4.1.1.15 Effects of Organic Additives in Ruthenium Systems

When the organic additive benzimidazole was used in a ruthenium/iodide catalyst system, significant changes were noted. Relatively small amounts of benzimidazole added to the ruthenium carbonyl/P(n-Bu)$_4$Br system cause an increased amount of ethanol product, as shown in Table 18. When a larger amount of benzimidazole was used, the amount of ethanol decreased but that of other oxygenates increased dramatically. Interestingly, when benzimidazole was replaced by indole, which is a close structural and electronic analog, the only change noted was an increase in the formation of ethanol. These results are shown in Table 19. Related organic compounds were also tested as promoters, but they had a negative effect on the catalyst system, as shown in Table 19.

When organic additive A58 was added to the ruthenium catalyst systems, both the molten phosphonium salt system and the iodide-promoted catalyst in NMP were found to produce more C_2 products, such as ethanol. The enhancement was particularly notable for the NMP system. Increased activities were also observed. Electron-withdrawing groups substituted on the additive seem to increase both the activity and the selectivity to higher alcohols in the NMP system, while electron-donating groups have the opposite effect. A76 had a slight negative effect on the catalyst activity in NMP solvent, but the production of ethanol and propanol increased significantly. Interestingly, no effect was observed in either system when the closely related A73 was added. Results of these experiments are reported in Table 20.

The addition of additives $KH_2B(pyrazole)_2$ or $KHB(pyrazole)_3$ to the NMP system affected the activity slightly. Also, the yield of C_2+ alcohols dropped to only about 10% (from about 20% when no additive was added) by weight of total product.

It has become clear that the additive benzimidazole is not stable at 230°C under catalytic conditions; it decomposes to

o-phenylenediamine and some C_1 fragment, most likely formic acid. Large quantities of o-phenylenediamine were observed by GC in these catalytic runs. 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 production of certain oxygenates when benzimidazole was used as additive may have resulted from the hydrogenation of the C_1 fragment formed from benzimidazole decomposition. Results of these experiments are reported in Table 20.

Three additional derivatives of the organic additive A58 were tested. As shown in Table 21, the total activity of the Ru/KI/NMP system did not change very much with the addition of these derivatives. However, like most other derivatives of A58 we have tested, they all enhanced the formation of ethanol. The effects of the adding the related additives A93 and A94 to the Ru/KI/NMP system were also similar. An enhancement of ethanol formation was observed while the activity was not affected. Additive A95, however, did increase the activity of the system.

Since A92 is a relatively low melting solid, we attempted to use it as a solvent for an otherwise unpromoted ruthenium catalyst system. The system of Ru/A92 is a relatively active one at the pressure of 5000 psi. Attempts to promote the catalyst activity and the formation of higher alcohols by the addition of iodide failed as neither an increase in activity nor an increase in ethanol formation were observed. Addition of HI or CoI_2 completely poisoned the system.

Interestingly, the combination of $Ru_3(CO)_{12}$ and A92 in toluene solvent forms an active catalyst system which produces mainly methanol and methyl formate. Unlike the system of ruthenium/A92 with no added solvent, the activity of this particular system was not affected much by the addition of iodide.

Table 18. Effects of Organic Additives

	SGHAM-L-#	1-57	1-63	1-65	2-7
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.25	0.31	1.25	1.25
3	Solvent	$P(n\text{-}Bu)_4Br$	$P(n\text{-}Bu)_4Br$	$P(n\text{-}Bu)_4Br$	$P(n\text{-}Bu)_4Br$
4	mL/g	15.0g	7.5g	15.0g	15.0g
5	Additive	Benzimidazole	Benzimidazole	Benzimidazole	Benzimidazole/$Rh(acac)_3$
6	mmol	3.8	7.6	30.5	30.5/1.0
7	Press.,psi	5000	5000	5000	5000
8	Temp.,°C	230	230	230	230
9	Time,hrs.	3.0	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0	1.0
11	MeOH,g	3.2	1.5	3.0	1.7
12	EtOH,g	2.8	0.2	1.6	0.85
13	n-PrOH,g	trace	trace	0.2	trace
14	n-BuOH,g	trace	trace	trace	trace
15	CH_3CHO,g	0.3	trace	0.1	0.0
16	Other Ox.,g	0.3	0.9	3.7	1.4
17	Tot. Prod.,g	6.6	2.6	8.6	4.0
18	% EtOH	43	8	19	21
19	C_2+/C_1 ratio	1.1	0.73	1.9	1.4

