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Alternating nitrous oxide / reductant cycles and the determination of copper area in supported copper catalysts

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Reduction, surface oxidation and re-reduction of a copper-on-silica catalyst has been investigated using hydrogen, carbon monoxide and nitrous oxide in a flow system with mass spectrometric determination. Hydrogen is more effective than carbon monoxide for the initial reduction of the catalyst as prepared in oxide form and the copper content can be accurately determined from the total gas consumption in both cases. However, carbon monoxide can quantitatively remove surface oxygen, deposited from nitrous oxide, at a temperature of 333 K, whereas the same process in hydrogen peaks at 383 K. A method for determining the quantity of surface copper by sequential N_2O/CO cycles under isothermal conditions has been established.

Keywords: copper on silica; nitrous oxide oxidation; carbon monoxide reduction

1. Introduction

A variety of methods have been described for the determination of the metal surface area in supported copper catalysts [1–14]. Nitrous oxide chemisorption, depositing one oxygen atom per two surface copper atoms, is perhaps the most satisfactory. Originally described in a static form by Dell et al. [4,5], it was subsequently developed in pulse form [6,7]. The latter method has been widely used but can give erratic results, possibly due to rapid overheating and sintering of small particles on initial exposure to high nitrous oxide pressures. Chinchen et al. [8] subsequently described the continuous flow breakthrough method, reactive frontal chromatography. Comparative studies by Bartley et al. [9] and by Thomas [10] both claim that this method is the most reliable although there are still disputes regarding its validity [11–13]. The general procedure involves reduction in hydrogen at ~ 500 K, cooling to 333–363 K, and exposure to a low concentration of N_2O in a flow system with measurement of the uptake by thermal conductivity or mass

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spectrometry. Repeat determinations have usually been done after a repeat reduction at the same temperature, although work by Bond and Namijo [14] indicates that hydrogen can remove oxygen deposited from N_2O at 403–423 K.

The present work compares H_2 and CO as reductants for a supported copper catalyst, both in its initial oxide form and following surface oxidation in N_2O. Carbon monoxide is very effective for re-reduction, sufficiently so that repeated surface area determinations are possible through alternating N_2O/CO cycles at a fixed temperature.

2. Experimental

The experiments were carried out in a continuous flow system which allowed switching between two streams using a 1/16″ 4-port valve. One stream was either ultrahigh purity helium or hydrogen in helium, the other any combination of hydrogen, helium, carbon monoxide or nitrous oxide (supplied via mass flow controllers) with a small amount of argon always present as a tracer. The catalyst sample was contained in a 5 mm i.d. Pyrex tube located in a cylindrical aluminium block closely fitting within a tube furnace. This could be programmed off a thermocouple in the block. Additional sheathed thermocouples located in the sample tube just above and below the sample itself showed a temperature gradient of less than ±4 K during ramping and less than ±0.5 K under isothermal conditions. The aluminium block was spirally wound with a 1/12″ o.d. stainless steel tube through which nitrogen gas cooled to as low as 85 K could be passed. This allowed cooling of the sample from above 573 K to below 333 K in less than 10 min. A second 4-port valve enabled switching of the stream leaving the reactor, or the bypass, to a quadrupole mass spectrometer (Vacuum Generators SX300). This was operated in multiple ion mode with measurements at $m/z = 2$ (H_2), 18 (H_2O), 28 (N_2 or CO), 32 (O_2), 40 (Ar), and 44 (N_2O or CO_2) once every 6 s. All signals were background corrected and those at $m/z = 28$ were adjusted for fragmentation from any N_2O and CO_2 also present. Most experiments were carried out with sample masses of 100–400 mg and a total flowrate of 60 cm^3(STP)/min of which about half was sampled into the mass spectrometer.

