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The Measurement of Copper Surface Areas by Reactive Frontal Chromatography[1]

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A technique, termed here "reactive frontal chromatography," which permits the evaluation of copper areas in oxide-supported copper catalysts in general is described. The aspect which relates to normal frontal chromatography is that of the flow switching technique, flows being changed from helium to a helium/nitrous oxide mixture. In this case, however, instead of simply observing the N_2O uptake as in normal frontal chromatography, the N_2O decomposes upon adsorption yielding N_2 in the gas phase, the oxygen being chemisorbed on the surface: this is the reactive aspect. Therefore before the N_2O breakthrough occurs, N_2 is evolved in an amount equivalent to the number of oxygen atoms chemisorbed on the copper surface. The technique has been calibrated against a sample of unsupported copper whose area is determined in the same apparatus by the BET method.

INTRODUCTION

Metal surface areas are normally measured by the chemisorption of a suitable adsorbate. Copper surface areas have been determined using carbon monoxide and hydrogen, although neither adsorbate is thought to yield accurate results (*1*). Attempts to use oxygen as adsorbate have also been largely unsuccessful as the ready chemisorption of oxygen on the copper surface is accompanied by a partial and slow oxidation of the bulk, the extent and stoichiometry of which depend markedly on the conditions used (*2*). However, a successful oxygen chemisorption technique has recently been described by Parris and Klier (*3*).

The reaction of nitrous oxide with copper has been used to evaluate metal surface areas of both pure and supported copper catalysts (*4–8*). This technique is based on the decomposition of ntirous oxide molecules on the surface of copper to produce chemisorbed oxygen atoms which generate gas phase nitrogen according to the process

$$N_2O_{(g)} + 2Cu_{(s)} \rightarrow N_{2(g)} + (Cu—O—Cu)_{(s)}$$

where s denotes surface atoms. Ultraviolet photoelectron spectroscopy has been used by Narita *et al.* (*9*) to confirm that, at temperatures below 100°C, the oxidation of copper by N_2O is sufficiently mild that only the surface copper is oxidised and that only to the Cu(I) oxidation state.

There is some disagreement between various investigators as to the optimum temperature at which the N_2O reaction should be carried out, and as to the effect of temperature on the extent of oxidation. Dell *et al.* (*4*) recommended exposure of copper to N_2O at 20°C, but this has been criticised by Scholten and Konvalinka (*6*) as giving irreproducible results. Scholten and Konvalinka favoured the use of temperatures 90–100°C to obtain more reproducible results and indicated that bulk oxidation commences at temperatures of ~120°C. Evans *et al.* (*8*) are in agreement with this, and suggested that the application of a single pulse of N_2O in excess of that required to oxidise all the surface copper at a tempera-

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[1] The technique described in this paper is the subject of ICI UK Patent Application 8512684 and enquiries regarding licenses to use this technique should be addressed to G. C. Chinchen.

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ture of 90°C provides a reliable measurement of copper surface area. This is in contrast to the results of Sengupta *et al.* (*10*), who suggest that there is a sharp increase in N_2O decomposition, indicating the onset of bulk oxidation, at 70°C. Osinga *et al.* (*5*), however, proposed that copper surface area measurements can be carried out with N_2O at temperatures of 20–120°C as bulk oxidation does not commence until 150°C. From a recent study by a microcalorimetric method, Giamello *et al.* (*11*) conclude that no substantial changes in the uptake of N_2O occur in the temperature range 20–80°C, in agreement with other authors (*5, 9*), and suggest that the extent of reaction is not kinetically controlled in that temperature range.

A variety of experimental techniques has been used to determine the extent of the reaction of N_2O with the surface of copper. Early work by Dell *et al.* (*4*) and Osinga *et al.* (*5*) measured the amount of nitrogen formed in a static system by freezing out excess N_2O and determining the residual pressure in a conventional volumetric apparatus. Scholten and Konvalinka (*6*) used both thermal conductivity and mass spectrometric methods to analyse the gas phase above a catalyst which had been dosed with N_2O. As already mentioned, the microcalorimetric method of Giamello *et al.* (*11*) has been used to monitor the interaction of N_2O with copper. Dvořák and Pašek (*7*) used a pulse chromatographic method in which pulses of N_2O were introduced into a helium stream as it passed over a sample of catalyst.