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 19. Effects of Organic Additives

	SGHAM-L-#	1-67	1-71	1-73[a]
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.25	1.25	1.25
3	Solvent	$P(n\text{-}Bu)_4Br$	$P(n\text{-}Bu)_4Br$	NMP
4	mL/g	15.0g	15.0g	15.0 mL
5	Additive	Indole	Indole/Quinoline	Indole
6	mmol	30.5	15.0/15.0	30.5
7	Press.,psi	5000	5000	5000
8	Temp.,°C	230	230	230
9	Time,hrs.	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	4.3	2.4	trace
12	EtOH,g	3.3	2.8	trace
13	n-PrOH,g	0.3	trace	-
14	n-BuOH,g	trace	trace	-
15	CH_3CHO,g	0.50	0.3	-
16	Other Ox.,g	trace	trace	-
17	Tot. Prod.,g	8.4	5.5	trace
18	% EtOH	39	51	-
19	C_2+/C_1 ratio	0.95	1.3	-

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

[a] Experimental procedure: B(5).

Table 19. Effects of Organic Additives (Cont'd)[a]

	SGHAM-L-#	6-51	6-52	6-53
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	2.2	2.2	2.2
3	Solvent	Toluene	Toluene	Toluene
4	mL	45	45	45
5	Additive	Phenazine	Anthranilamide	Quinoxaline
6	mmol	93	93	93
7	Press.,psi	6000	5000	5000
8	Temp.,°C	230	230	230
9	Time, hr.	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH, g	b	b	b
12	EtOH, g			
13	n-PrOH, g			
14	n-BuOH, g			
15	CH_3CHO, g			
16	Other Ox., g			
17	Tot.Prod., g			
18	% C_2+ alcohols			
19	C_2+/C_1 ratio			

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.

[a] Experiments conducted in last quarter of contract.

[b] No product formed.

Table 19. Effects of Organic Additives (Cont'd)[a]

	SGHAM-L-#	6-49	5-45	6-50
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	2.2	2.2	2.2
3	Solvent	Toluene	Toluene	Toluene
4	mL	45	45	45
5	Additive	2-aminothiophenol	Adenine	2-Iodoaniline
6	mmol	93	93	93
7	Press.,psi	6000	6000	6000
8	Temp.,°C	230	230	230
9	Time, hr.	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH, g	b	b	b
12	EtOH, g			
13	n-PrOH, g			
14	n-BuOH, g			
15	CH_3CHO, g			
16	Other Ox., g			
17	Tot.Prod., g			
18	% C_2+ alcohols			
19	C_2+/C_1 ratio			

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.

[a] Experiments conducted in last quarter of contract.

[b] No product formed.

Table 19. Effects of Organic Additives (Cont'd)[a]

	SGHAM-L-#	3-111	4-132	6-48
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	2.2	2.2	2.2
3	Solvent	Toluene	Toluene	Toluene
4	mL	45	45	45
5	Additive	DPA[b]	Phthalhyazide	DAAQ[c]
6	mmol	93	93	93
7	Press.,psi	6000	6000	6000
8	Temp.,°C	230	230	230
9	Time, hr.	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH, g	d	d	d
12	EtOH, g			
13	n-PrOH, g			
14	n-BuOH, g			
15	CH_3CHO, g			
16	Other Ox., g			
17	Tot.Prod., g			
18	% C_2+ alcohols			
19	C_2^+/C_1 ratio			

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.

[a] Experiments conducted in last quarter of contract.

[b] 2-(Diphenylphosphino)-N,N-dimethylanaline.

[c] Diaminoanthraquinone.

[d] No product formed.

