4.2.2.8 Reactivity of a Copper Cyclopentadienyl Complex

Earlier work in this project has shown that CuCl-NaOMe catalysts produce methanol and other oxygenates under low pressures (1000-2000 psi). Homogeneous copper catalysts appear to be implicated in these reactions. The reactivity of a soluble copper complex, $(C_5Me_5)Cu$, was investigated to determine whether this complex might be more reactive or stable than those otherwise present in the catalyst solutions. Results are given in Table 42. Methanol and other oxygenates were indeed formed, but the decomposition of the original copper complex and the formation of insoluble copper products in the final solution prevent any conclusions concerning the nature of the active species.

Table 42. Experiments with Copper Complexes

	SGHAM-V-#	3-105	3-109
1	Catalyst	Cp^*Cu[a]	Cp^*Cu[c]
2	mmol	6.0	6.0
3	Solvent	THF[b]	THF[b]
4	mL	60	60
5	Promoter	NaOMe	NaOMe
6	mmol	150	150
7	Pressure, psi	2000	2000
8	H_2/CO	1:1	1:1
9	Temp.,°C	100	100
10	Time, hrs	3.0	3.0
11	Wt.% MeOH	4.5	1.4
12	Wt.% EtOH	-	-
13	Solids	much	much
14	Solv. Decomp.	-	-

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

a $(C_5Me_5)Cu$ together with LiCl by-product of synthesis and red solids formed during handling.

b Tetrahydrofuran.

c $(C_5Me_5)Cu$ and LiCl.

4.2.2.9 The Copper/Methoxide System Under Standard Conditions

Previous work in this project had shown that systems composed of a copper(I) salt and sodium methoxide can convert syngas to methanol and methyl formate at a high rate under very mild conditions (100°C, 1000 to 2000 psi). However, higher alcohols were not produced and the lifetime of the catalyst was limited. The investigation was continued with the goals of extending the catalyst lifetime and shifting the products of the reaction to higher alcohols. One approach to these goals was to gain a better understanding of the catalyst system, since a knowledge of how it works may provide insights into how to achieve the desired changes.

Continued experiments were aimed primarily at reproducing previously reported results and establishing a standard set of conditions under which to operate. Table 43 reports the data from a number of these "standard" experiments. Both copper(I) iodide and chloride were investigated as catalyst precursors. The copper(I) iodide was found to be purer and easier to handle so it was chosen as the standard catalyst precursor. The standard charge consisted of 5 mmol copper(I) iodide and 110 mmol sodium methoxide. The other reaction conditions were chosen to be a H_2/CO ratio of 1:1 at 2000 psi with a temperature of 110°C. The solvent used for standard runs was diethyl carbitol (DEC) and the standard length of an experiment was set at three hours. Some variability in the results of the experiments was observed, particularly as a function of sodium methoxide purity. For example, the low gas uptake in run #74 is probably due to contamination of the sodium methoxide.

A curious result occurred when construction near the autoclaves forced a change from a 300 mL autoclave to one of 150 mL volume. Initial experiments in this autoclave were performed with half the volume of solvent (75 mL) and half the standard amounts of reactants. However, these systems showed very poor reactivity. It was found that if the full amounts of reactants (5 mmol CuI and 110

mmol NaOMe) were used in the smaller volume of solvent, full reactivity was restored. The reason for this behavior is unknown, but because of it all experiments were performed with the same amounts of reactants. Only the volume of solvent was changed depending upon the autoclave in use. Results from both autoclaves are listed in Table 43.

Key to Tables 43 to 55

SGHAM-G-#	
1 Catalyst	Copper species used as catalyst precursor.
2 mmol	Amount of copper species in mmoles.
3 NaOMe, mmol	Amount of sodium methoxide in mmoles.
4 Solvent	Solvent used for reaction.
5 mL	Volume of solvent.
6 Additive	Additive employed.
7 mmol	Amount of additive in mmoles.
8 Pressure, psi	Reaction pressure, psi.
9 H_2/CO	Synthesis gas molar (volume) ratio.
10 Temp.,°C	Reaction temperature.
11 Time, hrs	Reaction time in hours.
12 Uptake, psi	Gas uptake in psi.
13 Wt.% MeOH	Amount of methanol in final solution.
14 Wt.% MeOF	Amount of methyl formate in final solution.
15 Other Prods	Other products observed in final solution.

