2
DOE/PC/89786--T3

DOE/PC/89786--T3

DE92 001962

PROGRESS REPORT

A NOVEL PROCESS FOR METHANOL SYNTHESIS

Principal Investigators

John W. Tierney

Irving Wender

**Chemical and Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, PA 15261.**

Prepared for the Department of Energy

Grant No. DE-FG22-89PC89786

December 1, 1990 through February 28, 1991

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

APR 20 1961

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1	Rate of Methanol Synthesis at Various Cu-chromite Loadings (at constant KOME loading)	11
2	Rate of Methanol Synthesis at Various Cu-chromite Loadings (at constant KOME/Cu-chromite ratio)	12
3	Size Distribution for Fresh Cu-chromite Catalyst .	13
4	Size Distribution for Cu-chromite Catalyst	14
5	Effect of Speed of Agitation on Rate of Methanol Synthesis	15
6	Effect of Speed of Agitation on Rate of Methanol Synthesis (data from Liu ⁽⁶⁾)	16
7	Rate of Methanol Synthesis using Cu-chromites with Different Surface Areas	17

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
1	Rate of Methanol Synthesis as a Function of Cu-chromite Loading at Constant KOME Loading (steady state rate at 40 hrs)	18
2	Rate of Methanol Synthesis as a Function of Cu-chromite Loading at Constant KOME/Cu-chromite Ratio (steady state rate at 40 hrs)	19
3	Properties of Commercial and In-house Cu-chromite	20

1.0 ABSTRACT

A bench-scale reactor is being used to conduct studies of the conversion of synthesis gas to methanol by a novel process. During the last quarter, we provided evidence for a two step reaction in series as against the direct hydrogenation of CO. We believe that the carbonylation reaction takes place in the liquid phase adjacent to the solid catalyst surface while the hydrogenolysis reaction is restricted to the surface of Cu-chromite. A non-equilibrium film model was proposed to explain the unexpectedly high reaction rates and the increased tolerance of the process to CO. In this quarter, we looked at the effect of Cu-chromite loading and surface area. A Cu-chromite catalyst was synthesized in-house using a coprecipitation technique and its activity compared to a commercial catalyst. The effect of stirrer speed and feed flow rate on the rate of MeOH synthesis was also investigated. In the absence of mass transfer limitations⁽¹⁾, the rate of methanol synthesis (expressed per unit weight of the catalyst) varies with catalyst loading and feed flow rate. It is likely that a deactivating species is generated in-situ or is present in the feed.

2.0 INTRODUCTION

An experimental investigation of a new process, developed in our laboratory, for converting synthesis gas to methanol is being carried out. It has significant advantages over the conventional gas phase synthesis in that the recycle of unreacted material can be virtually eliminated and it operates at lower temperatures. The reaction is not significantly poisoned by CO_2 or H_2O . It has been demonstrated that the reaction proceeds with good rates at 150°C and 6.3 MPa pressure. It is likely that the overall reaction proceeds through methyl formate as an intermediate. However, the nature of the mixed catalyst comprised of an alkali methoxide (e.g. KOMe) and Cu-chromite and of the possible intermediates is not well understood. The thrust of this research program is to obtain a better understanding of the reaction and particularly of the role of the catalyst. This information should make it possible to scale up the process.

Two papers have been published^(1,2) reporting our studies. One is a study of the individual consecutive reactions: carbonylation of methanol to methyl formate followed by the hydrogenolysis of the methyl formate. The other paper is on the concurrent reactions in which a carbonylation catalyst (e.g. potassium methoxide) and a hydrogenolysis catalyst (e.g. Cu-chromite) are used in the same reactor. The current work is part of

a three and a half-year project which started in September, 1989.

In this report, a soluble catalyst refers to an alkali salt (e.g. potassium methoxide) added as a powder to the reactor (the powder is soluble in methanol). The Cu-chromite powder is referred to as a heterogeneous catalyst. A homogeneous reaction is thus one which takes place in the liquid solution (not on the surface of Cu-chromite) and a heterogeneous reaction is one which takes place on the surface of Cu-chromite. It is possible that the soluble salt is adsorbed on the Cu-chromite and the combination then functions as the catalyst or the catalyst precursor.