The standard 21.9 wt% copper-on-silica catalyst used in most experiments was prepared by deposition–precipitation [15] of copper hydroxide on to an aerosil-type silica of area 191 m^2/g (Degussa Aerosil 200). The filter cake was dried at 373 K and calcined in flowing air at 773 K. The resultant black product was crushed and sieved and samples of the 300 to 600 μm fraction loaded into the reactor. The initial reduction was in the form of a temperature programmed reduction (TPR), or stepwise TPR, with the temperature raised at 4 K/min in a 7% hydrogen/helium mixture to a temperature of 533 K and held there for a further two hours before cooling. The calcined sample will be referred to as 21.9% CuO/SiO_2 and the reduced version as 21.9% Cu/SiO_2.

3. Results and discussion

Fig. 1 illustrates the TPR of 21.9% CuO/SiO_2 in hydrogen. The reduction rate exhibited two maxima at 500 and 517 K. The temperature of the first maximum is typical for silica supported copper catalysts in general [16] while the origin of the second peak is less certain. It is more likely to correspond to reduction of a second species which interacts more strongly with the support than to the second stage of a sequential reduction $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$ [16]. As previously shown by Bond and Namijo [14], it is possible to calculate the copper content from the integrated hydrogen consumption assuming the reduction is represented exactly by

$$CuO + H_2 \rightarrow Cu + H_2O$$

For the catalyst here, the hydrogen consumption was 3490 μmol/g indicating 22.2 wt% copper in good agreement with the value obtained by atomic absorption analysis.

Fig. 2 shows the corresponding results for the TPR of the same catalyst in carbon monoxide. In this case it was possible to follow both reactant (CO) consumption and product (CO_2) production and, as expected, they exhibit a mirror image. Again there are two lower temperature peaks, at 452 and 472 K, but the quantities of CO and CO_2 corresponding to them (~1640 μmol/g) were approximately one-half that for the corresponding peaks with hydrogen. Additional CO consumption

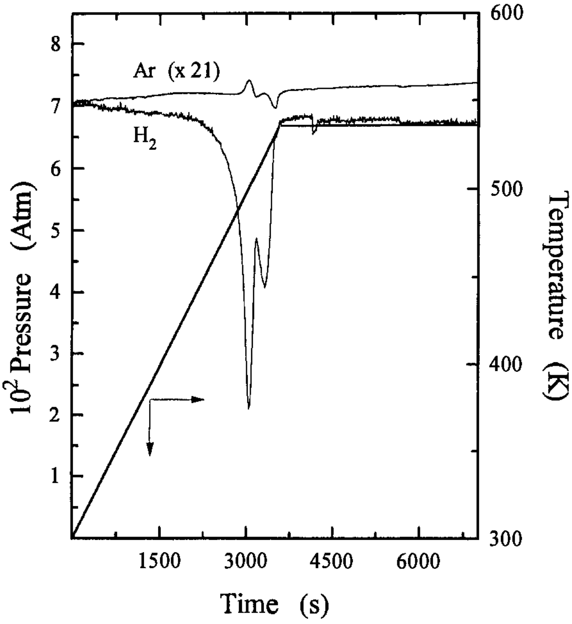

Fig. 1. Temperature programmed reduction of 21.9% CuO/SiO_2 (0.291 g) in 7.1% H_2/He at 60 cm^3(STP)/min.

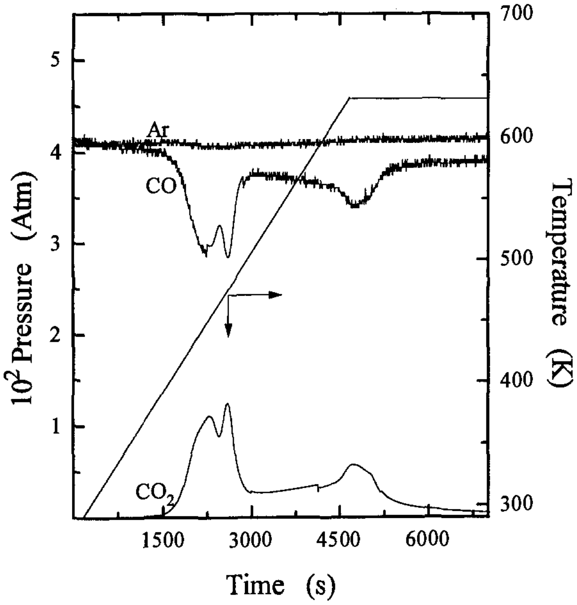

Fig. 2. Temperature programmed reduction of 21.9% CuO/SiO_2 (0.265 g) in 4.3% CO/He at 60 cm^3(STP)/min.

