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A Microcalorimetric Method for the Evaluation of Copper Surface Area in Cu–ZnO Catalyst

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The reaction of O_2 and N_2O with Cu, traditionally employed for the evaluation of copper surface area, has been investigated by adsorption microcalorimetry on some Cu–ZnO catalysts with different copper loadings. The oxidation of copper at room temperature proceeds in different ways with the two gases, yielding surface and bulk oxidation with O_2 and only a partial oxidation at the surface with N_2O ($\theta = 0.3$). The evaluation via oxygen adsorption at room temperature totally relies on a detailed investigation of the thermokinetics, where the accomplishment of the monolayer is marked by a sharp variation in the reaction kinetics. The heat of interaction of N_2O with copper does not vary with coverage or with Cu loading. It is therefore suggested that the evaluation of the heat released upon contact of copper-containing catalysts with an excess of N_2O can provide a precise and quick measurement of the copper surface area.

INTRODUCTION

The measure of the surface exposed by a metal when present in a mixed metal/oxide catalyst is of great importance, since it is often closely related to the catalytic activity (*1*). The evaluation of the free metal surface area in Cu-containing catalysts is usually made through the oxidation of the surface either with N_2O or O_2, and the comparison with the same reaction on a standard sample (e.g., Cu powders or evaporated films of known specific surface area). Among the various techniques proposed chemisorption is the one most often employed (*1–6*).

The interaction of O_2 is complex and temperature-dependent. The ready chemisorption of oxygen on the copper surface is accompanied by a partial and slow oxidation in the bulk, whose extent and stoichiometry depends, inter alia, upon the temperature (*7, 8*).

This process takes place at rather low temperature, even where also physisorption occurs, so that it is difficult to evaluate the oxygen uptake due to the plain surface oxidation. At 137 K Vasilievich *et al.* (*5*) observed a minimum in the oxygen uptake, which was interpreted as due to the absence of both bulk oxidation and appreciable physisorption. In fact, the adsorption at that temperature is not activated and the uptake corresponds to a composition of the surface layer close to Cu_2O.

N_2O decomposes at the Cu surface by the reaction:

$$N_2O_{(g)} \rightarrow N_{2(g)} + \tfrac{1}{2}O_{2(ads)}$$

According to calorimetric measurements by Dell, Stone, and Tiley (*9*), the heat of formation of the oxidized layer is the same with both O_2 and N_2O: this was taken as evidence that the surface phase arrived at was the same. LEED measurements by Ertl (*10*) have confirmed this hypothesis as far as the very early stages of reaction are concerned. The overall activity of N_2O is, however, much less than that of O_2: at room temperature only a fraction of the metallic surface is oxidized and bulk oxidation

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only takes place above 373 K (*9*). There is conflicting evidence about the temperature dependence of the surface oxidation of Cu by N_2O: between 293 and 373 K Osinga *et al.* on copper powders (*2*) and Sengupta *et al.* on Cu–ZnO catalysts (*6*) found no appreciable change in the N_2O uptake, whereas Scholten and Konvalinka on various copper powders and copper-based catalysts (*3*) observed an increase with temperature. Recently Narita *et al.* on Cu–SiO_2 samples (*11*) have found that only above 373 K did marked increases in surface oxidation occur.

Other discrepancies, e.g., the amount of N_2O decomposed per square meter of copper at room temperature, the coverage reached in such conditions, and the area of a single Cu surface site, arise among different authors (*2, 3, 9*).

Thus, two chemisorptive methods are now available to determine the free surface area of copper, namely that of Vasilievich *et al.* (*5*) and the more common one based on the evaluation of N_2O decomposed at room temperature (*9*). In an investigation of Cu–ZnO catalysts, which are active for the water-gas shift reaction, we have tackled afresh the problem of Cu oxidation by O_2 and N_2O.

In the present paper, attention is focussed on the use of microcalorimetry in the evaluation of the copper surface area. In a future paper details will be reported as to the energies and kinetics of the oxidative processes.