Table 43. The Copper/Methoxide System Under Standard Conditions

SGHAM-G-#	39	40	56	74	77
1 Catalyst	CuI	CuCl	CuI	CuI	CuI
2 mmol	5	5	5	5	5
3 NaOMe, mmol	110	110	110	110	110
4 Solvent[a]	DEC	DEC	DEC	DEC	DEC
5 mL	150	150	75	75	75
6 Additive	none	none	none	none	none
7 mmol	-	-	-	-	-
8 Press., psi	2000	2000	2000	2000	2000
9 H_2/CO	1:1	1:1	1:1	1:1	1:1
10 Temp.,°C	110	110	110	110	110
11 Time, hrs	3	3	3	3	3
12 Uptake, psi	4800	3750	3500	2100	5300
13 Wt.% MeOH	3.8	1.2	7.7	3.9	6.2
14 Wt.% MeOF	9.6	11.0	6.6	8.6	11.0
15 Other Prods	none	none	none	none	none

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] DEC = Diethyl carbitol.

4.2.2.10 Identification of Solids Formed in the Copper System

Significant progress has been made in identifying the solid products of the copper/methoxide catalyzed reactions. After high pressure experiments there is invariably present a large amount of dark solids. These solids can no longer produce active catalyst systems. Iodometric analysis has shown that the solids contain most or all of the copper initially charged to the reactor. Treatment of the solids with water separates a small amount of an insoluble solid from the major portion of the solids which is mildly basic and quite water soluble. The insoluble solid analyzes as reasonably pure copper metal and accounts for most of the copper present in the solids. Infrared spectroscopy of the solids has shown that they contain primarily sodium formate. This agrees well with the observation that the bulk of the solids consists of a mildly basic water soluble substance. The IR spectrum of the solids also displays smaller absorbances near those of sodium formate. Thus it has been shown that the copper(I) iodide and sodium methoxide initially added to the reactor are converted to sodium formate, a species similar to sodium formate, and probably copper metal. It cannot be said with certainty whether the copper metal is present in the solids as recovered from the reactor or is formed by reaction of some copper compound with the water used to separate the soluble and insoluble fractions of the solids. The mechanism of formation of the formate is still actively being investigated since the conversion of methoxide to formate may well be responsible for the deactivation of the catalyst.

When copper(I) iodide and sodium methoxide in diethyl carbitol were exposed to syngas at one atmosphere and heated, a reaction was observed to occur. A series of color changes led quickly to formation of a black solid. This black solid appeared to remain unchanged for the duration of the reaction, up to 6.5 hours. When the solid was separated from the liquid phase by

filtration in air it became red hot, indicating the presence of a very reactive species. The one atmosphere experiment was then repeated, but the separation of the solids was performed under a nitrogen atmosphere. The solids were then tested for catalytic activity in diethyl carbitol at 2000 psi and found to be mildly active. The liquid phase, with fresh sodium methoxide added, was also tested and found to be inactive. Infrared spectroscopy of the solids recovered from the one atmosphere reaction revealed the presence of only sodium methoxide. The copper species that was present either had no significant IR absorbances or was present in too small an amount to detect. After these solids were tested for reactivity, different solids were formed which were again examined by IR spectroscopy and found to contain sodium formate but no methoxide. Thus this series of experiments has demonstrated that copper(I) iodide and sodium methoxide react in the presence of syngas to form a solid which either is or can form the active catalyst. This solid contains sodium methoxide. After reaction at 2000 psi other solids are recovered which are no longer active and which contain sodium formate rather than sodium methoxide. The nature of the active copper species, the role of the sodium methoxide and the mechanism of formation of the sodium formate are still under investigation.

Results of experiments with the one atmosphere products are given in Table 44. The one atmosphere reactions were carried out using Procedure B(13) and the high pressure experiments were performed using Procedure B(12), both described in Appendix B.

