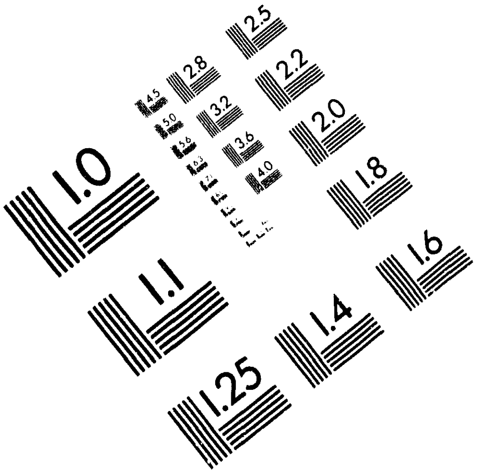

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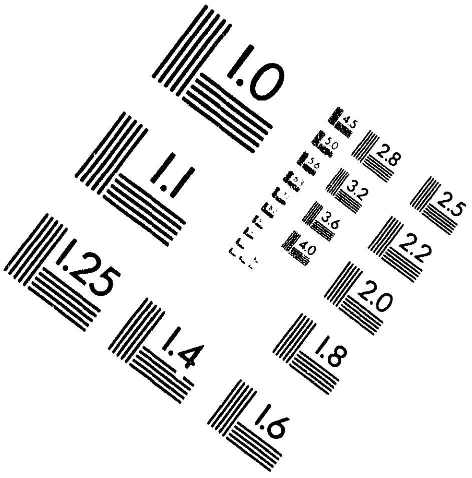

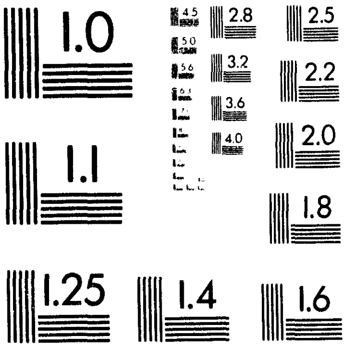

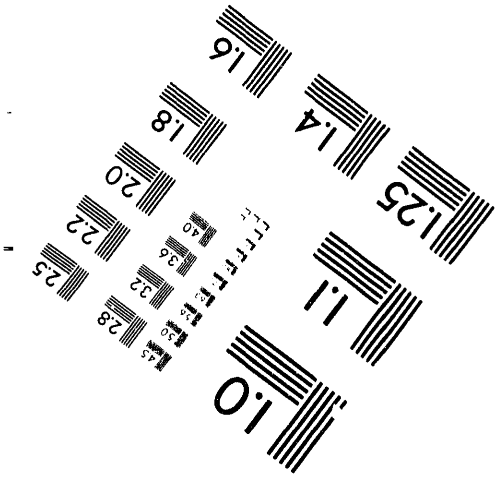

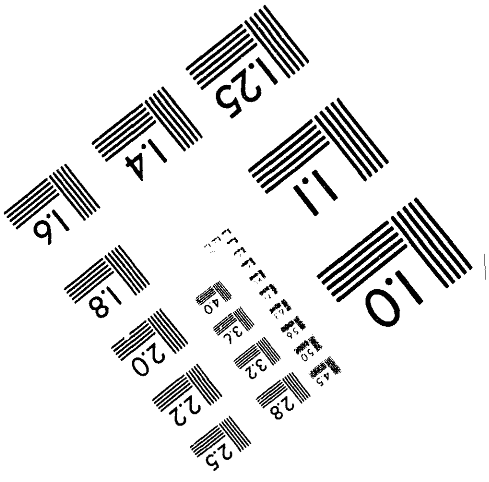

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A NOVEL PROCESS FOR METHANOL SYNTHESIS

Final Report

John W. Tierney
Irving Wender

Work Performed Under Contract Number: DE-FG22-89PC89786

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By

Chemical and Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, Pennsylvania 15261

January 25, 1994

PREFACE

This is the final report for a three year research program sponsored by the Department of Energy through the University Coal Research Program. The research was carried out by Dr. Vishwesh Palekar as part of the requirements for the PhD in Chemical Engineering in the Department of Chemical and Petroleum Engineering at the University of Pittsburgh. The work was supervised by Professors John W. Tierney and Irving Wender. Dr. Jeon Hung, a Research Associate in the Chemical and Petroleum Engineering Department, also made substantial contributions. The Department of Energy Project Officer was Robert Gormley. The material in this report is taken from Dr. Palekar's PhD dissertation.

In addition to this report, the following publications, presentations, and patents were produced as a result of this work.

Publications

V.M. Palekar, "Liquid Phase Synthesis of Methanol/Methyl Formate under Mild Conditions," Ph D Dissertation, University of Pittsburgh, (1993).

V.M. Palekar, J.W. Tierney and I. Wender, "Alkali Compounds and Copper Chromite as Low-Temperature Slurry Phase Methanol Catalysts," *Applied Catalysis A: General*, **103**, 105-122, (1993).

V.M. Palekar, H. Jung, J.W. Tierney and I. Wender, "Slurry Phase Synthesis of Methanol with a Potassium Methoxide/Copper Chromite Catalytic System,"*Applied Catalysis A: General*, **102**, 13-34 (1993).

Patents

"Methanol Synthesis Using a Catalyst Combination of Alkali or Alkaline Earth Salts and Reduced Copper Chromite," U.S. Patent 5,221,652, John W. Tierney, Irving Wender and Vishwesh M. Palekar, June 22, 1993.

Two additional patent applications are being processed.

Presentations

V.M. Palekar, H. Jung, J.W. Tierney and I. Wender, "A Low Temperature Synthesis of Methanol from Syngas," Spring Meeting, American Institute of Chemical Engineers, Houston TX, April (1993).

V. Palekar, J.W. Tierney and I. Wender, "The Effect of CO_2 and H_2O and Their Interaction in a Novel Slurry Phase Synthesis of Methanol," Pittsburgh Coal Conference, Pittsburgh PA, October 14-18 (1991).

V. Palekar, J.W. Tierney and I. Wender, "Catalytic Studies on a Novel Synthesis of Methanol," Summer National Meeting, American Institute of Chemical Engineers, Pittsburgh PA, August 18-21 (1991).

V. Palekar, J.W. Tierney and I. Wender, "A Novel Process for Methanol Synthesis," Department of Energy University Coal Research and Historically Black Colleges and Universities Contractors' Conference, Pittsburgh PA June 25-27 (1991).

V. Palekar, J.W. Tierney and I. Wender, "Methanol Synthesis Using an Alkali Methoxide/Cu Chromite Catalytic System," Thirtieth Annual Spring Symposium, Pittsburgh Cleveland Catalysis Society, Pittsburgh PA, May 29-31 (1991).

V. Palekar, J.W. Tierney and I. Wender, "Catalytic Studies on a Concurrent Methanol Synthesis in the Liquid Phase," 12th North American Meeting, Catalysis Society, Lexington KY, May 5-9 (1991).

V. Palekar, J.W. Tierney and I. Wender, "The Synthesis of Methanol by a Novel Method," AIChE Annual Meeting, Chicago IL, November 11-16, (1990)

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Z. Liu, V. Palekar, J.W. Tierney, I.Wender and Y.T. Shah, "Synthesis of Methanol in a Methanol-Rich Liquid Phase," AIChE Summer National Meeting, San Diego CA, August 19-22 (1990).

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Z. Liu, J.W. Tierney, Y.T. Shah and I. Wender, "Methanol Synthesis via Methyl Formate in a Slurry Reactor," Fuel Processing Technology, 23, 149-167 (1989).

Z. Liu, J.W. Tierney, Y.T. Shah and I. Wender, "Kinetics of Two-Step Methanol Synthesis in the Slurry Phase," Fuel Processing Technology, 185, 18 (1988).

ABSTRACT

The use of methanol (MeOH) as a fuel additive and in MTBE production has renewed interest in the search for improved MeOH processes. Commercial processes are characterized by high pressures and temperatures with low per pass conversion (10-12%). Efforts are underway to find improved MeOH synthesis processes. A slurry phase "concurrent" synthesis of MeOH/methyl formate (MeF) which operates under relatively mild conditions (100°C lower than present commercial processes) was the subject of investigation in this work. Evidence for a reaction scheme involving the carbonylation of MeOH to MeF followed by the hydrogenolysis of MeF to two molecules of MeOH - the net result being the reaction of H_2 with CO to give MeOH via MeF, is presented. Up to 90% per pass conversion and 98% selectivity to methanol at rates comparable to commercial processes have been obtained in spite of the presence of as much as 10,000 ppm CO_2 and 3000 ppm H_2O in the gas and liquid respectively.

The equilibrium concentration of MeF in liquid decreases rapidly with increasing temperature. Thermodynamic and reaction studies indicated that the synthesis is best carried out at a temperature in the range of 100-180°C and pressure between 30- 65 atm. A number of active catalytic systems including mixed catalysts comprised of alkali (Na, K, Rb and Cs) compounds and copper chromite as well as alkali impregnated copper chromite have been identified. The alkali hydroxide, formate, carbonate, bicarbonate and oxide are shown to be as active as the corresponding alkali methoxide. A $KOCH_3$/copper chromite mixed catalyst is likely to be the most favored catalyst combination due to its high stability under the operating conditions used. Evidence for a synergistic effect between the alkali methoxide and the copper chromite catalysts is presented. The copper chromite ensures the activity of the various alkali anions by conversion to the corresponding alkali methoxide. This interaction is responsible for high MeOH formation rates and increased tolerance to the presence of H_2O and CO_2.

Reaction studies indicated that the rate of MeOH formation is dependent on both the carbonylation and the hydrogenolysis reaction; the carbonylation reaction becomes more important at higher copper chromite loadings. The presence of small amounts of H_2O and CO_2 decreases the rate of carbonylation and results in a MeF concentration less than the equilibrium concentration under the operating conditions used. The alkali distributes itself between the liquid and the copper chromite surface; the latter likely results in site blockage decreasing the hydrogenolysis reaction rate.

The effect of process parameters such as temperature, pressure, H_2/CO ratio in the reactor, flow rate and catalyst loading were also investigated. The use of temperatures above 170°C at a pressure of 50 atm results in MeF being the limiting reactant. Small amounts of CH_4 are also formed. Significant MeOH synthesis rates at a pressure in the range of 40-50 atm. makes possible the elimination of an upstream shift reactor and the use of an air-blown syngas generator. The nature of the catalysts was studied and correlated with the behavior of the various species in the concurrent synthesis.

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1.0 INTRODUCTION

1.1 HISTORY OF THE CONCURRENT METHANOL SYNTHESIS

The two step reaction scheme for MeOH production via MeF is as follows,

$$CO + CH_3OH \rightleftharpoons HCOOCH_3 \qquad (1\text{-}1)$$

$$HCOOCH_3 + 2H_2 \longrightarrow 2CH_3OH \qquad (1\text{-}2)$$

The overall reaction from equations 1-1 and 1-2 is,

$$2H_2 + CO \longrightarrow CH_3OH \qquad (1\text{-}3)$$

It was first proposed by Christiansen(1)* in 1919 and then by BASF in 1925(2) that these two reactions could be carried out in two-stages for methanol synthesis. The two-stage methanol synthesis was subsequently described in other patents(3,4) as well as in a technical paper(5). A pilot plant based in Germany, is mentioned in a patent(6) issued in 1954, where the carbonylation reaction was carried out in a methanolic solution of sodium methoxide, and the hydrogenolysis reaction was carried out in a separate reactor in the gas phase using copper chromite as a catalyst. The specified conditions were 20-60 atm and 100- 170°C. In fact, reaction 1-1 has been reported to proceed fairly rapidly in the homogenous phase at only 80°C and 30-40 atm using sodium methoxide(7) while reaction 1-2 occurs on a heterogenous catalyst at about 110-180°C and 30 atm(8) catalyzed by copper

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*Parenthetical references placed superior to the line of text refer to the bibliography.

chromite. However, after this, nothing was published in the open literature about the two stage synthesis, probably due to the severe deactivating effect of species such as H_2O and CO_2 on the $NaOCH_3$ catalyst in the carbonylation reaction.

The first report of synthesizing MeOH in a single reactor came in 1982, when Aker Engineering reported an alkali or alkaline earth alkoxide/copper chromite mixed catalytic system in the liquid phase which could convert syngas to a mixture of MeOH and MeF in a single reactor at 110°C and pressures as low as 5 atm(9). (The reported value for the pressure seems questionable because of the low equilibrium conversion at 5 atm). This was followed by feasibility studies by Liu et al.(10) and Onsager et al.(11,12) who obtained high methanol synthesis rates at low temperatures ($T < 180°C$). Economic evaluations indicated that this concurrent synthesis could be competitive with present day technologies(12).

1.2 EQUILIBRIUM CO CONVERSION IN THE TWO-STAGE AND CONCURRENT SYNTHESES

Since the overall reaction in the two stage synthesis and the concurrent synthesis is the same as the direct synthesis, the overall thermodynamics must be the same. The synthesis of MeOH is exothermic; therefore the lower the operating temperature, the higher is the equilibrium conversion of CO. Equilibrium CO conversion for a H_2/CO feed ratio of 2 in a single reactor is shown in Figure 1. It can be seen that at a temperature of 150°C and a pressure of 63 atm, the equilibrium conversion is above 95%. High conversions can be obtained in the two-stage and the concurrent synthesis due to lower operating temperatures.

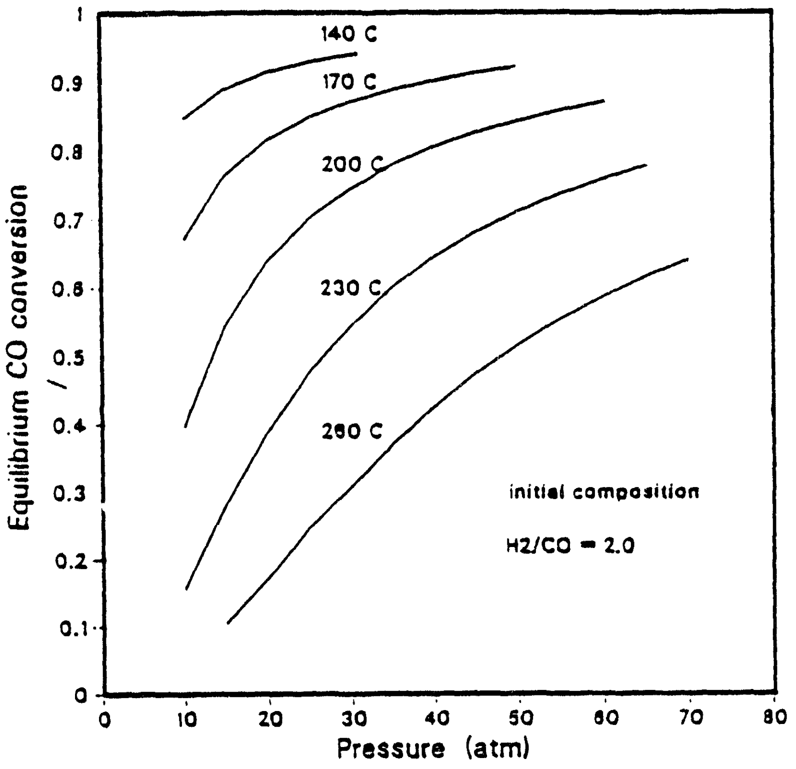


Figure 1. Equilibrium CO Conversion to MeOH for H_2/CO Feed Ratio of Two

1.3 CARBONYLATION OF ALCOHOL

The carbonylation of an alcohol is an exothermic reaction. For methanol carbonylation, ΔH_{298} = - 38.65 kJ/mol. A decrease in temperature and an increase in pressure tends to favor the reaction of MeOH to form MeF. Favored operating conditions are 80-100°C and 30-50 atm(3). The carbonylation of MeOH to MeF is an equilibrium reaction whose dependence on temperature and pressure under the above conditions is shown in Table 1(5). The reaction is a gas-liquid reaction and involves CO dissolution in MeOH. Alkali and alkaline earth metal alkoxides have traditionally been used as catalysts(7); the reaction in all cases is almost completely selective to MeF. $NaOCH_3$ is the most widely used catalyst.

The carbonylation reaction suffers from certain drawbacks. Even though the alkali methoxide has good solubility in MeOH, it is sparingly soluble in MeF. This implies that there must be an excess of MeOH in solution at all times. Some proposals to circumvent this problem have been made. According to a patent filed by Shell International(4), it is advantageous to replace the sodium alkoxide catalyst by alkoxides of heavier alkali metals (K, Rb, Cs). This results in two advantages. In addition to a higher solubility in the reaction mixture of the alkali alkoxides, as well as their corresponding formates, the alkoxides of K, Rb and Cs are reported to be more active than $NaOCH_3$. In fact, for the carbonylation of ethanol to ethyl formate, the nature of the alkali ions has also been shown to affect the alkoxide catalyst reactivity in the order: LiOEt < NaOEt < KOEt(13). This is also likely to hold true for MeF formation. It is consistent with the tenet that the alkali metal with the lower ionization potential, K(4.32V) < Na(5.12V) < Li(5.36V), should form the alkoxide ions, RO^- more easily(7). It would thus be expected that the performance of Rb and Cs alkoxides would be better than Na or K alkoxides.

Table 1. Equilibrium Conversion of MeOH for the Carbonylation Reaction(5)

Temperature (°C)	Pressure (H_2 + CO) (atm)	Equilibrium Conversion of MeOH (% by weight)
80	20	20
80	40	40
80	60	62
80	80	85
100	20	10
100	40	20
100	60	35
100	80	52

Another problem is that the alkali alkoxide (i.e. $NaOCH_3$) reacts with CO_2 and H_2O to form sodium methyl carbonate and sodium formate according to equations 1-4 and 1-5 respectively,

$$CH_3ONa + CO_2 \rightleftharpoons CH_3OCOONa \qquad (1\text{-}4)$$

$$CH_3ONa + H_2O \rightleftharpoons CH_3OH + NaOH$$

$$NaOH + CO \rightleftharpoons HCOONa$$

or

$$NaOH + HCOOCH_3 \rightleftharpoons HCOONa + CH_3OH \qquad (1\text{-}5)$$

thus deactivating the catalyst. The formation of HCOONa is particularly detrimental due to its low solubility in methanol, giving a white precipitate in the reaction mixture. Great care must be taken to remove all CO_2 and H_2O from the feed CO and MeOH; one report recommends cleanup levels of as much as 10 ppm CO_2 and 1 ppmv H_2O for the carbonylation reaction(14). It is worthwhile to note that the commercial Leonard process is carried out at these low levels of CO_2 and H_2O to prevent catalyst deactivation. Such cleanup levels incur huge costs and it would be advantageous if the level of tolerance could be increased.

Besides $NaOCH_3$, Liu et al.(15) tested $KOCH_3$ as a carbonylation catalyst resulting in improved rates for MeF synthesis. $RbOCH_3$ and $CsOCH_3$ have not been tested for the carbonylation reaction, but as explained earlier, should result in higher MeF formation rates. Imyanitov et al.(16) found the formate, carbonate, glycolate and phenolate of sodium to be active only above 150°C and 100 atm. It is noteworthy, that at milder conditions ($T < 150°C$, $P \approx 50$ atm), these compounds displayed negligible activity for the carbonylation reaction. The addition of transition metal complexes, such as $W(CO)_6$ or $Ru_3(CO)_{12}$, to $KOCH_3$ has been reported to increase its activity by providing a more electrophilic source of CO and by promoting the removal of trace water impurities by means of the water gas shift (wgs) reaction(17). In the commercial synthesis, it is claimed that addition of a proprietary additive to $NaOCH_3$ improved MeF yield at lower pressures(18).

Based on the fact that the reactions were found to be first order with respect to CO, a two-step mechanism involving RO^- as the reactive intermediate was suggested(19),

$$RO^- + CO \rightleftharpoons [COOR]^- \tag{1-6}$$

$$[COOR]^- + ROH \longrightarrow HCOOR + RO^- \tag{1-7}$$

where R is any alkyl group.

Investigators have studied the kinetics of the carbonylation reaction under varied conditions(7,15,20). Liu et al(15) and Gormley et al.(21) presented kinetic expressions which included both the forward and reverse reactions while Tonner et al.(7) considered only the forward reaction. In general, the forward reaction rate was found to be first order in MeOH and CO, while the reverse reaction was first order in MeF concentration. H_2 and N_2 were reported to act as inerts, having no effect on the MeF synthesis(16). This is of particular significance to the concurrent synthesis due to the presence of H_2 in large quantities.

1.4 HYDROGENOLYSIS OF ALKYL FORMATES

The hydrogenolysis reaction is exothermic (ΔH_{298} = - 52.6 kJ/mol for the hydrogenolysis of MeF). Low temperatures and high pressures favor the reaction. Equilibrium conversions, calculated assuming a gas phase reaction and taking into consideration the non-ideality of the species involved, are given in Table 2(22). It can be seen that conversion greater than 90% can be obtained under mild conditions of temperature and pressure. These high conversions are favorable for the concurrent synthesis, as it could eliminate syngas recycle, reducing recycle compression costs.

The hydrogenolysis of MeF has been studied at 110-180°C, in the gas(1,23,6,24) as well as in the liquid phase(15,16,25,26) at ambient and increased pressure. Early work was done by Christiansen(1) who studied the reaction in the gas phase as the second step in the two-stage MeOH synthesis over a 'more or less' reduced copper oxide at about 180°C. Patents were later issued for an 'Adkins-type' copper chromite catalyst yielding over 95% MeF conversion with 96% selectivity to MeOH in the gas phase(6). Sorum(27) reported better than 98% selectivity to MeOH by carrying out hydrogenolysis of MeF in the liquid phase.

Copper chromite, traditionally used for the low temperature hydrogenolysis of esters(28), is the favored catalyst for this reaction. The method of catalyst reduction affects its activity for MeF hydrogenolysis. Higher rates were reported by Sorum et al.(25), using liquid phase reduction in comparison to other investigators using gas phase reduction(15,26); this was attributed to better temperature control during reduction. These findings are compared in Table 3. It is noteworthy that Sorum and Onsager(25) used a MeF/MeOH mixture as charge in contrast to pure MeOH being used by the other investigators(15,26).

Table 2. Equilibrium Conversion of MeF During Hydrogenolysis

Temperature (°C)	Pressure (atm)	Equilibrium Conversion of MeF (mole%)*
100	20	95
100	40	96
100	60	97
100	80	97
140	20	92
140	40	93
140	60	94
140	80	95
180	20	87
180	40	89
180	60	91
180	80	91

* Initial H_2 to MeF ratio = 2.0

Table 3. Rate of MeF Hydrogenolysis Reported by Different Investigators

Temp. (°C)	Pressure (atm)	P_{H2}	P_{CO}	C_{MeF}	Rate of MeF Consumption by Hydrogenolysis Reaction (moles/min) * 10^3		
					Liu et al.[*]	Monti et al.[**]	Sorum and Onsager[***]
100	63	30.4	15.2	1.8	0.088	0.042	0.96
111	50	24.4	12.2	1.13	0.1	0.039	1.02
125	63	27.6	13.8	0.92	0.12	0.068	1.44
130	50	22.0	11.0	0.7	0.16	0.052	1.34
150	63	22.67	11.33	0.46	0.29	0.085	1.87
168	50	12.4	6.2	0.18	0.18	0.038	1.34
173	50	10.0	5.0	0.14	0.15	0.029	1.23

[*] 600 cc. MeF liquid
[**] 150 cc. MeF liquid
[***] 100 cc. MeF/MeOH liquid

Six commercial copper chromite catalysts were tested by Sorum and Onsager(25). Their relative activities are presented in Table 4. The catalysts were reduced overnight in H_2 in MeOH. The catalyst labeled G-89 (manufactured by United Catalysts Inc.) and the Ba-promoted catalysts were found to be active and stable at 413-458°K and 70 atm. These results were supported by Liu et al.(15) who found that the Mn-promoted catalyst displayed higher initial activity, though it deactivated faster than the Ba-promoted catalyst. Gormley et al.(29) tested Raney copper, Raney copper chromite and Girdler copper chromite in the liquid phase. The Girdler copper chromite catalyst was reported to display the lowest deactivation rate. Evans et al.(13) studied the activity of a variety of copper catalysts for the hydrogenolysis of ethyl formate in the gas phase and found Raney copper to be more active than other supported or unsupported copper-chromium catalysts, but, as shown by Gormley et al.(29), these Raney copper catalysts deactivate rapidly. Based on these results, the best catalysts in terms of activity and stability are the Ba or Mn-stabilized copper chromites. These were used in this work.

A number of investigators have proposed both power law and Langmuir-Hinshelwood type kinetic expressions for the hydrogenolysis of MeF in the liquid phase(15,25,26). For H_2 partial pressure > 70 atm, Sorum et al.(25) found the rate to be first order in MeF and independent of P_{H_2}, while Monti et al.(26) and Liu et al.(15) found it to be first order in P_{H_2} for $P_{H_2} < 70$ atm. The presence of CO was found to inhibit the hydrogenolysis reaction on the copper chromite surface resulting in a decrease in rate.

Carbon monoxide is a by-product of the hydrogenolysis reaction due to decarbonylation of MeF(23,8); the latter is favored at higher temperatures(23).

Table 4. Activities of Different Copper Chromite Catalysts(27)

Catalyst	Composition (% by weight)*			Conversion*** (%)
	Cu	Cr	Additive	
G-13**	42	26		19
G-22**	33	27	11% Ba	14
G-89	39	32	2.5% Mn	17
Cu-202 P	65	12		22
Cu-1106 P	31	30	9% Ba	9
Cu-1800 P	41	32		13

170°C, 100 atm, 1 h, 1.0 g catalyst loading and 11.7 mole% MeF in MeOH
* The remaining element is oxygen
** Manufactured by United Catalysts
*** % conversion = 100 * (MeF charged - MeF after reaction)/MeF charged

Although, CO has a detrimental effect on activity, the effect is reversible(15,21). The adsorption strength on the copper chromite active sites is greatest for MeF, next for CO and least for H_2(30). The presence of CO should inhibit hydrogen adsorption on the copper chromite surface. If the carbonylation reaction, in which CO is a reactant, is combined with the hydrogenolysis reaction, as in the concurrent synthesis the effect of CO assumes added importance considering its presence in large amounts. Other side products such as CO_2 and CH_4 in the liquid phase(25), and up to 10% CO_2, CH_4 and HCHO in the gas phase, have been reported(8).

1.5 TWO-STEP METHANOL SYNTHESIS IN SEPARATE REACTORS

As mentioned before, the carbonylation and hydrogenolysis steps can be carried out in series in two separate reactors to produce MeOH. However, hardly any information is available in the literature on the actual performance of a two-stage system, except for one patent(31) using $NaOCH_3$ for liquid phase carbonylation and copper chromite for gas phase hydrogenolysis as catalysts. The specified conditions were 20-60 atm and 100-170°C. Liu et al.(15) studied the two individual reactions with a view of combining them. Kinetic rate expressions for both the carbonylation of MeOH and the hydrogenolysis of MeF were derived. The effect of CO, CO_2 and H_2O on the individual reactions was also studied. CO_2 and H_2O strongly deactivated the carbonylation reaction while CO and CO_2 inhibited reactions on the copper chromite surface; the effect of CO_2 was found to be partially reversible.

A number of investigators have speculated on the possibility of combining the two steps but noted the disadvantages involved such as the presence of possible deactivating factors such as CO, CO_2 and H_2O(32,26). Gormley et al.(21) pointed out that the two step process would be uneconomical in comparison to the current commercial process unless the two steps could be combined in a single reactor.

1.6 CONCURRENT METHANOL SYNTHESIS

Synthesis of MeOH at low pressure and temperature in a single reactor would have advantages over present day direct processes, because of higher equilibrium conversion and lower equipment costs. Since the sum of the two individual reactions results in the same reaction as in the direct MeOH synthesis (equation 1-3), the thermodynamics of the overall reaction is the same as for the direct synthesis. The lower temperature of operation allows for potentially more CO to be converted. The equilibrium conversion of CO and the maximum selectivity to MeOH are listed in Table 5, taking into consideration, the non-ideality of reactants and products species(22).

In the concurrent synthesis, both the carbonylation and the hydrogenolysis reactions are carried out in a single slurry phase reactor. This requires a compromise in the operating conditions for the two individual reactions. Liu et al.(10) used temperatures from 100-180°C and pressures from 30-65 atm for the concurrent synthesis.

Since the reaction is restricted to the liquid phase, the operating conditions must be within the thermodynamically feasible region shown in Figure 2(10). The curve represents the temperature at which the vapor pressure of MeOH is equal to its equilibrium partial pressure according to the CO hydrogenation reaction. In the shaded region, the equilibrium partial pressure is greater than the vapor pressure and the concurrent synthesis is possible, while in the region to the right of the curve, MeOH remains in the gas phase due to a greater vapor pressure. Typical operating conditions for the concurrent synthesis are indicated by an (x) in the shaded region in comparison to the direct syntheses (e.g. ICI) in the gas phase.

Table 5. Equilibrium CO Conversion and Selectivity for the Concurrent Synthesis Reaction. (assuming no side reactions)(22)

Temperature (°C)	Pressure (atm)	Equilibrium Conversion of CO (mole%)*	Selectivity to MeOH (%)
100	5	85	98
100	10	91	98
100	30	97	98
140	5	53	98
140	10	73	98
140	30	88	97
180	10	30	97
180	30	70	97

* Initial H_2/CO ratio = 2

The first experimental evidence that the reactions can occur in a single reactor was provided by Imyanitov et al.(16) using a catalyst for MeF formation and a catalyst for its hydrogenation. Due to the deactivation of the $NaOCH_3$ catalyst in the presence of H_2O to yield HCOONa, Imyanitov et al.(16) examined the

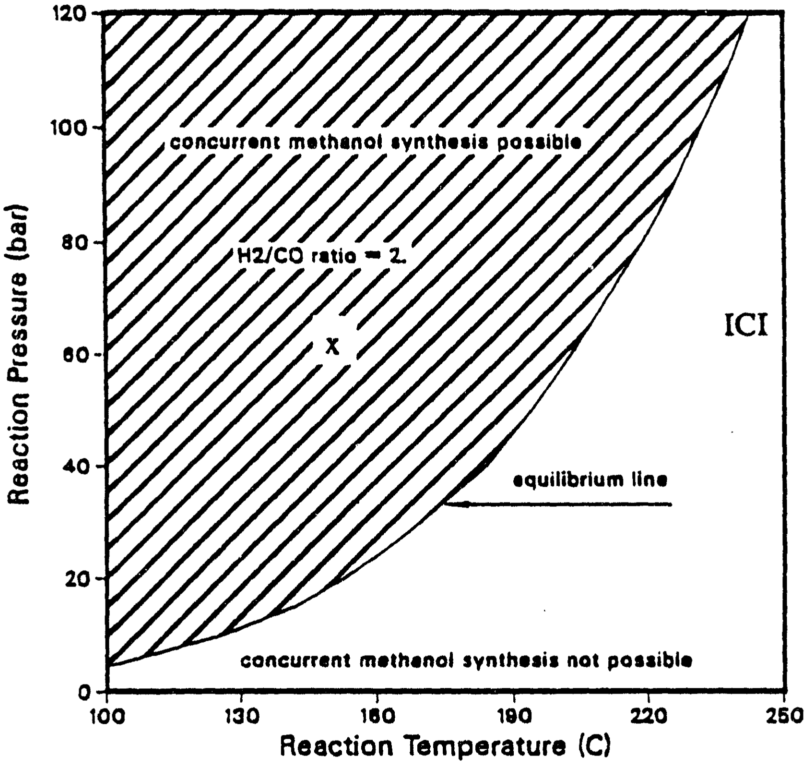


Figure 2. Thermodynamically Feasible Region for Concurrent Synthesis[(10)]

possibility of regenerating the active $NaOCH_3$ catalyst in a separate reactor. Ethylene glycol was used as a possible regenerating solvent. Under rather stringent conditions of temperatures greater than 150°C and pressures of 150-250 atm, it was claimed that significant amounts of MeOH were formed using either HCOONa or Na_2CO_3 and hydrogenolysis catalysts such as copper-chromium-calcium or copper on silica in a single reactor. No conversions or selectivities were reported. In the absence of the alkali compounds, MeOH was not formed or the rate of synthesis was several times lower. Their results are listed in Table 6. The main drawback is the severe conditions of operation. The use of MeOH itself as a solvent was not examined.

