4.1.2.4 Studies of Catalyst Composition

In initial studies we found that Ru and additives C4, A25, and A28 were the critical components of this novel catalyst system. More detailed studies of the effect on the ethanol selectivity of varying the catalyst components are recorded in Table 25.

In this series of experiments the temperature was maintained at 140°C. Additive C4 was held at a constant level while Ru, A25, and A28 were varied. The base case is W13-105 with an ethanol selectivity of 47.5%. In the absence of additive A25 the selectivity is reduced to 9% (W13-110). Doubling the Ru concentration (W13-113) increased the selectivity to 70%. At this increased Ru level the effect of varying additive A25 was studied in W17-8, W17-10, and W17-19. In the absence of A25 (W17-8) the selectivity is low. The best selectivity in this series, 72%, was obtained at Ru:A25 = 1:1 (W17-19). A further increase in the Ru (W17-1) resulted in a lower selectivity (64%) relative to W17-19, although the selectivity did increase with increasing A25 (W17-60, W17-64). The effect of varying the concentration of A28 is not clear. In comparing W17-22 and -24 to W13-113, the selectivity decreased upon both increasing and decreasing A28. A similar result was obtained with W17-19 and W17-55. However, in comparing W17-64 and W17-68 the selectivity increased slightly with increasing A28.

The data reported in Table 25 demonstrate that Ru, A25, and A28 all play an important role in determining the ethanol selectivity. More experimental details are given in Table 28.

Table 25. Ethanol Selectivity Determined by Catalyst Components

	Molar Ratio				
SGHAM-W-#	C4	Ru	A25	A28	EtOH Sel.,%[a]
13-105	1	1	1	20	47.5
13-110	1	1	0	20	9.0
13-113	1	2	1	20	70.4
17-8	1	2	0	20	16.4
17-10	1	2	0.5	20	35.2
17-19	1	2	2	20	72.3
17-22	1	2	1	10	52.8
17-24	1	2	1	40	31.5
17-55	1	2	2	40	29.0
17-1	1	3	1	20	63.9
17-60	1	3	2	20	69.8
17-64	1	3	3	20	70.8
17-68	1	3	3	40	71.1

See Table 28 for experimental details.

[a] Selectivity to ethanol plus ethanol equivalents (compounds easily converted to ethanol).

4.1.2.5 The Effect of Temperature on Homologation

The homologation reaction was carried out at several temperatures, and the results are reported in Table 26. (Full experimental results are given in Table 28.) Increasing the temperature above 140°C normally results in a decrease in ethanol selectivity. For example, W13-106 is a repeat of W13-105 (Table 25) with the exception that the reaction temperature was increased from 140°C to 155°C. The ethanol selectivity decreased from 47 to 41%. Similarly, the selectivity dropped from 70% in W17-60 (Table 25) to 53% in W17-72 upon increasing the reaction temperature ten degrees. However, decreasing the temperature to 130°C markedly increased the selectivity. In comparing W17-74 to W17-60, the ethanol selectivity increases to 80% at 130°C. In this case the ethanol rate is 2 M/hr and the methanol conversion is 65%.

The response to temperature exhibited by this catalytic system is different from that of the well-known Co-Ru-I homologation catalyst. In the case of the latter catalyst, increasing the temperature from 170 to 200°C increases the ethanol selectivity. It is generally accepted that the cobalt catalyst first produces acetaldehyde, which is then reduced to ethanol by ruthenium.

$$CH_3OH + H_2 + CO \longrightarrow CH_3C(O)H + H_2O$$

$$CH_3C(O)H + H_2 \longrightarrow CH_3CH_2OH$$

A series of experiments was carried out with our novel Ru-containing catalyst in order to study the product distribution as a function of reaction time. In these experiments the gas uptake, and hence the methanol conversion, was varied. The results are given in Table 27. The conditions and catalyst composition are the same as those used in W17-74, Table 26. At low methanol conversion, 20% (W17-77), the main product is acetaldehyde. As the

methanol conversion increases, the acetaldehyde selectivity decreases and the ethanol selectivity increases. Although not conclusive, these results suggest that acetaldehyde is formed first and then reduced to ethanol.

Table 26. Ethanol Selectivity at Different Temperatures

	Molar Ratio					
SGHAM-W-#	C4	Ru	A25	A28	Temp,°C	EtOH Sel.,%[a]
13-105	1	1	1	20	140	47.5
13-106	1	1	1	20	155	40.9
17-60	1	3	2	20	140	69.8
17-72	1	3	2	20	150	53.1
17-74	1	3	2	20	130	80.1

See Table 28 for experimental details.

[a] Ethanol plus ethanol equivalents.

