JOURNAL OF CATALYSIS **118,** 507–510 (1989)

An Improved Procedure for Estimating the Metal Surface Area of Supported Copper Catalysts

Supported Cu catalysts are of immense industrial importance, but a rapid and reliable method for estimating the exposed Cu metal surface, and hence the number of Cu atoms available to act catalytically, has not yet been described.

Attempts have been made (*1, 2*) to use CO chemisorption to count surface Cu atoms, but the results are uncertain because of extensive physical adsorption, especially when a support of high surface area is used, and because of the unknown CO/Cu_s stoichiometry. Several groups of workers have employed O_2 chemisorption, but the success of this method depends upon the conditions used and upon the state of the catalyst. Chemisorption of O_2 is accompanied by slow partial oxidation of the bulk metal at temperatures above ambient (*3*), and if the Cu crystallites are sufficiently small (i.e., <10 nm) they may be quickly and totally oxidized even at 77 K (*4*). Nevertheless this method can afford reliable results if the operating conditions are carefully controlled (*5*).

Attention in recent years has been concentrated however on the use of N_2O to form a layer of chemisorbed O atoms on the Cu metal surface (*4, 6–12*): the O/Cu_s ratio is believed to be 0.5. There is however no agreement as to the optimum temperature at which the reaction should be performed. Scholten and Konvalinka (*4*) and Evans *et al.* (*7*) favor 363–373 K because irreproducible results are obtained at lower temperatures and bulk oxidation is significant above 393 K. Other workers however believe that bulk oxidation starts as low as 340 K (*8*), although many have concluded that no substantial change in the uptake of N_2O occurs between 293 and 353 K (*9–11*).

A variety of techniques has also been used to determine the extent of the reaction of N_2O with Cu catalysts. Dell *et al.* (*6*) and Osinga *et al.* (*9*) employed a static system; they froze out unreacted N_2O and measured the residual N_2 volumetrically. Scholten and Konvalinka (*4*) used thermal conductivity to analyze the gas above the catalyst after dosing with N_2O, while Giamello *et al.* (*11*) have used microcalorimetry to follow the interaction. Various forms of the pulsed chromatographic method have also been tried (*12, 13*).

The method to be described minimizes the disadvantages (*5*) associated with the volumetric and pulse-flow methods, namely, the inherent inaccuracy associated with measuring very low N_2 pressures in the former case and the difficulty of identifying conditions giving complete reaction but no bulk oxidation in the latter. It involves reacting reduced Cu catalysts with pure N_2O under conditions expected to lead to the formation of a complete layer of O atoms having an O/Cu_s ratio of 0.5, but without oxidation of the bulk metal, and then determining the number of chemisorbed O atoms by temperature-programmed reduction (TPR). Whereas the methods used previously have derived this number by inference, the presence technique measures it directly and is therefore expected to be more accurate and reliable.

EXPERIMENTAL

Cu catalysts were prepared on three supports (Aerosil 200, Degussa Al_2O_3–C, and

0021-9517/89 $3.00

TABLE 1

Characteristics of Supported Cu Catalysts and Their Rates for CO_2 Hydrogenation at 673 K

Catalyst	Method[a]	Cu content (wt%)		Cu area ($m^2\ g_{Cu}^{-1}$)	Dispersion (%)	Rate ($mmol\ h^{-1}\ m^{-2}$)
		By AA	By TPR			
Cu/SiO_2	IE	6.3	3.8	335	52.0	0.076
10% Cu/SiO_2	DP	5.6	5.4	93	14.4	0.148
5% Cu/SiO_2	DP	4.2	3.6	253	39.2	0.060
10% Cu/SiO_2	Impr.	7.2	7.6	56	5.3	0.025
5% Cu/SiO_2	Impr.	4.3	4.4	33	5.3	0.061
10% Cu/TiO_2	Impr.	8.6	7.9	28	4.3	0.028
5% Cu/TiO_2	Impr.	5.0	3.1	66	10.3	0.029
10% Cu/Al_2O_3	Impr.	7.5	5.1	239	37.0	0.100
5% Cu/Al_2O_3	Impr.	4.1	4.3	199	30.4	0.051

[a] IE, ion exchange; DP, deposition–precipitation; Impr., impregnation.

Degussa P-25 TiO_2) by (i) impregnation to incipient wetness with a solution of $Cu(NO_3)_2$ (*14*), (ii) ion exchange with $[Cu(NH_3)_4]^{2+}$ (*15*), and (iii) deposition–precipitation of $Cu(OH)_2$ (*16*). Various Cu concentrations were used as shown in Table 1. Precursors were dried overnight in an air oven at 400 K and were then calcined for 5 h at 773 K in a stream of air. Cu contents were determined by atomic absorption (AA) spectroscopy (see Table 1), and also by TPR as described below.