(~1800 μmol/g) occurred above 480 K with a broad maximum near 633 K. In this case it seems that the high and low temperature reduction regions do correspond to sequential reduction. In particular, if the reduction was stopped at 473 K (i.e. when carbon monoxide consumption was half the total) then the resultant material would not chemisorb nitrous oxide at 333 K. Similarly, such samples exhibited near zero initial activity for the dehydrogenation of methanol, a reaction which requires zero valent copper [17]. Activity gradually developed over a period of 30 min as the catalyst was further reduced by the hydrogen produced by dehydrogenation. This, together with the results of figs. 1 and 2, shows that hydrogen is a better reducing agent than carbon monoxide for this type of supported copper catalyst as prepared in oxide form.

The interaction of nitrous oxide with hydrogen reduced catalysts was studied under a variety of conditions. The behaviour was the same whether the sample was purged with helium at the final reduction temperature and cooled in helium, or cooled to the desired temperature (300–363 K) in the hydrogen/helium mixture used for reduction and flushed to zero hydrogen signal. The hydrogen desorption process was then complete in less than 2 min as expected from the TPD results of Muhler et al. [11] showing maximum desorption rates at ~300 K.

Fig. 3 shows the result of exposing a reduced 21.9% Cu/SiO_2 sample to nitrous oxide at 333 K. The production of nitrogen followed the argon tracer with almost no delay. Nitrous oxide consumption was complete until its signal showed a step rise which crossed the fall in nitrogen consumption near the 50% mark for each (as

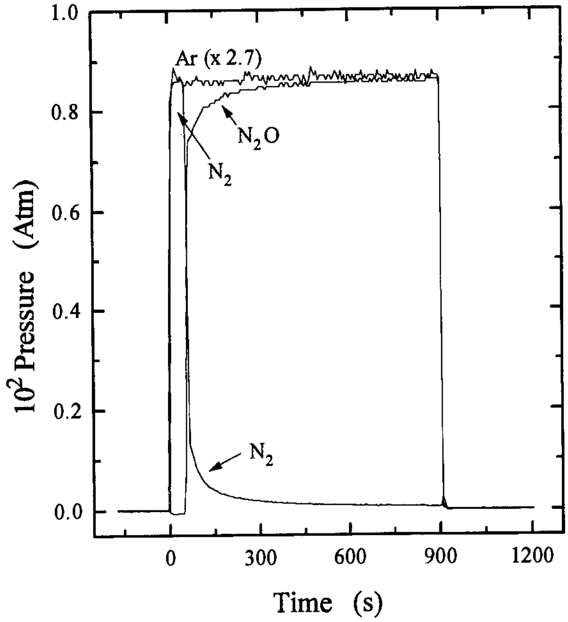

Fig. 3. Nitrous oxide consumption and nitrogen production following exposure of 21.9% Cu/SiO_2 (0.291 g) to 0.86% $N_2O/Ar/He$ at 60 cm^3(STP)/min at 333 K.

expected if the initial reactive adsorption is without holdup of either gas). However, a small amount of nitrous oxide consumption (and nitrogen production) continued in a process with a half life of ~30 s. When the feed stream was switched back to pure helium the signals due to nitrous oxide and argon fell in unison indicating that the surface oxidised catalyst did not retain any unreacted nitrous oxide. The "tails" in N_2O consumption, and N_2 production, may be due to small readjustments in the positions of initially deposited oxygen atoms from random ones to more regular arrays so as to allow fuller occupancy. They are less likely to be due to subsurface oxidation given the results of Bartley et al. [9] indicating that long equilibration (16 h in helium at 333 K) does not induce more uptake of N_2O.