Table 44. High Pressure Experiments with Products of One Atmosphere Reactions

	SGHAM-G--#	73	75	76
1	Catalyst[a]	Liquid + Solid	Liquid	Solid
2	mmol	-	-	-
3	NaOMe, mmol	0	110	0
4	Solvent[b]	DEC	DEC	DEC
5	mL	75	75	75
6	Additive	none	none	none
7	mmol	-	-	-
8	Pressure, psi	2000	2000	2000
9	H_2/CO	1:1	1:1	1:1
10	Temp.,°C	110	110	110
11	Time, hrs	3	3	3
12	Uptake, psi	1200	500	1700
13	Wt.% MeOH	4.0	1.4	5.7
14	Wt.% MeOF	3.6	0.1	4.8
15	Other Prods	none	none	none

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] Liquid and/or solid products derived from the reaction of 5 mmol CuI and 110 mmol NaOMe in DEC at 100°C under one atmosphere syngas (Experimental procedure B(13)).

[b] DEC = Diethyl carbitol.

4.2.2.11 New Solvents for the Copper/Methoxide System

A number of new solvents for the copper/methoxide system were investigated with the goal of increasing the activity and/or the lifetime of the catalyst system. Copper(I) salts are known to activate hydrogen best in pyridine solvents, with quinoline and 4-picoline giving the highest activity [1]. Therefore, the copper/methoxide system was investigated in these solvents. The results are presented in Table 45. The system was active in these solvents, though somewhat less so than in DEC. The products were not unusual, except that a trace of ethanol was formed in 4-picoline. Also reported in Table 45 is one experiment in dimethyl sulfoxide. It was felt that the solids formed during the reaction might be soluble in this very polar solvent. However, no reaction occurred.

1. Weller, S.; Mills, G.A. *J. Am. Chem. Soc.*, 1953, **75**, 769.

Table 45. New Solvents for the Copper/Methoxide System

	SGHAM-G-#	41	42	44
1	Catalyst	CuI	CuI	CuI
2	mmol	5	5	5
3	NaOMe, mmol	110	110	110
4	Solvent	Quinoline	4-Picoline	DMSO[a]
5	mL	150	150	150
6	Additive	none	none	none
7	mmol	-	-	-
8	Press., psi	2000	2000	2000
9	H_2/CO	1:1	1:1	1:1
10	Temp.,°C	110	110	110
11	Time, hrs	3	3	3
12	Uptake, psi	2650	3400	100
13	Wt.% MeOH	4.2	4.9	1.9
14	Wt.% MeOF	3.8	5.0	0.2
15	Other Prods	none	Ethanol	none

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] Dimethyl sulfoxide.

4.2.2.12 New Ligands for the Copper/Methoxide System

Another approach to modifying the reactivity of the copper/methoxide system has been to attach ligands to the copper in an effort to keep the copper species in solution. Several experiments were done with tetrakis(acetonitrile)copper(I) tetrafluoroborate. This complex displayed variable reactivity. The results of the experiments are listed in Table 46. In experiment #46 the system displayed an initial burst of high reactivity accompanied by an exotherm followed by very low activity. In experiment #47 only very low activity was observed, while in experiment #53 activity comparable to CuI was observed. In all cases the products were not unusual, with the exception of a trace of another oxygenate in run #53.

The ligand hydrotris(pyrazolyl)borate is known to coordinate to copper(I) and allow the formation of a stable carbonyl complex [1]. This ligand was synthesized, but attempts to prepare the carbonyl complex were unsuccessful. One experiment was performed with CuI with this ligand as an additive. No unusual reactivity was observed. The complex triphenylphosphinecopper(I) hydrotris(3,5-dimethylpyrazolyl)borate was successfully prepared. It was anticipated that under reaction conditions this complex might undergo replacement of the triphenylphosphine ligand with CO and that the resulting carbonyl complex might be catalytically active. However, this experiment was unsuccessful. The results of these experiments are shown in Table 47.

