

4.1.1.7 Comparison of Additives LaCl_3 and SmCl_3

Additive SmCl_3 has been found to be a useful promoter in other reactions involving syngas. We therefore have made several runs in which pure SmCl_3 , pure LaCl_3 , or a mixture of the two was used to determine if significant differences or synergism between the two exists. The data are given in Table 5. The runs with pure LaCl_3 and 1:1 $\text{LaCl}_3:\text{SmCl}_3$ both gave a total rate to alcohol of about 0.8 M/h. The first experiment with pure SmCl_3 gave a rate over double that, primarily due to a very large methanol rate. A repeat of this SmCl_3 run gave a rate of 0.87 M/h, so it seems likely that the high rate in the first run was the result of an unnoticed contamination. Selectivities in the three good runs were very similar. The promoting abilities of LaCl_3 and SmCl_3 thus appear to be very similar in general.

4.1.1.8 Comparison of Additives SmI_3 and SmCl_3

Additive SmI_3 is similar in composition to the beneficial additive SmCl_3 , and it was expected that the response of the Ru/I system to it would be similar. However, two runs conducted with SmI_3 showed significantly reduced activity as compared with similar runs with SmCl_3 , as shown in Table 6. Reasons for this difference are not understood, although impurities in the compounds added may be a possibility.

Key to Tables 5, 6, 7, and 8

SGHAM-B-#

1 Catalyst	Complex used as catalyst precursor.
2 mmol Ru	Amount of ruthenium used, mmoles.
3 Solvent	Reaction solvent, NMP = N-methylpyrrolidone.
4 mL	Amount of solvent employed.
5 Additive	Additive or additives used.
6 mmol	Amounts of additives used, mmoles.
7 Promoter	Additional promoters or additives used.
8 mmol	Amounts of promoter, mmoles.
9 Pressure, psi	Reaction pressure, psig.
10 H ₂ /CO	Syngas composition.
11 Temp, °C	Reaction temperature.
12 Time, hrs	Reaction time in hours.
13 Uptake, psi	Gas uptake during reaction in psi.
14 MeOH, M/h	Rate to methanol in moles/liter solution/hour.
15 EtOH, M/h	Rate to ethanol.
16 n-PrOH, M/h	Rate to n-propanol.
17 i-PrOH, M/h	Rate to i-propanol.
18 n-BuOH, M/h	Rate to n-butanol.
18 i-BuOH, M/h	Rate to i-butanol.
20 Alcohols, M/h	Rate to total alcohols.

Table 5. Comparison of Additives LaCl_3 and SmCl_3

SGHAM-B-#	49	50	51	55
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol Ru	6	6	6	6
3 Solvent	NMP	NMP	NMP	NMP
4 mL	75	75	75	75
5 Additive	$\text{LaCl}_3/\text{SmCl}_3$	SmCl_3	LaCl_3	SmCl_3
6 mmol	3/3	6	6	6
7 Promoter	I_2/NaI	I_2/NaI	I_2/NaI	I_2/NaI
8 mmol	5/15	5/15	5/15	5/15
9 Pressure, psi	6000	6000	6000	6000
10 H_2/CO	1.0	1.0	1.0	1.0
11 Temp, °C	230	230	230	230
12 Time, hrs	2.27	1.94	0.8	0.87
13 Uptake, psi	6000	6000	6000	6000
14 MeOH, M/h	0.26	1.06	0.13	0.24
15 EtOH, M/h	0.44	0.75	0.51	0.47
16 n-PrOH, M/h	0.07	0.09	0.09	0.09
17 i-PrOH, M/h	0.02	0.01	0.002	0.01
18 n-BuOH, M/h	0.01	0.01	0.02	0.02
19 i-BuOH, M/h	0.03	0.02	0.04	0.04
20 Alcohols, M/h	0.83	1.94	0.80	0.87

Experimental procedure: B(1); Analytical procedure: C(2); Key on page 41.

Table 6. Comparison of Additive SmI_3 with SmCl_3

SGHAM-B-#	76	77	50
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol Ru	6	6	6
3 Solvent	NMP	NMP	NMP
4 mL	75	75	75
5 Additive	$\text{SmI}_3 \cdot 3\text{H}_2\text{O}$	$\text{SmI}_3 \cdot 3\text{H}_2\text{O}$	SmCl_3
6 mmol	6	6	6
7 Promoter	I_2/NaI	I_2/NaI	I_2/NaI
8 mmol	5/15	5/15	5/15
9 Pressure, psi	6000	6000	6000
10 H_2/CO	1:1	1:1	1:1
11 Temp, °C	230	230	230
12 Time, hrs	3.00	3.00	1.94
13 Uptake, psi	3330	2960	6000
14 MeOH, M/h	0.02	0.02	1.06
15 EtOH, M/h	0.11	0.01	0.75
16 n-PrOH, M/h	0.03	0.03	0.09
17 i-PrOH, M/h	0.01	0.00	0.01
18 n-BuOH, M/h	0.01	0.01	0.01
19 i-BuOH, M/h	0.01	0.01	0.02
20 Alcohols, M/h	0.19	0.08	1.94

Experimental procedure: B(1); Analytical procedure: C(2); Key on page 41.