Table 27. Ethanol Selectivity vs. Methanol Conversion

		Selectivity, %	
SGHAM-W-#	MeOH Conv.,%	AcH[a]	EtOH[b]
17-77	20	58	19
17-78	35	35	42
17-80	54	26	48
17-74	65	15	56

See Table 28 for experimental details.

[a] Acetaldehyde plus acetaldehyde equivalents in dimethyl acetal.
[b] Ethanol only.

Key to Tables 28, 67, 72, and 76

SGHAM-W-#	
1 Catalyst	Compound added as catalyst precursor.
2 mmol	Amount of catalyst precursor, mmoles.
3 Cocatalyst	Compound added as cocatalyst.
4 mmol	Amount of cocatalyst added, mmoles.
5 Additive	Catalyst additives employed.
6 mmol	Amount of catalyst additive, mmoles.
7 Promoter	Other promoter employed.
8 mmol	Amount of promoter, mmoles.
9 MeOH(mL)	Amount of methanol used.
10 Pressure,psi	Reaction pressure in psig.
11 H_2/CO	Syngas molar (volume) ratio.
12 Temp.,°C	Reaction temperature.
13 Time,hr	Reaction time in hours.
14 Uptake,psi	Gas uptake in psi.
15 Product Sel.%	Molar selectivity to products:
16 EtOH	Free ethanol
17 EtOH Eq.	Ethanol equivalents
18 Total EtOH	Total ethanol
19 Other Oxy.	Other oxygenates

Table 28. Methanol Homologation Experiments

	SGHAM-W-#	13-105	13-106	13-110	13-113
1	Catalyst	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$
2	mmol	2	2	2	4
3	Cocatalyst	C4	C4	C4	C4
4	mmol	2	2	2	2
5	Additive	A25	A25	none	A25
6	mmol	2	2	0	2
7	Promoter	A28	A28	A28	A28
8	mmol	40	40	40	40
9	MeOH, mL	40	40	40	40
10	Pressure, psi	975	975	975	975
11	H_2/CO	2:1	2:1	2:1	2:1
12	Temp.,°C	140	155	140	140
13	Time, hrs	1.22	0.55	0.57	2.7
14	Uptake, psi	950	617	771	3350
15	Product Sel.%				
16	EtOH	25.2	13.6	2.3	43.0
17	EtOH Eq.	22.2	27.3	6.6	27.4
18	Total EtOH	47.5	40.8	8.9	70.4
19	Other Ox.	52.25	59.1	91.1	29.6

Experimental procedure: B(2); Analytical procedure: C(2); Key on page 115.

Table 28. Methanol Homologation Experiments (Cont'd)

	SGHAM-W-#	17-1	17-8	17-10	17-19
1	Catalyst	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$
2	mmol	6	4	4	4
3	Cocatalyst	C4	C4	C4	C4
4	mmol	2	2	2	2
5	Additive	A25	none	A25	A25
6	mmol	2	-	1	4
7	Promoter	A28	A28	A28	A28
8	mmol	40	40	40	40
9	MeOH, mL	40	40	40	40
10	Pressure, psi	975	975	975	975
11	H_2/CO	2:1	2:1	2:1	2:1
12	Temp.,°C	140	140	140	140
13	Time, hrs	1.83	0.75	0.63	3.15
14	Uptake, psi	2777	926	694	3663
15	Product Sel.%				
16	EtOH	40.7	5.65	14.7	46.3
17	EtOH Eq.	23.1	10.8	20.4	26.5
18	Total EtOH	63.8	16.4	35.2	72.7
19	Other Ox.	36.1	83.6	64.8	27.3

Experimental procedure: B(2); Analytical procedure: C(2); Key on page 115.

Table 28. Methanol Homologation Experiments (Cont'd)

	SGHAM-W-#	17-22	17-24	17-55	17-60
1	Catalyst	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$
2	mmol	4	4	4	6
3	Cocatalyst	C4	C4	C4	C4
4	mmol	2	2	2	2
5	Additive	A25	A25	A25	A25
6	mmol	2	2	4	4
7	Promoter	A28	A28	A28	A28
8	mmol	20	80	80	40
9	MeOH, mL	40	40	40	40
10	Pressure, psi	975	975	975	975
11	H_2/CO	2:1	2:1	2:1	2:1
12	Temp.,°C	140	140	140	140
13	Time, hrs	1.0	0.62	1.5	2.0
14	Uptake, psi	1198	538	1277	2540
15	Product Sel.%				
16	EtOH	33.3	11.1	18.0	46.6
17	EtOH Eq.	19.4	20.3	11.3	23.2
18	Total EtOH	52.7	31.5	29.3	69.8
19	Other Ox.	47.2	68.5	70.7	30.2

Experimental procedure: B(2); Analytical procedure: C(2); Key on page 115.