Liu et al.(10) studied the reaction in 1000 cc. and 300 cc. slurry autoclaves using $KOCH_3$ and a copper chromite catalyst containing small amounts of Ba or Mn, at temperatures of 140-180°C and pressures of 38-62 bar. External catalyst reduction was used in the 1000 cc. reactor while in situ reduction was used in the 300 cc. reactor. They found that the MeF concentration in the liquid was near equilibrium and concluded that the hydrogenolysis reaction may be rate controlling. The rates of MeOH synthesis obtained experimentally were higher than those predicted based on the individual reactions. Obviously, the concurrent synthesis is not a simple summation of the two individual reactions. The cause of this anomalous behavior was postulated to be due to possible interaction between the $KOCH_3$ and copper chromite catalysts, but no insight into the nature of this interaction was provided.

The effect of CO_2 in the feed was also studied by Liu et al.(10) The presence of 2% and 6% of CO_2 in the inlet syngas stream severely inhibited the reaction but this effect was shown to be reversible. It was proposed that the presence of water

Table 6. Imyanitov et al.'s Results for the Concurrent Synthesis in a Batch Reactor using Various Catalysts*

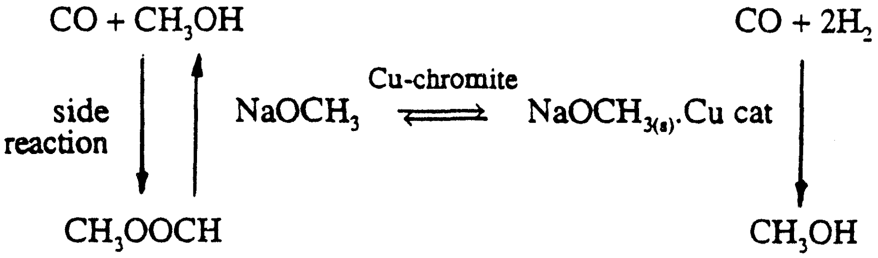
Homogeneous Catalyst	Heterogeneous Catalyst	Pressure (atm)	Rate of MeOH Formation (h^{-1})
No catalyst	Copper chromium	150	No reaction
Sodium carbonate	"	150 250	0.13 0.20
Sodium formate	"	150 250	0.25 0.40
No catalyst	Copper on silica	150	0.20
Sodium formate	"	100 150	0.40 0.60

100 ml. MeOH, 0.04 g-equivalent sodium salt, 8.5 g hydrogenation catalyst, 200°C, H_2:CO = 2:1

could also contribute to premature catalyst deactivation and inhibit initial performance(22).

There are at least two possibilities when the alkali methoxide (e.g. $KOCH_3$) and copper chromite are in the same reactor -- a) $KOCH_3$ and copper chromite influence the activity of each other but act as two separate catalysts, b) the $KOCH_3$ adsorbs on the copper chromite and forms the active catalyst.

Onsager et al.(11) believe that the active catalyst for the synthesis of MeOH in the concurrent synthesis is formed when the methoxide, dissolved in methanol or any other organic solvent such as cyclohexane, is contacted with the copper chromite; the methoxide is adsorbed on the copper chromite surface. They report that MeOH is formed primarily by direct hydrogenation of CO on the resultant catalyst surface (heterogenous methoxy adsorbed copper chromite). The reaction scheme proposed is shown below.



The carbonylation of MeOH to MeF is reported to be a side reaction. While some MeOH may be formed by hydrogenolysis of MeF, the predominant reaction is a direct hydrogenation on the copper chromite which has methoxide adsorbed on its surface. Small amounts of dimethyl ether and H_2O were also identified in the liquid analysis. No higher alcohols were reported.

In addition to $NaOCH_3$ and $KOCH_3$, Onsager et al.(12) used $Ba(OCH_3)_2$ with copper chromite as catalysts for the concurrent synthesis. They stressed the need to eliminate all CO_2 and H_2O from the reaction system. This is inconsistent with their proposed mechanism, since the direct synthesis is known to give improved performance with CO_2 in the feed syngas (H_2 + CO). Activities were reported to be enhanced by the use of a solvent with a dielectric constant lower than that of MeOH. MeOH synthesis rates almost doubled using cyclohexane as a solvent(11). A kinetic rate expression was proposed; the rate of MeOH formation was first order in both the $NaOCH_3$ and copper chromite catalyst loadings and the total pressure.

1.7 SUMMARY

The concurrent synthesis has definite advantages over the direct synthesis route to MeOH. While it has been proved that such a route is technically feasible, very little information is available on the effects of the process parameters. The importance of factors such as CO, CO_2, H_2O and process parameters such as temperature, pressure, flow rate, H_2/CO ratios in the reactor and catalyst loading needs to be examined in greater detail.

The role played by the different catalysts such as alkali compounds as well as the possible interaction of these compounds with copper chromite needs to be examined. The use of other more active promoters and alternate catalysts needs to be probed. The reaction scheme for MeOH synthesis in the presence of alkali compound/copper chromite catalysts is intriguing and needs to be examined for a better understanding of the process chemistry.

2.0 OBJECTIVES OF THIS RESEARCH

The principle objective of this work is to investigate a multi- step, single stage concurrent synthesis of MeOH and MeF. The synthesis operates under mild conditions, in the temperature range of 100-180°C and pressures of 30-65 atm yielding high conversions per pass. A typical catalyst system includes a mixed catalyst comprised of alkali compounds and copper chromite or alkali promoted copper chromite. The specific objectives of this study were as follows,

- To determine the effect of alternate catalysts on the concurrent synthesis. These included various soluble salts of alkali metals (Na, K, Rb and Cs) along with copper chromite as well as alkali impregnated copper chromite. Efforts were focussed on finding more active catalysts for MeOH synthesis and studying the interaction of the alkali compounds or adsorbed alkali with the copper chromite catalyst.
- To study possible reaction pathways involved. This included identifying the phase(s) in which the reactions take palce (whether homogeneous/heteogeneous or totally heterogeneous).
- To study the formation of by-products and their effect on the concurrent synthesis rate. The effect of possible deactivating molecules such as CO, CO_2 and H_2O was to be investigated. Of particular interest was the behavior of these species during reaction.
- To study the effect of operating variables on the reaction, including reaction temperature, pressure, catalyst loading, flow rate and feed gas composition on MeOH formation rate in the concurrent synthesis.
- To develop suitable kinetic rate expressions for the reactions.

3.0 EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 OPERATING PROCEDURE

The two reactions, carbonylation and hydrogenolysis are carried out in the same reactor. MeOH is not only a reactant, but it also serves as the solvent. A sketch of the concurrent synthesis experimental setup is shown in Figure 3. The method of operation is described below.

A 300 cc. stainless steel autoclave reactor obtained from Autoclave Engineers was used. Reactions were normally carried out in a semi- continuous manner with liquid batch and the gas being continually removed as product. The reactor was pressurized to the reaction pressure and leak tested for a minimum of 15 minutes, the pressure being controlled by a back pressure regulator (0-273.5 atm, Tescom, Inc.). The catalyst was reduced at 170°C, either in situ or external to the reactor; the procedure is described later. After reduction, the temperature was decreased to the reaction temperature (typically 150°C) and controlled flows of H_2, CO and in some cases CO_2, from pressurized cylinders obtained from Linde (custom grade, 99.9% purity), individually metered by on-line Brooks mass flow controllers (Model 5850C, maximum flow rate of 1000 cc/min under standard conditions) were introduced into the reactor at the desired composition. The mixed gases were bubbled through a dip tube into the reactor filled with 150 cc. MeOH and the catalyst (typically a mixed $KOCH_3$/copper chromite combination).

The effluent gas was removed from the reactor by an outlet line located at the

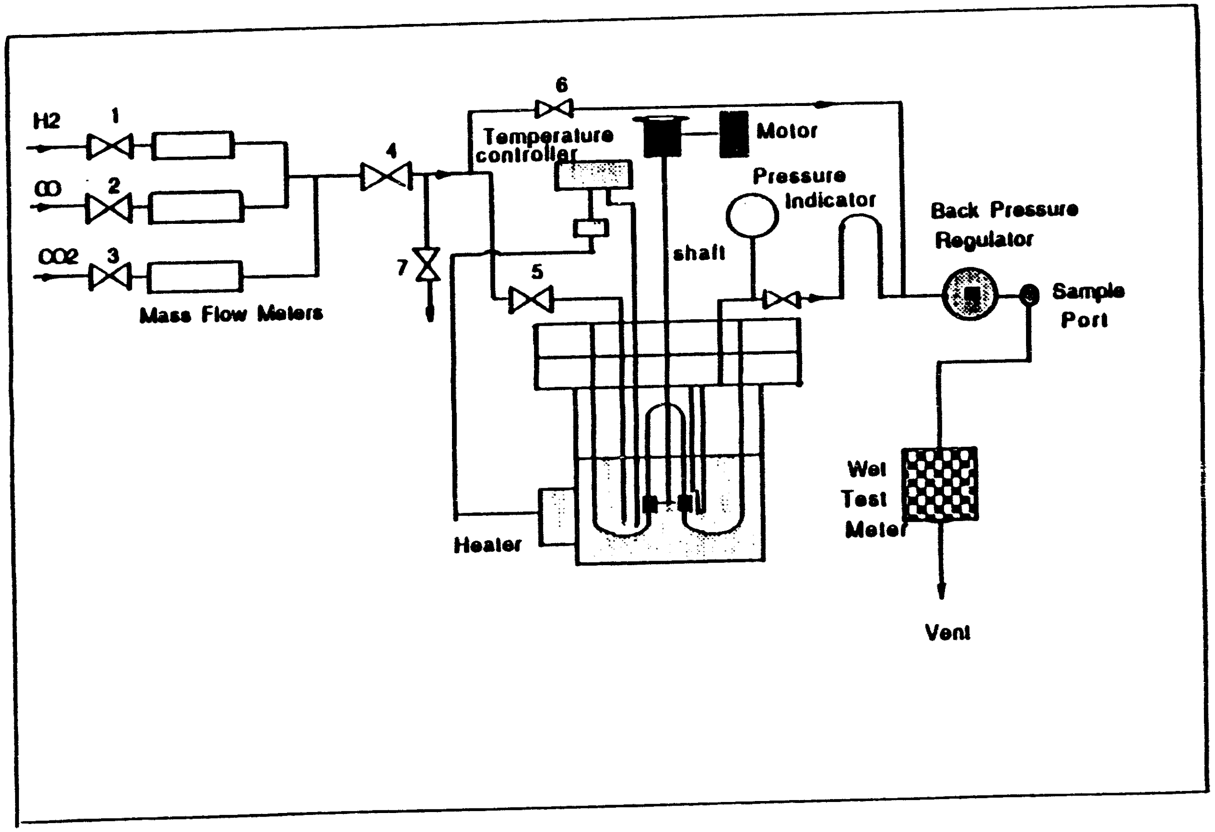


Figure 3. Schematic of Experimental Setup

top of the reactor. The outlet line was heated with heating tape to prevent condensation of the volatile components in the line leading to the sample port. However, the possibility of some condensation in the lines out of the reactor cannot be ruled out. The gases passed through a filter packed with a 2 micron frit to prevent any catalyst entrainment and then into the back pressure regulator where the pressure was reduced to 1 atm. The flow rate of the effluent gas was measured by a calibrated wet test flow meter (Precision Scientific Inc.) before the gas was vented.

Gas and liquid analyses were carried out an regular intervals using an HP 5880 gas chromatograph (GC) equipped with Porapak Q and Carbosieve S columns and a thermal conductivity detector. Liquid samples were taken through a tube connected to the inlet line. No liquid product was removed except for liquid sampling. The feed CO was passed through a 4 Å molecular sieve and activated charcoal purifiers to remove CO_2 and $Fe(CO)_5$ from the feed gas. The CO contained an average of 0.3% CO_2 which was diluted to 0.1% after the CO was mixed with H_2 and almost completely removed by the molecular sieve purifier. No H_2O was present in the feed gas.

3.2 CATALYSTS

The Ba promoted copper chromite hydrogenolysis catalyst was obtained from Calsicat Division of Mallinckrodt, Inc. The physical properties of the catalyst are given in Table 7.

The carbonylation catalysts were obtained from various sources; the $KOCH_3$,

Table 7. Physical Properties of the Barium-Promoted Copper Chromite Catalyst (obtained from manufacturer)*

Type	81C-83B, Calsicat Division,Mallinckrodt, Inc.
	Black powder
Surface area, m^2/g	103
Bulk density, g/cc	0.64
Cu, wt%	32.1
Cr, wt%	29.0

* No analysis available for barium

HCOOK and Rb_2O were from Aldrich Chemical Company, Inc. (99%), the KOH, KCl and $CsOH.H_2O$ were from Mallinckrodt (AR grade), the $CsHCO_3$ was procured from Strem Chemicals. Inc. (99%), the HCOOCs from Cabot Chemicals (Technical Grade). The MeOH and MeF were from Fischer Scientific (A.C.S Certified - 99.9% purity). All were used as such.

The copper chromite and alkali compound were weighed on a Mettler PC 2000 electronic balance (error ± 2 mg) and added to a clean reactor. About 150 cc. of MeOH was added to the autoclave. Analysis of the liquid MeOH showed a H_2O content of 0.2%-0.4%. After the MeOH and the catalyst were added, the reactor was sealed by tightening the threaded bolts.

In addition to the mixed catalysts comprised of alkali compounds and copper chromite, two other modes of alkali incorporation into the copper chromite were used in this work. One technique used was coprecipitation, in which a copper chromite catalyst containing potassium was prepared by coprecipitating copper nitrate (Fischer Scientific Co.) with barium nitrate ($Ba(NO_3)_2.3H_2O$, Aldrich Chemical Co.) and potassium dichromate with ammonium hydroxide according to the procedure suggested by Conner et al.(33). The resultant catalyst precursor was filtered, dried overnight at 110°C and pulverized. This complex was then thermally decomposed in air and the resultant black powder washed with water and dried overnight at 120°C. Another copper chromite catalyst not containing any potassium was prepared by a slight modification of the method suggested by Conner et al.(34) in which ammonuim dichromate was used instead of potassium dichromate to precipitate the catalyst precursor. The overall reaction can be represented by equations 3-1 and 3-2.

$$2Cu(NO_3)_2 + NH_4Cr_2O_7 + 4NH_4OH \longrightarrow 2Cu(OH)NH_4CrO_4 + 4NH_4NO_3 + H_2O \qquad (3\text{-}1)$$

$$2Cu(OH)NH_4CrO_4 \xrightarrow{\Delta} CuO.CuCr_2O_4 + N_2 + 5H_2O \qquad (3\text{-}2)$$

Another method used was the incipient wetness technique in which potassium or cesium was impregnated on the surface of copper chromite. Catalysts with different loadings of potassium (up to 12%) and cesium (up to 3%) on copper chromite were prepared by this technique using potassium carbonate or cesium carbonate, respectively, as the precursor compound. In this method, the precursor compound was dissolved in water and then added dropwise to the catalyst so as just to wet the surface of copper chromite. The resultant powder was dried overnight at 110°C, pretreated in hydrogen using a ramp rate of 1°/min for 6 hours to 400°C followed by isothermal treatment at 400°C for 4 hours. This treatment did not alter the surface area and the X-ray diffraction pattern of the oxidized hydrogen pretreated potassium decorated copper chromite.

3.2.1 CATALYST CHARACTERIZATION

The copper chromites were characterized by BET, Mercury Porosimetry, X-ray diffraction, atomic absorption and scanning electron microscopy. The surface areas of the catalysts before and after reaction were measured using an N_2 BET point technique at liquid N_2 temperatures. The sizes and distribution of the pores as well as the porosity were characterized by Mercury Porosimetry using a Micromeritics 2600 Surface Area Analyzer at the University of Pittsburgh facility UPARC. A Phillips X-ray diffractometer (XRD) using Cu-Kα radiation at 40 KV and 20 mA was used to obtain X-ray diffraction patterns of the copper chromites before and after reaction. A Perkin Elmer Model 380 Atomic Absorption (AA) Spectrophotometer (wavelength, 766.5 nm, slit width, 2nm) was used to measure the distribution of potassium between the liquid and the copper chromite surface. The sum was found to be within 10% of the potassium added initially. Scanning electron microscopy (SEM) was carried out for structural and morphological investigation using a JEOL 35 CX SEM (25 KV electron beam).

3.3 OPERATING CONDITIONS

The range of operating conditions used in this study is listed in Table 8.

Table 8. Range of Operating Conditions for the Concurrent Synthesis

Temperature	80-150°C
Total pressure	52-64 atm.
Initial catalyst loading	
Alkali salt	0.007-0.028 gmoles/liter
Copper chromite	20-40 gm./liter
Initial MeOH loading	150 ml.
Feed rate at 1 atm. and 25°C	75-125 cc/min
Stirrer speed	750-1150 rpm.
Feed rate (H_2/CO)	1.0-2.0

3.4 CATALYST REDUCTION

The copper chromite catalysts were reduced both in situ as well as external to the reactor. In situ liquid phase reduction in the concurrent synthesis has the advantage of eliminating an external reduction step. In situ liquid phase reduction was carried out in a stream of pure H_2 at 170°C and reaction pressure (typically 63 atm). Liquid and gas analyses showed that no MeF is formed during reduction. External reduction was also carried out with a temperature ramp to 170°C in 3 hours and then maintaining the temperature at 170°C for 4 hours. The catalyst was then forced into the reactor using pressurized N_2 without exposing to air.

At the start of reaction, the amount of H_2O present in the liquid is that present in the MeOH charge plus, in the case of in situ reduction, that generated due to catalyst reduction. For in situ reduction, the amount of water formed during reduction was found to correspond to the reduction of $CuO,CuCr_2O_4$ to $Cu^o,CuCrO_2$. These calculations are given in Appendix C.

3.5 METHOD OF CALCULATION

The MeOH synthesis rate was assumed to be one-half the rate of H_2 consumption in moles/h, while the MeF formation rate was assumed to be equal to the CO disapearance rate in moles/h. The MeOH synthesis rate was then calculated as follows,

1. The flow rate of gas coming out of the reactor was measured by the wet test meter (calibrated in ft/min) and converted to cc/min.
2. The product gas composition was measured by injecting samples of the gas into the G.C. and converted to mole fraction as described above. The outlet flow rate multiplied by the mole fraction of the individual component gave the outlet flow rate of that component.
3. The inlet flow rate of the H_2 and CO introduced into the reactor were read off mass flow meters and converted to cc/min. using calibration charts for the individual flow meters. The individual mass flow meters were calibrated using a wet test meter at the exit under reaction conditions, the wet test meter being calibrated using a soap bubble flow meter.
4. The difference of the H_2 and CO flow rates in and out of the reactor was the H_2 and CO consumed in MeOH and MeF synthesis respectively in the reactor.
5. The H_2 consumption in cc/min. was converted to moles/min at standard atmospheric conditions, since both the inlet and the outlet flow rates were calibrated at these conditions.
6. The MeOH synthesis rate is then one-half the rate of H_2 consumption

> while the MeF synthesis rate is equal to the rate of CO consumption in moles/min. The MeOH synthesis rate was converted to moles/h/kg cat by dividing by the weight of copper chromite catalyst loaded into the reactor at the start of reaction.

Error analysis for measurements of MeOH and MeF rates of formation based on the rate of consumption of the non-condensibles namely H_2 and CO respectively, showed a standard error of 2.6% about the mean at a 95% confidence level.

4.0 RESULTS AND DISCUSSION

4.1 GENERAL RESULTS

In the concurrent synthesis, MeOH is formed as a liquid. The conditions at which this is possible are prescribed by the thermodynamically feasible region shown in Figure 2(10). In this region, the equilibrium partial pressure of MeOH (according to the CO hydrogenation reaction) is greater than its vapor pressure at a particular temperature; MeOH is thus formed as a liquid. Liu et al.(10) obtained high MeOH formation rates at temperatures of 140-160°C and pressures of 40-65 atm. An operating pressure of 63 atm. was typically used in this work. From Figure 2, at a total pressure of 63 atm., the maximum temperature that can be used for MeOH to be a liquid is 205°C.

The concurrent synthesis is highly selective to MeOH. Four main reactions proceed simultaneously in the reactor. They are the carbonylation of MeOH to MeF (reaction 1-1), the hydrogenolysis of MeF to two moles of MeOH (reaction 1-2), and the side reactions -- the wgs reaction (reaction 4-1) and dehydration of MeOH to give dimethyl ether (DME) (reaction 4-2).

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \tag{4-1}$$

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O \tag{4-2}$$

At 150°C, 63 atm total pressure and feed $H_2/CO = 2$, the gas phase is mainly H_2 and CO while the liquid product is predominantly MeOH and MeF. The composition of a typical gas sample at steady state is 66% H_2, 33% CO and 0.8-1% CO_2 as the non-condensible components. A typical liquid sample at steady state has a composition of 1.8 mole% MeF, 98.1 mole% MeOH, traces of H_2O and DME and dissolved gases including CO, H_2 and CO_2. Traces of formaldehyde (< 0.05 mole%) were also detected in the gas analysis. At 150°C, up to 90% per pass conversion with 99% selectivity to MeOH has been obtained. The only other side reaction in which CO and H_2 participated was the wgs reaction and the extent of this reaction was limited by the rate of dehydration of methanol to dimethyl ether. A maximum rate of 0.36 moles/h/kg cat was obtained under baseline conditions (150°C, 63 bar and 105 cc/min feed rate) for the wgs reaction, based on CO_2 measurements in the effluent gas. This resulted in a maximum error of 1.8 % in the rate of methanol formation. A summary of the runs made is presented in Appendix A.

4.2 THERMODYNAMICS

The maximum amount of MeF that can be formed in the concurrent synthesis is governed by the carbonylation equilibrium. The fugacity coefficients for the gas were determined for all components while the activity coefficients were evaluated only for MeOH and MeF, since they comprise almost 99% of the liquid product. The activity coefficients for the other components were assumed to be unity. These calculations are shown in Appendix B. The system is non-ideal at our normal operating conditions and this is taken into account in the rest of this work.

The equilibrium concentration of MeF in the liquid is an important variable. It is a function of the operating temperature and the CO partial pressure in the reactor. Liu et al.(15) measured the equilibrium MeF mole fraction in the presence of about 10 ppm of H_2O. In the concurrent synthesis, the concentration of H_2O at steady state is a 1000 ± 100 ppm of H_2O at 150°C and 63 atm total pressure. The equilibrium MeF concentration for the carbonylation reaction was measured at 150°C in the presence of about 1000 ppm H_2O in the liquid (Appendix A) and was found to agree well with the measurements of Liu et al(15). The equilibrium carbonylation equation of Liu et al.(15), K_e = 3.37E-7 exp(3780/T), was extrapolated to give the mole fraction of MeF at equilibrium at various temperatures. These are shown in Figure 4. The MeF mole fraction at equilibrium indicated as the ordinate in Figure 4 sets the upper limit for the MeF concentration in the reactor. In the absence of other effects, the highest rate of MeOH formation at a particular operating temperature is obtained when the MeF concentration is equal to its equilibrium concentration.

For the wgs reaction, the mole fraction of CO_2 in the gas can be related to the mole fraction of H_2O in the liquid by the governing equation, $y_{CO_2} = 5.9\ x_{H_2O}$. At 150°C and 63 atm, DME is present almost completely in the gas phase (conditions are above the critical point) and leaves the reactor along with the product gas. Very small amounts of DME ($\approx$ 0.1- 0.3%) are formed, the level remaining constant throughout the run, mainly due to the non-acidic nature of the catalytic system and the low temperature of operation. Although the extent of reaction is small, it is important since it fixes the amount of H_2O present in the system at steady state.

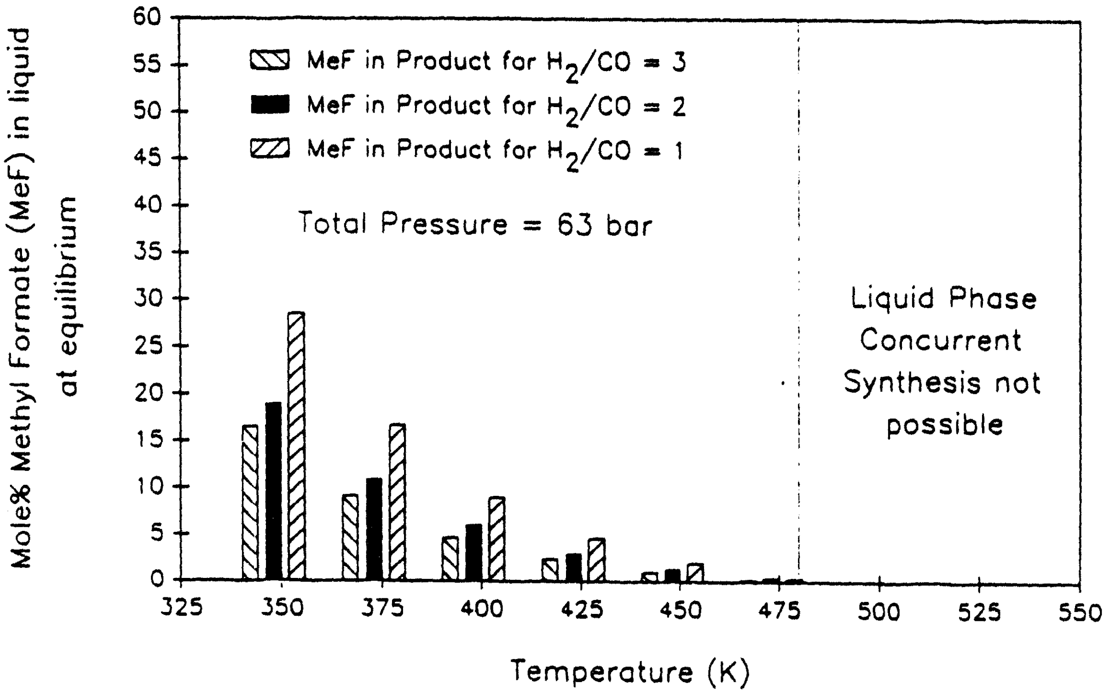


Figure 4. Equilibrium MeF Concentration in the Concurrent Synthesis as a Function of Temperature

4.3 TRANSIENT BEHAVIOR DURING REACTION START-UP

A typical run is preceded by catalyst reduction in situ in a stream of pure H_2. At reaction start-up, synthesis gas is introduced into the reactor which is filled with H_2, at a space velocity of 2340 l/h/kg catalyst. It takes about 3 hours for the CO concentration to reach steady state in the liquid agitated reactor (see Appendix B). The increase in CO drives the wgs reaction, resulting in a simultaneous increase in the CO_2 concentration in the reactor. The wgs reaction results in depletion of H_2O in the liquid. The buildup of CO and the depletion of H_2O offset each other, resulting in CO_2 concentration in the gas going through a maximum as shown in Figure 5. This is a common feature for every run.

At the start of the reaction, no MeF is formed due to the high levels of H_2O present ($\approx$ 0.4-0.6 % in liquid) and CO_2 generated ($\approx$ 2.5-3.0 %). These high levels prevent MeF formation due to the deactivation of the methoxide catalyst by formation of the formate and the methyl carbonate respectively(7). The highest level of CO_2 corresponds to a low MeOH production rate. With the removal of CO_2 in the product gas, the concentration of CO_2 and H_2O are continually depleted. As the H_2O and consequently CO_2 are reduced below 3,000 ppm and 10,000 ppm in the liquid and gas respectively, MeF is formed by the carbonylation reaction.

During reactor start-up, the changes in the MeF, H_2O and DME compositions based on gas analyses are shown in Figure 6. Upon depletion of H_2O in the liquid and CO_2 in the reactor (latter shown in Figure 5), MeF starts building up. MeOH is then formed. The total induction period for MeOH synthesis typically is about 35 hours. A typical plot of the progress of the reaction versus time on stream is shown

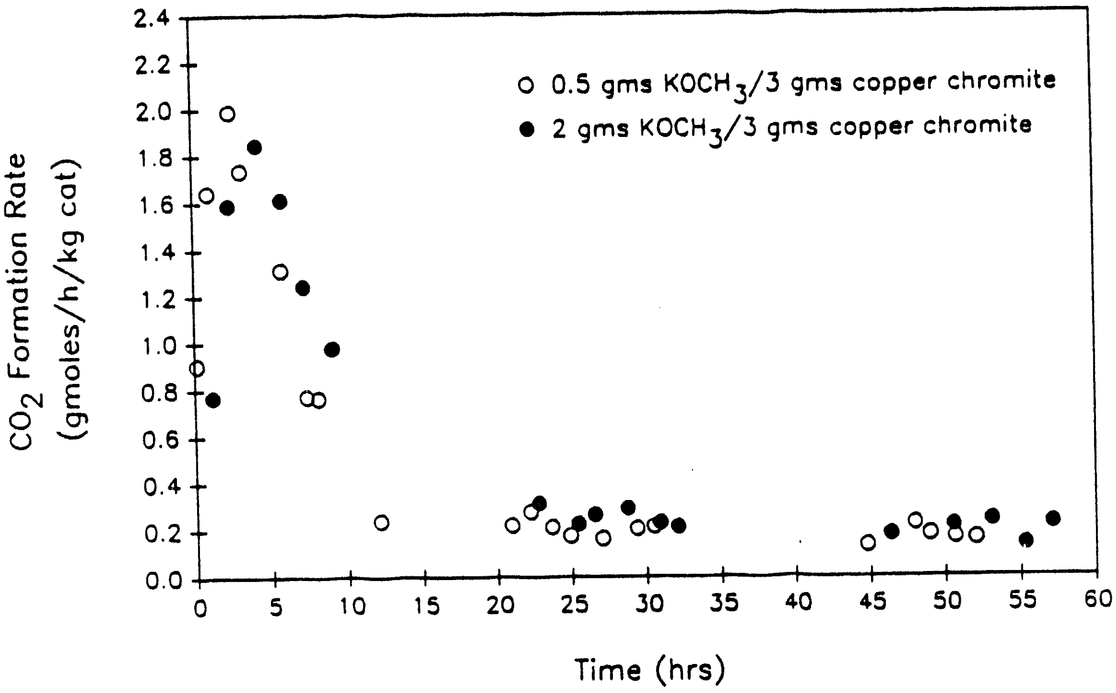


Figure 5. Production Rate of CO_2 with Time

in Figure 7. It is essentially comprised of three parts - (a) time required for the H_2O and CO_2 to be reduced to tolerable levels (shown by dotted line in Figure 7), (b) time for MeF formation, and (c) time for the conversion for MeF to MeOH. At steady state, the rate of MeF formation by the carbonylation reaction is equal to the rate of MeOH formation by the hydrogenolysis reaction.

In spite of the presence of potential deactivating factors such as CO, CO_2 and H_2O, the concurrent synthesis yields high MeOH synthesis activity with a deactivation rate as low as 0.39 %/day for a mixed $KOCH_3$/copper chromite catalyst. The rates obtained in the concurrent synthesis at low loadings are comparable to present day commercial processes(35,36,37). Under typical reaction conditions, a steady state gas analysis shows 0.65-0.8 mole% CO_2. Evidently, this level of CO_2 is tolerated by the concurrent synthesis. A typical liquid composition contains 0.1-0.15 mole% H_2O. At temperatures above 170°C for a pressure of 63 atm and above 168°C for a pressure of 50 atm, a small amount of CH_4 (< 0.2 mole%) was seen in the gas analysis. However, no CH_4 was detected below 160°C, suggesting that CH_4 plays an insignificant role in the concurrent synthesis. No higher alcohols were detected in the GC analysis for any of the runs.