We have now developed a flow, as distinct from a pulse, chromatographic method in which the copper-containing sample is exposed to a dilute mixture of N_2O in inert gas, viz. helium. The technique, which we have termed "reactive frontal chromatography," permits the accurate and convenient routine evaluation of copper areas and is particularly suitable for *in situ* measurements, i.e., the evaluation of copper areas of catalyst samples whilst they are in a reactor. As in normal frontal chromatography we use a flow switching technique, the flow being changed from helium to a helium/N_2O mixture. However, we do not simply observe the N_2O uptake as in normal frontal chromatography. On adsorption the N_2O decomposes giving N_2 in the gas phase, the oxygen being chemisorbed on the surface: this is the reactive aspect. Hence, before N_2O breakthrough occurs, N_2 is evolved in an amount equivalent to the number of oxygen atoms chemisorbed on the copper surface. Since the reaction is quantitative, reacting to half-monolayer coverage (*6*), i.e., 5×10^{14} oxygen atoms/cm^2 or 2×10^{-15} cm^2/oxygen atom, the surface area (m^2) of the copper is obtained by multiplying the total number of molecules of nitrogen evolved by 2×10^{-19}. The technique has been conveniently calibrated against a sample of unsupported copper whose area was determined in the same apparatus by the BET method.

Reactive frontal chromatography has a number of distinct advantages over pulse methods: less complicated hardware is required, the method is faster and requires less operator involvement, a diluted N_2O can be used which keeps the system more isothermal, and the volume of N_2 evolved is more easily and accurately determined.

EXPERIMENTAL

Apparatus. The apparatus used in the technique development is shown diagramatically in Fig. 1. Basically it consists of a glass U-tube (40 cm long and 0.4 cm i.d.) which is used to contain the crushed copper-containing catalyst or material. The U-tube is housed in a normal gas chromatographic oven. The U-tube may also be immersed in a liquid-nitrogen bath to allow *in situ* measurements of total surface area at 77 K. A six-port pneumatic valve was used to switch between the various required gas flows, i.e., reduction gas (H_2/N_2), helium, nitrous oxide, and carbon monoxide.

The hydrogen (Air Products) was 99.99%

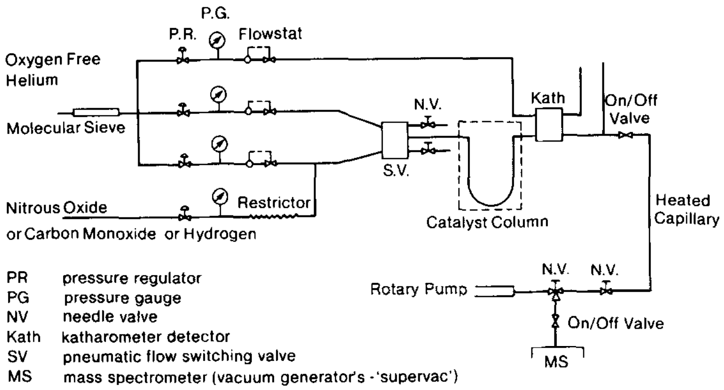

FIG. 1. Diagrammatic representation of apparatus.

pure; carbon monoxide (Matheson) was 99.997% pure; the nitrous oxide (Air Products) was 99.9% pure, the 0.1% impurity being oxygen. All these gases were used direct from the cylinder without further purifications, any correction which might have been required for the 0.1% oxygen impurity in the nitrous oxide was negligible.

The helium (British Oxygen Co.) was purified by passing through a "Rare Gas Purifier" (British Oxygen Co., Mk 3) which consisted of columns in series, containing titanium granules at 700°C for the removal of nitrogen and oxygen; copper oxide (also at 700°C) to remove hydrocarbons, hydrogen, and carbon monoxide; and a molecular sieve (at ambient temperature) to remove water and carbon dioxide. The oxygen content in the exit gas was <1 ppm on a Hersch Oxygen Meter (Engelhard Industries Ltd.).

