

#### 4.3.1.4 Studies of Catalyst Composition and Precursors

In our initial studies of the novel methanol homologation system, we found that Ru and additives C4, A25, and A28 are critical components of the catalyst. Some of our earlier results with this catalyst are shown in Table 65. The homologation catalyst is normally charged as a mixture of Ru, C4, A25 and A28 to a reactor containing methanol. Ru is typically charged as  $\text{RuCl}_3$ , which is very soluble in methanol.  $\text{RuCl}_3$  is converted to C16 under reaction conditions. When mixed together in methanol at 22°C, C4 rapidly reacts with A25 to form C17. C17 is converted under reaction conditions into other species which have not yet been identified.

We have examined the effect of varying the type of catalyst precursors utilized in the catalyst charge. The results are reported in Table 66. In runs 13-111 and 18-9 the Ru is charged as C8 and C9. C8 is not very soluble in methanol. Run 13-111 is comparable to run 13-110 (Table 65). The lower ethanol selectivity in 13-111 may be a result of the reduced ruthenium solubility. C15 is similar to  $\text{RuCl}_3$  and the activity and ethanol selectivity are similar to run 17-60 (Table 65). C9 and C10 are ruthenium complexes containing the elements of A25. In both cases the ethanol selectivity is less than 30%.

Various compounds containing C4 were examined as catalyst precursors. In run 17-87, C4 was replaced with C11 which does not readily react with A25. The catalyst activity was very low. C12 and C13 are compounds containing the elements of C4 and A25 but in different molar amounts. The ethanol selectivity is somewhat lower with C12 than with C4 and A25. C13 resulted in an ethanol selectivity of 80.1% at 140°C (run 17-82). The selectivity decreased when the reaction was carried out at 130 and 150°C.

As noted in Table 65, in the absence of A25 very little ethanol is obtained. Other additives similar to A25 were obtained and examined in the homologation reaction. The results are

reported in Table 66. In these experiments Ru was charged as  $\text{RuCl}_3$ . Replacing A25 with the other additives resulted in less active catalysts and much lower ethanol selectivities. For example, the highest ethanol selectivity in these runs, 47.3%, was obtained in run 17-126 with A33. In experiments with A32, A34 and A35 there was little gas uptake and ethanol was a minor product. Except for A25 none of the other additives readily reacted with C4 prior to catalysis. Therefore, C14, a compound derived from C4 and A36, was prepared. C14 is chemically similar to C13. Run 18-26 utilizing C14 can be compared with 18-24 where a mixture of C4 and A36 was charged. The ethanol selectivity increased by 16% with C14. Although A32-A37 are chemically similar to A25, some of their other physical properties are quite different. The results obtained with A32-A37 have directed us toward the choice of other additives with properties that reflect more subtle changes in A25.

A28 was replaced with A3, A45 and A46. In terms of ethanol selectivity the best results were obtained with A45. In each case the catalyst activity and ethanol selectivity was less than with A28.

The data listed in Table 66 indicates that markedly different results can be obtained depending on the compounds utilized in the catalyst charge. The catalyst consisting of C4,  $\text{RuCl}_3$ , A25 and A28 can give ethanol selectivities of 80%. It appears that C4 and A25 must interact prior to catalysis in order to obtain an active catalyst. We have also found that A25 reacts with A28 to form A30. For example, in run 17-60 (Table 65) A30 was observed in the liquid products by NMR. The identity of A30 was verified by an authentic sample prepared via a known synthetic procedure. Different results were obtained in 17-74 (Table 65). At the end of this run A25 had been converted into a mixture of A30 and A31 in about 1:1 molar ratio (based on NMR). The identity of A31 is not known. Note that the temperature is  $140^\circ\text{C}$  and  $130^\circ\text{C}$  for runs 17-60 and 17-74, respectively. At  $140^\circ\text{C}$  the conversion of A25 to A30 is complete whereas at  $130^\circ\text{C}$  the 1:1 mixture of A30 and A31 is rapidly formed and remains constant through out the

run. That the ethanol selectivity is higher at 130°C and may be a consequence of the A30/A31 mixture.