EXPERIMENTAL

CuO–ZnO samples have been obtained by addition of Na_2CO_3 and NaOH to aqueous solutions of copper and zinc nitrates and decomposition at 583 K of the precipitate to form an oxidic two-phase system according to a procedure thoroughly described elsewhere (*12*). Reduction of CuO to Cu has been carried out with H_2 in a flow system at 483 K. Prior to exposure to the atmosphere and transfer into the calorimetric cell, the samples underwent a limited oxidation with a flow of very diluted O_2 in inert gas to prevent loss of specific surface area. Static reduction was then performed in the calorimetric cell with several doses of 100 Torr H_2 at 483 K.

Microcrystalline samples of pure Cu have been obtained from a solution of copper nitrate by the same procedure. The surface area of these samples ranged between 1 and 2.5 m^2g^{-1} (BET, σ_{Kr} = 19.5 Å^2).

Samples with Cu contents of, respectively, 3, 15, and 30% (mole fraction) have been studied and will accordingly be referred to as Cu–ZnO/3, Cu–ZnO/15, and Cu–ZnO/30. The specific surface areas of precursor oxides (BET, σ_{N_2} = 16.2 Å^2) ranged between 45 and 60 m^2g^{-1} and no significant variations were found upon reduction, as opposed to what has been reported by other authors (*13*).

Calorimetric measurements have been carried out by means of a Tian–Calvet microcalorimeter connected to a volumetric apparatus which enabled the dosing of small amounts of O_2 and N_2O (*14, 15*). The amount of catalyst employed was kept as low as possible in order to avoid any parasitic kinetic effect; it ranged between 0.25 and 1 g, for the highest and the lowest copper loadings, respectively. As N_2O decomposes on the catalyst giving rise to N_2, no change in pressure is observed during the reaction if the oxygen is all chemisorbed. To check for the presence of unreacted N_2O a cold finger was inserted in the volumetric frame.

In both experiments with N_2O and O_2 successive small doses of the reacting gas were admitted until no detectable heat emission was recorded. We assumed that after the last dose no further reaction could occur under the experimental conditions adopted. For each dose the heat evolved and the oxygen uptake have been determined. Provided that the amount of heat released in successive doses is of the same order of magnitude a semi-quantitative description of the kinetics can be made by measuring the peak breadths t_m, $t_{1/2}$, $t_{1/10}$,

TABLE 1

Oxygen Uptakes at Room Temperature from N_2O and O_2

Sample	(1) Cu loading (μmol g^{-1})	(2) Oxygen uptake from N_2O decomposition (μmol($\frac{1}{2}O_2$) · g^{-1})	(3) Oxygen uptake from O_2 adsorption (μmol($\frac{1}{2}O_2$) · g^{-1})	(4) O/Cu from oxygen adsorption
Cu–ZnO/3	327	19	140	0.44
Cu–ZnO/15	1810	48	435	0.25
Cu–ZnO/30	3600	112	900	0.26

and t_0 which are the times necessary to reach the maximum deviation and, respectively, one-half and one-tenth of it; t_0 is the duration of the whole heat signal (*15*). Obviously, the larger these times, the slower the phenomenon.

The chemisorption of O_2 at low temperature and the interaction of N_2O in the temperature range 293–353 K have been performed by injecting small doses of gas in a flow system equipped with a thermal conductivity detector and a silica gel column for detection of the residual N_2O or O_2.

Oxygen and nitrous oxide were Specpure gases from Matheson Ltd.

RESULTS

Blank experiments showed that the interaction of both N_2O and O_2 with the support (ZnO) alone is negligible when compared to the reaction with copper-containing samples.

Nitrous Oxide

The oxidation experiments have been carried out using very small doses of N_2O (1 to 5 μmol). No residual N_2O was detectable after reaction of every single dose, except the last one in each run. The process terminates abruptly, and is not followed by any secondary phenomenon. The amounts of reacted N_2O are reported in the second column of Table 1.

In Fig. 1 the integral heat evolved (Q^{int}) vs the oxygen uptake (n_a) is reported for the three Cu–ZnO samples examined. The experimental points are satisfactorily fitted by a single straight line passing through the origin, the slope of the line corresponding to a heat of interaction of 317 kJ (mol N_2O)$^{-1}$. This means that, within the experimental error, the heat of interaction does not depend upon either the coverage or the Cu loading.

