

4.3.1.6 Further Studies of Catalyst Additives

Earlier work in this project had shown that additives C4 and A25 are critical components of the catalyst. In the absence of one or both, the homologation reaction was not observed. Previous work carried out with additives similar to A25 found only three additives, A37, A47 and A53, that resulted in catalysts generating ethanol with selectivities greater than 60%. These additives are structurally similar to A25, but in addition possess a common feature not found in the other A25-type additives that yielded poor homologation catalysts. Further work has been done on other A25-type additives that possess the same characteristics of A37, A47 and A53. The results are reported in Table 71. All of the runs reported in Table 71 were carried out at 975 psig with $H_2/CO = 2:1$.

Catalysts containing additives A82 to A86 result in ethanol selectivities of 54.2% to 68.4%. These selectivities approach those obtained with A25. Additives A82 to A86, A37, A47 and A53 fall in a general class of additives with similar structural and electronic properties. Additives A81 and A87 (Table 71, runs 21-48 and 21-76) fall outside the scope of this general class and result in poor homologation catalysts. Thus, it appears that the important factors leading to good A25-type additives have been identified.

It appeared important to synthesize more additives that fall within this class with the goal of optimizing the desirable structural and electronic properties. However, none of the additives which would be of interest in this regard have been reported in the literature. Thus, we have devised a short, general synthesis of this type of additive.

The first step in this synthesis has been reported in the literature. We have carried out this step and obtained a quantitative yield of a key intermediate; this is an improvement over the 50% yield reported in the literature. The second step of

the synthesis is unknown, but enough literature precedent exists to suggest that it should be successful. We have found this to be the case and have successfully applied it to the synthesis of two precursors of A25-type additives. The success of this step indicates that this synthesis will find broad applicability to the preparation of these additives. The third step in this synthesis is well known in the literature and we have been able to apply it to the synthesis of A25 and two new A25-type additives, A91 and A102. These additives are structurally quite similar but possess different electronic properties. Additive A25 has electronic properties which lie between these two extremes. These additives should give us information in future catalyst testing on the electronic effects governing this chemistry.

We have briefly investigated the use of lower catalyst and promoter concentrations than have normally been used. The goal here is to find a catalyst which will operate efficiently at much more dilute conditions. This would reduce catalyst cost and allow us to carry out more screening studies on new additives. Run 4-KGM-77 (Table 72) shows that a tenfold reduction in catalyst and promoter concentration results in a lower reaction rate, as expected (a standard run would show a gas uptake of ca. 3000 psi in the same time period). A total ethanol selectivity of 56% is observed, which is less than that typically obtained at higher catalyst/promoter concentrations (75-80%). Run 4-KGM-81 shows that increasing the Ru concentration results in a slower reaction rate but a higher total ethanol selectivity.

We have studied the effects of adding promoters of another type to the C4-Ru-A25-A28 catalysts. The results are given in Table 73. All the runs reported in Table 73 were carried out for 2.5 hours at 140°C and 975 psig. In a typical homologation experiment the activity of the C4-Ru-A25-A28 catalyst appears to diminish during the course of the reaction. It is thought that the loss in activity reflects dissociation of A25 from an C4-A25 complex that is formed under homologation reaction conditions. In runs carried out with A25:A24 = 1:0.5 to 1:1.5 (21-86, 89, 94) the

catalyst activity does not appear to diminish. The rate of gas consumption is constant throughout the reaction. (In a run with the C4-Ru-A25-A28 catalyst, carried out to the same methanol conversion, the rate of gas consumption eventually decreases.) NMR analysis indicates that A25 has remained bound to C4 through the entire reaction. Similar results have been found with catalysts containing A25:A88 and A25:A89. With A25:A88 = 1:1.5, the ethanol selectivity is increased by 5% to 80%, relative to the base case without A88 (run 21-82). No loss in activity was observed. Interestingly, decreasing A88 such that A25:A88 = 1:0.5 results in a very active catalyst (run 21-120). There is no indication of catalyst deactivation; the ethanol selectivity is however reduced by 10%.

Additives C4 and A25 were charged as the complex C13 along with RuCl₃, A28 and various amounts of A88. Run 21-125 does not contain A88. In this case the ethanol selectivity is 83%. Addition of A88 (runs 21-127 and 21-130) results in slight increases in the amount of gas consumed and the ethanol selectivity. The rate of gas uptake was relatively constant during the 2.5 hr reaction time.

Our previous studies found that at the end of a standard homologation reaction A25 is recovered as a mixture of A30 and A31. As A25 dissociates from the A25-C4 complex under reaction conditions, A25 reacts with A28 to form A30. As A30 is produced, the concentration of A25 must decrease. This means that the active catalyst concentration must fall, presumably leading to a decline in the rate of ethanol production. The significance of the results reported in Table 73 for the A25:A90 mixtures is that A25 is not converted to A30 under reaction conditions. NMR of the recovered catalyst components indicates that A25 is recovered only as an A25-C4 complex.

Additional experiments have been carried out with A88. The results are reported in Table 74. All the runs reported in Table 74 were carried out for 2.5 hrs at 140°C and 975 psig. In comparing runs 23-10, 21-120, and 23-12 with the standard run (21-82) it is

apparent that over a certain range A88 increases the ethanol rate and selectivity. This occurs only when a low level of A88 is utilized (23-10). In run 23-10 the activity of the catalyst did not appear to diminish over the course of the reaction. NMR analysis of the recovered catalyst components from 23-10 show that very little A30 is formed and that the major portion of A25 is recovered as as an A25-A9 complex.