3.0 RESEARCH OBJECTIVES

Principal research objectives are,

- 1) To determine the effect of alternate catalysts on the synthesis. This will include modified copper chromite catalysts in addition to soluble catalysts in the form of methoxides or similar salts.
- 2) To determine the nature of the active catalyst in this reaction and the effect of deactivating agents such as CO_2 , H_2O and CO .
- 3) To determine the rate limiting steps in this reaction to aid in scale-up. The effect of catalyst loading and reactor volume are of special importance.
- 4) To develop mathematical models which can be used to predict the rates of reaction and are suitable for use in scale-up of the reaction.

4.0 CURRENT WORK

In this quarter, we studied the effect of Cu-chromite loading and surface area and the effect of feed flow rate on the rate of MeOH synthesis.

4.1 Effect of Cu-chromite Loading

Our previous studies indicate that the hydrogenolysis reaction is the rate-determining step⁽³⁾. The soluble catalyst, typically KOMe, interacts with the Cu-chromite perhaps by generating an active site(s) for the hydrogenolysis reaction. An optimal ratio of the soluble to the heterogeneous catalyst was found⁽⁴⁾. A non-equilibrium film model⁽³⁾ was proposed in which the surface area of Cu-chromite is a key factor.

According to the principles of reaction kinetics, the rate of MeOH synthesis should be proportional to the concentration of Cu-chromite if hydrogenolysis is rate limiting. The rates of MeOH formation (expressed per unit weight of the catalyst) at constant KOMe loading were found to decrease with increased amount of the Cu-chromite catalyst (Figure 1; Table 1). One possibility is that the Cu-chromite may interact with the KOMe. To investigate this, the rate of MeOH synthesis was studied as a function of Cu-chromite loading at constant KOMe/Cu-chromite ratio (Figure 2).

Based on unit weight of the hydrogenolysis catalyst, higher MeOH formation rates (Table 2) were observed for lower catalyst loadings. The non-linear change in reaction rate with amount of catalyst suggests that other factors influence the rate at different loadings. These could include: (1) equilibrium for the hydrogenolysis reaction, (2) mass transfer limitations, (3) generation of other deactivating species in the reaction medium or entering with the feed. These possible effects are examined in the following discussion,

If a reaction is near equilibrium, the amount of catalyst has little effect on the rate. It has been shown previously from equilibrium calculations that the carbonylation reaction is in equilibrium in the bulk liquid and the hydrogenolysis reaction is far from equilibrium under the reaction conditions being used⁽³⁾. Equilibrium, therefore, does not limit the hydrogenolysis reaction.

4.2 Effect of Mass Transfer

Two kinds of mass transfer limitations are likely to exist in this three phase system, namely gas-liquid and liquid-solid mass transfer⁽⁵⁾. The former is mainly a function of the turbulence in the medium and can be identified by studying the effect of the speed of agitation on the MeOH synthesis rate. The mass transfer from liquid to solid is mainly a function of the

particle size of the catalyst. The particle size distribution of the heterogeneous Cu-chromite catalyst determined by a Microtrac size analyzer before and after reaction are shown in Figure 3. Although the distribution of particle sizes is bimodal, it is noteworthy that the particle sizes are small, of the order of about 10 microns before reaction and about 20 microns after reaction. It is unlikely that diffusion inside the catalyst pores would be limiting under these conditions, eliminating the possibility of liquid-solid mass transfer limitation. The rate of MeOH synthesis was studied at various agitation speeds for 15% loading of Cu-chromite, maintaining a 1:6 ratio of KOMe to Cu-chromite. The effect of stirring speed for a catalyst loading of 15 wt% (worst case scenario) is shown in Figure 4. The rate of MeOH synthesis was found to be independent of the stirring speed even at stirring speeds of the order of 250 rpm. Since all the experiments are carried out at a stirring rate of the order of 1500-2000 rpm, gas-liquid mass transfer is not rate limiting for the concurrent synthesis. Liu found a similar behavior for lower catalyst loadings⁽⁶⁾ This is shown in Figure 5.

