

4.2.1.3 Studies of Methanol Homologation with Cobalt Catalysts

Because of the small amounts of methanol observed relative to higher alcohols in some of our cobalt-catalyzed reactions, a study of the homologation of methanol under similar conditions was undertaken. We initially found (Table 33) that higher alcohol formation from methanol is somewhat more favorable (higher turnovers and/or selectivity) with $\text{Co}_2(\text{CO})_8/3,4,5\text{-trimethoxytoluene}$ mixtures than with similar $\text{Co}_2(\text{CO})_8/\text{neat MeOH}$ or MeOH/toluene mixtures. These effects were seen at 180°C (V2-8, 20), 200°C (V2-25, 30), and 240°C (V1-130, V2-1, 4). In addition, the formation of solids and other oxygenates noted in neat methanol were not detected in the presence of 3,4,5-trimethoxytoluene. We concluded that 3,4,5-trimethoxytoluene may hinder the formation of products resulting from methanol carbonylation while enhancing cobalt stability. Further studies showed that (i) higher alcohol formation depends upon the $\text{MeOH}/3,4,5\text{-trimethoxytoluene}$ molar ratio; (ii) cobalt stability also depends upon the 3,4,5-trimethoxytoluene/Co ratio, with precipitation occurring when this ratio was below 1:1 (V2-69); and (iii) higher alcohols were obtained with a maximum rate of 2.5 M/h (V2-47). Attempts to achieve higher rates to alcohols at a higher temperature, 210°C , showed cobalt precipitation (V2-80) even when using the same $\text{MeOH}/3,4,5\text{-trimethoxytoluene}$ ratio that provided optimum alcohol formation and a stable system at 200°C (V2-47).

The possibility that a bulk dilution effect might be responsible for our results was partially discounted by different results obtained in comparison runs conducted with MeOH/toluene mixtures (V2-52, 60, 64, 64R). The same dilution effects should be seen with toluene as with 3,4,5-trimethoxytoluene. However, runs containing toluene showed less favorable formation of higher alcohols. More dramatic differences between systems based on toluene and those based on 3,4,5-trimethoxytoluene are evident from

the maximum alcohol formation and cobalt stability obtained in the 3,4,5-trimethoxytoluene-containing runs (V2-37, 69, 69R), as well as from the responses of the alcohol rate to the amounts of 3,4,5-trimethoxytoluene or toluene in these systems.

It appears that 3,4,5-trimethoxytoluene improves the formation of higher alcohols both via enhanced methanol homologation, and through increasing the cobalt stability. Nevertheless, a further increase in the activity of these systems is required prior to the evaluation of these systems under more relevant industrial conditions. The beneficial effects associated with the presence of 3,4,5-trimethoxytoluene may be a consequence, at least in part, of improved carbon monoxide solubility and/or coordinative interaction between 3,4,5-trimethoxytoluene and $\text{Co}_2(\text{CO})_8$ or related complexes. The low stability observed for the cobalt system in methanol, a high polarity solvent, suggests that these two factors are more important in our case than any polarity change introduced by using 3,4,5-trimethoxytoluene.

Key to Table 33

SGHAM-V-#

1 mmol Co	mmoles of cobalt used, added as $\text{Co}_2(\text{CO})_8$.
2 Solvent	Solvent used.
3 mL/mmol	Volume and mmoles of solvent used.
4 Cosolvent	Cosolvent employed.
5 mL/mmol	Amount of cosolvent in mL and mmoles.
6 Promoter	Additional promoter used.
7 mmol	Amount of promoter added.
8 Pressure, psi	Reaction pressure in psig.
9 H_2/CO	Syngas composition, molar (volume) ratio.
10 Temp., °C	Reaction temperature.
11 Time, hrs	Reaction time in hours.
12 Wt.% MeOH	Percent by weight of individual products in final reaction solution.
13 Wt.% EtOH	
14 Wt.% n-PrOH	
15 Wt.% n-BuOH	
16 Wt.% Other Ox.	Percent by weight of other oxygenates observed.
17 Turnovers, alc	Turnovers to higher alcohols; mmol alc/mmol Co.
18 Selectivity, %	Mmol higher alcohols formed/mmol MeOH converted.
19 EtOH, M/h	Rates to products in moles/liter solution/hr.
20 n-PrOH, M/h	
21 n-BuOH, M/h	
22 Alcohols, M/h	Total rate to higher alcohols.
23 Methane, mole %	Amount of CH_4 in gas phase at end of reaction.
24 CO_2 , mole %	Amount of CO_2 in gas phase at end of reaction.
25 Solids	Amount of solids observed in final solution.