Because of its very small specific surface area it was not possible to carry out a similar detailed experiment on pure Cu. A rough estimate of the heat of reaction of N_2O with such a sample was however obtained by contacting it with one substantial dose: within the experimental uncertainties

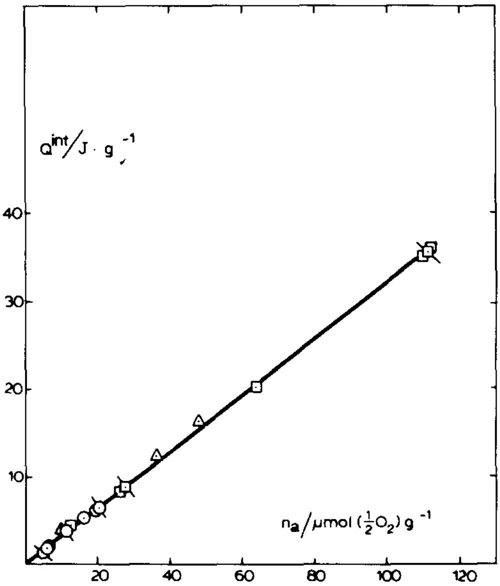

FIG. 1. Integral heat vs oxygen uptake from N_2O decomposition (○ Q, Cu–ZnO/3; △, Cu–ZnO/15; □, Cu–ZnO/30; ●, pure Cu).

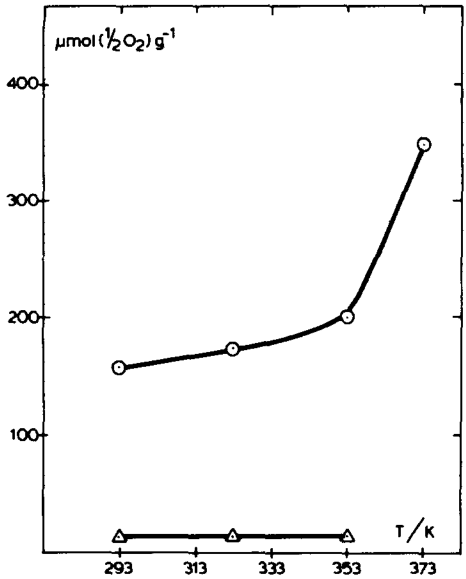

FIG. 2. N_2O uptake vs temperature in flow system on Cu–ZnO/30 (○) and on pure Cu (△).

the value obtained, reported as a single point in Fig. 1, also falls on the straight line.

The heat emission peaks have a shape close to those found in fast processes. Upon increasing coverage, however, the rate of heat emission slightly decreases. The variation of the total N_2O uptake with the reaction temperature has been investigated by the flow method in the range 293–373 K on Cu–ZnO/30 and on pure Cu. The results are reported in Fig. 2. They show only very slight increases in the extent of the reaction with temperature below 353 K, not even detectable on pure copper. On the other hand above 353 K a marked increase occurs. At 373 K the amount of N_2O dissociated is twice that at 300 K.

Oxygen at Room Temperature

Molecular oxygen is irreversibly taken up when admitted to the samples. However, the interaction shows a definite pressure-dependence from the very initial stages of oxidation, as a residual O_2 pressure is always observed at the end of the heat emission. Measurements have been stopped when the heat emission was negligibly small.

The integral heat (Q^{int}) vs oxygen uptake is reported in Fig. 3a for the Cu–ZnO/3 sample. Data for the same system as partial molar heat ($\Delta Q^{\text{int}}/\Delta n_a$) vs oxygen uptake are plotted in Fig. 3b. Except for the initial dose, which shows a higher differential heat, this quantity has a constant value over a wide range of coverage (181 kJ ($\frac{1}{2}$ mol $O_2)^{-1}$) and then abruptly drops to much lower values for the final adsorption (ranging between 30 and 80 kJ ($\frac{1}{2}$ mol $O_2)^{-1}$ on various samples). The basic features of the diagrams in Fig. 3 are the same for the other two Cu–ZnO systems and for the pure Cu sample: in all cases a strong interaction takes place at constant heat (except for a few doses at the lowest coverage) and is then followed by a weak adsorption. The most interesting fact is that on all samples

