CATALYTIC SYNTHESIS OF METHANOL FROM HYDROGEN AND CARBON MONOXIDE ON A COPPER-ZINC OXIDE SUPPORTED CATALYST

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INTRODUCTION

Most kinetic studies of methanol synthesis over Cu/ZnO catalysts have been carried out using mixtures of carbon monoxide and hydrogen. But in some cases (1) the synthesis gas has also contained carbon dioxide (2). Power rate laws as well as complicated rate expressions have been proposed over the years. The detailed kinetics of the surface processes is virtually unknown. With the exception, perhaps, of the near-atmospheric work by Saida and Ozaki (3), investigations of the kinetics of methanol synthesis over Cu/ZnO catalysts have been done at pressures on the order of 75 atm (1,4-8). A major drawback of several such kinetic studies is the use of integral reactors.

In this study, we investigate the kinetics of methanol synthesis over a commercial Cu/ZnO/Al₂O₃ catalyst in a differential reactor at pressures in the range from 3 to 15 atm and temperatures between 250 and 290°C (9).

EXPERIMENTAL METHOD

A high pressure unit is used for the kinetic experiments (9). The reactor system consists of a U-tube made of stainless steel 304, 0.95 cm OD and 0.09 cm thick. The U-tube is suspended vertically in a Techné fluidized sand bath SBS-4. In the direction of flow, the U-tube contains a length of glass wool, a preheating section of Potters silica glass spheres P-047, a second length of glass wool to isolate the catalyst bed from the glass spheres and a final glass wool plug above the catalyst bed to prevent carry-over of the catalyst (9). Omega iron-constantan thermocouple probes TT-J-30 are used for temperature measurements. Our data reveal that the fixed bed we use is isothermal (9). The reactor system is pressurized by a Grove back pressure regulator 91W. The reactor effluent is led to a Carle sampling valve 7707. During analysis, the effluent sample is carried by the carrier gas (hydrogen) to a Varian Aerograph Gas Chromatograph 202-B. A Chromosorb 102 column permits separation of CO, CO₂, and methanol. The gas chromatograph is coupled with a Houston Instrument chart recorder A521X-14K to enable qualitative and quantitative analysis of the effluent. Based on gas chromatographic analysis of CO bubbled through methanol at different temperatures, it is concluded that the weight percent of the components in the reactor effluent can be estimated by using Dietz's thermal conductivity weight factors (10).

A 5 g Cu/ZnO/Al₂O₃ catalyst sample (C79-2-01 of United Catalysts, Inc., Kentucky) of average size equal to 0.077 cm is reduced with hydrogen at 1 atm and 290°C for 15 hours (9). No further pretreatment is done during the rest of the experimental span. A reaction interval of one hour is found to be sufficient to produce reproducible steady-state product distributions. Steady state reaction data are collected at temperatures between 250 and 290°C, pressures in the range of 3 to 15 atm, H₂/CO = 2.1 - 2.4.
and total flow rates between 70 and 120 cc/min (STP). The catalyst composition measured with a Dispersive Analyzer is on an oxygen free basis: 40.6 wt.% Cu, 50.3 wt.% Zn and 9.1 wt % Al. The specific surface area of this catalyst, determined by BET with N<sub>2</sub>, is 37.8 m<sup>2</sup>/g.

RESULTS

The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is tested at three temperatures, 250, 270 and 290 °C. Typical measured steady state conversions are summarized in Table 1 along with the conditions used. No deactivation of the catalyst is observed at the experimental conditions studied, based on periodic tests conducted at "standard conditions" which were chosen to be 11.2 atm, 250 °C and H<sub>2</sub>/CO ratio equal to 2.3. As a consequence of a rigorous design of our differential reactor, heat and mass transfer effects are negligible (9).