Table 33. Methanol Homologation with Cobalt Systems

SGHAM-V-#	1-130	2-1	2-4	2-8	2-20
1 mmol Co	17.3	17.3	17.3	17.3	17.3
2 Solvent	MeOH	MeOH	MeOH	MeOH	MeOH
3 mL/mmol	15/500	15/500	75/2344	75/2344	16/500
4 Cosolvent	3-T ^a	Toluene	-	-	3-T ^a
5 mL/mmol	60/330	60/651	-	-	60/330
6 Promoter	-	-	-	-	-
7 mmol	-	-	-	-	-
8 Pressure, psi	6000	6000	6000	6000	6000
9 H ₂ /CO	1:1	1:1	1:1	1:1	1:1
10 Temp., °C	240	240	240	200	200
11 Time, hrs	3	3	3	3	3
12 Wt.% MeOH	5.7	17.0	68.7	40.0	3.7
13 Wt.% EtOH	8.4	0.3	8.0	16.0	13.4
14 Wt.% n-PrOH	2.1	-	3.5	-	3.1
15 Wt.% n-BuOH	-	-	-	-	-
16 Wt.% Other Ox.	-	-	-	11.1	-
17 Turnovers, alc	5.4	0.2	5.7	9.6	8.7
18 Selectivity, %	54	10	33	26	76
19 EtOH, M/h	0.64	0.02	0.61	1.2	0.93
20 n-PrOH, M/h	0.12	-	0.20	-	0.16
21 n-BuOH, M/h	-	-	-	-	-
22 Alcohols, M/h	0.76	0.02	0.81	1.2	1.09
23 Methane, mole %	10.0	1.8	7.3	11.5	10.2
24 CO ₂ , mole %	3.2	0.23	3.7	2.8	7.2
25 Solids	trace	much	much	much	none

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 144.

^a 3,4,5-Trimethoxytoluene.

Table 33. Methanol Homologation with Cobalt Systems (Cont'd)

SGHAM-V-#	2-25	2-30	2-37	2-43	2-47
1 mmol Co	17.3	17.3	17.5	17.5	17.5
2 Solvent	MeOH	MeOH	MeOH	MeOH	MeOH
3 mL/mmol	16/500	75/2344	16/500	32/1000	32/1000
4 Cosolvent	3-T ^a	-	3-T ^a	3-T ^a	3-T ^a
5 mL/mmol	60/330	-	60/330	43/242	28/154
6 Promoter	-	-	-	-	-
7 mmol	-	-	-	-	-
8 Pressure, psi	6000	6000	6000	6000	6000
9 H ₂ /CO	1:1	1:1	1:1	1:1	1:1
10 Temp., °C	180	180	200	200	200
11 Time, hrs	3	3	1.5	1.5	1.5
12 Wt.% MeOH	4.2	34.4	4.4	11.4	21.0
13 Wt.% EtOH	9.2	12.2	9.6	13.7	15.8
14 Wt.% n-PrOH	2.2	1.6	2.0	3.0	1.6
15 Wt.% n-BuOH	-	-	-	-	-
16 Wt.% Other Ox.	-	10.8	0.7	2.7	4.1
17 Turnovers, alc	6.1	8.8	6.5	9.7	10.6
18 Selectivity, %	57	25	61	52	44
19 EtOH, M/h	0.67	0.89	1.4	2.0	2.3
20 n-PrOH, M/h	0.12	0.10	0.2	0.2	0.2
21 n-BuOH, M/h	-	-	-	-	-
22 Alcohols, M/h	0.79	0.99	1.60	2.3	2.5
23 Methane, mole %	5.0	8.8	7.0	8.9	12.7
24 CO ₂ , mole %	3.2	4.6	3.1	4.3	9.7
25 Solids	none	none	none	none	none

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 144.

^a 3,4,5-Trimethoxytoluene.