TPR apparatus of standard design (*17*) was modified to allow flows of (i) 5% H_2 in Ar, (ii) pure Ar, and (iii) pure N_2O to be passed sequentially through the reactor and detector. A normal TPR was first performed on a calcined sample: this permitted an estimate of the Cu content, assuming that calcination in each case afforded CuO, and also produced a reduced Cu catalyst thoroughly free from all adsorbed species and in a suitable state for reaction with N_2O. The heating rate was 5 K min^{-1} and the flow rate of the gas was 40 $cm^3\ min^{-1}$. Reduction peaks were symmetrical, having values of T_{max} of about 473 K, with an accompanying smaller peak at 503–573 K. Reduction was stopped at 623 K in order to avoid sintering of the Cu crystallites. This temperature appeared to be high enough to secure complete reduction to Cu metal, but it is a further advantage of this method that the H_2 consumption in this first TPR may be used to give a direct estimate of the amount of reduced Cu present in the sample (see Table 1). The detector response was calibrated by injecting doses of pure H_2.

The sample was then cooled to the reaction temperature, normally 333 K, in O_2-free Ar (obtained by passing Ar through a bed of SiO_2-supported MnO) and after 30 min pure N_2O was allowed to flow over the sample for 1 h at this temperature (flow rate 81 $cm^3\ min^{-1}$). The N_2O flow was then replaced by Ar and the sample cooled to room temperature. The H_2/Ar mixture was then introduced and a second TPR carried out. A peak due to the reduction of the adsorbed O atoms was observed: it was symmetrical, and values of T_{max} were in the range 403–423 K, i.e., significantly lower than for the principal peak in the reduction of CuO. After the second TPR, a further calibration with a dose of pure H_2 was carried out, and the number of surface Cu atoms, Cu_s, computed assuming $O/Cu_s = 0.5$. The dispersion, Cu_s/Cu_{tot}, was then calculated using the Cu content as determined by TPR, and also the Cu surface area (assuming 1.47×10^{19} atoms m^{-2}, this being the mean for the three low Miller Index planes).

RESULTS AND DISCUSSION

A selection of the results is shown in Table 1. Except in two cases, the agreement between the Cu contents as estimated by AA spectroscopy and by TPR is satisfactory. The observed dispersion is markedly dependent on both the support and the method of preparation. With SiO_2, ion exchange and deposition–precipitation both afford high dispersions, markedly better than those obtained with the impregnation method. This last method, however, gives quite good dispersions with Al_2O_3 but not with TiO_2. Kuijpers *et al.* (*18*) reported that a 10% Cu/SiO_3 catalyst made by deposition–precipitation had a metal area of 90 $m^2\ g_{Cu}^{-1}$, in very good agreement with what we find (Table 1).

The Cu content of the Cu/SiO_2 catalyst made by ion exchange seems high (~6%). On the basis of an assumed Si–OH concentration of $3 \times 10^{18}\ m^{-2}$ (*19*), the maximum Cu content is calculated to be 3.2%. As has been recently pointed out (*19*), such a high value is probably caused by the precipitation of $Cu(OH)_2$ from the solution of $[Cu(NH_3)_4]^{2+}$ in the pores as the pH is lowered by washing. This method therefore in fact closely resembles the deposition–precipitation method. The so-called ion exchange method has been reported (*19*) to give well-dispersed Cu particles (Cu area 249 $m^2\ g_{Cu}^{-1}$ for 4.1% Cu/SiO_2, measured as described by Wainwright *et al.* (*7*)), in agreement with the first and third entries in Table 1.

As noted above, the reaction of the N_2O with the Cu surface was normally conducted at 333 K. In order to determine the sensitivity of the resulting estimate of the number of O atoms chemisorbed to the reaction temperature, measurements were also made with the 10% Cu/Al_2O_3 catalyst using temperatures of 343 and 363 K. Values for the Cu areas obtained were, respectively, 241 and 242 $m^2\ g_{Cu}^{-1}$, in excellent agreement with the value of 239 $m^2\ g_{Cu}^{-1}$ given in Table 1, where the temperature used was 333 K. These results suggest very strongly that the reaction temperature used is not critical and that no bulk oxidation occurs (at least with this catalyst) up to 363 K.