A mass spectrometer and a katharometer were available as detection equipment. The flow of gas to the mass spectrometer was controlled by a needle valve, which allowed a flow of 20 cm^3/min to pass to the MS system and 5 cm^3/min to be vented. This system ensured that the katharometer was maintained at its calibration pressure.

The katharometer was calibrated by injection of known volumes of gas and recording the chart area proportional to it,

$$\text{i.e., } K = \frac{\text{mol (injected)}}{\text{area}}.$$

This calibration constant K (mol cm^{-2}) can be converted into another one, K^1 (mol cm^{-4}), by multiplying by the chart speed and dividing by the carrier gas flow rate.

$$\text{i.e., (mol cm}^{-4}\text{) } K^1 = K \times \frac{\text{chart speed}}{\text{flow rate}}.$$

Gas phase concentration is then given by multiplying K^1 by the height of the deflection from the baseline. The katharometer can therefore be used in this way to calibrate the mass spectrometer.

The copper-containing materials used in these experiments were a commercial copper–zinc oxide/alumina catalyst containing approximately 60% CuO, 30% ZnO, and 10% Al_2O_3 and an unsupported copper oxide (AnalaR BDH) whose purity was quoted as >98%, the major quoted impurities being alkali sulfates (<0.3%).

Method. The experimental method was to charge approximately 4 g of copper-containing material to the glass U-tube and then measure its total surface area using N_2 at −196°C. The material was then reduced in a 5% H_2/He gas stream at a temperature of 240°C until no further water evolution was observed by mass spectrometry. The temperature was then lowered under a flow of helium until all the hydrogen had been swept from the system (any hydrogen remaining on the copper will desorb into the helium stream during the cooling from 240°C to ambient temperature, the peak maximum temperature of the hydrogen desorption spectrum on copper(110) being 50°C (*12*)). The total surface area of the reduced material was measured by nitrogen adsorption at −196°C and for copper area determination the reduced material was held at 60°C under a flow of helium which was then replaced by a N_2O/He flow (ca. 6% N_2O in He, flow rate 25 cm^3/min). The eluted gases were monitored, on line, first on the katharometer detector and then on the mass spectrometer, following $m/e = 28$ (N_2) and 44(N_2O). A typical reactive frontal chromatogram is shown in Fig. 2. A check on the amount of oxygen deposited on the surface of the copper by reaction with N_2O was made by reducing the oxidised copper with carbon monoxide. This was done by the frontal method. First, the N_2O flow was switched off and then swept out of the system. The temperature was then raised to 240°C under He flow (25 cm^3 min^{-1}) when the flow was changed to a CO/He stream (6% CO in He, 25 cm^3 min^{-1}). The reaction involved is

$$CO_{(g)} + Cu_{(s)} \rightarrow CO_{(a)} \qquad \text{(a = adsorbed species)} \quad (2)$$

$$CO_{(a)} + O_{(s)} \rightarrow CO_{2(g)} \quad (3)$$

which has been shown to be facile (*13*), Reaction (3) having an activation energy of 6 kcal mol^{-1}. The eluted gases were monitored, as before, on line, using katharometer and mass spectrometer detectors in series. A typical reactive frontal chromatogram of this type is shown in Fig. 3.

Having re-reduced the copper its total surface area was again measured using nitrogen adsorption at −196°C. This sequence of N_2O treatment, CO reduction, and total surface area measurement was repeated several times.

Calculation. The calculation of copper areas from the frontal chromatograms such as Figs. 2 and 3 is a relatively simple procedure. For instance, in the case of N_2O decomposition it is merely necessary to calculate the volume of N_2 produced as follows:

$$\text{Volume of } N_2 \text{ produced } (cm^3) = F \cdot C \cdot S/100R$$

where F = flow rate of reaction gas (cm^3 min^{-1}) determined using a bubble flow meter,
C = % N_2O in reaction gas,
S = chart distance between start of N_2 production and N_2O breakthrough (cm),
R = chart speed (cm min^{-1}).