Table 33. Methanol Homologation with Cobalt Systems (Cont'd)

SGHAM-V-#	2-52	2-57	2-60	2-64	2-69
1 mmol Co	17.5	17.5	17.5	17.5	17.5
2 Solvent	MeOH	MeOH	MeOH	MeOH	MeOH
3 mL/mmol	48/1500	75/2344	32/1000	16/500	70/2187
4 Cosolvent	Toluene	-	Toluene	Toluene	3-T ^a
5 mL/mmol	28/304	-	53/576	60/652	6/35
6 Promoter	-	-	-	-	-
7 mmol	-	-	-	-	-
8 Pressure, psi	6000	6000	6000	6000	6000
9 H ₂ /CO	1:1	1:1	1:1	1:1	1:1
10 Temp., °C	210	200	200	200	200
11 Time, hrs	1.5	1.5	1.5	1.5	1.5
12 Wt. % MeOH	27.3	44.0	17.4	14.4	36.0
13 Wt. % EtOH	12.5	14.6	8.9	0.7	12.0
14 Wt. % n-PrOH	0.8	1.6	0.5	-	1.2
15 Wt. % n-BuOH	-	-	-	-	-
16 Wt. % Other Ox.	2.3	8.0	0.2	-	7.9
17 Turnovers, alc	7.1	8.4	5.3	0.34	7.9
18 Selectivity, %	33	25	36	10	26
19 EtOH, M/h	1.8	2.0	1.3	0.10	1.75
20 n-PrOH, M/h	0.1	0.2	0.1	-	0.13
21 n-BuOH, M/h	-	-	-	-	-
22 Alcohols, M/h	1.9	2.2	1.4	0.10	1.88
23 Methane, mole %	9.2	14.8	5.7	1.0	15.2
24 CO ₂ , mole %	3.1	16.7	0.3	0.3	11.3
25 Solids	trace	much	some	some	some

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 144.

^a 3,4,5-Trimethoxytoluene.

Table 33. Methanol Homologation with Cobalt Systems (Cont'd)

SGHAM-V-#	2-69R	2-64R	2-80
1 mmol Co	17.5	17.5	17.5
2 Solvent	MeOH	MeOH	MeOH
3 mL/mmol	70/2187	16/500	48/1500
4 Cosolvent	3-T ^a	Toluene	3-T ^a
5 mL/mmol	6/35	60/652	28/154
6 Promoter	-	-	-
7 mmol	-	-	-
8 Pressure, psi	6000	6000	6000
9 H ₂ /CO	1:1	1:1	1:1
10 Temp., °C	200	200	210
11 Time, hrs	1.5	1.5	1.5
12 Wt.% MeOH	36.4	14.4	21.3
13 Wt.% EtOH	16.0	1.1	15.2
14 Wt.% n-PrOH	1.4	-	0.7
15 Wt.% n-BuOH	-	-	-
16 Wt.% Other Ox.	7.6	-	1.4
17 Turnovers, alc	10.3	0.6	9.1
18 Selectivity, %	32	15	36
19 EtOH, M/h	2.3	0.16	2.2
20 n-PrOH, M/h	0.2	-	0.1
21 n-BuOH, M/h	-	-	-
22 Alcohols, M/h	2.5	0.16	2.3
23 Methane, mole %	16.4	0.91	17.7
24 CO ₂ , mole %	12.2	-	11.8
25 Solids	some	some	some

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 144.

^a 3,4,5-Trimethoxytoluene.

4.2.1.4 Reactions of Novel Cobalt Catalysts

Complexes with coordinated pentamethylcyclopentadienyl ligand, C_5Me_5 , have been shown to survive, at least for a short time, under relatively high pressures of syngas. This stability provides the opportunity to test the reactivity of specific transition metal complexes and, in principle, to assess the importance of several chemical factors (e.g., oxidation state, ligands, etc.) on their ability to yield oxygenates. As a test of this concept, a cobalt-based system containing $(C_5Me_5)Co(CO)_2$ in combination with the additive LuH_3 gave methanol under a syngas pressure of 3000 psi, as shown in Table 34. Infrared spectroscopic studies of the final solutions under ambient conditions showed that the initial complex had changed into other uncharacterized complexes containing terminal carbonyl ligands.