Table 28. Methanol Homologation Experiments (Cont'd)

	SGHAM-W-#	17-64	17-68	17-72	17-74
1	Catalyst	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$
2	mmol	6	6	6	6
3	Cocatalyst	C4	C4	C4	C4
4	mmol	2	2	2	2
5	Additive	A25	A25	A25	A25
6	mmol	6	6	4	4
7	Promoter	A28	A28	A28	A28
8	mmol	40	80	40	40
9	MeOH, mL	40	40	40	40
10	Pressure, psi	975	975	975	975
11	H_2/CO	2:1	2:1	2:1	2:1
12	Temp.,°C	140	140	150	130
13	Time, hrs	2.2	3.25	1.0	4.5
14	Uptake, psi	2422	2250	2436	3038
15	Product Sel.%				
16	EtOH	51.8	62.3	30.7	56.1
17	EtOH Eq.	19.0	8.7	22.4	24.0
18	Total EtOH	70.8	71.0	53.1	80.1
19	Other Ox.	29.1	29.0	46.8	19.8

Experimental procedure: B(2); Analytical procedure: C(2); Key on page 115.

Table 28. Methanol Homologation Experiments (Cont'd)

	SGHAM-W-#	17-77	17-78	17-80
1	Catalyst	$RuCl_3$	$RuCl_3$	$RuCl_3$
2	mmol	6	6	6
3	Cocatalyst	C4	C4	C4
4	mmol	2	2	2
5	Additive	A25	A25	A25
6	mmol	4	4	4
7	Promoter	A28	A28	A28
8	mmol	40	40	40
9	MeOH, mL	40	40	40
10	Pressure, psi	975	975	975
10	H_2/CO	2:1	2:1	2:1
11	Temp.,°C	130	130	130
12	Time, hrs	0.5	1.25	3.0
13	Uptake, psi	500	1200	2190
14	Product Sel.%			
15	EtOH	19.1	42.86	47.8
16	EtOH Eq.	42.4	33.14	28.4
17	Total EtOH	61.5	76.0	76.2
18	Other Ox.	38.5	24.0	23.7

Experimental procedure: B(2); Analytical procedure: C(2); Key on page 115.

4.1.3 Task 1 Summary

Direct Syngas Conversion

Certain soluble ruthenium species, in combination with iodide promoters, catalyze the conversion of H_2/CO into methanol. A small amount of work prior to the initiation of this contract indicated that significant amounts of higher alcohols (ethanol, propanol, and butanols) could be produced under certain conditions. Research under this contract has attempted to more fully explore the potential of modified ruthenium catalysts for the production of mixed alcohol products from syngas, particularly at pressures below 6000 psi, and preferable at pressures from 1000 to 3000 psi.

Prior to the initiation of this contract, it was discovered that the addition of specific lanthanide metal complexes to the ruthenium catalyst significantly increased the overall catalytic activity and the selectivity to C_2+ alcohols. During this contract we have investigated several aspects of these lanthanide-promoted catalysts with respect to the conversion of H_2/CO into mixed alcohols. The goal of this work has been to improve the activity and higher alcohol selectivity, as well as to investigate the mechanism of this conversion. Specifically, we have investigated the effects of total iodide concentration, acidity, and solvent polarity on activity and selectivity. In addition, we have studied the effect of adding known methanol hydroformylation catalysts.

With the lanthanide-promoted catalysts, we have observed total ROH rates of up to 1.6 mol/l/hr and C_2+ selectivities (relative to total ROH) over 80 weight %. Typically, carbon selectivities to alcohols (relative to all liquid products) are in excess of 95%. The major gaseous products are methane and carbon dioxide. These products are generally formed in approximately equivalent amounts and usually constitute 30 to 50% (on a product mole basis) of all reaction products.

We have determined that increasing the total iodide level in

the Ru/I/lanthanide catalyst decreases the activity, but increases the C_2+ alcohol selectivity. Replacement of NaI with I_2 as the iodide source decreases the activity and increases the C_2+ selectivity. We assume that this is an acidity effect since I_2 reacts with H_2 to yield HI. Thus, there is considerable flexibility, via pH variation, with regard to activity and selectivity using this modified ruthenium catalyst. In the absence of the lanthanide additive, both the rates and selectivities are significantly lower. In the case of tri-n-propylphosphine oxide solvent, the effect of acidity on rates and selectivity is the same in both the presence and absence of the lanthanide additive. However, in the case of N-methylpyrrolidone solvent, the effect of acidity in the absence of the additive is opposite that observed in its presence.

A study of product distribution as a function of H_2/CO conversion (i.e., reaction time) indicated that it is likely that the higher alcohol products are being formed from methanol by a homologation mechanism. The relative selectivity to higher alcohols increased relative to methanol at the longer reaction times.