Table 19. Effects of Organic Additives (Cont'd)

	SGHAM-L-#	1-55	1-75
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.25	1.25
3	Solvent	$P(n\text{-}Bu)_4Br$	$P(n\text{-}Bu)_4Br$
4	mL/g	15.0g	15.0g
5	Additive	Imidazole	Sodium imidazolate
6	mmol	3.8	11.0
7	Press.,psi	5000	5000
8	Temp.,°C	230	230
9	Time,hrs.	3.0	5.0
10	H_2/CO	1.0	1.0
11	MeOH,g	3.9	2.1
12	EtOH,g	1.4	1.8
13	n-PrOH,g	-	-
14	n-BuOH,g	-	-
15	CH_3CHO,g	trace	trace
16	Other Ox.,g	-	-
17	Tot. Prod.,g	5.3	3.9
18	% EtOH	26	46
19	C_2+/C_1 ratio	0.36	0.86

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 20. Effects of Organic Additives in Ruthenium Systems

	SGHAM-L-#	3-17	2-65	1-109
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.25	1.25	1.25
3	Solvent	NMP	NMP	NMP
4	mL/g	30 mL	30 mL	30 mL
5	Additive	KI	KI/A58	KI/A58
6	mmol	9.0	9.0/1.9	9.0/3.0
7	Press.,psi	6000	6000	6000
8	Temp.,°C	230	230	230
9	Time,hrs	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	3.1	3.3	3.6
12	EtOH,g	0.86	2.1	1.5
13	n-PrOH,g	trace	0.11	0.10
14	n-BuOH,g	trace	trace	trace
15	CH_3CHO,g	0.10	1.3	1.5
16	Other Ox.,g	0.47	1.2	0.89
17	Tot. Prod.,g	4.53	8.0	7.6
18	% C_2+ alcohols	19	28	21
19	C_2+/C_1 ratio	0.46	1.4	1.1

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 20. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	3-58	2-107	4-46
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	2.2	2.2	2.2
3	Solvent	NMP	NMP	NMP
4	mL/g	50 mL	50 mL	50 mL
5	Additive	KI	KI/A74	KI/A75
6	mmol	19	19/2.5	19/2.6
7	Press.,psi	6000	6000	6000
8	Temp.,°C	230	230	230
9	Time,hrs	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	4.2	4.3	3.3
12	EtOH,g	1.1	4.0	2.3
13	n-PrOH,g	0.15	0.60	0.23
14	n-BuOH,g	0.0	trace	trace
15	CH_3CHO,g	0.47	1.0	0.57
16	Other Ox.,g	0.33	0.73	0.63
17	Tot. Prod.,g	6.3	10.6	7.0
18	% C_2+ alcohols	20	43	36
19	C_2+/C_1 ratio	0.5	1.5	1.1

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 20. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	2-96	3-23	4-52
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.25	1.25	1.25
3	Solvent	NMP	NMP	NMP
4	mL/g	30 mL	50 mL	50 mL
5	Additive	KI/A73	KI/Benz[a]	KI/o-Phen[b]
6	mmol	9.0/2.3	9.0/51	9.0/4.6
7	Press.,psi	6000	6000	6000
8	Temp.,°C	230	230	230
9	Time,hrs	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	3.02	3.9	3.8
12	EtOH,g	0.56	0.73	2.0
13	n-PrOH,g	trace	trace	0.24
14	n-BuOH,g	trace	0.0	trace
15	CH_3CHO,g	0.10	trace	0.61
16	Other Ox.,g	0.35	2.8	0.9
17	Tot. Prod.,g	4.0	7.5[c]	7.6
18	% C_2+ alcohols	14	10	30
19	C_2+/C_1 ratio	0.33	0.9	1.0

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

[a] Benzimidazole.

[b] o-Phenylenediamine.

[c] In this experiment, 3.7g (37 mmol) of o-phenylenediamine was detected by GC.

Table 20. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	4-54	4-58[a]
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.25	1.25
3	Solvent	$P(n\text{-}Bu_4)Br$	NMP
4	mL/g	15.0 g	50 mL
5	Additive	o-Phen[b]	KI/o-Phen[b]
6	mmol	9.0	9.0/9.3
7	Press.,psi	5000	6000
8	Temp.,°C	230	230
9	Time,hrs	3.0	3.0
10	H_2/CO	1.0	1.0
11	MeOH,g	2.1	3.4
12	EtOH,g	1.3	1.8
13	n-PrOH,g	0.18	0.21
14	n-BuOH,g	trace	trace
15	CH_3CHO,g	trace	0.28
16	Other Ox.,g	0.84	1.2
17	Tot. Prod.,g	4.42	6.9
18	% C_2+ alcohols	33	51
19	C_2+/C_1 ratio	1.1	1.0

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

[a] Experimental procedure: B(5).

