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The Chemical State of Copper during Methanol Synthesis

Reply to Chinchen and Waugh

Copper-based methanol synthesis catalysts have been the subject of many studies (1–14). Some of them have focused on the nature of the active Cu site(s) but the subject is still rather controversial. All researchers find metallic Cu as the predominant Cu species on $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ catalysts during methanol synthesis; however, the amount and catalytic importance of the small concentrations of Cu^+ accompanying Cu is at the center of a controversy. The amount of Cu^+ ions present during methanol synthesis can depend, among other things, on catalyst composition (1, 10), gas composition (e.g., presence of CO_2, H_2O), and reaction conditions.

Chinchen and Waugh (12) have presented some data which show that ICI's proprietary $CuO/ZnO/Al_2O_3$ catalyst of unspecified composition contains both metallic and oxidized Cu under real methanol synthesis conditions with CO_2/CO ratios exceeding 0.3. The presence of oxidized Cu was inferred from N_2O chemisorption data which showed that up to 40% of the Cu surface atoms did not chemisorb atomic oxygen from N_2O due to site blocking by adsorbed atomic oxygen from the methanol synthesis reaction. Though, in general, the detection of oxygen chemisorbed on a metal does not necessarily prove the presence of "oxidized" metal with measurable electron delocalization (15–17) we believe the trend in oxygen coverage of Cu with CO_2/CO ratio to be interesting. It appears that with a very high CO_2/CO ratio of 1 there is a quarter monolayer of oxygen on Cu during steady-state methanol synthesis conditions. Chinchen and Waugh state that an extrapolation of their data to a CO_2/CO ratio of 0.08, used in our study (9), would result in less than 2% oxidized Cu and thereby support our results in our XPS study. We found, using a feed gas of 73% H_2, 25% CO, and 2% CO_2, only *metallic* Cu with a detection limit of 2% for oxidized Cu. Oxidized copper (Cu^+) was, however, readily detected when catalysts were briefly exposed to oxygen.

The feed composition containing 2% CO_2 may be unusual for commercial operations but it is certainly rather typical for published research. We chose the feed composition based on a study by Klier *et al.* (13, 14) in which they showed a maximum methanol synthesis rate at this 2% CO_2 concentration. The major role of CO_2 in the feed gas is to avoid catalyst deactivation (4, 6). Many studies have been reported of active Cu-based catalysts using feeds not containing CO_2 at all. In fact, the catalyst used in our study (9) was able to produce methanol up to 75% of equilibrium conversion at conditions of 500 psig, 250°C, and a space velocity of 650 hr^{-1} using a feed mole composition of 66.6% H_2 and 33.3% CO with no CO_2 present.

We believe that there is sufficient evidence in the literature that completely reduced Cu-based catalysts are very good methanol synthesis catalysts (4, 7, 9). Thus, metallic copper sites must be active sites for this reaction. On the other hand, there is also evidence of incomplete copper reduction under certain reaction conditions leading to a mixture of mainly Cu and some Cu^+. The question of whether Cu^+ is another or even a much more active site for methanol formation than Cu has not yet

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been answered. It would have been interesting if Chinchen and Waugh had shown a correlation between the performance of their catalysts and the amount of surface oxidized copper. We know of only one study (*10*) that shows a relationship between Cu^+ surface concentration and methanol synthesis activity. However, this relationship was found for a copper/chromia catalyst where Cu^+ was stabilized by the formation of $CuCrO_2$. No CO_2 was used in the feed gas (67% H_2, 33% CO). In our own work, attempts to correlate methanol synthesis rates with relative amounts of Cu and Cu^+ were not successful because the reduction of CuO to Cu was completed at the onset of measurable CO conversion at about 130°C (*9*). We did, however, observe Cu^+ as intermediate in the reduction of Cu^{2+} to Cu and, as already mentioned, after only minute air exposure of used catalysts.

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