All of the homologation experiments reported here were carried out at pressures below 1000 psi. With the exception of run 18-3, experiments which produced ethanol and equivalents with selectivities greater than 65% formed these products at rates in the range of 1 to 3 moles per liter of solution per hour. The complete record of data for this section is given in Table 67.

Table 65. Earlier Results with the Methanol Homologation System

SGHAM-W-#	Molar Ratio				Temp., °C	EtOH Sel., %
	C4	Ru	A25	A28		
13-110	1	1	0	20	140	9.0
13-105	1	1	1	20	140	47.5
17-60	1	3	1	20	140	69.8
17-74	1	3	2	20	130	80.1

See Table 28 for experimental details.

Table 66. Effects of Catalyst Composition Changes

SGHAM-W-#	Catalyst, molar ratio	Temp., °C	EtOH Sel.,%
13-111	C4:C8:A25:A28 = 1:1:1:20	140	31.4
18-9	C4:C15:A25:A28 = 1:2:1:20	140	74.2
17-101	C4:C9:A28 = 1:2:20	140	23.0
17-99	C4:C10:A28 = 1:1:20	140	22.9
17-87	C11:Ru:A25:A28 = 1:3:2:20	140	16.5
17-95	C12:Ru:A28 = 1:3:20	140	69.6
17-82	C13:Ru:A28 = 1:3:20	140	80.1
18-1	C13:Ru:A28 = 1:3:20	130	76.9
18-12	C13:Ru:A28 = 1:3:20	150	no analysis
17-108	C4:Ru:A32:A28 = 1:2:1:20	140	13.6
17-112	C4:Ru:A33:A28 = 1:2:1:20	140	34.3
17-126	C4:Ru:A33:A28 = 1:2:1:20	155	47.3
18-4	C4:Ru:A34:A28 = 1:2:1:20	140	28.1
18-10	C4:Ru:A35:A28 = 1:2:1.5:20	140	25.5
18-24	C4:Ru:A36:A28 = 1:2:1:20	140	35.2
18-28	C4:Ru:A37:A28 = 1:2:1:20	140	24.1
18-26	C14:Ru:A28 = 1:2:1	140	51.7
18-3	C4:Ru:A25:A3 = 1:2:1:20	140	74.6
18-20	C4:Ru:A25:A45 = 1:2:1:15	140	50.2
18-32	C4:Ru:A25:A45 = 1:2:2:15	140	68.5
18-38	C4:Ru:A25:A46 = 1:2:1:20	140	49.2

See Table 67 for experimental details.

Table 67. Methanol Homologation Experiments

SGHAM-W-#	17-82	17-87	17-95	17-99
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	C10
2 mmol	6.00	6.00	6.00	2.00
3 Cocatalyst	C13	C11	C12	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	none	A25	none	none
6 mmol	0.0	4.00	0.0	0.0
7 Promoter	A28	A28	A28	A28
8 mmol	40.00	40.00	40.00	40.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Pressure, psi	975	975	975	975
11 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
12 Temp., °C	140	140	140	140
13 Time, hr	3.66	1.00	2.00	0.50
14 Uptake, psi	4064	223	2375	450
15 Product Sel. %				
16 EtOH	47.98	12.54	45.26	7.95
17 EtOH Eq.	32.05	4.00	24.38	15.02
18 Total EtOH	80.04	16.55	69.64	22.97
19 Other Oxy.	19.96	83.45	30.36	77.03

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 115.

Table 67. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	17-101	17-108	17-112	17-126
1 Catalyst	C9	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	none	A32	A33	A33
6 mmol	0.0	2.00	2.00	2.00
7 Promoter	A28	A28	A28	A28
8 mmol	40.00	40.00	40.00	40.00
9 MeOH(mL)	40.00	40.00	40.00	40.00
10 Pressure,psi	975	975	975	975
11 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
12 Temp., °C	140	140	140	155
13 Time,hr	0.75	1.00	1.00	1.00
14 Uptake,psi	383	100	139	250
15 Product Sel.%				
16 EtOH	5.38	12.82	4.99	22.23
17 EtOH Eq.	17.64	13.57	29.27	25.10
18 Total EtOH	23.01	26.39	34.26	47.33
19 Other Oxy.	76.99	73.61	65.74	52.67

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 115.