Several experiments were carried out with a C13-Ru-A28 catalyst but with added A25. C13 is a metal catalyst that contains A25. We were interested in determining if A25 would increase catalyst performance in the same way previously observed with A88 (compare 21-125 and 21-130). As indicated by run 21-134, A25 has little effect on catalyst activity until a high level is added (run 23-8) and the activity diminishes. NMR of the recovered catalyst components showed only A30, there was no indication of C13. These results indicate that A88 is unique in promoting the homologation reaction with the C13 based catalyst.

Several new catalyst components were evaluated. The results are reported in Table 75. All the runs reported in Table 75 were carried out for 2.5 hrs at 140°C and 975 psig. C19, C20, and C21 are metal additives that contain A24. In all cases the activity is very low and little ethanol is generated.

A complete record of the experiments carried out in this part of the project is given in Table 76.

Table 71. Effects of Catalyst Composition Changes

SGHAM-W-#	Catalysts, molar ratio	EtOH sel.%
21-48	C4:Ru:A81:A28 = 1:2:2:20	19.3
21-54	C4:Ru:A82:A28 = 1:2:2:20	54.2
21-56	C4:Ru:A83:A28 = 1:2:2:20	58.2
21-68	C4:Ru:A84:A28 = 1:2:2:20	68.4
21-71	C4:Ru:A85:A28 = 1:2:2:20	59.0
21-73	C4:Ru:A86:A28 = 1:2:2:20	60.1
21-76	C4:Ru:A87:A28 = 1:2:2:20	12.6

See Table 76 for experimental details.

Table 72. Methanol Homologation Experiments

SGHAM-KGM-#	4-81	4-77
1 Catalyst	C22	C22
2 mmol	1.0	0.4
3 Cocatalyst	C13	C13
4 mmol	0.2	0.2
5 Additive	-	-
6 mmol	-	-
7 Promoter	A28	A28
8 mmol	4	4
9 MeOH (mL)	40.0	40.0
10 Pressure, psi	1000	975
11 H ₂ /CO	2:1	2:1
12 Temp., °C	139	139
13 Time, hr	2.5	2.5
14 Uptake, psi	361	575
15 Product Sel. %		
16 EtOH	58	31
17 EtOH eq.	13	25
18 Total EtOH	71	56
19 Other Oxy.	29	44

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.
 Experiments done in final quarter of contract.

Table 73. Effects of Additional Promoters on the Standard Catalyst

SGHAM-W-#	Catalysts, molar ratio	Gas uptake	EtOH sel. %
21-82 (std.)	C4:Ru:A25:A28 = 1:2:1:20	3000	75.7
21-86	C4:Ru:A25:A24:A28 = 1:2:1:0.5:20	2886	75.7
21-89	C4:Ru:A25:A24:A28 = 1:2:1:1:20	2770	75.0
21-94	C4:Ru:A25:A24:A28 = 1:2:1.5:1:20	2298	72.3
21-96	C4:Ru:A25:A88:A28 = 1:2:1.5:1:20	2945	80.3
21-120	C4:Ru:A25:A88:A28 = 1:2:0.5:1:20	4150	71.0
21-99	C4:Ru:A25:A89:A28 = 1:2:1.5:1:20	1550	71.4
21-125	C13:Ru:A28 = 1:2:20	2400	83.1
21-127	C13:Ru:A88:A28 = 1:2:0.5:20	2500	85.8
21-130	C13:Ru:A88:A28 = 1:2:1.5:20	2782	84.6

See Table 76 for experimental details.

Table 74. Effects of Additional Promoters on the Standard Catalyst^a

SGHAM-W-#	Catalysts, molar ratio	gas uptake	EtOH sel. %
21-82 (Std.)	C4:Ru:A25:A28 = 1:2:1:20	3000	75.7
23-10	C4:Ru:A25:A88:A28 = 1:2:1:0.25:20	3581	85.1
21-120	C4:Ru:A25:A88:A28 = 1:2:1:0.5:20	4150	71.0
23-12	C4:Ru:A25:A88:A28 = 1:2:1:1:20	1550	67.3
21-125 (Std.)	C13:Ru:A28 = 1:2:20	2400	83.1
21-130a	C13:Ru:A88:A28 = 1:2:1:20	2782	84.6
21-134	C13:Ru:A25:A28 = 1:2:1:20	2350	82.3
23-8	C13:Ru:A25:A28 = 1:2:2:20	1600	77.9

See Table 76 for experimental details.

^a Experiments done in final quarter of contract.

Table 75. Effect of Catalyst Composition Changes^a

SGHAM-W-#	Catalysts, molar ratio	gas uptake	EtOH sel. %
21-133	C19:Ru:A25:A28 = 1:2:1:20	412	13.6
23-1	C13:C20:A28 = 1:2:20	200	48.0
23-7	C13:C21:A28 = 1:2:20	100	9.3

See Table 76 for experimental details.

^a Experiments done in final quarter of contract.

