JOURNAL OF CATALYSIS 97, 374–384 (1986)

The Specific Copper Surface Areas in Cu/ZnO Methanol Synthesis Catalysts by Oxygen and Carbon Monoxide Chemisorption: Evidence for Irreversible CO Chemisorption Induced by the Interaction of the Catalyst Components

G. E. PARRIS[1] AND K. KLIER

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

Received January 25, 1985; revised September 4, 1985

The chemisorption of oxygen and carbon monoxide has been employed to determine the copper metal surface areas of Cu/ZnO methanol synthesis catalysts in the compositional range Cu/ZnO = 0/100 to 100/0. The total, reversible, and irreversible adsorption capacities for oxygen and carbon monoxide have been measured at 78 and 293 K, respectively. The reversible CO capacities show good linearity with the irreversible O_2 capacities and lie on a line connecting the capacity for pure copper with that, at zero intercept, of pure zinc oxide. Thus, the crystalline copper surface areas in these biphase catalysts have been evaluated from the specific irreversible adsorption of O_2 on pure copper having surface stoichiometry Cu : O = 2 : 1. The reversible CO chemisorption also is a measure of the copper metal surface area but irreversible CO chemisorption is associated with defect sites, attributed to nonmetallic copper species in zinc oxide. A critical comparison with another traditionally employed method, N_2O decompositive chemisorption, shows that the low temperature adsorption of O_2 is the preferred, reliable technique for the determination of crystalline copper surface areas.

INTRODUCTION

Several techniques have been developed and applied to the evaluation of specific metal surface areas in supported metal catalysts (*1*). Of these methods, chemisorption from the gas phase is by far the most extensively utilized with carbon monoxide (*2–10*), hydrogen (*3, 4, 11, 12*), and oxygen (*4, 13–15*) being the more frequently used adsorbates, but nitrous oxide decomposition (*16–19*) and hydrogen–oxygen titrations (*20, 21*) have also been used. The techniques require, however, that the adsorbate form a chemisorbed monolayer and that a simple stoichiometric relationship exist between the number of molecules and the number of surface atoms. This is not always the case as adsorption stoichiometry can be particle size dependent (*3, 21*), kinetically restricted to submonolayers, or complicated by the diffusion of the adsorbate into subsurface layers.

One of the key questions in the mechanism of methanol synthesis from carbon monoxide and hydrogen has been associated with the relative role of the catalyst components. Historically, the successful catalysts for methanol synthesis utilized zinc oxide, ZnO (*22*). The additions of chromia, Cr_2O_3, or alumina, Al_2O_3, to the zinc oxide-based catalysts were found to be beneficial as supports for extending catalyst life as promoters to enhance the catalytic activity for synthesis of methanol. These catalysts operate at high pressures (>20 MPa) and temperatures (573–623 K), however. The further addition of copper oxide to these catalysts resulted in much higher methanol synthesis activity at lower pressures (2–10 MPa) and temperatures (523 K) than observed with the pure components only, or with the ZnO/Cr_2O_3 and ZnO/

---

[1] Present address: Air Products & Chemicals, Inc., P.O. Box 538, Allentown, Pa. 18105.

0021-9517/86 $3.00

Al_2O_3 catalysts (*23, 24*). In addition, the method of preparation of copper catalysts was found to be an important factor (*25*). These observations indicated that the final state of copper in the $Cu/ZnO/Al_2O_3$ catalysts determined their high activity and selectivity for the production of methanol.

In a series of studies of the Cu/ZnO biphase catalysts that involved the determination of activity and selectivity (*26*), characterization by X-ray diffraction and electron microscopy (*27*), and observations of optical spectra (*28*), experimental results suggested that, in addition to a crystalline part, varying amounts of copper exist in an amorphous solute form in ZnO depending on the Cu/Zn elemental composition. It is therefore important to determine the crystalline copper surface area in this catalyst system. This task is not an easy one to accomplish since crystalline copper chemisorbs few gases strongly and in those cases when it does, such as oxygen via N_2O decomposition or O_2 dissociative chemisorption, there is concern as to the reliability of the results. Some investigators suggested that no standard method to measure active surface areas of copper catalysts exists (*29*).

The present study deals with the chemisorption of carbon monoxide and oxygen on the Cu/ZnO methanol synthesis catalysts with the aim to determine the crystalline part of the copper surface area in these catalysts. Chemisorption of these two gases has been investigated in a wide range of pressures for the whole compositional range Cu/ZnO = 0/100 to 100/0. Reversible and irreversible portions of each adsorbate were determined for each of the Cu/ZnO ratios. The results obtained herein are critically evaluated and compared with the literature in terms of practicality and reliability of the chemisorption methods for the copper metal area determination in the presence of an oxide phase.

EXPERIMENTAL

Catalysts. The Cu/ZnO = 0/100–100/0 catalysts were coprecipitated from nitrate solution by Na_2CO_3 and calcined according to procedures previously described in detail (*26, 30*). The calcined CuO/ZnO samples were placed between plugs of glass wool in a Pyrex U-tube with glass beads to preheat the reducing gas. The U-tube, which had an inner thermowell concentric with the outer wall of one arm, was then glass blown onto a volumetric chemisorption apparatus and protected with greaseless stopcocks. A static vacuum of 10^{-6} Torr was typically obtained.