4.3 Effect of Deactivating Species

It is likely that a deactivating species is either formed in the reaction or is present in the feed gases and is continually fed in to the reactor. The former could arise from the presence of deactivating agents such as H₂O and CO₂. While the use of increased

amounts of catalyst has led to increased production of CO_2 , it has not been possible to correlate the change in rate with changes in CO_2 and H_2O concentration, and it seems that these species are not the main cause of the non-linear behavior. Another possibility is that a transient deactivating species is formed or enters with the feed. Though such a species has not yet been identified, mathematical expressions (Appendix A) qualitatively show that this could result in a non-linear behavior. These possibilities will be examined in the future.

4.4 Effect of Feed Flow Rate

The rate of MeOH synthesis should be independent of the inlet syngas flow rate to the reactor using a stoichiometric feed composition in the well stirred reactor. However, the rate decreases with a decrease in the inlet flow rate. The MeOH synthesis rate at different flow rates for a mixed catalyst comprised of KOMe and Cu-chromite is summarized in Table 3.

It is likely that the non-linearity with Cu-chromite loading and effect of flow rate are related as the stripping rate of gas leaving the reactor decreases when the catalyst loading is increased (more reaction) or feed rate is decreased. A constant rate of inhibiting by-product will have a higher residence time in the reactor at lower flow rates and may affect a larger amount of catalyst at higher catalyst loadings. As shown in Appendix A, this

accounts qualitatively for the experimental observations.

4.5 Effect of Cu-chromite Surface Area

To study the effect of Cu-chromite surface area on the rate of MeOH synthesis, a Cu-chromite catalyst was prepared in our laboratory by the method suggested by Adkins et al⁽⁷⁾. This involves the precipitation of an ammonium salt according to the reaction,

The basic ammonium salt is then decomposed according to the reaction,

The properties of this catalyst are compared with the commercial Cu-chromite in Table 3. As shown by Monnier et al.⁽⁸⁾, the Cu-chromite surface area is a function of the Cu/Cr ratio. The rates of MeOH synthesis obtained with the two catalysts are compared in Figure 6. The two catalysts are similar in their surface morphologies as indicated by their XRD spectra; they differ, however, in their surface areas. The rates of MeOH formation (Figure 6) thus indicate that the Cu-chromite surface area does influence the rate. This is in agreement with the non-equilibrium film theory as proposed earlier⁽³⁾ which implies that a larger surface area would lead to higher MeOH formation rates.

5.0 FUTURE WORK

Studies will be carried out to investigate the activity and nature of the reactions with other catalysts for MeOH synthesis. Different salts will be investigated for their catalytic activity and to test the Cu-chromite regeneration hypothesis. The effect of addition of small amounts of MeF to the reaction feed will be tested in the hope of decreasing the initial transient period. Cu-chromites with different surface areas will be tested to investigate the effect on the rate of MeOH synthesis. The effect of different amounts of CO_2 and H_2O in the reaction mixture will be investigated.