Table 76. Methanol Homologation Experiments

SGHAM-W-#	21-48	21-54	21-56
1 Catalyst	RuCl ₃	RuCl ₃	RuCl ₃
2 mmol	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4
4 mmol	2.00	2.00	2.00
5 Additive	A81	A82	A83
6 mmol	4.00	4.00	4.00
7 Promoter	A28	A28	A28
8 mmol	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00
10 Pressure, psi	975	975	975
11 H ₂ /CO	2:1	2:1	2:1
12 Temp., °C	140	140	140
13 Time, hr	1.00	3.70	2.00
14 Uptake, psi	462	1338	1489
15 Product Sel. %			
16 EtOH	8.59	33.78	33.25
17 EtOH eq.	10.68	20.48	24.96
18 Total EtOH	19.28	54.26	58.21
19 Other Oxy.	80.72	45.74	41.79

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

Table 76. Methanol Homologation Experiments (Cont.'d)

SGHAM-W-#	21-68	21-71	21-73
1 Catalyst	RuCl ₃	RuCl ₃	RuCl ₃
2 mmol	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4
4 mmol	2.00	2.00	2.00
5 Additive	A84	A85	A86
6 mmol	4.00	4.00	4.00
7 Promoter	A28	A28	A28
8 mmol	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00
10 Pressure, psi	975	975	975
11 H ₂ /CO	2:1	2:1	2:1
12 Temp., °C	140	140	140
13 Time, hr	2.00	2.20	2.00
14 Uptake, psi	2300	1543	1540
15 Product Sel. %			
16 EtOH	36.44	37.66	38.27
17 EtOH eq.	31.91	21.37	21.85
18 Total EtOH	68.36	59.03	60.12
19 Other Oxy.	31.64	40.97	39.88

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

Table 76. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	21-76	21-82
1 Catalyst	RuCl ₃	RuCl ₃
2 mmol	4.00	4.00
3 Cocatalyst	C4	C4
4 mmol	2.00	2.00
5 Additive	A87	A25
6 mmol	4.00	2.00
7 Promoter	A28	A28
8 mmol	20.00	20.00
9 MeOH (mL)	40.00	40.00
10 Pressure, psi	975	975
11 H ₂ /CO	2:1	2:1
12 Temp., °C	140	140
13 Time, hr	1.00	2.50
14 Uptake, psi	250	3000
15 Product Sel. %		
16 EtOH	5.63	47.11
17 EtOH eq.	6.94	28.64
18 Total EtOH	12.57	75.75
19 Other Oxy.	87.43	24.25

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

Table 76. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	21-86	21-89	21-94
1 Catalyst	RuCl ₃	RuCl ₃	RuCl ₃
2 mmol	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4
4 mmol	2.00	2.00	2.00
5 Additive	A25:A24	A25:A24	A25:A24
6 mmol	1:2	2:2	3:2
7 Promoter	A28	A28	A28
8 mmol	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00
10 Pressure, psi	975	975	975
11 H ₂ /CO	2:1	2:1	2:1
12 Temp., °C	140	140	140
13 Time, hr	2.50	2.50	2.50
14 Uptake, psi	2886	2770	2298
15 Product Sel. %			
16 EtOH	49.91	48.85	45.45
17 EtOH eq.	25.80	26.14	26.88
18 Total EtOH	75.71	74.99	72.33
19 Other Oxy.	24.29	25.01	27.67

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

Table 76. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	21-96	21-99	21-120
1 Catalyst	RuCl ₃	RuCl ₃	RuCl ₃
2 mmol	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4
4 mmol	2.00	2.00	2.00
5 Additive	A25:A88	A25:A89	A25:A88
6 mmol	3:1	3:1	1:2
7 Promoter	A28	A28	A28
8 mmol	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00
10 Pressure, psi	975	975	975
11 H ₂ /CO	2:1	2:1	2:1
12 Temp., °C	140	140	140
13 Time, hr	2.50	2.50	2.50
14 Uptake, psi	2945	1550	4150
15 Product Sel. %			
16 EtOH	53.98	42.66	44.83
17 EtOH eq.	26.34	28.78	26.02
18 Total EtOH	80.32	71.43	70.85
19 Other Oxy.	19.68	28.57	29.15

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

Table 76. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	21-125	21-127	21-130
1 Catalyst	RuCl ₃	RuCl ₃	RuCl ₃
2 mmol	4.00	4.00	4.00
3 Cocatalyst	C13	C13	C13
4 mmol	2.00	2.00	2.00
5 Additive	none	A88	A88
6 mmol	4.00	1.00	3.00
7 Promoter	A28	A28	A28
8 mmol	20.00	20.00	20.00
9 MeOH(mL)	40.00	40.00	40.00
10 Pressure,psi	975	975	975
11 H ₂ /CO	2:1	2:1	2:1
12 Temp., °C	140	140	140
13 Time,hr	2.50	2.50	2.50
14 Uptake,psi	2400	2500	2782
15 Product Sel. %			
16 EtOH	55.09	57.19	55.77
17 EtOH eq.	28.09	28.66	28.84
18 Total EtOH	83.18	85.84	84.61
19 Other Oxy.	16.82	14.16	15.39