1. Bruce, M.I.; Ostazewski, A.P.P. *J. Chem. Soc., Dalton Trans.*, **1973**, 2433.

Table 46. Experiments with Tetrakis(acetonitrile)copper(I) Tetrafluoroborate

	SGHAM-G-#	46	47	53
1	Catalyst[a]	$Cu(MeCN)_4BF_4$	$Cu(MeCN)_4BF_4$	$Cu(MeCN)_4BF_4$
2	mmol	5	5	5
3	NaOMe, mmol	110	110	110
4	Solvent[b]	DEC	DEC	DEC
5	mL	150	150	150
6	Additive	none	none	none
7	mmol	-	-	-
8	Pressure	2000	2000	2000
9	H_2/CO	1:1	1:1	1:1
10	Temp.,°C	110	110	110
11	Time, hrs	3	3	3
12	Uptake, psi	2000	310	3300
13	Wt.% MeOH	2.2	1.9	3.6
14	Wt.% MeOF	5.6	0.7	6.2
15	Other Prods	none	none	trace

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] $Cu(MeCN)_4BF_4$ = tetrakis(acetonitrile)copper(I) tetrafluoroborate.

[b] DEC = Diethyl carbitol.

Table 47. Experiments with Hydrotris(pyrazolyl)borate Ligands

SGHAM-G-#	52	60
1 Catalyst	CuI	$(PPh_3)Cu(DMHTPB)$[a]
2 mmol	5	5
3 NaOMe, mmol	110	110
4 Solvent[b]	DEC	DEC
5 mL	150	75
6 Additive	KHTPB[c]	none
7 mmol	5	-
8 Pressure	2000	2000
9 H_2/CO	1:1	1:1
10 Temp.,°C	110	110
11 Time, hrs	3	3
12 Uptake, psi	3000	200
13 Wt.% MeOH	1.7	0.3
14 Wt.% MeOF	7.8	0
15 Other Prods	none	none

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] Triphenylphosphinecopper(I)hydrotris(3,5-dimethylpyrazolyl)borate.

[b] DEC = Diethyl carbitol.

[c] Potassium hydrotris(pyrazolyl)borate.

4.2.2.13 Investigation of the Reactivity of Cupric Methoxide

It had been considered possible that the catalyst in the copper/methoxide systems might be finely divided copper metal and that the reaction might thus be heterogeneous. Copper(I) methoxide, which should be formed in these systems, is known to decompose to copper metal, methanol and formaldehyde [*1*]. Cupric methoxide is reported to do the same thing at elevated temperatures. Therefore, cupric methoxide could be prepared and studied in a pure form while copper(I) methoxide could not. Cupric methoxide was prepared by reaction of cupric bromide and sodium methoxide in methanol. When tested alone for catalytic activity in DEC, cupric methoxide was inactive. After the reaction, very finely divided copper metal was recovered from the autoclave. Cupric methoxide in the presence of sodium methoxide did produce an active system. However, when the cupric methoxide was first reacted with syngas at 2000 psi and 110°C to form copper metal, then cooled and supplied with sodium methoxide, no reaction occurred on restoring heat and pressure. These results, summarized in Table 48, indicate that neither copper metal alone nor copper metal and sodium methoxide are the active catalyst. The reactivity of cupric methoxide and sodium methoxide probably stems from partial reduction of the cupric methoxide to a copper(I) species which then reacts with the sodium methoxide to produce the usual catalyst.

1. Costa, G.; Camus, A.; Marsich, N. *J. Inorg. Nucl. Chem.*, 1965, **27**, 281.

Table 48. Investigation of the Reactivity of Cupric Methoxide

	SGHAM-G-#	59	63	66
1	Catalyst[a]	$Cu(OMe)_2$	$Cu(OMe)_2$	$Cu(OMe)_2$
2	mmol	10	14	10
3	NaOMe, mmol	0	110	110[b]
4	Solvent[c]	DEC	DEC	DEC
5	mL	75	75	75
6	Additive	none	none	none
7	mmol	-	-	-
8	Pressure, psi	2000	2000	2000
9	H_2/CO	1:1	1:1	1:1
10	Temp.,°C	110	110	110
11	Time, hrs	3	3	3[d]
12	Uptake, psi	0	4000	500
13	Wt.% MeOH	0.4	8.2	NA[e]
14	Wt.% MeOF	0	12.3	NA[e]
15	Other Prods	none	none	none

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] $Cu(OMe)_2$ = Cupric methoxide.