Table 34. Experiments with Cobalt Complexes

SGHAM-V-#	3-118	3-122	3-126	3-129
1 Catalyst	$\text{Cp}^*\text{Co}(\text{CO})_2^{\text{a}}$	$\text{Cp}^*\text{Co}(\text{CO})_2^{\text{a}}$	$\text{Cp}^*\text{Co}(\text{CO})_2^{\text{a}}$	$\text{Cp}^*\text{Co}(\text{CO})_2^{\text{a}}$
2 mmol	2.0	4.0	4.0	4.0
3 Solvent	MeCN	MeCN	CH_2Cl_2	TG ^b
4 mL	60	60	75	75
5 Promoter	LuH_3	LuH_3	LuH_3	LuH_3
6 mmol	2.8	2.8	2.8	2.8
7 Pressure, psi	3000	3000	3000	3000
8 H_2/CO	1:1	1:1	1:1	1:1
9 Temp., °C	200	200	200	220
10 Time, hrs	3.0	3.0	5.0	5.0
11 Wt.% MeOH	0.12	0.7	-	2.0
12 Wt.% EtOH	-	-	-	-
13 Solids	some	much	much	much
14 Solv. Decomp.	-	-	-	-

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 140.

^a $(\text{C}_5\text{Me}_5)\text{Co}(\text{CO})_2$.

^b Tetraglyme.

4.2.2 Copper Catalysts

4.2.2.1 Introduction

The goal of Task 2 is to develop novel catalysts for the conversion of synthesis gas to higher mixed alcohols. Several potential catalyst systems have therefore been tested. Some of the research has been directed toward a known [1] copper catalyst system which produces methanol and methyl formate at moderate pressures (500-2000 psi) and very low temperatures (80-120°C) when sodium methoxide (NaOMe) is used as the promoter. Under these conditions, we have observed the production of oxygenates at rates of about 1.5 mol/l/hr, about half of this mixture being methanol. Higher alcohols were not observed. The attractive operating conditions of this catalyst indicated that it was worthwhile to determine if it could be altered to produce higher alcohols. Operating conditions have been varied, and the effect of the solvent and base components of the catalyst have been investigated. Various additives have also been tested. This was of special interest since we earlier (prior to October 1, 1984) discovered that several additives had a significant effect on the rate of the reaction. By use of these additives, it has been possible to essentially double the activity of the system.

Experiments have also been conducted to determine how the products are formed in this system and to attempt to identify the species responsible for the remarkable activity of this system under very mild conditions.

1. Japanese patent application JA 57-128,642 (1982), to Mitsui Petrochemical.

4.2.2.2 Effect of Solvent in the Cu/Base System

The solvent diethyl carbitol (DEC) has been used in most of the runs with the Cu/base system. It exhibited complete stability under the conditions employed and gave reasonably consistent rates to MeOH. In contrast, when 18-crown-6 was employed as a solvent, much lower rates were seen even though DEC and 18-crown-6 are both ethers. These results are recorded in Table 35. Added methanol strongly inhibited activity even when it was used in a 1:30 mixture with DEC. The reason for this inhibition is not obvious.

4.2.2.3 Effect of the Type of Base in the Cu/Base System

A number of experiments were conducted in which the NaOMe component of the catalyst was replaced with other bases. The data are recorded in Table 36. Those bases included potassium hydroxide, sodium formate, sodium ethoxide, and potassium t-butoxide. In all cases, no activity was observed. These results are in disagreement with those previously reported by Mitsui.

Key to Tables 35, 36, and 37

SGHAM-B-#

1 Copper	Form of copper added.
2 mmol	Amount of copper complex added, mmoles.
3 Additive	Catalyst additive.
4 mmol	Amount of catalyst additive in mmoles.
5 Additive	Catalyst additive.
6 mmol	Amount of catalyst additive in mmoles.
7 Solvent	Reaction solvent; DEC = Diethyl carbitol.
8 mL	Amount of solvent employed, mL.
9 Temp., °C	Reaction temperature.
10 Pressure	Reaction pressure, psig.
11 H ₂ /CO	Syngas molar ratio.
12 Time, h	Reaction time in hours.
13 Uptake, psi	Gas uptake in psig.

Table 35. Effect of Solvent in the Cu/Base System

SGHAM-B-#	34	13	21	24	23
1 Copper	CuCl	CuCl	CuCl	CuCl	CuCl
2 mmol	5	5	5	5	5
3 Additive	NaOMe	NaOMe	NaOMe	NaOMe	NaOMe
4 mmol	110	110	110	110	110
5 Additive	-	-	-	-	-
6 mmol	-	-	-	-	-
7 Solvent	DEC	MeOH	DEC/MeOH	DEC/MeOH	18-Crown-6
8 mL	150	150	145/5	145/5	150
9 Temp., °C	110	110	110	110	110
10 Pressure	2000	2000	2000	2000	2000
11 H ₂ /CO	1.00	1.00	1.00	1.00	1.00
12 Time, h	3	4	4	4	4
13 Uptake, psi	4850	1000	1080	600	200

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 153.