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

Table 76. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	21-133	21-134	23-1	23-7	23-8
1 Catalyst	RuCl ₃	RuCl ₃	C20	C21	C13
2 mmole	4.0	4.0	4.0	4.0	4.0
3 Cocatalyst	C19	C13	C13	C13	C13
4 mmol	2.0	2.0	2.0	2.0	2.0
5 Additive	A25	A25	none	none	A25
6 mmol	2.0	1.0	0	0	2.0
7 Promoter	A28	A28	A28	A28	A28
8 mmol	20.0	20.0	20.0	20.0	20.0
9 MeOH (mL)	40.0	40.0	40.0	40.0	40.0
10 Pressure, psi	975	975	975	975	975
11 H ₂ /CO	2:1	2:1	2:1	2:1	2:1
12 Temp., °C	140	140	140	140	140
13 Time, hr	2.5	2.5	2.5	2.5	2.5
14 Uptake, psi	412	2350	200	100	1600
15 Product Sel. %					
16 EtOH	0.0	56.6	26.0	0.0	50.7
17 EtOH eq.	13.6	25.7	22.0	9.3	27.2
18 Total EtOH	13.6	82.3	48.0	9.3	77.9
19 Other Oxy.	86.3	17.6	52.0	90.6	22.0

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

Table 76. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	23-10	23-13
1 Catalyst	RuCl ₃	RuCl ₃
2 mmol	4.0	4.0
3 Cocatalyst	C4	C4
4 mmol	2.0	2.0
5 Additive	A25:A88	A25:A88
6 mmol	2.0:0.5	2.0:2.0
7 Promoter	A28	A28
8 mmol	20.0	20.0
9 MeOH (mL)	40.0	40.0
10 Pressure, psi	975	975
11 H ₂ /CO	2:1	2:1
12 Temp., °C	140	140
13 Time, hr	2.5	2.5
14 Uptake, psi	3581	1550
15 Product Sel. %		
16 EtOH	58.9	44.7
17 EtOH eq.	26.1	22.6
18 Total EtOH	85.1	67.3
19 Other Oxy.	14.9	32.6

Experimental procedure: B(2); Analytical procedure: C(9); Key on page 115.

4.3.2 Task 3 Summary

Research in Task 3 has been conducted on the novel methanol homologation system which produces ethanol and other products under relatively low pressures. Studies of the catalyst chemistry have been carried out, with an emphasis on the involvement of catalyst additives and precursors in the catalytic chemistry. Studies have also been done to explore the effects of a number of reaction variables on this catalyst system.

Because of the many variables involved in the methanol homologation system, it was felt that the best approach to gaining an understanding of how each affects the behavior of the system was through statistically designed experiments. These experiments would allow the determination of which variables were most important for obtaining high conversion rates of methanol to ethanol with high selectivity, and at what levels optimum results could be obtained.

In preparation for statistically designed sets of experiments, the reaction was scaled up from 40 to 150 mL of methanol in a larger autoclave. No problems were encountered, and results analogous to those obtained at the smaller scale were observed.

A first designed set of experiments explored the effects of six variables: temperature, pressure, ruthenium, and the amounts of three additives. The experiments did not generate data of sufficient quality for quantitative correlations to be made, but did suggest conditions under which a second designed set might be more successful. The second designed set varied only temperature, ruthenium, and two additives, over somewhat narrower ranges. This designed set provided excellent quantitative correlations between the variables studied and the rate and selectivity of ethanol production. The results showed that conditions for highest rate and highest selectivity are mutually exclusive within the range of variables investigated. The highest rate to ethanol is achieved at high temperature, high ruthenium, and low levels of A25 catalyst

additive. The highest selectivity requires low temperature and high A25.

Several experiments were carried out with added solvents (in addition to the methanol normally used). Although earlier work with cobalt-based homologation systems showed increased selectivity with added solvents, these experiments did not result in increased selectivity. However, from a practical standpoint the reactant methanol may be an advantageous solvent for this reaction.

Earlier work in this project demonstrated the importance of two specific catalyst additives in the new homologation system. Work has been done to attempt to use additives similar to one of these, both to learn about the essential characteristics of the additive and to try to further enhance the rate and selectivity. Further work identified several more additives of this type which effectively promote the methanol homologation reaction. It appears that we have identified the important factors defining good catalyst additives for this system. To synthesize more additives that fall within this class, with the goal of optimizing the desirable structural and electronic properties, we have developed a general synthetic route to such compounds.

The rate of reaction with the homologation system has frequently been observed to decrease with time. Various factors could be responsible for this observation, including the possibility of product inhibition at high methanol conversions. It has now been found, however, that the use of additional additives of a certain type give a constant rate of gas consumption throughout the reaction. No loss in activity is observed, and in some cases the ethanol selectivity actually increases.

5.0 CONCLUSIONS AND OPPORTUNITIES FOR FUTURE RESEARCH

This research project was directed toward the discovery, identification, and investigation of homogeneous catalytic systems which could convert syngas to alcohols useful as fuels or fuel additives. As general guidelines, we hoped to find catalytic systems which could produce mixtures of methanol containing at least 30% higher alcohols, with a 90% selectivity to alcohols among the liquid products. These systems should be stable and should operate at pressures below 6000 psi, with lower pressures being most preferable. Rates to alcohol products of 2.0 moles/liter of solution/hr or greater would indicate that the systems might have practical potential.

Potential homogeneous catalytic systems were broadly studied with these goals in mind. Many novel approaches and ideas were conceived and evaluated experimentally. Some approaches were found to have little potential at their present stage of development or knowledge. Significant progress has been made on two approaches to the production of ethanol and higher alcohols; direct conversion of syngas to alcohols with ruthenium catalysts, and the homologation of methanol to ethanol.