Prior to initiating the reduction, the U-tube was purged by flowing a 2% H_2 in N_2 gas mixture through the catalyst bed for 20–30 min at room temperature, the gas mixture being first scrubbed by an oxygen getter. The catalyst was then heated, with a cylindrical heater positioned around the bed, at 3–4 K min^{-1} to a final temperature of 523 K while monitoring and maintaining flow of 2% H_2/N_2 gas at 40 cm^3 min^{-1}. Reduction times at 523 K were always 1.5 to 2 times the time necessary for stoichiometric reduction of CuO to Cu^0 and depended on the weight of catalyst used, usually 0.5 to 1 g, and its copper content. In the calculation of the reduction time it was assumed that reduction of CuO initiated at 483 K since in separate experiments water vapor was detected in the effluent at this point of the temperature ramp.

Upon termination of reduction, the sample temperature was lowered to, and equilibrated at, 473 K under a flowing 2% H_2/N_2 mixture. The flow of gas was then stopped, and exit and entrance stopcocks closed to protect the sample from atmosphere. The sample was evacuated at 473 K for 10–16 h before adsorption studies. Different specimens of each composition were used for CO and O_2 chemisorption studies.

Surface area measurement. The adsorbate gas was argon and the measurement of its isotherms at 78 K was straightforward. The condensation pressure, P_0 of argon was determined by a graphical method presented elsewhere (*31*). Here the P_0 of nitrogen was measured by inserting a nitrogen gas thermometer into the cryogenic liquid N_2 bath, and from a calibration plot of P_0 for argon versus P_0 for nitrogen the P_0 of argon was ascertained. The surface areas were calculated from BET plots using an argon cross-sectional area of 0.168 nm^2 (*34*).

CO chemisorption. Carbon monoxide isotherms were measured at 293 ± 0.2 K, the sample U-tube being immersed in a water bath. Helium was used to measure the dead space. To determine the amount of reversible and irreversible carbon monoxide adsorption, an adsorption isotherm was measured to approximately 120 Torr equilibrium pressure (isotherm I). Following this measurement, the sample was evacuated for 10 min; then a second isotherm (II) completed. This second isotherm corresponds to the reversibly adsorbed CO and the difference between isotherms I and II to the irreversibly adsorbed CO. Pressure measurements were made with a MKS 315 BH-1000 Torr differential manometer. Zero stability was ±0.05 Torr.

O_2 chemisorption. Oxygen chemisorption experiments were performed at 78 K, sample temperature being measured with a 1 K resolution Omega 2160A digital thermometer. A liquid nitrogen bath was placed about the U-tube before admission of oxygen to the reduced catalyst specimens. An argon adsorption run was then made in which between 5–8 points were recorded in the relative pressure range $0.5 \leq P_E/P_0 \leq 0.30$. The BET equation was used for surface area calculations. After the adsorbed argon was pumped off at room temperature for about 30 min, the sample was again cooled in liquid nitrogen and the dead space determined using helium. The helium was then pumped off keeping the sample U-tube immersed in liquid nitrogen.

In this manner the desired temperature of 78 K was maintained as evidenced by thermometry prior to and during the oxygen admissions. Due care was taken by admitting oxygen slowly and in small doses to minimize sample warming due to the evolution of adsorption heat. The maximum observed temperature rise was 5–6 K during the initial doses.

The determination of the amount of oxygen chemisorption parallels the procedure outlined in carbon monoxide chemisorption except that isotherms were run only to approximately 6 Torr and the sample degassing schedule was different. According to Rhodin (*39, 40*) there is no pressure dependence of the Cu_2O layer thickness on copper at 78 K and for pressures in the range 0.001 to 100 Torr. While weak O_2 chemisorption and physisorption do occur on top of this irreversible O_2 chemisorption these can be removed by the degassing schedule employed (vide infra). However, because these weak adsorptions do occur it was necessary, using this method, to determine isotherms to some convenient and measurable pressure such that the weak adsorptions could be measured and the irreversible O_2 capacity estimated by difference. After isotherm I was run to approximately 6 Torr the sample was evacuated at 78 K for 2½ h.

The sample was then warmed to room temperature, while degassing, over a 30- to 40-min period and degassing continued for 1 h. Once this degassing was complete the sample was again prepared for a second oxygen isotherm II by cooling in helium until 78 K was attained and repeating the aforementioned steps. The essentials of this procedure had been described by Zettlemoyer *et al.* (*32*). The irreversibly chemisorbed oxygen is obtained by the difference between isotherms I and II. Pressure measurements were made using a MKS 77H-30 Torr differential manometer and zero stability of ±0.002 Torr was achieved.