Table 36. Effect of the Type of Base in the Cu/Base System

SGHAM-B-#	34	26	22	16	33	Non-Contract
1 Copper	CuCl	CuCl	CuCl	CuCl	CuCl	CuCl
2 mmol	5	5	5	5	5	5
3 Additive	NaOMe	NaOEt	KOt-Bu	NaOF	B(OMe) ₃	KOH
4 mmol	110	110	110	110	10 mL	110
5 Additive	-	-	-	-	-	-
6 mmol	-	-	-	-	-	-
7 Solvent	DEC	DEC	DEC	DEC	DEC	DEC
8 mL	150	150	150	150	150	150
9 Temp., °C	110	110	110	110	110	110
10 Pressure	2000	2000	2000	2000	2000	2000
11 H ₂ /CO	1.00	1.00	1.00	1.00	1.00	1.00
12 Time, h	3	4	4	4	3	4
13 Uptake	4850	170	490	0	0	50

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 153.

4.2.2.4 Effect of Additives on the Cu/Base System

A number of additives were screened for promoting effect on the Cu/base system. Standard conditions of 110°C and 2000 psi 1:1 H₂/CO were used. Activity, as measured by total gas uptake, is shown in Table 37 for a standard run with Cu/NaOMe only and for runs with various additives. Additives IrCl₃, FeBr₂, and Fe₂(CO)₉ acted as very potent inhibitors for the production of MeOH and other oxygenates. Mercury metal had little effect when it was present in an amount equal to the amount of copper, but in larger amounts, it was also an inhibitor. We have previously observed that SmCl₃ is a promoter of catalytic activity in the Cu/base system, and when it was used in conjunction with IrCl₃, some activity was restored, but the gas uptake remained much less than would be expected for Cu/NaOMe only. Additive UCl₄, similar in nature to SmCl₃, also acted as a promoter, but a comparison of the UCl₄ run with previous data for SmCl₃ indicated it is not as potent as SmCl₃.

Table 37. Effect of Additives on the Cu/Base System

SGHAM-B-#	8-DCB-Z-82	20	11	34
1 Copper	CuCl	CuCl	CuCl	CuCl
2 mmol	5	5	5	5
3 Additive	NaOMe	NaOMe	NaOMe	NaOMe
4 mmol	110	110	110	110
5 Additive	SmCl ₃	UCl ₄	Hg	-
6 mmol	5	5	5	-
7 Solvent	DEC	DEC	DEC	DEC
8 mL	150	150	150	150
9 Temp., °C	110	110	110	110
10 Pressure	2000	2000	2000	2000
11 H ₂ /CO	1.00	1.00	1.00	1.00
12 Time, h	4	4	3	3
13 Uptake, psi	10870	6430	5210	4850

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 153.

Table 37. Effect of Additives on the Cu/Base System (Cont'd)

SGHAM-B-#	3	8	12	7	2
1 Copper	CuCl	CuCl	CuCl	CuI	CuI
2 mmol	5	5	5	5	5
3 Additive	NaOMe	NaOMe	NaOMe	NaOMe	NaOMe
4 mmol	110	110	110	110	110
5 Additive	IrCl ₃ /SmCl ₃	Fe ₂ (CO) ₉	Hg	FeBr ₂	IrCl ₃
6 mmol	5/5	5	25	5	5
7 Solvent	DEC	DEC	DEC	DEC	DEC
8 mL	150	150	150	150	150
9 Temp., °C	110	110	110	110	110
10 Pressure	2000	2000	2000	2000	2000
11 H ₂ /CO	1.00	1.00	1.00	1.00	1.00
12 Time, h	4	4	3	4	4
13 Uptake, psi	1190	290	290	230	0

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 153.

