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NOTES

Mechanism of Methanol Synthesis from Carbon Monoxide and Hydrogen on Copper Catalysts

INTRODUCTION

The synthesis of methanol over copper catalysts is still the subject of much controversy (*1, 2*). Recent work on the synthesis of methanol (*3–5*) from $CO_2/CO/H_2$ mixtures has shown that methanol is formed from carbon dioxide and that, for a variety of copper catalysts, the rate of synthesis is proportional to the copper metal area. These catalysts were all prepared by coprecipitation of copper and other salts and, on reduction, contained a substantial proportion of metallic copper (in the range 15–70 wt%). In contrast, Burch (*6, 7*) and Denise *et al.* (*8*) find pronounced support effects with different copper catalysts in methanol synthesis from CO/H_2 and CO_2/H_2 mixtures. Other sometimes conflicting support effects have been reported for methanol synthesis from carbon monoxide/hydrogen mixtures. Although synthesis activity (lower than in mixtures containing carbon dioxide) was found in Cu/ZnO catalysts (*9, 10*) and a commercial $Cu/ZnO/Al_2O_3$ catalyst (*11*), another commercial $Cu/ZnO/Al_2O_3$ catalyst has no detectable activity in the absence of carbon dioxide (*12, 13*). Temperature-programmed reaction spectroscopy with unsupported polycrystalline copper (*5*) showed that no methanol was formed from a carbon monoxide/hydrogen mixture. Further, copper catalysts prepared from intermetallic precursors (*14, 15*) have exceptional activity for methanol synthesis, far beyond that expected from the measured copper metal areas. In this note we examine possible mechanisms of methanol synthesis from carbon monoxide and hydrogen on supported copper catalysts.

POSSIBLE MECHANISMS

Two broad categories of reaction mechanism can be identified:

(a) Type I: Carbon monoxide, adsorbed on the copper surface, is hydrogenated by the addition of hydrogen atoms while the C–O bond remains intact. A second C–O bond is neither formed nor broken.

(b) Type II: Carbon monoxide (or a partially hydrogenated intermediate, e.g., HCO) reacts with an oxygen atom on the catalyst surface to give an intermediate, typically a formate, which contains two C–O bonds. Subsequent reaction leads overall to methanol and the reformation of the surface oxygen atom.

With CO/H_2 reaction mixtures of very low carbon dioxide content and hence low oxidizing power the coverage of adsorbed oxygen on the copper surface is very low (*4, 5*). Thus, for mechanisms of Type II the adsorbed oxygen which participates in intermediate formation must be associated with the support phase. On catalysts of unsupported copper, or with supports (e.g., silica) in which the oxygen atoms of the oxide are unlikely to be available for reaction, the Type I mechanism is the only plausible route.

At low concentrations of adsorbed oxygen, little of the adsorbed carbon monoxide will be removed as carbon dioxide (the main reaction in $CO_2/CO/H_2$ mixtures) and the residence time could be long enough for hydrogenation to give methanol. Experimental results with CO/H_2 mixtures over low-area, unsupported copper (*5*), when no methanol was observed, and copper/silica

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catalysts (*6, 7*), found to be of low specific activity, indicate that Type I is an intrinsically slow route, compared with other routes from carbon monoxide or carbon dioxide. Since adsorbed carbon monoxide is bonded to copper through the carbon atom, whereas methoxy, for example, is bonded through the oxygen, the reversal of an intermediate must occur at some stage in the reaction. This may account for the relatively slow rate of reaction.

The formation of a dioxygenate intermediate from carbon monoxide requires an additional oxygen atom and this must be derived from the support under carbon monoxide/hydrogen mixtures. The dioxygenate intermediate is probably formate, but the arguments used apply to other possible intermediates, e.g., H_2CO_2. Bulk formates can be produced from carbon monoxide by reaction with a strong base. The reaction of carbon monoxide with alumina and magnesia (*16*) has been shown to produce surface formates in the appropriate temperature range (375–575 K). Surface formates are similarly formed on zirconia by carbon monoxide (*17*). Adsorbed formates have been detected on Cu/ZnO catalysts (*1*). Thus the Type II mechanism requires copper to be supported on a basic oxide. All the copper catalysts reported (*6–8, 14, 15*) to have high activity in the conversion of CO/H_2 mixtures to methanol have a basic oxide support.

The adsorbed formates on magnesia and alumina exist as a bidentate species (*16*) and these appear also to be the main types on copper metal surfaces (*18*). Two main types of formates can be distinguished on copper metal/basic oxide catalysts: formate is adsorbed either on the surface of the support oxide alone or at the periphery between the copper surface and the support oxide. Peripheral formate formed from carbon monoxide adsorbed on the copper could have one oxygen bonded to copper and the other as part of the oxide lattice. Jin *et al.* (*19*) have shown that carbon monoxide adsorbed on platinum in a Pt/CeO_2 catalyst can react with lattice oxygen at the metal/oxide interface. Ghiotti *et al.* (*20*) found a peripheral carbonyl formed by carbon monoxide chemisorption on Cu/ZnO catalysts.

The reactions of a formate intermediate are probably critical in determining the overall rate of methanol synthesis by Type II. Evidence that the hydrogenolysis of formate is the rate-controlling step (*5*) has been confirmed by Mueller and Griffin (*21*). Direct hydrogenolysis, through spillover from the hydrogen adsorbed on copper, would then regenerate the hydroxyl group on the support surface. Hydrogen dissociation on copper metal surfaces is fast enough to account for observed rates of methanol synthesis (*5, 22*), even on alloy-based catalysts.