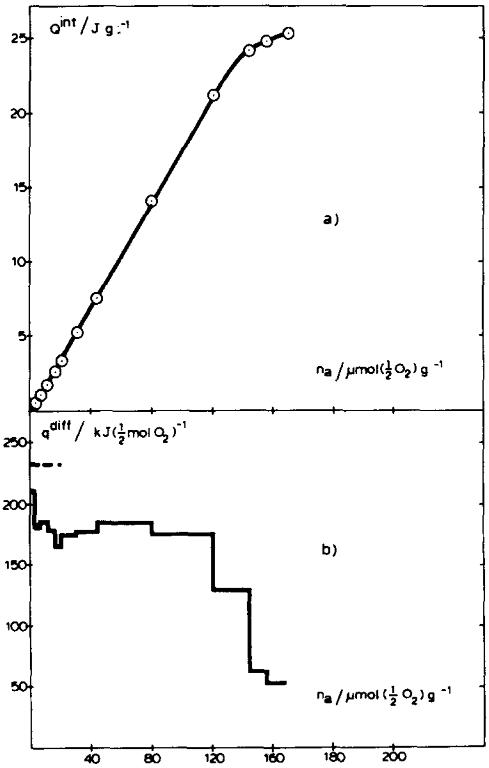

FIG. 3. Integral heat (a) and partial molar heat (b) vs oxygen uptake from O_2 adsorption and N_2O decomposition (b, dashed line) on Cu–ZnO/3.

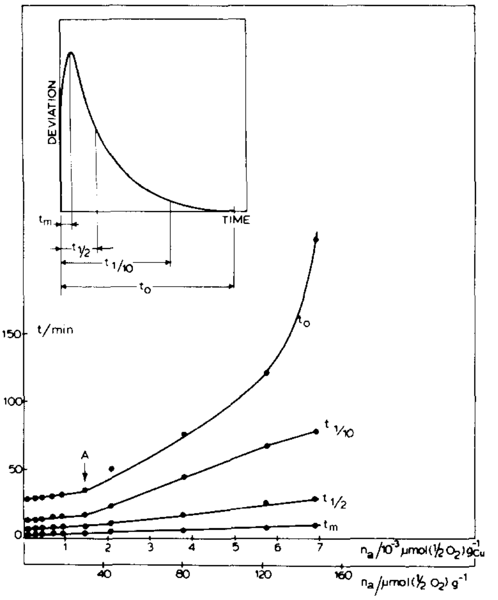

FIG. 4. Variation of peak breadth parameters with successive increments of oxygen coverage, on Cu–ZnO/3. Inset: Schematic thermogram defining peak breadth parameters t_m, $t_{1/2}$, $t_{1/10}$, and t_0.

the molar heat of the strong interaction (181 kJ ($\frac{1}{2}$ mol O_2)$^{-1}$) is the same on the three samples. The coverage at which the strong interaction stops is reported in Table 1 (column 3).

In spite of the constancy of the heat of interaction, the kinetics of adsorption vary dramatically with coverage. Figure 4 illustrates the kinetic aspects of O_2 adsorption. The thermokinetic data t_m, $t_{1/2}$, $t_{1/10}$, and t_0, measured as sketched in the inset, are reported in the figure as a function of O_2 uptake on Cu–ZnO/3. The process, rather fast at the very beginning, becomes progressively slower, and t_m, $t_{1/2}$, $t_{1/10}$, and t_0 are observed to increase almost linearly up to a coverage (point A in the figure) after which the increase with coverage is more marked. Adsorption on differently Cu-loaded samples showed the same kinetic features.

The amount of oxygen irreversibly held at low temperature by the Cu powder as a function of the temperature is shown in Fig. 5. As already stated, such data have been obtained in a He flow system by O_2 successive pulses. The oxygen uptake is constant in the range 80 to 140 K at 4.9 ± 0.04 μmole m^{-2} whereas, at higher temperature, the adsorbed amount increases.