4.1.1.9 Use of Ruthenium Cyclopentadienyl Complexes

For many metals, cyclopentadienyl ligands are among the most tenacious ligands known, and their steric bulk can often alter the nature of reactions taking place on the metal. We have synthesized two complexes, $[(C_5H_5)RuI(CO)_2]$ and $[(C_5Me_5)Ru(CO)_2]_2$, by published procedures and screened them for activity. We had hoped to learn two things. First, will complexes of this type survive the conditions employed in the catalytic runs (230-250°C and 6000 psi syngas), and if they do, will they give different selectivity from the usual source of ruthenium, $Ru_3(CO)_{12}$. Data for these runs are given in Table 7. In general, it can be seen that overall activity is reduced compared to a run using $Ru_3(CO)_{12}$, indicating that the complexes must survive to some extent. Selectivity to higher alcohols is slightly increased, but this usually happens when the overall activity drops. These results indicate that the complexes do survive to some extent at reaction conditions, and the cyclopentadienyl ligands mainly function as inhibitors. Two runs in pure dicyclopentadiene solvent were also attempted to try to swamp the ruthenium in a sea of ligands. Two side-reactions of the solvent prevented us from gaining any useful knowledge.

Table 7. Use of Ruthenium Cyclopentadienyl Complexes

SGHAM-B-#	37	38	39	40
1 Catalyst	CpRu(CO) ₂ I	CpRu(CO) ₂ I	[Cp*Ru(CO) ₂] ₂	CpRu(CO) ₂ I
2 mmol Ru	6	6	6	6
3 Solvent	NMP	NMP	NMP	NMP
4 mL	75	75	75	75
5 Additive	I ₂	I ₂	I ₂	I ₂
6 mmol	5	5	5	5
7 Promoter	NaI	NaI	NaI	NaI
8 mmol	15	15	15	15
9 Pressure, psi	6000	6000	6000	6000
10 H ₂ /CO	1.0	1.0	1.0	1.0
11 Temp, °C	230	230	230	250
12 Time, hrs	3	3	2.55	3
13 Uptake, psi	4150	5670	6000	4710
14 MeOH, M/h	0.16	0.17	0.34	0.004
15 EtOH, M/h	0.23	0.27	0.45	0.13
16 n-PrOH, M/h	0.04	0.05	0.06	0.03
17 i-PrOH, M/h	0.003	0.001	0.02	0.001
18 n-BuOH, M/h	0.01	0.01	0.01	0.01
19 i-BuOH, M/h	0.03	0.04	0.02	0.02
20 Alcohols, M/h	0.47	0.54	0.90	0.2

Experimental procedure: B(1); Analytical procedure: C(2); Key on page 41.

Table 7. Use of Ruthenium Cyclopentadienyl Complexes (Cont'd)

SGHAM-B-#	41	42	43	46	48
1 Catalyst	Cp*Ru ^a	Cp*Ru ^a	Cp*Ru ^a	Cp*Ru ^a	CpRu(CO) ₂ I
2 mmol Ru	6	6	6	6	6
3 Solvent	NMP	NMP	NMP	NMP	NMP
4 mL	75	75	75	75	75
5 Additive	I ₂	I ₂	I ₂	I ₂	I ₂
6 mmol	5	5	5	5	5
7 Promoter	NaI	NaI	NaI	NaI	NaI
8 mmol	15	15	15	15	15
9 Pressure, psi	6000	6000	6000	6000	6000
10 H ₂ /CO	1.0	1.0	1.0	1.0	1.0
11 Temp, °C	250	240	220	230	230
12 Time, hrs	2.75	2.58	3	3	1.42
13 Uptake, psi	6000	6000	4950	5970	6100
14 MeOH, M/h	0.01	0.22	0.36	0.16	0.53
15 EtOH, M/h	0.13	0.26	0.24	0.28	0.28
16 n-PrOH, M/h	0.03	0.03	0.03	0.04	0.05
17 i-PrOH, M/h	0.004	0.001	0.004	0.002	0.01
18 n-BuOH, M/h	0.004	0.004	0.01	0.01	0.01
19 i-BuOH, M/h	0.01	0.01	0.02	0.02	0.05
20 Alcohols, M/h	0.19	0.52	0.66	0.51	0.93

Experimental procedure: B(1); Analytical procedure: C(2); Key on page 41.

^a [(C₅Me₅)Ru(CO)₂]₂.