Table 67. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-1	18-3	18-4	18-9
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	Ru(acac) <sub>3</sub>
2 mmol	6.00	4.00	4.00	4.00
3 Cocatalyst	C13	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	none	A25	A34	A25
6 mmol	0.0	2.00	2.00	2.00
7 Promoter	A28	A3	A28	A28
8 mmol	20.00	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Pressure, psi	975	975	975	975
11 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
12 Temp., °C	130	140	140	140
13 Time, hr	4.00	3.20	2.00	3.00
14 Uptake, psi	2418	122	100	2125
15 Product Sel. %				
16 EtOH	55.14	7.73	12.23	47.85
17 EtOH Eq.	21.72	66.91	15.82	26.41
18 Total EtOH	76.86	74.64	28.04	74.27
19 Other Oxy.	23.14	25.36	71.96	25.73

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 115.



Table 67. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-10	18-12	18-20	18-24
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	6.00	4.00	4.00
3 Cocatalyst	C4	C13	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	A35	none	A25	A36
6 mmol	3.00	0.0	2.00	2.00
7 Promoter	A28	A28	A45	A28
8 mmol	20.00	20.00	30.00	20.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Pressure, psi	975	975	975	975
11 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
12 Temp., °C	140	150	140	140
13 Time, hr	1.00	1.00	3.50	1.30
14 Uptake, psi	167	839	1300	1030
15 Product Sel. %				
16 EtOH	2.14	no anal	3.27	10.27
17 EtOH Eq.	23.42	-	46.96	24.88
18 Total EtOH	25.56	-	50.23	35.15
19 Other Oxy.	74.44	-	49.7	64.85

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 115.

Table 67. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-26	18-28	18-32	18-38
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	4.00	4.00	4.00
3 Cocatalyst	C14	C4	C4	C4
4 mmol	1.00	2.00	2.00	2.00
5 Additive	none	A37	A25	A25
6 mmol	0.0	2.00	4.00	2.00
7 Promoter	A28	A28	A45	A46
8 mmol	20.00	20.00	30.00	40.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Pressure, psi	975	975	975	975
11 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
12 Temp., °C	140	140	140	140
13 Time, hr	2.50	0.75	4.00	2.75
14 Uptake, psi	830	419	1044	860
15 Product Sel. %				
16 EtOH	37.57	9.71	40.36	23.02
17 EtOH Eq.	14.13	14.37	28.12	26.22
18 Total EtOH	51.70	24.09	68.47	49.24
19 Other Oxy.	48.30	75.91	31.53	50.76

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 115.

#### 4.3.1.5 Studies of Catalyst Additives and Solvents

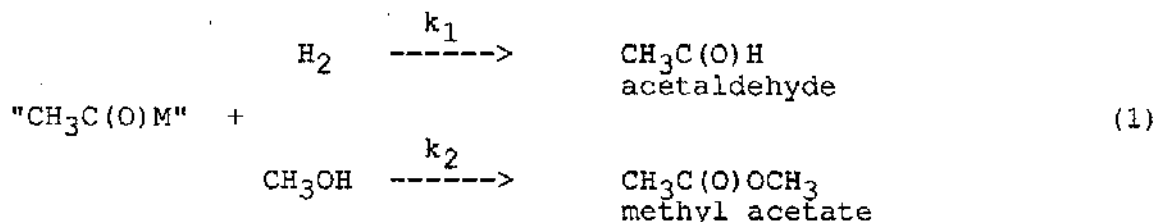
Earlier work in this project had shown that catalyst additives C4 and A25 are critical components of the catalyst. In the absence of one or both, the homologation reaction is not observed. Additives similar to A25 were prepared and examined in our earlier work. In general, catalysts containing additives other than A25 were found to be markedly less active, and ethanol selectivities were less than 40%. Further studies of alternative additives were conducted; the results are reported in Table 68.