4.4 SALIENT DIFFERENCES IN THE CONCURRENT SYNTHESIS

When the carbonylation catalyst, $KOCH_3$ and the hydrogenolysis catalyst, copper chromite are put together in a single reactor, the resultant concurrent synthesis does not behave as predicted based on the individual reactions. Higher experimental rates and increased tolerance to CO_2 than predicted from the individual reactions are obtained(10).

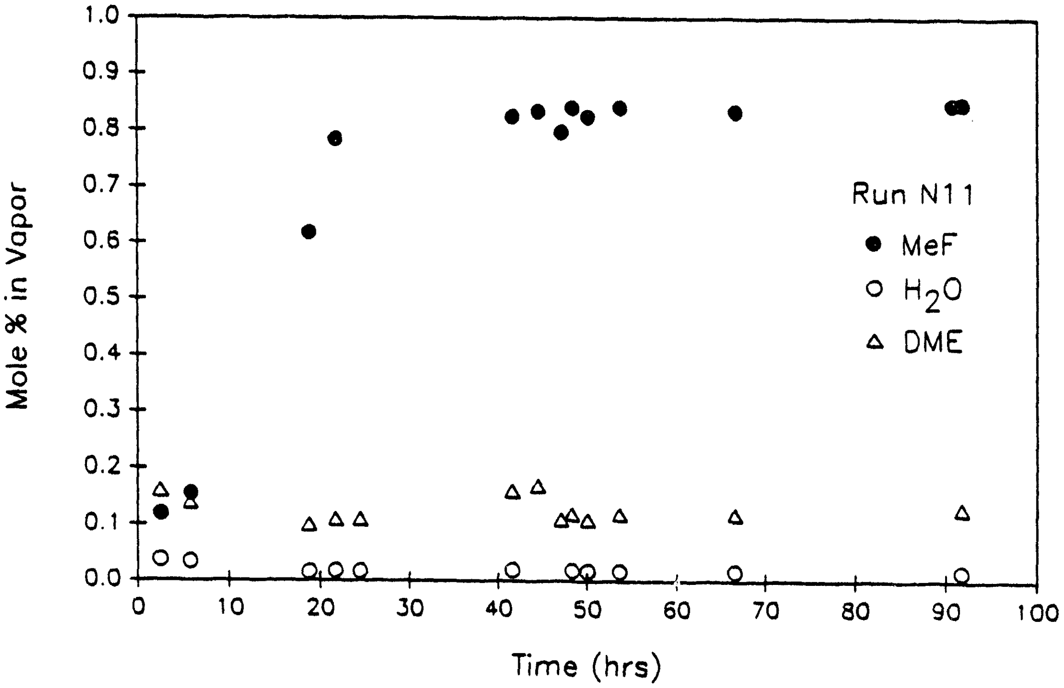


Figure 6. Variation of MeF, DME and Water with Time

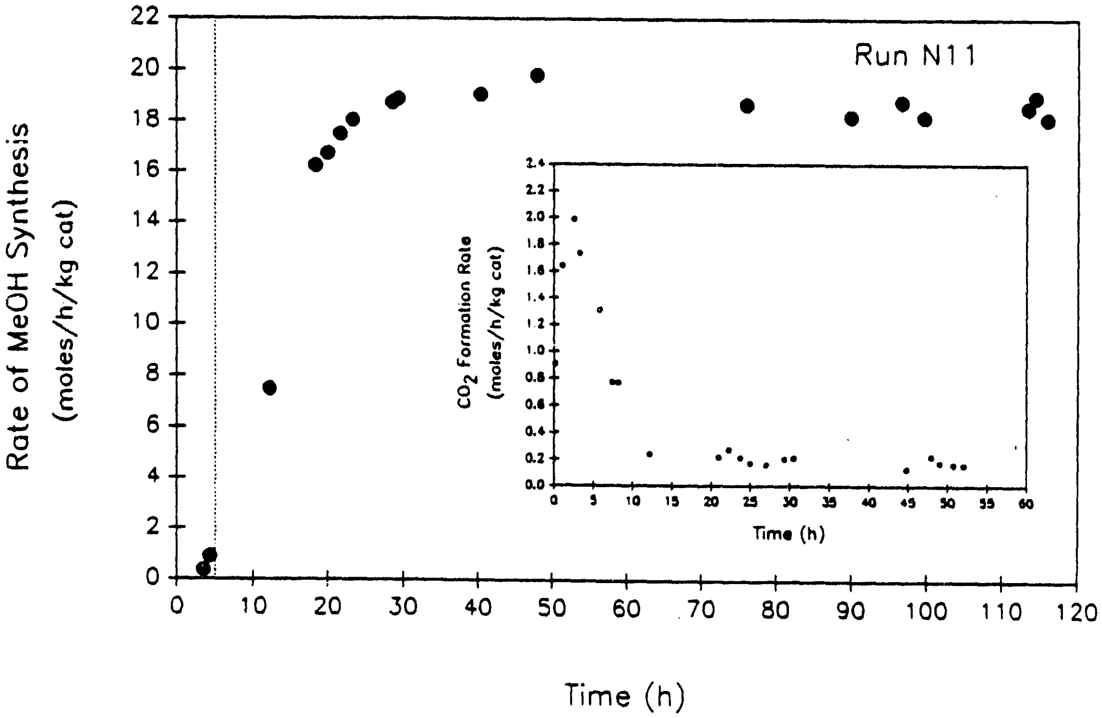


Figure 7. Typical Rate of MeOH Synthesis vs Time During Start-up

The rate of concurrent methanol synthesis is compared in Table 9 with the calculated rate of carbonylation of MeOH (in the presence of about 10 ppm water(22)) and the rate of MeF hydrogenolysis under typical concurrent reaction conditions using the equation of Liu et al(15). In an almost anhydrous environment, the carbonylation rate is three orders of magnitude higher than the concurrent synthesis rate, which is higher than the hydrogenolysis rate. From the predicted carbonylation and the hydrogenolysis rates, it would seem likely that in the concurrent synthesis, the MeF is in equilibrium and the rate of MeOH synthesis is controlled by the hydrogenolysis rate. However, this is not the case, as is substantiated later. In the concurrent synthesis, the MeF is found not to be in equilibrium.

The concurrent synthesis operates with about 1000 ppm H_2O in the liquid. It is known that $KOCH_3$ reacts with H_2O giving alkali formates (e.g. HCOOK) severely deactivating the active catalyst. Hence, the rate of carbonylation at 150°C was measured in the presence of 1000 ppm water. This is shown in Table 10 as a function of CO partial pressure. It can be seen that the H_2O severely decreases the carbonylation rate to 0.099E-3 moles/min. Under these conditions, the hydrogenolysis rate as predicted from the equation of Liu et al.(15) is 0.03E-3 moles/min, assuming that MeF is in equilibrium (Table 9). The measured concurrent synthesis rate (0.95E-3 moles/min - Table 9) is significantly higher than the individual rates. If the concurrent reaction were a simple summation of the carbonylation and the hydrogenolysis reactions, then the rate of methanol synthesis could be calculated from the individual reaction rates. Evidently, this is not the case. The results given in Tables 9 and 10 suggest a synergistic behavior of the carbonylation and the hydrogenolysis reactions. In addition, increased tolerance to CO_2 levels to as much as 10,000 ppm in the gas and H_2O levels as much as 3000 ppm in the liquid were found.

One possibility is that formation of MeOH does not proceed through MeF, but is formed by the direct hydrogenation of CO. The latter was proposed by Onsager et al.(11) where MeOH was believed to be formed predominantly by direct hydrogenation of CO on a copper chromite surface containing adsorbed methoxide. The carbonylation of methanol to methyl formate was proposed to be a side reaction. If this were true, it could explain the observed behavior of the concurrent synthesis. Evidence for MeOH formation via MeF is presented below.

4.5 REACTION PATHWAYS

At start-up, the reactor is filled with MeOH and the MeF composition increases slowly. The rate of MeOH formation during reactor start-up as a function of gas phase MeF concentration is plotted in Figure 8 for five duplicate runs at 150°C and 63 atm. The MeF in the gas phase should be in equilibrium with the MeF in the liquid; the linear relationship shown in Figure 8 indicates that MeOH formation is proportional to MeF concentration and supports the view that MeOH formation proceeds via MeF. The spread in the data in Figure 8 is possibly due to condensation of the MeF in the product lines. Additional evidence for the formation of MeOH via MeF is shown in Figure 9 in which typical conversions of CO and H_2 during start-up as a function of reaction time are given. When CO is introduced in the reactor (initially filled with H_2), the CO conversion is high at first and then rapidly levels off (Figure 9). Once the CO concentration reaches steady state, its conversion corresponds to its utilization in the carbonylation

Table 9. Rate of Concurrent Synthesis in Comparison to Predicted Rate of Individual Carbonylation and Hydrogenolysis Reactions

Reaction	Rate (moles/min) * 10^3
Concurrent Methanol Synthesis[a] (Experimental)	0.95
Carbonylation of Methanol[b]	142
Hydrogenolysis of Methyl Formate[c]	0.3

[a] T = 150°C, P = 63 bar, Hydrogen partial pressure = 22.67 bar, Carbon monoxide partial pressure = 11.33 bar, 0.0476 moles/l potassium methoxide, 20 g/l copper chromite, 150 cc. methanol charge, 1000 ppm water at steady state

[b] T = 150°C, Carbon monoxide pressure = 11.33 bar, 0.0476 moles/l potassium methoxide, 10 ppm water in reactor; initial rate of carbonylation predicted from carbonylation rate equation by Liu et al.[10]

[c] T = 150°C, P = 63 bar, Hydrogen partial pressure = 22.67 bar, Carbon monoxide partial pressure = 11.33 bar, 20 g/l copper chromite, Concentration of methyl formate = 3.1 mole% (equilibrium concentration under these conditons according to the carbonylation reaction); predicted from hydrogenolysis rate equation by Liu et al.[10]

Table 10. Rate of Concurrent Synthesis in Comparison to Predicted Rate of Individual Carbonylation and Hydrogenolysis Reactions in the Presence of 1000 ppm H_2O

Reaction	Rate (moles/min) * 103
Concurrent Methanol Synthesis[a] (Experimental) (Run N11)	0.95
Carbonylation of Methanol[b]	0.099
Hydrogenolysis of Methyl Formate[c]	0.3

[a] T = 150°C, P = 63 bar, Hydrogen partial pressure = 22.67 bar, Carbon monoxide partial pressure = 11.33 bar, 0.0476 moles/l potassium methoxide, 20 g/l copper chromite, 150 cc. methanol charge, 1000 ppm water at steady state

[b] T = 150°C, Carbon monoxide pressure = 11.33 bar, 0.0476 moles/l potassium methoxide, 1000 ppm water in reactor; initial rate of carbonylation reaction (experimental)

[c] T = 150°C, P = 63 bar, Hydrogen partial pressure = 22.67 bar, Carbon monoxide partial pressure = 11.33 bar, 20 g/l copper chromite, Concentration of methyl formate = 3.1 mole% (equilibrium concentration under these conditons according to the carbonylation reaction); predicted from hydrogenolysis rate equation by Liu et al.[10]

reaction. As the MeF concentration in the reactor rises, H_2 reacts and its conversion follows the build-up of MeF. The reaction of H_2 appears to be proportional to the MeF present in the reactor, indicating that CO and H_2 are involved in separate reactions, namely the carbonylation and the hydrogenolysis reactions, respectively. The predominant pathway for MeOH formation appears to be through MeF, although it is possible that some MeOH is formed directly from CO and H_2.

A number of other observations support the claim that the formation of MeOH proceeds via MeF in the concurrent synthesis. These are as follows,

1) During reaction start-up, high levels of H_2O (5,000-7,000 ppm in liquid from catalyst reduction and H_2O in the methanol charge) and CO_2 formed by the wgs reaction retard MeF formation by removing the methoxide catalyst as HCOOK and CH_3OCOOK respectively(7,15). During this time, little MeOH or MeF is formed, indicating that MeF is needed for MeOH formation. On depletion of H_2O (below 3,000 ppm) and CO_2 (below 10,000 ppm), MeF formation proceeds, which in turn gives MeOH.

2) The induction period for methanol formation is sensitive to MeF concentration. If the MeOH is formed via MeF, then addition of MeF at the start of the reaction should result in a decreased induction period. Figure 10 does indeed show a decreased induction period when 1.2 mole% of MeF was present at the start of reaction, supporting the view that MeF must be present for MeOH to be formed.

3) The direct hydrogenation of CO/CO_2 is slow at 150°C on copper based

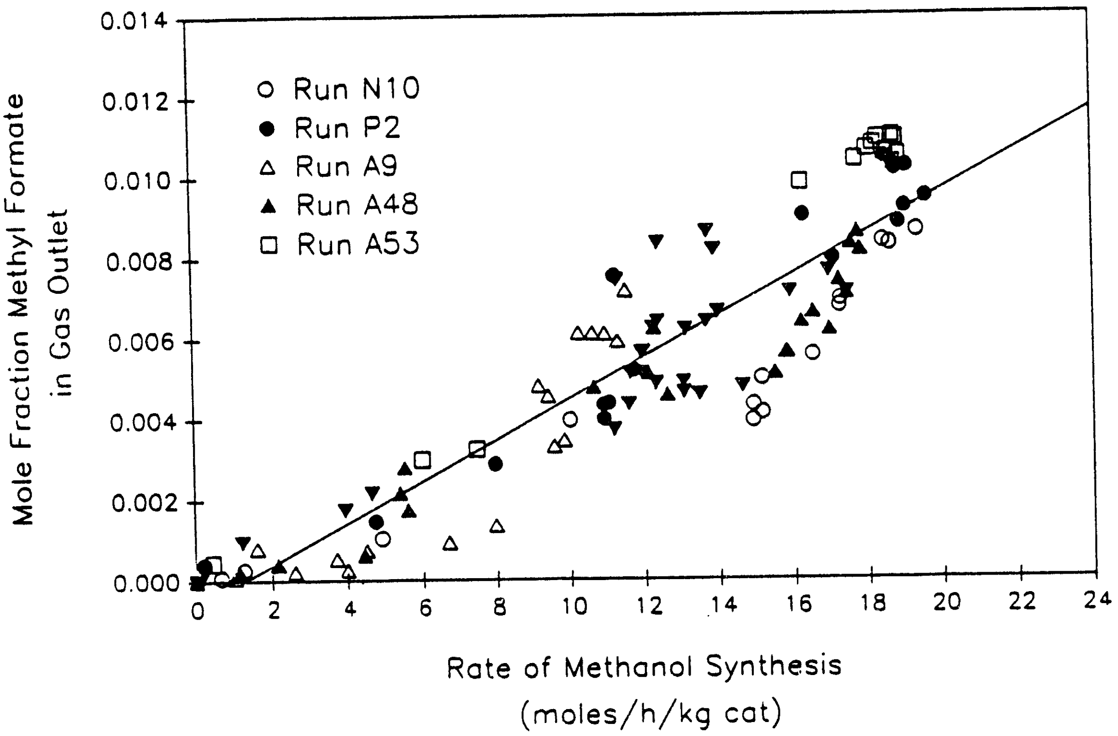


Figure 8. Rate of MeOH Synthesis as a Function of MeF Concentration in the Gas Phase

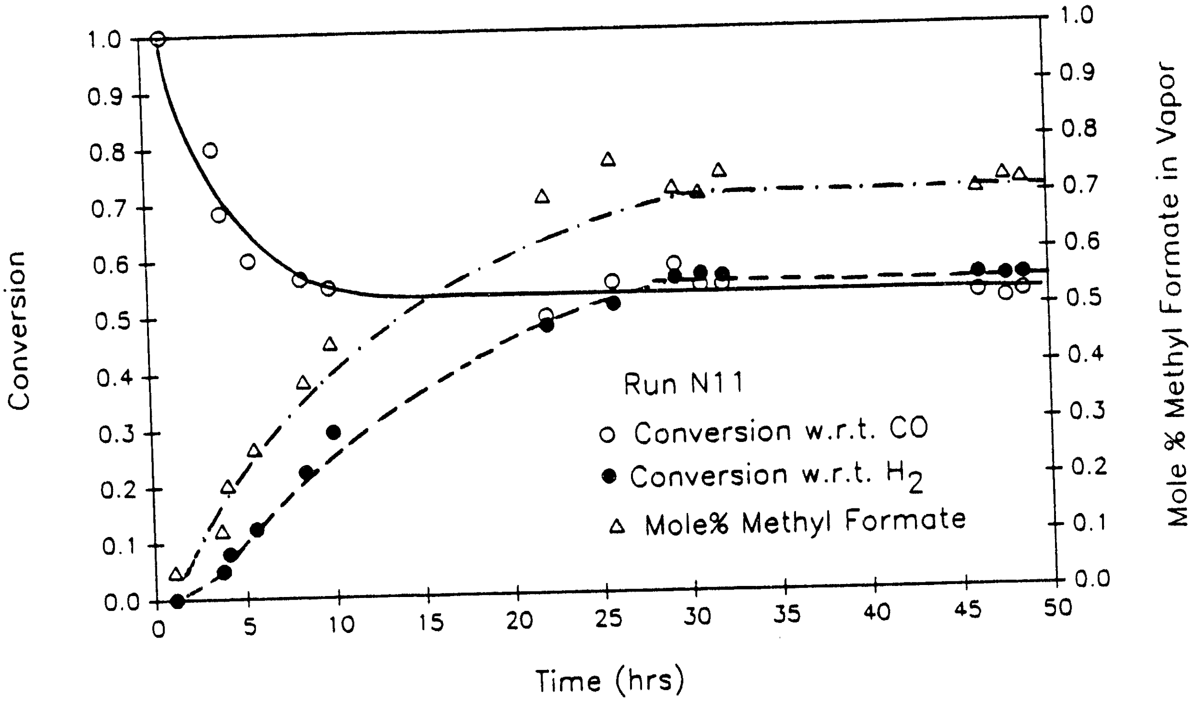


Figure 9. Typical Conversion of CO and H_2 with Time

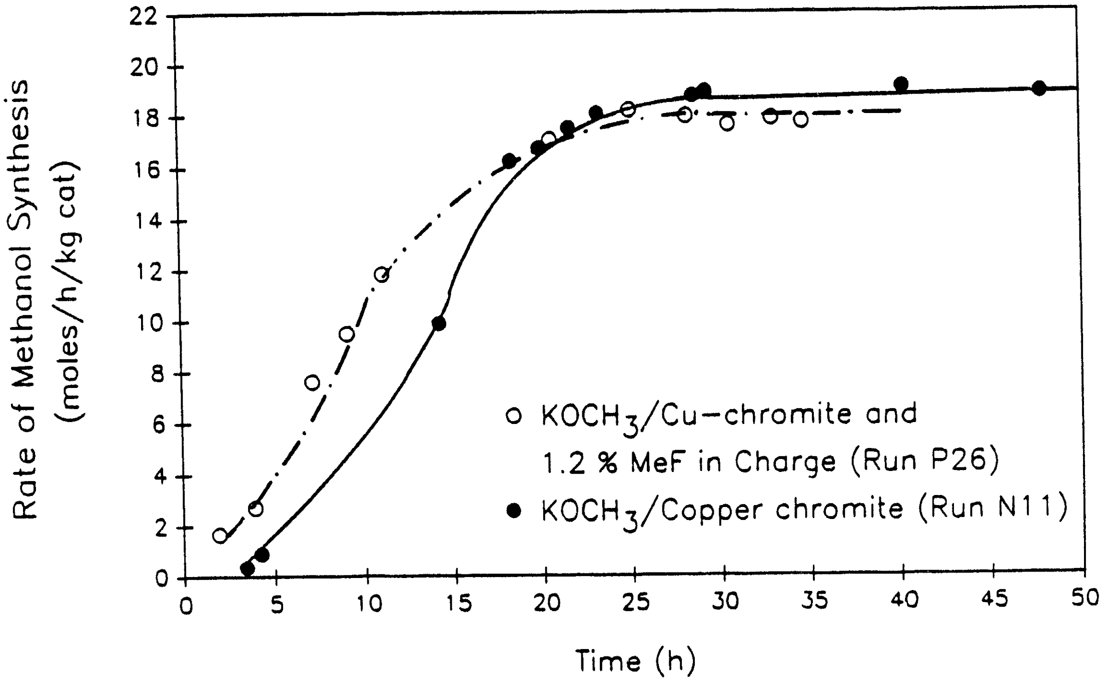


Figure 10. Effect of MeF in Charge on Induction Period

catalysts(38) and is unlikely to contribute to MeOH formation at the low temperature. In contrast, the carbonylation and the hydrogenolysis reactions take place at considerably milder conditions(32,39). This further emphasizes the role of MeF as the predominant source of MeOH, as against direct hydrogenation of CO/CO_2 at 150°C.

Having presented evidence for the formation of MeOH in a series reaction proceeding via MeF, it is important to establish the nature of the active catalyst for the reactions in the concurrent synthesis. To investigate whether formation of MeF in the concurrent synthesis is indeed catalyzed by CH_3OK, the activity of the mixed $KOCH_3$/copper chromite catalyst was compared to a coprecipitated potassium-containing copper chromite catalyst prepared by the method described earlier in this dissertation(33,34). The barium promoted and the prepared coprecipitated copper chromite catalysts had approximately the same composition (Cu/Cr ratio of 0.9). The rates of MeF formation during start-up for these catalysts are compared in Figure 11. The coprecipitated catalyst shows a longer induction period than the mixed catalyst. Analysis by atomic absorption of the liquid sample for potassium at the end of the reaction using coprecipitated copper chromite showed that 15% of the potassium cation had leached into the liquid where it could react with methanol to form $KOCH_3$ according to reaction 4-3.

$$CH_3OH + K^+ \rightleftharpoons CH_3OK + H^+ \qquad (4\text{-}3)$$

The increased induction period for the coprecipitated catalyst can be explained by the slow diffusion of alkali out of the bulk matrix into the liquid or on to the surface of copper chromite. The carbonylation reaction may take place either in solution or on the surface of the copper chromite catalyst with adsorbed $KOCH_3$. It is well known that the formation of MeF by the carbonylation reaction is homogeneously catalyzed by CH_3OK(7,15,1). It is likely that, in the concurrent synthesis, the formation of MeF takes place in the homogeneous liquid phase, although its formation on the copper chromite surface with adsorbed $KOCH_3$ cannot be ruled out.

4.6 LIQUID PHASE COMPOSITION OF MeF

In an anhydrous medium, the carbonylation reaction is two orders of magnitude faster than the hydrogenolysis reaction (Table 9). In the presence of small amounts of H_2O in the liquid, as in the concurrent synthesis, the rate of MeF formation is decreased (Table 10). If this rate in the concurrent synthesis is comparable to the rate of MeF disappearance by hydrogenolysis, then the MeF will not be in equilibrium. The MeF concentration was measured for the concurrent synthesis, at 150°C, 63 bar, 0.5 grams $KOCH_3$ and 3 grams copper chromite for various H_2/CO ratios. This is presented in Table 11, together with the calculated equilibrium MeF in mole percent. It can be seen that MeF concentration in the liquid is below the equilibrium concentration and hence the carbonylation reaction does not proceed to equilibrium in the concurrent synthesis. This means that both carbonylation and hydrogenolysis reactions influence the rate of MeOH formation; neither step controls under baseline conditions in the concurrent synthesis.

Since MeOH formation occurs via MeF, there is a distinct possibility of an interaction between the two catalysts resulting in the observed behavior in the concurrent synthesis. Four rather non-exclusive possibilities can prevail when

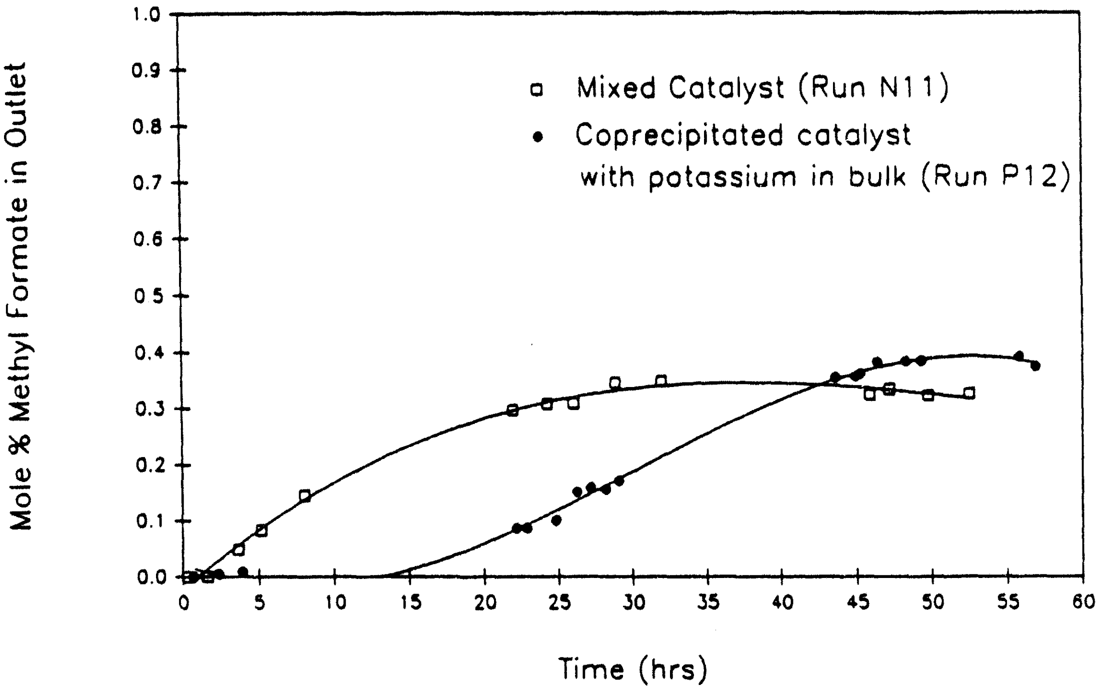


Figure 11. Mole Fraction MeF in Outlet for a Mixed $KOCH_3$/Copper Chromite and Coprecipitated Copper Chromite Catalysts

Table 11. MeF Mole Fraction Under Baseline Conditions at Various H_2/CO Ratios

Feed H_2/CO	H_2/CO in Reactor	CO Partial Pressure (atm)	Equilibrium MeF Concentration (mole%)	Experimental MeF in Liquid (mole%)
3.1 (Run A48)	4.6	6.07	1.5	0.79
2.92 (Run A48)	4.3	6.41	1.65	-
2.6 (Run A48)	3.6	7.39	1.93	0.83
2.0 (Run N11)	2.0	11.33	3.1	1.75
1.2 (Run A48)	0.6	21.25	5.7	4.43
1.0 (Run A48)	0.45	23.45	6.2	5.2
0.55 (Run A48)	0.2	28.33	7.45	7.3

using the combined catalytic system: (a) the two catalysts act separately with no interaction; (b) the $KOCH_3$ catalyzes the carbonylation reaction but is also adsorbed on the surface of copper chromite; (c) the two catalysts interact to form a new catalyst system; and (d) the copper chromite can function as more than an ester hydrogenolysis catalyst.

4.7 COMPARISON OF THE ACTIVITY OF A $KOCH_3$/COPPER CHROMITE SYSTEM WITH THAT OF COPPER-ZINC OXIDE

We compared the activity of copper chromite with copper-zinc oxide, the catalyst for the direct synthesis, with and without $KOCH_3$ (Table 12). Under concurrent synthesis conditions (110-180°C), copper chromite is known to be a better hydrogenolysis catalyst(8,25,40) than copper-zinc oxide(41). The $KOCH_3$/copper chromite and the $KOCH_3$/copper-zinc oxide catalysts have equal loadings of $KOCH_3$ and should result in equal rates of MeF formation, unless the hydrogenolysis catalyst affects the carbonylation reaction. As seen in Figure 12, the rate of methyl formate formation is higher for the $KOCH_3$/copper chromite than for $KOCH_3$/copper-zinc oxide. In the concurrent synthesis, both H_2O and CO_2 react with $KOCH_3$ to form potassium formate and potassium methyl carbonate respectively. The carbonylation activity in the presence of copper chromite indicates that potassium formate and the potassium methyl carbonate are converted to $KOCH_3$ by a copper chromite catalyzed hydrogenolysis reaction, restoring the carbonylation activity of $KOCH_3$ for MeF synthesis. The copper-zinc oxide cannot regenerate $KOCH_3$ as effectively at 150°C resulting in a lower MeF formation rate (Figure 12). In a MeOH solvent, copper chromite catalyzes three reactions; the hydrogenolysis of MeF to MeOH, the wgs reaction and reaction with various alkali compounds to regenerate the alkoxide.

As shown in Figure 13, copper-zinc oxide alone and the copper chromite alone result in low methanol formation rates; the $KOCH_3$/copper chromite combination is a much more active catalyst. Almost no MeF is formed using copper-zinc oxide alone, under concurrent synthesis conditions. The low methanol synthesis rates with the $KOCH_3$/copper-zinc oxide (Figure 13) in spite of the presence of some MeF (Figure 12), indicates that copper-zinc oxide is a poor catalyst for MeF hydrogenolysis. The copper chromite catalyst by itself also shows some activity. Two possible explanations are that the copper chromite has some activity for the direct hydrogenation of CO, or that the presence of traces of potassium in the reactor from previous runs leads to formation of MeF and hence to MeOH formation. The presence of alkali impurity in copper chromite catalysts has been reported to significantly influence MeOH synthesis activity, albeit at 250°C(42). Traces of potassium were indeed detected in the liquid and on the solid copper chromite surface at the end of the run along with traces of MeF. The contribution of residual potassium in the reactor to the MeOH formation rate at 150°C is likely to be small; the low catalytic activity of the copper chromite catalyst by itself is probably due to direct hydrogenation of CO.

One explanation for the lower hydrogenolysis activity of copper- zinc oxide is its likely tendency to be converted more easily to Cu^0 under the reducing environment in the concurrent synthesis. In comparison, the presence of barium in the copper chromite stabilizes Cu^+, known to be an active site for hydrogenolysis of esters(8). $BaCrO_4$ is believed to inhibit complete reduction of divalent copper by stabilization of Cu^+ as $CuCrO_2$(23).