We have also performed a number of runs using Cp (cyclopentadienyl) or Cp* (pentamethylcyclopentadienyl) complexes as the ruthenium component of the normal catalyst charge. The goal was to determine if such complexes could be stable under the relatively vigorous conditions (230-250°C, 6000 psi 1:1 H_2/CO) employed, and if such complexes could exhibit altered reactivity or selectivity. The experiments show that considerable stability does exist under reaction conditions, especially for the Cp* complex. This is demonstrated by the overall reduction in activity observed. An increase in C_2+ products is also observed, but such results normally occur when the overall rate decreases, so no special influence on selectivity can be ascribed to the Cp or Cp* ligands.

The addition of water to the initial catalyst charge was found to reduce reaction rate substantially even though stoichiometry requires that water be formed whenever higher alcohols are produced from syngas. It is normally observed that much of this water is shifted to CO_2 and H_2 as it is formed. The presence of

added water at the 7 volume percent level in a catalytic solution brings about a significant decrease in catalyst rate. Since substantial amounts of the added water remain after catalysis, this water is probably deactivating the catalyst precursor. It appears, however, that water formed by the catalyst under normal test conditions never builds up to this level, so inhibition by water is not expected to present a significant problem in this system. This indicates the importance of the inherent water-gas shift activity of this catalyst to its total performance.

Experiments with halide-promoted ruthenium catalysts for direct conversion of syngas to alcohols were carried out in several novel solvents. Although good catalyst stability and alcohol productivity were seen, solvent degradation was found to be a problem. The use of Lewis acids in combination with these catalyst systems showed in some cases a shift in product selectivity, but again solvent stability was less than desirable.

Several novel additives, members of a family of metal complexes, have been identified which significantly alter the selectivity and/or the activity of the basic iodide-promoted catalytic system. One of these additives nearly triples the activity of the basic iodide-promoted system in NMP solvent (to a total alcohol rate of about 1.2 M/hr), and at the same time increases the C_2+ alcohol fraction from 10 to 80 wt.%. Most interesting is the observation that some of these additives allow the formation of alcohol products at good rates under significantly lower pressures than previously observed; substantial activity is observed at 3000 psi of syngas pressure. Other related additives have been tested which change the selectivity to higher alcohols without affecting the total reaction rate significantly.

The effects of using phosphonium halides as solvents were studied during the contract. Some of these materials are molten at reaction temperatures and therefore appear to be suitable solvents. Experiments have been carried out with various additives in these solvents which improve the rate and/or selectivity to higher alcohols. Use of the novel additives described immediately above

in tetrabutylphosphonium bromide solvent gives good rates to alcohols (ca. 1.2 M/hr), but the selectivity to alcohols in the liquid product (56 wt.%) is not as good as in NMP solvent. In NMP solvent, this number is typically above 80 wt.%.

Continued investigation of this class of additives demonstrated that a number of similar additives have similar catalytic characteristics. A particular additive was found to increase the production of n-propanol, especially in the molten phosphonium salt system. Furthermore, it was demonstrated that the addition of synthetic precursors of one of these additives to the molten phosphonium salt system gave catalytic effects very similar to those of the additive itself.

Modifications of this additive have also been investigated. The introduction of electron-donating or electron-withdrawing groups sometimes can cause significant changes in catalyst behavior. In this case, neither gave an increase in activity, although changes in selectivity were evident. Electron-donating groups seem to retard the homologation steps of this particular system, while electron-withdrawing groups caused the system to produce other oxygenates.

Organic compounds similar to those included in some of the metal-containing additives tested have also been used as catalyst additives. In several cases, enhanced selectivities and activities to higher alcohols were observed. Electron-withdrawing groups substituted on the additive seem to increase both the activity and the selectivity to higher alcohols, while electron-donating groups have the opposite effect.

It has become clear that benzimidazole, an additive reported by others to be a useful promoter for ruthenium catalysts, is not stable at 230°C under catalytic conditions. It decomposes to o-phenylenediamine and a C_1 fragment, most likely formic acid. Interestingly, o-phenylenediamine in low concentration was shown to be a mild promoter for the formation of certain oxygenates by these catalyst systems. At high concentrations, however, it retarded the catalyst activity. The enhanced activity when benzimidazole was

used as additive may have resulted from the hydrogenation of the C_1 fragment formed from benzimidazole decomposition.

Studies have been carried out on a particular class of organic additives with the catalyst system of ruthenium carbonyl in organic solvents. It has been discovered that one member of this class has the ability to substantially increase the syngas conversion activity of the ruthenium catalyst in several types of organic solvents. The system with this modification is reasonably active even at pressures as low as 3000 psi. Although this particular system does not yield C_2+ alcohols (methanol is the major product), additional additives or cocatalysts have been found to enhance the formation of ethanol. It is presumed that the addition of these latter compounds forms a homologation catalyst system so that some of the methanol produced from syngas is transformed to ethanol in a second reaction step.