RESULTS

Surface Areas by Argon Adsorption

While it was not the intent of this work to analyze pore size distribution characteristics since a complete study of these proper-

TABLE 1

Surface Area of Copper Metal and Zinc Oxide in the Binary Cu/ZnO Catalysts

Catalyst composition (Cu/ZnO)	Cu surface area (m^2/g catalyst)	ZnO surface area[a] (m^2/g catalyst)	Total surface area (m^2/g catalyst)
0/100	—	24.1	24.1
10/90	4.9	30.1	35.0
20/80	8.9	27.6	36.5
30/70	16.0	23.3	39.3
40/60	6.5	8.5	15.0
50/50	5.7	5.4	11.1
67/33	3.9	3.5	7.4
100/0	0.62	—	0.62

[a] ZnO surface area = total surface area − Cu surface area.

ties has been made by Bulko (*33, 34*), surface areas were measured to ensure that samples were representative of those used in catalyst testing studies. Excellent agreement between surface areas reported herein, in the last column of Table 1, and those measured by Bulko *et al.* were obtained.

Oxygen Chemisorption

The isotherms (I) for oxygen on the Cu/ZnO = 20/80, 30/70, 40/60, and 50/50 specimens are shown in Fig. 1 and those on the Cu/ZnO = 0/100, 10/90, 67/33, and 100/0 specimens in Fig. 2. These isotherms are separated for clarity of presentation only. Pure zinc oxide was subjected to the same reducing atmosphere of 2% H_2/N_2 gas at 523 K (*26, 33*) as the copper-containing catalysts prior to the chemisorption measurements.

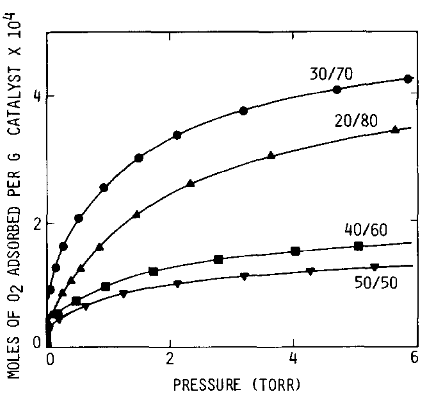

FIG. 1. Oxygen adsorption isotherms (I) on the Cu/ZnO = 20/80, 30/70, 40/60, and 50/50 catalysts at 78 K.

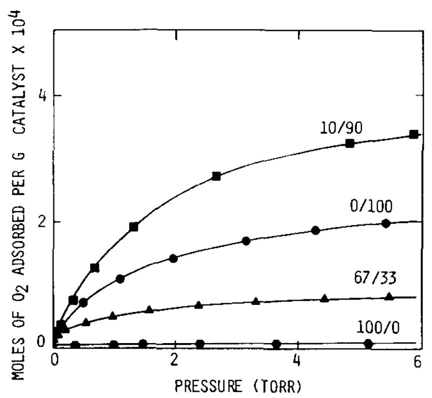

FIG. 2. Oxygen adsorption isotherms (I) on the Cu/ZnO = 0/100, 10/90, 67/33,and 100/0 catalysts at 78 K.

Figure 3 illustrates separately the oxygen

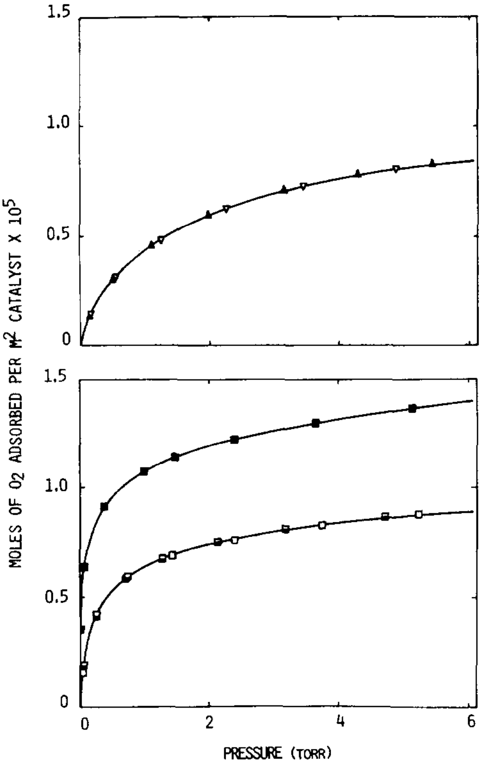

FIG. 3. Oxygen adsorption isotherms at 78 K on Cu/ZnO = 0/100 and 100/0. Isotherm I (▲, ■) comprises reversible plus irreversible oxygen adsorption; isotherms II (▽, □) and III (⬓) comprise reversible adsorption only.

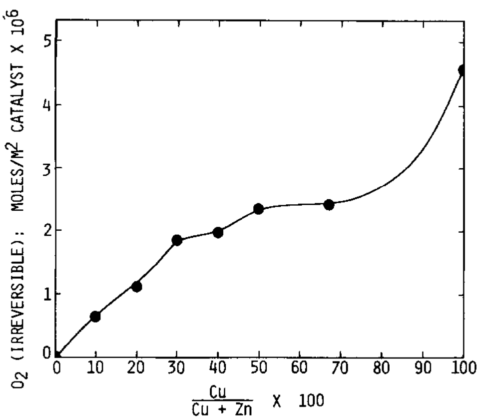

FIG. 4. The dependence of the irreversible oxygen adsorption at 78 K on the Cu/ZnO ratio in the binary copper–zinc oxide catalysts.

adsorption results obtained for isotherms I and II on Cu/ZnO = 0/100 and 100/0, respectively. A third isotherm III is also shown in this figure for pure copper. This isotherm was obtained, subsequent to isotherm II, by performing the same degassing schedule employed between isotherms I and II in order to confirm that *all* irreversible O_2 chemisorption had occurred in isotherm I. It is noted that in these and all other samples, isotherms I and II are nearly parallel and that isotherm I has an apparent "zero" pressure intercept which corresponds to the difference between isotherms I and II, indicating that irreversible oxygen chemisorption occurs. Isotherms II and III represent reversibly adsorbed oxygen only and consequently the magnitude of the total adsorption occurring in isotherm I is a summation of reversibly and irreversibly adsorbed species. The irreversible oxygen capacities obtained from differences between isotherms I and II for all Cu/ZnO catalysts investigated are plotted in Fig. 4 as a function of the catalyst composition.