An alternative route is the reaction of adsorbed formate with methanol product to give methyl formate, which then migrates to the copper surface to undergo hydrogenolysis to methanol:

$$OH_{(a)} + CO \rightarrow HCOO_{(a)}$$

$$HCOO_{(a)} + CH_3OH \rightarrow HCOOCH_3 + OH_{(a)}$$

$$HCOOCH_3 + 4H_{(a)} \rightarrow 2CH_3OH$$

Bases catalyze the formation of methyl formate from carbon monoxide and methanol (*23*). Methyl formate hydrogenolysis is fast enough to account for the observed rates of methanol synthesis over conventional catalysts. The specific rates of methanol synthesis on copper/zinc oxide catalysts (*5*), extrapolated to 475 K and 100 kPa on the basis of first order in hydrogen and an activation energy of 100 kJ mol^{-1}, are about 10^{-5} mol $CH_3OH(m^2\ Cu)^{-1}\ h^{-1}$. The observed (*24*) rate specific of methyl formate hydrogenolysis under the same conditions is 1.2×10^{-3} mol $CH_3OH(m^2\ Cu)^{-1}$. Monti *et al.* (*24*) found the hydrogenolysis reaction to be 0.45 order in methyl formate, so a steady-state level of methyl formate in methanol synthesis can be calculated: it corresponds to about 0.01% of methyl formate in the methanol product. Thus, the formation and hydrogenolysis of methyl formate is a plausible mechanism for methanol production from CO/H_2 mixtures over copper/zinc oxide catalysts. However, it cannot be the only route as the initiation of the reaction via methyl formate clearly requires methanol formation by another path, e.g., direct hydrogenation. A positive order in methanol might also be expected in methanol synthesis kinetics but this has not been reported (*1*, *2*).

Catalysts derived from rare earth/copper alloys are much more active than conventional catalysts for methanol synthesis (*14*, *15*). A similar calculation to that above (in which the BET area of the catalyst is used, rather than measured copper area) gives a lower limit to the synthesis rate of about 10^{-2} mol CH_3OH m^{-2} h^{-1}. This indicates that methyl formate hydrogenolysis is not fast enough, unless the rate of methyl formate hydrogenolysis on alloy-derived catalysts is several orders of magnitude faster than that on the copper/silica catalyst used by Monti *et al.* (*24*).

THE HIGH ACTIVITY OF ALLOY-BASED CATALYSTS

The high activity of copper catalysts derived from rare earth/copper alloys does not arise from the copper metal crystallites present in the catalysts, but probably originates in "very highly dispersed" copper present on, or, more likely, within, the surface of the rare earth oxide (*15*). Both Type I and Type II mechanisms appear possible. The energetics of adsorption of hydrogen and carbon monoxide would be different on bulk copper metal and on a cluster containing only a few copper atoms in a rare-earth oxide matrix, so large differences in rates of methanol synthesis by Type I mechanism could be expected. Also the small Cu cluster size facilitates the hydrogen spillover or peripheral reaction required for the Type II mechanism. The strong basicity of the support oxides (ceria, thoria, and rare earth oxides) would promote the conversion of carbon monoxide to formate, etc.

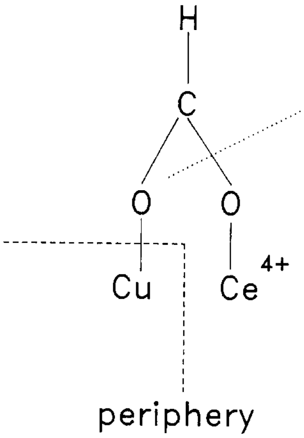

FIG. 1. Possible structure of formate intermediate adsorbed at the periphery between a copper cluster and the ceria support in Cu/CeO_2 catalysts derived from copper–cerium alloys.

Simple geometrical calculations indicate that peripheral reactions could be important in alloy-based catalysts. If, for example, the copper clusters active in these catalysts contain 5–14 atoms (from an *fcc* unit cell face to a complete *fcc* unit cell), then the fraction of peripheral copper atoms, Φ, is 0.8–0.3. In precipitated copper catalysts the copper crystallites are 5–10 nm in size and $\Phi \sim 2 \times 10^{-4}$ for these catalysts. Thus the ratio of rates at the periphery for catalysts of similar copper content would be

$$\frac{\Phi \text{ (alloy-based catalyst)}}{\Phi \text{ (precipitated catalyst)}} \sim 3000.$$

This can be compared with the experimental rate ratio of $\sim 10^3$, so it is improbable that a peripheral reaction fast enough to account for the high activity of alloy-based catalysts would be of much significance in precipitated catalysts.

A formate group adsorbed at the periphery between a copper cluster and a support of the type shown in Fig. 1 differs from formate on either copper metal or a basic oxide (ZnO, CeO_2, etc.): a consideration of bond energies suggests that hydrogenolysis of peripheral formate should be facile. Experiments with labeled carbon and oxygen reactants to distinguish between various reaction mechanisms on alloy-based catalysts are in progress.

The mechanisms presented in this note have much in common with those suggested for CO/H_2 reactions on palladium catalysts (*2*). This relationship is explored further elsewhere (*25*).

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