CHEMISORPTION OF CO, CO_2, O_2 AND H_2 ON THE Cu/ZnO METHANOL SYNTHESIS CATALYSTS

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INTRODUCTION

Historically the successful catalysts for methanol synthesis from synthesis gas have always utilized zinc oxide. The addition 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 and as promoters to enhance the catalytic activity for synthesis of methanol. These catalysts operate at high pressures (>200 atm) and temperatures (573-623 K), however. The addition of copper oxide to these catalysts resulted in much higher methanol synthesis activity at lower pressures (75 atm) and temperatures (523 K) than observed with the pure components only, or with the ZnO/Cr_2O_3 and ZuO/Al_2O_3 catalysts, (1,2). In addition, the method of preparation of copper catalysts was found to be an extremely important factor(3).

These observations implied that the final state of copper in the mixed $Cu/ZnO/M_2O_3$ catalysts critically determined their high activity and selectivity for the production of methanol. The present work was undertaken to determine the chemisorption properties of CO, CO_2, O_2 and H_2 for a series of binary copper-zinc oxide methanol synthesis catalysts and thereby clarify the reason for the observed mutual promotion effect between Cu and ZnO by identifying the nature of the reactive centers in methanol synthesis catalysts based on copper.

EXPERIMENTAL

The Cu/AnO = 0/100-100/0 catalysts were coprecipitated from nitrate solution by Na_2CO_3, calcined and reduced with H_2/N_2 = 2/98 vol according to a procedure previously described in detail (3,4). The adsorption experiments were conducted in a glass high vacuum volumetric adsorption apparatus with a stationary background vacuum of 10^{-4} Pa. The catalysts were reduced on the adsorption system without exposure to air.

The CO and H_2 isotherms were measured at 293 K up to a final pressure of approximately 16 kPa. The weak and strong capacities were determined as follows: (1) run an adsorption isotherm on a reduced and activated sample, (2) evacuate the sample for 10 minutes then run a second isotherm, and (3) this second isotherm corresponds to the weakly adsorbed gas and the difference between the first and second isotherms is the strongly adsorbed gas. Oxygen chemisorption experiments were conducted at 78 K according to the procedure of Zettlemoyer et al (6). Surface area measurements were made using the BET method with argon as adsorbate.

Carbon dioxide isotherms were studied at 523 K and 293 K on pure ZnO and on the Cu/ZnO = 30/70 catalyst sample. For analysis of the gas phase composition in mixed gas CO/CO_2 redox studies a Varian VGA-100 quadrapole gas analyzer was installed on the chemisorption apparatus. The full details of these experiments are reported elsewhere (5).

RESULTS AND DISCUSSION

CO, O_2 and H_2 Chemisorption

The total CO capacities plotted in Figure 1 are seen to increase with increasing copper content in the binary Cu/ZnO catalysts, with maximum coverage obtained for pure copper. While no adsorption of CO was observed on pure ZnO at 293 K, the saturated coverage obtained for CO on copper is Θ = 0.15-0.18 using the range of site densities estimated for copper surfaces. The strong CO fraction however, shows a double humped feature with broad maxima at the Cu/ZnO = 30/70 and 67/33 compositions. In Figure 2 is shown a comparison between the weak CO and irreversible O_2 chemisorption data. It can be seen from the figure that weak CO capacities show good linearity with irreversible O_2 adsorption, has zero intercept and correctly predicts the observed CO capacity on pure copper.

The series of binary Cu/ZnO catalysts studied here may be divided into two groups, Cu/ZnO = 0/100-30/70 and 40/60-67/33 compositions, which are distinguishable by their crystallite sizes and morphological constitutions as reported earlier (7). Also, a substantial portion of copper was found to be X-ray amorphous (8) and scanning transmission electron microscopy analyses showed this amorphous copper to be in the ZnO phase (7). In an attempt to correlate the chemisorption behavior determined here, with the microstructure and distribution of elements reported earlier in the catalyst particles, four models are proposed below to describe the adsorption behavior of oxygen and carbon monoxide. They are as follows:

Model I — Irreversible O_2 and weak and strong CO adsorption occurs on copper crystallites only.