Halide-promoted ruthenium catalytic systems were shown to be capable of selectively producing alcohols directly from syngas. In some modifications studied, the fraction of ethanol and higher alcohols in the product was 80% and higher, although the total rates in these cases, being less than 2 mol/l/hr, would require improvement. Some modifications were studied which gave good rates of syngas conversion, but a substantial amount of the product was oxygenates other than alcohols, such as acetate esters. Other modifications have recently been found which can produce an alcohol mixture containing 30% of the C₂+ alcohols, and do so at good rates -- 3 mol/l/hr at pressures of 5000 psi. These systems contain novel catalyst additives or promoters which impart enhanced activity to the catalyst, at the same time maintaining good

selectivity to alcohols. An additional benefit of these additives appears to be their ability to give the catalyst good activity in simple, inexpensive solvents such as alcohols. Use of alcohols as solvents could also have the effect of increasing the yield of C₂+ alcohols if desired, since recycle of methanol or ethanol to the system leads to their conversion to higher alcohols. The catalytic systems which accomplish these conversions appear to have good potential for further improvements; enhanced rates at lower reaction pressures would be the most significant change. The concept of using the alcohols themselves as solvents and recycling the lower alcohols to the system to enhance the higher alcohol yield also deserves further study.

Ethanol is a useful liquid fuel or fuel additive. Previous attempts in the literature to produce ethanol from syngas have often taken the approach of first converting the syngas to methanol, followed by a methanol homologation step. Although methanol production is a demonstrated process, known methanol homologation catalysts were not active or selective enough to make this route feasible. Some of our research was conducted on methanol homologation, since this process is likely to be involved in direct syngas conversion catalysts which produce ethanol and higher alcohols. In these studies, a novel methanol homologation catalyst was discovered which operates with good rates and selectivities at much lower pressures than previously possible — typical reaction pressures are below 1000 psi. Because this represented a significant advance over previous technology, research was continued on this novel system. This work has led to further improvements; rates to ethanol and products easily converted to ethanol of greater than 2 mol/l/hr with selectivities of around 80% are typically observed. Recent results indicate that a class of promoters has several beneficial effects on the catalyst behavior in this system, including improved stability of the catalyst. The process by which this and other catalyst additives present in this system operate is not well understood. Further work is necessary to more fully explore the effects of these

additives, and to better define the potential of this novel catalytic system.

The concept of using homogeneous catalysts to produce fuel alcohol mixtures from synthesis gas has been demonstrated in this project. Advances have been made on the direct conversion of syngas to alcohols with ruthenium catalysts and on the homologation of methanol to ethanol with the novel catalyst system. Each of these areas appears to have potential for future development, and important chemical and process questions remain to be explored in more detail. Research on these two approaches to ethanol and higher alcohols will be continued under a new contract, No. DE-AC22-86PC90013. In addition to the continued chemical investigations, work under this contract will address the economics of processes based on these approaches.

6.0 APPENDIXES

6.1 APPENDIX A. USE OF CODE SYSTEM

A code system has been used in this report and throughout the contract period to identify proprietary data or information which may be the subject of future patents. The code system consists of three classifications, each member of which is assigned a number.

Category A encompasses additives, such as ligands, metal complexes, or salts, which apparently function as catalyst promoters.

Category C consists of catalysts or cocatalysts.

Category S includes solvents for catalytic reactions.

Use of the code system has been approved by the Chief Office of Patent Counsel, U.S. Department of Energy, 9800 South Cass Avenue, Argonne, Illinois 60439.

6.2 APPENDIX B. PROCEDURES FOR CATALYST TESTING

Procedure B(1)

A 150cc 316 stainless steel magnedrive autoclave was used for catalyst testing. The cleaned autoclave was purged with nitrogen, charged with the reactants (solids, then liquids), sealed and pressurized to 300 psi CO. This pressure was held for several minutes to ensure that there were no leaks. The reactor was heated to the specified temperature and then pressurized with the desired gas to 250 psi above the specified operating pressure. The pressure was maintained within ± 250 psi of the operating pressure by repressurizing as necessary. After completion of the run, the reactor was rapidly cooled to 25°C and a gas sample was taken. It was then slowly vented and the product solution was collected and analyzed. The reactor was washed with several solvents under superambient temperature and pressure, then disassembled and washed manually.

Procedure B(2)

A 100 cc Hastelloy magnedrive autoclave was used for catalyst testing. The cleaned autoclave was purged with nitrogen, charged with the reactants, sealed and pressured to 400 psig with synthesis gas of the desired composition. The reactor was maintained at 400 psig for 10 minutes to check for leaks. The reactor was then heated to the desired temperature and pressured with synthesis gas to 25 psi above the specified pressure. The pressure was maintained within ± 25 psi of the operating pressure by repressurizing as necessary. After the experiment was completed, the reactor was cooled to 20°C. The gas was vented and the liquid products were collected in a chilled bottle fitted with a septum. The reactor was washed with various solvents until the rinses appeared clean. The reactor was periodically disassembled and cleaned, as required.

Procedure B(3)

A 150 mL 316 stainless steel magnedrive autoclave was used for catalyst testing. The cleaned autoclave was purged with nitrogen, charged with the reactants (via syringe or from a nitrogen-blanketed Schlenk tube), sealed and pressurized to 1000 psi with 1:1 H₂/CO. This pressure was held for several minutes to ensure that there were no leaks. The pressure was increased to 3500-4000 psi and the reactor was heated to the specified temperature. The pressure was then brought to the required value. The pressure was maintained within \pm 500 psi of the specified operating pressure by repressurizing as necessary. After completion of the run, the reactor was rapidly cooled to below 20°C, and a gas sample was taken in some instances. The reactor was slowly vented, and the product solution was collected and analyzed. The reactor was washed with several solvents under superambient temperature and pressure, then disassembled and washed manually.