DISCUSSION

Our experiments have confirmed the literature data that N_2O is much less reactive than O_2, as far as the reacted amounts are concerned (Table 2); N_2O only engages a fraction of the surface whereas O_2 forms many oxidized layers and possibly, in the case of very small particles such as on Cu–ZnO/3, involves the whole particles. The nature of the calorimetric results allows various energetic and kinetic features of the oxidative phenomena to be considered.

Energetics of O_2 and N_2O Interactions

The value of 181 kJ per half mole of O_2 obtained in the O_2 reaction is close to the standard enthalpy of formation of Cu_2O (167.5 kJ mol^{-1}) (*16*). Furthermore the Cu(II) ESR spectrum, clearly evidenced in the oxide precursor, was totally absent even after prolonged contact with oxygen of the reduced samples (*17*).

We therefore come to the conclusion that the oxidized phase is Cu_2O, as would be expected since this is the oxidized compound of copper more stable at room temperature.

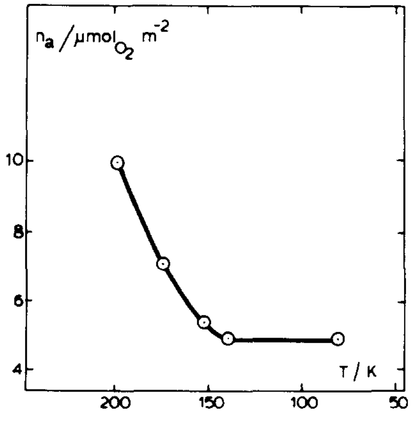

FIG. 5. Oxygen uptake vs temperature in flow system on pure Cu.

TABLE 2

Surface Uptake of Oxygen and Cu Surface Area

Sample	(1) Oxygen uptake from N_2O decomposition (10^{-3} $\mu mol(\frac{1}{2}O_2) \cdot g_{Cu}^{-1}$)	(2) Oxygen uptake from O_2 adsorption at point A (10^{-3} $\mu mol(\frac{1}{2}O_2) \cdot g_{Cu}^{-1}$)	(3) (1)/(2)	(4) Copper surface area ($m^2 \cdot g_{Cu}^{-1}$)	(5) $\bar{d}^a$ (Å)
Cu–ZnO/3	0.92	1.45 ± 0.10	0.63 ± 0.03	166	41
Cu–ZnO/15	0.41	0.6 ± 0.1	0.60 ± 0.10	74	92
Cu–ZnO/30	0.49	0.8 ± 0.1	0.62 ± 0.08	87	77

[a] Mean volume-surface diameter ($\bar{d} = 6V/S_{Cu}$, where V is the volume of 1 g Cu).

The coincidence between the molar heat of O_2 reaction on pure Cu and Cu–ZnO catalyst seems to rule out any particular role of ZnO in the oxidation. The roughness of the measurement on pure Cu must however be kept in mind.

In the case of N_2O the molar heat of reaction can actually be interpreted as due to the adsorption of half a mole of O_2 coming from the decomposition of N_2O, provided that the enthalpy of formation of N_2O (+82.5 kJ ($\frac{1}{2}$ mol $O_2)^{-1}$) is subtracted from the value of 317 kJ ($\frac{1}{2}$ mol $O_2)^{-1}$: this gives 234.5 kJ ($\frac{1}{2}$ mol $O_2)^{-1}$.

Such a value, constant in the whole range of coverage, is larger by 53 kJ ($\frac{1}{2}$ mol $O_2)^{-1}$ than the one in the O_2 case, as reported in Fig. 3b (dashed line). Only at very low O_2 coverage does the differential heat of O_2 adsorption (Fig. 3b) tend to the N_2O value, in agreement with the observation that on copper monocrystals the very initial stages of oxidation are much the same for both N_2O and O_2 (*10*). The difference between the heat of interaction of O_2 and N_2O can be accounted for by a model in which O_2 builds up several layers of Cu_2O, whereas N_2O oxidizes some exposed Cu atoms only, so that the oxidized phase has little relationship to bulk Cu_2O. As a consequence the related heat must be different.