[b] Added after one hour reaction.

[c] DEC = Diethyl carbitol.

[d] Total reaction time 1 hr without NaOMe, 2 hrs with NaOMe.

[e] Not analyzed.

4.2.2.14 Redox Control in the Copper/Methoxide System

Since a substantial amount of copper metal is recovered from the solids produced by the catalytic reactions and since copper metal has been shown not to be the catalyst, it was felt that reduction of the copper(I) to copper metal might be responsible for deactivation of the catalyst. Therefore several attempts were made to control the oxidation state of the copper by preventing or reversing any reduction of copper(I) occurring during the reactions. In one experiment run in 4-picoline solvent, cupric acetate was used as an additive. Cupric acetate reacts with copper metal in picoline to produce two moles of copper(I). However, the presence of the cupric acetate inhibited the reaction rather than promoting it. Experiments were also performed with iodine as the oxidative additive. Reactivity was only slightly diminished and the products of the reaction included small amounts of other oxygenates, but the expected increase in catalyst lifetime was not observed. The results of these experiments are presented in Table 49.

Table 49. Redox Control in the Copper/Methoxide System

SGHAM-G-#	49	50	51
1 Catalyst	CuI	CuI	CuI
2 mmol	5	5	5
3 NaOMe, mmol	110	110	110
4 Solvent[a]	4-Picoline	DEC	DEC
5 mL	150	150	150
6 Additive	$Cu(OAc)_2$[b]	I_2	I_2
7 mmol	50	20	50
8 Pressure, psi	2000	2000	2000
9 H_2/CO	1:1	1:1	1:1
10 Temp.,°C	110	110	110
11 Time, hrs	3	3	3
12 Uptake, psi	1200	3600	2500
13 Wt.% MeOH	3.3	4.2	3.1
14 Wt.% MeOF	1.1	8.7	4.7
15 Other Prods	none	trace	trace

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] DEC = Diethyl carbitol.

[b] Cupric acetate.

4.2.2.15 Investigation of Other Bases in the Copper System

The function of the methoxide in the copper/methoxide system was probed by trying to replace it with other bases. One possibility was that the methoxide was functioning simply as a strong base and/or nucleophile. Since amides have similarly high basicity and nucleophilicity, they were tested. The most closely related amide would be sodium amide. However, this base displayed no reactivity with copper(I) iodide in diethyl carbitol. The sodium amide was recovered apparently unchanged from the reaction. Since the lack of reactivity might have been the result of poor solubility, the more soluble lithium diisopropyl amide was tested. It also displayed no reactivity. The results of these experiments are found in Table 50.

It is reasonable to assume that the copper(I) iodide and sodium methoxide from which the catalyst is produced first react to form copper(I) methoxide. Copper(I) methoxide is known to be thermally unstable, decomposing to copper metal, methanol and formaldehyde. A likely intermediate in this decomposition is copper hydride, produced by β-hydride elimination from copper(I) methoxide, a reaction not without precedent. Copper hydride has also been postulated as an intermediate in the thermal decomposition of other copper(I) alkoxides [*1*]. Therefore, it seemed likely that if copper hydride were the active catalyst, systems composed of copper(I) iodide and other alkoxides should show reactivity similar to that of sodium methoxide systems. In fact, the original Japanese patent application which reported the copper/methoxide system claimed that all alkoxides produce active systems. In previous work with this system sodium ethoxide was examined and found not to produce an active system.