[b] o-Phenylenediamine.

Table 20. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	3-32	3-48	3-64
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	2.2	2.2	2.2
3	Solvent	NMP	NMP	NMP
4	mL/g	50g	50 mL	50 mL
5	Additive	KI/A76	$KI/KH_2B(pyrazole)_2$	$KI/KHB(pyrazole)_3$
6	mmol	19/2.5	19/2.0	19/2.7
7	Press.,psi	6000	6000	6000
8	Temp.,°C	230	230	230
9	Time,hrs	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	2.2	4.1	4.8
12	EtOH,g	2.1	0.50	0.59
13	n-PrOH,g	0.71	trace	trace
14	n-BuOH,g	trace	trace	trace
15	CH_3CHO,g	trace	trace	trace
16	Other Ox.,g	0.42	trace	trace
17	Tot. Prod.,g	5.4	4.6	5.4
18	% C_2+ alcohols	52	11	11
19	C_2+/C_1 ratio	1.5	0.12	0.13

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 21. Effects of Organic Additives in Ruthenium Systems

SGHAM-L-#	3-72	4-96	4-94
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmol	2.2	1.8	2.2
3 Solvent	NMP	NMP	NMP
4 mL/g	50.0	50.0	50.0
5 Additive	KI/A96	KI/A97	KI/A98
6 mmol	3.2/3.2	1.9/3.0	3.2/3.0
7 Press.,psi	6000	6000	6000
8 Temp.,°C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	3.5	2.7	3.5
12 EtOH,g	1.5	2.3	1.4
13 n-PrOH,g	0.2	0.53	0.11
14 n-BuOH,g	0.0	0.0	0.0
15 CH_3CHO,g	0.6	0.74	0.75
16 Other Ox.,g	1.0	0.0	0.88
17 Tot. Prod.,g	6.8	6.3	6.8
18 % C_2+ alcohols	25	45	22
19 C_2+/C_1 ratio	0.94	1.3	0.94

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 21. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	5-5	2-127	2-125
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	2.2	2.2	2.2
3	Solvent	NMP	NMP	NMP
4	mL/g	40.0	40.0g	40.0g
5	Additive	A94	KI/A95	KI/A93
6	mmol	91	19/108	19/93
7	Press.,psi	6000	6000	6000
8	Temp.,°C	230	230	230
9	Time, hrs	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	3.8	6.1	4.1
12	EtOH,g	2.3	2.0	2.2
13	n-PrOH,g	0.0	0.17	trace
14	n-BuOH,g	0.0	0.0	0.0
15	CH_3CHO,g	0.0	0.0	0.0
16	Other Ox.,g	0.2	0.65	0.25
17	Tot. Prod.,g	6.3	8.8	6.6
18	% C_2+ alcohols	37	25	33
19	C_2+/C_1 ratio	0.66	0.44	0.61

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 21. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	2-117	2-123	2-125
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.8	1.8	1.8
3	Solvent	A92	A92	A92
4	mL/g	15.0g	20.0g	20.0g
5	Additive	-	KI	NaI
6	mmol	-	9.0	9.0
7	Press.,psi	5000	5000	5000
8	Temp.,°C	230	230	230
9	Time, hrs	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	10.3	8.6	4.5
12	EtOH,g	0.0	0.11	0.17
13	n-PrOH,g	0.0	0.0	0.0
14	n-BuOH,g	0.0	0.0	0.0
15	CH_3CHO,g	0.0	0.0	0.0
16	Other Ox.,g	1.0	1.22	0.46
17	Tot. Prod.,g	11.3	9.9	5.1
18	% C_2+ alcohols	0.0	1.0	3.0
19	C_2+/C_1 ratio	0.0	0.10	0.09

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 21. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	5-7	5-11
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	1.8	1.8
3	Solvent	A92	A92
4	mL/g	20.0g	20.0g
5	Additive	HI	CoI_2
6	mmol	22	3.2
7	Press.,psi	5000	5000
8	Temp.,°C	230	230
9	Time, hrs	3.0	3.0
10	H_2/CO	1.0	1.0
11	MeOH,g	NA[a]	NA[a]
12	EtOH,g		
13	n-PrOH,g		
14	n-BuOH,g		
15	CH_3CHO,g		
16	Other Ox.,g		
17	Tot. Prod.,g		
18	% C_2+ alcohols		
19	C_2^+/C_1 ratio		

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

[a] Product not analyzed due to formation of a gum-like material; no liquid remained.