Methanol is the main product at the conditions studied. Carbon dioxide and water (in trace amounts) are formed as side products. No other by-products are observed at the conditions used. It is observed that the reaction rate increases as the temperature increases in the temperature range 250 to 290 °C. Also, the reaction rate increases as the total pressure increases at constant temperature and H<sub>2</sub>/CO ratio (Table 1). Note that at 250 and 270 °C the methanol synthesis reaction in our system is far from equilibrium whereas at 290 °C the reverse reaction becomes important.

Starting with power rate laws, several rate expressions were tried to fit our data. Emphasis was laid, on rate expressions containing a small number of parameters. The reaction rate was found to be approximately proportional to the total pressure. This enabled us to eliminate several rate expressions if the observed dependence of rate on total pressure was not followed (9).

Since evidence for the formyl (CHO-) and the methoxy (CH<sub>3</sub>OH-) species has been reported for Cu/ZnO catalysts during methanol synthesis (1,2,11), two parameter and three parameter kinetic models which can be derived from Langmuir-Hinshelwood type rate expressions were tried. These contained rate determining steps involving a bimolecular surface reaction between an absorbed hydrogen atom and either a methoxy or a formyl adsorbed species. The form of such rate expressions examined is

\[ r = k \left( P_{CO} P_{H_2}^2 - \frac{P_{MeOH}}{K_{eq}} \right) P_{CO}^a P_{H_2}^b \]  

(1)

It is found that the best possible fit is obtained with the rate expression (9)

\[ r = k \left( P_{CO} P_{H_2}^2 - \frac{P_{MeOH}}{K_{eq}} \right) P_{CO}^\theta P_{H_2}^{\theta m} \]  

(2)

where \( k = k_0 \exp \left( \frac{-E}{RT} \right) \) and \( n = -1.30 \pm 0.03 \). The Arrhenius plot of the temperature dependence of \( k \) is presented in Figure 1. With a single pre-exponential factor and a single overall activation energy obtained from linear regression of the rate constant data, large deviations (30-40%) are observed between predicted and measured reaction rates. Therefore, it is proposed that there is a decrease in the overall activation energy with temperature (Fig. 1). The overall activation energies and the corresponding pre-exponential factors computed at each temperature from Figure 1, are presented in Table 2. The error

319
accompanying the estimation of the activation energy is about ± 1000 cal/gmol based on the error involved in calculating the activation energy from the Arrhenius plot and the 15% maximum relative error in observed reaction rates. Equation 2 fits all our data with a maximum relative error of less than 15% (Fig. 2).

DISCUSSION

From the structure of rate Equation 2 we note that (i) the kinetics of the reverse reaction is accounted for; (ii) this rate expression contains only two parameters, the rate constant and an empirical constant, n (1,3,6,9); (iii) the reaction rate depends on a positive power of partial pressure of hydrogen and on a negative power of the partial pressure of carbon monoxide (1,9); and (iv) the measured overall activation energy decreases with increasing temperature (Table 2).

The term $P_{\text{H}_2}^{0.6}$ (Eq. 2) represents a formyl species, CHO-, formed by a reactive collision between CO and an adsorbed hydrogen atom. Mechanisms proposed by Herman et al., (4) and Kung (11) involve the formyl species as one of the surface intermediates. Assuming the formyl species to be the most abundant surface intermediate and the last reaction step of both mechanisms to be rate determining, a rate expression similar to Equation 2 can be derived (9,12).

In the mechanism reported in (4), the intermediates are proposed to be bonded to the surface cation via the carbon atom. Such a proposal is feasible for noble-metal catalysts because relatively strong metal carbon bonds can be formed, and there is ample evidence that CO adsorbs molecularly on these metals with the carbon end pointing towards the metal (11). However, it is proposed that the large dipole moments and the relatively uneven electron density distribution on oxide surfaces favor bonding of the surface to the oxygen atom of the intermediate (11). Thus a methoxy type derivative should be more likely.

