DE86014812

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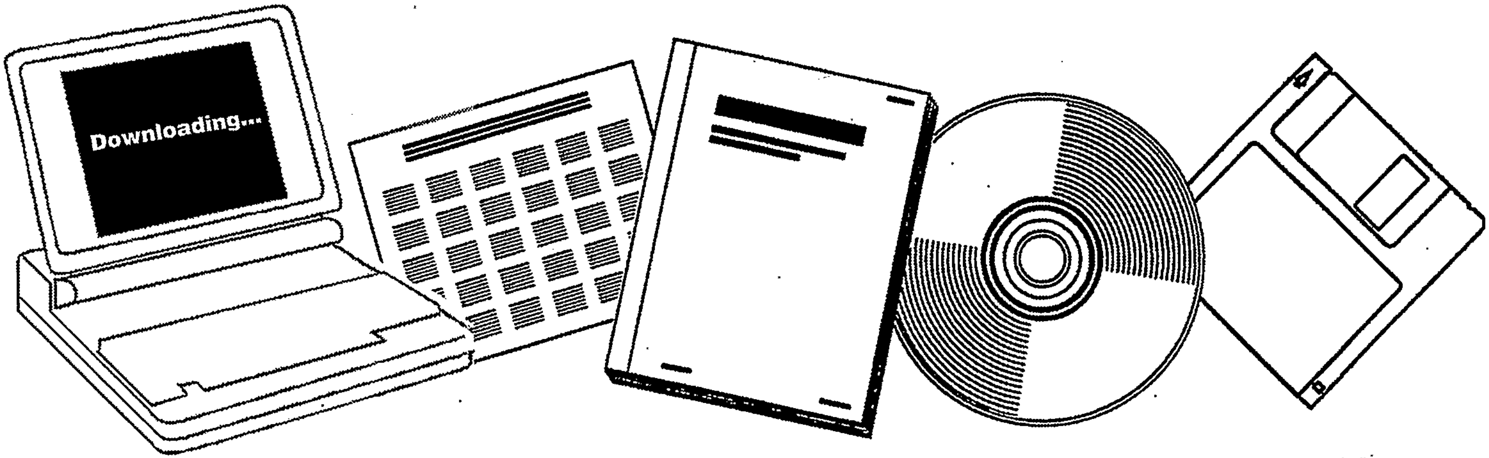
MINNESOTA UNIV., MINNEAPOLIS

30 JUN 1986



DIRECT ALCOHOL SYNTHESIS REACTIONS ON COBALT MODIFIED METHANOL CATALYSTS

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DOE/ER/13392--1

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Prepared 06/30/86

ABSTRACT

We are studying the adsorption and reaction properties of Cu--ZnO, Co--ZnO and Co--Cu--ZnO catalysts intended for the direct synthesis of methanol and higher alcohols from CO:H_2 mixtures. Our principal goals are (1) to understand the adsorption behavior of highly dispersed metals in ZnO-based catalysts; and (2) to determine the importance of these adsorption sites in alcohol synthesis reactions. Results obtained during the first year for the binary Cu-ZnO systems indicate that for sub-monolayer coverages of Cu(e.g., less than 10^{15} Cu atoms/m^2 of ZnO), the Cu species are present in an electron deficient (i.e., partially oxidized) metallic state. This state is characterized by abnormally high values for the vibrational frequency of adsorbed CO, and by a significant barrier to oxygen adsorption. The methoxy and formate intermediates produced during methanol decomposition are both more stable on these supported Cu surfaces than on bulk Cu. These Cu species are also quite active for CH_2O hydrogenation, which indicates that the rate limiting step in methanol synthesis is instead the hydrogenation of the formate intermediate. Work is in progress to determine whether Cu maintains this electron deficient state under alcohol synthesis conditions, and whether a similar state also occurs for Co supported on ZnO.

INTRODUCTION

The direct synthesis of methanol and higher alcohols from $CO:H_2$ synthesis gas mixtures is expected to have an increasing role in meeting the energy needs of the United States (HERMANN 1984). The decreasing availability and ease of processing of known domestic petroleum resources, together with the establishment of emissions control regulations which restrict the use of lead-based octane promoters, is placing an increasing burden on refiners' octane upgrading capacity (ANDERSON 1986). The use of methanol and/or blends of higher alcohols as octane enhancers offers the most promising alternative approach for relieving this pressure.

