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PROGRESS REPORT

A NOVEL PROCESS FOR METHANOL SYNTHESIS

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1.0 ABSTRACT

A bench-scale reactor is being used to study the conversion of synthesis gas to methanol (MeOH) in the liquid phase by a novel method. In previous reports, we provided evidence for a two step reaction consisting of a carbonylation reaction taking place mainly in the "film" close to a copper chromite surface followed by a hydrogenolysis reaction taking place on the surface of the copper chromite. The interaction between the two catalysts enhances the rate of methanol formation. In this quarter, we reexamined the equilibrium concentration for methyl formate and obtained data at higher loadings of copper chromite.

2.0 INTRODUCTION

A new method for converting synthesis gas to MeOH, which was developed in our laboratory and which we call the concurrent synthesis of MeOH, is being investigated. The method has advantages over the conventional gas phase synthesis in that recycle of unreacted material can be greatly reduced and temperature is lower. The reaction is tolerant to CO_2 or H_2O. It has been demonstrated that the reactions proceed with good rates at 150°C and 63 bar pressure. We have previously provided evidence that the formation of MeOH proceeds through MeF in the concurrent synthesis. However, the nature of the mixed catalyst, comprised of an alkali methoxide (e.g. KOMe) and copper chromite and of the possible intermediates is not understood. The thrust of this research program is to obtain a better understanding of the reaction and particularly of the role of the catalyst(s). This information should help 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 reactions: the carbonylation of MeOH to MeF and the hydrogenolysis of MeF to MeOH. The other paper describes the concurrent reaction in which a carbonylation catalyst (e.g. KOMe) and a hydrogenolysis catalyst (e.g. copper chromite) are used in the same reactor. A number of papers are under preparation for publication. 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 compound (e.g. KOMe) added as a powder to the reactor (the powder is soluble in MeOH); the copper chromite is referred to as a heterogeneous catalyst. A "homogeneous" reaction is one which takes place in the liquid solution (not on the surface of copper chromite) and a heterogeneous reaction is one which takes place on the surface of copper chromite. It is possible that the soluble salt is adsorbed on the copper 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 various catalysts on the synthesis of MeOH. 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 and H_2O.

3) To determine the rate-limiting step(s) in this reaction. 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 which would be useful in eventual scale-up of the reaction.

4.0 CURRENT WORK

In this quarter, we reexamined the equilibrium condition for MeF in the concurrent synthesis and obtained data at high loadings of copper chromite.

4.1 Liquid Phase Composition of MeF

We had previously reported that MeF is formed in equilibrium amounts in all our runs. This led to the conclusion that the hydrogenolysis of MeF was the rate determining step. However, there was a difference in the experimental MeF concentration in the liquid and the equilibrium concentration predicted by Liu et. al.(2) We therefore reexamined the equilibrium mole fractions predicted by Liu for the carbonylation reaction. This was done by contacting MeOH and CO in a 300 ml autoclave at the desired temperature (150°C) and waiting until there was no further pressure change. A typical plot of pressure versus time is shown in Figure 1. The equilibrium mole percent MeF was obtained by analyzing the equilibrium liquid. Both the forward and the reverse reaction were studied (the latter, by starting with MeF as charge). The equilibrium compositions and equilibrium constants for three pressures for both the forward and reverse reaction are shown in Tables 1 and 2. The equilibrium ratios vary consistently with pressure. The equilibrium MeF concentration was then plotted versus CO partial pressure. As shown in Table 3, these values agree well with those predicted by Liu et al.(2) although there is more difference at the lower partial pressures of CO.