Procedure B(4)

Into a specially designed glass liner, the catalyst and additive(s) were charged along with 15.0 g of P(n-Bu)₄Br (or other specified solvent). The glass liner was then placed into a 150 mL rocker bomb autoclave. The system was pressurized with nitrogen to 80 psig and vented, a total of three times. The system was then pressurized with syngas to 200 psig, vented, pressurized to 1000 psig syngas and tested for possible leaks. Then it was heated to 230°C and pressurized to 5000 psig (or other specified pressure) for a desired period (usually 3.0 hr) with adjustment of pressure back to the specified level as uptake of gas occurred. After the desired time of reaction, the system was cooled to room temperature, vented and purged with nitrogen. The glass liner was taken out and the content analyzed by GC methods.

Procedure B(5)

In experiments where a liquid organic solvent was used, the catalyst and additives were charged into a 150 mL Hastelloy C magnedrive autoclave along with the solvent under argon. The reactor was sealed, pressurized with 80 psi of nitrogen, and vented. It was then pressurized to 300 psi with syngas and again vented. This purging was then repeated once more before the system was pressurized to 1000 psi of syngas. At this point, the system was tested for possible leaks. It was then heated to the desired temperature. After the desired temperature was reached, the system was pressurized to the desired level with syngas. The temperature and pressure were then kept constant for the desired reaction period. Afterwards, the reactor was rapidly cooled to room temperature by a cool water jacket.

Procedure B(6)

High pressure runs were conducted in a 300 mL Hastelloy C magnedrive autoclave. The catalyst and solvent were charged to the reactor, the reactor head was secured, and the system was flushed with nitrogen. Premixed 1:1 H₂/CO (or other gases as required) was charged to the reactor to a pressure of 300 psi, and heating and stirring were commenced. When the desired temperature was reached, more gas was added to bring the pressure up to 100 psi over the nominal operating pressure. The reaction was allowed to proceed until the reactor pressure dropped to 100 psi under the nominal operating pressure, then 200 psi gas was introduced. Pressure was maintained in this manner, at \pm 100 psi of the specified reaction pressure over the entire reaction time. The reactor was then cooled to 20°C, a sample was taken from the gas phase of the reactor, and the liquid phase was dumped into a crown-capped bottle.

Procedure B(7)

Stoichiometric reactions of the Everitt's salt system with CO were performed in the following manner. A solution containing 5 mM sodium amminepentacyanoferrate(II), 20 mM methanol and 0.1 M KCl was prepared and the pH adjusted to 3.5 with 1 M HCl. The solution was purged with CO at one atmosphere for 30 minutes. The pH was then readjusted to 3.5. An approximately 90 cm² platinum mesh cylinder was coated with 3×10^{-7} mol/cm² Prussian Blue by potentiostatting it at +0.5 V vs. Ag/AgCl in a solution containing 10 mM ferric chloride and 10 mM potassium ferricyanide and passing 2.6 coulomb of charge. The Prussian Blue coating was then reduced to Everitt's salt at 0 V in nitrogen-purged 0.1 M KCl solution. The catalyst solution and approximately 0.1 g n-propanol internal standard were loaded into a short column with a medium frit at the bottom through which CO was introduced. The solution was purged with CO, then the Everitt's salt coated electrode was quickly transferred to the catalyst solution. After the Everitt's salt coated electrode was loaded into the column, a sample of the solution was taken, the CO turned off and the cell stoppered. After approximately 7.5 hours of reaction a sample of the solution was removed and its methanol content compared with that of the initial sample by gas chromatography. For these experiments, only the ratio of the response of the methanol to the n-propanol internal standard was measured to determine if there had been any increase in methanol concentration.

Procedure B(8)

Electrocatalytic experiments with diaquobis(oxalato)chromate were performed as follows. A solution containing 20 mM methanol and either 0.1 M KCl or pH 3.5 phthalate buffer was prepared and the exact concentration of methanol determined by GC analysis. A known weight of this solution, about 60 g, was mixed with enough

potassium diaquobis(oxalato)chromate(III) to give a 5 mM solution. The pH of the solution with KCl was about 3 so no adjustment was necessary. The solution was loaded into a cell composed of an inner compartment of 3.0 cm diameter with a medium frit at the bottom, contained within a 400 mL beaker. An approximately 90 cm² platinum mesh cylinder was coated with 3×10^{-7} mol/cm² Prussian Blue by potentiostatting it at +0.5 V vs Ag/AgCl in a solution containing 10 mM ferric chloride and 10 mM potassium ferricyanide and passing 2.6 coulomb of charge. The Prussian Blue coated electrode was placed in the center compartment and a platinum counter electrode and the Ag/AgCl reference electrode were placed in the outer compartment. The inner compartment was sealed with a rubber stopper through which passed a copper wire for electrical connection to the electrode, a pipet for the CO purge and a gas outlet which was connected to a cold trap at -78°C for collecting any methanol washed out by the CO purge. The solution was purged with CO for 15 minutes and then a potential of -0.9 V was applied to the electrode to reduce the Prussian Blue to Everitt's salt. The reaction was run for three hours with continuous CO purge and with a constant potential of -0.9 V applied. After the reaction the solution from the inner compartment was collected, along with rinses from the inner compartment and the cold trap. This solution was weighed, and then acetonitrile internal standard was weighed in. The final methanol content was determined by GC analysis and compared with the known amount of methanol added.