Table 21. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	6-6	6-8	6-12
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7	4.7
3	Solvent	Toluene	Toluene	Toluene
4	mL/g	40.0g	40.0g	40.0g
5	Additive	A92	A92	A92
6	mmol	93	93	93
7	Press.,psi	6000	4000	3000
8	Temp.,°C	230	230	230
9	Time, hrs	3.0	3.0	3.0
10	H_2/CO	1.0	1.0	1.0
11	MeOH,g	13.5	14.1	4.3
12	EtOH,g	0.20	0.1	0.0
13	n-PrOH,g	0.0	0.0	0.0
14	n-BuOH,g	0.0	0.0	0.0
15	CH_3CHO,g	0.0	0.0	0.0
16	Other Ox.,g	10.4	1.81	0.37
17	Tot. Prod.,g	24.1	16.0	4.7
18	% C_2+ alcohols	0.0	0.0	0.0
19	C_2+/C_1 ratio	0.32	0.10	0.0

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 21. Effects of Organic Additives in Ruthenium Systems (Cont'd)

	SGHAM-L-#	4-119	4-121
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7
3	Solvent	Toluene	p-Xylene
4	mL/g	40.0g	40.0g
5	Additive	A92/PPNI[a]	A92/KI
6	mmol	93/7.5	93/19
7	Press.,psi	6000	6000
8	Temp.,°C	230	230
9	Time, hrs	3.0	3.0
10	H_2/CO	1.0	1.0
11	MeOH,g	6.9	9.6
12	EtOH,g	1.9	1.4
13	n-PrOH,g	trace	trace
14	n-BuOH,g	0.0	0.0
15	CH_3CHO,g	0.0	0.0
16	Other Ox.,g	2.9	3.8
17	Tot. Prod.,g	11.8	14.8
18	% C_2+ ROH	16	10
19	C_2+/C_1 ratio	0.59	0.28

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

[a] PPNI = bis(triphenylphosphine)iminium iodide.

4.1.2 Ruthenium Catalysts for Methanol Homologation

4.1.2.1 Introduction

It is apparent that a difficult step in the production of higher alcohols is the first step in the process, the initial activation of CO and H_2. One way to circumvent this problem is to use methanol as a starting material along with syngas. Since methanol is inexpensive, readily available, and easily manufactured from syngas, it is an excellent feedstock for these reactions. Some research was therefore directed toward the investigation of methanol homologation as a route to higher alcohols.

The reductive carbonylation of methanol, i.e., the reaction of methanol with synthesis gas to yield acetaldehyde, as shown below, is normally carried out with a cobalt-iodide catalyst at 160-180°C and 3000-6000 psig.

$$CH_3OH + H_2 + CO \text{ -----> } CH_3C(O)H + H_2O$$

In most cases the acetaldehyde selectivities are 55 to 80%. In 1983 at UCC, we discovered a novel catalyst that markedly lowered the required operating pressure. In this case the reaction conditions are 170°C and 1000 psig and the acetaldehyde selectivity approaches 75%. This system is unlike many related catalytic systems which only carbonylate methanol in reactions with synthesis gas. That is, in many other systems H_2 is not "activated" and only esters and carboxylic acids are obtained. A patent application covering this technology was submitted to the U.S. Patent Office in 1984.

The addition of ruthenium to a cobalt-iodide catalyst is known to result in the formation of ethanol. It is thought that Ru hydrogenates acetaldehyde, the net reaction being homologation of methanol.

$$CH_3OH + 2\ H_2 + CO \text{ ------> } CH_3CH_2OH + H_2O$$

A Co-Ru-I catalyst requires operating conditions of 180°C and 4000 to 8000 psig. Ethanol rates are typically 3 to 6 M/hr and selectivities are at best 85%. We have extended our previous work by studying a ruthenium catalyst with a cocatalyst. Here, the objective is to produce ethanol or higher alcohols at low operating pressure via methanol homologation.