Controlling the selectivity of alcohol synthesis reactions is also of broader scientific interest in the context of catalyst design. The reactions that are involved offer an excellent opportunity to test our ability to identify and subsequently predict the kinetic behavior of complex, multi-functional catalytic networks. The two catalyst preparation factors which most strongly influence the reaction selectivity, namely alkali promotion and active metal dispersion, are also subjects of interest to the catalytic community in their own right.

Methanol synthesis is practiced commercially using Cu/Al/ZnO or Cu/Cr/ZnO mixtures (KLIER 1982). Operating at pressures between 50 and 75 atmospheres and temperatures between 473 and 523 K, these catalysts achieve a CH_3OH selectivity of better than 99%. This selectivity reflects the ability of the catalyst to activate CO hydrogenation, without permitting CO dissociation (i.e., the initial step in methanation and/or Fischer-Tropsch chemistry).

Our current understanding of Cu/ZnO catalysts and the CH_3OH synthesis mechanism is described in recent review articles (KLIER 1982, KUNG 1980). More recent work has focussed on several remaining questions of scientific interest, including the relative importance of the formate vs. formyl species as the first hydrogenated intermediate, the role of CO_2 (or H_2O) in the reactant gas mixture, and whether the reaction occurs on metallic Cu clusters or at atomically dispersed Cu sites. Understanding these questions is important for improving the preparation methods for Cu/ZnO based catalysts, and for developing bi-functional catalysts for higher alcohols and other chemical products (SHELDON 1983).

Non-agricultural ethanol and other short chain alcohols are currently manufactured by hydration of the corresponding olefin (SHERMAN 1981). Higher alcohols are also produced from their preceding olefin homologs, via a two-step sequence of carbonylation using a homogeneous Rh or Rh:Co catalyst to produce the corresponding aldehyde, followed by hydrogenation in a separate reactor to produce the alcohol. To eliminate the reliance on olefin feedstocks of the former processes, and to eliminate the operating complexity associated with handling the homogeneous catalysts for the latter processes, research is needed toward direct synthesis of alcohols from $CO:H_2$ mixtures via mechanisms that involve the intermediate synthesis of CH_3OH rather than olefins. Specific needs include:

- Finding ways to activate CH_3OH for CO insertion using heterogeneous catalysts.
- Ways to accomplish the subsequent carbonylation and hydrogenation reactions efficiently in the same reactor.
- Ways to combine the methanol synthesis and subsequent homologation steps in a single process stream, preferably within a single reactor.

Two routes have been demonstrated for higher alcohol synthesis using heterogeneous catalysts. Alkali promoted Cu/ZnO catalysts produce significant yields of short chain and branched alcohols (SMITH 1984, KLIER 1982). The chain growth mechanism which leads to products with molecular weights greater than C_2H_5OH appears to be base-catalyzed aldol condensation, as evidenced by the fact that chain growth effectively ceases with 2-methyl-1-propanol product. The role of the alkali promoter in facilitating the synthesis of C_2H_5OH itself is less clear. It has been proposed that the alkali cation activates $CH_3O_{(a)}$ for CO insertion:

$$CH_3O_{(a)} + CO_{(a)} \longrightarrow CH_3COO_{(a)}$$

This step is analogous to the CO insertion step into $OH_{(a)}$ groups that has been suggested as the route to the $HCOO_{(a)}$ intermediate in the CH_3OH synthesis reaction (NATTA 1957). The latter proposal is based on the known promotional effect of alkali cations in the homogeneous formate reaction. Enhancement of the CH_3OH synthesis rate on alkali-promoted Cu/ZnO catalysts has been reported.

The second demonstrated route to higher alcohols is the formation of an alcohol mixture which contains a Shultz-Flory distribution of chain lengths, using Cu/Co/Al/Zn/Na oxide mixtures (COURTY 1982). The role of each component in these complex catalysts has not been resolved. The reaction selectivity for alcohols is extremely sensitive to the exact composition, in particular to the presence of alkali. The fact that a distribution of hydrocarbon products is also observed that has a similar value for the chain propagation parameter suggests strongly that both sets of products involve a common chain growth process, probably resembling conventional Fischer-Tropsch chemistry (FUJIMOTO 1985). The selectivity to alcohols is then determined by the chain termination (desorption) step, as it is affected by the catalyst composition.