In run 18-109 with A26, the reaction consumed 300 psi in 7 minutes and then stopped. The temperature was very difficult to control due to the exothermic nature of the reaction. Lower temperature runs (118-110 and 18-112) resulted in better temperature control. In each case gas consumption was low and in 18-112 the ethanol selectivity was only 9.1%. Additives A47 (18-54, EtOH = 64.8%), A37 (18-116, EtOH = 60.2%) and A53 (21-16, EtOH = 71.6%) resulted in catalysts that yielded ethanol with selectivities >60%. The catalyst containing A53 approaches the activity and ethanol selectivity obtained with A25. The results with A47, A37 and A53 demonstrate that additives other than A25 will work.

Several experiments were carried out with  $H_2/CO = 1:1$  at various temperatures and pressures. The results are reported in Table 69. Neither the operating pressure nor the amount of Ru utilized had much impact on the ethanol selectivity. The highest ethanol selectivity, 50.1%, was obtained at 140°C and 500 psig. Decreasing the pressure decreased the activity as judged by the amount of gas consumed per unit time.

The homologation reaction was carried out with various solvents at constant catalyst composition and reaction conditions. The results are reported in Table 69. For comparison, run 17-19 (no solvent, same reaction conditions) is included in Table 69. In these experiments the methanol:solvent ratio was 1:1 by volume.

Except for diglyme solvent (18-87, EtOH = 70.9%) the ethanol selectivities are markedly less than in the no-solvent case. There is no correlation of catalyst activity or product selectivity with solvent polarity. It was anticipated that the ethanol selectivity would increase by the addition of a solvent. This effect has been observed in the cobalt-catalyzed reductive carbonylation of methanol. In that case, it was thought that the metal-acyl intermediate (" $\text{CH}_3\text{C}(\text{O})\text{M}$ ", equation 1) reacts with  $\text{H}_2$  or methanol to yield acetaldehyde or methyl acetate, respectively.



A solvent decreases the methanol concentration whereas the  $\text{H}_2$  concentration (assuming the  $\text{H}_2$  partial pressure remains constant) remains relatively unchanged. The net effect is that the reaction of the acyl intermediate " $\text{CH}_3\text{C}(\text{O})\text{M}$ " with  $\text{H}_2$  becomes more favored ( $k_1[\text{H}_2] > k_2[\text{CH}_3\text{OH}]$ ) and the amount of acetaldehyde increases. The decreased catalyst activity and ethanol selectivity (except in diglyme) may indicate that the solvent is not acting as a simple diluent in the homologation reaction.

Several runs were carried out with a catalyst consisting of C4-C6-Ru-A25-A28. The results are listed in Table 70 (18-41, 68, 70, 73, 75, and 76). It was thought that C6, in combination with  $\text{RuCl}_3$ , would lead to a better acetaldehyde hydrogenation catalyst and higher ethanol selectivities. Run 18-41 resulted in an ethanol selectivity of 80% which is 8% higher than for the corresponding run without C6 (17-19, Table 69). Increasing A25 (18-73) or  $\text{RuCl}_3$  (18-70), or decreasing  $\text{RuCl}_3$  (18-68) resulted in ethanol selectivities less than 70%.

Table 68. Effects of Catalyst Composition Changes

SGHAM-W-#	Catalysts, molar ratio	Temp., °C	EtOH Sel.,%
18-51	C4:Ru:A8:A28 = 1:2:2:20	165	43.3
18-53	C4:Ru:A53:A28 = 1:2:1:20	140	19.3
18-105	C4:Ru:A54:A28 = 1:2:2:20	140	3.6
18-109	C4:Ru:A26:A28 = 1:2:2:20	140	6.6
18-110	C4:Ru:A26:A28 = 1:2:2:20	115	not analyzed
18-112	C4:Ru:A26:A28 = 1:2:2:20	95	9.1
18-113	C4:Ru:A55:A28 = 1:2:2:20	140	26.2
18-115	C4:Ru:A36:A28 = 1:2:2:20	140	32.2
18-50	C4:Ru:A36:A28 = 1:2:3:20	165	not analyzed
18-54	C4:Ru:A47:A28 = 1:2:1.5:20	140	64.8
18-56	C4:Ru:A48:A28 = 1:2:2:20	140	24.8
18-59	C4:Ru:A49:A28 = 1:2:2:20	140	17.0
18-60	C4:Ru:A49:A28 = 1:2:1.35:20	120	37.9
18-114	C4:Ru:A50:A28 = 1:2:2:20	140	15.4
18-116	C4:Ru:A37:A28 = 1:2:2:20	140	60.2
18-121	C4:Ru:A37:A28 = 1:2:2:20	150	12.5
18-122	C4:Ru:A51:A28 = 1:2:2:20	140	9.4
18-123	C4:Ru:A52:A28 = 1:2:2:20	140	4.8
21-16	C4:Ru:A53:A28 = 1:2:2:20	140	71.6

See Table 70 for experimental details.