4.1.2.2 Effects of Catalyst Additives on Homologation

We have found that ethanol is obtained in good yield with a ruthenium-containing catalyst at 140°C and 950 psig. Initial results indicated rates to ethanol (and products easily converted to ethanol) of approximately 2-4 M/hr and a selectivity to ethanol approaching 50%.

The choice of catalyst additives in this homologation system has a powerful effect on catalyst activity and selectivity, as shown by the data recorded in Table 22. Experiment W-94 is the base case with no additive. Use of the additive A24 reduces the activity by one-half. The most interesting results are obtained with related additives in experiments W-70, 97, 99, and 103, which show a broad range of activity. The increased activity and subsequent increase in ethanol selectivity observed for some of these additives may possibly be due to their effects on the metal components which facilitate the hydrogen activation process, thus leading to increased acetaldehyde formation.

A more detailed presentation of the data is given in Table 23. The catalyst system without additive (experiment W-94) generates about 20% ethanol and equivalents, while addition of A25 (run W-99) results in a substantial increase in ethanol and its equivalents. Run W-105 is a repeat of run W-99 but with the H_2:CO ratio increased to 2:1. In this case, ethanol and its equivalents account for nearly 50% of the products.

4.1.2.3 Screening of Other Catalysts for Homologation

Several other potential catalysts were screened for activity, as shown in Table 24. In all cases the reaction conditions were 140°C and 975 psig (H_2/CO = 1:1). Many catalysts tested were inactive under these mild conditions. Others generated only small amounts of ethanol, with higher selectivities to other oxygenates.

Table 22. Effects of Catalyst Additives on Homologation

SGHAM-W-#	Additive	Uptake,psi	Time, hr	Ethanol + Eq.,%
94	-	900	1.2	20.0
95	A24	500	1.1	6.1
70	A21	615	2.2	7.6
97	A8	1086	1.6	20.6
99	A25	2510	1.7	38.5
103	A26	490	1.0	4.7

See Table 23 for experimental details.

Key to Tables 23 and 24

SGHAM-W-#	
1 Catalyst	Complex used as catalyst precursor.
2 mmol	Amount of complex added, in mmoles.
3 Cocatalyst	Complex used as cocatalyst.
4 mmol	Amount added, in mmoles.
5 Additive	Additive used in reaction.
6 mmol	Amount added, in mmoles.
7 Promoter	Promoter employed for reaction.
8 mmol	Amount added, in mmoles.
9 MeOH, mL	Amount of methanol used, mL.
10 Pressure, psi	Reaction pressure, psi.
11 H_2/CO	Synthesis gas volume (molar) ratio.
12 Temp.,°C	Reaction temperature.
13 Time, hrs	Reaction time in hours.
14 Uptake, psi	Gas uptake in psi.
15 Wt.% EtOH	Amount of ethanol produced, in wt.%.
16 Wt.% EtOH Eq.	Equivalents of ethanol in other compounds.
17 Wt.% Other Ox.	Other oxygenates produced, in wt.%.

Table 23. Methanol Homologation Experiments

	SGHAM-W-#	68	70	71	75	77	78
1	Catalyst	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$
2	mmol	2.0	2.0	2.0	2.0	2.0	2.0
3	Cocatalyst	C4	C4	C4	C4	C4	C4
4	mmol	2.0	2.0	2.0	2.0	2.0	2.0
5	Additive	A20	A21	A20	A22	A23	A20
6	mmol	2.0	2.0	4.0	2.0	2.0	2.0
7	Promoter	A28	A28	A28	A28	A28	A28
8	mmol	40	40	40	40	40	40
9	MeOH, mL	42.5	42.5	42.5	42.5	42.5	42.5
10	Pressure, psi	975	975	975	975	975	975
11	H_2/CO	1:1	1:1	1:1	1:1	1:1	1:1
12	Temp.,°C	140	140	140	140	140	105
13	Time, hrs	1.0	2.2	0.5	0.75	0.75	2.5
14	Uptake, psi	800	615	625	838	681	404
15	Wt.% EtOH	2.5	3.1	2.1	3.2	3.2	0
16	Wt.% EtOH Eq.	6.1	4.5	8.6	13.2	12.0	0
17	Wt.% Other Ox.	91.4	92.4	89.3	83.6	84.8	100

Experimental procedure: B(2); Analytical procedure: C(1); Key on page 105.