Carbon Monoxide Chemisorption

The CO isotherms shown in Fig. 5 have a character which indicated that adsorption was completed at subatmospheric pressures. Pure ZnO which was treated with the same reducing atmosphere did not adsorb CO at 293 K. Of the total CO uptake approximately 95% was reversibly chemisorbed on pure reduced copper, though the cumulative error in the adsorbed amount can be as large as 12% relative on this low area specimen at 100 Torr pressure. By comparison the reversible CO chemisorption on the Cu/ZnO = 30/70 catalyst was only 72% of the total uptake and the cumulative error accounts for <2% of the uptake.

The specific CO capacities plotted in Fig. 6 are seen to increase with increasing copper content in the catalyst, with maximum coverage obtained for pure copper. These capacities are given for the pressure of 100 Torr, at which the adsorption isotherms are near saturation as demonstrated in Fig. 5. The irreversible CO fraction, however, shows a double-humped feature with maxima at the Cu/ZnO = 30/70 and 67/33 catalyst compositions.

DISCUSSION

The adsorption characteristics of the pure components—Cu and ZnO—and the

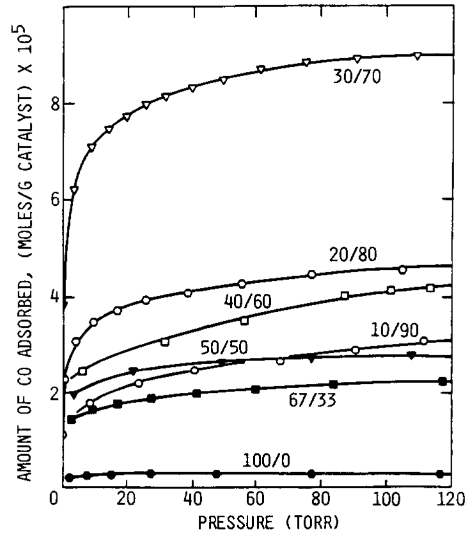

FIG. 5. Carbon monoxide chemisorption isotherms (I) at 293 K on the binary Cu/ZnO catalysts. The labels at the individual isotherms denote the molar composition Cu/ZnO.

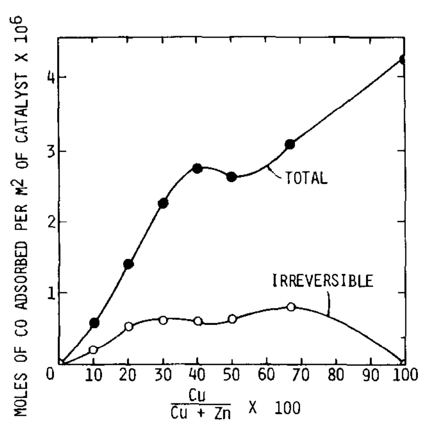

FIG. 6. The dependence of the carbon monoxide saturation adsorption (TOTAL) and irreversible adsorption (IRREVERSIBLE) on the Cu/ZnO ratio in the binary copper–zinc oxide catalysts.

composite Cu/ZnO catalysts will be discussed separately.

Pure Components: Cu and ZnO

Oxygen adsorption on copper has been used in earlier studies as a tool for determining specific copper areas in catalysts. Vasilevich *et al.* (*13*) recommended chemisorption of oxygen at 137 K to determine copper surface areas in catalysts containing copper, zinc, chromium, and/or aluminum. Their choice of temperature was one of expediency since at 78 K additional multilayer adsorption of O_2 occurs and the quantity of physically adsorbed gas must be determined. It is shown below that the 78 K isotherm method gives equally good results in terms of surface stoichiometry. Moreover, the lower temperature of 78 K was deemed advantageous to prevent undesirable long-term effects associated with a slow diffusion and oxide growth (*39, 40*).

It can be seen from Fig. 3 (top) that the adsorption of oxygen on zinc oxide is completely reversible. This result indicates that the zinc oxide remains essentially stoichiometric after exposure to a reducing atmosphere of 2% H_2 in N_2 at 523 K since irreversible O_2 adsorption would perhaps be induced on oxygen vacancies and/or interstitial zinc atoms. The activity of ZnO in isotopic exchange, photodesorption, conductivity, and catalytic oxidation depends on the outgassing temperature *in vacuo* and it has been reported that room temperature hydrogen chemisorption proceeds only after 673 K activation (*35*).