6.0 REFERENCES

- 1) Z. Liu, J. W. Tierney, Y. T. Shah and I. Wender, Methanol Synthesis via Methyl Formate in a Slurry Reactor, **Fuel Processing Technology**, 23, 1989, p. 149-167.
- 2) Z. Liu, J. W. Tierney, Y. T. Shah and I. Wender, Kinetics of the Two Step Methanol Synthesis in the Slurry Phase, **Fuel Processing Technology**, 18, 1988, p. 185-199.
- 3) A Novel Process for Methanol Synthesis, progress report submitted to the Department of Energy, November 30, 1990.
- 4) A Novel Process for Methanol Synthesis, progress report submitted to the Department of Energy, February 28, 1990.
- 5) O. Livenspiel, **Chemical Reaction Engineering**, John Wiley and Sons, Inc., New York, 1985.
- 6) Z. Liu, **PhD. Dissertation**, submitted to the University of Pittsburgh, Pittsburgh, PA, 1988.
- 7) H. Adkins, E. E. Burgoyne and H. J. Schneider, The Copper-Chromium Oxide Catalyst for Hydrogenation, **American Chemical Society Journal**, 72, 1950, p. 2626-2629.
- 8) J. R. Monnier, M. J. Hanrahan and G. Apai, A Study of the Catalytically Active Copper Species in the Synthesis of Methanol over Copper-Chromium Oxide, **Journal of Catalysis**, 1989, p. 119-126.

Figure 1: Rate of Methanol Synthesis at Various Cu-chromite Loadings (at constant KOME loading)

Figure 2: Rate of Methanol Synthesis at Various Cu-chromite Loadings (at constant KOMe/Cu-chromite ratio)

Figure 3(a): Size Distribution for Fresh Cu-chromite Catalyst

Figure 3(b): Size Distribution for Cu-chromite Catalyst

Figure 4: Effect of Speed of Agitation on Rate of Methanol Synthesis

Figure 5: Effect of Speed of Agitation on Rate of Methanol Synthesis (data from Liu⁽⁶⁾)

Figure 6: Rate of Methanol Synthesis using Cu-chromites with Different Surface Areas

Table 1: Rate of Methanol Synthesis as a Function of Cu-chromite
Loading at Constant KOME/Cu-chromite Ratio
(steady state rate at 40 hrs)

Amount of Catalyst wt. KOME/ wt. Cu-chromite	Rate of Methanol Synthesis gmoles/h/kg cat
0.5/ 3.0	20.67
1.0/ 6.0	10.03
2.76/ 17.75	2.32

Note: Ratio of KOME to Cu-chromite is 1:6.

Table 2: Rate of Methanol Synthesis as a Function of Cu-chromite
Loading at Constant KOME Loading
(steady state rate at 40 hrs)

Amount of Catalyst wt. KOME/ wt. Cu-chromite	Rate of Methanol Synthesis gmoles/h/kg cat
1.0/ 3.0	19.05
1.0/ 6.0	10.03

Note: KOME loading is constant.

Table 3: Properties of Commercial and In-house Cu-chromite

Type	Commercial ^a	In-house
Nominal Composition	32.1 wt% Cu 29.0 wt% Cr	- -
Cu/Cr molar ratio	0.905	0.9
Ba/Cu molar ratio	-	0.11
Surface Area (m ² /gm)		
Before reaction	100.3 (103) ^b	18.785
After reaction	110.06	18.386
Average Diameter (microns)		
Before reaction	11.99 ^c	-
After reaction	18.80 ^c	-
Bulk Density (g/cc)	0.64	-

^a Manufactured by Calsicat, Mallinckrodt Inc.

^b Surface area provided by the manufacturer

^c Measured using a Microtrac Size Analyzer

APPENDIX A

The rate of methanol synthesis was found to vary with feed flow rate and the amount of the catalyst. Qualitatively, it was found that the rate of MeOH synthesis expressed per gram of catalyst increased with an increase in the feed flow rate and with a decrease in the amount of catalyst present. This anomalous behavior was previously explained assuming the formation of a deactivating species in the reaction mixture. This seemed likely in the presence of a large number of possible deactivating factors in the reaction medium like H_2O and CO_2 . However, changes in the concentration of these species to account for changes in the rate of MeOH synthesis were not identified. In light of this, a further search was undertaken to isolate the cause of this behavior. A guard bed was introduced in the CO line to remove possible contaminants such as iron carbonyl. It has been known that these impurities exist in CO and do affect the rate of MeOH synthesis (especially in the direct MeOH synthesis). A modelling effort was undertaken on the lines similar to our previous modelling effort, encompassing the effect of a deactivating species entering the reactor with the feed. The equations are listed below.