Model II — Irreversible O_2 and weak CO are adsorbed on copper crystallites; strong CO adsorbs on solute copper.

Model III — Irreversible O_2 is adsorbed on copper crystallites and solute copper. Weak and strong CO are on copper crystallites.

Model IV — Irreversible O_2 is adsorbed on copper crystallites and solute copper. Weak CO on copper crystallites, strong CO on solute copper.

It is apparent from Figure 2 that the sites for weak CO and irreversible O_2 are the same and can readily be attributed to the crystalline copper phase. Further, the strong CO capacities cannot be correlated directly with irreversible O_2 capacities and Models I, III and IV are therefore discarded. On this basis, using the specific adsorption of O_2 on pure copper as well as the measured total surface areas the copper and zinc oxide surface areas in the composite catalysts were determined and the results are shown in Table 1. The methanol synthesis activity does not correlate with either the ZnO or Cu surface areas in the individual catalysts.

With the zinc oxide surface areas available a test can be made of the dependence of strong CO capacities on the surface concentration of solute copper assuming the surface concentration to be proportional to the bulk concentration reported by Bulko et al (8). The plot of surface coverage by strong CO against the concentration of copper solute shown in Figure 3 has a linear portion for each morphology. Therefore, if the strongly bound CO molecules titrate the surface copper solute sites, then the basal (0001) ZnO planes tend to accomodate more solute copper atoms than the prism (1010) planes, which predominate in the compositional ranges Cu/ZnO = 40/60-67/33 and 0/100-30/70 respectively. Since the basal plane of ZnO is formally electrostatically charged while the prism plane is not, its higher accomodation of copper is consistent with the idea that the solute copper species are also charged. These solute copper sites are therefore considered to be the active centers for strong carbon monoxide adsorption and the adsorption characteristics of CO and O_2 are adequately described by Model II.

The amounts of weakly adsorbed hydrogen is proportional to that of irreversibly adsorbed O_2 but the relationship is not linear. Further, the weak H_2 capacities lie above the capacities predicted by pure copper metal and cannot be accounted for by total H_2 coverage on metallic copper surface. Without further evidence therefore, adsorption of H_2 on copper solute sites on the ZnO phase, created by the Cu-ZnO interactions, cannot be excluded.

Redox Behavior with CO/CO_2 Mixtures

The studies on the redox behavior of the Cu/ZnO catalysts were done on, and are of particular interest for the Cu/ZnO = 30/70 catalyst since it is the most active one and was used by Chatikavanij (9) in CO_2 kinetic studies.

The CO_2 isotherms at 523K on a freshly reduced (2% H_2 in N_2) show that there is a very strong interaction of this gas with the Cu/ZnO = 30/70 catalyst, this interaction being stronger but apparently less extensive than with pure ZnO. No carbon monoxide was found in the gas phase when pure CO_2 was added. Upon addition of CO at 523 K to a freshly reduced catalyst, however, a build up of CO_2 in the gas phase was detected. The time dependence of the partial pressure of desorbed CO_2 is shown in Figure 4 for pure ZnO as well as Cu/ZnO = 30/70 samples. There was no preexposure to CO_2 in the samples of Figure 4 and the ZnO areas used in all samples were similar. Also, addition of CO_2 to CO-reduced then outgassed samples gave CO in the gas phase, and as Figure 5 shows, irrespective of whether or not CO_2 is initially present on the surface, the amount of CO_2 desorbed upon CO addition depends only upon the mole fraction of CO in the gas phase.

The redox equilibrium can be represented using the defect notation of Kofstad (12) by the equation

$$CO_{2(g)} + V_o \overset{Kg}{\rightleftharpoons} CO_{(g)} + O_o \qquad 1)$$

where the subscript g denotes gas phase O_o is a lattice oxygen anion and V_o is a lattice oxygen anion vacancy. Adsorption equilibrium for CO and CO_2 on the catalyst surface are given by equations (2) and (3)

$$CO_{2(g)} \overset{K_{CO_2}}{\rightleftharpoons} CO_{2(s)} \qquad 2)$$

$$CO_{(g)} \overset{K_{CO}}{\rightleftharpoons} CO_{(s)} \qquad 3)$$

where subscript s denotes surface.