On the other hand, Fig. 3 (bottom) shows that on pure copper the initial doses of oxygen in isotherm I give rise to a large amount of irreversibly adsorbed oxygen with equilibrium pressure less than 10^{-3} Torr. The additional adsorption of oxygen which occurs on top of this surface oxide layer can be removed by the degassing treatment employed as shown by isotherm II. A subsequent measurement, isotherm III, also shows that oxygen chemisorption was completed in isotherm I. The difference between isotherms I and II gives 4.57×10^{-6} mol of O_2 irreversibly chemisorbed per square meter of copper. For copper metal the areas per metal atom in the (100), (110), and (111) planes are 0.065, 0.092, and 0.0563 nm^2, respectively (*36*). If it is assumed that the three major planes are present in equal amounts an average site area of 0.0711 nm^2 is obtained and is equivalent to 1.41×10^{19} copper atoms m^{-2}. However, site densities ranging from 1.35×10^{19} to 1.7×10^{19} surface copper atoms m^{-2} have been used in the literature (*16, 18b, 36*). Kington and Holmes (*37*), using O^{2-} ionic radii and the spacing of Cu atoms in the metal, pointed out that there is not room for every surface copper atom to adsorb an oxygen ion (O^{2-}) and that a complete layer should be formed at $\theta = 0.42$ of an atomic monolayer. Thus, using an equilibrium distribution in which the major planes are equally abundant, 1.4×10^{19} Cu atoms m^{-2} and $\theta_{max} = 0.42$, it can be calculated that monolayer coverage of oxide ions corresponds to 4.92×10^{-6} mol O_2 m^{-2} copper. This agrees well with the measured value of 4.57×10^{-6} mol O_2 m^{-2}, the value of 4.6×10^{-6} mol O_2 m^{-2} calculated from the data of Zettlemoyer *et al.* (*32*) when an argon area of 0.168 nm^2 is used instead of

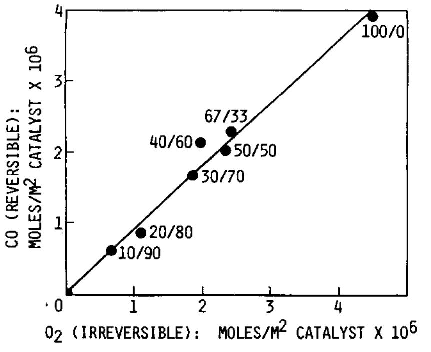

FIG. 7. The relation between the amounts of weakly chemisorbed carbon monoxide at 293 K and irreversibly chemisorbed oxygen at 78 K, indicating that these two adsorbates are a measure of copper metal surface area.

0.14 nm^2 to determine their surface areas, and the approximate surface stoichiometry of Cu/O = 2/1 observed by others (*37–41*) from O_2 adsorption studies.

The chemisorption of carbon monoxide at 293 K follows a somewhat similar pattern in that there is no measured uptake on pure ZnO, but chemisorption does take place on pure copper metal. From Fig. 6 the saturated coverage obtained for CO on copper is $\theta = 0.18$, assuming single site adsorption, and it is reversibly adsorbed. This result is in good agreement with the coverages of $\theta = 0.20$ to 0.25 obtained at ambient temperatures by several investigators (*18a, 42, 43*) and further attests to the low saturated coverage of CO reached on copper surfaces.

Binary Cu/ZnO Catalysts

The physical and chemical interactions of copper with zinc oxide might be expected to alter the adsorptive characteristics of oxygen and carbon monoxide in the composite catalysts and potentially give complex results. In the following discussion a comparison is made between oxygen and carbon monoxide chemisorption data in order to determine (i) the crystalline copper and zinc oxide surface areas and (ii) the origin of induced, strong chemisorption of carbon monoxide shown in Fig. 5 for the binary Cu/ZnO catalysts.

It is first pointed out that there is a good correlation between the irreversible oxygen chemisorption and reversible CO chemisorption. In Fig. 7 is shown a plot of reversible CO capacities against irreversible O_2 capacities, in moles per square meter of catalyst. The reversible CO capacities show good linearity with irreversible O_2 capacities in the whole compositional range in which the chemisorption data for Cu/ZnO catalysts lie on a line connecting the capacity of pure copper with that, at zero intercept, of pure zinc oxide. These results suggest that the sites for reversible CO and irreversible O_2 are the same and can be readily attributed to the crystalline copper phase. Further, in view of the fact that only weak CO adsorption occurs on pure copper, and since there is no systematic dependence of irreversible CO capacities on irreversibly adsorbed O_2, it can be concluded that the binary catalysts show an enhanced irreversible CO chemisorption. This enhanced CO chemisorption is attributed to defects extraneous to the copper metal surface, such as solute copper ions in the zinc oxide matrix suggested earlier (*27, 28*) or hydroxyl groups that are induced by the presence of copper that interact with CO to make surface formate (*44*), or some other not yet precisely characterized defect in the binary catalysts.

Some support for the conclusion that no irreversible oxygen adsorption occurs on these extraneous defects at 78 K may be derived from the results obtained for pure copper metal. It has been shown that the experimental procedure adopted in this work gives irreversible oxygen adsorption which reproduces other results reported in the literature and yields surface stoichiometry indicative of Cu_2O formation. Under the low temperature regime (78 K) no further oxygen adsorbs irreversibly on top of this Cu_2O layer. If the defect sites for irreversible CO are $Cu^{\delta+}$ ions in the ZnO matrix they are not expected to further chemisorb oxygen irreversibly, similarly as the Cu_2O surface layer on metallic copper does not.