4.8 THE ROLE OF COPPER CHROMITE IN MeF FORMATION

At 80°C, for a CO partial pressure of 11.33 bar ($H_2/CO = 2$ in reactor), 19% of MeF should be obtained in the liquid, as predicted by Liu et al.(15), the rest being methanol (Figure 4). As mentioned earlier, in carbonylation of MeOH to MeF at

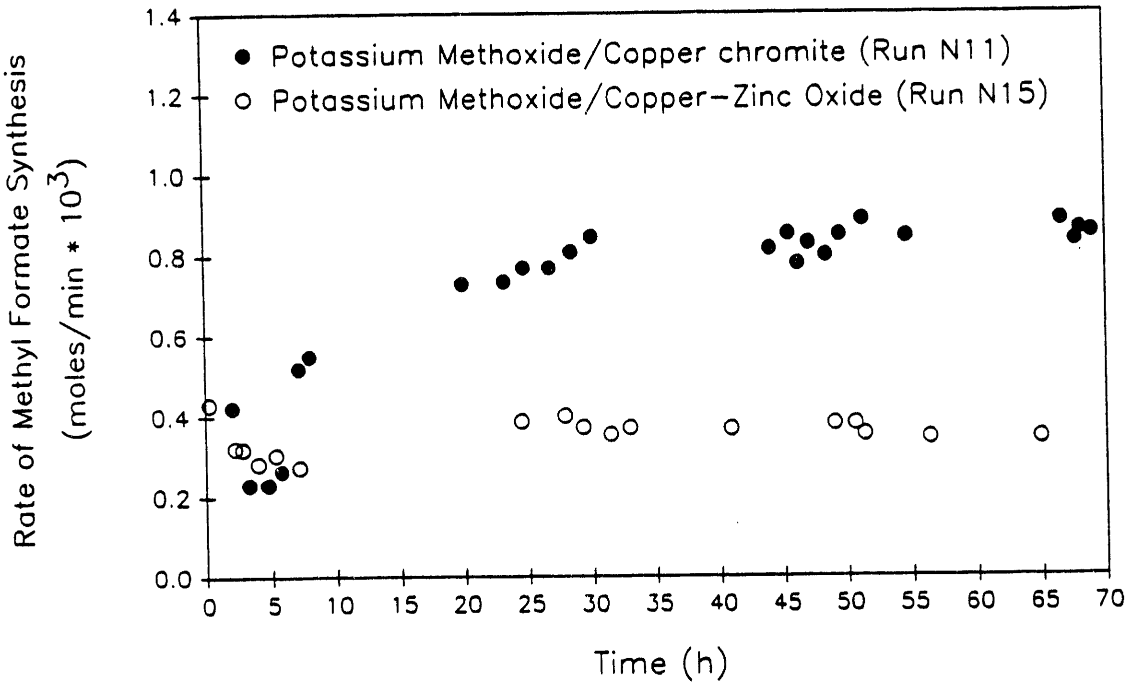


Figure 12. Rate of MeF Synthesis for a $KOCH_3$/Copper Chromite and $KOCH_3$/Cu-ZnO Catalyst Systems

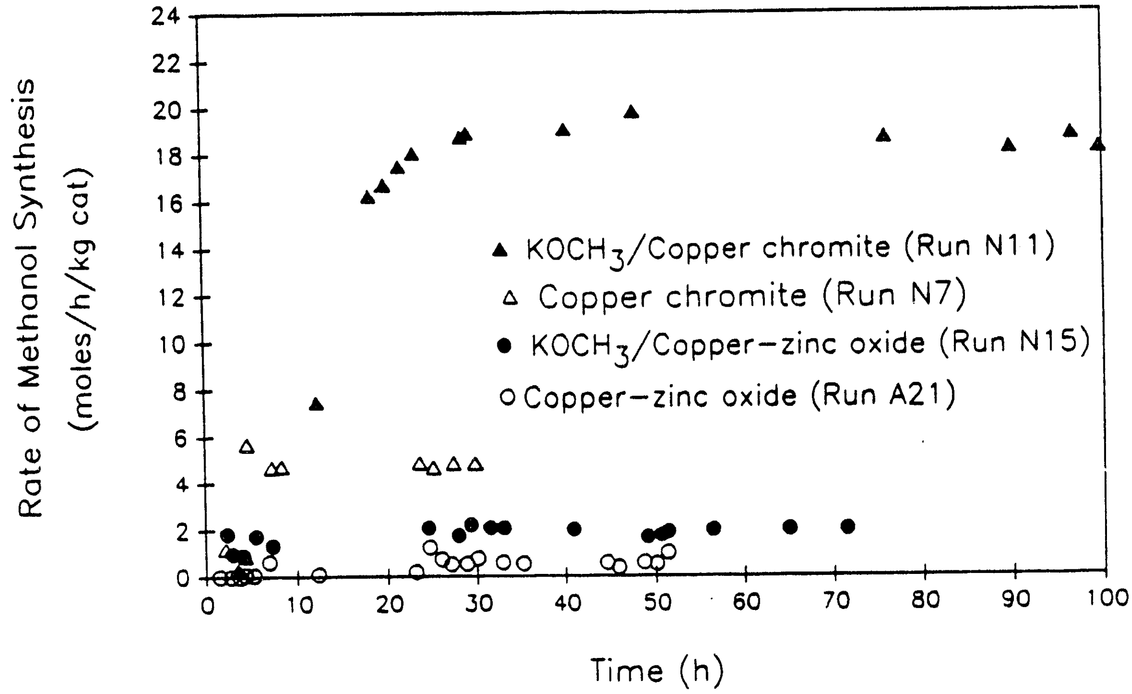


Figure 13. Rate of MeOH Synthesis for Copper Chromite and Copper-Zinc Oxide With and Without $KOCH_3$

80°C, high MeF formation rates are obtained only when H_2O and CO_2 are reduced to less than 10 ppm levels(7,15). The rate of MeF formation in the concurrent synthesis in the presence of about 1000 ppm water, as measured by CO consumption during a run in which the temperature was varied from 80°C to 150°C, is shown in Figure 14. At 80°C, the rate of formation is less than 0.3E-4 moles/min resulting in negligible MeF in spite of the predicted equilibrium composition (19 mole%). MeF starts to form when the temperature is increased above 100°C. The concurrent methanol synthesis occurs above 100°C; at these temperatures, the copper chromite regenerates the methoxide catalyst by facilitating hydrogenolysis of the potassium formate and the potassium methyl carbonate. The coproduction of MeOH and MeF in the presence of small amounts of H_2O and CO_2 is best carried out above 100°C.

A regeneration scheme is proposed in Figures 15 and 16 in which potassium formate and potassium methyl carbonate are converted to $KOCH_3$ by hydrogenolysis on the copper chromite surface, maintaining the $KOCH_3$ concentration in solution. This results in increased tolerance of the concurrent synthesis to the presence of H_2O and CO_2. Such transformations have been suggested by Bybell et al.(41) for intermediate moieties on copper-zinc oxide catalysts at 250°C for the direct synthesis of MeOH. Imyanitov et al.(16) have also proposed the possibility of $KOCH_3$ regeneration from the formate in the presence of ethylene glycol as solvent.

To confirm the regeneration cycle (Figures 15 and 16), we tested potassium formate, which is inactive in the carbonylation reaction(16), along with copper chromite for activity in the concurrent synthesis. Indeed, potassium formate is as active a catalyst as potassium methoxide (Table 12), supporting the proposal that

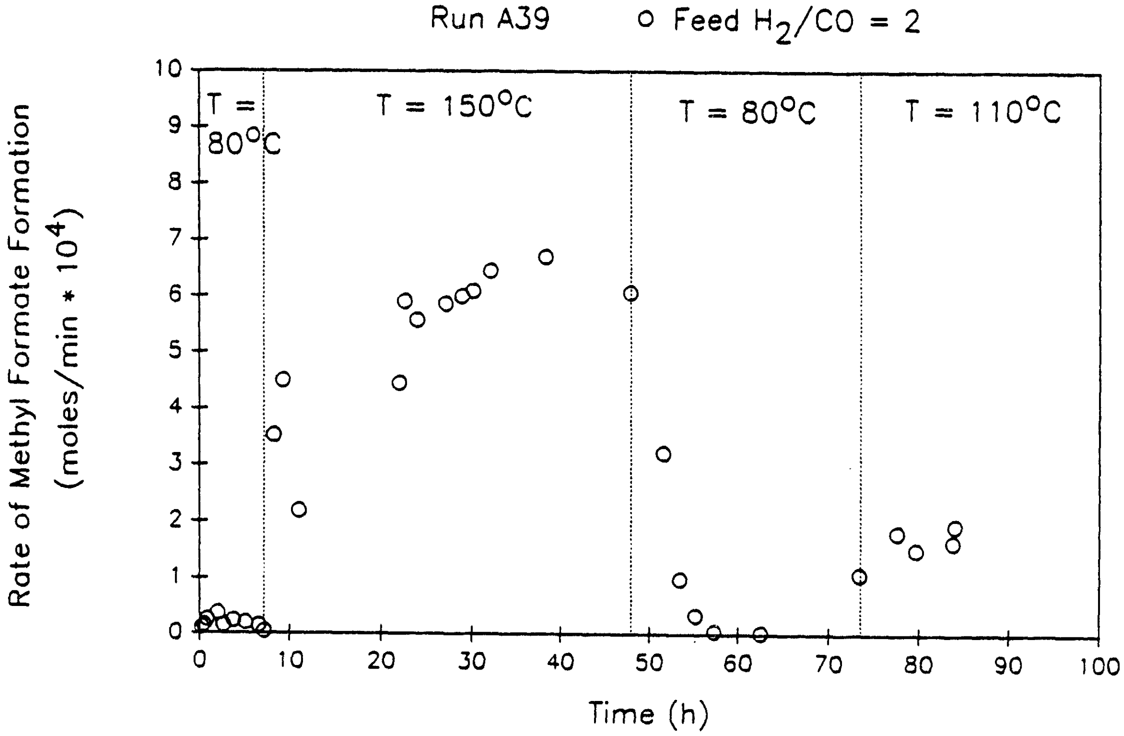


Figure 14. Rate of MeF Formation as a Function of Temperature

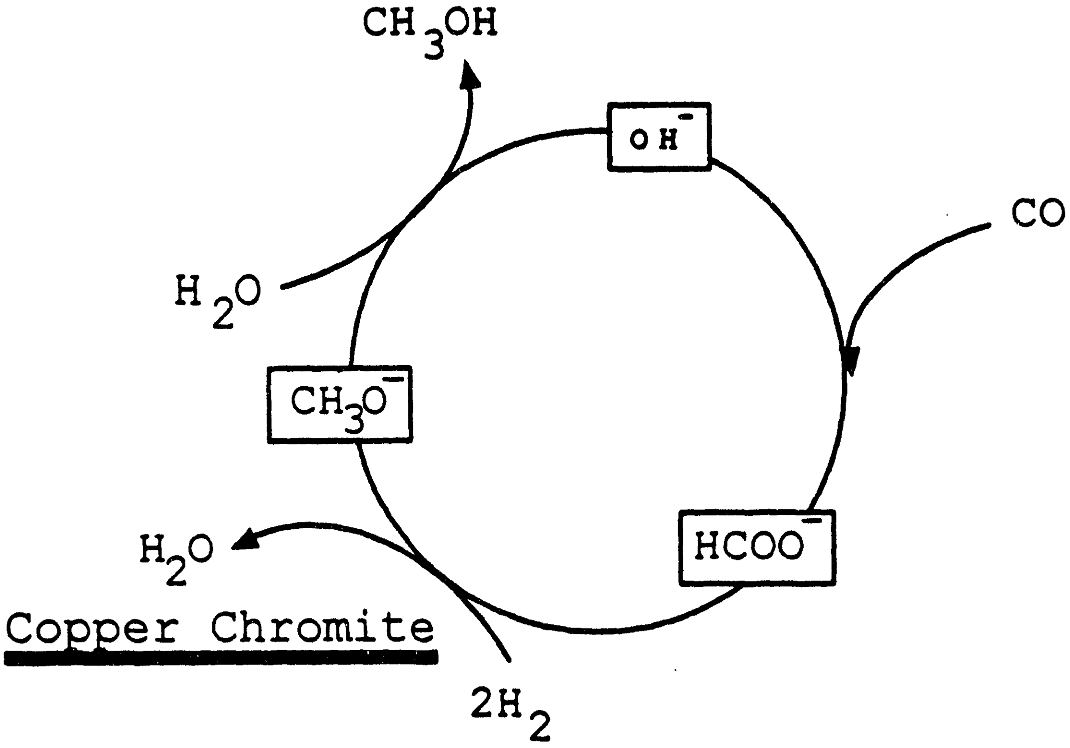


Figure 15. Proposed Regeneration of $KOCH_3$ from H_2O Deactivation in the Presence of Copper Chromite

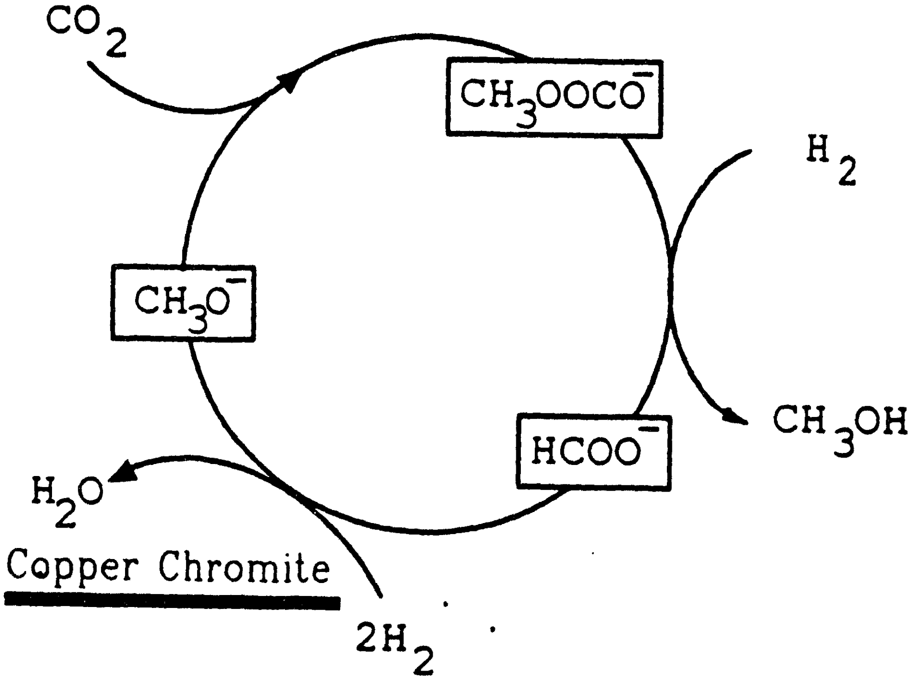


Figure 16. Proposed Regeneration of $KOCH_3$ from CO_2 Deactivation in the Presence of Copper Chromite

copper chromite maintains $KOCH_3$ concentration. Even KOH is an active catalyst (Table 12), reacting on the copper chromite surface to generate $KOCH_3$, as shown in Figure 15. The activity of potassium methyl carbonate could not be tested since it is not available in a stable form. However, its activity is likely to be similar to that of potassium methoxide.

Table 12. Activities of KOH and HCOOK in Comparison to CH_3OK with Copper Chromite in the Concurrent Synthesis

Soluble Salt	Loading moles/l	Rate of Methanol Synthesis moles/h/kg cat*
CH_3OK (Run N11)	0.048	19.0
KOH (Run A8)	0.057	19.62
HCOOK (Run A19)	0.048	19.25

* Steady state rate at the end of 40 hours; rate based on 20 g/l of copper chromite catalyst.

When $KOCH_3$ is added to a MeOH solution, in the presence of small amounts of water, the $KOCH_3$ is removed as HCOOK. An equilibrium is likely to be attained in the bulk between the CH_3O^- and the $HCOO^-$ formed. Table 13 shows the $[HCOO^-]/[CH_3O^-]$ ratio at equilibrium as a function of the temperature and H_2O concentration, calculated using the free energies of formation. Under normal operating conditions, the equilibrium favors formation of $HCOO^-$, the ratio of $[HCOO^-]/[CH_3O^-]$ decreasing with increasing temperature. However, the wgs reaction on the copper chromite surface leads to a reduction of H_2O concentration on the surface, so that the concentration of CH_3OK in solution is restored.

If the methoxide catalyst is regenerated by the copper chromite, the rate of carbonylation reaction should be high in the region close to the copper chromite surface. This region may be represented by a "film" close to the copper chromite surface. An overall reaction model is proposed in which MeF is formed by homogeneous carbonylation near the copper chromite surface and in the bulk liquid, coupled with regeneration of the methoxide catalyst on the copper chromite surface. This is followed by heterogeneous hydrogenolysis of MeF to yield MeOH.

The formation of MeF in the carbonylation reaction is postulated to occur by a two step mechanism involving the addition of CO to the methoxide anion according to equations 4-4 and 4-5(19).

$$CH_3O^- + CO \longrightarrow CH_3OCO^- \qquad (4\text{-}4)$$

$$CH_3OCO^- + CH_3OH \rightleftharpoons HCOOCH_3 + CH_3O^- \qquad (4\text{-}5)$$

The hydrogenolysis of MeF to MeOH on the copper chromite surface has been postulated to proceed via a hemiacetal intermediate obtained by hydrogenation of the surface methoxycarbonyl species as shown in equation 4-6(25),

$$\begin{aligned} HCOOCH_3 &\longrightarrow CH_3OCO_{(a)} \xrightarrow{2H} CH_3OCHOH_{(a)} \\ &\longrightarrow CH_3O_{(a)} + HCOH_{(a)} \xrightarrow{3H} 2CH_3OH \qquad (4\text{-}6) \end{aligned}$$

Table 13. Calculated Equilibrium Ratio of [HCOOK]/[CH_3OK] in Solution as a Function of Temperature and H_2O Concentration

Temp °C	CO Partial Pressure atm	Mole Fraction H_2O in Liquid	Mole Fraction MeF in Liquid	Equilibrium Constant K_e	$\frac{[HCOOK]}{[CH_3OK]}$
25	10	0.001	1.30	4704.9	12.59
25	10	0.01	1.30	4704.9	125.91
25	20	0.001	1.66	4704.9	28.59
25	20	0.01	1.66	4704.9	285.90
110	10	0.001	0.94	720.8	3.47
110	10	0.01	0.94	720.8	34.64
110	20	0.001	0.96	720.8	7.29
110	20	0.01	0.96	720.8	72.91
130	10	0.001	0.93	520.0	2.14
130	10	0.01	0.93	520.0	21.43
130	20	0.001	0.95	520.0	4.42
130	20	0.01	0.95	520.0	44.18
150	10	0.001	0.92	387.0	1.52
150	10	0.01	0.92	387.0	15.17
150	20	0.001	0.94	387.0	3.09
150	20	0.01	0.94	387.0	30.85

The methoxycarbonyl (CH_3OCO^-) is common to reactions 4-4 and 4-6. One possibility is that, in the presence of both catalysts, CH_3OK near a partially reduced copper chromite can generate the methoxycarbonyl intermediate on the copper chromite surface which in turn will give MeOH according to equation 4-6. This would indicate that formation of MeOH in the concurrent synthesis is largely a surface phenomenon; in this case, the rate of MeOH synthesis should be proportional to the copper chromite loading. This is not consistent with the results obtained in this study; the data will be discussed later.

Since the reaction medium is MeOH, there is likely to be a preponderance of CH_3O^- groups on the copper chromite surface(43,44). If this were a surface phenomenon, the incorporation of CO into the Cu-O bond of $CH_3O_{(a)}$ would form a Cu-C bonded methoxycarbonyl intermediate on the surface which would yield a Cu-O bonded surface hemiacetal moiety according to equation 4-6. This is unlikely on copper surfaces; the Cu-O bond is more stable than the Cu-C bond for MeOH synthesis(45).

Adsorbed formates have been reported to be MeOH synthesis intermediates on copper-zinc oxide catalysts at 250°C(46). These Cu-O bonded surface species may also be present on the copper chromite catalyst in the concurrent synthesis as a result of methoxide catalyst deactivation. Figure 17 shows the proposed transformations of the different species in the concurrent synthesis - the concentration of CH_3O^- is maintained by its regeneration from the formate; it then functions as a catalyst for carbonylation of MeOH to MeF. The MeF then is adsorbed on the surface via a methoxycarbonyl species(25) which undergoes hydrogenolysis to MeOH probably through a hemiacetal intermediate (Figure 17). It is likely that formate, methoxide and methoxycarbonyl species all exist at various stages on the copper chromite surface.

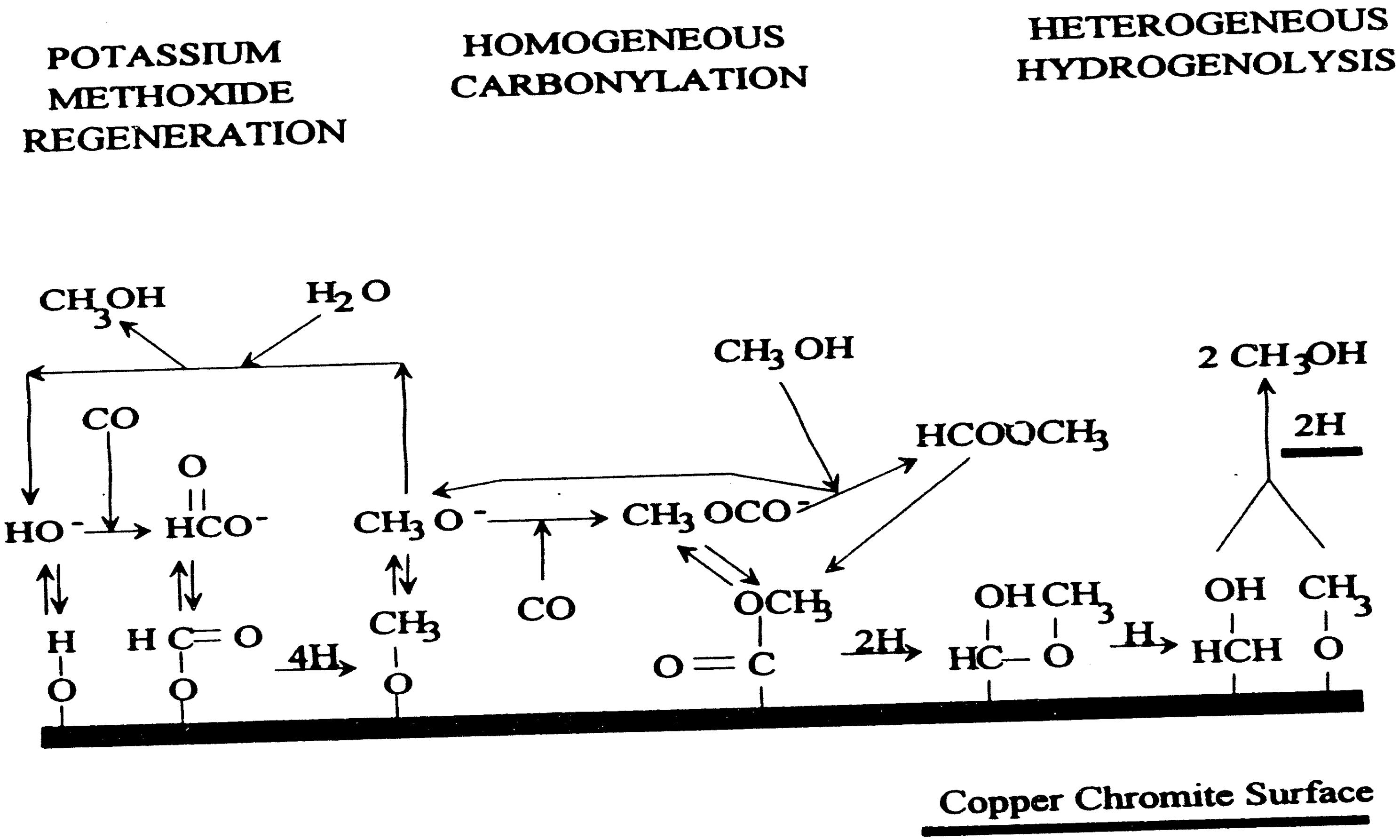


Figure 17. Proposed Transformations in the Concurrent Synthesis

4.9 EFFECT OF $KOCH_3$ LOADING ON RATE OF METHANOL FORMATION

Under our standard concurrent synthesis conditions (T = 150°C, P = 63 bar, $H_2/CO = 2$), the MeF concentration is less than equilibrium concentration as discussed in Section 5.4. Therefore, MeOH formation is governed by the rates of both carbonylation and hydrogenolysis reactions; neither reaction rate is controlling. The concentration of $KOCH_3$ catalyst should influence the rate of MeOH formation. The effect of $KOCH_3$ concentration in the charge at a constant loading of copper chromite is shown in Figure 18. The maximum MeOH formation rate was identified at a concentration of 0.048 moles/l $KOCH_3$ in the charge.

The concentration of MeF in the liquid for different $KOCH_3$ loadings is shown in Table 14. As expected, an increase in $KOCH_3$ concentration results in increased MeF concentration. At lower $KOCH_3$ loadings, this results in increased MeOH synthesis rates. However, at higher $KOCH_3$ loadings (beyond the maximum shown in Figure 18), in spite of the higher MeF concentration, the rate of MeOH synthesis decreases. This effect could be attributed to the blocking of the active hydrogenolysis sites on the copper chromite surface, resulting in decreased MeOH synthesis activity.

To ascertain the effect of alkali blockage on the copper chromite surface, the rates of hydrogenolysis on copper chromite are compared in the presence and absence of CH_3OK (Table 15). It can be seen that the presence of CH_3OK results in a decrease in the rate of H_2 consumption. The CH_3OK also catalyzes the decarbonylation reaction resulting in CO formation which could cause a decrease

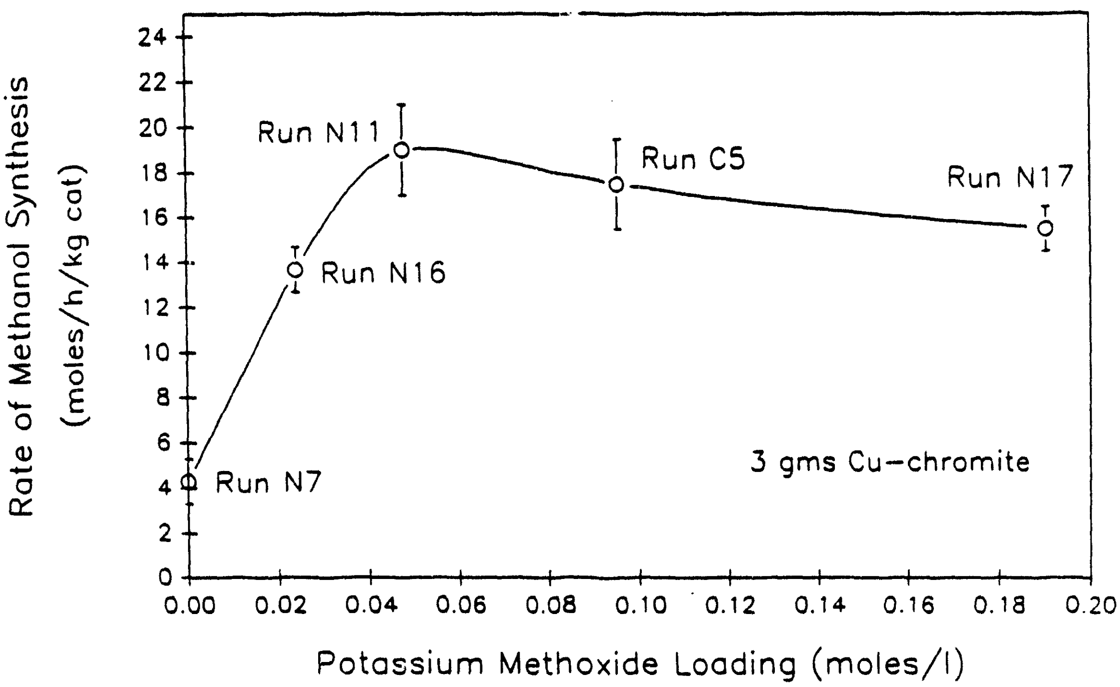


Figure 18. Rate of MeOH Synthesis as a Function of $KOCH_3$ Loading

in the rate. Whether inhibition of the hydrogenolysis reaction is due to alkali blockage or to CO formed because of the presence of alkali is difficult to determine.

Table 14. Mole Fraction of MeF as a Function of $KOCH_3$ Loading

CH_3OK Loading (moles/l)	MeF Concentration in Liquid (mole%)	Equilibrium MeF Concentration (mole%)	Rate of MeOH Synthesis[a] (moles/h/kg cat)
0.024 (Run A20)	1.17	3.1	13.66
0.048 (Run A48)	1.79	3.1	19.0
0.19 (Run A54)	2.45	3.1	15.52

[a] Steady state MeOH synthesis rate at 40 hours reaction time based on 20 g/l copper chromite.

At any time, the potassium on the copper chromite surface could exist as HCOOK or CH_3OK. The cation and the anion in both these compounds can exist on the surface hydrogenolysis sites. It is difficult to identify the blocking effect due to individual species. For simplicity, the site blocking will be referred to as alkali (in this case, potassium) site blocking, though this encompasses the possibility that the effect may be due to the formate or methoxide anion.

Table 15. Rate of H_2 Consumption in the Hydrogenolysis Reaction with and without $KOCH_3$

Reaction	Rate of H_2 Consumption (moles/h/kg cat)
Hydrogenolysis Reaction	93[a]
Hydrogenolysis Reaction in the Presence of $KOCH_3$ (Run A11)	34[b]

[a] Initial rate of MeOH synthesis by the hydrogenolysis reaction, predicted using the equation proposed by Liu et al.(22) at 150°C and 63 atm. total pressure using pure MeF as feed, H_2 partial pressure of 34 atm. and 20 g/l copper chromite catalyst concentration.

[b] Initial rate of MeOH synthesis by the hydrogenolysis reaction (experimental) in the presence of 0.048 moles/l CH_3OK catalyst at 150°C and 63 atm. total pressure using pure MeF as feed, H_2 partial pressure of 34 atm. and 20 g/l copper chromite catalyst concentration.

It has previously been shown that both KOH and HCOOK are active catalysts. For different loadings, the reaction rate for KOH and HCOOK is similar to that of $KOCH_3$ (Figure 19). This is additional evidence for the proposed role of copper chromite in the regeneration of potassium methoxide in solution.

The rate of MeF formation in the concurrent reaction is compared with that predicted by Liu et al.(15) for the carbonylation reaction (Table 16). The initial rate

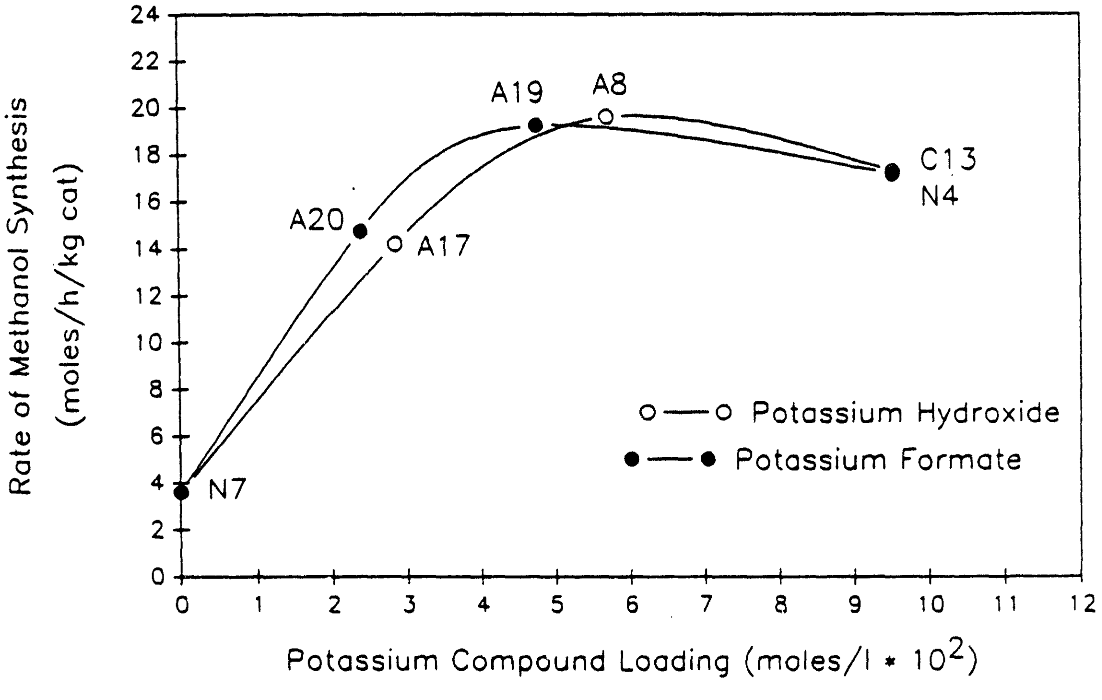


Figure 19. Rate of MeOH Synthesis as a Function of KOH and HCOOK Loading

is the rate at three hours after introduction of CO, when MeF starts to form. At this time the H_2O in the reactor has been depleted to about 3000 ppm. The steady state rates are at 40 hours of reaction time when the H_2O concentration has decreased to about 1000 ppm. The rates of MeF formation (both initial and steady state) in the concurrent synthesis are lower than predicted due to the higher amounts of H_2O and CO_2 present (about 10 ppm was present in the carbonylation reaction(22)). The steady state rates are also significantly higher than the initial rates due to the decreased H_2O concentration. An increase in the initial rates with increasing $KOCH_3$ concentration is consistent with that found for the carbonylation reaction. At steady state, the rate of MeF formation is equal to the rate of MeOH formation; as expected, the trend in the steady state MeF rates (Table 15) is similar to the trend in MeOH synthesis presented in Figure 18.