In the mechanism proposed in (11), the formation of the methoxy intermediate from the formyl species involves rupture of two bonds and formation of three bonds. An elementary step is expected not to involve multiple bond ruptures and formations. This proposed elementary step of such a mechanism must therefore be looked upon cautiously in the absence of independent evidence that supports such a step.

The indication of the formyl species from the kinetics observed and the examination of the shortcomings of the mechanisms proposed in (4,11) allow us to suggest the mechanism (9)

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} \\
\text{CO} & \quad \text{C} \\
\text{I} & \quad \text{O} \\
\text{CH}_2\text{OH} + \text{H} & \quad \text{O}
\end{align*}
\]

for the supported Cu/ZnO catalyst we used. Here the symbols * , \(0\) and \(v\) represent a metal cation, a zinc or an oxygen site, and an oxygen vacancy respectively. "I" represents a likely intermediate between the formyl and methoxy species (9). Its possible structure needs to be investigated.

Rate equation 2 can be derived from this mechanism by assuming that the formyl species is the most abundant surface intermediate and that the surface reaction between the methoxy species and an
adsorbed hydrogen atom is the rate determining step (Agny, 1984). The main difference between this mechanism and the mechanism reported in (11) is the addition of an intermediate I between the formyl and methoxy intermediates.

Recently, coadsorption of CO and H$_2$ on ZnO and Cu/ZnO catalysts has been investigated at 270 K and subatmospheric pressures by Saussey et al., (13). The infrared spectrum of a mixture of CO and H$_2$ adsorbed on ZnO or Cu/ZnO reveals a pair of weak bands which have been assigned to vibrations of a surface formyl species. This is to our knowledge, the first report presenting direct evidence for a formyl species resulting from CO and H$_2$ interaction on Cu/ZnO catalysts. Deluzarche et al. (14) claim to have identified, by reactive scavenging, the formyl species on nickel. Kung (11) presents certain organometallic chemistry analogs to substantiate the formyl and methoxy species as intermediates in the mechanism he has proposed for methanol synthesis on ZnO and Cu/ZnO catalysts. These findings support our suggestion that adsorbed formyl species can be the most abundant surface intermediate (9), although further studies are necessary for such a proposal.

Formaldehyde has never been observed as an intermediate in methanol synthesis over ZnO or Cu/ZnO catalysts. A plausible explanation, perhaps, is that formaldehyde being a highly reactive intermediate undergoes rapid conversion in some species like the methoxy. Saida and Ozaki (3), who have studied the kinetics of methanol synthesis over a Cu/ZnO/Cr$_2$O$_3$ catalyst at near atmospheric pressures, conclude that quantitative interpretation of their data is possible only by assuming a reaction sequence involving formaldehyde. In a very recent work, Tawarah and Hansen (15) have investigated the kinetics of methanol decomposition over ZnO in the temperature range 563 to 613 K. Based on their observations, they confirmed the presence of formaldehyde in the reactor effluent with a mass spectrometer and with chemical methods. Invoking the principle of microscopic reversibility, it may be concluded that some of those intermediates (15) participate in the methanol synthesis reaction.

Ample evidence exists for the methoxy species on ZnO and ZnO/Cr$_2$O$_3$ catalyst (16-19). Since the active forms appear to be the metal cations for both ZnO and Cu/ZnO catalysts, it seems reasonable to assume the formation of methoxy species on the Cu/ZnO catalysts. Recently, the methoxy species has also been observed on a Cu/ZnO catalyst during methanol synthesis (20). For Cu/ZnO catalysts it is proposed that the intermediates, in the course of their progress towards the product methanol, orient themselves to form the more favorable oxygen-surface bond (11). These arguments lend support to the inclusion of a methoxy intermediate in the mechanism proposed for methanol synthesis over a Cu/ZnO/Al$_2$O$_3$ catalyst.