TABLE 2

Comparison of the Copper Crystallite Sizes by Oxygen Chemisorption and X-Ray Line Broadening

Cu/ZnO[a]	Cu crystallite sizes (nm)	
	Oxygen	X-Ray[b]
10/90	7.1	5.5
20/80	7.2	4.5
30/70	5.5	7.3 (5.9[200],6.6[111])[c]
40/60	28.0	31.0
50/50	44.0	40.0
67/33	89.0	92.0

[a] CuO/ZnO in wt%.

[b] Reference (*33*).

[c] Average values measured on eight Cu/ZnO = 30/70 samples (*47*).

Likewise, surface hydroxyls are not known to chemisorb oxygen irreversibly.

On the basis of the above conclusions the specific adsorption of oxygen on pure copper may be used to determine the copper surface areas in the composite catalysts. The zinc oxide area is then given by the difference between total BET area and copper areas calculated from irreversible oxygen chemisorption. These quantities are summarized in Table 1 for the whole compositional range studied and, in light of Fig. 7, are a reflection of Fig. 4 which shows that the fractional copper surface area increases monotonically with copper content in the composites. Using the crystalline copper content reported by Bulko *et al.* (*28*) and assuming spherical particles, the copper crystallite sizes have been calculated from the data in Table 1, and are compared in Table 2 with those values determined by X-ray line broadening (*33*). Good agreement between the two sets of data is shown in this table.

In another study (*44*), the Cu/ZnO catalyst was examined by optical diffuse reflectance after being subjected to various gas treatments and was observed to possess surface hydroxyl groups. However, that catalyst was degassed at room temperature following reduction, whereas the present catalysts were degassed at 473 K and are unlikely to possess a significant amount of surface hydroxyl groups. With the zinc oxide surface areas available, Table 1 allows a test to be made of the dependence of irreversible CO capacities on the defect concentrations of solute copper in zinc oxide obtained by other methods. Using the data of Bulko *et al.* (*28*) and assuming the nominal solute $Cu^{\delta+}$ surface concentration to be proportional to bulk concentration, the plot of the surface coverage by irreversible CO against the concentration of copper solute shown in Fig. 8 has a linear portion for each morphology. An earlier electron microscopic examination of the Cu/ZnO catalysts had shown that the zinc oxide phase in specimens with composition Cu/ZnO ≤ 30/70 had prism $(10\bar{1}0)$ morphology while those with composition Cu/ZnO ≥ 40/60 had basal (0001) morphology (*27*). Therefore, if the irreversibly bound CO molecules titrate the surface copper solute sites, the ZnO (0001) planes tend to accumulate more of the solute copper atoms than the $(10\bar{1}0)$ planes. Since the basal

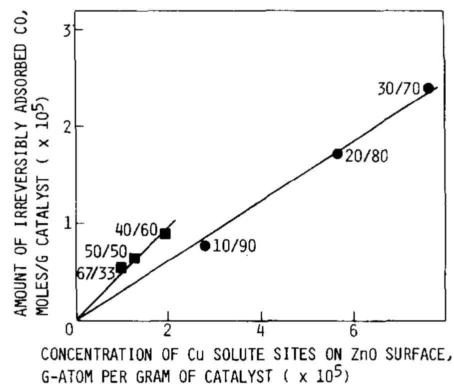

FIG. 8. The dependence of the amount of irreversibly chemisorbed carbon monoxide on the concentration of copper solute sites on ZnO surface, calculated from the bulk concentrations reported in Ref. (*28*), estimated from X-ray diffraction and the ZnO surface areas in Table 1. The $(10\bar{1}0)$ prism planes of ZnO are exposed in the Cu/ZnO = 10/90, 20/80, and 30/70 catalysts and the (0001) basal planes of ZnO are exposed in the Cu/ZnO = 40/60, 50/50, and 67/33 catalysts.

plane is formally electrostatically charged while the prism plane is not, the accumulation of copper is consistent with the idea that the copper species are also charged and tend to neutralize the excess charges on the (0001) planes.

The Nitrous Oxide Decomposition Method

An alternative approach to oxygen chemisorption for determining copper surface areas has been proposed in the N_2O decomposition method (*16–19*). This method is based on the decomposition of N_2O molecules on a copper surface which is accompanied by the liberation of one nitrogen molecule. The experimental approaches have typically been either (i) to measure the residual nitrogen pressure in a conventional volumetric adsorption apparatus after freezing out excess N_2O, or (ii) to employ a pulsed gas chromatographic method. Both approaches have been utilized in the temperature range 273–413 K. More recently, a microcalorimetric method has been used and proposed as a quick method for copper surface area determination (*45*).