The copper areas have then been obtained from the volumes of N_2 produced, assum-

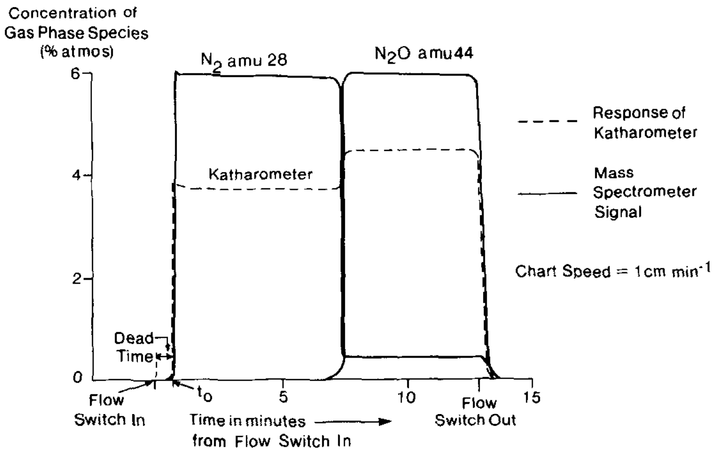

FIG. 2. Nitrous oxide in helium over reduced copper catalyst.

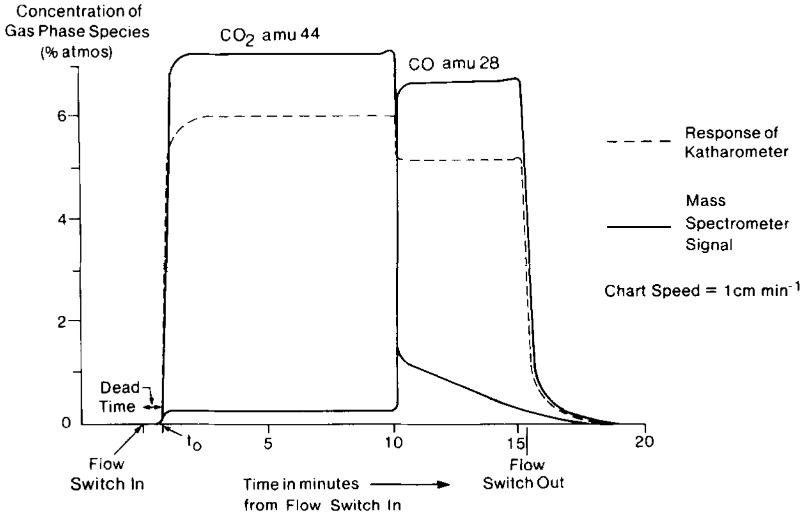

FIG. 3. Carbon monoxide in helium over oxidised copper catalyst.

ing that saturation coverage occurred at 5.0 × 10^{14} oxygen atoms/cm^2 copper surface (*14*).

RESULTS AND DISCUSSION

The results of the BET measurements of the total surface area of the AnalaR cupric oxide and of the reduced material are listed in Table 1, together with the copper metal areas measured by N_2O decomposition at 60°C, and afterwards by CO reduction (at 240°C) of the surface oxide so formed. The metal surface areas are expressed per unit weight of copper metal formed by reduction of the oxide. The reduced copper has a much lower surface area (4.6 m^2/g) than the starting cupric oxide (16.3 m^2/g).

TABLE 1

Copper Metal Area of Reduced Copper Oxide by (i) BET Method, (ii) N_2O Decomposition, and (iii) CO Reduction after Oxidation by N_2O. All at 1 Atmosphere Total Pressure[a]

Sample	Copper metal area (m^2/g Cu)		
	(i) By BET N_2 adsorption at −196°C	(ii) By N_2O decomposition at 60°C	(iii) By CO reduction at 240°C after N_2O treatment
1	4.67	4.61	4.63
2	5.21	4.91	4.84
3	5.26	4.39	5.00
4	5.05	4.33	4.52

[a] BET area by method of Bowker *et al.* (*18*).