The alkali methoxide or formate is distributed between the liquid and the copper chromite surface. The distribution of potassium between the liquid and the copper chromite surface at the end of the reaction under ambient conditions, as measured by atomic absorption (Figure 20) can be represented by a Freundlich type isotherm ($\theta = 1.34\ C^{0.78}$ - where θ is the surface coverage of potassium in moles potassium per g of copper chromite catalyst and C is the concentration of potassium in the liquid in moles/l). A significant fraction of the potassium (25%) is adsorbed on the copper chromite surface at ambient conditions and this should also be true under concurrent synthesis operating conditions, though the coefficients in the Freundlich equation will be different. Under ambient conditions, in all cases, about 75% of the alkali was present in the liquid at the end of reaction, the rest being on the solid surface. The adsorbed alkali may play a role in the blocking of the hydrogenolysis sites on the copper chromite surface.

Table 16. Rate of MeF Formation as a Function of $KOCH_3$ Loading

CH_3OK Loading (gmoles/l)	MeF Synthesis Rate Predicted By Liu et al. (moles/min)	Methyl Formate Sythesis Rate in the Concurrent Synthesis (moles/min)	
		Initial	Steady State
0.024 (Run A20)	$71 * 10^{-3}$	$0.3 * 10^{-3}$	$0.68 * 10^{-3}$
0.048 (Run N11)	$142 * 10^{-3}$	$0.36 * 10^{-3}$	$0.95 * 10^{-3}$
0.095 (Run C5)	$285 * 10^{-3}$	$0.41 * 10^{-3}$	$0.85 * 10^{-3}$
0.19 (Run A54)	$570 * 10^{-3}$	$0.44 * 10^{-3}$	$0.78 * 10^{-3}$

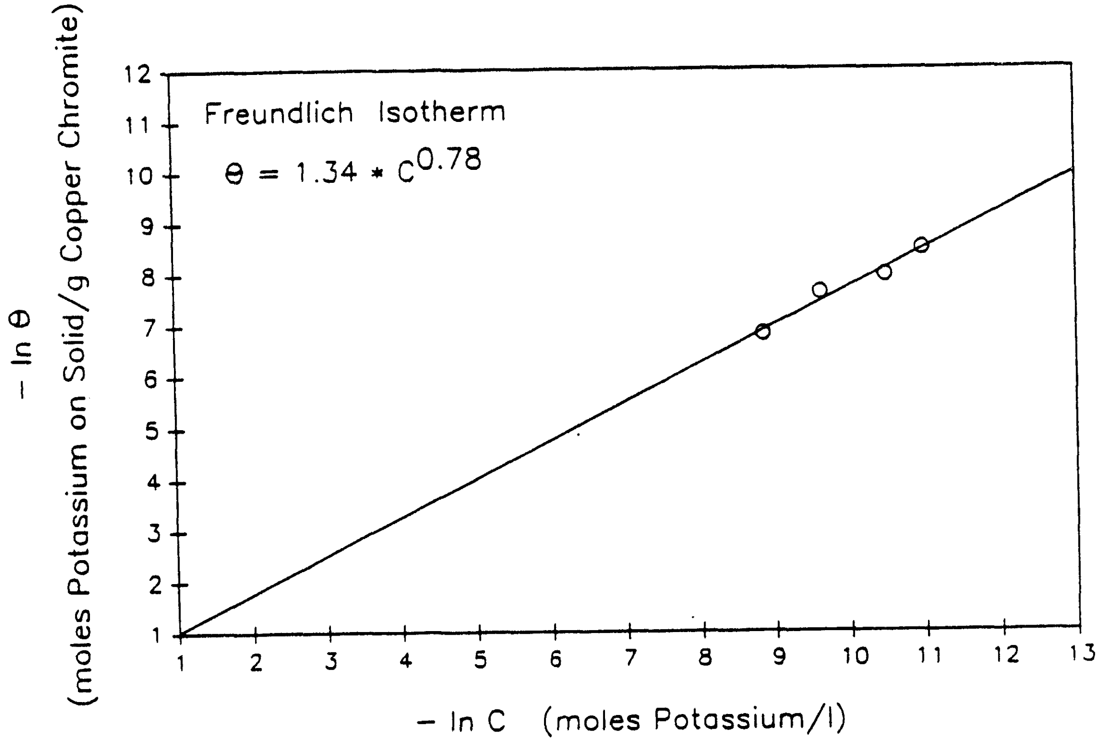


Figure 20. Distribution of Potassium Between the Bulk Liquid and the Copper Chromite Surface Under Ambient Conditions

4.10 OTHER POTASSIUM COMPOUNDS AS CATALYSTS

Traditionally, alkali metal alcoholates have been used as catalysts for the synthesis of MeF. The above discussion showed that KOH and HCOOK are converted to the active CH_3OK catalyst. By regeneration with ethylene glycol in a separate reactor, Imyanitov et al.(16) showed that Na_2CO_3 was also active. This could imply that alkali compounds such as K_2CO_3 could be active in the concurrent synthesis. K_2CO_3 and KCl were tested for activity in the concurrent synthesis. As seen in Table 17, except for the low activity of the chloride, all compounds are active for the synthesis of MeOH; MeF is formed in each case. Since the methoxide ion is needed for MeF production, these compounds are all converted to the active CH_3OK. Possible transformations are shown in Figure 21. The low activity of the chloride is comparable to the case with no addition of alkali compound. It may also be that the chloride anion renders the copper chromite inactive due to poisioning.

4.11 SODIUM, RUBIDIUM AND CESIUM COMPOUNDS AS CATALYSTS

Sodium, rubidium and cesium compounds were also tested for MeOH synthesis activity. As with potassium, the activity of the hydroxide and the formate of cesium and the hydroxide of sodium are similar to that of their respective methoxides (Table 18). This is additional evidence for the conversion of the alkali formate to the alkali methoxide in the presence of copper chromite. It is noteworthy that none of these alkali compounds have been reported as catalysts for the carbonylation reaction. The lower activities of the cesium compounds in

Table 17. Activities of Potassium Compounds in the Concurrent Synthesis

Soluble Catalyst		Rate of MeOH Synthesis* moles/h/kg cat
Type	Loading moles/l	
CH_3OK (Run N1)	0.095	18.1
KOH (Run A16)	0.095	18.3
HCOOK (Run A26)	0.095	17.9
K_2CO_3	0.048	11.6
KCl (Run N6)	0.095	4.5
No Alkali Compound (Run N7)	-	3.3

* Steady state rate at the end of 40 hrs based on 20 g/l barium stabilized copper chromite catalyst

comparison to the corresponding potassium compounds seem out of place

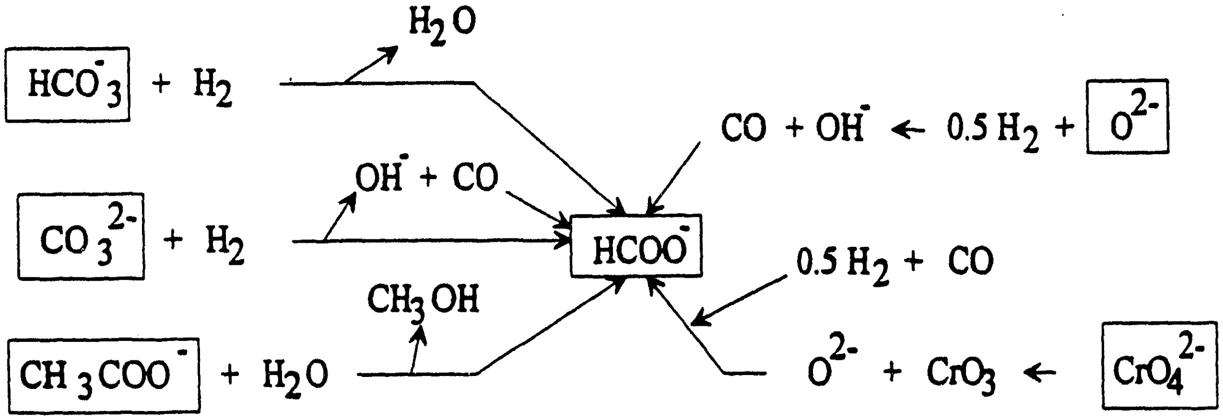


Figure 21. Possible Transformations Between the Different Alkali Anions in Solution

particularly in light of findings by Tonner et al.(7) that carbonylation rates decrease in the order Cs > K > Na. Possible reasons for this behavior are discussed later.

Table 18. Activities of Sodium, Rubidium and Cesium Compounds with Copper Chromite in the Concurrent Synthesis

Soluble Catalyst		Rate of Methanol Synthesis* moles/h/kg cat
Type	Loading moles/l	
CH_3ONa (Run A31)	0.048	15.1
CH_3ONa (Run C10)	0.095	13.2
NaOH (Run A15)	0.048	15.3
CsOH (Run A24)	0.024	11.5
CsOH (Run A22)	0.048	15.0
HCOOCs (Run C12)	0.095	14.1
Rb_2O (Run A23)	0.048	16.8
$CsHCO_3$ (Run C11)	0.056	15.1
Cs_2CrO_4 (Run A3)	0.024	11.4

[*] Steady state rate at the end of 40 hrs based on 20 g/l copper chromite catalyst

4.12 ALKALINE EARTH COMPOUNDS AS CATALYSTS

It was first reported by Petrole Informations(9) that, in addition to alkali methoxides, alkaline earth methoxides were also catalysts for MeOH synthesis in conjunction with copper chromite. Onsager et al. used $Ba(OCH_3)_2$ as a catalyst although its activity was much lower than that of $NaOCH_3$(12). The activities of four alkaline earth compounds with copper chromite are shown in Table 19; the rates of methanol formation are lower than those with the alkali compounds. The greater ionization potential of the alkaline earth metals results in a decreased ability to release the anion, which is reflected in low MeF concentrations (< 20% of equilibrium values for the cases considered) resulting in low MeOH formation rates. As with alkali, the non-methoxide alkaline earth anions are converted to the respective methoxides in the presence of copper chromite.

4.13 ACTIVITIES OF DIFFERENT ALKALI METHOXIDES IN THE CONCURRENT SYNTHESIS

It is proposed that the alkali compound adsorbed on the surface of copper chromite blocks hydrogenolysis sites, affecting the rate of MeOH synthesis (Figure 18). To test this effect, four alkali alkoxides were used with copper chromite in the concurrent synthesis. Their activities are listed in Table 20. The $KOCH_3$/copper chromite catalyst gives the highest MeOH formation rate. As expected, the MeF concentration in the liquid increases from sodium to cesium, with decreasing ionization potential of the alkali metal (Table 21). The activity of $KOCH_3$ is understandably higher than $NaOCH_3$. In addition, the lower solubility of HCOONa in MeOH might also contribute to the lower activity. At the end of

Table 19. Rate of MeOH Synthesis with Different Alkaline Earth Compounds and Copper Chromite

Soluble catalyst		Rate of Methanol Synthesis*
Type	Loading (moles/l)	moles/h/kg cat
$Ba(OCH_3)_2$ (Run A2)	0.043	4.2
$Ba(OH)_2$ (Run P27)	0.095	2.5
BaO (Run P28)	0.095	2.3
$Mg(OCH_3)_2$ (Run P3)	0.047	1.2

* Steady state rate at the end of 40 hrs; rate based on 20 g/l of heterogeneous copper chromite catalyst.

reaction, small amounts of a white precipitate of HCOONa was found in the reaction mixture under ambient conditions. This was not the case for the potassium, rubidium and cesium methoxides. For the rubidium and cesium methoxides, in spite of the increased MeF concentration, the MeOH formation activities are consistently lower. This may be due to the fact that the larger size of the rubidium and cesium ions results in more hydrogenolysis sites being covered, lowering MeOH formation rates. Since the carbonylation reaction takes place near the copper chromite surface, the formation of MeF may require the alkali methoxide to diffuse into pores of the catalyst. Diffusion into the pores of copper chromite (average pore size is 35-40 Å) may be hindered with increasing alkali size. The initial rate of MeF formation increases in the order Na < K < Rb < Cs (Table 21) and the steady state rates show a maximum for $KOCH_3$. This is consistent with the rates of MeOH synthesis shown in Table 20). Additional support for the lower rates with cesium compounds is obtained by comparing the activities of the hydroxides and formates of cesium and potassium (Table 18). In all cases, the potassium compounds are more active that the corresponding cesium compounds.

4.14 RATE OF MeOH SYNTHESIS AT HIGHER COPPER CHROMITE LOADINGS

The rate of MeOH synthesis is influenced by the copper chromite catalyst loading (Figure 22). The MeOH synthesis rate expressed per kilogram of copper chromite decreased with increasing copper chromite loading, although the amount of MeOH formed (moles/h) increased. At constant $KOCH_3$ loading, an increase in copper chromite loading results in a lower MeF concentration in the liquid, decreasing the MeOH synthesis rate. In the case of 0.095 moles/l $KOCH_3$ and 20 g/l copper chromite, the MeF concentration was found by interpolation to be 2.12 mole%, while for 0.095 moles/l $KOCH_3$ and 40 g/l copper chromite, the MeF was 1.58 mole%. The decreased rate of MeOH synthesis (Figure 22) indicates that the carbonylation reaction is limiting at higher copper chromite loadings.

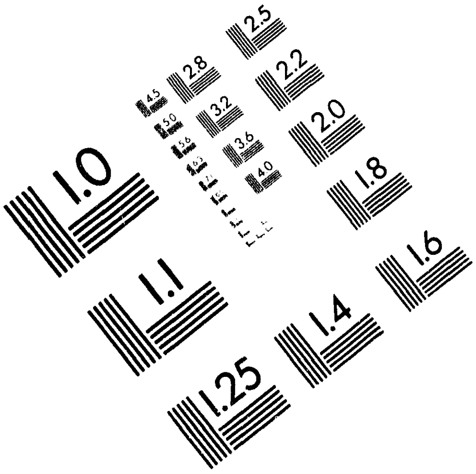
From the above discussion, it is apparent that the low MeOH synthesis rates at high catalyst loading cannot be overcome by addition of more $KOCH_3$. For example, for 0.25 moles/l $KOCH_3$ and 40 g/l copper chromite loading, the MeF

Table 20. Rate of MeOH Synthesis with Different Alkali Methoxides

Soluble Catalyst		First Ionization Potential of Alkali Metal Volts	MeF Concentration in Liquid mole%	Rate of MeOH Synthesis[a] moles/h/kg cat
Type	Loading gmole/l			
CH_3ONa (Run A31)	0.048	5.14	1.4	15.1
CH_3OK (Run A48)	0.048	4.34	1.8	19.0
CH_3ORb (Run A14)	0.048	4.18	2.4	16.7
CH_3OCs (Run A12)	0.048	3.89	2.7	14.7

[a] Steady state rate at the end of 40 hrs based on 20 g/l copper chromite catalyst.

reached 92% of the equilibrium concentration (Run A52); however, the rate of MeOH formation per kg of copper chromite catalyst was lower (Figure 22). The effect of increased MeF concentration is offset by a decreased number of hydrogenolysis sites available due to site blockage; the actual rate of MeOH synthesis depends on the magnitude of these effects.



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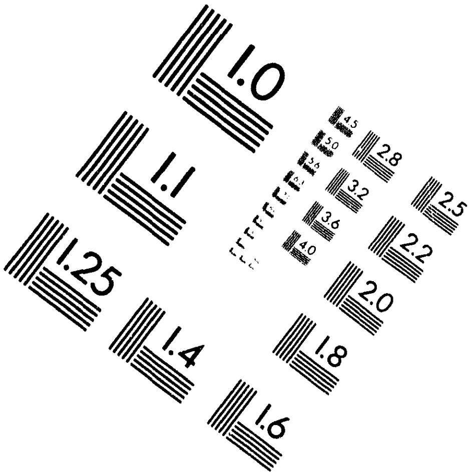

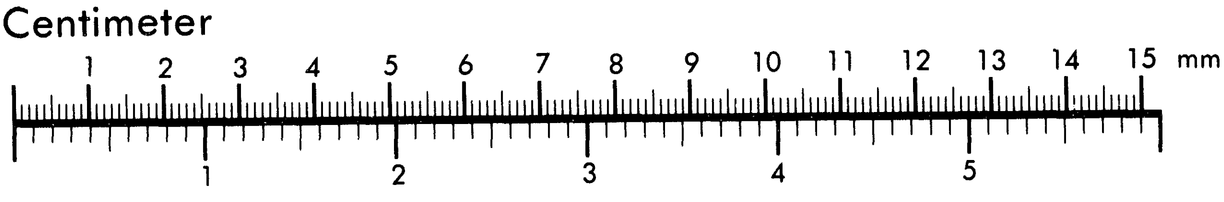

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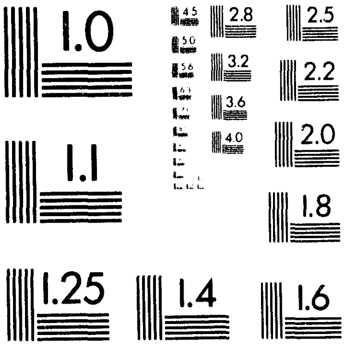

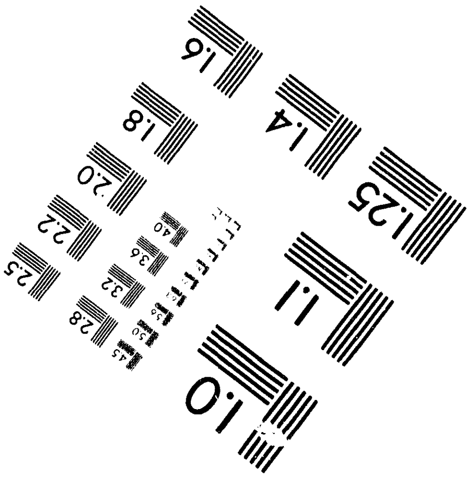

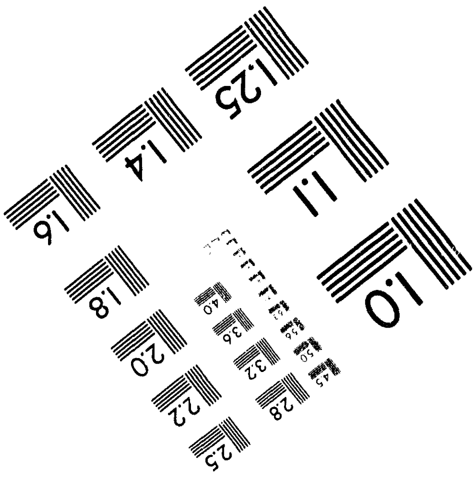

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Table 21. Rate of MeF Synthesis with Different Alkali Methoxides

Soluble Catalyst		First Ionization Potential of Alkali Metal Volts	Rate of Methyl Formate Synthesis (moles/min)	
Type	Loading mole/l		Initial	Steady State
CH_3ONa (Run A31)	0.048	5.14	$0.15 * 10^{-3}$	$0.75 * 10^{-3}$
CH_3OK (Run N11)	0.048	4.34	$0.36 * 10^{-3}$	$0.95 * 10^{-3}$
CH_3ORb (Run A14)	0.048	4.18	$0.43 * 10^{-3}$	$0.83 * 10^{-3}$
CH_3OCs (Run A12)	0.048	3.89	$0.46 * 10^{-3}$	$0.74 * 10^{-3}$

[*] Steady state rate at the end of 40 hours based on 20 g/l copper chromite catalyst.

The volumetric productivity at high catalyst loadings is low. This can be improved by increasing the MeF concentration in solution to as close to equilibrium as possible. One strategy to increase the carbonylation rate is to add an agent such as a transition metal (other than iron or nickel) carbonyl which has been shown to increase the turnover frequency for MeF formation by providing a more activated CO species(17). These strategies to improve reactor productivity need to be examined in greater detail.

The rate of MeOH synthesis was also examined at a 15% catalyst loading at the optimum catalyst ratio for the 2.5% loading case. The results are compared in Figure 23. The rate of MeOH synthesis expressed per gram of copper chromite catalyst decreases with increasing catalyst concentration. The carbonylation reaction seems to limit the rate of MeOH formation at the higher loading.

4.15 NATURE OF ALKALI INTERACTION IN THE CONCURRENT SYNTHESIS

Potassium impregnated copper chromites were tested for activity in the concurrent synthesis. Different amounts of potassium were impregnated by the incipient wetness technique using potassium carbonate as a precursor and then activated in a stream of pure H_2 at 400°C. The rate of MeOH synthesis as a function of potassium loading is shown in Figure 24. The rate of MeOH formation is high for the 5.7% potassium loading but is about 0.65 that of the $KOCH_3$/copper chromite catalyst (Figure 18). A salient feature is the sharp decrease in rate between 5.7% and 11.3% potassium loading (Figure 24). It is noteworthy that the monolayer coverage of potassium on the copper chromite used in this study corresponds to a loading of 12%. One possible explanation is that the ratio of adsorbed potassium to copper chromite (moles potassium/g copper chromite) (see Section 5.9 for details) is 3.5E-4 for the 5.3 wt% potassium impregnated catalyst and 5.6E-4 for the 11.3 wt% potassium loading (Table 22). The increased adsorption may result in blockage on the surface of the copper chromite

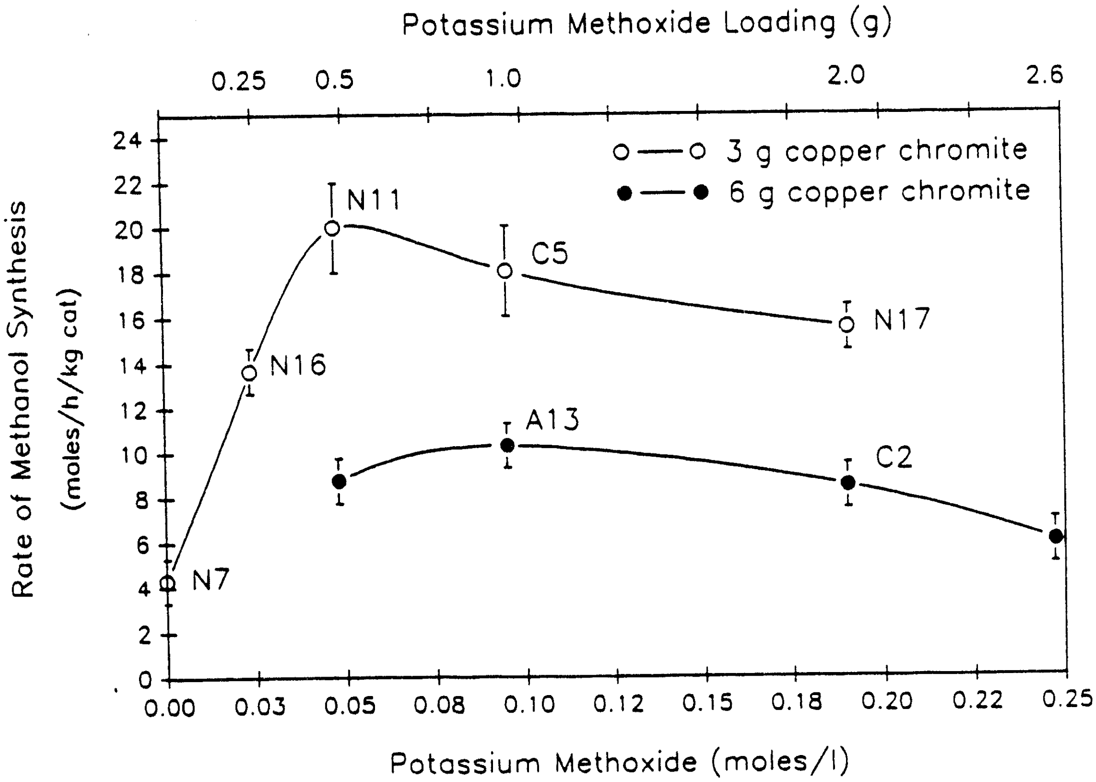

Figure 22. Rate of MeOH Synthesis for Two Copper Chromite Loadings

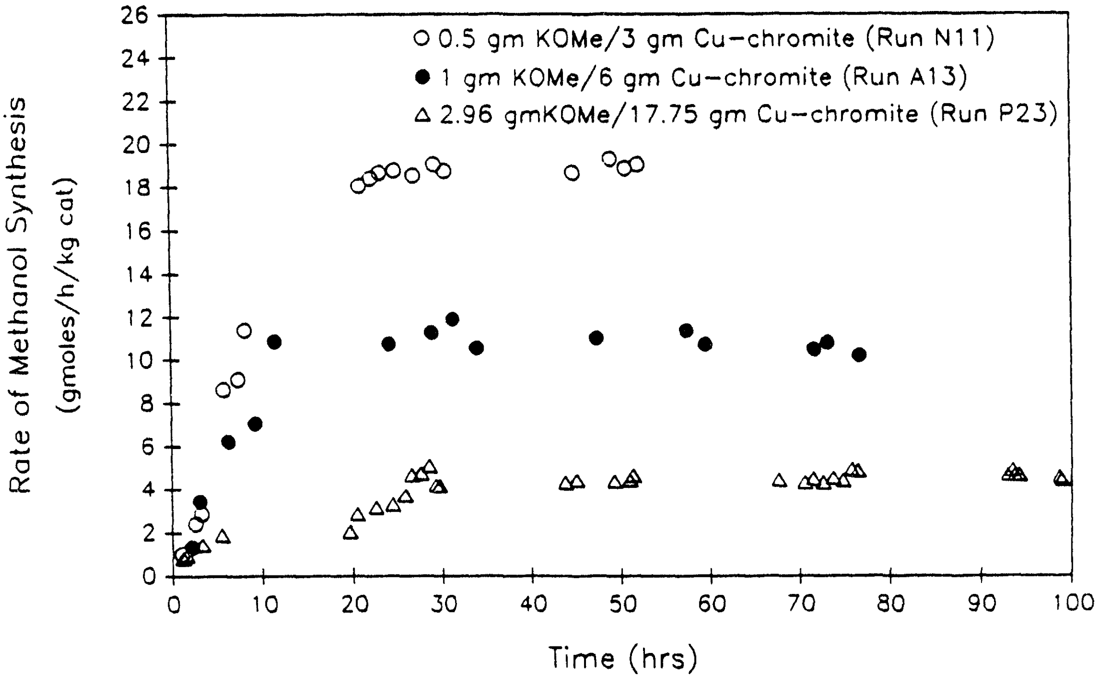

Figure 23. Rate of MeOH Synthesis for Three Heterogeneous Catalyst Loadings

accounting for the low MeOH formation rates. The lower rates with the impregnated catalysts (Figure 24) in comparison to the mixed $KOCH_3$/copper chromite catalyst (Figure 18) may be due to the stronger chemical interaction between the alkali and the copper chromite surface.

It is interesting to compare the nature of the alkali/copper chromite catalyst in the concurrent synthesis with alkali promoted copper-zinc oxide catalysts at 250°C for the direct synthesis. Klier et al.(30) have shown by infrared studies that the latter proceeds via a surface formate precursor; the surface alkali on copper-zinc oxide at 250°C serves to increase the activity per site for MeOH formation rather than the number of active sites. The resultant effect is promotion of the rate of the direct hydrogenation of CO to MeOH. In addition, increased amounts of higher alcohols have been reported(41). In the concurrent synthesis, the postulated alkali blockage of the hydrogenolysis sites may lead to a decreased number of available sites; the activity per site is probably unchanged. No higher alcohols or esters other than MeF are formed in the concurrent synthesis, a result of the low temperature of operation (below the Huttig temperature of 179°C for copper).

4.16 ACTIVITIES OF DIFFERENT COPPER CHROMITES FOR THE CONCURRENT SYNTHESIS

A number of copper chromite catalysts were examined for their MeOH synthesis activity (Table 23). A high surface area Ba- stabilized, G-89 (United Catalysts)(10) and a Mn-stabilized copper chromite yielded high methanol synthesis activities (Table 23). Deactivation rates were higher for the copper chromites containing Mn. However, a deactivation rate over 75 hours of 1.3 %/day

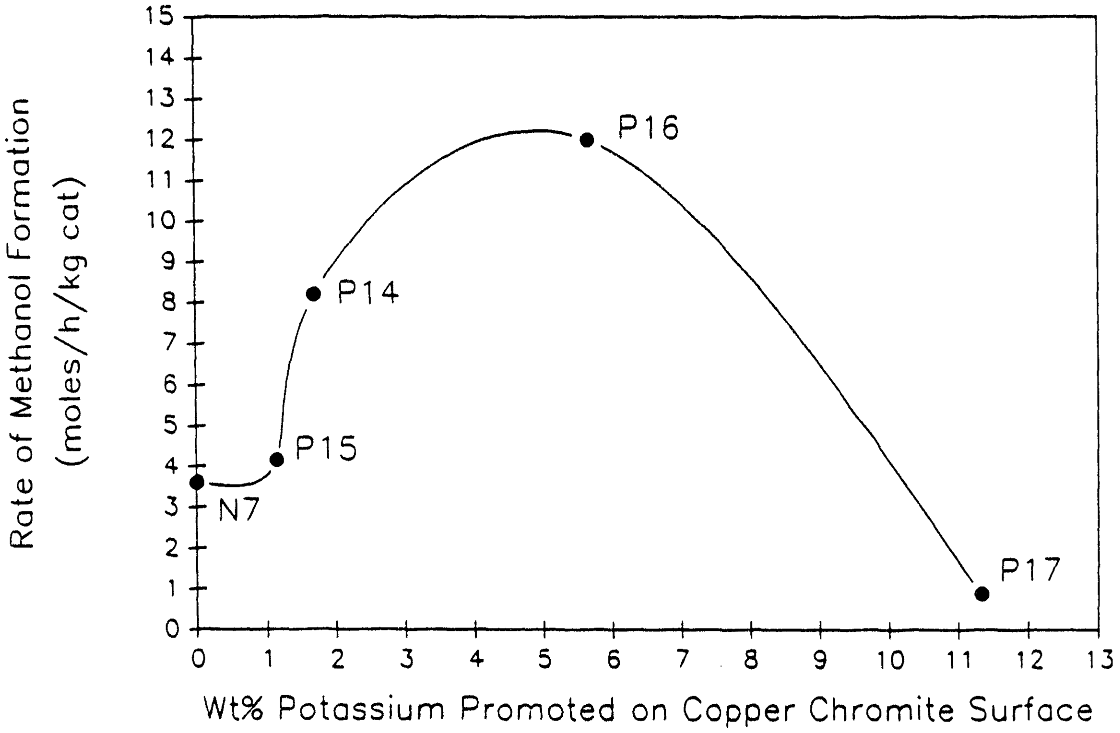

Figure 24. Effect of Potassium Loading on the Rate of MeOH Synthesis For Potassium Impregnated Copper Chromite

Table 22. Distribution of Potassium Between Liquid and the Copper Chromite Surface for Potassium Impregnated Copper Chromite Catalysts At Ambient Conditions

Wt% Potassium Impregnated on Copper Chromite	Total Moles Potassium moles * 10^3	Concentration of Potassium in Liquid moles/ml * 10^5	Potassium in Liquid moles * 10^3	Potassium on Copper Chromite moles * 10^3	$\frac{\text{Moles Potassium Adsorbed} * 10^4}{\text{g Copper Chromite}}$ θ
5.7 (Run P16)	4.3	2.12	3.3	1.1	3.5
11.3 (Run P17)	8.7	3.06	3.7	5.0	5.6

for the G-89 catalyst is better than the 3.0 %/day deactivation rate previously reported(10) due to removal of iron carbonyls from the CO feed which are detrimental for copper chromite catalysts.

The surface area of the Ba-stabilized copper chromite seems to influence its MeOH synthesis activity (Figure 25). The XRD analyses of the Ba-stabilized copper chromites showed that the surface morphology was the same in all cases. Catalyst particle size measurements indicated that the particle sizes before reaction were similar in the three cases (≈ 20-30 μm). Although, the catalysts were not tested for available surface sites, it is likely that the reduced surface area catalysts have smaller number of active sites.