The following assumptions have been made in the mathematical representation of the effect of a deactivating agent entering with the feed or being generated in-situ on the rate of

methanol synthesis.

- 1) There is no mass transfer limitations in the reactor. This has been shown to be the case in our reactor system⁽⁶⁾.
- 2) The contents of the reactor are well mixed.
- 3) Isothermal conditions prevail at steady state operation.
- 4) The rate of methanol formation is directly proportional to the concentration of the heterogeneous catalyst.
- 5) The stoichiometric H_2/CO ratio required is 2.0. This has been shown to be the case by product gas analysis in a gas chromatograph.
- 6) The consumption of H_2 is solely in the formation of methanol. Thus the net rate of methanol formation is equal to one-half the rate of H_2 consumption.
- 7) The rate of generation of the deactivating species is independent of the feed rate and the concentration of the heterogeneous catalyst.

The following nomenclature has been used in the equations listed below,

R_1	Rate of methanol synthesis (gmoles/min)
R_2	Rate of production of the deactivating species (gmoles/min)
F_1	Total feed mass flow rate (gmoles/min)
F_2	Total exit mass flow rate (gmoles/min)
Y_1	Mole fraction of the deactivating species in the feed gas
Y_2	Mole fraction of the deactivating species in the outlet gas

C_0	Initial concentration of catalyst taken (gms/liter)
C	Concentration of active catalyst in the reactor (gms/liter)
α	Proportionality factor for the deactivating species
K_1	Rate constant assuming a pseudo-first order rate expression

If a deactivating species is present in the feed or is generated in the reaction medium, it can cause the feed flow rate and catalyst loading to affect the rate of methanol synthesis as described below,

Assuming the rate of methanol synthesis to be proportional to the amount of heterogeneous catalyst, the rate of methanol formation can be expressed as,

$$R_1 = K_1(1-\alpha y_2)C \quad (1)$$

It is assumed that the ratio of H_2/CO equals 2 in the feed gas. This is the stoichiometric requirement and the net rate of methanol formation is then equal to one half of the rate of hydrogen consumption, assuming that at steady state all the hydrogen is consumed in the formation of methanol via the hydrogenolysis of methyl formate. A mass balance over H_2 results in,

$$R_1 = \frac{1}{2} \left(\frac{2F_1}{3} - \frac{2F_2}{3} \right) = \frac{F_1 - F_2}{3} \quad (2)$$

1. Presence of a Deactivating Agent in the Feed

Effect of feed flow rate on methanol synthesis rate

To find the effect of flow rate on reaction rate, we differentiate R_1 w.r.t. F_1 keeping all the other variables constant including the amount of catalyst added. It is assumed that the deactivating agent is in equilibrium on the solid surface and thus at steady state the amount of active catalyst is constant. Differentiating equation (1) leads to,

$$\frac{dR_1}{dF_1} = -K_1 \alpha C \frac{dy_2}{dF_1} \quad (3)$$

which results in,

$$\frac{dy_2}{dF_1} = -\frac{1}{K_1 \alpha C} \frac{dR_1}{dF_1} \quad (4)$$

Differentiating equation (2) results in,

$$\frac{dR_1}{dF_1} = \frac{1}{3} \left(1 - \frac{dF_2}{dF_1} \right) \quad (5)$$

which leads to,

$$\frac{dF_2}{dF_1} = 1 - 3 \frac{dR_1}{dF_1} \quad (6)$$

If the deactivating agent enters in the feed and there is no generation in the reaction medium then at steady state, a mass balance over the deactivating agent (accumulation = 0) results in,

$$F_1 y_1 - F_2 y_2 = 0 \quad (7)$$

Differentiating equation (7) results in,

$$y_1 - y_2 \frac{dF_2}{dF_1} - F_2 \frac{dy_2}{dF_1} = 0 \quad (8)$$

Substituting equations (4) and (6) in (8) we have,

$$y_1 - y_2 + 3y_2 \frac{dR_1}{dF_1} + \frac{F_2}{K_1 \alpha C} \frac{dR_1}{dF_1} = 0 \quad (9)$$

which results in,

$$\frac{dR_1}{dF_1} = \frac{1 - \frac{y_1}{y_2}}{3 + \frac{F_2}{K_1 \alpha C y_2}} \quad (10)$$