Kinetic Aspects of O_2 and N_2O Reactions

The thermokinetic data in Fig. 4 show that within a process at constant differential heat, the rate of O_2 reaction slows down at increasing coverage: thermokinetics parameters range, in fact, between values typical of a quasi-instantaneous phenomenon (initial points) and values indicating a very slow thermal emission (last points). The abrupt decrease in the rate of heat evolution (observable around the point A) suggests a change in process, namely the end of the oxidation of the surface and the occurrence, from point A onward, of reaction with subsurface and bulk copper. In fact uptakes at the point A seem to be determined by the Cu surface area only, as they are strictly proportional to the N_2O uptake (Table 2, columns 1, 2, 3). The measure of O_2 uptakes at the point A thus constitute a novel method for the determination of the Cu surface. The process can be thought of as either a two-dimensional oxidation, followed by the reaction with the bulk, or as the building up of oxidized patches of different thickness lying nearby patches of bare metal, as pointed out by Rhodin (*8, 18*). Although the latter picture seems more feasible we note that the actual values of the ratio of N_2O/O_2 uptakes would suggest the former description.

More recent results by Habraken *et al.* (*19*) on the adsorption of oxygen on Cu single crystals also favor a model in which, under low oxygen pressure, a first chemisorbed oxygen layer is completed before any reaction with bulk or subsurface copper ions begins.

The coverage in oxygen atoms from N_2O would be about 0.3 if the point A repre-

TABLE 3

Oxygen Uptake on Pure Cu as Determined by Different Authors

Oxidizing agent	Ref.	Oxygen uptake/m² Cu		Number of Cu atoms/m² Cu	Surface area of a single Cu site (Å)	O/Cu[a]
		N (cm^3)	Oxygen atoms			
N_2O at room temperature	(*9*)	0.11 ± 0.01*	2.95×10^{18}	14.7×10^{18}*	6.8	0.2
	(*2*)	0.176 ± 0.01*	4.73×10^{18}	13.5×10^{18}*	7.41	0.35
	(*3*)	0.176	4.70×10^{18}*	$17. \times 10^{18}$*(*15*)	5.88	0.275
	This work	0.126 ± 0.05	$3.4 \pm 0.2 \times 10^{18}$	—	—	0.30
O_2 at low temperature	(*5*)	0.135 ± 0.015	$7.4 \pm 0.8 \times 10^{18}$	13.9×10^{18}	7.2*	0.5
	This work	0.11 ± 0.01	5.91×10^{18}	—	—	—

Note. Asterisks indicate values given by the authors.

[a] In the case of a full 2Cu/O monolayer the limiting value is 0.5.

sented the completion of a two-dimensional oxidation with ratio 1 : 2 oxygen to surface-Cu. This value falls in the range proposed for the O/surface-Cu ratio by other authors (Table 3): it is noteworthy that the actual number of Cu atoms exposed per unit area is not involved in our case.

Some authors have reported that N_2O decomposition is slower than the adsorption of O_2 (*3, 9*). Scholten and Konvalinka (*3*) have ascribed their finding that the N_2O uptake increases from 273 to 363 K to a high activation energy of dissociation and to a marked variation of it with coverage. We have found, on the contrary (Fig. 2), that no substantial changes in the uptake occur in the range 293–353 K, in agreement with data reported by other authors (*2, 6, 11*). This suggests that the extent of reaction is not kinetically controlled in the mentioned temperature range.

The decomposition of N_2O on our samples does not appear to be substantially more activated than the reaction with O_2 at the same extent of surface oxidation. Figure 6 reports the thermokinetic parameters measured in the reaction with N_2O (full line) and O_2 at the initial stages (dashed line) as a function of oxygen coverage.

The reaction of N_2O appears to be only slightly slower than that of O_2 at comparable coverages, i.e., far below the oxygen monolayer, and to slow down with coverage to only a very little extent, as also O_2 does. These observations seem to rule out the idea that N_2O decomposition stops for kinetic reasons at $\theta \cong 0.3$, and to support the concept that the decomposition at room temperature only occurs at particular sites, then poisoned by adsorbed oxygen atoms. The rate of N_2O decomposition at these particular surface sites is only slightly higher than that of O_2–Cu interaction in the same range of coverage and must be char-

