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LETTERS TO THE EDITORS

The Chemical State of Copper during Methanol Synthesis

Industrial methanol synthesis catalysts are generally based on $CuO/ZnO/Al_2O_3$ or $CuO/ZnO/Cr_2O_3$ systems. There has been much discussion recently about the mechanism of synthesis on these catalysts and it is clearly not yet fully understood (*1*, *2*). Indeed there is still controversy about the nature of the active sites and more specifically about the chemical state of the copper component during methanol synthesis.

Herman *et al.* (*3*) studied these catalysts systems and suggested that the active phase was a Cu^+ solution in ZnO where Cu^+ nondissociatively chemisorbs CO and ZnO activates the H_2. A different view was expressed by Andrew (*4*) who from a study of methanol and water-gas shift catalysts presented a case for copper being the only active component and that the role of zinc oxide was to adsorb poisons present in the synthesis gas. Raney Cu–Zn catalysts have been shown to be active in methanol synthesis (*5*) and the greatest activity was exhibited by catalysts containing approximately 97 wt% copper (*6*). The authors concluded that in the hydrogenation of carbon monoxide to methanol copper was the active component in fully extracted Raney Cu–Zn catalysts. However, Herman *et al.* (*3*) claimed that reduced pure copper oxide had zero activity for methanol synthesis within detection limits. This observation has been ascribed to sintering of the copper (*6*), and a number of authors have found that the catalyst activity for methanol synthesis from $CO/CO_2/H_2$ synthesis gas was proportional to the copper surface area (*4*, *7*). It seems that more than one mechanism may lead to methanol but that under the conditions usually employed industrially, i.e., with synthesis gases containing both CO and CO_2, the hydrogenation of CO_2 predominates (*7*, *8*) and copper is the active component.

Some work has been done to elucidate the chemical state of the copper in the working catalyst surface, using XPS. Okamoto *et al.* (*9*) studied coprecipitated CuO/ZnO catalysts reduced at 250°C with H_2 and found that they contained a monovalent copper species in the surface, when the chemical composition was <25 wt% CuO. In high copper content catalysts (>25 wt% CuO) the predominant copper metal species was well-dispersed metal particles whereas in low copper content catalysts (<10 wt% Cu) the major copper metal species was a two-dimensional epitaxial copper layer over ZnO. They concluded that both the two-dimensional copper metal layer and the monovalent copper species were formed by reduction of Cu^{2+} dissolved in a ZnO lattice whereas the well-dispersed metal particles originated from crystalline and amorphous copper oxide phases. The two-dimensional copper metal species was found to be preferentially reoxidised to Cu^+ when exposed to air at ambient temperature and it was suggested that the two-dimensional species is the catalytically active one for methanol synthesis. Apai *et al.* (*10*) also found a surface concentration of Cu^+ stable to hydrogen reduction at 270°C for copper/chromia catalysts and correlated the surface concentration of Cu^+ with methanol synthesis activity (for a synthesis gas of 67% H_2/33% CO). They claimed that this was the first established direct evidence for Cu^+ as the associative CO (i.e., alcohol-producing) site on these catalysts.

In contrast, Fleisch and Mieville (*11*, *12*) coupled a minireactor to a surface analysis instrument via a high-vacuum sample transfer system and were able to study the sur-

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face of a commercial $CuO/ZnO/Al_2O_3$ catalyst (UCI C18-HC) by XPS after it had been operating at 2 atm pressure in a methanol synthesis feed gas of 73% H_2, 25% CO, and 2% CO_2 at 250°C. They concluded that the surface was entirely metallic copper, ZnO, and Al_2O_3.

In this report N_2O chemisorption data are presented from *in situ* studies on a commercial $CuO/ZnO/Al_2O_3$ (60 : 30 : 10) methanol synthesis catalyst which has been operating in microreactor systems at pressures up to 100 atm. These data strongly suggest that the working surface of this catalyst is by no means entirely metallic copper under typical methanol synthesis conditions, and has up to 40% of a monolayer of oxygen atoms on it depending on the CO_2/CO ratio of the synthesis gas.