Our research is aimed at examining a third, potentially unique route for higher alcohol synthesis on catalysts which contain atomicly dispersed Co species. We wish to determine whether these species may support CO insertion chemistry similar to that known for homogeneous Co clusters (e.g., CH_3OH carbonylation) (ORCHIN 1981, SLOCUM 1980). Obviously there is an enormous difference in the local environments of a homogeneous Co cluster dissolved in an alcohol solvent and a Co atom dispersed on the surface of an oxide support in a heterogeneous catalyst. Nevertheless, there is at least one early report that a 2:1 ZnO:CoO catalyst showed ca. 40% selectivity for C_2H_5OH synthesis (NATTA 1957).

The key issue in the possible role of the homologation route vs. the alkali-promoted routes is the preparation method and operating conditions that are needed to stabilize these isolated CO sites. Highly dispersed Co catalysts can be prepared by ion exchange (BRUNELLE 1973), or by deposition of Co carbonyl clusters (ICHIKAWA 1979). It must be demonstrated whether such high dispersion can be maintained on a ZnO support, and whether an alkali promoter has a greater effect on the alcohol selectivity of Co sites. It is also possible that the alkali promoter and the ZnO support will have a synergistic effect on alcohol selectivity.

Our research program is aimed at identifying and performing the essential kinetic, spectroscopic, and adsorption experiments needed to answer these questions. We will measure the rates and selectivities of the elementary reaction steps of the proposed surface intermediates in the direct synthesis of higher alcohols, using both temperature programmed desorption and transient and steady state kinetic techniques. We will correlate these results with the composition, preparation method, and operating condition of the catalyst surface (e.g., oxidation state). In particular, we wish to identify the relative importance of dispersion, oxidation state, and alkali promotion in determining the activity and selectivity of the CO component of these catalysts.

PROGRESS: YEAR ONE

Our work during the first year has focussed on characterizing the reactivity of the different Cu species present in Cu/ZnO catalysts. This has involved primarily adsorption, decomposition, and spectroscopic measurements of CH_3OH on various Cu/ZnO mixtures, using a combined IR-TPD cell. We have also completed two reactor flow systems for steady state kinetic experiments with gas chromatographs for product analysis. One system is operated at 1 atm, and has been used for mechanistic studies of the hydrogenation kinetics of the CH_2O intermediate. The second system has been operated at pressures up to 50 atm, and is used for CO hydrogenation measurements.

In our adsorption/decomposition studies, we have shown that Cu dispersed on ZnO shows unique kinetic behavior for the decomposition of CH_3OH. This behavior is different from that exhibited by bulk Cu (WACHS 1979) or pure ZnO (ROBERTS 1985). Samples are prepared by depositing Cu onto ZnO powders (Kadox 25), using impregnation with $Cu(NO_3)_2$ solution, followed by drying, calcining, and in-situ reduction. Methanol is then adsorbed at room temperature, and the product evolution is monitored using a mass spectrometer as the sample is heated to 673 K.

For a freshly reduced sample, the observed CH_3OH decomposition behavior is essentially identical to that observed for pure ZnO. Decomposition occurs sequentially via $CH_3O_{(a)}$ and $HCOO_{(a)}$ intermediates, which decompose with apparent activation energies of 41 and 43 kcal/mole, respectively. These are the same values as observed for pure ZnO. However, if the sample is pre-oxidized using surface area titration with either O_2 or N_2O, then new $CH_3O_{(a)}$ and $HCOO_{(a)}$ decomposition channels are observed with apparent activation energies of 34 and 37 kcal/mole, respectively. These processes are assigned to Cu sites that have been activated by the pre-oxidation step. The amount of CH_3OH which decomposes in these new channels is much less (ca. only 15%) than the number of Cu surface atoms determined by O_2 titration, which in turn is several times less than the total amount of Cu deposited during the preparation step.

Together with separate spectroscopic measurements of adsorbed CO on the same samples, these results lead us to conclude that the new CH_3OH decomposition channel is due to CH_3OH molecules adsorbed on the ZnO support at the perimeter of the Cu clusters. The role of the pre-oxidation step is surmised to provide reactive $O^=$ anions on the surface of the Cu clusters, which react with neighboring $CH_3O_{(a)}$ species on the ZnO support during the TPD experiment. The reactivity of these $O^=$ anions is further indicated by the fact that CO_2 rather than CO is the product of the $HCOO_{(a)}$ decomposition step. The increased lability of these $O^=$ species may be attributed to the weaker energy of Cu-O bonds, relative to their Zn-O counterparts.