Using equations (1)-(3) a model equation was developed (5) for the redox equilibria data shown in Figure 5. It was estimated from fitting the data that

$$\frac{K_{CO}}{K_{CO_2}} = 1.3$$

and

$$Kg = 40$$

The value obtained for Kg is neither that for the redox equilibrium of pure ZnO nor pure Cu_2O. This result points to the presence of a compound of intermediate composition such as might be realized from a disolution of copper in zinc oxide as proposed earlier (4). Klier et al (10), in a quantitative study of the kinetics of methanol synthesis for the Cu/ZnO = 30/70 catalyst in the presence of CO_2, reported three sets of constants with which best fits were obtained for three cases involving competitive adsorption schemes of CO, CO_2 and H_2. The values given above for Kg and K_{CO}/K_{CO_2} are consistent with the values they report for the scheme wherein CO_2 competes with both CO and H_2, but CO and H_2 are adsorbed on different sites.

The solubility limit of copper (II) oxide in zinc oxide is 4-6% (11,12) whereas Bulko et al (8) measured up to 16.8%. Since it was earlier concluded that the copper solute species is a charged entity it appears substantiated that the solute copper species exist as copper (I) in zinc oxide.

CONCLUSIONS

The following important conclusions emerge from this work:

1. The sites for weak CO and irreversible O_2 adsorption are the same and readily attributable to the crystalline copper phase.
2. The methanol synthesis activity does not correlate with either the ZnO or Cu surface areas in the composite catalysts.
3. Strong CO chemisorption is associated with the surface copper solute sites which are preferentially accommodated on the electrostatically charged basal plane of ZnO.
4. The ZnO phase in the composite catalyst undergoes redox equilibria in CO/CO_2 mixtures at 523 K with an equilibrium constant that is different from those for pure ZnO or Cu_2O.
5. The solute copper species exist as copper (I) in zinc oxide and are probably the reactive centers in methanol synthesis from synthesis gas.

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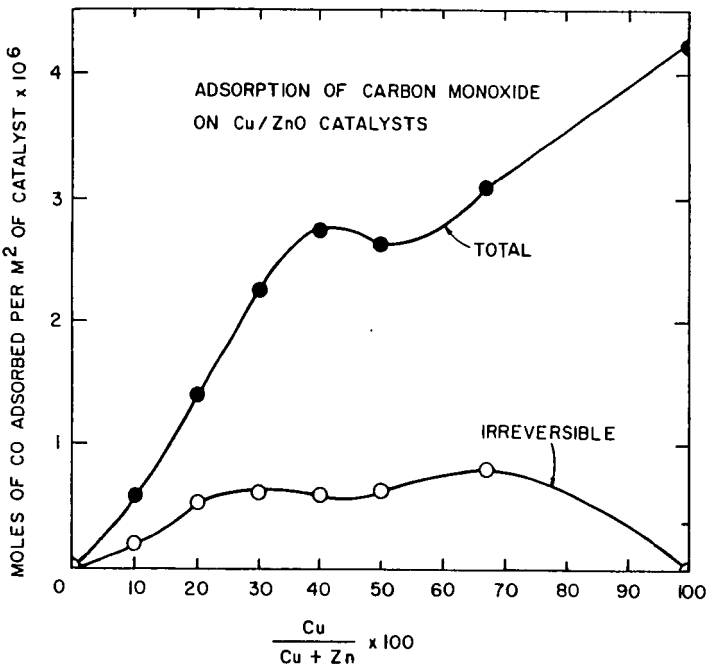

Figure 1. The dependence of the carbon monoxide saturation adsorption (total) and irreversible adsorption (irreversible) on the Cu/ZnO ratio in the binary copper-zinc oxide catalysts.