Table 69. Effects of Solvents and Reaction Conditions

SGHAM-W-#	C4:Ru:A25:A28	Solvent	Temp., °C	Pressure, psig	H <sub>2</sub> /CO	EtOH Sel.,%
18-97	1:2:2:20	----	140	975	1:1	45.2
18-100	1:2:2:20	----	140	750	1:1	41.8
18-102	1:1:2:20	----	140	750	1:1	41.0
21-28	1:0.5:2:20	----	140	750	1:1	41.7
21-25	1:2:1:20	----	140	500	1:1	50.1
17-19	1:2:2:20	none	140	975	2:1	72.7
18-85	1:2:2:20	DEC <sup>a</sup>	140	975	2:1	57.3
18-87	1:2:2:20	Diglyme	140	975	2:1	70.9
18-91	1:2:2:20	1,4-Dioxane	140	975	2:1	14.9
18-94	1:2:2:20	DPE <sup>b</sup>	140	975	2:1	56.5
21-30	1:2:2:20	NMP <sup>c</sup>	140	975	2:1	45.7
21-35	1:2:2:20	Toluene	140	975	2:1	44.4
21-39	1:2:2:20	DMF <sup>d</sup>	140	975	2:1	0.0

See Table 70 for experimental details.

<sup>a</sup> Diethyl carbitol.

<sup>b</sup> Diphenyl ether.

<sup>c</sup> N-Methylpyrrolidone.

<sup>d</sup> N,N-Dimethylformamide.

Key to Table 70

SGHAM-W-#

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

Table 70. Methanol Homologation Experiments

SGHAM-W-#	18-41	18-44	18-46
1 Catalyst	Co(OAc) <sub>2</sub> /RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	2/2	1.00	1.00
3 Cocatalyst	C4	C4	C4
2 mmol	2.00	0.50	0.50
5 Additive	A25	A25	A25
6 mmol	4.00	1.00	2.00
7 Promoter	A28	A28	A28
8 mmol	20.00	10.00	10.00
9 MeOH (mL)	40.00	40.00	40.00
10 Solvent	none	none	none
11 mL	0.00	0.00	0.00
12 Pressure, psi	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1
15 Temp., °C	140	165	165
16 Time, hr	5.75	2.50	2.20
17 Uptake, psi	3200	1097	1090
18 Product Sel. %			
19 EtOH	50.23	29.51	31.94
20 EtOH Eq.	29.60	31.63	27.01
21 Total EtOH	79.83	61.13	58.96
22 Other Oxy.	20.17	38.87	41.04

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.



Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-48	18-50	18-51	18-53
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	0.75	1.00	1.00	4.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	0.25	0.50	0.50	2.00
5 Additive	A25	A36	A8	A53
6 mmol	0.50	1.50	1.00	2.00
7 Promoter	A28	A28	A28	A28
8 mmol	7.50	10.00	10.00	40.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Solvent	none	none	none	none
11 mL	0.00	0.00	0.00	0.00
12 Pressure, psi	975	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14 Temp., °C	165	165	140	140
15 Time, hr	1.50	2.50	1.50	0.75
16 Uptake, psi	450	490	620	450
17 Product Sel. %				
18 EtOH	21.46	NA <sup>a</sup>	15.94	7.67
19 EtOH Eq.	21.16	NA <sup>a</sup>	27.36	11.64
20 Total EtOH	42.62	NA <sup>a</sup>	43.30	19.31
21 Other Oxy.	57.38	NA <sup>a</sup>	56.70	80.69