Out initial kinetic studies have been aimed primarily at verifying the activity of the catalysts studied above. In addition, measurements of CH_2O hydrogenation kinetics have been performed using our 1 atm reactor. These studies have provided new insight regarding the nature of the rate limiting step in the CH_3OH synthesis reaction, as explained below.

All of the rate expressions for CH_3OH synthesis reported by earlier authors have contained a H_2 pressure dependence that is greater than first order (KLIER

1982). Conventionally, this is interpreted to mean that the rate limiting step is the addition of either the third or fourth H atom to the adsorbed $CH_2O_{(a)}$ or $CH_3O_{(a)}$ intermediate, respectively. However, this appears to be at inconsistent with reports that Cu/ZnO catalysts have very high activity for a wide range of aldehyde hydrogenation reactions (VERDAGE 1982).

Our kinetic measurements have shown that CH_2O is also rapidly hydrogenated on Cu/ZnO catalysts. For a reactor space time of W/F = 2 gm-hr/mole, complete conversion of CH_2O is achieved at 423 K; i.e., at much lower temperature than required for CH_3OH synthesis. Moreover, the subsequent reaction of CH_2O with the CH_3OH product is even faster. Thus it appears highly unlikely that the hydrogenation of gas phase CH_2O is the rate limiting step in CH_3OH synthesis. This accounts for the fact that gas phase CH_2O has never been reported in the CH_3OH product stream.

Instead, we propose that the rate limiting step is the hydrogenation of the chemisorbed $CH_2O_{2(a)}$ intermediate that is produced by hydrogenation of $HCOO_{(a)}$:

$$HCOO_{(a)} \overset{+H(a)}{\longleftrightarrow} CH_2OO_{(a)} \xrightarrow[\text{RLS}]{+H(a)} CH_3O_{(a)}$$

The limiting kinetics of the second step is due to the need to dissociate the second C-O bond that is formed when CO is stabilized on the surface as $HCOO_{(a)}$ at the beginning of the synthesis process.

Our high pressure reactor has just become operational. Preliminary measurements using a 1 wt.% Cu/ZnO catalyst show that for reactor conditions of W/F = 3 gm-hr/mole, p = 50 atm, T = 493 K, and a reactant mixture containing $CO:CO_2:H_2$ = 24:6:70, a CO conversion of 2% is obtained. The reaction is slightly greater than first order with respect to total pressure. No higher alcohols are observed on the unpromoted Cu/ZnO catalysts.

REFERENCES

Anderson, E. V., Chem. & Eng. News, April 14, 1986 p. 18.

Brunnele, J. R., and A. Sugier; Comptes Rendus. Acad. Sci. Ser. C 276 1545 (1973).

Courty, P., D. Durand, E. Freund, and A. Sugier; J. Molec. Catal. 17 241 (1982).

Fujimoto, K., and T. Oba; Applied Catal. 13 289 (1985).

Herman, R. G., in Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals (R.G. Herman, ed. Plenum, NY 1984) p.1.

Ichikawa, M.; J. Catal. 59 67 (1979).

Klier, K.; Adv. Catal. 31 243 (1982).

Kung, H. H.; Catal. Rev., Sci. & Eng. 22 235 (1980).

Linn, F. N., and F. Pinnella, in Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals (ibid) p. 53.

Natta, G., U. Colombo, and I. Pasquon; in Catalysis Vol. 5 (P. H. Emmett, ed., Reinhold, 1957) p. 131.

Roberts, D. L., and G. L. Griffin; J. Catal. 95 617 (1985).

Sheldon, R. A., in Chemicals from Synthesis Gas (D. Reidel, Dordrecht (1983) pp. 75-85.

Sherman, P. D. Jr., and P. R. Kavasmaneck, in "Ethanol" (Kirk Othmer Encyclopedia of Chemical Technology, Wiley, Third Ed. 1981) Vol. 9, p. 338.

Slocum, D. W., in Catalysis in Organic Synthesis (W. H. Jones, ed., Academic Press, 1980) p. 245.

Smith, K. J., and R. B. Anderson; J. Catal. 85 428 (1984).

Verdage, G. A., and K. Klier; J. Catal. 77 558 (1982).

Wachs, I. E., and R. J. Madix; J. Catal. 53 208 (1978).