Measurements were made to determine the ease with which the oxygen deposited from nitrous oxide could be removed by exposure to reducing agents. Fig. 4 shows the results obtained using carbon monoxide at 333 K. It is clear that surface re-reduction is possible at this surprisingly low temperature. Carbon dioxide was produced immediately but its pressure was less than that of the corresponding decrease in carbon monoxide pressure because some of the latter adsorbs on the re-reduced copper surface as that is created. Carbon dioxide production and carbon monoxide consumption both exhibited some tails attributable to a slower rate of reduction for some of the deposited oxygen possibly due to stronger binding to particular sites. When the feed stream was switched back to helium the carbon monoxide signal lagged that of the argon tracer as carbon monoxide desorbed from the copper. When the re-reduced sample was exposed to nitrous oxide the resultant signals

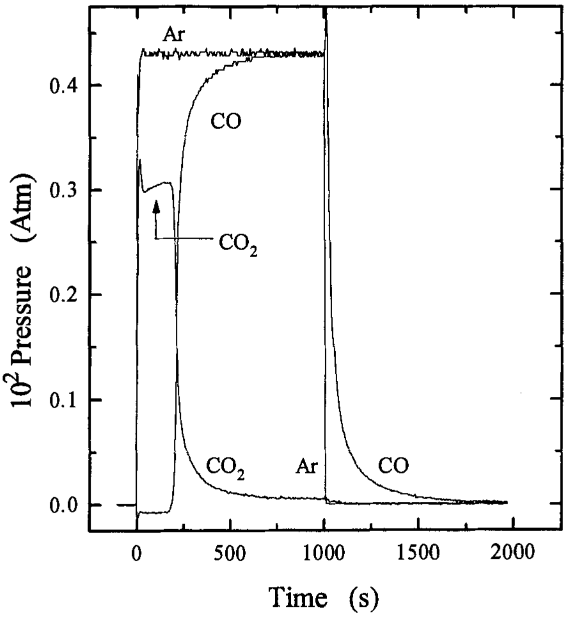

Fig. 4. Carbon monoxide consumption and carbon dioxide production following exposure of 21.9% Cu/SiO_2 (0.291 g) to 0.86% $N_2O/Ar/He$ at 60 cm^3(STP)/min at 333 K.

were very similar to those of fig. 3. Thus cycles with nitrous oxide and carbon monoxide are repeatable with similar results.

Table 1 lists the gas consumptions and productions measured during a series of successive cycles at 333 K. In each case the integrated areas for N_2O, N_2, CO_2 and gross CO consumption were obtained by integration to lines obtained by extrapolation of the step changes corresponding to cessation of rapid surface oxidation (or re-reduction) to the baseline. Inclusion of the "tails" to each peak would add ~8% to each value. The quantities of CO adsorbed correspond to the amounts desorbed following the switch from CO/Ar/He to He as calculated from the area between the carbon monoxide signal and the normalised argon one. The net CO consump-

Table 1
Gas consumption and production during alternating N_2O/CO cycles on 21.9% Cu/SiO_2 at 333 K

	N_2O oxidation		CO reduction			Net CO loss[a]
	N_2 formed[a]	N_2O loss[a]	CO_2 formed[a]	gross CO loss[a]	CO adsorbed[a]	
cycle 1	98	94	106	157	56	101
cycle 2	94	95	100	140	39	101
cycle 3	100	87	102	147	49	98
average	97	92	103	148	48	100

[a] In µmol/g.

tion (i.e. that involved in surface re-reduction) is then obtained by difference. The internal agreement between N_2 production, N_2O consumption, CO_2 production and net CO consumption is very good given that there may be some systematic errors in the mass spectrometer calibrations for the various gases. Similarly, there is little fall-off in the values from cycle to cycle indicating that surface oxygen deposited from nitrous oxide is fully removed by reaction with carbon monoxide at the same temperature.