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 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

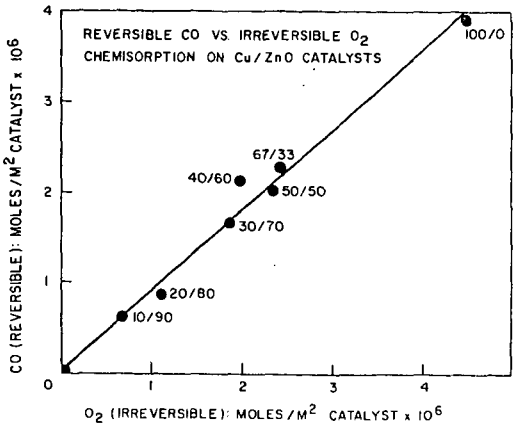

Figure 2. The relation between the amounts of weakly chemisorbed carbon monoxide and irreversibly chemisorbed oxygen indicating that these two adsorbates are a measure of copper metal surface area.

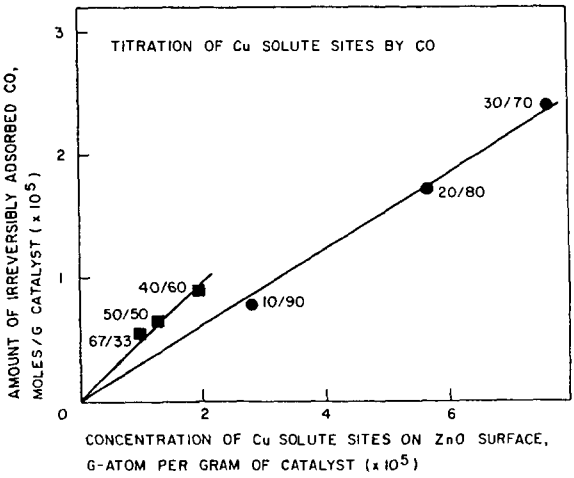

Figure 3. The dependence of the amount of irreversibly chemisorbed carbon monoxide on the concentration of amorphous copper found by X-ray diffraction and by STEM. The (1010) prism planes of zinc oxide are exposed in the Cu/ZnO = 10/90, 20/80, and 30/70 catalysts and the (0001) basal planes of ZnO are exposed in the Cu/ZnO = 40/60, 50/50, and 67/33 catalysts.

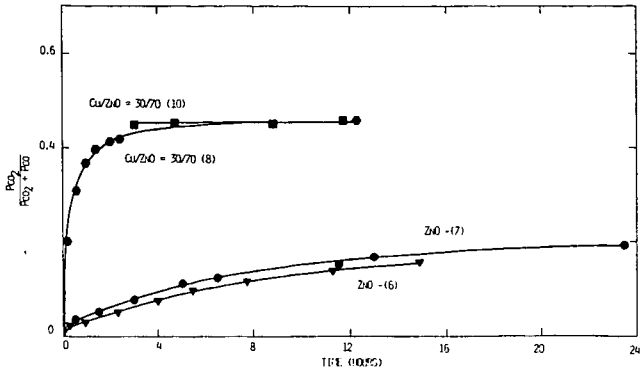

Figure 4. The time dependence of CO_2 partial pressure over ZnO and Cu/ZnO catalysts after CO is admitted to catalyst prereduced in H_2/N_2 = 2/98 vol. % at 523K.

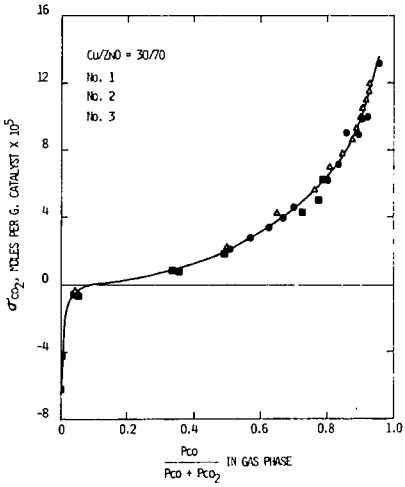

Figure 5. The dependence of σ_{CO_2}, defined as the cummulative amount of CO_2 desorbed from the catalyst surface less the initial amount of CO_2 adsorbed prior to the addition of CO, on the mole fraction of CO in the gas phase.