.4 as proposed by Muhler et al. [1], will be seriously in error. The nitrous oxide method which has been calibrated using the low index faces of copper single crystal [8–10] and also polycrystalline copper [4] would appear to be more accurate.

Finally, the proposition that some estimate might be made of the population of the low index crystal faces on the surface of the supported copper by modelling the hydrogen desorption spectrum also appears to be invalidated by fig. 2. The peak maximum temperature for the hydrogen desorption from the copper is seen to be 317 K from that figure. The highest peak maximum temperature obtained by Anger et al. for hydrogen desorption from the three low index copper faces was 325 K from copper (110) [2]. When due allowance is made for the different heating rates (3 $K s^{-1}$ Anger, 10 K min this work) this value reduces to 295 K which is considerably lower than the 317 K observed for catalyst B. We would be unable to model the hydrogen desorption spectrum of catalyst B on the basis of the published low index face hydrogen desorption spectra. On reflection this would hardly appear to be surprising since one would expect to find a significant proportion of high index planes on the small particles which constitute a high surface area catalyst.

References

[1] M. Muhler, L.P. Nielson, E. Tornqvist, B.S. Clausen and H. Topsoe, Catal. Lett. 14 (1992) 241.

[2] A. Anger, A. Winkler and K.D. Rendulic, Surf. Sci. 220 (1989) 1.

[3] G.C. Chinchen, P.J. Denny, J.R. Jennings, M.S. Spencer and K.C. Waugh, Appl. Catal. 36 (1988) 1.

[4] G.C. Chinchen, C.M. Hay, H.D. Vandervell and K.C. Waugh, J. Catal. 103 (1987) 79.

[5] K.C. Waugh, Appl. Catal. 43 (1988) 315.

[6] K.C. Waugh, Catal. Today 15 (1992) 51.

[7] M. Bowker, H. Houghton and K.C. Waugh, J. Chem. Soc. Faraday Trans. I 77 (1981) 3023.

[8] F.H.P.M. Habraken and G.A. Bootsma, Surf. Sci. 88 (1979) 285.

[9] F.H.P.M. Habraken and G.A. Bootsma, Surf. Sci. 87 (1979) 383.

[10] F.H.P.M. Habraken, C.M.A.M. Mesters and G.A. Bootsma, Surf. Sci. 97 (1980) 264.