4.17 THE CATALYST SYSTEM

The catalytic system used in the concurrent synthesis falls in the general category of mixed catalysts consisting of alkali compounds and copper chromite or alkali impregnated copper chromite. The alkali compounds are soluble and ionize in MeOH at temperatures above 100°C. It is likely that the CH_3O^- anion is the active catalyst for the formation of MeF.

The heterogeneous copper chromite catalyst is normally favored for the hydrogenolysis of esters at low temperatures. These catalysts typically contain a copper oxide and a copper chromite ($CuCr_2O_4$) spinel phase. The most commonly used method for the preparation of a compound containing these two components is that suggested by Adkins et al.(33,34). A basic ammonium salt containing copper and chromium is prepared by reaction 4-7 and then decomposed with careful control of the exotherm to give copper chromite according to reaction 4-8.

Table 23. Rate of MeOH Synthesis with Different Copper Chromites

Run No.	Type of Copper Chromite Cu%/Cr%/Ba%/Mn% (Surface Area)	Rate of MeOH Synthesis* gmoles/h/kg cat	Average Deactivation Rate %/day
P3	Ba stabilized copper chromite** 28.33/25.15/7.21/0 (103 m2/gm)	21.0	0.37
A36	Ba stabilized copper chromite** 31.7/28.7 (55 m2/gm)	16.896	1.04
P13	Ba stabilized copper chromite {Cu/Cr=0.9, Ba/Cu=0.11} (18.785 m2/gm)	10.623	2.77
A35	Ba stabilized copper chromite* 34.8/30.4	16.991	0.79
A38	G-89 (United Catalysts) 37.7/29.1/0.05/1.7	18.618	1.315
A34	Mn stabilized copper chromite* 31.1/32.2 (26 m2/gm)	18.967	2.36

* Steady state rate measured at the end of 40 hrs; based on copper chromite catalyst loading.

** Catalyst furnished by the Calsicat division of Mallinckrodt. Inc.

All experiments were carried out with 20 gms/l loading of Cu-chromite and 0.0476 gms potassium methoxide in 150 ml. methanol charge.

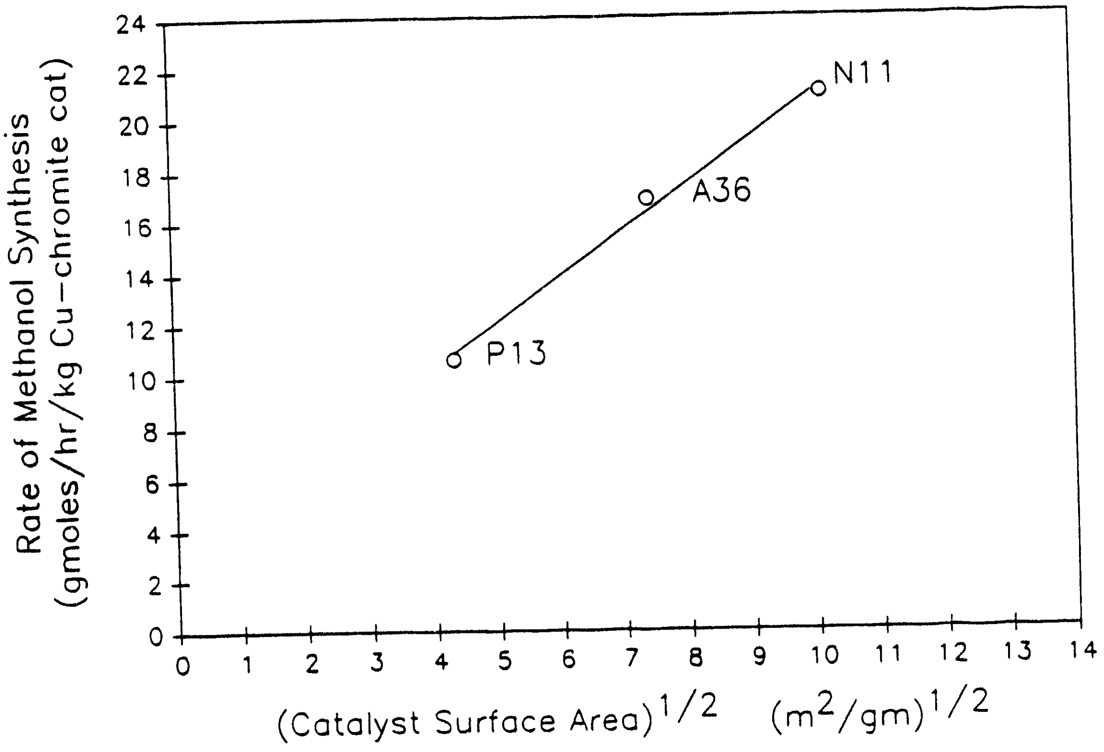

Figure 25. Rate of MeOH Synthesis as a Function of Catalyst Surface Area for Ba-stabilized Copper Chromite

$$\begin{aligned}&2Cu(NO_3)_2 + NH_4Cr_2O_7 + 4NH_4OH \longrightarrow \\ &\quad 2Cu(OH)NH_4CrO_4 + 4NH_4NO_3 + H_2O \qquad (4\text{-}7)\end{aligned}$$

$$2Cu(OH)NH_4CrO_4 \xrightarrow{\Delta} CuO.CuCr_2O_4 + N_2 + 5H_2O \qquad (4\text{-}8)$$

Additives such as Ba or Mn are added to the copper chromite to act as stabilizers by formation of $BaCrO_4$ or $MnCrO_4$ respectively. It is known that precipitation parameters for the copper chromite affect its subsequent catalytic properties. Onsager et al.(47) recommend a pH of 6 to obtain an active copper chromite catalyst.

X-ray powder diffraction traces of these catalysts show a poorly defined crystalline pattern in the unreduced state. The only identifiable peaks were those corresponding to CuO and $CuCr_2O_4$ phases with $BaCrO_4$ for the barium stabilized copper chromites (Figure 26). These have also been identified by other investigators(23,40). After in situ reduction or after reaction, all the peaks in the X-ray trace disappeared except for the G-89 copper chromite catalyst which retained some crystallinity (Figures 26 and 27). For the Ba-stabilized copper chromite, at the end of reaction, the surface areas for the mixed catalysts as well as for the potassium impregnated catalysts were essentially unchanged implying that sintering was not the cause of catalyst deactivation. The unchanged surface areas, in spite of the disappearance of the small crystalline peaks, indicated that the Ba-stabilized copper chromite is predominantly amorphous in nature.

In contrast, the copper chromite catalysts with and without potassium prepared in this laboratory by the incipient wetness and by coprecipitation techniques showed higher crystallinity containing CuO and $CuCr_2O_4$ phases. However, after reaction, all catalysts seemed to lose their crystallinity as shown in Figure 26.

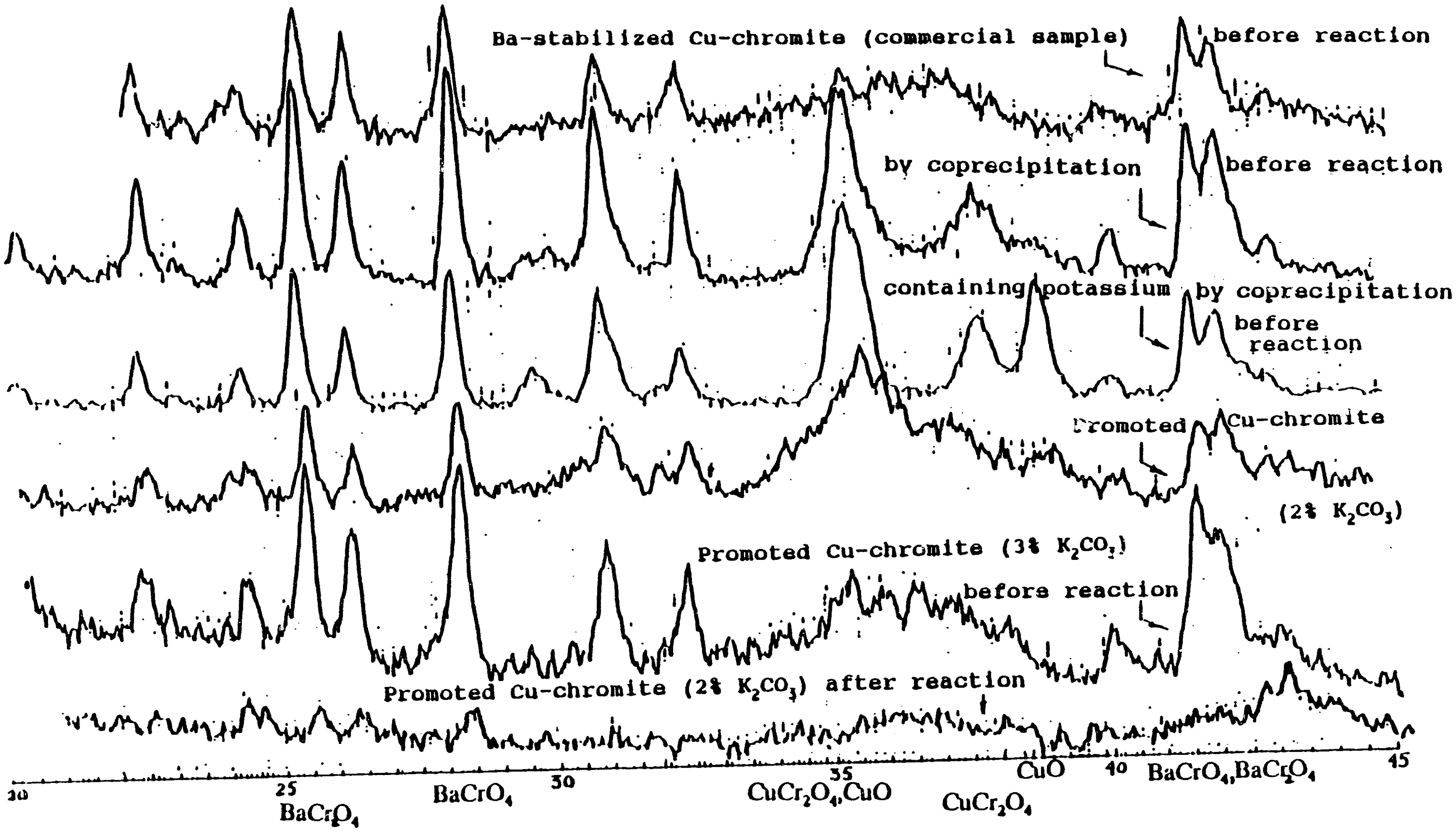

Figure 26. XRD traces for Ba-stabilized Copper Chromite Before and After Reaction

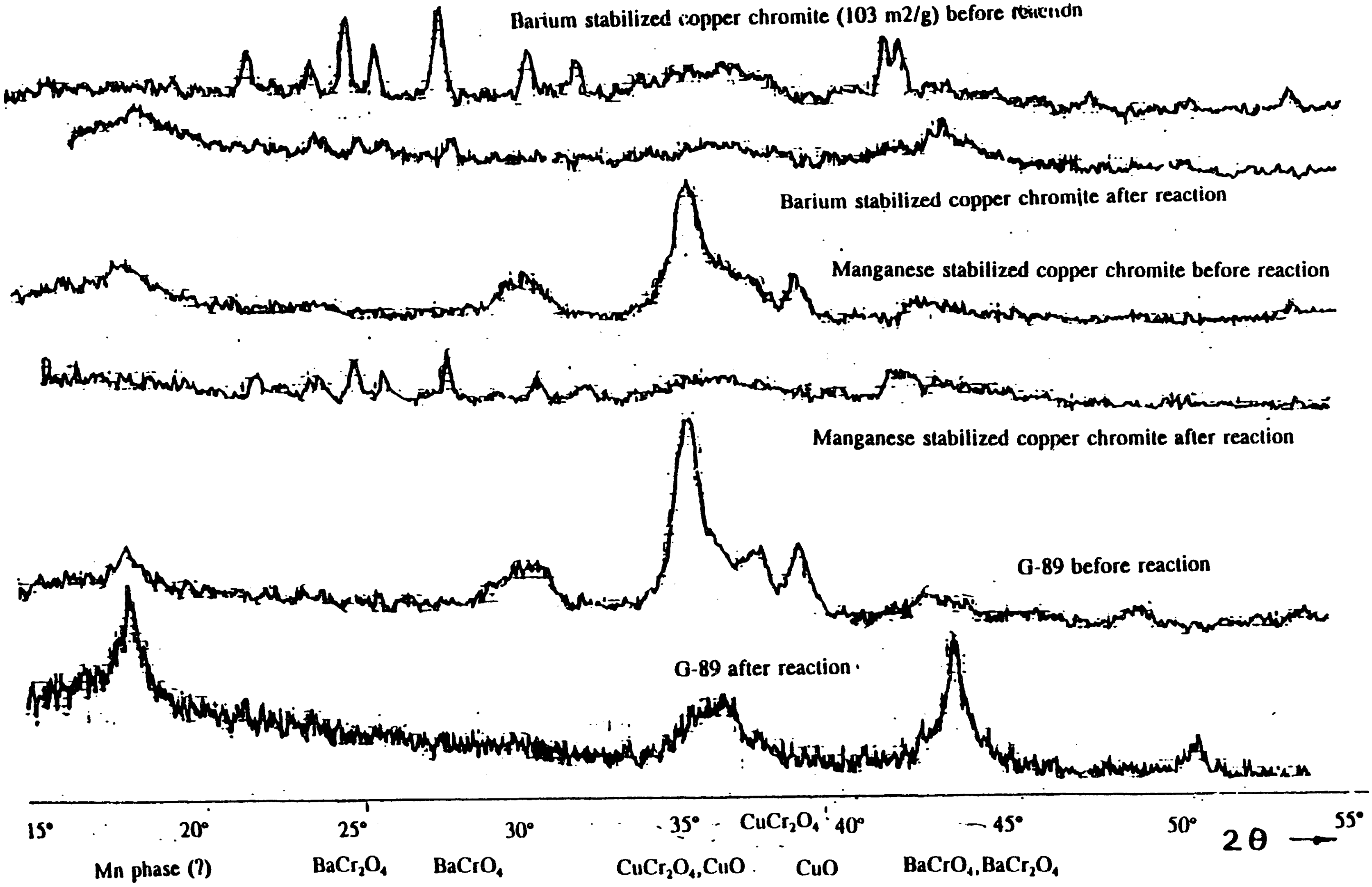

Figure 27. XRD traces for a Mn-stabilized and G-89 Copper Chromites Before and After Reaction

A scanning electron micrograph image of the unreduced barium-stabilized copper chromite showed two distinct phases, one comprised mainly of flat platelet like structures likely to be a chromium rich phase having a high surface area, the other an agglomerated structure containing aggregates of small particles, likely to be a copper-rich phase (Figure 28). This is consistent with our X-ray diffraction analysis of the Ba-stabilized copper chromite catalyst. For the potassium promoted copper chromite, in addition to the two regions mentioned above small globular agglomerates were evident on the surface. These probably correspond to the potassium impregnated on the copper chromite surface (Figure 29).

We measured the amount of water formed during in situ reduction for 20 g/l and 40 g/l of copper chromite. The water was found to correspond to the reduction of a $CuO/CuCr_2O_4$ phase to a $CuCrO_2$ phase; it seems likely that Cu^+ is the desired oxidation state for the concurrent methanol synthesis. Detailed calculations are shown in Appendix C. Monnier et al.(40) have also identified Cu^+ in the $CuCrO_2$ phase formed on reduction of a copper chromite catalyst as the active site for the direct methanol synthesis although others such as Cu^{2+}(34), Cu^0 dispersed on $CuCr_2O_4$(48), Cu^0 on or mixed with Cr_2O_3(49), Cu_2O or CuO on $CuCr_2O_4$ or Cu^0 on $Cu_2Cr_2O_4$(28) have been proposed as active species.

Size analyses of the copper chromite particles before reaction were obtained in a Microtrac size analyzer and showed a size distribution in the range of 2 to 88 microns, mainly concentrated between 5.5 to 62 microns with an average size of 30 microns. After reaction, this range shifted to a smaller particle range with an average size of 20 microns. The mean crystallite size before reaction calculated using the Scherrer formula was found to be 136Å.

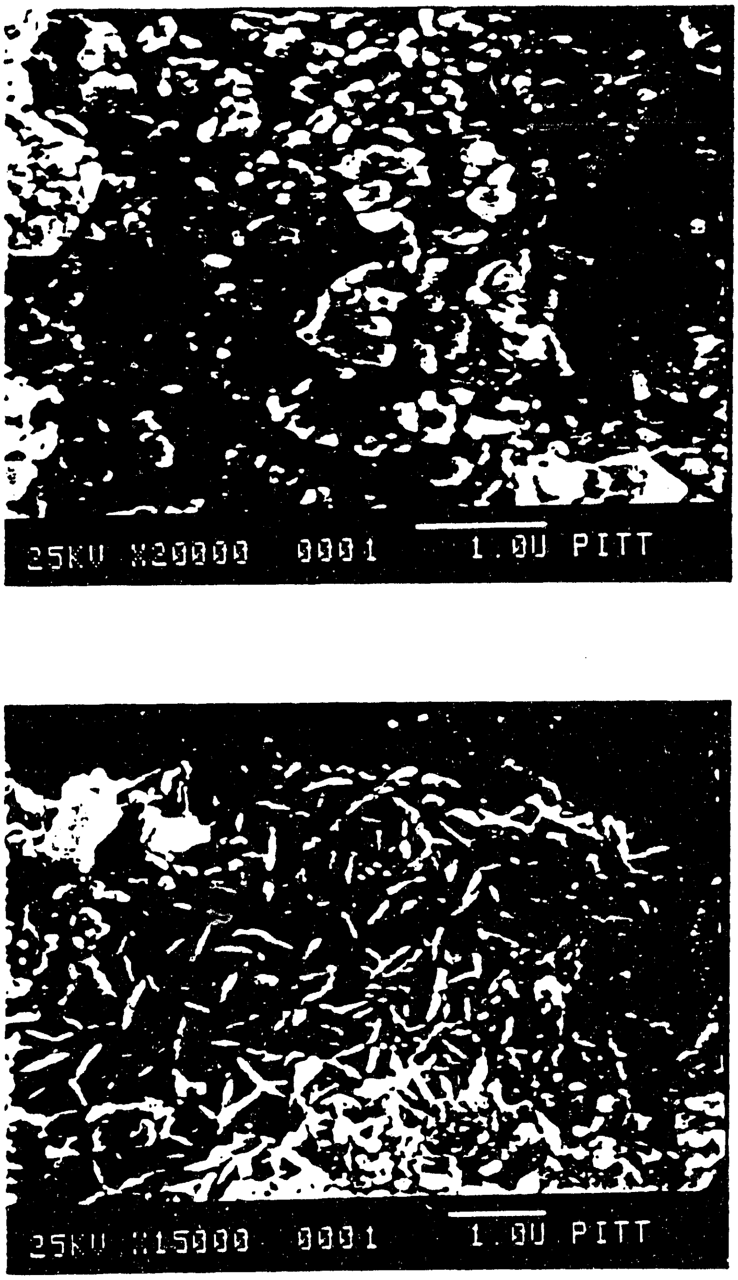

Figure 28. SEM images of Ba-stabilized Copper Chromite

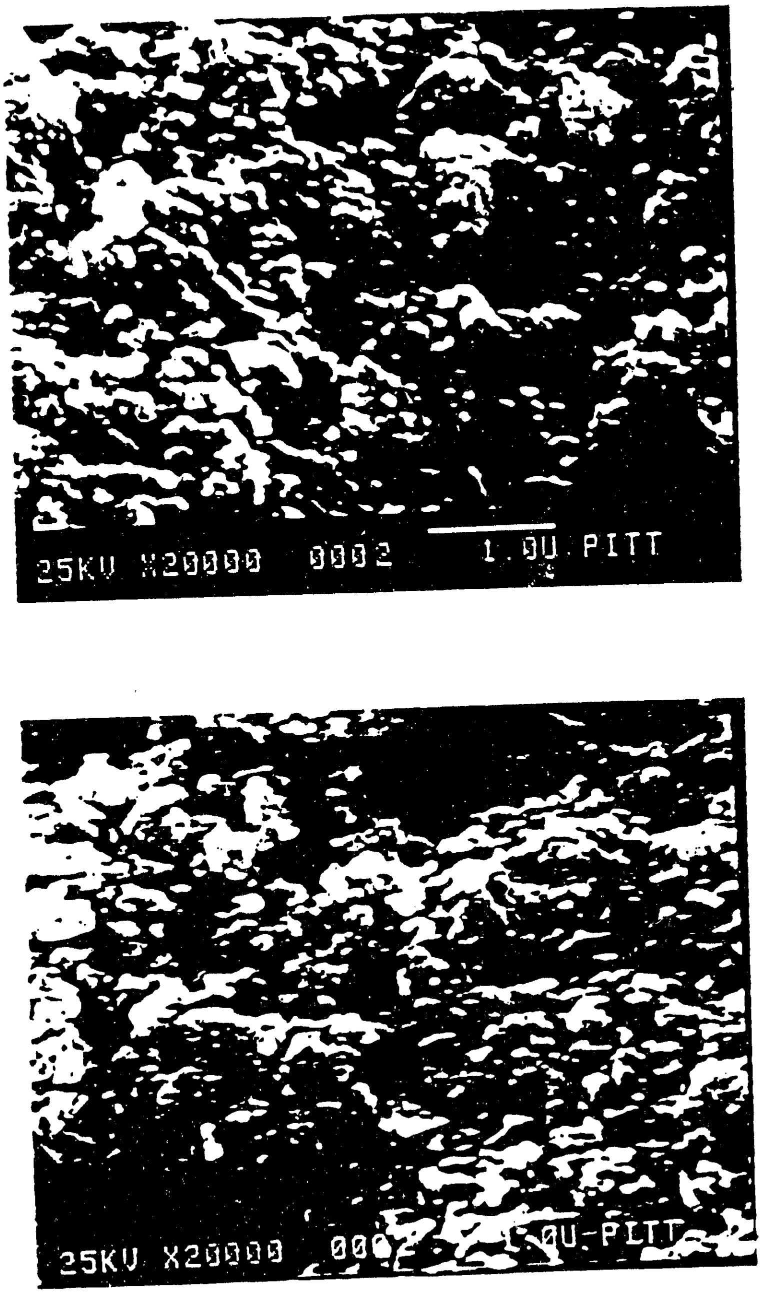

Figure 29. SEM images of Potassium Impregnated Ba-stabilized Copper Chromite

The pore size distribution for the Ba-stabilized copper chromite before and after reaction is shown in Figure 30. It can be seen that the copper chromite had an average pore size of 40 Å at the end of reaction. The larger pores probably correspond to inter-particle pores while the micropores correspond to intra-particle pores.

4.18 CATALYST REDUCTION

The reduction procedure for copper chromite has been reported to influence its MeOH synthesis activity(23). Lower hydrogenolysis activity was obtained by Monti et al.(26) using gas phase reduction than that obtained by Sorum et al.(25) with liquid phase reduction. Miya et al.(50) report that adding MeOH to copper chromite during the reduction period increased catalyst activity. The difference was attributed to poorer control of the reduction exotherm. Studies using TPR have shown that temperatures in the range of 165 to 185°C are optimum for partially reducing the copper chromite to Cu^{+}(48).

The MeOH synthesis activity was measured using external gas phase reduction and in situ liquid phase reduction in a stream of pure H_2 at 170°C (Table 24). For external reduction, a slow temperature ramp rate of 0.8°/min was used to prevent the formation of hot spots. The rate of MeOH formation for gas phase reduction is slightly lower than for in situ reduction. For external reduction, the amount of H_2O present in the charge seemed to have little effect on the rate of MeOH formation. No sintering of the copper chromite catalyst was ever found after reduction; the surface areas measured by BET before and after reaction were similar. The progress of the concurrent reaction was found to be similar in all cases; this is

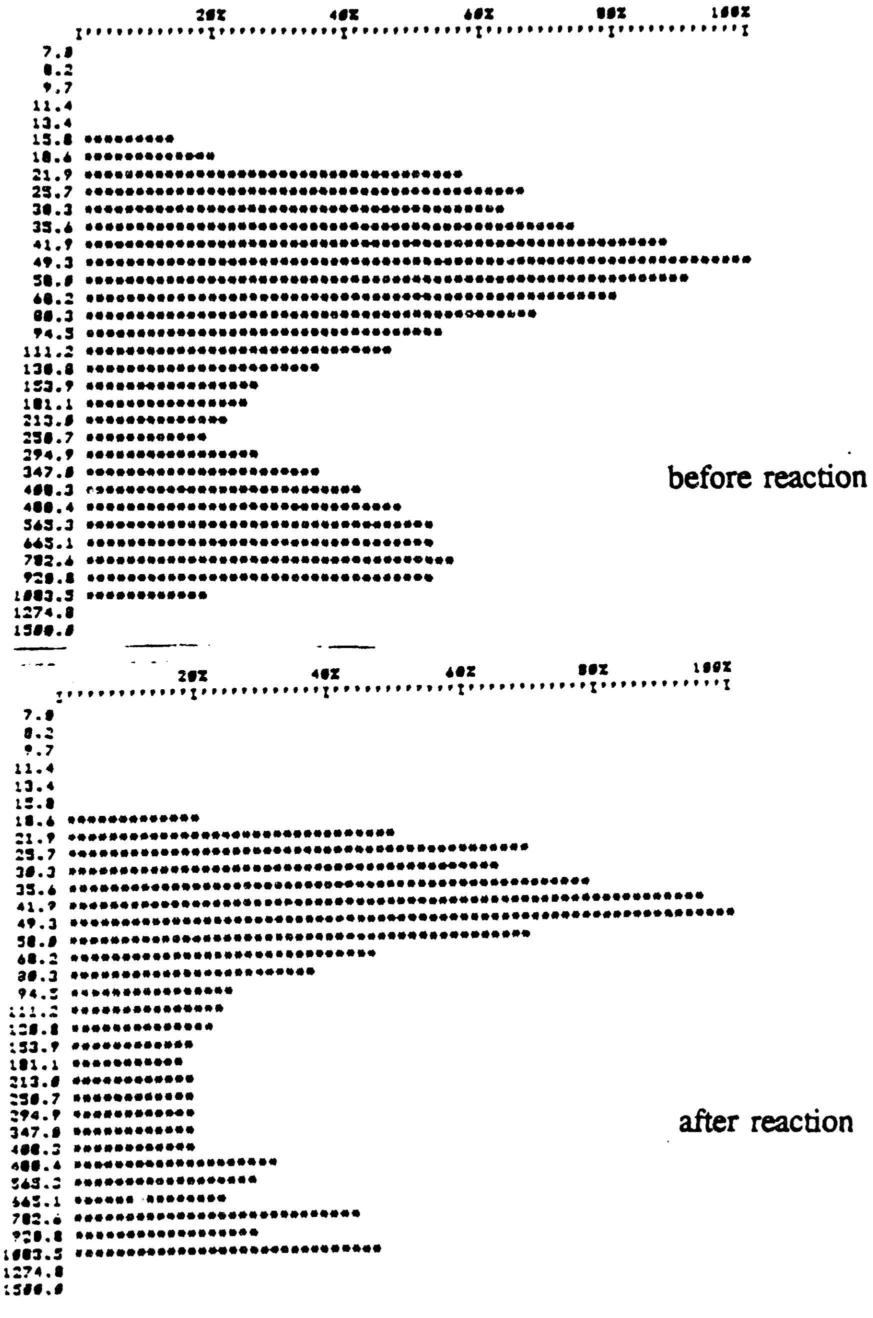

Figure 30. Pore Size Distribution of Copper Chromite Catalyst Before and After Reaction

expected, since the copper chromite is in a similar reducing atmosphere at all times. Unless otherwise indicated, all runs were made using in situ liquid phase reduction with H_2 at 170°C, with both copper chromite and $KOCH_3$ charged to the reactor.

Table 24. Rate of MeOH Synthesis with Three Catalyst Different Reduction Methods

Method of Copper Chromite Reduction	Rate of Methanol Synthesis* gmoles/h/kg cat
In situ reduction with $KOCH_3$ (approx 0.6% H_2O in charge) (Run N11)	19.0
Gas phase external reduction (0.96% H_2O in charge) (Run A10)	17.13
Gas phase external reduction (0.26% H_2O in charge) (Run A9)	18.85

* Steady state rate measured at the end of 40 hrs based on copper chromite catalyst loading.

All experiments were carried out with 20 gms/l loading of Cu-chromite and 0.048 gmoles/l potassium methoxide in 150 ml. methanol charge.

The fresh MeOH charged to the reactor contains about 0.2-0.3 mole% H_2O. In addition, H_2O is the product of catalyst reduction when H_2 is used as a reductant. In the concurrent synthesis, the H_2O formed during reduction corresponded to the reduction of the $CuO,CuCr_2O_4$ phase to the $Cu^0,CuCrO_2$ phase implying that Cu^+ is the likely active state for the concurrent reaction. Typically, with 3 g of copper chromite, about 0.4-0.5 mol% H_2O was present in the liquid at the start of the reaction. Upon introduction of CO in the reactor under H_2 pressure, the wgs reaction gives CO_2 which leaves along with the product stream, leading to a continual depletion of H_2O in the reactor. At steady state, the only source of H_2O in the concurrent synthesis is that resulting from dehydration of MeOH to DME.

4.19 DIFFUSION EFFECTS

The effects of external and internal diffusion on the intrinsic kinetics of MeOH formation were studied. Since gas-liquid and solid-liquid external mass transfer is related to the stirring speed, the rate of MeOH synthesis was studied as a function of the speed of agitation. Different stirring speeds from 97 to 3000 rpm were used in a random manner to confound the effect of previous histories in the reactor. For a 2.5 wt% catalyst loading Liu(22) found a significant decrease in rate only when the stirring speed was reduced to 97 rpm. This effect was verified for a 15 wt% copper chromite catalyst loading when the rate decreased only for speeds below 250 rpm (Figure 31). Thus, under normal conditions of operation (agitation rates of 1800-2000 rpm; 3 % catalyst loading), it is unlikely that external mass transfer limitations exist in the present system.

To test for internal pore diffusion limitations, the copper chromite was sieved and three particle sizes were examined as shown in Table 25. The rates of MeOH synthesis show a small change with particle size. One possibility is that due to the narrow size distribution of the catalyst particles (2-30 μm), the differences are not pronounced. The pore size distribution showed an average pore size of 40 Å. It is likely that these dimensions can result in pore diffusion limitations, particularly since H_2, CO, MeOH and $KOCH_3$ have to diffuse into the pores. More work is needed.