It has been reported that the copper(I) alkoxides most likely to form copper hydride on thermal decomposition are secondary alkoxides, particularly 3-pentoxide, 2-pentoxide, and the alkoxide

of benzhydrol [1]. Table 51 reports results of some experiments with copper(I) iodide and different secondary alkoxides. Sodium 3-pentoxide was formed in situ by reaction of sodium amide and 3-pentanol. The copper/3-pentoxide system was unreactive, but in this case the ammonia formed was not removed from the solution and an excess of 3-pentanol may have been present. Potassium isopropoxide was prepared by reaction of potassium metal and isopropanol. Again no reactivity was observed, but this system probably also contained excess alcohol. The sodium salts of 2-pentanol and benzhydrol were formed as before by reaction of the alcohol with sodium amide, but in these experiments the ammonia was removed under vacuum before the material was loaded into the autoclave. Also, care was taken to have a small excess of sodium amide so that no unreacted alcohol remained. No reaction was observed with the benzhydrol product but sodium 2-pentoxide did produce a mildly active system. Gas uptake occurred and a number of products were formed. The products of the reaction included small amounts of methanol, methyl formate, other oxygenates, and some unidentified products. Though the reactivity was low, this experiment demonstrates that alkoxides other than methoxide can produce similar catalyst systems.

The above results support the theory that the active catalyst is a copper hydride species. One attempt was made to produce copper hydride in situ by reaction of copper(I) iodide with lithium aluminum hydride. This experiment failed, but it was subsequently found that lithium aluminum hydride deactivates a standard copper(I) iodide/sodium methoxide system, so the failure of the copper hydride experiment would be expected. Other experiments which produced copper hydride are described in a later section.

1. Whitesides, G.M.; Sadowski, J.S.; Lilburn, J. *J. Am. Chem. Soc.*, 1974, **96**, 2829.

Table 50. Substitution of Amides for Methoxide in Copper/Methoxide Systems

	SGHAM-G-#	43	65
1	Catalyst	CuI	CuI
2	mmol	5	5
3	NaOMe, mmol	0	0
4	Solvent[a]	DEC	DEC
5	mL	150	75
6	Additive	$NaNH_2$	$LiN(iPr)_2$[b]
7	mmol	110	110
8	Pressure, psi	2000	2000
9	H_2/CO	1:1	1:1
10	Temp.,°C	110	110
11	Time, hrs	3	3
12	Uptake, psi	450	0
13	Wt.% MeOH	0.1	0
14	Wt.% MeOF	0	0
15	Other Prods	none	ethanol

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] DEC = Diethyl carbitol.

[b] Lithium diisopropylamide.

Table 51. Substitution of Other Alkoxides for Methoxide in Copper/Methoxide Systems

	SGHAM-G-#	62	64	67	68
1	Catalyst	CuI	CuI	CuI	CuI
2	mmol	5	5	5	5
3	NaOMe, mmol	0	0	0	0
4	Solvent[a]	DEC	DEC	DEC	DEC
5	mL	75	75	75	75
6	Additive	Na_2Pent[b]	KiOPr[c]	Na_3Pent[d]	NaBenz[e]
7	mmol	110	110	110	110
8	Pressure	2000	2000	2000	2000
9	H_2/CO	1:1	1:1	1:1	1:1
10	Temp.,°C	110	110	110	110
11	Time, hrs	3	3	3	3
12	Uptake, psi	300	0	1300	0
13	Wt.% MeOH	0	0	0.2	0
14	Wt.% MeOF	0	0	0.2	0
15	Other Prods	none[f]	none[f]	traces[f]	none

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] DEC = Diethyl carbitol.

[b] Sodium 2-pentoxide.

[c] Potassium isopropoxide.

[d] Sodium 3-pentoxide.

[e] Sodium salt of benzhydrol.

[f] Substantial amounts of the alcohol and formate ester derived from the alkoxide and traces of the ketone derived from the alkoxide were observed.

4.2.2.16 Attempts to Increase Hydrogenation Activity

Several experiments were performed in an attempt to enhance the hydrogenation activity of the catalyst system and perhaps produce higher alcohols. One approach was to increase the total pressure from 2000 psi to 6000 psi while maintaining the H_2/CO ratio at 1:1. This change did not significantly alter the product distribution but did shorten catalyst lifetime. Another approach used was to maintain the 2000 psi operating pressure, but to change the H_2/CO ratio to 2:1. This change also significantly decreased the catalyst lifetime without altering the products of the reaction. The results of these experiments are presented in Table 52.