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

<sup>a</sup> Not analyzed; solution lost during recovery process.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-54	18-56	18-59	18-60
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	4.00	4.00	2.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	1.00
5 Additive	A47	A48	A49	A49
6 mmol	2.50	4.00	2.20	1.35
7 Promoter	A28	A28	A28	A28
8 mmol	40.00	40.00	40.00	28.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Solvent	none	none	none	none
11 mL	0.00	0.00	0.00	0.00
12 Pressure, psi	975	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14 Temp., °C	140	140	140	120
15 Time, hr	2.00	1.00	1.00	2.50
16 Uptake, psi	1596	445	977	758
17 Product Sel. %				
18 EtOH	39.09	1.75	1.44	15.14
19 EtOH Eq.	25.71	23.13	15.56	22.80
20 Total EtOH	64.81	24.87	17.00	37.95
21 Other Oxy.	35.19	75.13	83.00	62.05

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-68	18-70	18-75	18-76
1 Catalyst	Co(OAc) <sub>2</sub> /RuCl <sub>3</sub>	Co(OAc) <sub>2</sub> /RuCl <sub>3</sub>	Co(OAc) <sub>2</sub>	Co(OAc) <sub>2</sub>
2 mmol	4/1	8/4	1.00	4.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	A25	A25	A25	A25
6 mmol	4.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmol	40.00	40.00	40.00	40.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Solvent	none	none	none	none
11 mL	0.00	0.00	0.00	0.00
12 Pressure, psi	975	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14 Temp., °C	140	140	140	140
15 Time, hr	2.75	2.50	2.75	2.20
16 Uptake, psi	2330	1700	850	610
17 Product Sel. %				
18 EtOH	47.46	37.05	12.10	1.77
19 EtOH Eq.	22.24	28.45	42.22	45.33
20 Total EtOH	69.69	65.50	54.32	47.10
21 Other Oxy.	30.31	34.50	45.68	52.90

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-73	18-85	18-87	18-91
1 Catalyst	Co(OAc) <sub>2</sub> /RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4/4	4.00	4.00	4.0
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	A25	A25	A25	A25
6 mmol	8.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmol	40.00	40.00	40.00	40.00
9 MeOH(mL)	40.00	20.00	20.00	20.00
10 Solvent	none	DEC <sup>a</sup>	Diglyme	1,4-Dioxane
11 mL	0.00	20.00	20.00	20.00
12 Pressure, psi	975	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14 Temp., °C	140	140	140	140
15 Time, hr	1.00	2.00	2.00	2.00
16 Uptake, psi	1450	1540	2030	380
17 Product Sel. %				
18 EtOH	37.39	30.23	45.75	6.83
19 EtOH Eq.	29.71	27.06	25.20	8.11
20 Total EtOH	67.10	57.30	70.94	14.94
21 Other Oxy.	32.90	42.70	29.06	85.06

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

<sup>a</sup> Diethyl carbitol.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-94	18-97	18-100	18-102
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	4.00	4.00	2.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	A25	A25	A25	A25
6 Mol	4.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmol	40.00	40.00	40.00	20.00
9 MeOH (mL)	20.00	40.00	40.00	40.00
10 Solvent	DPE <sup>a</sup>	none	none	none
11 mL	20.00	0.00	0.00	0.00
12 Pressure, psi	975	975	750	750
13 H <sub>2</sub> /CO	2:1	1:1	1:1	1:1
14 Temp., °C	140	140	140	140
15 Time, hr	2.00	2.00	2.30	2.50
16 Uptake, psi	1720	2568	2100	1980
17 Product Sel. %				
18 EtOH	25.60	19.48	19.25	19.98
19 EtOH Eq.	30.98	25.80	22.57	21.02
20 Total EtOH	56.58	45.27	41.82	41.00
21 Other Oxy.	43.42	54.73	58.18	59.00