We have studied several solvents for this additive-modified system, and have found that the polar solvent sulfolane gives good rates to alcohols, including C2+ alcohols. This system, Ru/A16/KI/A92 is also a very selective system for producing only alcohols. Unlike systems previously described which involve the use of metal-containing additives such as A38 and its derivatives, this system produces only small amounts of other oxygenates such as acetate esters. Furthermore, the rate of formation of C_2+ alcohols is very respectable. For example, at 5000 psi, the rate to C_2+ alcohols is 1.4 M/h with a molar selectivity to C_2+ alcohol of 60%; methanol is the other product and the rate of its formation is 0.94 M/h.

Because of potential drawbacks of sulfolane solvent, such as cost and possible decomposition, other solvents were also tested. Tetrahydrofuran (THF) appeared to give encouraging results. At 5000 psi, a total rate to alcohols of 3.4 mol/l/hr was observed, and 29% of the alcohols fraction was C_2+ alcohols. The yield of other oxygenates was low, at about 8 wt.% of the liquid product. Experiments in alcohol solvents are most interesting. Methanol solvent gave quite good activity, although a net loss in methanol was observed. This apparently results from homologation of a

substantial amount of this alcohol to ethanol and higher alcohols. Ethanol solvent has also given encouraging results. At 5000 psi, a total alcohol rate of 3.1 mol/l/hr was achieved, and 31% of the alcohol fraction was C_2+ alcohols. Only 4 wt.% of the liquid product was other oxygenates. These results indicate that alcohols themselves may be the best solvents for these reactions. By recycling the light alcohols methanol and ethanol to the reaction, the yield of higher alcohols could be substantially enhanced.

Methanol Homologation

A ruthenium-containing catalyst system has been discovered which converts methanol to ethanol upon reaction with syngas at very low pressures and temperatures -- 950 psi and 140°C. For the first time homologation of methanol can be effectively carried out at reaction pressures less than 1000 psig. The activity and selectivity are strongly dependent on the catalyst additive utilized.

The importance of having each of four catalyst components present during the reactions has been demonstrated, and the effects of reaction temperature have been explored. Lower temperatures have a significant effect on increasing the selectivity to ethanol. Selectivities to ethanol of 80% and rates of 2 M/hr have been observed; these are close to the best reported for the standard Co-Ru-I catalyst (rate of 4 M/hr, selectivity of 85%) which requires high temperature-high pressure operation. Turnover frequencies for the new catalyst are in the range of 20 to 40 moles ethanol per g-atom Ru per hour.

Studies of this catalyst were continued under Task 3 of this contract, which consists of a more thorough study of the fundamental chemistry and process characteristics of catalyst systems most deserving of further work. Additional results are therefore reported under the Task 3 heading.

4.2 Task 2 - Development of Novel Catalysts

The objective of Task 2 was to design systems for the production of alcohols from syngas based on new homogeneous catalysts, preferably those comprising non-noble metals. This has therefore involved catalyst screening studies with potential catalytic systems based on metals which had previously shown little or no activity for homogeneous syngas conversion. Catalysts screened included complexes of cobalt, copper, iron, palladium, rhenium, and others.

4.2.1 Cobalt Catalysts

4.2.1.1 Introduction

A search was conducted for a homogeneous cobalt catalyst system active for the conversion of syngas into mixtures of fuel alcohols. Previous literature reports identified cobalt as one of the most suitable metals for such a purpose. The earlier work shows that cobalt catalysts can produce alcohol products, but rates are very low under practical conditions. Nevertheless, confusion was prevalent concerning the roles of solvents in these catalytic systems. Reaction solvents can have substantial effects on the stability of a catalyst, and large improvements in cobalt stability are probably required if such a catalyst system is to be practical. Thus the identification of a practical cobalt catalytic system will unavoidably involve the search for a suitable solvent, and our approaches were planned following this premise.

Since higher alcohols may be formed in these systems by homologation of initially-formed methanol, a few experiments were also carried out on the homologation of added methanol.

Some specific cobalt complexes were tested as catalyst precursors, to investigate the possibility that they would provide more stable catalyst systems.

4.2.1.2 Studies of Novel Solvents with Cobalt Catalysts

A series of cobalt-solvent combinations has been investigated based on analogies with other catalytic systems. Several of these combinations were found to be inactive, even in the presence of promoters (Table 29). Others, however, were found to be active catalytic systems. For instance, 3,4,5-trimethoxytoluene, an oxygen-containing organic solvent, appears to promote improved performance for higher alcohol formation relative to toluene solvent in standard runs (Table 30). The 3,4,5-trimethoxytoluene solvent appears to improve the stability of the cobalt catalyst. For example, a much smaller amount of cobalt precipitation is visually detected after 240°C runs in 3,4,5-trimethoxytoluene: toluene than in comparable runs in toluene.