4.2.2.5 Esters as Substrates in the Cu/Base System

A typical run with the Cu/base system forms other oxygenates, mainly methyl formate, in addition to MeOH. It was of interest to determine if some or all of the MeOH formed in this system could result from the hydrogenation of methyl formate. Runs were therefore conducted using solvent DEC with moderate amounts of one of four different esters added: methyl formate, ethyl formate, methyl acetate, and ethyl acetate. Results are shown in Table 38. Under pure hydrogen atmosphere at standard conditions, the methyl formate was hydrogenated, and methanol was produced. The other esters were not effectively hydrogenated. When we attempted to repeat these experiments in pure methyl formate or ethyl formate as both solvent and substrate, no activity was observed. Apparently the catalyst is deactivated by the pure ester solvent.

Key to Table 38

SGHAM-B-#

1 Copper	Form of copper added.
2 mmol	Amount of copper complex added, mmoles.
3 Additive	Catalyst additive.
4 mmol	Amount of catalyst additive in mmoles.
5 Additive	Catalyst additive.
6 mmol	Amount of catalyst additive in mmoles.
7 Solvent	Reaction solvent; DEC = Diethyl carbitol.
8 mL	Amount of solvent employed, mL.
9 Temp., °C	Reaction temperature.
10 Pressure	Reaction pressure, psig.
11 H ₂ /CO	Syngas molar ratio.
12 Time, h	Reaction time in hours.
13 Uptake, psi	Gas uptake in psig.
14 MeOH, %	Methanol produced, wt.% of total solution.
15 MeOCHO, %	Methyl formate present, wt.% of solution.
16 EtOH, %	Ethanol present, wt.% of solution.
17 EtOCHO, %	Ethyl formate present, wt.% of solution.

Table 38. Esters as Substrates in the Cu/Base System

SGHAM-B-#	14	18	19	75
1 Copper	CuCl	CuCl	CuCl	CuCl
2 mmol	5	5	5	5
3 Additive	NaOMe	NaOMe	NaOMe	NaOMe
4 mmol	110	110	110	110
5 Additive	MeOCHO	EtOAc	MeOAc	EtOCHO
6 mmol	50 mL	50 mL	50 mL	50 mL
7 Solvent	DEC	DEC	DEC	DEC
8 mL	100	100	100	100
9 Temp., °C	110	110	110	110
10 Pressure	1000	1000	1000	1000
11 H ₂ /CO	1/0	1/0	1/0	1/0
12 Time, h	3	3	3	3
13 Uptake, psi	2880	0	50	2130
14 MeOH, %	28.17	0.423	3.9	7.15
15 MeOCHO, %	3.91	8.21	-	0.07
16 EtOH, %	-	-	-	trace
17 EtOCHO, %	-	-	-	21.62

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 160.

4.2.2.6 Copper Catalyst Recycle Experiments

Solids are present at the conclusion of all of the copper catalyst runs, and it was of interest to try to determine if the actual catalysis was homogeneous or heterogeneous in nature. Several experiments were conducted to explore this question, and the results are given in Table 39. Three standard CuX/NaOMe runs were made at 110°C and 2000 psi syngas, and all showed the expected activity. The solids were removed from the first by filtration, and the pale yellow solution was recharged to the reactor under the same conditions. No uptake of syngas occurred. The solids were also removed from the second standard run, but in this case, the solids were recharged to the reactor along with fresh solvent. This combination also showed no activity. When this run was removed from the reactor, very little solid remained in the reaction liquid. Addition of NaOMe to this run solution did not produce an active system either. Finally, the solids were isolated from the third standard run and recharged to the reactor along with additional NaOMe and fresh solvent. This combination also failed to show reactivity. The reason for the loss of activity in these recycle experiments is not understood.

Table 39. Recycle Experiments for the CuX/NaOMe System

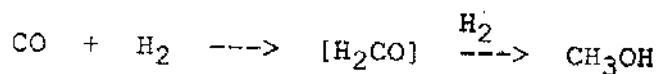
SGHAM-B-#	Catalyst	Uptake, psi	Area % MeOH	Area % Other Ox.
28	Standard	4700	6.91	14.78
29	Solution from 28	90	6.12	13.45
30	Standard	7550	5.09	9.03
31	Solid from 30	90	0.08	0
32	31 + 110 mmol NaOMe	40	0.41	0.39
34	Standard	4850	7.88	17.31
35	Solid from 34 + 110 mmol NaOMe	160	0.68	2.53

Experimental procedure: B(6); Analytical procedure: C(5).