Routine and reproducible measurement of copper surface areas is available by monitoring the reaction of N_2O with copper atoms under suitable conditions and the basic method has been well documented (*13–17*). The most convenient form of this method for *in situ* applications is that of frontal chromatography (*18*) and the measurement of copper areas by this technique using a gas composition of up to 10% N_2O in helium has been developed (*19*). This frontal chromatographic method is readily employed in the microreactors commonly used for assessing methanol synthesis catalyst activity, by first depressurising and sweeping out the synthesis gas from the reactor with inert gas and cooling to near ambient temperature before establishing a flow of the required N_2O/He gas mixture through the reactor. The N_2 front produced may be monitored using a thermal conductivity detector or a mass spectrometer as available. With such an *in situ* technique available, the apparent copper area of a sample of catalyst can be measured after it is first activated (i.e., reduced) in the standard H_2/N_2 gas mixture and again after various exposures to synthesis gas at typical industrial methanol synthesis conditions. Measurement of the apparent copper surface area by the N_2O method after exposure to methanol synthesis conditions gives a direct measure of the degree of oxygen atom coverage of the copper under steady-state methanol synthesis conditions, any apparent decrease from the initial area being actually oxygen atom site blocking of the reaction $N_2O + Cu \rightarrow N_2 + Cu_2O$, providing no sintering of the copper has occurred. By rereducing the catalyst surface with the H_2/N_2 gas mixture after such measurements and then redetermining the copper area it is possible to assess the extent of any irreversible surface changes (e.g., sintering) which have occurred during operation in the microreactor. In practice, very little irreversible loss of copper area occurs if the exposure to methanol synthesis conditions is brief, e.g., the 6 h or so generally required to reach steady operation and obtain a reliable assessment of the catalyst activity. Consequently, it is only necessary to carry out the rereduction and redetermination of the copper area to obtain a reliable assessment of the state of the copper in the catalyst if the exposure to methanol synthesis conditions has been much longer. Since oxygen adsorbs on copper (110) in a p(2 × 1) structure (*20*), only half of the fraction of the total copper area affected by oxygen is covered by the oxygen, that is,

$$\text{Oxygen coverage (monolayers)} = \frac{\text{Initial Copper Area} - \text{Apparent Copper Area}}{\text{Initial Copper Area} \times 2}.$$

Measurements of this type have been made by the authors on several independent microreactor systems using samples of a commercial $CuO/ZnO/Al_2O_3$ (60 : 30 : 10) methanol synthesis catalyst at various stages of its industrial life. The state of the copper surface has been assessed after operation in the microreactors at pressures up to 100 atm, temperatures of 250–280°C and in methanol synthesis gases of various compositions for periods of up to 140 h. Table 1 summarises the results of these measurements.

TABLE 1

Copper Areas of $CuO/ZnO/Al_2O_3$ (60 : 30 : 10) Catalyst after Various Treatments

Initial copper area after reduction, m^2/g catalyst charged	Apparent copper area after reaction in synthesis gas, m^2/g catalyst charged	Rereduced copper area after reaction, m^2/g catalyst charged	Oxygen coverage of copper monolayers	Synthesis conditions			
				Time at conditions (h)	Pressure (atm)	Temp (°C)	Gas composition
—	17.4	21.4	0.09	140	100	280	$CO/CO_2/H_2/N_2$: 10, 3, 67, 20
—	20.5	26.4	0.11	140	100	280	$CO/CO_2/H_2/N_2$: 10, 3, 67, 20
33.1	14.0	—	0.29	6	50	250	$CO/CO_2/H_2/He$: 14, 14, 46, 26
21.6	11.4	—	0.24	6	50	250	$CO/CO_2/H_2/He$: 14, 14, 46, 26
9.0	4.0	—	0.28	6	50	250	$CO/CO_2/H_2/He$: 11, 11, 60, 18
24.9	5.5	23.1	0.39	6	50	250	$CO/CO_2/H_2/He$: 10, 13, 52, 28
23.2	17.1	23.0	0.13	24	1	300	CO_2/H_2: 99.9, 0.1

The results show that after being subjected to typical methanol synthesis conditions, between 9 and 40% of the copper surface has oxygen atoms on it. Furthermore, the degree of oxidation of the surface is shown to be affected by the composition of synthesis gas, particularly the CO_2/CO ratio. For a CO_2/CO ratio of 1.0, the oxygen coverage of the copper surface is about 25–30%, falling to only 9–11% for a CO_2/CO ratio of 0.3 and rising to nearly 40% for a CO_2/CO ratio of 1.3. There are insufficient data to assess the effect of pressure and temperature on the oxygen coverage, but an experiment at atmospheric pressure showed that a 13% oxygen coverage of the copper surface was obtained after the reduced catalyst was subjected to an atmosphere of 99.9% CO_2/0.1% H_2 for 24 h at 300°C.

In their recent Note in this journal, Fleisch and Mieville (*12*) used a methanol synthesis feed gas of 73% H_2, 25% CO, and 2% CO_2 at a pressure of 2 atm and concluded that the copper surface was entirely metallic. This rather unusual methanol synthesis gas (80% H_2, 10% CO, 10% CO_2 is more typical industrially with copper catalysts) has a CO_2/CO ratio of only 0.08 and from a rough extrapolation of the data in Table 1 might be expected to result in an oxygen coverage of the copper surface of less than 2%, which would probably be undetected by their XPS technique.

In summary, we have found that the surface of $CuO/ZnO/Al_2O_3$ methanol synthesis catalyst contains both metallic and oxidised copper under real methanol synthesis conditions and the proportion of oxidised surface depends on the precise composition of the synthesis gas; the greater the CO_2/CO ratio the more oxidised is the copper surface.

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