The decomposition of nitrous oxide copper proceeds with a high heat of reaction (*18a*) although per se this may not be detrimental. The reaction is apparently also rapid and thus facilitates its use in a gas chromatographic configuration (*18b*). However, because it was shown that the extent of surface and bulk oxidation can introduce significant error at elevated temperatures (*16*), an effect of reaction-induced temperature transients may be envisioned. This temperature transient will be dependent on the initial column temperature, size of the N_2O pulse, and specific copper surface areas. That the kinetics of N_2O decomposition for small and large crystallite sizes of copper are different has already been demonstrated by Scholten and Konvalinka (*16*). It is this property of the dynamic chemisorptive methods that makes their application at high temperatures highly dependent on the details of the experimental setup and on the performance of the measurement. In addition, discrepancies concerning the amount of N_2O decomposed per square meter of copper and the area of a single copper site (*16–18*), as well as the possible dependence of decomposition/chemisorption temperature on the support (*18b, 45, 46*), exist among the different reports.

On the other hand, static methods utilizing N_2O or O_2 dissociative chemisorption cannot be used at ambient and higher temperatures because of bulk oxidation which accompanies the surface reactions. Oxygen chemisorption which forms surface oxygen anions, as does N_2O decomposition, proceeds to a limiting oxide layer thickness of 1.7 to 7.0 nm at 273–353 K (*39, 40*) and involves bulk oxidation of the metal. At 77 K, where the present oxygen chemisorption capacities were measured, the limiting oxide layer thickness is only 0.4 nm (*39, 40*) and since the ionic radius of O^{2-} is 0.28 nm it corresponds to the formation of a Cu_2O monolayer, consistent with the surface stoichiometry obtained by irreversible O_2 chemisorption at low temperatures. N_2O will not decompose at these low temperatures, however, to give any defined Cu : O stoichiometry, and therefore, the static oxygen method at low temperatures appears more reliable in the static regime.

CONCLUSIONS

The chemisorption of oxygen carbon monoxide has been employed to determine the crystalline copper surface areas in Cu/ZnO methanol synthesis catalysts in the compositional range Cu/ZnO = 0/100 to 100/0. The total, reversible, and irreversible adsorption capacities for oxygen and carbon monoxide have been measured at 78 and 293 K, respectively. For the composites, the reversible CO capacities at 293 K show good linearity with the irreversible O_2 capacities at 78 K and lie on a line connecting the capacity for pure copper with that, at zero intercept, of pure zinc oxide. Thus, the crystalline copper surface areas in these biphase catalysts have been evaluated from the specific irreversible adsorption of O_2 on pure copper having surface stoichiometry Cu : O = 2 : 1. A critical analysis with another traditionally employed method, N_2O decompositive chemisorption, shows that the low temperature adsorption of O_2 is the preferred, reliable technique for determination of the crystalline copper surface areas in composite catalysts. The irreversible CO capacities are proportional to the bulk concentration of solute copper in zinc oxide estimated by independent methods, but higher specific chemisorption capacities are found for the basal (0001) than for the prism $(10\bar{1}0)$ morphologies. This result indicates a preference of the basal zinc oxide planes for the copper solute species.

ACKNOWLEDGMENT

This research was supported in part by U.S. Department of Energy Grants ET-78-S-01-3177 and DE-FG22-83PC60786.

Note added in proof. Two recent reports provide additional evidence, or an indication thereof, of CO chemisorption on the Cu/ZnO catalysts that is stronger than that on metallic copper. In the first of these two reports, B Fubini, V. Bolis, and E. Giamelo carried out a calorimetric study of CO adsorption on ZnO and Cu/ZnO specimens (*Thermochim. Acta* **85,** 23, 1985) and have noted that while a substantial fraction of the adsorption sites for CO have energies expected for Cu(O)–CO bond, some sites did exhibit a higher interaction heat, which may be attributed to the coordination of CO onto Cu(I). In the second and more recent of the two communications, G. Ghiotti, F. Boccuzzi, and A. Chiorino (*Chem. Commun., 1985,* 1012) report a 1580-cm^{-1} IR absorption band for CO on a Cu/ZnO specimen found in addition to the usual CO absorptions around 2100 cm^{-1}. The 1580-cm^{-1} band is assigned by Ghiotti, Boccuzzi, and Chiorino to CO carbon-down on copper and side-on on zinc ions of the zinc oxide surface, and these authors propose that the binding site is copper particle–zinc oxide interface. In principle, neither the presently reported adsorption evidence for irreversible CO nor calorimetry nor IR spectroscopy can *locate* the copper or copper-induced defect on which the CO molecule is bound. However, the results of these experiments agree in that a part of the CO adsorbate is more strongly bonded on the Cu/ZnO specimens than on the separate Cu metal and ZnO components.