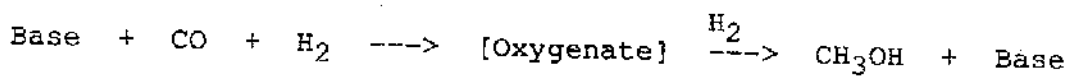
4.2.2.7 Effect of Amine Trapping Agents on the Copper System

The copper/base system is interesting from a mechanistic point of view, and we have attempted to test the possibility that one of the two routes shown below is operable:

Formaldehyde Route



Hydrogenolysis Route



From a practical standpoint, the chances of modifying the copper system to produce higher alcohols would be much greater if the production of methanol is going through a formaldehyde intermediate rather than another oxygenate intermediate which is hydrogenolyzed to form the methanol. We reasoned that if production of methanol proceeds through a free or bound formaldehyde, one might be able to trap it by reaction with an amine. Amines are known to react under fairly mild conditions with formaldehyde to give the corresponding methyl-substituted amine. This reaction is much less likely with the alternative oxygenate intermediate. Reaction of the amine directly with methanol is also possible, but it was hoped that this would not occur under the conditions used.

The results from a number of experiments involving trapping by added piperidine are given in Table 40. A standard copper/base run, made in a 2:1 mixture of the normal solvent and piperidine, shows a reduction of activity to 1/3 of its usual value as measured by gas uptake. The primary products are methanol and N-formyl-piperidine. Copper catalysts have previously been reported to carbonylate amines to formylamines, and we have confirmed that the CuX/NaOMe catalyst is highly active for that carbonylation

reaction. In contrast, very little N-methylpiperidine, the expected product of a formaldehyde intermediate, is observed, and the usual other oxygenates are absent also. Separate tests have shown that, at the normal catalytic reaction temperature of 110°C, the other oxygenates react with piperidine to form N-formylpiperidine and small amounts of N-methylpiperidine even in the absence of catalyst. In contrast, methanol does not react at all with piperidine at that temperature in the presence of catalyst, but formaldehyde (added as paraformaldehyde) produces substantial amounts of N-methylpiperidine and N-formylpiperidine in a 2:1 ratio. N-formylpiperidine essentially functions as an inert solvent for the system because when a run is conducted in a 1:1 solvent mixture of N-formylpiperidine and the usual solvent, normal activity to methanol and other oxygenates is observed.

Two additional experiments were conducted in this set showed that an active copper catalyst was necessary for the trapping to occur. As shown in Table 41, a mixture of piperidine and paraformaldehyde in the presence of DEC solvent, NaOMe, and CuCl which was deactivated by prior exposure to MeOH gave very little N-methylpiperidine, the trapping product.

Another complicating aspect of the trapping experiments is the rapid carbonylation of piperidine to N-formylpiperidine in the presence of the copper catalyst. A run was conducted to determine whether N-formylpiperidine could effectively trap a formaldehyde intermediate. The formation of moderate amounts of N-methylpiperidine from N-formylpiperidine and paraformaldehyde in the presence of the CuX/NaOMe catalyst, along with moderate activity for the conversion of syngas to MeOH and other oxygenates, indicates that the amine trapping experiments can distinguish between a formaldehyde intermediate and another intermediate. It appears that a formaldehyde intermediate is not a significant pathway in the CuX/NaOMe-catalyzed conversion of syngas to MeOH and other oxygenates.

Key to Table 40

SGHAM-B-#

1 mmol CuCl	Amount of CuCl charged, mmoles.
2 Solvent	Solvents used, volumes indicated below.
3 mL	PIP = piperidine, NFPIP = N-formylpiperidine.
4 Promoter	Promoter used, NaOMe = sodium methoxide.
5 mmol	Amount of promoter used, mmoles.
6 Pressure, psi	Reaction pressure, psig.
7 H ₂ /CO	Syngas composition, or other gas used.
8 Temp., °C	Reaction temperature.
9 Time, hrs	Reaction time in hours.
10 Uptake, psi	Gas uptake during reaction.
11 Area % PIP	Piperidine, amount observed by G.C. in area %.
12 Area % NMPIP	N-methylpiperidine.
13 Area % NFPIP	N-formylpiperidine.
14 Area % MeOH	Methanol.
15 Area % Other Ox.	Other oxygenates.