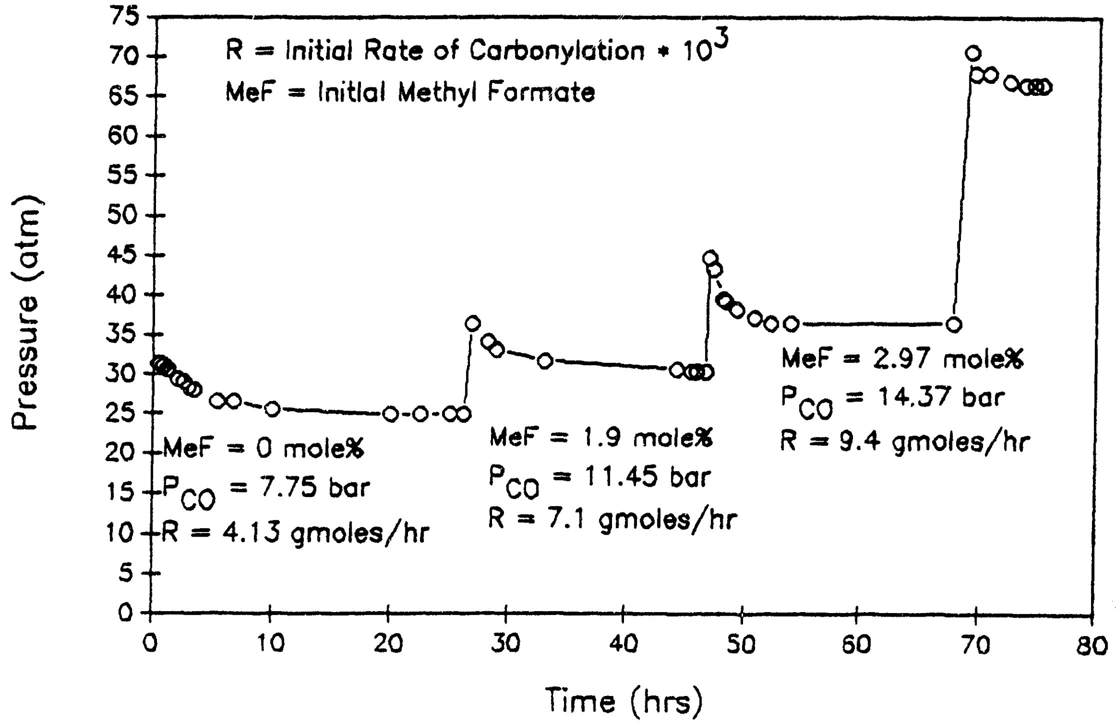

Figure 1. Plot of pressure versus time for measurement of equilibrium concentration of methyl formate in carbonylation reaction. Temperature, 150°C; 0.5 grams KOMe; initial charge 150 cc MeOH.

The mole percent MeF measured in a baseline run (T = 423 K, P = 63 bar, 0.5 grams $KOCH_3$, 3 grams copper chromite) is presented in Table 3 together with the equilibrium MeF mole percent. It can be seen from Table 3 that the MeF is not in equilibrium and hence neither the carbonylation nor the hydrogenolysis reactions is controlling.

Since methanol is produced from methyl formate, the rate of MeOH formation is proportional to MeF concentration. As shown in Table 4, an increase in $KOCH_3$ loading results in increased MeF concentration in the liquid, the MeF approaching equilibrium at higher loadings. We have previosly shown that using three grams of copper chromite, the rate of MeOH synthesis is a maximum when 0.5 grams $KOCH_3$ are used(3) and that for low loadings of $KOCH_3$, the rate of MeOH synthesis increases with increased MeF levels in the liquid. Using larger amounts of KOMe the rate of MeOH synthesis decreases, although the MeF concentration increases (Table 4). This may be due to alkali blocking of the hydrogenolysis sites on the surface of copper chromite at the high $KOCH_3$ loading.

4.2 Effect of Heterogeneous Catalyst Loading on the Rate of Methanol Synthesis

At low loadings of $KOCH_3$, the carbonylation reaction is not at equilibrium, indicating that the rate of carbonylation is limiting the extent of reaction. At the high $KOCH_3$ loadings, the carbonylation reaction is close to equilibrium as indicated by the MeF composition, and hence MeOH formation is controlled by the hydrogenolysis reaction. High $KOCH_3$ loadings may result in alkali blocking some of the available sites for hydrogenolysis. The rate of MeOH formation as a function of copper chromite loading is shown in Figure 2. MeOH synthesis rates are expressed per kg of copper chromite and decrease with an increase in copper chromite loading although the amount of MeOH formed (gmoles/hr) increases. This behavior is in agreement with an alkali site blocking hypothesis. Although the rate of reaction per gram of catalyst is high for low loadings, it may be difficult to get high volumetric productivity using high catalyst loadings. More work is needed to improve reactor volumetric productivity.

We have previously studied the behavior of sodium, potassium, rubidium and cesium methoxide together with copper chromite(4) and found that the highest reaction rate was obtained using $KOCH_3$. This was unexpected since $CsOCH_3$ is more effective for carbonylation(2,5). This difference may be due to increased site blocking by the larger cesium cation on the surface of copper chromite.