4.20 EFFECT OF REACTION TEMPERATURE

The effect of temperature is manifested in the rates of the reactions, vapor pressures of the solution components and solubilities of CO and H_2. The solubilities of H_2 and CO in MeOH and MeF are functions of temperature and could affect the rate of reaction. The MeOH synthesis rate may change as a function of the H_2 concentration in the liquid. The solubilities of CO and H_2 were calculated using the equations presented by Liu(22) are listed in Section 5.25. However, the temperature affects the rate directly because of the exponential relation of the rate with temperature. The effect of reaction temperature on MeOH synthesis rate was studied at a feed H_2/CO ratio of two for the $KOCH_3$/copper chromite mixed catalyst at two different reaction pressures (Figure 32). Since the carbonylation reaction is not in equilibrium, the concentration of MeF is a function of temperature and the slope of the ln(rate) vs 1/T plot (Figure 32) will vary with temperature. At 910 psig, an average apparent activation energy of 8 kcal/mole is obtained. This activation energy includes the activation energy of the carbonylation and the hydrogenolysis reactions. At an operating pressure of 50 bar, the MeOH synthesis rate increases up to 168°C, after which it decreases. Liu et al.(10) also found the rate of MeOH formation to be lower at 180°C than at

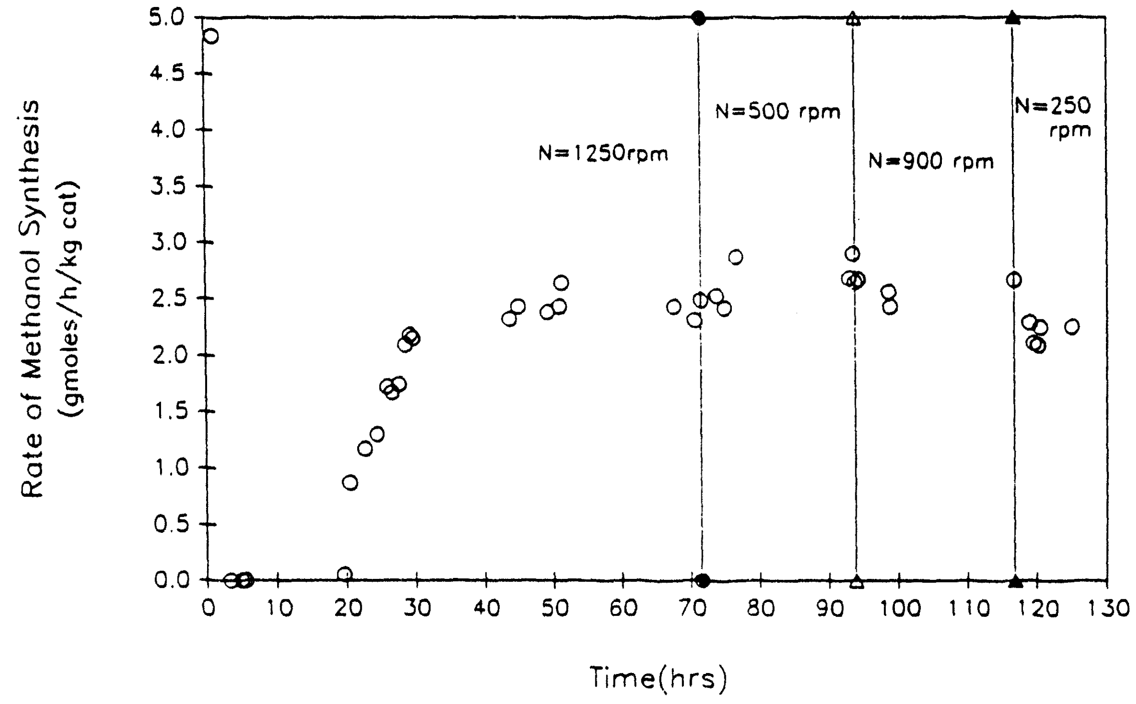

Figure 31. Rate of MeOH Synthesis as a Function of Stirring Speeds for a 15% Catalyst Loading

Table 25. Effect of Catalyst Particle Size on Rate of MeOH Synthesis

Size of Copper Chromite Particles	Rate of Methanol Synthesis* (moles/h/kg cat)
greater than 106 mm (Run A44)	17.1
between 53 and 106 mm (Run A46)	17.4
less than 38 mm (Run A45)	17.8

* Steady state rate at the end of 40 hours

160°C, for a feed H_2/CO of 3. Such an effect can either be due to a change in the reaction mechanism or due to the reduced concentration of MeF. Although small amounts of CH_4 are formed above 170°C at 50 bar pressure, it is unlikely to be a major cause of reduced activity. One possibility for decreased reaction at 170°C, is that the MeF concentration is low and limits the hydrogenolysis reaction leading to decreased MeOH formation rates. The amount of CO_2 and H_2O in the gas decreases with decreasing temperature while the mole fraction of CO and H_2 in the vapor increases. These results suggest that any contribution to the decrease in rate due to deactivating factors such as CO, CO_2 and H_2O is due to the presence of CO rather than to CO_2 or H_2O. H_2 does not have a deactivating effect on the concurrent synthesis(16). No higher alcohols or other side products were formed under any of these conditions.

4.21 EFFECT OF TOTAL PRESSURE

The effect of total pressure at a feed H_2/CO ratio of two was studied for the $KOCH_3$/copper chromite and the $NaOCH_3$/copper chromite systems (Figure 33). A decrease in total pressure results in a decrease in the partial pressures of H_2 and CO. Lower CO partial pressure results in decreased MeF concentration and reduced copper chromite surface coverage. These effects tend to offset each other in the concurrent synthesis since CO competes for sites on the copper chromite surface.

A 20% reduction in operating pressure, results in about a 15% drop in rate of MeOH synthesis (Figure 33). The use of lower operating pressures in the concurrent synthesis is desirable for synthesis gas derived from coal gasification which is normally operated at 30-40 atm. If the gasification pressure could be raised to about 55 atm and the concurrent synthesis run at 50 atm, the direct use of gasifier derived synthesis gas would eliminate compression costs for the feed to the MeOH reactor. In Integrated Gasification Combined Cycle (IGCC) and other applications, the unconverted syngas at 50 atm can be fed directly to a gas turbine to produce steam for power generation.

High MeOH synthesis rates at low (H_2 + CO) partial pressures could allow the use of air in upstream CH_4 reforming to generate syngas, as the N_2 rich synthesis

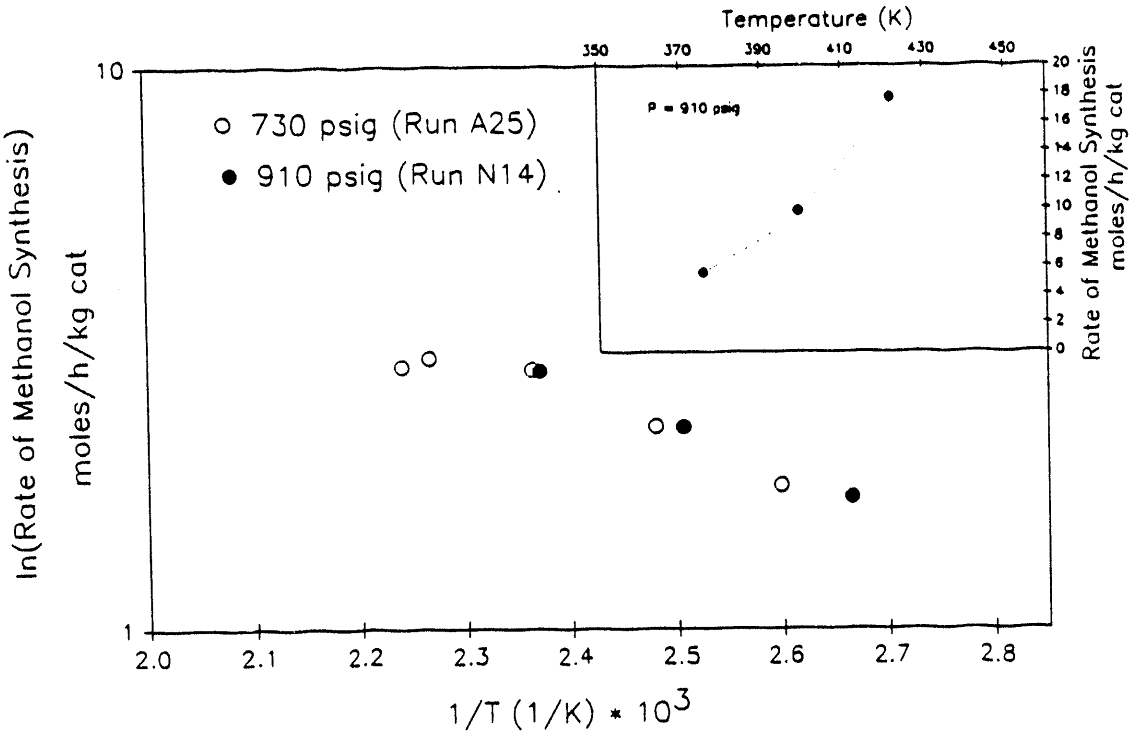

Figure 32. Effect of Temperature on Rate of Methanol Synthesis

gas can then be directly used in MeOH synthesis. Since the syngas generation cost

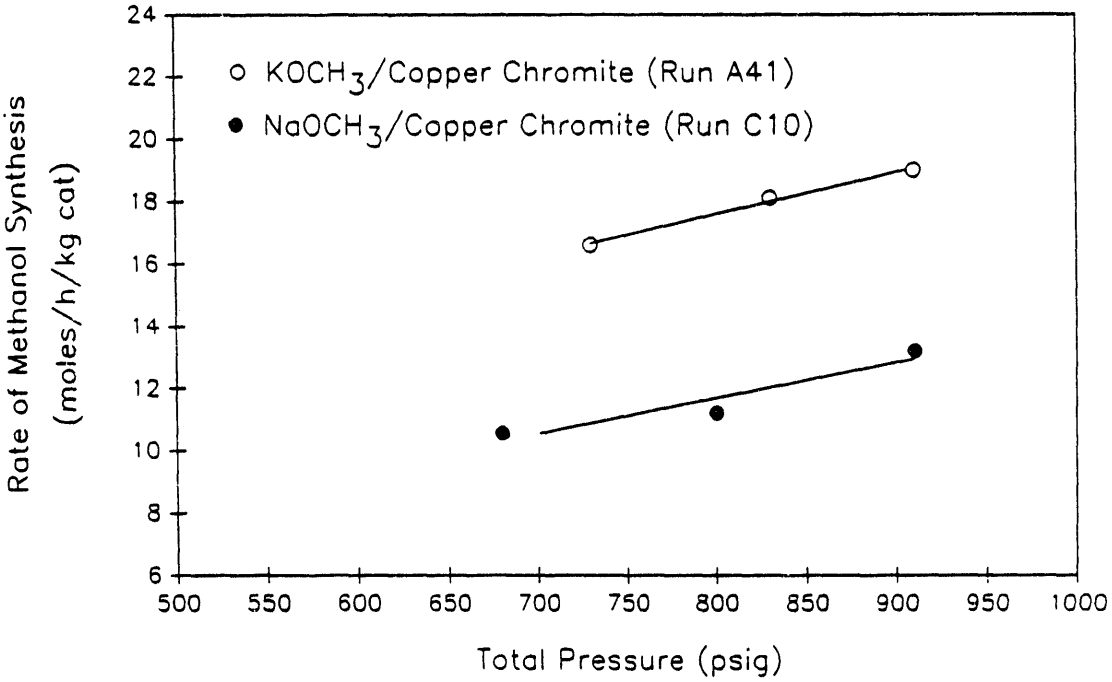

Figure 33. Effect of Pressure on Rate of Methanol Synthesis

and particularly the cost of oxygen in CH_4 reforming contributes almost 65% of the battery limit cost, the use of air in the reformer may provide considerable savings in the overall economics of the concurrent MeOH synthesis.

4.22 EFFECT OF H_2/CO RATIO

The effect of the H_2/CO ratio that exists in the vapor phase is an important parameter influencing the rates of the individual reactions. In the concurrent synthesis, the stoichiometric requirement for MeOH is two, so a feed gas lean in H_2 would lead to an even leaner H_2/CO ratio in the reactor and vice versa. The concurrent reaction was tested with different feed H_2/CO ratios (Table 26) using in situ liquid phase reduction. The H_2/CO ratios were arbitrarily changed to avoid the effect of previous history in the reactor. The average deactivation rate was used to correct the rate to that at the end of 40 hrs (see Appendix D). In spite of increasing MeF concentration in the reactor with increasing CO partial pressure, the rate of MeOH formation shows a maximum at a $H_2/CO = 0.6$ in the reactor (Figure 34). This implies that the H_2 concentration becomes limiting for lean H_2/CO ratios in the reactor. The deactivation rate seems to be a function of the CO partial pressure; a higher CO partial pressure results in more rapid deactivation (Table 26).

An $H_2/CO \approx 3$ is obtained via methane reforming, while $H_2/CO < 1$ is obtained via coal gasification. Considerable MeOH synthesis activity was obtained with both these gas ratios in the reactor. This could imply that H_2/CO feeds need not be shifted and can be used as such in the concurrent synthesis. For a feed H_2/CO ratio of 0.69, typical of syngas obtained from a Texaco gasifier, it was found that the rate was 28% less than the rate with a feed syngas ratio of two. After 85 hrs of operation, the feed syngas ratio was increased to 2.0 (normal operation); the MeOH formation rate increased but remained less than the rate under normal operating conditions by 14%, after correcting for the average deactivation rate. This indicates that CO does lead to some irreversible deactivation of the copper chromite catalyst. Traces of CH_4 were obtained at a feed $H_2/CO < 0.69$, but no higher alcohols or side products were detected.

Table 26. Rate of MeOH Synthesis as a Function of H_2/CO Ratio

H_2/CO Ratio in Feed	H_2/CO Ratio in Reactor	Rate of MeOH Synthesis* moles/h/kg cat	Average Deactivation Rate** (%/day)
3.0 (Run A33)	4.57	13.5	0.34
2.0 (Run N11)	2.0	19.0	0.37
1.0 (Run A48)	0.45	19.5	0.85
0.69# (Run A30)	0.39	13.62	1.46
0.5## (Run A32)	0.2	13.0	1.87

* Steady state rate measured at the end of 40 hrs; based on 0.5 gms $KOCH_3$ and 3 gms copper chromite catalyst loading.

** Average deactivation rate from best fit line.

\# Typical of syngas produced by gasification from a Texaco gasifier.

\## Typical of syngas produced by gasification from a Shell gasifier.

The H_2:CO stoichiometry is two for MeOH and one for MeF. As shown In

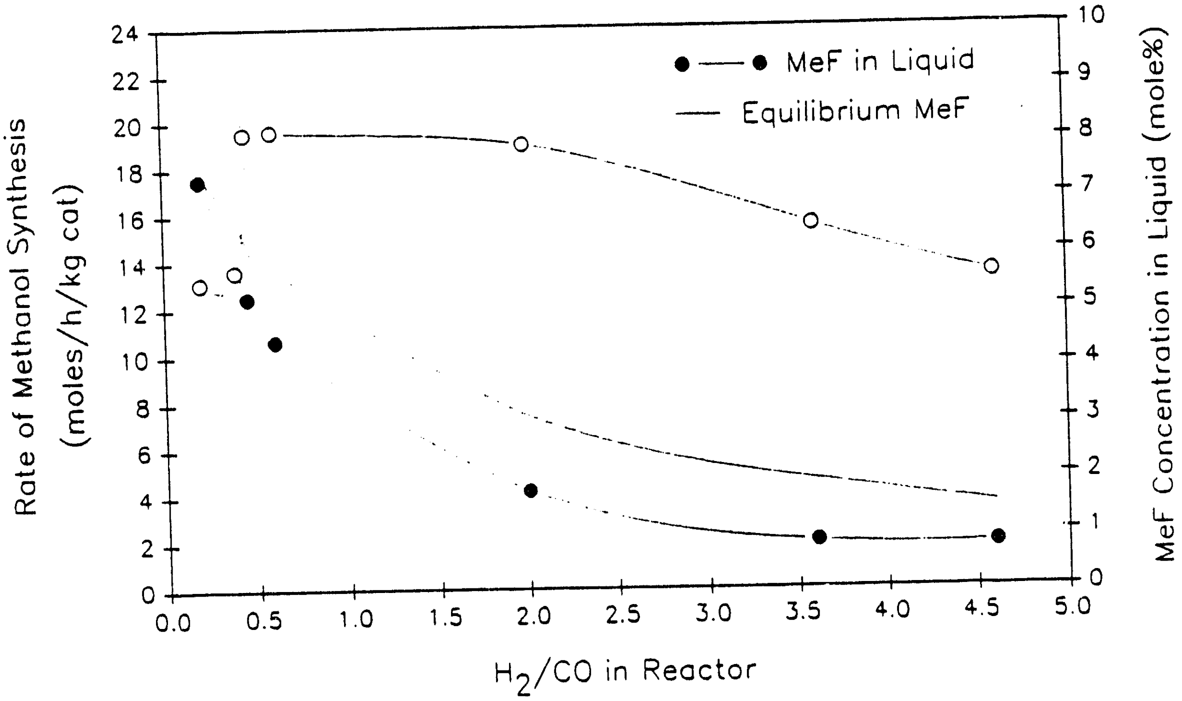

Figure 34. Mole Fraction MeF as a Function of H_2/CO Ratio

Figure 35, the concurrent synthesis can be tuned to obtain pure MeOH or pure MeF as product by using a synthesis gas ratio of two or one in the reactor respectively and recyling the unwanted product back to the reactor.

4.23 EFFECT OF H_2O AND CO_2 ON METHANOL SYNTHESIS ACTIVITY

The effect of varying amounts of water in the reactor charge on the rate of MeOH synthesis is shown in Figure 36. Up to 1% H_2O in the charge is tolerated by the concurrent synthesis. The amount of H_2O in the reactor continuously decreases due to loss by vaporization and removal as CO_2 produced via the wgs reaction. The only source of H_2O at steady state is by dehydration of MeOH to give DME. For a starting H_2O concentration of 3.5%, it takes longer for the reaction to proceed. From Figure 36, the rate picks up at about 25 hours corresponding to 1.6 mole% CO_2 in the vapor and 0.3 mole% H_2O in the liquid. It is conceivable that the MeOH formation rate will reach the levels achieved by the runs at lower H_2O concentrations, since the water concentration in the liquid is being continually depleted.

There are at least two ways that H_2O may affect the MeOH synthesis rate. One is the removal of the $KOCH_3$ as the formate and the other is by promoting the sintering of copper chromite. The former is known to be severe. The latter is unlikely since under concurrent synthesis conditions, surface area measurements have ascertained that there is no hydrothermal sintering of the copper chromite catalyst at the end of reaction.

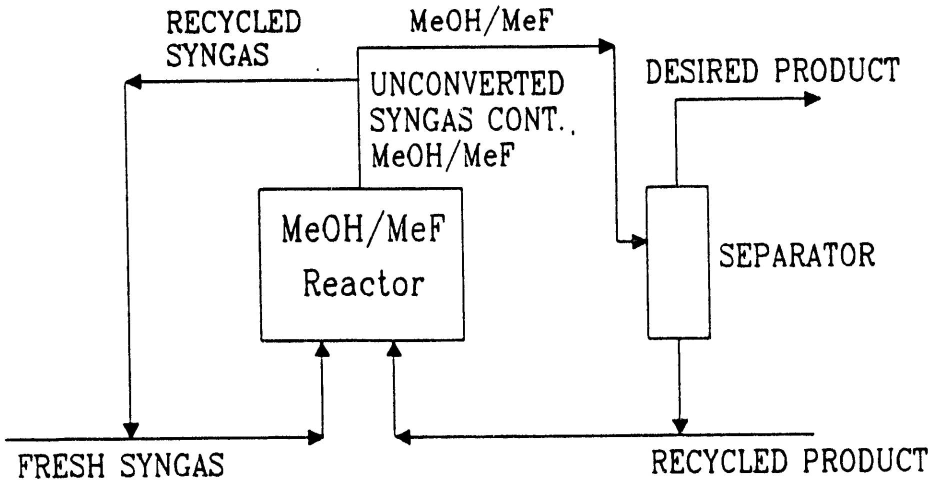

Figure 35. The Concurrent Synthesis Can Produce Pure MeOH or MeF as Product

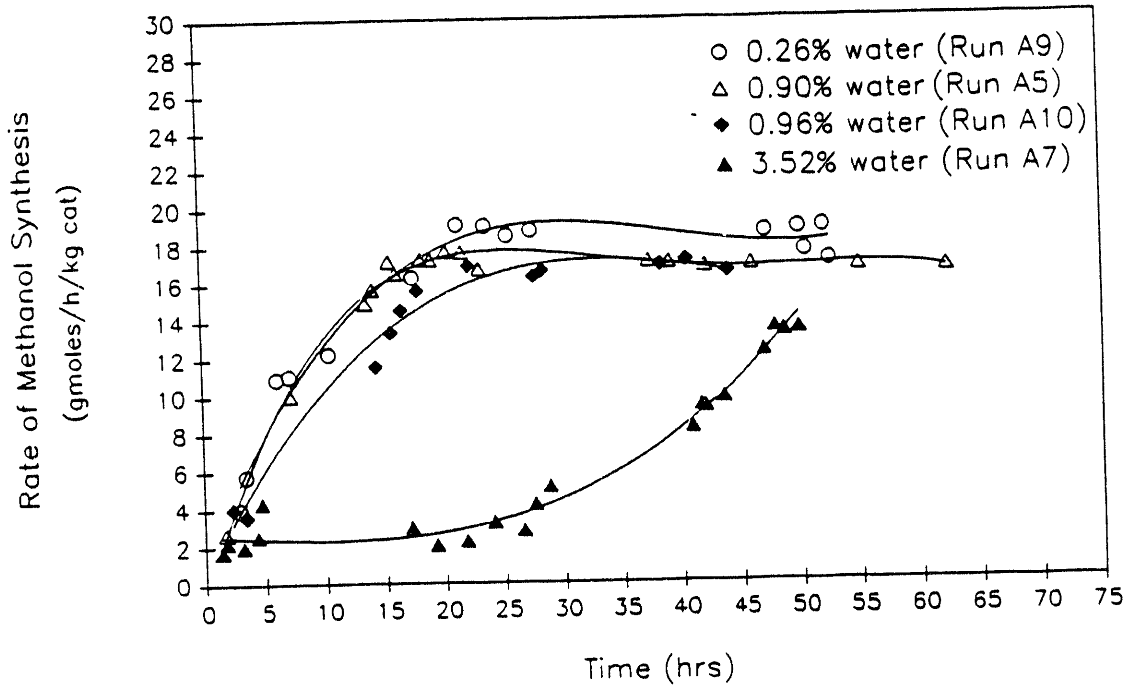

Figure 36. Effect of H_2O in Charge on Rate of MeOH Synthesis

CO_2 is also known to have a detrimental effect by removal of the alkali methoxide as the alkali methyl carbonate and by competitively inhibiting reactions on the copper chromite surface(15). Liu et al.(10) showed that 2% and 6% CO_2 in the feed is detrimental to the concurrent synthesis. The effect of small amounts of CO_2 on the rate of MeOH synthesis is examined in Figure 37. It is evident that levels of CO_2 below 1% in the reactor are tolerated by the concurrent synthesis. The introduction of CO_2 results in a decrease in MeF concentration (Figure 38), due to removal of the $KOCH_3$ catalyst. For CO_2 up to 1%, the copper chromite helps regenerate the $KOCH_3$ catalyst resulting in a recovery of the MeF formation rate as shown in Figure 39. At higher CO_2 concentrations, the CO_2 limits the ability of copper chromite to regenerate the $KOCH_3$ catalyst. This leads to a subsequent reduction in MeF concentration in the reactor resulting in lowered MeOH synthesis rates.

4.24 EFFECT OF SOLVENT ON MeOH SYNTHESIS ACTIVITY

The rate of the concurrent MeOH synthesis is partially dependent on the rate of carbonylation catalyzed by the methoxide anion. The nucleophilicity of the methoxide anion is known to be a function of the hydrogen bonding capability of the solvent. It is reported that the presence of a protic solvent such as MeOH renders the methoxide anion less nucleophilic(51). The presence of alkali cations is believed to decrease this hydrogen bonding(51). Onsager et al. claimed that the use of a solvent with a lower dielectric constant than MeOH increased the rate of MeOH synthesis(11); the reason for this is not stated. One possibility is the reduced hydrogen bonding ability and another is the increased solubility of the reacting gases CO and H_2 in these solvents. Indeed as shown in Table 28, the solubilities of

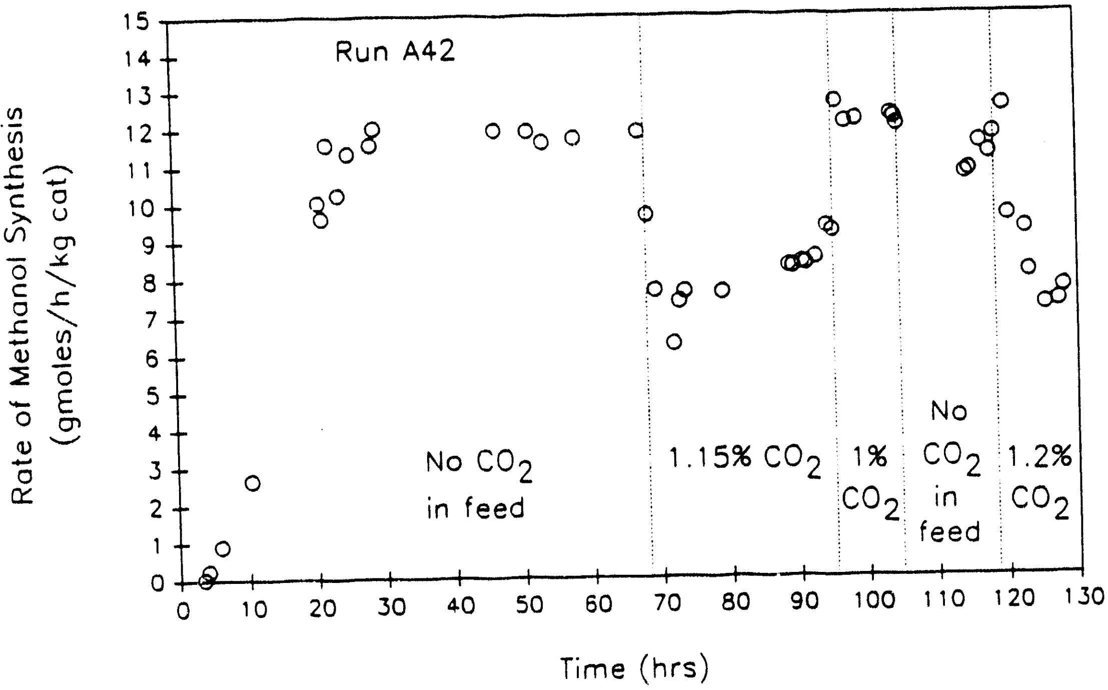

Figure 37. Effect of CO_2 on Rate of MeOH Synthesis

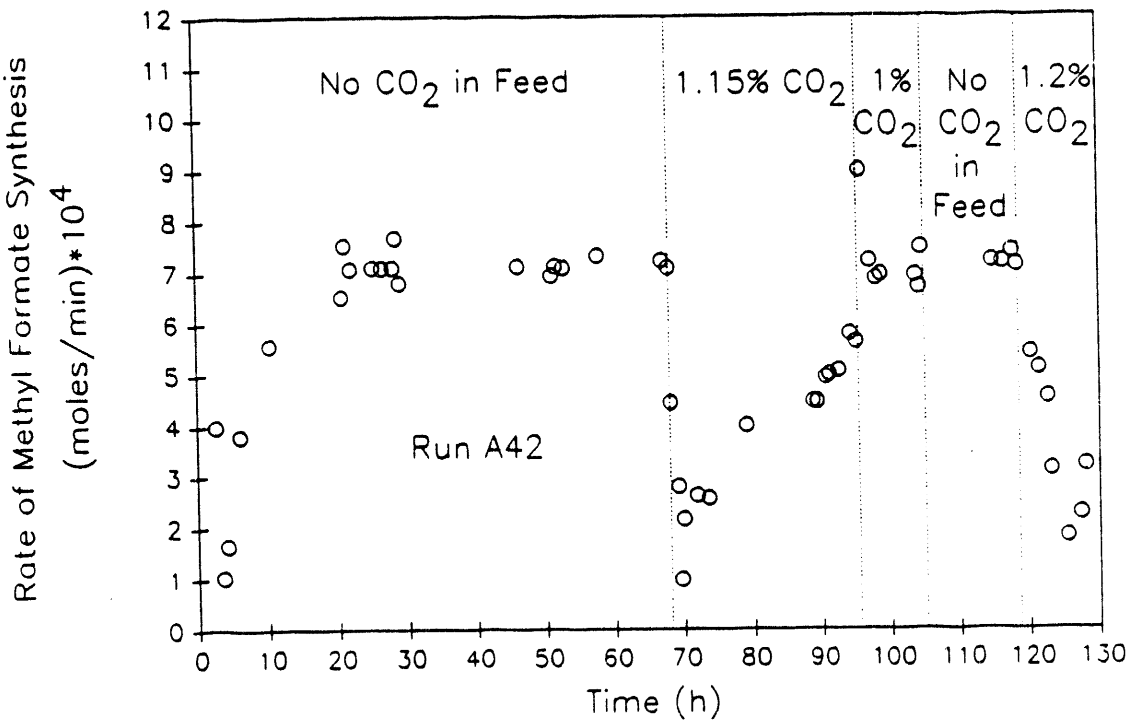

Figure 38. Effect of CO$_2$ on Rate of MeF Synthesis

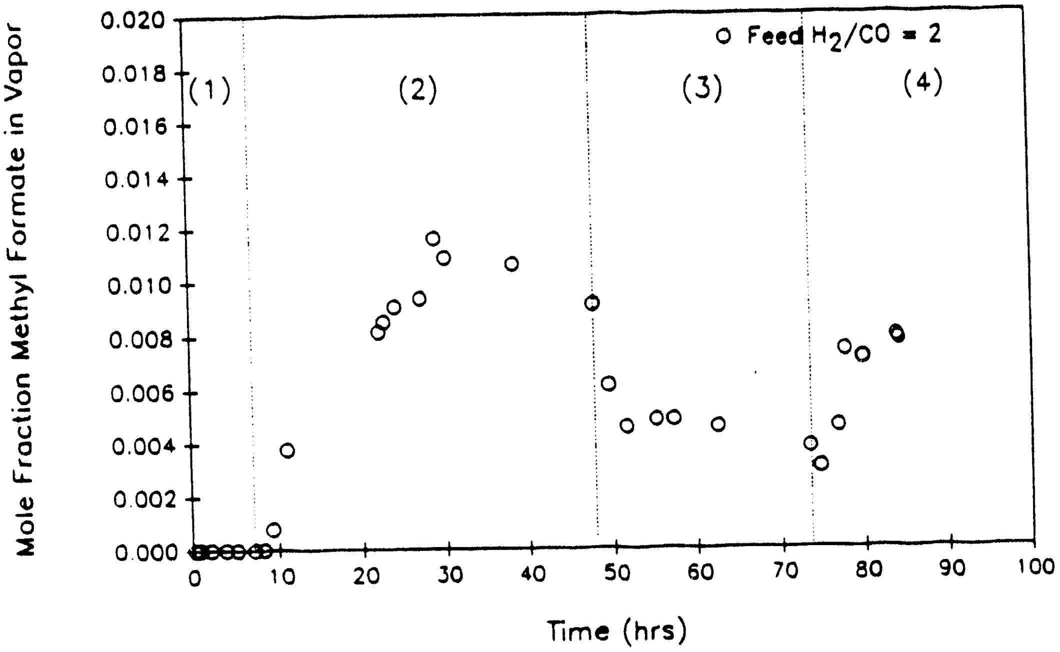

Figure 39. Effect of CO_2 on MeF Concentration in the Gas Phase

CO and H_2, calculated using the equation of Chang et al.(52,53), are higher. Cyclohexane is reported to be an active solvent(11).

We tested the activity of the $KOCH_3$/copper chromite catalyst system in cyclohexane (CYC)/MeOH (2:1) as solvent at 63 atm total pressure. As shown in Table 28, the activity in a pure MeOH solvent is higher than in a CYC/MeOH solvent. This was due to the lower CO and H_2 partial pressures (Table 28). The lower CO partial pressure resulted in a lower MeF concentration. The effect of the use of CYC on MeOH synthesis activity is contrary to that of Onsager et al.(11) who reported almost a 100% increase in MeOH formation activity. This effect needs to be investigated in greater detail.

The use of certain solvents other than MeOH may have some advantages. The use of a high boiling aprotic (low dielectric constant) solvent may be a good choice i.e. triglyme. This could provide a more nucleophilic methoxide anion(51) and also reduce formation of H_2O by the MeOH dehydration reaction. The reduced H_2O could increase the rate of MeF formation which in turn will increase MeOH formation activity.