Table 40. Amine Trapping Experiments

SGHAM-B-#	63	64	65
1 mmol CuCl	5	5	5
2 Solvent	DEC/PIP	DEC/PIP/MeOH	DEC/PIP/MeOCHO
3 mL	67/33	33/33/33	33/33/33
4 Promoter	NaOMe	NaOMe	NaOMe
5 mmol	110	110	110
6 Pressure, psi	2000	100	100
7 H ₂ /CO	1	H ₂	H ₂
8 Temp., °C	110	110	110
9 Time, hrs	3	3	3
10 Uptake, psi	1520	10	50
11 Area % PIP	0.0	45.5	0.0
12 Area % NMPIP	0.3	0.0	1.9
13 Area % NFPIP	36.5	0.0	45.2
14 Area % MeOH	4.9	18.9	15.8
15 Area % Other Ox.	0.0	0.0	1.1

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 166.

Table 40. Amine Trapping Experiments (Cont'd)

SGHAM-B-#	66	67	68
1 mmol CuCl	5	5	5
2 Solvent	DEC/PIP/H ₂ CO	DEC/PIP/EtOCHO	DEC/PIP/MeOH/MeOCHO
3 mL	67/33/10g	33/33/33	25/25/25/25
4 Promoter	NaOMe	NaOMe	NaOMe
5 mmol	110	110	110
6 Pressure, psi	2000	100	100
7 H ₂ /CO	1	H ₂	H ₂
8 Temp., °C	110	110	110
9 Time, hrs	3	3	3
10 Uptake, psi	100	120	40
11 Area % PIP	18.0	0.8	0.0
12 Area % NMPIP	13.2	0.5	0.8
13 Area % NFPIP	7.5	34.6	41.5
14 Area % MeOH	2.9	2.5	30.1
15 Area % Other Ox.	0.0	0.0	0.5

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 166.

Table 40. Amine Trapping Experiments (Cont'd)

SGHAM-B-#	69	70	72
1 mmol CuCl	-	5	5
2 Solvent	PIP/MeOCHO	DEC/PIP	DEC/NFPIP
3 mL	50/50	67/33	50/50
4 Promoter	-	NaOMe	NaOMe
5 mmol	-	110	110
6 Pressure, psi	20	1000	2000
7 H ₂ /CO	N ₂	CO	1
8 Temp., °C	110	110	110
9 Time, hrs	3	3	3
10 Uptake, psi	0	200	2610
11 Area % PIP	0.0	0.0	0.0
12 Area % NMPiP	0.0	0.0	2.1
13 Area % NFPIP	72.7	36.1	47.1
14 Area % MeOH	14.4	0.6	5.7
15 Area % Other Ox.	12.5	0.0	4.2

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 166.

Key to Table 41

SGHAM-B-#

1 mmol CuCl	Amount of CuCl employed.
2 mmol NaOMe	Amount of NaOMe added.
3 mL DEC	Amount of solvent DEC used.
4 mL PIP	Amount of trapping agent piperidine added.
5 mL NFP	Amount of trapping agent N-formylpiperidine.
6 g (CH ₂ O) _n	Amount of paraformaldehyde added.
7 Temp., °C	Reaction temperature.
8 Pressure, psi	Reaction pressure.
9 Gas charged	Gas used to pressurize the reactor.
10 Time, hrs	Reaction time in hours.
11 Uptake, psi	Gas uptake in psi.
	Percent by weight in final reaction solution:
12 Wt.% MeOH	MeOH = methanol
13 Wt.% MeOF	MeOF = methyl formate
14 Wt.% PIP	PIP = piperidine
15 Wt.% NFPIP	NFPIP = N-formylpiperidine
16 Wt.% NMPIP	NMPIP = N-methylpiperidine; trapping product.

Table 41. Effects of Amine Trapping Agents

SGHAM-B-#	74	80
1 mmol CuCl	5 ^a	5
2 mmol NaOMe	110	110
3 mL DEC	50	50
4 mL PIP	50	-
5 mL NFPIP	-	50
6 g (CH ₂ O) _n	10	10
7 Temp., °C	110	110
8 Pressure, psi	100	2000
9 Gas charged	H ₂	1:1 H ₂ /CO
10 Time, hrs	3.0	3.0
11 Uptake, psi	80	900
12 Wt. % MeOH	2.36	4.82
13 Wt. % MeOF	-	3.90
14 Wt. % PIP	50.23	-
15 Wt. % NFPIP	3.63	48.20
16 Wt. % NMPIP	0.05	3.36

Experimental procedure: B(6); Analytical procedure: C(5); Key on page 170.

^a Catalyst deactivated by previous exposure to methanol.