There can be considered to be three possible ways of CO$_2$ formation (i) the Boudouard reaction, (ii) the water gas shift reaction, and (iii) oxidation-reduction of the catalyst. In our reaction system, the carbon and oxygen balances based on CO in the feed and CO, CO$_2$ and CH$_3$OH in the reactor effluent are always closed. This enables us to suggest that the Boudouard reaction can be eliminated as a source of CO$_2$ (9).

Van Herwijnen and Dejong (21) have investigated the kinetics and mechanism of the water gas shift reaction on a Cu/ZnO catalyst in the range of 172 to 230 °C and pressures ranging from 1 to 6 atm. With a feed mixture containing CO, N$_2$ and small amounts of H$_2$O, they find their Cu/ZnO catalyst to be active in the forward direction of this reaction. This finding allows us to suggest that at our experimental conditions (250–290 °C, 3–15 atm), such a reaction is likely.
Herman et al., (4) have tested a Cu/ZnO/Al₂O₃ catalyst for a H₂/CO (76/24) mixture without CO₂. Although this catalyst is found to be selective to methanol, it is rapidly and irreversibly deactivated. Their examination of the catalyst by optical spectroscopy reveals only the pink color that is characteristic of copper. They attribute this to oxidation-reduction of the catalyst.

In view of these arguments and lack of any spectroscopical analysis of our catalyst, both the water gas shift reaction and oxidation-reduction of the catalyst are probably responsible for the formation of CO₂ at the conditions of our experiments.

SUMMARY

The kinetics of methanol synthesis from carbon monoxide and hydrogen over a commercial Cu/ZnO/Al₂O₃ catalyst has been investigated at temperatures between 250 and 290 °C and pressures between 3 and 15 atm. The highest catalytic activity is observed at 290 °C. A two parameter kinetic model that quantitatively describes the observed patterns is presented. It is also proposed that the formyl species, CHO-, appears to be the most abundant surface intermediate, and the rate determining step seems to be the surface reaction between the methoxy intermediate and an adsorbed hydrogen atom. Based on this study and current knowledge of supported Cu/ZnO catalysts, a mechanism for the methanol synthesis is proposed. The main feature of this mechanism is the shift from a carbon-surface bond to an oxygen-surface bond during the course of reaction.

NOMENCLATURE

\[ E = \text{Activation energy, cal/gmol} \]
\[ k = \text{Rate constant, gmol/g\text{-}cat/sec/atm} \]
\[ k_0 = \text{Pre-exponential factor, gmol/g\text{-}cat/sec/atm} \]
\[ K_{eq} = \text{Equilibrium constant of the methanol synthesis reaction} \]
\[ n = \text{Empirical constant} \]
\[ r = \text{Reaction rate, gmol/g\text{-}cat/sec} \]
\[ R = \text{Universal gas constant, cal/gmol/K} \]
\[ T = \text{Temperature of reaction, K} \]
REFERENCES


ACKNOWLEDGEMENTS

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TABLE 1.
Steady State Data of Methanol Synthesis of Cu/ZnO/Al₂O₃ Catalyst C79-2-01 of United Catalysts, Inc.

<table>
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<th>Run #</th>
<th>Reactor Temperature (°C)</th>
<th>Reactor Pressure (atm)</th>
<th>H₂ / CO F</th>
<th>Flow Rate at STP (cc/min)</th>
<th>Conversion of CO to Methanol (%)</th>
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* Trace amounts.

TABLE 2.
Pre-exponential Factors and Overall Activation Energies for Methanol Synthesis over Cu/ZnO/Al₂O₃ Catalyst C79-2-01 of United Catalysts, Inc.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pre-exponential Factor (nmol/g-cat/sec/atm)</th>
<th>Overall Activation Energy (cal/gmol)</th>
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<td>290</td>
<td>48</td>
<td>25,000 ± 1,000</td>
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324
Figure 1. Arrhenious Plot for the Methanol Synthesis Reaction in our System (Eq. 2).

Figure 2. Comparison Between Measured Reactions Rates and Predicted Reaction Rates (Eq. 2).