Table 27. H_2 and CO Solubilities in Various Solvents Under Concurrent Synthesis Conditions

Partial Pressure bar	Temp. oK	Solubility of H2 in Solvent (gmole/cc) * 10^3				
		n-hexane	cyclo-hexane	n-decane	n-tetra-decane	Methanol
20	423	0.1936	0.1812	0.1792	0.1238	0.147
	398	0.1665	0.1543	0.1526	0.1077	0.1166
	373	0.1394	0.1273	0.1259	0.0916	0.0889
30	423	0.2776	0.2476	0.2737	0.1861	0.2208
	398	0.2420	0.2143	0.2328	0.1626	0.1749
	373	0.2064	0.1811	0.1919	0.1390	0.1334
40	423	0.3529	0.2979	0.3715	0.2487	0.2945
	398	0.3122	0.2631	0.3157	0.2181	0.2333
	373	0.2715	0.2284	0.26	0.1875	0.1778
45	423	0.3874	0.3170	0.4216	0.2801	0.331
	398	0.3454	0.2833	0.3582	0.2461	0.2624
	373	0.3034	0.2496	0.2948	0.2121	0.2

Partial Pressure bar	Temp. oK	Solubility of CO in Solvent (gmole/cc) * 10^3				
		n-hexane	cyclo-hexane	n-decane	n-tetra-decane	Methanol
15	423	0.2723	0.1658	0.1265	0.102	0.1356
	398	0.2426	0.1519	0.1164	0.0948	0.1055
	373	0.213	0.1381	0.1063	0.0875	0.07876
20	423	0.3515	0.2260	0.1682	0.1359	0.1808
	398	0.3149	0.2062	0.1549	0.1262	0.1406
	373	0.2784	0.1864	0.1417	0.1166	0.105
30	423	0.4926	0.3541	0.2512	0.2033	0.2718
	398	0.4467	0.3202	0.2316	0.1889	0.2109
	373	0.4008	0.2862	0.2121	0.1745	0.1575
40	423	0.6105	0.4923	0.3333	0.2703	0.3616
	398	0.5613	0.4414	0.3078	0.2513	0.2813
	373	0.5122	0.3905	0.2823	0.2323	0.21

Table 28. Effect of Cyclohexane as Solvent on the Rate of MeOH Synthesis

Solvent	Conc. of Methyl Formate in Liquid Experimental (mole%)	Equilibrium Conc. of Methyl Formate in Liquid (mole%)	Rate of Methanol Synthesis (gmoles/h/kg cat)	CO Partial Press. (bar)
Methanol/Cyclohexane (1:2)	2.36	2.94	14.98	10.63
Methanol	5.2	6.28	19.5	23.45

Feed $H_2/CO = 1$

5.0 CONCLUSIONS

The concurrent synthesis is well suited for the manufacture of MeOH/MeF in the slurry phase, in a single reactor, under relatively mild conditions. Under typical operating conditions of 100-180°C and 30-65 atm, a reaction scheme involving the carbonylation of MeOH to MeF followed by the hydrogenolysis of MeF to two molecules of MeOH results in a net reaction of H_2 with CO to give MeOH. Inspite of the presence of potential deactivating agents such as H_2O and CO_2, up to 90% per pass conversion and 98% selectivity to methanol at rates comparable to commercial processes have been obtained. In addition, the formation of MeOH at 150°C and 63 atm is tolerant to the presence of as much as 10,000 ppm CO_2 and 3000 ppm H_2O in the gas and liquid respectively.

A number of active catalytic systems including mixed catalysts comprised of alkali (Na, K, Rb and Cs) compounds and copper chromite as well as alkali impregnated copper chromite were identified. The alkali hydroxide, formate, carbonate, bicarbonate and oxide are as active as the corresponding alkali methoxide. It is proposed that copper chromite catalyzes the reaction of alkali formate and alkali methyl carbonate to the corresponding methoxide, maintaining its concentration in solution. A $KOCH_3$/copper chromite mixed catalyst is likely to be the most favored catalyst combination due to its high stability under the operating conditions used. A synergistic effect exists between the alkali methoxide and the copper chromite catalysts; this interaction is responsible for high MeOH formation rates and increased tolerance to the presence of H_2O and CO_2.

Reaction studies indicated that MeF concentration in the liquid is less tha the equilibrium concentration; the rate of MeOH formation is dependent on both the carbonylation and the hydrogenolysis reaction. The carbonylation reaction becomes more important at higher copper chromite loadings. The rate of MeOH synthesis displays a maximum at an optimum CH_3OK/copper chromite catalyst loading. The alkali distributes itself between the liquid and the copper chromite surface; the latter likely results in site blockage decreasing the hydrogenolysis reaction rate.

A number of barium and manganese stabilized copper chromites were found to be active for MeOH synthesis with low deactivation rate with time onstream. It is likely that Cu^+ is the active oxidation state under typical operating conditions. The effect of process parameters such as temperature, pressure, H_2/CO ratio in the reactor, flow rate and catalyst loading were also investigated. The use of temperatures above 170°C at a pressure of 50 atm, results in MeF being the limiting reactant. Small amounts of CH_4 is also formed. The rate of methanol synthesis decreases by only 12% for a 20% reduction of toal pressure; significant MeOH synthesis rates at pressure in the range of 40-50 atm. makes possible the elimination of an upstream shift reactor and the use of an air-blown syngas generator. A H_2/CO ratio of 0.6 in the reactor results in the highest rate. This implies efficient performance with syngas derived from coal gasification.

APPENDIX A.

APPENDIX A.

DATA SUMMARY

Table 29. Data Summary for C Series Runs (without getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)[*]		Feed H_2/CO Ratio	Rate of Methanol Synthesis[*][~] moles/h/kg cat	Comments
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)			
C2	150	63	CH_3OK (0.19)	Copper Chromite (40)	2.0	9.17	f.r. = 105
C3	150	63	-	1.1% K-Promoted Copper Chromite (40)	2.0	7.78 6.33	f.r. = 118 f.r = 65
C5	150	63	CH_3OK (0.096)	Copper Chromite (20)	2.0	17.22 14.58	f.r. = 105 f.r. = 75 d.r. = 0.79
C6	150	63	HCOOCs (0.096)	Copper Chromite (20)	2.0	11.54	f.r. = 105
C10	150	63 56 47	CH_3ONa (0.096)	Copper Chromite (20)	2.0	13.2 11.1 11.24 9.98	f.r. = 105 f.r. = 78 f.r. = 105 f.r. = 105
C11	150	63	$CsHCO_3$ (0.056)	Copper Chromite (20)	2.0	15.66	f.r. = 105
C12	150	63	HCOOCs (0.096)	Copper Chromite (20)	2.0	14.1	f.r. = 105
C13	150	63	HCOOK (0.096)	Copper Chromite (20)	2.0	17.6 13.8	f.r. = 105 f.r. = 75

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
[*] 150 cc. MeOH charge
[~] Steady state rate at the end of 40 hours based on copper chromite loading.

Table 30. Data Summary for N Series Runs (without getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)*		Feed H_2/CO Ratio	Rate of Methanol Synthesis** moles/h/kg cat	Comments
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)			
N1	150	63	CH_3OK (0.096)	Copper Chromite (20)	2.0	17.9	f.r. = 105
N2	150	63	CH_3OK (0.096)	Copper Chromite (20)	2.0	16.0	f.r. = 105
N3	150	63	HCOOCs (0.096)	Copper Chromite (20)	2.0	13.6 10.96	f.r. = 105 f.r. = 75 d.r. = 2.88
N4	150	63	KOH (0.096)	Copper Chromite (20)	2.0	17.84 13.72	f.r. = 105 f.r. = 75
N6	150	63	KCl (0.096)	Copper Chromite (20)	2.0	4.5	f.r. = 105
N7	150	58	-	Copper Chromite (20)	2.0	3.2	f.r. = 105
N8	150	50	-	Copper Chromite (20)	2.0 1.0	2.2 1.8	f.r. = 75 f.r. = 50
N9	150 120	63	CH_3OK (0.096)	Copper Chromite (20)	1.5 1.0 2.0	18.2 13.0 8.0	f.r. = 87 f.r. = 70 f.r. = 105
N10	150	63	CH_3OK (0.096)	Copper Chromite (20)	2.0	17.6	f.r. = 105

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
* 150 cc. MeOH charge
** Steady state rate at the end of 40 hours based on copper chromite loading.

Table 31. Data Summary for N Series Runs, contd. (without getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)'		Feed H_2/CO Ratio	Rate of Methanol Synthesis'' moles/h/kg cat	Comments
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)			
N11	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	19.0	f.r. = 105
						16.0	f.r. = 75
						23.0	f.r. = 135
N12	90	63	CH_3OK (0.048)	Copper Chromite (20)	Only CO	0.48E-4*	f.r. = 35
	150	63			Only CO	3.21E-4*	
N13	80	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	3.7	f.r. = 105
	150					19.02	
	100					4.12	
N14	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	18.3	f.r. = 105
	100					4.54	
	125					10.1	
N15	150	63	CH_3OK (0.096)	Copper-Zinc Oxide (20)	2.0	2.0	f.r. = 105
N16	150	63	CH_3OK (0.024)	Copper Chromite (20)	2.0	13.66	f.r. = 105
N17	150	50	CH_3OK (0.19)	Copper Chromite (20)	2.0	15.52	f.r. = 105

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
' 150 cc. MeOH charge
'' Steady state rate at the end of 40 hours based on copper chromite loading.
* Rate of MeF formation in moles/min.

Table 32. Data Summary for P Series Runs (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)[′]		Feed H_2/CO Ratio	Rate of Methanol Synthesis[″] moles/h/kg cat	Comments
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)			
P1	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	19.38	f.r. = 105
P2	150	63	-	0.8% Cs-Promoted Copper Chromite[•] (20)	2.0	4.92	f.r. = 105
P3	150	63	$Mg(OCH_3)_2$ (0.047)	Copper Chromite (20)	2.0	1.2	f.r. = 105
P4	150	63	-	Cs-Promoted Copper Chromite[•] (20)	2.0	3.28	f.r. = 105
P5	150	63	-	Copper Chromite (20)	Only H_2	-	Batch Expt.
P6	150	63	-	1.1% K-Promoted Copper Chromite (20)	Only H_2	-	Batch Expt.
P7	150	50	-	Copper Chromite (20)	Reduction by H_2	-	Batch Expt.

f.r - feed flow rate (cc/min)

[′] 150 cc. MeOH charge

[″] Steady state rate at the end of 40 hours based on copper chromite loading.

[•] Unactivated catalyst

Table 33. Data Summary for P Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)[']		Feed H_2/CO Ratio	Rate of Methanol Synthesis[**] moles/h/kg cat	Comments
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)			
P8	150	63	-	0.6% K-Promoted Copper Chromite[*] (20)	2.0	3.58	f.r. = 105
P9	150	63	-	1.1% K-Promoted Copper Chromite[*] (20)	2.0	7.25	f.r. = 105
P10	150	63	-	1.7% K-Promoted Copper Chromite[*] (20)	2.0	5.19	f.r. = 105
P12	150	63	-	Copper Chromite Containing K[---] (20)	2.0	5.7	f.r. = 105
P13	150	63	CH_3OK (0.048)	Copper Chromite[--] (20)	2.0	10.62	f.r. = 105
P14	150	63	-	1.7% K-Promoted Copper Chromite[--] (20)	2.0	8.21	f.r. = 105
P15	150	50	-	1.1% K-Promoted Copper Chromite[--] (20)	2.0	4.17	f.r. = 105

f.r - feed flow rate (cc/min)

['] 150 cc. MeOH charge

[**] Steady state rate at the end of 40 hours based on copper chromite loading.

[*] Unactivated catalyst

[--] Activated catalyst (reduced in H_2 at 400°C)

[---] Catalyst prepared by coprecipitation.

Table 34. Data Summary for P Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)[*]		Feed H_2/CO Ratio	Rate of Methanol Synthesis[**] moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
P16	150	63	-	5.7% K-Promoted Copper Chromite[--] (20)	2.0	12.51	f.r. = 105	2.2
P17	150	63	-	11.3% K-Promoted Copper Chromite[--] (20)	2.0	0.87	f.r. = 105	2.8
P20	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	18.8	f.r. = 105	2.0
						13.2	f.r. = 60	
P22	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	18.9	f.r. = 105	2.1
						14.3	f.r. = 75	1.8
						13.1	f.r. = 60	1.6
						9.8	f.r. = 43	
P23	150	63	CH_3OK (0.29)	Copper Chromite (120)	2.0	4.3	1250 rpm	
						4.1	500 rpm	
						4.4	900 rpm	
						3.8	250 rpm	
							f.r. = 105	3.2
						4.0	f.r. = 75	3.1
P26	150	63	CH_3OK[•] (0.048)	Copper Chromite (20)	2.0	13.2	f.r. = 105	-
P27	150	63	$Ba(OH)_2$ (0.095)	Copper Chromite (20)	2.0	2.5	f.r. = 105	-
P28	150	63	BaO (0.095)	Copper Chromite (20)	2.0	2.3	f.r. = 105	0.85

f.r - feed flow rate (cc/min)

[*] 150 cc. MeOH charge

[**] Steady state rate at the end of 40 hours based on copper chromite loading.

[•] 145 cc. MeOH and 5 cc. MeF charge (reduced to 1.2% MeF in liquid after reduction).

[--] Activated catalyst (reduced in H_2 at 400°C)

Table 35. Data Summary for A Series Runs (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)[*]		Feed H_2/CO Ratio	Rate of Methanol Synthesis[**] moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
A1	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	14.6 12.2 11.4	f.r. = 105 f.r. = 75 f.r. = 60	1.45
A2	150	63	$Ba(OCH_3)_2$ (0.048)	Copper Chromite (20)	2.0	4.2 3.9	f.r. = 105 f.r. = 75	-
A3	150	63	Cs-chromate (0.048)	Copper Chromite (20)	2.0	11.43	f.r. = 105	2.4
A4	150	63	CH_3OK (0.048)	Copper Chromite (22.3)	2.0	18.6 14.1	f.r. = 105 f.r. = 75	2.0
A5	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	17.5	f.r. = 105 0.9% H_2O in charge	1.7
A6	150	63	-	5.7% K-Promoted Copper Chromite (20)	2.0	12.4 9.98	f.r. = 105 f.r. = 45	-
A7	150	63	CH_3OK (0.048)	Copper Chromite (20.8)	2.0	18.2	f.r. = 105 3.52 H_2O in charge	-
A8	150	63	KOH (0.057)	Copper Chromite (20)	2.0	19.62	f.r. = 105 d.r. = 1.28	-

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)

[*] 150 cc. MeOH charge

[**] Steady state rate at the end of 40 hours based on copper chromite loading.

Table 36. Data Summary for A Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)[a]		Feed H_2/CO Ratio	Rate of Methanol Synthesis[aa] moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
A9	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	18.8	f.r. = 105 0.26% H_2O in charge	1.76
A10	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	17.3	f.r. = 105 0.96% H_2O in charge	-
A11	150	63	CH_3OK[*] (0.048)	Copper Chromite (20)	Only H_2	34[**]	f.r. = 90	-
A12	150	63	CH_3OCs (0.048)	Copper Chromite (20)	2.0	14.73	f.r. = 105 d.r. = 0.91	-
A13	150	63	CH_3OK (0.096)	Copper Chromite (40)	2.0	10.4	f.r. = 105	1.58
A14	150	63	CH_3ORb (0.048)	Copper Chromite (20)	2.0	16.68	f.r. = 105 d.r. = 0.59	2.4
A15	150	63	NaOH (0.024)	Copper Chromite (20)	2.0	13.33 11.0	f.r. = 105 d.r. = 1.47 f.r. = 75	1.43
A16	150	63	KOH (0.095)	Copper Chromite (20)	2.0	18.28	f.r. = 105 d.r. = 1.6	1.29

f.r - feed flow rate (cc/min)

[a] 150 cc. MeOH charge

[aa] Steady state rate at the end of 40 hours based on copper chromite loading.

[*] 150 cc. MeF charge

[**] Initial rate of MeOH synthesis by hydrogenolysis (moles/h/kg cat)

Table 37. Data Summary for A Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)[*]		Feed H_2/CO Ratio	Rate of Methanol Synthesis[**] moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
A17	150	63	KOH (0.029)	Copper Chromite (20)	2.0	14.21 13.7	f.r. = 105 d.r. = 1.25 f.r. = 75	1.95 1.73
A19	150	63	HCOOK (0.048)	Copper Chromite (20)	2.0	19.25	f.r. = 105 d.r. = 0.92	-
A20	150	63	HCOOK (0.024)	Copper Chromite (20)	2.0	14.74	f.r. = 105 d.r. = 1.61	1.17
A21	150	63	-	Copper-Zinc Oxide (20)	2.0	0.58	f.r. = 105	< 0.1
A22	150	63	CsOH (0.048)	Copper Chromite (20)	2.0	15.0	f.r. = 105 d.r. = 3.62	2.79
A23	150	63	Rb_2O (0.048)	Copper Chromite (20)	2.0	16.75	f.r. = 105 d.r. = 6.24	2.28
A24	150	63	CsOH (0.024)	Copper Chromite (20)	2.0	11.48	f.r. = 105 d.r. = 1.83	-
A25	150	56.1	CH_3OK (0.048)	Copper Chromite (20)	2.0	18.6	f.r. = 105	1.7
	150	50.7				17.12		1.4
	168	50.7				20.81		-
	130	50.7				9.87		2.3
	112	50.7				6.05		2.5
	173	50.7				18.57		-

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
[*] 150 cc. MeOH charge
[**] Steady state rate at the end of 40 hours based on copper chromite loading.

Table 38. Data Summary for A Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)*		Feed H_2/CO Ratio	Rate of Methanol Synthesis** moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
A26	150	63	HCOOK (0.095)	Copper Chromite (20)	2.0	16.86	f.r. = 105 d.r. = 1.36	-
A27	150	63	1:5 CH_3OK:$NaOCH_3$ (7.96E-3 : 0.0403)	Copper Chromite (20)	2.0	18.42	f.r. = 105	-
A28	150	63	1:5 CH_3OK:$NaOCH_3$ (4.03E-3 : 0.0199)	Copper Chromite (20)	2.0	13.80	f.r. = 105	1.22
A29	150	63	1:5 CsOH:$NaOCH_3$ (7.07E-3 : 0.0405)	Copper Chromite (20)	2.0	15.06	f.r. = 105	-
A30	150	63	CH_3OK (0.048)	Copper Chromite (20)	0.69	13.38	f.r. = 123 d.r. = 1.46	7.0
A31	150	63 43	CH_3ONa (0.048)	Copper Chromite (20)	2.0	15.1 12.54	f.r. = 105 d.r. = 0.66 f.r. = 105	1.4
A32	150	63	CH_3OK (0.048)	Copper Chromite (20)	0.5	13.1	f.r. = 120 d.r. = 1.87	7.3
A33	150	63	CH_3OK (0.048)	Copper Chromite (20)	3.0	13.9	f.r. = 140	0.8

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
* 150 cc. MeOH charge
** Steady state rate at the end of 40 hours based on copper chromite loading.

Table 39. Data Summary for A Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)'		Feed H_2/CO Ratio	Rate of Methanol Synthesis** moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
A34	150	63	CH_3OK (0.048)	Mn-stabilized Copper Chromite (20)	2.0	18.97	f.r. = 105 d.r. = 2.36	2.1
A35	150	63	CH_3OK (0.048)	Ba-stabilized Copper Chromite* (20)	2.0	16.99	f.r. = 105 d.r. = 0.79	-
A36	150	63	CH_3OK (0.048)	Ba-stabilized Copper Chromite-- (20)	2.0	16.89	f.r. = 105 d.r. = 1.04	-
A37	150	63	CH_3OK (0.048)	-	2.0	2.2E-4---	f.r. = 105	-
A38	150	63	CH_3OK (0.048)	G-89 (20)	2.0	18.62	f.r. = 105 d.r. = 1.32	-
A39	80 150 80 110	30 50 50 50	CH_3OK (0.048)	Copper Chromite (20)	2.0	0.2E-4--- 7.4E-4--- 0.3E-4*** 1.82E-4***	f.r. = 105	-
A40	80 150	30 46	CH_3OK (0.048)	Copper Chromite (20)	0.5	2.4E-4 9.8E-4	f.r. = 120	-
A41	150	63 57 53	CH_3OK (0.048)	Copper Chromite (20)	2.0	0.05 0.04 0.04	f.r. = 105 10% CO_2 in feed	-

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
' 150 cc. MeOH charge
** Steady state rate at the end of 40 hours based on copper chromite loading.
* Ba-stabilized copper chromite (Cu-34.8%, Cr-30.4%)
-- Ba-stabilized copper chromite (Cu-31.7%, Cr-28.7%; Surface Area S_A = 55 m^2/g)
*** Rate of MeF Formation (moles/min)

Table 40. Data Summary for A Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)*		Feed H_2/CO Ratio	Rate of Methanol Synthesis** moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
A42	150	48	CH_3OK (0.048)	Copper Chromite (20)	1.0	11.94	f.r. = 105, No feed CO_2	-
						8.35	1.15% CO_2	
						12.2	f.r. = 140, 1% CO_2	
						11.78	No feed CO_2	
						7.68	1.2% CO_2	
A43	150	48	CH_3OK (0.048)	Copper Chromite (20)	2.0	10.64 7.73 3.2	f.r. = 105, No feed CO_2 0.8% CO_2 1.2% CO_2	-
A44	150	63	CH_3OK (0.048)	Copper Chromite (20) > than 106 mm	2.0	17.1	f.r. = 105	1.73
A45	150	63	CH_3OK (0.048)	Copper Chromite (20) < 53 mm	2.0	17.8	f.r. = 105	-
A46	150	63	CH_3OK (0.048)	Copper Chromite (20) > 53 mm and < 106 mm	2.0	17.4	f.r. = 105	-
A48	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	17.02	f.r. = 105	1.75
					2.6	15.5		0.85
					2.92	14.4		-
					3.1	13.4		0.79
					1.0	18.7		5.2
					0.55	13.7		7.7

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
* 150 cc. MeOH charge
** Steady state rate at the end of 40 hours based on copper chromite loading.

Table 41. Data Summary for A Series Runs, contd. (with getter)

Run No.	Temp. °C	Pressure atm	Catalyst Type (Catalyst Loading)$^{\prime}$		Feed H_2/CO Ratio	Rate of Methanol Synthesis$^{\prime\prime}$ moles/h/kg cat	Comments	Mole Fraction MeF in Liquid
			Soluble Compound (moles/l)	Heterogeneous Catalyst (g/l)				
A49	150	7.75$^{\bullet}$ 11.45$^{\bullet}$ 14.37$^{\bullet}$	CH_3OK (0.384)	-	Only CO	6.9E-5^{--} 11.8E-5$^{\bullet\bullet}$ 15.6E-5^{--}	Batch expt.	1.9 2.97 4.0
A50	150	3.28$^{\bullet}$ 15.55$^{\bullet}$ 36.44$^{\bullet}$	CH_3OK (0.048)	Copper Chromite (20)	Only CO	-	Batch expt.	0.96 3.53 5.05
A51	150	63	CH_3OK (0.048)	Copper Chromite (20)	1.0	14.98	f.r. = 105 Cyclohexane/MeOH (2:1) as solvent	2.36
A52	150	63	CH_3OK (0.25)	Copper Chromite (20)	1.8	6.14	f.r. = 105	3.30
A53	150	63	CH_3OK (0.048)	Copper Chromite (20)	2.0	17.5 19.1 13.8	f.r. = 105 f.r. = 135 f.r. = 75	1.74 1.86 1.45
A54	150	63	CH_3OK (0.19)	Copper Chromite (20)	2.0	14.9	f.r. = 105	2.45

f.r - feed flow rate (cc/min)
d.r. - deactivation rate (%/day)
$^{\prime}$ 150 cc. MeOH charge
$^{\prime\prime}$ Steady state rate at the end of 40 hours based on copper chromite loading.
$^{\bullet}$ CO partial pressure
$^{--}$ Initial rate of carbonylation (moles/min)

APPENDIX B.

APPENDIX B.
THERMODYNAMICS

B.0.1 FUGACITY AND ACTIVITY COEFFICIENTS IN THE CONCURRENT STNTHESIS

In order to evaluate the composition of the reaction mixture at equilibrium, the non-ideality of the system has be taken into account. This requires the evaluation of the fugacity coefficients for the gas and the activity coefficients for the liquid under the conditions of operation. Figure 40 lists the various components in this three phase system. In this work, the fugacity coefficients were evaluated for all the gaseous species involved while the liquid phase activity coefficients were evaluated for MeOH and MeF only, since they comprise more than 99.9% of the liquid composition. A number of techniques are available for the computation of these non-ideality parameters. The fugacity coefficients (ϕ_i) were evaluated by two methods -- 1) by corresponding states using values of $\phi_i^{(0)}$ and $\phi_i^{(1)}$ and the Pitzer accentric factor α_i(54,55) and 2) by Tsonopoulos equation for non- polar fluids(55). The fugacity coefficients, at 150°C, listed in Table 42, agree within 5% except for H_2 and DME. Other than H_2, CO and CO_2, the rest of the components are considerably non-ideal under concurrent synthesis conditions.

The activity coefficients can be calculated independently using an equation of state such as the Wilson equation or by the Raoult's Law using vapor-liquid equilibrium and the individual component vapor pressures and the gas phase fugacities. Vapor-liquid data at 25°C and pressure between 200 and 600 mm are

Gas	Liquid	Solid
H_2 CO CH_3OH $HCOOCH_3$ CO_2 CH_3OCH_3	CH_3OH $HCOOCH_3$ H_2O $KOCH_3$ CATALYST DISSOLVED GASES	Cu-CHROMITE

Figure 40. Components in the Three Phase Concurrent Synthesis

available in the DECHEMA compilation. The fugacity coefficient at 25°C and at low pressures were calculated based on corresponding states(54,55) and the activity coefficients were calculated using the Raoult's Law. Then, it was assumed that the liquid activity coefficients do not change much with temperature and pressure. This was done as data for the variation of activity coefficients for MeF as a

Table 42. Gas Phase Fugacity Coefficients at 150°C in the Concurrent Synthesis

Component	Fugacity Coefficient at 150°C	
	Corresponding States Approach	Tsonopoulos Equation
H_2	1.24	1.04
CO	1.02	1.02
CO_2	0.91	0.91
MeOH	0.55	0.52
MeF	0.43	0.43
H_2O	0.52	0.56
DME	0.81	0.68

function of temperatures were not available. The activity coefficients (γ_i) of MeOH and MeF as a function of MeF mole fraction (x_{MeF}) were represented by equations B-1 and B-2 respectively.

$$\gamma_{MeOH} = 4.813 - 21.812\, x_{MeF} + 65.735\, x_{MeF}^2 - 109.89\, x_{MeF}^3 + 91.32\, x_{MeF}^4 - 29.27\, x_{MeF}^5 \quad \text{(B-1)}$$

$$\gamma_{MeF} = 2.542 - 5.067\, x_{MeF} + 4.868\, x_{MeF}^2 - 1.599\, x_{MeF}^3 \quad \text{(B-2)}$$

B.0.2 EQUILIBRIUM MeF COMPOSITION

The carbonylation equilibrium was measured in the presence of 1000 ppm H_2O at 150°C by contacting MeOH and CO in the 300 cc. autoclave at 150°C and waiting until there was no further pressure change and analyzing the equilibrium liquid using a gas chromatograph. Since the carbonylation reaction is known to be deactivated by the presence of small amounts of H_2O, the approach to equilibrium in the presence of 1000 ppm H_2O would be slow. Hence, to eliminate error, both the forward and the reverse carbonylation reactions were studied (the latter by starting with MeF as charge). The average of the equilibrium composition in the forward and the reverse carbonylation was assumed to be the true equilibrium composition. The forward carbonylation reaction as three starting CO partial pressures is shown in Figure 41. The equilibrium MeF concentration at 150°C, obtained by the forward and the reverse carbonylation reaction experiments, can be correlated to the CO partial pressure by equations B-3 and B-4 respectively. The average of the values predicted by the two equations at a particular CO partial pressure is taken to be the equilibrium MeF composition. Using this technique, the measured equilibrium MeF mole fraction (x_{MeF}) agreed within 10% with that predicted by Liu et al.(15), as shown in Table 43.

$$x_{MeF} = -5.82E{-1} + 3.16E{-1} \times P_{CO} \quad \text{(B-3)}$$

$$x_{MeF} = 2.06E{-1} + 2.57E{-1} \times P_{CO} \quad \text{(B-4)}$$

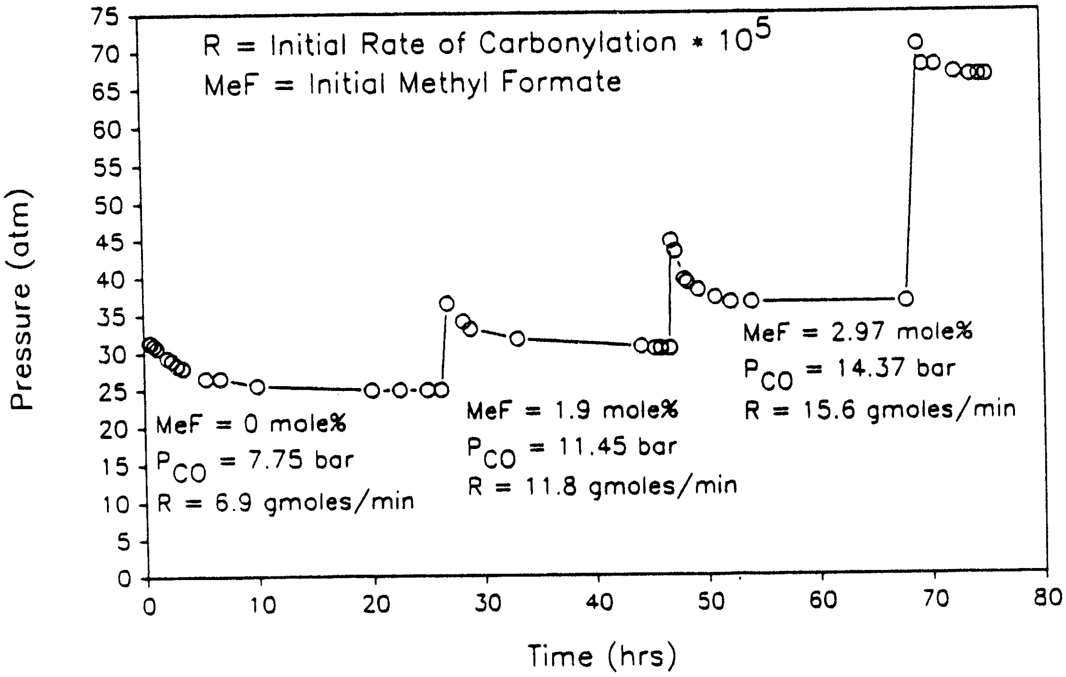

Figure 41. Typical Carbonylation Experiment to Measure Equilibrium MeF Concentration

Table 43. Equilibrium Constant for the Carbonylation Reaction Measured by the Forward and Reverse Reactions

Total Pressure (atm)	Partial Pressure of CO (atm)	Conc. MeF measured at equilibrium (mole%)	Conc. MeF predicted by Liu et al. (mole%)	$K_e = \frac{x_{MeF} \cdot 10^3}{x_{MeOH} * P_{CO}}$
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	4.1	2.9

Total Pressure (atm)	Partial Pressure of CO (atm)	Conc. MeF measured at equilibrium (mole%)	Conc. MeF predicted by Liu et al. (mole%)	$K_e = \frac{x_{MeF} \cdot 10^3}{x_{MeOH} * P_{CO}}$
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

The initial rates of carbonylation as a function of CO partial pressure were also calculated. These are shown in Table 44. As expected, the initial rates of carbonylation increase with an increase in CO partial pressure. These rates are much lower than the rates of MeF formation in the concurrent synthesis.

Table 44. Initial Carbonylation Rates as a Function of CO Partial Pressures

CO Partial Pressure (atm) (Run A49)	MeF Concentration in Liquid (mole %)	Initial Rate of Carbonylation (moles/min)
7.75	0	$6.9 * 10^{-5}$
11.45	1.9	$11.8 * 10^{-5}$
14.37	3.0	$15.6 * 10^{-5}$

T = 150°C, P = 63 atm, $H_2/CO = 2$

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