Since y_2 is always greater than y_1 , the R.H.S. is always positive and hence as the flow rate decreases, the rate of methanol formation decreases. This also means that,

$$0 < \frac{dR_1}{dF_1} < 1 \quad (11)$$

Effect of catalyst amount on methanol synthesis rate

If the feed flow rate is kept constant and the catalyst concentration is changed, by differentiating equation (1) with respect to the catalyst concentration, we have,

$$\frac{dR_1}{dC} = K_1(1-\alpha y_2) - K_1\alpha C \frac{dy_2}{dC} \quad (12)$$

and from (2)

$$\frac{dR_1}{dC} = -\frac{1}{3} \frac{dF_2}{dC} \quad (13)$$

At steady state from equation (7),

$$F_1 y_1 - F_2 y_2 = 0 \quad (14)$$

On differentiation with respect to the catalyst amount we have,

$$y_2 \frac{dF_2}{dC} + F_2 \frac{dy_2}{dC} = 0 \quad (15)$$

Incorporating (12) and (13) in equation (15) results in,

$$\frac{dR_1}{dC} = \frac{K_1(1-\alpha y_2)}{1 + \frac{3K_1\alpha C y_2}{F_2}} \quad (16)$$

As C increases, F_2 decreases and y_2 increases resulting in a decrease in dR_1/dC . Thus an increase in the catalyst concentration decreases the rate of reaction expressed per gram of the catalyst.

2. Generation of a Deactivating Species in the Reaction

Effect of flow rate on methanol synthesis rate

Another possibility is that a deactivating species is formed in the reaction medium (e.g. CO_2 or H_2O). Assuming that this deactivating agent is formed solely in the reactor and is independent of the feed flow rate and the catalyst concentration, a material balance over the deactivating species results in,

$$R_2 = F_2 y_2 \quad (17)$$

Differentiating (17) with respect to the feed rate results in,

$$\frac{dR_2}{dF_1} = F_2 \frac{dy_2}{dF_1} + y_2 \frac{dF_2}{dF_1} = 0 \quad (18)$$

Substituting dy_2/dF_1 from equation (4) and dF_2/dF_1 from equation (6) in (18) and rearranging, we get,

$$\frac{dR_1}{dF_1} = \frac{1}{3 + \frac{F_2}{K_1 \alpha C y_2}} \quad (19)$$

Using the same argument as before, since the R.H.S. is positive the rate of methanol formation will decrease with a decrease in the feed flow rate.

Effect of catalyst concentration on methanol synthesis rate

Assuming that R_2 is independent of the amount of catalyst, differentiating equation (17) with respect to the catalyst concentration C and combining equations (12) and (13) results in,

$$\frac{dR_1}{dC} (F_2 + 3K_1 \alpha C y_2) = K_1 (1 - \alpha y_2) F_2 \quad (20)$$

This on rearrangement gives,

$$\frac{dR_1}{dC} = \frac{K_1 (1 - \alpha y_2)}{1 + \frac{3K_1 \alpha C y_2}{F_2}} \quad (21)$$

which is the same as (16). It qualitatively explains the observation that the rate of methanol formation (expressed per gram

of catalyst) decreases with an increase in the catalyst loading.

In the above discussion, it has been assumed that the rate of formation of the deactivating species is independent of the catalyst concentration. This may not necessarily be true. In fact if a deactivating species is being generated then the rate of generation is likely to be proportional to the heterogeneous catalyst concentration. Thus, if $R_2 = K_{\text{deact}}C$ then $dR_2/dC = K_{\text{deact}}$ (constant). This introduces an additional complexity in the equation which would have to be accounted for.

END

**DATE
FILMED**

12/11/91