Table 52. Attempts to Increase the Hydrogenation Activity of the Copper/Methoxide System

	SGHAM-G-#	72	78	58
1	Catalyst	CuI	CuI	CuI
2	mmol	5	5	5
3	NaOMe, mmol	110	110	110
4	Solvent[a]	DEC	DEC	DEC
5	mL	75	75	75
6	Additive	none	none	none
7	mmol	0	0	0
8	Pressure, psi	6000	6000	2000
9	H_2/CO	1:1	1:1	2:1
10	Temp.,°C	110	110	110
11	Time, hrs	3	3	3
12	Uptake, psi	340	1670	900
13	Wt.% MeOH	1.4	2.3	5.9
14	Wt.% MeOF	1.3	11.4	2.7
15	Other Prods	none	none	none

Experimental procedure: B(12); Analytical procedure: C(7); Key on page 176.

[a] DEC = Diethyl carbitol.

4.2.2.17 The Involvement of Copper Hydride in the Copper/Methoxide System

Earlier work had suggested that the active copper species might be a copper hydride. The copper hydride would be formed by β-hydride elimination from cuprous methoxide. Hydrogenation of CO has also been observed with a system composed of copper(I) iodide and sodium 3-pentoxide. Cuprous 3-pentoxide has been proposed to undergo thermal decomposition to form copper hydride.

In order to further explore the involvement of copper hydride in the copper/methoxide system, other methods of introducing copper hydride into the reaction were sought. One alternative to cuprous alkoxides is the use of copper(I) tetrahydroborates. It has been reported [*1*] that some copper tetrahydroborates may decompose thermally to form copper hydride according to equation (1).

$$CuBH_4 \quad \text{------>} \quad CuH + BH_3 \qquad (1)$$

With phosphine ligands, copper tetrahydroborate complexes are stable at room temperature, but can decompose on heating. Therefore the complex bis(triphenylphosphine)copper(I) tetrahydroborate was synthesized and its activity for CO hydrogenation tested. Results of the experiments are summarized in Table 53.

In the presence of the usual 110 mmol sodium methoxide, the copper tetrahydroborate complex was moderately active. However, in the absence of sodium methoxide, no gas uptake occurred and no products were produced. The gas uptake with sodium methoxide, 1600 psi, was considerably lower than a typical experiment with CuI. However, an experiment with the standard CuI/NaOMe system run immediately after the copper tetrahydroborate experiments also consumed only 1600 psi of syngas. Investigation showed that the apparent low gas uptake was caused by a leak in the gas inlet valve to the autoclave. In the absence of the leak both experiments

would have displayed higher uptakes. Therefore it can be concluded that the copper tetrahydroborate system is approximately as active as the CuI system for CO hydrogenation.

However, it cannot be said with certainty that the reactivity of the copper tetrahydroborate system resulted from thermal decomposition to copper hydride. Since the copper tetrahydroborate complex was only reactive in the presence of sodium methoxide, it is possible that the methoxide simply displaced the tetrahydroborate and produced the usual copper methoxide catalyst. If the copper tetrahydroborate complex did decompose to copper hydride, then the sodium methoxide must still be involved in the CO hydrogenation even after formation of copper hydride.

In order to establish with some certainty the involvement of copper hydride in the copper/methoxide system, it was decided to synthesize copper hydride directly. Copper hydride was prepared by reaction of copper(I) iodide and diisobutylaluminum hydride in pyridine at -50°C [2]. The copper hydride was precipitated with ether and washed several times with ether at -78°C. Since in its pure form copper hydride is not very stable at room temperature, the copper hydride and diethyl carbitol to be used as solvent were kept at -78°C until just before use. The DEC was then thawed and the solid and liquid added to the autoclave. The results of the experiments are reported in Table 54.