Row 1 of Table 1 lists the values of the copper metal areas obtained: (i) by N_2 adsorption at −196°C (the BET method), (ii) N_2O decomposition at 60°C, and (iii) by CO reduction of the surface oxide produced by N_2O decomposition at 60°C. The copper metal had been obtained by reduction of the oxide in the "normal" way, i.e., in a hydrogen stream (5% H_2 in He) raising the temperature from 110 to 240°C at a programmed rate of increase of 0.25°C min^{-1} and maintaining the temperature at 240°C until no further evolution of water was observed. The results of all three methods are within 2% of each other, confirming that the method of reactive frontal chromatography using N_2O decomposition at 60°C is a valid method for the determination of copper areas.

Rows 2 to 4 of Table 1 are repeats of the process, i.e., total surface area measurement by N_2 adsorption at −196°C, N_2O decomposition at 60°C, and CO reduction of the oxidised surface at 240°C. These continue to show reasonable agreement between the areas evaluated using N_2 adsorption, N_2O decomposition, and CO reduction.

Effect of reaction temperature. Changing the temperature at which the N_2O was dosed on the copper had no effect on the amount of N_2O which decomposed (see Table 2). This appears to accord with the results of Habraken and Bootsma (*14*) who indeed found a small negative temperature dependence of N_2O decomposition on copper single crystal on changing the crystal temperature. However, it seems to conflict with the findings of Scholten and Konvalinka (*6*) who found a small activation energy of 2 kcal mol^{-1} (temperature range 0 to 90°C, with no temperature dependence above 90°C where bulk oxide formed) for N_2O decomposition. This could suggest that their measurements were affected by diffusional limitations.

Effect of varying the N_2O partial pressure. The copper surface areas evaluated at different N_2O partial pressures (varying from 7 to 36%, 1 atm total pressure) are listed in Table 3. As expected, since the reaction proceeds to completion at half-monolayer coverage of oxygen, changing the N_2O did not markedly affect the value obtained for copper area. What did change, however, was the time to N_2O breakthrough: the higher the N_2O partial pressure, the shorter was the time to breakthrough. Indeed, increasing the N_2O partial pressure is a useful method of reducing the length of time to breakthrough and hence of reducing the time of the experiment, the only caveat being that, for a given supported copper catalyst, one should ensure that the N_2O partial pressure is not such that all of the reaction is complete within a few seconds. As a rough guide, initially working below 10% N_2O is advisable.

TABLE 2

Effect of Temperature on N_2O Decomposition Measurements

Temperature of N_2O decomposition (°C)	Copper metal area (m^2/g Cu)	
	By N_2O decomposition	By CO reduction at 240°C after N_2O treatment
25	4.18	4.91
38	4.08	—
60	4.33	4.52
90	4.24	4.29

TABLE 3

Copper Surface Areas Evaluated Using Different N_2O Partial Pressures at a Total Pressure of 1 atm

Percentage of N_2O in He (%)	Copper surface area from N_2O decomposition (m^2/g Cu)
7.0	4.11
9.8	3.98
13.7	3.87
17.0	3.81
19.0	3.51
22.0	3.51
36.0	3.58

The gradual fall in copper area during these experiments is caused by ageing of the sample and has been observed on all samples, including supported copper materials when they have been subjected to such consecutive cycles of oxidation/reduction.

Reaction probabilities. The remarkably sharp reactive frontal chromatograms (Fig. 2) imply an extremely high reaction probability. In fact, the reactive sticking probability of N_2O on all the low index faces of copper is sufficiently high that, at the temperature (60°C) and dosages used, reaction to saturation will be almost instantaneous. On the (110) face, the initial sticking probability, S_0, is 0.15, $\theta_{\max} = 0.5$ (5×10^{14} atoms cm^{-2}) for 10^5 Langmuir dosage: on the (100) face $S_0 = 5 \times 10^{-5}$, $\theta_{\max} = 0.5$; and on the (111) face $S_0 = 10^{-8}$ (at 60°C) ($S = Ae^{-10,400/RT}$, $R = 1.987$ cal K^{-1}, mol^{-1}, $A = 0.09$) (*15*). Since the N_2O partial pressure of 0.08 bar corresponds to a dosage of 6×10^7 Langmuir s^{-1}, even in the worst case of the (111) surface, saturation coverage will be achieved in 1 sec. This is consistent with our observation of a sharp breakthrough of N_2, virtually instantaneous upon the encounter of the N_2O with the copper surface. Furthermore, since N_2 and N_2O have different thermal conductivities, there is a step change in the katharometer response at the breakthrough (Fig. 2). Use of the mass spectrometer detector confirmed that no N_2O was being eluted with the N_2.