Procedure B(9)

Electrocatalytic experiments with amminepentacyanoferrate were performed as follows. A solution was prepared containing approximately 20 mM methanol, 5 mM sodium amminepentacyanoferrate(II) and 0.1 g n-propanol internal standard in either 0.1 M KCl or pH 3.5 phthalate buffer. The solution was purged with CO for 30 minutes. The pH of the unbuffered solution was adjusted both before and after the CO purge. The reactions were performed

in an H-cell in which the compartments were separated by a medium frit and the working compartment was equipped with a three-way stopcock for maintaining an inert atmosphere or a purge of gas. The working electrode was either a 2.6 cm² platinum wire or an 8 cm² platinum foil. The working electrodes were coated with 3 x 10⁻⁷ mol/cm² Prussian Blue by potentiostatting them at +0.5 V vs Ag/AgCl in a solution containing 10 mM ferric chloride and 10 mM potassium ferricyanide and passing 0.075 or 0.23 coulomb of charge. The counterelectrode was either the platinum foil or a stainless steel spatula. With the wire electrode, the reference electrode was located in the working compartment, but with the platinum foil as working electrode the reference electrode had to be located in the counter compartment. Before the reactions the cell was loaded with 0.1 M KCl and the Prussian Blue coated electrode was reduced at 0 V to Everitt's salt. Then, under nitrogen purge, the KCl solution was removed from both compartments and replaced with the catalyst solution. The working compartment contained about 10 mL of solution. Not all of the catalyst solution was used, and the remaining portion was retained for comparison with the product solution by GC analysis. After loading the catalyst solution into the cell, it was purged with CO and then the electrode potential was set at either 0 or -0.4 V. During the reaction the CO purge was either continued at a much reduced rate, or the CO was passed over the surface of the solution to exclude oxygen.

Procedure B(10)

High pressure runs were conducted in a 300 mL Hastelloy C magedrive autoclave. Solutions were prepared containing 20 mM methanol, 10 mM catalyst and n-propanol internal standard in either 0.1 M KCl or pH 3.5 phthalate buffer. The solutions were purged with CO for 30 minutes before being charged to the reactor. The unbuffered solutions were adjusted to pH 3.5 both before and after the CO purge. An 8 cm² platinum foil was coated with 3 x 10⁻⁷ mol/cm² Prussian Blue by potentiostatting it at +0.5 V vs Ag/AgCl

in a solution containing 10 mM ferric chloride and 10 mM potassium ferricyanide and passing 0.23 coulomb of charge. The Prussian Blue coated platinum foil was mounted via a platinum wire looped through a hole in the baffle of the autoclave. The reactor was purged with nitrogen, the electrode and catalyst solution were charged to the reactor, the reactor head was secured and the system was flushed with nitrogen. Approximately 180 mL of solution was charged into the autoclave while 20 mL was retained for comparison by GC analysis with the product solution. Premixed 1:1 H₂/CO was charged into the reactor to a pressure of 1000 psi, and heating and stirring were commenced. When the desired temperature was reached, more gas was added to bring the pressure up to about 100 psi over the nominal operating pressure. Had any gas been consumed, the pressure would have been maintained within ± 100 psi of the specified reaction pressure. At the conclusion of the reaction the reactor was cooled to 20°C and the solution dumped into a crown-capped pressure bottle.

Procedure B(11)

A 100 mL stainless steel magnedrive minireactor was used for catalyst testing. Catalyst solutions (35 mL) which contained the metal salt and ligand were prepared under nitrogen and charged to the minireactor. After purging the reactor with syngas, the reactor was pressurized to 100 psig and sodium borohydride solution (2 mL) was injected by pressure-lock syringe. The syngas pressure was increased to 600 psi and the reactor was heated to 100°C. Upon reaching this temperature, the pressure was increased to 950 psig. The reactor was monitored for gas uptake for several hours. The minireactor was allowed to cool to ambient temperature and the pressure was vented down to 200 psig. The contents were discharged, weighed, and analyzed by gas chromatography.

Procedure B(12)

Catalyst testing was performed in either a 300 mL or a 150 mL Hastelloy C magnedrive autoclave. The cleaned autoclave was purged with nitrogen, charged with the reactants, sealed and pressured to 1000 psi with synthesis gas of the desired composition. This pressure was held for 15 minutes to ensure that there were no leaks. The pressure was then increased to the desired operating pressure and the temperature raised to 110°C. The pressure was maintained to within ± 200 psi by repressurizing as necessary. After completion of the run the reactor was cooled to below 20°C and a gas sample was taken in some instances. The reactor was slowly vented and the product solution was collected and analyzed. The reactor was washed with several solvents, then disassembled and washed manually.

Procedure B(13)

Experiments at one atmosphere were performed as follows. The reactants and solvent were charged to a 250 mL three neck flask equipped with a thermometer, a gas inlet extending below the surface of the liquid and a gas outlet tube. The solution was stirred magnetically. To collect the volatile products the gas outlet was connected to a trap placed in a dry ice/isopropanol bath at -78°C. The gas outlet was passed through a flow meter to monitor the flow rate, which was approximately 450 mL/min. The system was purged with 1:1 H₂/CO for several minutes and then heated to 100°C. At the conclusion of the reaction the flow of gas was stopped and the material was collected either for analysis or for further use. When the products were to be used for further experiments, the flask was transferred to a nitrogen atmosphere glove box where the solid and liquid phases were separated by filtration. The solids were then washed twice each with diethyl carbitol and diethyl ether and were briefly dried under nitrogen.