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

<sup>a</sup> Diphenyl ether.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-105	18-109	18-110	18-112
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	A54	A26	A26	A26
6 mmol	4.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmol	20.00	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Solvent	none	none	none	none
11 mL	0.00	0.00	0.00	0.00
12 Pressure, psi	975	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14 Temp., °C	140	140	115	95
15 Time, hr	1.00	1.00	1.00	1.50
16 Uptake, psi	300	300	270	477
17 Product Sel. %				
18 EtOH	0.00	0.00	NA <sup>a</sup>	1.81
19 EtOH Eq.	3.61	6.62	NA <sup>a</sup>	7.34
20 Total EtOH	3.61	6.62	NA <sup>a</sup>	9.15
21 Other Oxy.	96.39	93.38	NA <sup>a</sup>	90.85

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

<sup>a</sup> Not analyzed; solution lost during recovery process.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-113	18-114	18-115	18-116
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	A55	A50	A36	A36
6 mmol	4.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmol	20.00	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Solvent	none	none	none	none
11 mL	0.00	0.00	0.00	0.00
12 Pressure, psi	975	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14 Temp., °C	140	140	140	140
15 Time, hr	1.40	1.00	1.00	2.40
16 Uptake, psi	490	431	650	7
17 Product Sel.				
18 EtOH	13.06	1.89	15.07	34.10
19 EtOH Eq.	13.15	13.57	17.15	26.10
20 Total EtOH	26.21	15.45	32.22	60.21
21 Other Oxy.	73.79	84.55	67.78	39.79

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	18-121	18-122	18-123
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	3.40	4.00	4.00
3 Cocatalyst	C4	C4	C4
4 mmol	1.70	2.00	2.00
5 Additive	A36	A51	A52
6 mmol	3.40	2.00	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 Solvent	none	none	none
11 mL	0.00	0.00	0.00
12 Pressure, psi	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1
14 Temp., °C	150	140	140
15 Time, hr	1.00	1.00	0.50
16 Uptake, psi	100	240	200
17 Product Sel. %			
18 EtOH	1.85	0.74	0.67
19 EtOH Eq.	10.70	8.63	4.13
20 Total EtOH	12.56	9.37	4.81
21 Other Oxy.	87.44	90.63	95.19

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.



Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	21-16	21-21	21-25
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4.00	4.00	4.00
3 Cocatalyst	C4	C18	C4
4 mmol	2.00	1.00	2.00
5 Additive	A47	A47	A25
6 mmol	4.00	4.00	2.00
7 Promoter	A28	A28	A28
8 mmol	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00
10 Solvent	none	none	none
11 mL	0.00	0.00	0.00
12 Pressure, psi	975	975	500
13 H <sub>2</sub> /CO	2:1	2:1	1:1
14 Temp., °C	140	140	140
15 Time, hr	4.50	2.75	2.00
16 Uptake, psi	1900	585	1085
17 Product Sel. %			
18 EtOH	46.45	28.46	24.09
19 EtOH Eq.	25.14	26.86	25.92
20 Total EtOH	71.60	55.32	50.01
21 Other Oxy.	28.40	44.68	49.99

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

Table 70. Methanol Homologation Experiments (Cont'd)

SGHAM-W-#	21-28	21-30	21-35	21-39
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	1.00	4.00	4.00	4.00
3 Cocatalyst	C4	C4	C4	C4
4 mmol	2.00	2.00	2.00	2.00
5 Additive	A25	A25	A25	A25
6 mmol	4.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmol	20.00	20.00	20.00	20.00
9 MeOH (mL)	40.00	20.00	20.00	20.00
10 Solvent	none	NMP <sup>a</sup>	Toluene	DMF <sup>b</sup>
11 mL	0.00	20.00	20.00	20.00
12 Pressure, psi	750	975	975	975
13 H <sub>2</sub> /CO	1:1	2:1	2:1	2:1
14 Temp., °C	140	140	140	140
15 Time, hr	1.75	2.00	2.00	1.00
16 Uptake, psi	2050	1000	1490	320
17 Product Sel. %				
18 EtOH	21.14	16.97	14.00	0.00
19 EtOH Eq.	20.65	28.70	30.45	0.00
20 Total EtOH	41.79	45.67	44.45	0.00
21 Other Oxy.	58.21	54.33	55.55	100.00

Experimental procedure: B(2); Analytical procedure: C(8); Key on page 262.

<sup>a</sup> N-Methylpyrrolidone.

<sup>b</sup> N,N-Dimethylformamide.