The hydrogen of CO_2 (the reverse water–gas shift reaction) was performed in a glass recirculation system (*20*): catalysts were initially reduced at 523 K for 1 h 80 Torr H_2, the H_2O being removed continuously by condensation. In seeking to relate the observed rates at 673 K (Table 1) to the measured Cu areas, one must assume that the areas produced by this reduction schedule and in the TPR procedure are the same. The TP reduction achieved a higher temperature (623 K) but used a lower H_2 pressure (40 Torr), the effects of which may compensate.

The reliability of the TPR method for estimating Cu areas is shown by the generally satisfactory correlation between Cu areas and rates of CO_2 hydrogenation (Table 1). Catalysts having low activity have Cu areas in the range 28–66 $m^2\ g_{Cu}^{-1}$, whereas those of high activity (10–25 mmol $h^{-1}\ g_{Cu}^{-1}$) have areas in excess of 200 $m^2\ g_{Cu}^{-1}$. The only exception to this generalization is the 10% Cu/SiO_2 made by deposition–precipitation, which shows high activity, notwithstanding a somewhat low Cu area. These results will be described more fully in a future publication.

We conclude that the use of TPR to estimate O atoms formed on Cu surfaces by dissociation of N_2O constitutes a direct, tolerant, and simple method for determining Cu surface area, dispersion, and particle size in supported Cu catalysts. TPR permits a distinction to be drawn between chemisorbed O atoms and Cu formed by overoxidation, and a separate assessment of each where necessary. A given sample may also be speedily reexamined in order to refine the accuracy of the measurement.

ACKNOWLEDGMENT

S.N.N. gratefully acknowledges financial support from the Government of the Republic of Cameroon.

REFERENCES

1. Emmett, P. H., and Skau, N., *J. Amer. Chem. Soc.* **65,** 1029 (1943).
2. Sinfelt, J. H., Taylor, W. F., and Yates, D. J. C., *J. Phys. Chem.* **69,** 95 (1965).
3. Allen, J. A., and Mitchell, J. W., *Discuss. Faraday Soc.* **8,** 1815 (1950).
4. Scholten, J. J. F., and Konvalinka, J. A., *Trans. Faraday Soc.* **65,** 2465 (1965).
5. Parris, G. E., and Klier, K., *J. Catal.* **97,** 374 (1986).
6. Dell, R. M., Stone, F. S., and Tiley, P. F., *Trans. Faraday Soc.* **49,** 195 (1953).
7. Evans, J. W., Wainwright, M. S., Bridgwater, A. J., and Young, D. J., *Appl. Catal.* **7,** 75 (1983).
8. Sengupta, G., Gupta, D. K., Kundu, M. L., and Sen, S. P., *J. Catal.* **67,** 223 (1983).
9. Osinga, T. J., Linsen, B. G., and van Beet, W. P., *J. Catal.* **7,** 277 (1967).
10. Narita, K., Takeyawa, N., Kobayashi, H., and Toyoshima, I., *React, Kinet. Catal. Lett.* **19,** 91 (1982).
11. Giamello, E., Fubini, B., Lauro, P., and Bossi, A., *J. Catal.* **18,** 108 (1970).
12. Dvorak, B., and Pasek, J., *J. Catal.* **18,** 108 (1970).
13. Chinchen, G. C., Hay, C. M., Vandervell, H. D., and Waugh, K. C., *J. Catal.* **103,** 79 (1987).
14. Bond, G. C., "Heterogeneous Catalysis: Principles and Applications," 2nd ed. Oxford Chemistry Series, 1987.
15. Satterfield, C. N., "Heterogeneous Catalysis in Practice." McGraw–Hill, New York, 1980.
16. Geus, J. W., *in* "Heterogeneous Catalysis in Practice." McGraw–Hill, New York, 1980.
17. Gentry, S. J., Hurst, N. W., and Jones A., *J. Chem. Soc. Faraday Trans. 1* **77,** 603 (1981).
18. Kuijpers, E. G. M., Tjepkema, R. B., van der Wal, W. J. J., Mesters, C. M. A. M., Spronck, S. F. G. M., and Geus, J. W., *Appl. Catal.* **25,** 139 (1986).
19. Lee, J. C., Trimm, D. L., Kohler, M. A., Wainwright, M. S., and Cant, N. W., *Catal. Today* **2,** 643 (1988).
20. S. N. Namijo, Ph.D. thesis, Brunel University, 1988.

GEOFFREY C. BOND
STEPHEN N. NAMIJO

Department of Chemistry
Brunel University
Uxbridge UB8 3PH, United Kingdom

Received August 18, 1988; revised February 9, 1989