REFERENCES

1. Whyte, T. E., Jr., *Catal. Rev.* **8,** 117 (1973).

2. Van Hardeveld, R., and Hartog, F., *Adv. Catal.* **22,** 75 (1972).

3. Topsoe, H., Topsoe, N., Bohlbro, H., and Dumesic, J. A., *Stud. Surf. Sci. Catal.* **7A,** 247 (1980).

4. Smith, J. S., Thrower, P. A., and Vannice, M. A., *J. Catal.* **68,** 270 (1981).

5. Scholten, J. J. F., and Von Montfoort, A., *J. Catal.* **1,** 85 (1962).

6. Boudart, M., Delbouille, A., Dumesic, J. A., Khammouma, S., and Topsoe, H., *J. Catal.* **37,** 486 (1975).

7. Brunauer, S., and Emmett, P. H., *J. Amer. Chem. Soc.* **59,** 1553 (1937).

8. Hughes, T. R., Houston, R. J., and Sieg, R. P., *Ind. Eng. Chem. Process Res. Dev.* **1,** 95 (1962).

9. Dorling, T. A., and Moss, R. L., *J. Catal.* **7,** 378 (1967).

10. Cormach, D., and Moss, R. L., *J. Catal.* **13,** 1 (1969).

11. Spenadel, L., and Boudart, J., *J. Phys. Chem.* **64,** 205 (1960).

12. Goodwin, J. G., Jr., *J. Catal.* **68,** 227 (1981).

13. Vasilevich, A. A., Shapiro, G.P., Alekseev, A. M., Semenova, T. A., Markina, M. I., Vasileva, T. A., and Budkina, O. G., *Kinet. Catal.* **16**(6), 1363 (1975).

14. Shchibrya, G. G., Maksimova, N. P., Dadugina, N. G., Rudnitskii, L. A., and Alekseev, A. M., *Kinet. Catal.* **16**(4), 979 (1975).

15. Andrew, S. P. S., "Post Congress Symposium of the 7th International Congress on Catalysis, Osaka, Japan, July 7, 1980," paper 12.

16. Scholten, J. J. F., and Konvalinka, J. A., *Trans. Faraday Soc.* **65,** 2465 (1969).

17. Osinga, Th. J., Linsen, B. G., and Van Beek, W. P., *J. Catal.* **7,** 277 (1967).

18. (*a*) Dell, R. M., Stone, F. S., and Tiley, P. F., *Trans. Faraday Soc.* **49,** 195 (1953). (*b*) Evans, J. W., Wainwright, M. S., Bridgewater, A. J., and Young, D. J., *Appl. Catal.* **7,** 75 (1983).

19. Dvorak, G., and Pasek, J., *J. Catal.* **18,** 108 (1970).

20. Benson, J. E., and Boudart, M., *J. Catal.* **4,** 704 (1965).

21. Wilson, G. R., and Hall, W. K., *J. Catal.* **17,** 190 (1970).

22. Klier, K., *Adv. Catal.* **31,** 252 (1982).

23. Patart, M., French Patent 540,343 (Aug. 1921).

24. Brocker, F. J., German Patent 2,116,949 (1972); assigned to BASF.

25. Audibert, Q., and Raineau, A., *Ind. Eng. Chem.* **20,** 1105 (1928).

26. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56,** 407 (1979).

27. Mehta, S., Simmons, G. W., Herman, R. G., and Klier, K., *J. Catal.* **57,** 339 (1979).

28. Bulko, J. B., Herman, R. G., Simmons, G. W., and Klier, K., *J. Phys. Chem.* **83,** 3118 (1979).

29. Baglin, E. G., Atkinson, G. B., and Nicks, L. J., *Ind. Eng. Chem. Proc. Res. Dev.* **20**(1), 87 (1981).

30. Parris, G. E., Ph.D. thesis, Lehigh University, Bethlehem, Pa. (1982).

31. Din, F., "Thermodynamic Functions of Gases," Vol. 2. Butterworths, London, 1956.

32. Zettlemoyer, A. C., Yu, Y. F., Chessick, J. J., and Healey, F. H., *J. Phys. Chem.* **61,** 1319 (1957).

33. Bulko, J. B., Ph.D. thesis, Lehigh University, Bethlehem, Pa. (1980).

34. Herman, R. G., Pendleton, P., and Bulko, J. B., "Advances in Materials Characterization," Materials Science Research, Vol. 17, p. 109. Plenum, New York, 1983.

35. Roberts, D. L., and Griffin, G. L., ACS Division of Fuel Chemistry, Preprints, Vol. 29, No. 5, p. 226 (Aug. 1984).

36. Kington, G. L., and Holmes, J. M., *Trans. Faraday Soc.* **49,** 417 (1953).

37. Kington, G. L., and Holmes, J. M., *Trans. Faraday Soc.* **49,** 425 (1953).

38. Thurston, E. F. W., *Trans. Faraday Soc.* **64,** 2181 (1968).

39. Rhodin, T. N., Jr., *J. Amer. Chem. Soc.* **72,** 5102 (1950).

40. Rhodin, R. N., Jr., *Adv. Catal.* **5,** 39 (1953).

41. Quinn, C M., and Roberts, M. M., *Trans. Faraday Soc.* **60,** 899 (1964).

42. Allen, J. A., and Mitchell, J. W., *Discuss. Faraday Soc.* **4,** 309 (1950).

43. Pritchard, J., *Trans. Faraday Soc.* **59,** 437 (1963).

44. Vedage, G. A., Pitchai, R., Herman, R. G., and Klier, K., "8th International Congress on Catalysis, Berlin (West), July 1984.

45. Giamello, E., Fubini, B., Lauro, P., and Bossi, A., *J. Catal.* **87,** 443 (1984).

46. Navita, K., Takezawa, N., Kobayaoki, H., and Toyoshima, I., *React. Kinet. Catal. Lett.* **19,** 91 (1982).

47. Klier, K., Chatikavanij, V., Herman, R. G., and Simmons, G. W., *J. Catal.* **74,** 343 (1982).