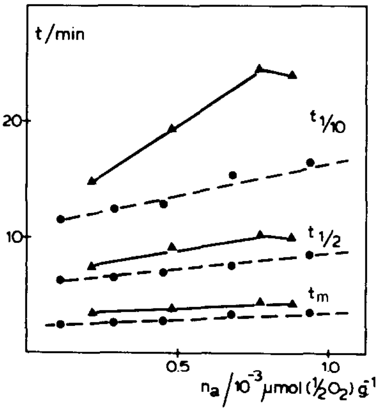

FIG. 6. Comparison between thermokinetics of nitrous oxide decomposition (full line) and oxygen adsorption (dashed line) on Cu–ZnO/3 in corresponding ranges of oxygen coverage. Variation of peak breadth parameters (t_m, $t_{1/2}$, $t_{1/10}$) with successive increments of oxygen coverage.

acterized by very low activation energy. As the reaction involves the remaining Cu atoms of the surface mainly above 353 K, we infer that this latter process requires a definitely higher activation energy.

Extent of Oxidation and Cu Surface Area

To calculate the surface areas of copper from the adsorbed amounts of N_2O and O_2, it is necessary, as already stated, to know the extent of adsorption on samples of known area (pure Cu). The results in the literature, as well as our own data on Cu powders, are reported in Table 3. Let us consider first the uptakes per square meter of Cu (first column). The data on N_2O decomposition by Osinga *et al.* (*2*) and by Scholten and Konvalinka (*3*) coincide, although conflicting evidence was found about the temperature dependence of the reaction. The one by Dell *et al.* (*9*) is definitely lower. This value has been criticized and explained by an overevaluation of the Cu surface as determined by krypton adsorption because of the adopted value of the Kr cross-sectional area, thought to be much lower (*2*). More recent data, however, show that the choice was basically correct (*20, 21*). Our datum lies between the value of Dell *et al.* and those proposed independently by Osinga *et al.* and by Scholten and Konvalinka. The value of the free metal surface area and particle size obtained for supported Cu samples on the basis of the present datum for N_2O decomposition on pure Cu are reported in Table 2 (columns 4 and 5.).

The O_2 uptake at low temperature is in fair agreement with that proposed by Vasilievich *et al.* (*5*). However, recent results on the adsorption of O_2 on Cu–ZnO catalysts, which will be discussed in a future paper, indicate a dependence of adsorption values upon the O_2 partial pressure in the gas flow. This obviously discounts the possibility of using the flow method with oxygen as a standard method for measuring free copper surface areas.

There is little agreement among the various authors about the number of atoms exposed by Cu powders per square meter (Table 3), which ranges from 17×10^{18} (when assuming a 70% preferential exposure of the (111) face (22)) to 13.5×10^{18} (in the hypothesis that the (111), (100), and (110) faces are equally exposed (*2*)). As a consequence of this and of the spreading of the data in the earlier columns, the O/Cu ratio attained upon oxidation is rather uncertain. We recall that our own value of 0.30 is not based on the knowledge of the number of Cu atoms at the unit surface.

CONCLUSIONS

The results afford some new detail about an old but important system. N_2O decomposes on Cu–ZnO with little activation energy in the whole range of coverage (up to about 0.3 O/Cu). The differential heat is constant with coverage and does not depend upon the copper content. Its actual value is higher than that for half a mole of oxygen, suggesting that the surface phases arrived at are different. Oxygen too is adsorbed at constant differential heat: a sudden change in the rate of heat evolution reveals the beginning of the reaction with the bulk.

It has been shown that microcalorimetry can help in the evaluation of the surface area of copper in Cu-containing catalysts. In fact the measurement of evolved heats is far more precise than that of adsorbed amounts by volumetric techniques. In the case of O_2 adsorption at room temperature the integral heat evolved (or the amount adsorbed) up to the point A in Fig. 4 (determined on a calorimetric base only) is a possible measure of the free metal surface area.

However, the room-temperature decomposition of N_2O is by far the best way to determine the copper surface area. As the molar heat of reaction is constant on all kinds of sample, and as the absence of any secondary reaction is confirmed, it suffices to contact a sample with one single dose of N_2O, exceeding the total capacity, to determine the maximum integral heat evolved and thus the surface area.

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