A limited comparative test with 2,4,6-trimethoxytoluene shows the better performance of 3,4,5-trimethoxytoluene in the formation of higher alcohols (Table 30). The reasons for this difference are not obvious.

Another approach has consisted of a search for nucleophilic solvents capable of activating the cobalt species without the inhibitory effect previously reported for most of such solvents. The solvent N-phenylcarbazole, a nitrogen-containing organic solvent, appeared to be a suitable candidate. A preliminary test showed that higher alcohols are indeed formed in N-phenylcarbazole: toluene solvent mixtures (Table 30).

Further experiments with $Co_2(CO)_8$/N-phenylcarbazole mixtures (Table 31) have shown that alcohols can be produced under several conditions, although in lesser amounts than in similar systems containing 3,4,5-trimethoxytoluene or 2,4,6-trimethoxytoluene.

Additional work with $Co_2(CO)_8$ mixtures containing 3,4,5-trimethoxytoluene and 2,4,6-trimethoxytoluene (Table 31) demonstrated that some of these catalysts yield alcohol mixtures containing ethanol and methanol as the major and minor components, respectively, even under mild conditions. In addition, $Co_2(CO)_8$/

2,4,6-trimethoxytoluene mixtures were found to favor formation of higher alcohols, although to a lesser extent than 3,4,5-trimethoxytoluene-containing systems. The low proportion of methanol in these products may have resulted from enhanced homologation reactions in the presence of 3,4,5-trimethoxytoluene and 2,4,6-trimethoxytoluene.

The reactivity of cobalt-2,5-dimethoxytetrahydrofuran mixtures was examined, due to the relationship of that solvent with other solvents previously applied for these reactions. It was found that these mixtures did not yield appreciable amounts of higher alcohols. Instead, as shown in Table 32, extensive solvent decomposition occurred with the resultant formation of methanol. Unusually good cobalt stability was observed, however. Attempts to improve the catalytic activity and cobalt stability by addition of polydentate phosphine ligands, as shown in Table 32, were not successful. As a result, studies of 2,5-dimethoxytetrahydrofuran were discontinued.

Key to Tables 29 and 30

SGHAM-V-#	
1 mmol Co	Amount of cobalt used, mmoles; $Co_2(CO)_8$ except as noted.
2 Solvent	Solvent or solvents used.
3 mL	Volume of solvents used; NMP = N-methylpyrrolidone.
4 Promoter	Additional promoter used.
5 mmol	Amount of promoter used, in mmoles.
6 Pressure, psi	Reaction pressure in psig.
7 H_2/CO	Syngas composition, molar ratio.
8 Temp.,°C	Reaction temperature.
9 Time, hrs	Reaction time in hours.
10 Wt.% MeOH	Percent by weight of individual products in final reaction solution.
11 Wt.% EtOH	
12 Wt.% n-PrOH	
13 Wt.% n-BuOH	
14 Wt.% Other Ox.	Percent by weight of other oxygenates observed.

Table 29. Experiments with Cobalt Catalysts

SGHAM-V-#	1	4	8	12
1 mmol Co	10.0	5.0[a]	5.0[a]	5.0[a]
2 Solvent	Sulfolane/18-crown-6	Sulfolane	Sulfolane	Sulfolane
3 mL	68/7	75	75	75
4 Promoter	NaCN	NaCN	Na_2HPO_4	H_3PO_4
5 mmol	10	25	6	6
6 Pressure, psi	6000	6000	6000	6000
7 H_2/CO	1.0	1.0	1.0	1.0
8 Temp.,°C	220	200	200	200
9 Time, hrs	3	3	4	3
10 Wt.% MeOH	-	-	-	-
11 Wt.% EtOH	-	-	-	-
12 Wt.% n-PrOH	-	-	-	-
13 Wt.% n-BuOH	-	-	-	-
14 Wt.% Other Ox.	-	-	-	-

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 130.

[a] $Co(acac)_3$ used.

Table 29. Experiments with Cobalt Catalysts (Cont'd)

SGHAM-V-#	16	20	22	25
1 mmol Co	5.0[a]	5.0[a]	3.4[a]	12.0
2 Solvent	H_3PO_4	1,3-Propanesultone	Sulfolane	NMP
3 mL	50	60	50	45
4 Promoter	-	-	Na_2HPO_4	DBTS[b]
5 mmol	-	-	4.3	32
6 Pressure, psi	6000	6000	6000	6000
7 H_2/CO	1.0	1.0	1.0	1.0
8 Temp.,°C	200	200	240	270
9 Time, hrs	4	4	2	3
10 Wt.% MeOH	-	-	-	-
11 Wt.% EtOH	-	-	-	-
12 Wt.% n-PrOH	-	-	-	-
13 Wt.% n-BuOH	-	-	-	-
14 Wt.% Other Ox.	-	-	-	-

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 130.