As with the copper tetrahydroborate system, no reactivity was observed in the absence of sodium methoxide. However, in the presence of 110 mmol sodium methoxide, the system was the most active one ever observed in the 150 mL autoclave. The gas uptake was 4480 psi and 7.0% methanol and 12.6% methyl formate were produced. A standard run using copper(I) iodide run immediately afterwards consumed 3270 psi syngas and produced 5.8% methanol and 10.5% methyl formate. The copper hydride system was also examined at 1000 psi in an attempt to extend its lifetime, but the opposite effect was noted. Copper hydride also hydrogenated CO in the presence of sodium ethoxide. The activity was considerably lower than with methoxide, but CuI displays no activity with ethoxide.

This is presumably because copper(I) ethoxide decomposes through a radical mechanism, producing copper metal rather than copper hydride. The ethanol and ethyl formate produced by the copper hydride/sodium ethoxide system was derived from the ethoxide, but the methanol and methyl formate could have come only from hydrogenation of CO.

Unlike the copper tetrahydroborate system, it is highly unlikely that methoxide displaced hydride from copper hydride to produce the usual copper methoxide catalyst. Also, if that were the case the sodium ethoxide system should have been inactive. Thus these results point very strongly to the involvement of copper hydride in the copper/methoxide system. But these results also clearly point to the importance of methoxide, or other alkoxide, in these systems since even copper hydride is inactive in the absence of alkoxide. The results agree with previous indications that it is loss of methoxide that is deactivating the copper/methoxide system.

1. Bianchini, C.; Ghilardi, C.A.; Meli, A.; Midollini, S.; Orlandini, A. *Inorg. Chem.*, 1985, **24**, 924.

2. Whitesides, G.M.; San Filippo, J. Jr. *J. Am. Chem. Soc.*, 1970, **92**, 6611.

Table 53. CO Hydrogenation by Bis(triphenylphosphine)copper(I) Tetrahydroborate

SGHAM-G-#	79	81	82
1 Catalyst[a]	P_2CuBH_4	P_2CuBH_4	CuI
2 mmol	5	5	5
3 NaOMe, mmol	110	0	110
4 Solvent[b]	DEC	DEC	DEC
5 mL	75	75	75
6 Additive	none	none	none
7 mmol	0	0	0
8 Pressure, psi	2000	2000	2000
9 H_2/CO	1:1	1:1	1:1
10 Temp.,°C	110	110	110
11 Time, hrs	3	3	3
12 Uptake, psi	1600	0	1600
13 Wt.% MeOH	3.4	0	5.3
14 Wt.% MeOF	4.1	0	8.8
15 Other Prods	none	none	none

Experimental procedure: B(14); Analytical procedure: C(7); Key on page 176.

[a] P_2CuBH_4 = bis(triphenylphosphine)copper(I) tetrahydroborate.

[b] DEC = Diethyl carbitol.

Table 54. Reactivity of Copper Hydride Systems

	SGHAM-G-#	85	86	87	89	88	90
1	Catalyst	CuH	CuH	CuI	CuH	CuH	CuH
2	mmoles	5	5	5	5	5	5
3	NaOMe, mmol	0	110	110	110	0	0
4	Solvent[a]	DEC	DEC	DEC	DEC	DEC	DEC
5	mL	75	75	75	75	75	75
6	Additive[b]	none	none	none	none	NaOEt	NaOEt
7	mmol	0	0	0	0	110	110
8	Press, psi	2000	2000	2000	1000	2000	1000
9	H_2/CO	1:1	1:1	1:1	1:1	1:1	1:1
10	Temp.,°C	110	110	110	110	110	110
11	Time, hrs	3	3	3	3	3	3
12	Uptake, psi	0	4480	3270	2980	280	720
13	Wt.% MeOH	0	7.0	5.8	3.6	1.0	2.0
14	Wt.% MeOF	0	12.6	10.5	5.1	1.2	1.5
15	Other Prods	none	none	none	none	none[c]	none[c]

Experimental procedure: B(14); Analytical procedure: C(7); Key on page 176.

[a] DEC = Diethyl carbitol.

[b] NaOEt = sodium ethoxide.

[c] Products included ethanol and ethyl formate derived from ethoxide.