There is a substantial body of evidence to show that nitrous oxide deposits one oxygen atom for every two surface copper atoms i.e.

$$2Cu(s) + N_2O(g) \rightarrow Cu_2O(s) + N_2(g)$$

in which case re-reduction by CO is necessarily

$$Cu_2O(s) + CO(g) \rightarrow 2Cu(s) + CO_2(g)$$

On this basis the dispersion of the copper (i.e. the percentage of its atoms which are exposed at the surface) can be calculated without further assumption. The value for the 21.9% Cu/SiO_2 used here is 5.7% corresponding to a particle size of approximately 18 nm assuming uniform spheres. With 1.46×10^{19} copper atoms per square metre of surface [18] the copper area is 8.0 m^2/g.

As can be seen from table 1 the amount of carbon monoxide adsorbed on the re-reduced surface is about half the gas production consumption in the oxidation/re-reduction cycles indicating a CO/Cu ratio of about 0.25 which is consistent with the results of De Rossi et al. [19] and of Kohler et al. [20].

Tests were carried out with hydrogen to see if it too could remove oxygen deposited on copper during exposure to nitrous oxide at 333 K. Results are shown in fig. 5. It is clear that hydrogen is less effective than carbon monoxide. There was some hydrogen consumption at 333 K but it did not reach a maximum until 383 K during a temperature ramp commenced after 7 min of exposure. The total amount of hydrogen consumed during re-reduction was ~93 μmol/g in good agreement with that found for carbon monoxide. Thus cycling in N_2O then H_2 as reported by Bond and Namijo [14] is a feasible way of carrying out repetitive determinations but it is less convenient than the N_2O/CO procedure described here, since unlike the latter, it cannot be carried out at fixed temperature.

The difference in reduction efficiency conforms to surface science studies which show that the rate of removal of absorbed oxygen from Cu(110) by carbon monoxide is several orders of magnitude faster than by hydrogen [21,22]. It is also in accord with the schematic potential energy barriers presented by Campbell and Ernst [23] in connection with the water–gas shift equilibrium on Cu(110). The main barrier in reduction by CO (the $CO_s + O_s$ step) is ~70 kJ/mol, whereas reduction by H_2 confronts two significant barriers, H_2 dissociation (~60 kJ/mol) and the $OH_s + H_s$ step which is higher still (~80 kJ/mol). While these values are unlikely to carry over exactly to the high oxygen coverages applying here, the relative reduction efficiencies observed here are qualitatively consistent with them.

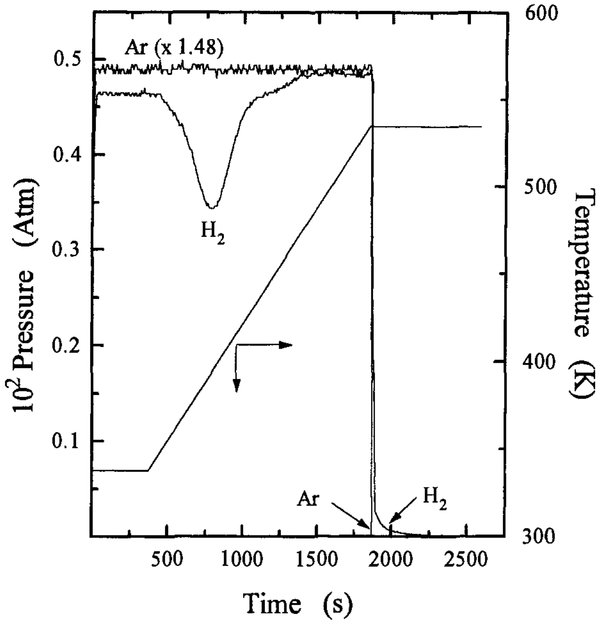

Fig. 5. Temperature programmed reduction of 21.9% Cu/SiO_2 (0.291 g) that had been reoxidised in N_2O to 0.495% $H_2/Ar/He$ at 60 cm^3(STP)/min.

The foregoing shows that H_2-TPR of the calcined material, with subsequent exposure to N_2O/CO cycles, is a feasible way to determine respectively, total copper and surface copper in copper on silica catalysts. The general applicability of the method has been tested for a variety of other copper based catalysts and the results will be presented together with the results for catalytic testing of the same materials at a later date.

Acknowledgement

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