[a] $Co(acac)_3$ used.

[b] Dibenzothiophenesulfone.

[c] Dibenzothiophene.

Table 29. Experiments with Cobalt Catalysts (Cont'd)

SGHAM-V-#	29	32	36	40
1 mmol Co	4.8[a]	10.2	11.0	12.2
2 Solvent	Sulfolane	NMP	NMP	Tetramethylurea
3 mL	50	45	50	50
4 Promoter	NaCN	DBT[c]	DBT[c]	-
5 mmol	15	10	9.9	-
6 Pressure, psi	6000	6000	6000	6000
7 H_2/CO	1.0	1.0	1.0	1.0
8 Temp.,°C	270	280	210	240/260
9 Time, hrs	2	3	4	4
10 Wt.% MeOH	-	-	-	-
11 Wt.% EtOH	-	-	-	-
12 Wt.% n-PrOH	-	-	-	-
13 Wt.% n-BuOH	-	-	-	-
14 Wt.% Other Ox.	-	-	-	-

Experimental procedure: B(1); Analytical procedure: C(2); Key on page 130.

[a] $Co(acac)_3$ used.

[c] Dibenzothiophene.

Table 30. Experiments with Cobalt Catalysts

	SGHAM-V-#	45	50	56	61
1	mmol Co	8.5	32.6	35.6	38.5
2	Solvent	Toluene/NPC[a]	Toluene/NPC[a]	Toluene/3-T[b]	Toluene
3	mL	40/30	42/30	15/40	61
4	Promoter	-	-	-	-
5	mmol	-	-	-	-
6	Pressure, psi	6000	6000	6000	6000
7	H_2/CO	1.0	1.0	1.0	1.0
8	Temp.,°C	240/270	215	240	215
9	Time, hrs	3	2	6	6
10	Wt.% MeOH	trace	0.5	1.0	2.4
11	Wt.% EtOH	trace	1.5	4.5	1.0
12	Wt.% n-PrOH	-	0.5	1.2	-
13	Wt.% n-BuOH	-	-	trace	-
14	Wt.% Other Ox.	-	-	1.2	trace

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 130.

[a] N-Phenylcarbazole.

[b] 3,4,5-Trimethoxytoluene.

Table 30. Experiments with Cobalt Catalysts (Cont'd)

	SGHAM-V-#	66	70	74	78
1	mmol Co	18.3	18.1	19.0	17.8
2	Solvent	Toluene	Toluene	Toluene	Toluene
3	mL	60	60	60	60
4	Promoter	-	-	-	-
5	mmol	-	-	-	-
6	Pressure, psi	6000	6000	6000	6000
7	H_2/CO	1.0	1.0	1.0	1.0
8	Temp.,°C	215	240	240	215
9	Time, hrs	3	3	2	3
10	Wt.% MeOH	0.6	0.3	0.4	0.5
11	Wt.% EtOH	-	trace	-	-
12	Wt.% n-PrOH	-	-	-	-
13	Wt.% n-BuOH	-	-	-	-
14	Wt.% Other Ox.	-	-	-	-

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 130.

Table 30. Experiments with Cobalt Catalysts (Cont'd)

	SGHAM-V-#	80	84	87	91	96
1	mmol Co	36.8	18.8	37.2	17.8	17.7
2	Solvent	Tol[a]	Tol[a]/3-T[b]/2-T[c]	Tol[a]/2-T[c]	Tol[a]/3-T[b]	Tol[a]/3-T[b]
3	mL	60	20/20/20	20/40	20/40	20/40
4	Promoter	-	-	-	-	-
5	mmol	-	-	-	-	-
6	Press., psi	6000	6000	6000	6000	6000
7	H_2/CO	1.0	1.0	1.0	1.0	1.0
8	Temp.,°C	240	240	215	215	240
9	Time, hrs	6	2	6	4	4
10	Wt.% MeOH	2.0	1.0	3.0	1.3	1.0
11	Wt.% EtOH	0.6	0.2	3.0	6.0	3.2
12	Wt.% n-PrOH	-	-	0.3	1.4	0.8
13	Wt.% n-BuOH	-	-	trace	-	0.1
14	Wt.% Oth.Ox.	-	-	0.2	trace	0.3

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 130.

[a] Toluene.

[b] 3,4,5-Trimethoxytoluene.

[c] 2,4,6-Trimethoxytoluene.