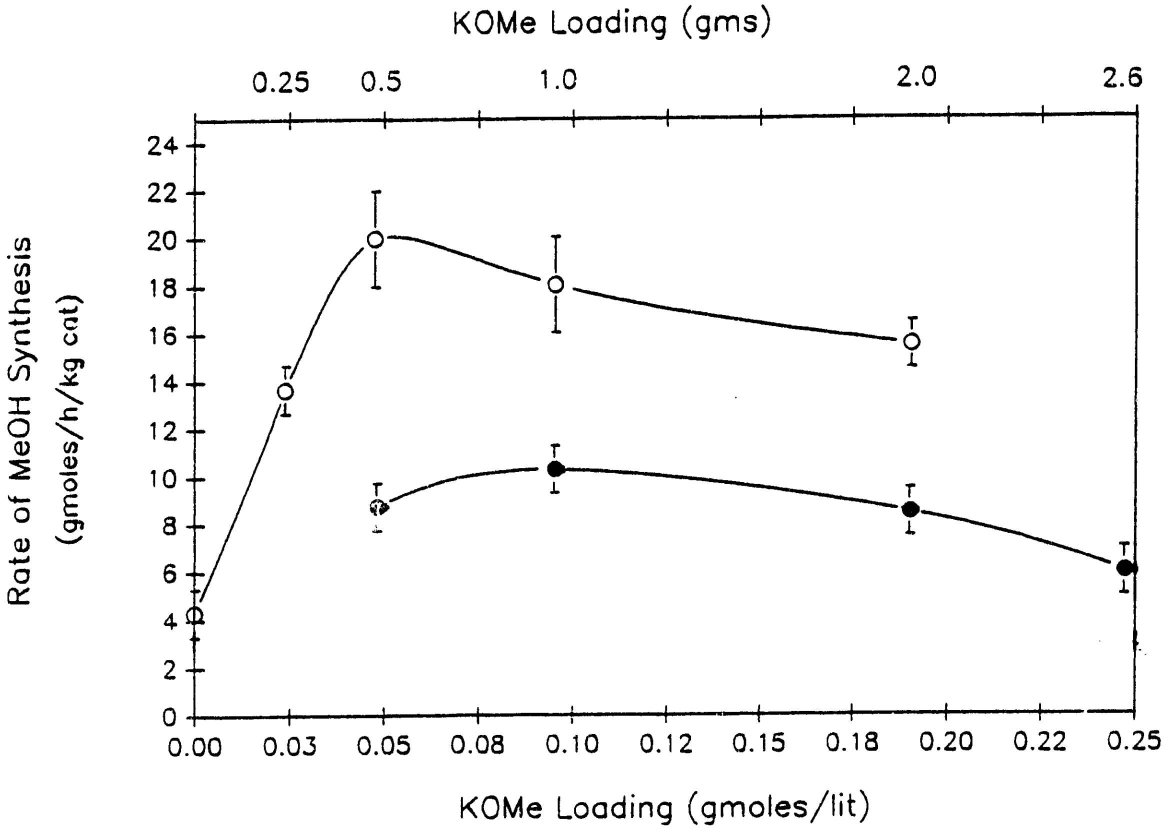

Figure 2. Rate of Methanol Synthesis as a Function of KOMe Loading for Three Grams (○) and Six Grams (●) of Copper Chromite. Temperature, 150°C; P, 63 bar; H_2/CO, 2; Methanol Charge, 150 cc.

Table 1: Concentration of MeF in Liquid by the Forward Carbonylation Reaction

Total Pressure (bar)	Partial Pressure of CO (bar)	Mole Percent MeF measured at equilibrium	Equilibrium MeF predicted by Liu et al. (mole%)	$K_c = \frac{x_{MeF} * 103}{x_{MeOH} * P_{CO}}$
24.86	7.75	1.9	2.17	2.5
30.31	11.44	2.97	3.17	2.67
36.45	14.37	4.0	4.10	2.9

Table 2: Concentration of MeF in Liquid by the Reverse Carbonylation Reaction

Total Pressure (bar)	Partial Pressure of CO (bar)	Mole Percent MeF measured at equilibrium	Equilibrium MeF predicted by Liu et al. (mole%)	$K_c = \frac{x_{MeF} * 103}{x_{MeOH} * P_{CO}}$
18.38	2.93	0.96	1.02	3.2
32.7	12.96	3.53	3.57	2.82
41.9	18.87	5.05	5.12	2.82

For our standard run, i.e. T = 423.15 K, P = 63 bar, P_{CO} = 11.33 bar

Equilibrium MeF mole percent should lie between 2.95 and 3.15.

Average MeF equilibrium mole percent = 3.1

Table 3: Experimental Methyl Formate Concentration as a Function of CO Partial Pressure. Temperature, 423 K; 0.5 grams $KOCH_3$; 3 grams Copper Chromite.

Feed H_2/CO	H_2/CO in Reactor	CO Partial Pressure (bar)	Equilibrium MeF Conc. (mole%)	Equilibrium MeF Predicted by Liu et al. (mole%)	MeF in Liquid (Measured) (mole%)
3.1	4.6	6.07	1.5	1.705	0.79
2.92	4.3	6.41	1.65	1.799	
2.6	3.6	7.39	1.93	2.06	0.83
2.0	2.0	11.33	3.1	3.13	1.75
1.2	0.6	21.25	5.7	5.79	4.43
1.0	0.45	23.45	6.2	6.28	5.2
0.55	0.2	28.33	7.45	7.49	7.3

Table: 4 Methyl Formate Mole Fraction in Liquid as a Function of $KOCH_3$ Loading

$KOCH_3$ Loading gms	Methyl Formate in Liquid mole%	Equilibrium Methyl Formate mole%
0.25	1.17	3.1
0.5	1.79	3.1
2.0	2.45	3.1

5.0 FUTURE WORK

Work will continue on measurement of the activity of other catalysts for MeOH synthesis. Kinetic and process modeling will be continued into the next quarter. Preparation of the final report will begin.

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.

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