Table 23. Methanol Homologation Experiments (Cont'd)

	SGHAM-W-#	81	92	94	95	97	99
1	Catalyst	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$	$RuCl_3$
2	mmol	4.0	2.0	2.0	2.0	2.0	2.0
3	Cocatalyst	C4	C4	C4	C4	C4	C4
4	mmol	2.0	2.0	2.0	2.0	2.0	2.0
5	Additive	A22	A20	-	A24	A8	A25
6	mmol	4.0	2.0	-	2.0	2.0	2.0
7	Promoter	A28	A28	A28	A28	A28	A28
8	mmol	40	40	40	40	40	40
9	MeOH, mL	42.5	42.5	42.5	42.5	42.5	42.5
10	Pressure, psi	975	975	975	975	975	975
11	H_2/CO	1:1	1:1	1:1	1:1	1:1	1:1
12	Temp.,°C	140	165	165	140	140	140
13	Time, hrs	0.55	0.3	1.2	1.1	1.6	1.7
14	Uptake, psi	491	310	930	500	1086	2510
15	Wt.% EtOH	1.0	0.5	7.2	0.5	10.7	18.0
16	Wt.% EtOH Eq.	1.7	4.8	12.8	5.6	9.9	20.5
17	Wt.% Other Ox.	97.3	94.7	80.0	93.9	79.4	61.5

Experimental procedure: B(2); Analytical procedure: C(1); Key on page 105.

Table 23. Methanol Homologation Experiments (Cont'd)

	SGHAM-W-#	103	105
1	Catalyst	$RuCl_3$	$RuCl_3$
2	mmol	2.0	2.0
3	Cocatalyst	C4	C4
4	mmol	2.0	2.0
5	Additive	A26	A25
6	mmol	2.0	2.0
7	Promoter	A28	A28
8	mmoles	40	40
9	MeOH, mL	42.5	42.5
10	Pressure, psi	975	975
11	H_2/CO	1:1	2:1
12	Temp.,°C	140	140
13	Time, hrs	1.0	1.1
14	Uptake, psi	490	950
15	Wt.% EtOH	0.5	25.0
16	Wt.% EtOH Eq.	4.2	21.3
17	Wt.% Other Ox.	95.3	53.7

Experimental procedure: B(2); Analytical procedure: C(1); Key on page 105.

Table 24. Screening of Other Catalysts for Homologation

	SGHAM-W-#	73	82	83	84	85	88
1	Catalyst	$RuCl_3$	Co[a]	$RuCl_3$	Co[a]	Pd[b]	Mn[c]
2	mmol	2.0	2.0	2.0	2.0	2.0	2.0
3	Cocatalyst	-	-	Co[a]	C4	C4	C4
4	mmol	-	-	2.0	2.0	2.0	2.0
5	Additive	A20	A20	A20	A20	A20	A20
6	mmol	2.0	2.0	2.0	2.0	2.0	2.0
7	Promoter	A28	A28	A28	A28	A28	A28
8	mmol	40	40	40	40	40	40
9	MeOH, mL	42.5	42.5	42.5	42.5	42.5	42.5
10	Press., psi	975	975	975	975	975	975
11	H_2/CO	1:1	1:1	1:1	1:1	1:1	1:1
12	Temp.,°C	140	140	140	140	140	140
13	Time, hrs	1.5	2.0	1.0	1.5	1.5	1.66
14	Uptake, psi	0	0	0	10	10	650
15	Wt.% EtOH	0	0	0	0	0	1.0
16	Wt.% EtOH Eq	0	2.0	0	3.0	2.0	3.0
17	Wt.% Oth.Ox.	0	98.0	0	97.0	98.0	96.0

Experimental procedure: B(2); Analytical procedure: C(1); Key on page 105.

[a] $Co(OAc)_2 \cdot 4H_2O$.

[b] $Pd(OAc)_2.2H_2O$.

[c] $Mn(NO_3)_3 \cdot 4H_2O$.