Key to Table 31

SGHAM-V-#	
1 mmol Co	mmoles of cobalt used; added as $Co_2(CO)_8$.
2 Solvent	Solvent or solvents used.
3 mL	Volume of solvent used.
4 Cosolvent	Cosolvent employed.
5 mL/mmol	Amount of cosolvent in mL and mmoles.
6 Pressure, psi	Reaction pressure, psig.
7 H_2/CO	Syngas composition, molar (volume) ratio.
8 Temp.,°C	Reaction temperature.
9 Time, hrs	Reaction time in hours.
10 Wt.% MeOH	Percent by weight of individual products in final reaction solution.
11 Wt.% EtOH	
12 Wt.% n-PrOH	
13 Wt.% n-BuOH	
14 Wt.% Other Ox.	Percent by weight of other oxygenates observed.
15 Solids	Amount of solids observed in final solution.

Table 31. Experiments with Cobalt Catalysts

	SGHAM-V-#	1-101	1-106	1-111
1	mmol Co	35.7	35.7	17.5
2	Solvent	Toluene	Toluene	Toluene
3	mL	20.0	20.0	20.0
4	Cosolvent	3-T[a]	3-T[a]	2-T[b]
5	mL/mmol	40/260	40/260	40/260
6	Pressure, psi	6000	6000	6000
7	H_2/CO	1:1	1:1	1:1
8	Temp.,°C	215	190	215
9	Time, hrs	4	4	4
10	Wt.% MeOH	-	-	-
11	Wt.% EtOH	7.0	3.5	1.8
12	Wt.% n-PrOH	1.8	0.4	1.8
13	Wt.% n-BuOH	0.2	-	-
14	Wt.% Other Ox.	3.8	0.6	0.4
15	Solids	some	none	none

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 137.

[a] 3,4,5-Trimethoxytoluene.

[b] 2,4,6-Trimethoxytoluene.

Table 31. Experiments with Cobalt Catalysts (Cont'd)

	SGHAM-V-#	1-115	1-119	1-124
1	mmol Co	17.5	32.6	17.3
2	Solvent	Toluene	Toluene	Toluene
3	mL	40.0	40.0	1.0
4	Cosolvent	N-PC[a]	N-PC[a]	3-T[b]
5	mL/mmol	30/143	30/143	60/340
6	Pressure, psi	6000	6000	6000
7	H_2/CO	1:1	1:1	1:1
8	Temp.,°C	215	240	240
9	Time, hrs	3	3	3
10	Wt.% MeOH	1.2	1.1	0.6
11	Wt.% EtOH	0.6	1.1	4.7
12	Wt.% n-PrOH	-	0.3	0.8
13	Wt.% n-BuOH	-	-	-
14	Wt.% Other Ox.	-	-	-
15	Solids	trace	some	none

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 130.

[a] N-phenylcarbazole.

[b] 3,4,5-Trimethoxytoluene.

Key to Tables 32, 34, 42 and 58

SGHAM-V-#	
1 Catalyst	Complex added as catalyst precursor.
2 mmol	Amount of complex in mmoles.
3 Solvent	Solvent used for reaction.
4 mL	Volume of solvent.
5 Promoter	Promoter employed.
6 mmol	Amount of promoter in mmoles.
7 Pressure, psi	Reaction pressure, psi.
8 H_2/CO	Synthesis gas molar (volume) ratio.
9 Temp.,°C	Reaction temperature.
10 Time, hrs	Reaction time in hours.
11 Wt.% MeOH	Amount of methanol observed in final solution.
12 Wt.% EtOH	Amount of ethanol observed in final solution.
13 Solids	Solids observed in final solution.
14 Solv. Decomp.	Solvent decomposition, weight percent.

Table 32. Experiments with Cobalt Catalysts

	SGHAM-V-#	3-26	3-26R	3-67	3-82	3-93
1	Catalyst	$Co_2(CO)_8$	$Co_2(CO)_8$	$Co_2(CO)_8$	$Co_2(CO)_8$	$Co_2(CO)_8$
2	mmol	6.0	6.0	6.0	6.0	6.0
3	Solvent	DMT[a]	DMT[a]	DMT[a]	DMT[a]	DMT[a]
4	mL	75	75	75	75	75
5	Promoter	-	-	P3[b]	P3[b]	P4[d]
6	mmol	-	-	3.7	15.0	12
7	Pressure, psi	6000	6000	6000	6000	6000
8	H_2/CO	1:1	1:1	1:1	1:1	1:1
9	Temp.,°C	175	175	175	175	175
10	Time, hrs	3.0	3.0	2.0	2.0	2.0
11	Wt.% MeOH	19.0[c]	19.0[c]	16.0	3.8	12.0[c]
12	Wt.% EtOH	1.0	1.0	1.2	-	0.5
13	Solids	trace	trace	some	much	much
14	Solv. Decomp.	98.0	96.0	14.3	76	-

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

[a] 2,5-Dimethoxytetrahydrofuran.

[b] 1,1,1-Tris(diphenylphosphino)ethane.

[c] Formed mainly as a result of solvent decomposition.

[d] Tris(2-diphenylphosphinoethyl)phosphine.