Measurement on supported copper catalysts. Experiments with zinc oxide (obtained by calcining freshly precipitated zinc carbonates) which had been reduced in the standard way already described, showed that it did not decompose N_2O at 60°C. The technique developed here should thus be applicable to typical supported copper catalysts, to evaluate their specific copper areas.

A considerable number of repeat determinations of the copper surface area of the commercial copper catalyst already described (reduced by the standard technique) was carried out in several set-ups operating the reactive frontal chromatographic technique. For these experiments where the sample copper surface area was much higher than that of the unsupported copper samples a reaction gas mix of 2.5% N_2O in helium was used with a flow rate of 90 cm^3/min over samples of about 2 g of catalyst. Only a katharometer detector was used. By way of comparison the copper surface area of this same catalyst was repeatedly assessed using a typical pulse technique (*7*, *8*). The results are shown in Table 4.

TABLE 4

Copper Surface Areas of Reduced Copper–Zinc Oxide/Alumina Catalyst

Data	Method		
	Frontal Chromatographic		Pulse
	Unit 1	Unit 2	
No of Observations	33	39	16
Copper area (m^2/g) arithmetic mean	32.9	32.8	38.7
Standard deviation	1.17	1.40	3.94
Confidence limits (95%) for mean copper area	32.9 ± 0.41	32.8 ± 0.45	38.7 ± 2.1

Statistical *t*-testing indicated no significant difference between units 1 and 2, the two reactive frontal chromatographic units. Whilst there is clearly a systematic difference in mean value between the two techniques, of more importance is the much greater reproducibility obtained by the reactive frontal chromatographic units. This is no surprise as there are many more potential sources of error in the pulse technique. The frontal chromatographic technique requires no ancillary analytical equipment, but only some form of thermal conductivity detector, and the method is immediate and obviates the need in the pulse method of (a) deciding when the asymptotically low N_2 level has been reached and (b) summing the amounts of N_2 obtained from the separate N_2 pulses up to the asymptotic N_2 level.

The frontal chromatographic method for measuring copper areas has been used recently by the authors to study the relationship between activity and copper area in methanol synthesis catalysts and to assess the degree of oxidation of the copper surface during methanol synthesis (*16*, *17*).

CONCLUSIONS

Most of the conclusions derive from the fact that the activation energy for the reaction $N_2O_{(g)} \rightarrow N_{2(g)} + O_{(s)}$ (g = gas, s = surface) on a copper surface is 0 to 2 kcal mol^{-1} so that the probability of reaction per collision is at worst 6×10^{-2} at 60°C; they are as follows:

1. The reactive frontal chromatographic lineshapes are extremely sharp (collision rate 10^{23} collisions sec^{-1}, reaction probability 6×10^{-2} per collision), both the N_2 lineshape from the decomposition reaction and the N_2O lineshape, after completion of the decomposition reaction, being rectangular. This allows for easy integration of the N_2 evolved and hence of the $O_{(s)}$ deposited, which itself saturates the copper surface at half-monolayer coverage; hence copper areas can be evaluated.
2. All of the N_2O is decomposed to $N_{2(g)}$

and $O_{(s)}$ until half-monolayer coverage is achieved and since N_2 and N_2O have distinctly different thermal conductivities a katharometer detector can easily distinguish between them upon completion of the decomposition. This obviates the need for gas chromatographic analysis (necessary with the pulse method) or for expensive mass spectrometry.

3. Because of its immediacy and ease of integration of the N_2 evolved ($O_{(s)}$ deposited), the method is an improvement over the pulsed N_2O technique for the measurement of copper areas.

4. Combination of the oxidation of the copper surface by N_2O at 60°C followed by its reduction by CO at 240°C is a powerful means of determining both the copper area and its degree of oxidation.

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