Procedure B(14)

Catalyst testing was performed in a 150 mL Hastelloy C magnedrive autoclave. The cleaned autoclave was purged with nitrogen, charged with the reactants, sealed and pressured to 1000 psi with synthesis gas of the desired composition. This pressure was held for 15 minutes to ensure that there were no leaks. The pressure was then increased to the desired operating pressure and the temperature raised to 110°C. The pressure was maintained to within 200 psi by repressurizing as necessary. After completion of the run the reactor was cooled to below 20°C and a gas sample was taken in some instances. The reactor was slowly vented and the product solution was collected and analyzed. The reactor was washed with several solvents, then disassembled and washed manually.

Procedure B(15)

Catalyst testing was performed in a 300 mL Hastelloy C magnedrive autoclave. The cleaned autoclave was purged with nitrogen, charged with reactants, liquids first, then solids, sealed and pressured to 600 psi with synthesis gas of the desired composition. This pressure was held for 15 minutes to ensure that there were no leaks. The temperature and pressure were then raised to the desired operating levels. The pressure was maintained to within 200 psi by repressurizing as necessary. After completion of the run the reactor was cooled to below 20°C and a gas sample was taken in some instances. The reactor was slowly vented and the product collected in a crown-capped bottle precooled to 0°C. The reactor was washed with several solvents, then disassembled and washed manually.

Procedure B(16)

The catalyst and additives were charged into a 150 mL or a 300 mL magnedrive Hastelloy autoclave along with the solvent under nitrogen. The reactor was sealed, pressurized with 80 psi of nitrogen, and vented. The system was then pressurized to 300 psi with syngas and again vented. This purging with syngas was repeated once more before pressurizing to 1000 psi with syngas. The system was tested for possible leaks. It was then heated to the desired temperature. After this temperature was reached, the system was pressurized to the desired pressure. The temperature and pressure were kept constant for the reported reaction period. Afterwards, the reactor was rapidly cooled to room temperature by a cool water jacket.

6.3 APPENDIX C. PROCEDURES FOR PRODUCT ANALYSIS

Procedure C(1)

Analysis of gaseous products was done isothermally using a Carle Analytical Gas Chromatograph, Series S. Liquid products were analyzed using a Hewlett-Packard 5840 Gas Chromatograph equipped with a 30 m DB 1701 F.S.O.T. capillary column and a Hewlett-Packard 5880 Gas Chromatograph equipped with a 6 ft × 1/4 in Tenax 60/100m column.

Procedure C(2)

Analysis of gaseous products was done isothermally using a Carle Analytical Gas Chromatograph, Series S. Liquid products were analyzed using a Varian gas chromatograph equipped with a 30 m DB 1701 F.S.O.T. capillary column.

Procedure C(3)

Analyses of gaseous products were done isothermally using a Carle Analytical Gas Chromatograph, Series S. Liquid products were analyzed using a Hewlett-Packard 5880A Gas Chromatograph equipped with a 6 ft × 1/8 in Tenax 60/100m column attached to a thermal conductivity detector and with a 50 m Igepal Co990 glass capillary column attached to a flame ionization detector.

Procedure C(4)

Liquid organic product analyses were performed on a Hewlett-Packard model 5840 gas chromatograph equipped with flame ionization detector and a 30m × 0.32mm Durabond 1701 capillary column, with an initial temperature of 40°C and a final temperature of 280°C.

Procedure C(5)

Analysis of gaseous products was done isothermally using a Carle Analytical Gas Chromatograph, Series S. Liquid product analyses were performed on a Varian 3700 capillary gas chromatograph using either a Durabond 1701 30m × .32mm capillary column, or a DB-1 30m × .32mm capillary column. The internal standard method using methyl propionate as internal standard was used to quantify the products.

Procedure C(6)

Liquid product analyses were performed on a Hewlett-Packard HP5890A gas chromatograph using a DB 1701 30m × 0.32mm capillary column attached to a flame ionization detector. Products were quantified using acetonitrile or n-propanol as internal standards.

Procedure C(7)

Liquid product analyses were performed on a Hewlett-Packard HP5890A gas chromatograph using a DB 1701 30m × 0.32mm capillary column attached to a flame ionization detector. Products were quantified using cyclohexane as an internal standard.

Procedure C(8)

Liquid product analyses were performed on a Varian 3700 capillary gas chromatograph equipped with a Durabond 1701 30m × 0.32mm capillary column.

Procedure C(9)

Liquid product analyses were performed on a Hewlett-Packard HP5890A gas chromatograph using a DB 1701 30m × 0.32mm capillary column attached to a flame ionization detector. Products were

quantified using acetonitrile as an internal standard. Gas samples were analyzed using a Carle Analytical Gas Chromatograph, Series S.

Procedure C(10)

The organic products were analyzed by gas chromatographic methods. The analyses were carried out using a Hewlett-Packard Model 5880 equipped with a 6 ft \times 1/8 in packed Tenax column. The initial and final temperatures for this instrument were set at 40 and 200°C, respectively. Analyses were also carried out using a HP-5840A instrument equipped with a 30m \times 0.32mm DB-1 capillary column. The initial and final temperatures were set at 40 and 280°C, respectively.