4.1.1.10 Effect of Added Water

The stoichiometry of the reaction of syngas to give C₂+ alcohols requires that water be formed. Water is not usually observed in the product mix of Task 1 runs presumably because it is converted to CO₂ and H₂ by the action of CO and metal catalysts in the water-gas shift reaction. However, when we added 20 volume % water to the initial catalyst/solvent charge of a standard Ru/I/LaCl₃ run and subjected the mixture to normal catalytic conditions, the rate of gas uptake was quite slow in comparison to a similar run without the water. The weight of the recovered liquid was much lower than normal, and the primary liquid carbon-containing product was methanol. Karl Fischer titration of the liquid showed that it still contained 7% water. At these relatively high levels, water apparently significantly inhibits the conversion of syngas and especially the formation of higher alcohols by this catalyst system. Water is probably deactivating the catalyst precursor; but it is possible that the rate at which water can be removed by shifting limits the rate of formation of higher alcohols.

Additional experiments were therefore carried out with smaller amounts of added water. The data from these runs (see Table 8) show that even relatively small amounts of water (7% by volume) can cause substantial alteration in catalytic activity. Water by-product formed during normal catalytic runs never builds up to this level; it is apparently converted to CO₂ through the water-gas shift reaction as it is formed. These results indicate the significant benefit of being able to carry out the water-gas shift reaction under normal catalytic conditions, since it prevents water from accumulating and causing catalyst rate reductions.

Table 8. Effects of Water Addition to Ruthenium Catalyst

SGHAM-B-#	57	78	79	50
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol Ru	6	6	6	6
3 Solvent	NMP	NMP	NMP	NMP
4 mL	75	75	75	75
5 Additive	$\text{LaCl}_3/\text{H}_2\text{O}$	$\text{LaCl}_3/\text{H}_2\text{O}$	$\text{LaCl}_3/\text{H}_2\text{O}$	LaCl_3
6 mmol	6/15 mL	6/5 mL	6/10 mL	6
7 Promoter	I_2/NaI	I_2/NaI	I_2/NaI	I_2/NaI
8 mmol	5:15	5:15	5:15	5:15
9 Pressure, psi	6000	6000	6000	6000
10 H_2/CO	1:1	1:1	1:1	1:1
11 Temp, °C	230	230	230	230
12 Time, hrs	3.00	3.00	3.00	1.94
13 Uptake, psi	2470	5650	3510	6000
14 MeOH, M/h	0.68	0.57	0.74	1.06
15 EtOH, M/h	0.09	0.33	0.36	0.75
16 n-PrOH, M/h	0.02	0.01	0.01	0.09
17 i-PrOH, M/h	0.06	0.01	0.01	0.01
18 n-BuOH, M/h	0.02	0.01	0.01	0.01
19 i-BuOH, M/h	0.01	0.01	0.01	0.02
20 Alcohols, M/h	0.88	0.94	1.14	1.94

Experimental procedure: B(1); Analytical procedure: C(2); Key on page 41.

4.1.1.11 Effects of Various Solvents on Ruthenium Catalysts

Other work in this project has shown that certain solvents can significantly stabilize cobalt catalysts for syngas conversion. Therefore further tests have been carried out with related solvents in the presence of other metal catalyst systems which exhibit good activity for syngas conversion. Results are presented in Table 9. Tests with the active iodide-promoted ruthenium system in the solvent veratrole (1,2-dimethoxybenzene) yielded methanol and ethanol, but degradation of veratrole into 2-methoxyphenol was noted. Longer reaction times led to increased solvent degradation. Nevertheless, the good catalyst stability observed in this system indicated that the 2-methoxyphenol product might be useful as a solvent. Results indicate that Ru-NaI systems yield mixtures of alcohols in the 2-methoxyphenol solvent. The production of fuel alcohols in this solvent appears to be greater than in more conventional solvents such as sulfolane. Unfortunately, solvent decomposition was also detected for 2-methoxyphenol-based systems.

Key to Tables 9 and 10

SGHAM-V-#

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

Table 9. Effects of Solvents on Ruthenium Catalysts

SGHAM-V-#	3-38	3-42	3-57	3-70
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	2.0	2.0	6.0	6.0
3 Solvent	Veratrole	Veratrole	Sulfolane	2-Methoxyphenol
4 mL	75	75	75	75
5 Promoter	NaI	NaI	NaI	NaI
6 mmol	20.0	20.0	20.0	20.0
7 Pressure, psi	6000	3000	6000	6000
8 H_2/CO	1:1	1:1	1:1	1:1
9 Temp, °C	240	240	240	240
10 Time, hrs	2.5	5.5	4.0	3.0
11 Wt.% MeOH	4.7	3.5	1.6	2.8
12 Wt.% EtOH	1.8	1.7	0.9	1.4
13 Solids	some	trace	none	some
14 Solv. Decomp.	3.0	15.0	-	14.3

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 50.

4.1.1.12 Effects of Lewis Acids on Ruthenium Catalysts

The possibility of shifting the selectivity of Ru-NaI-veratrole or -2-methoxyphenol systems away from methanol and toward higher alcohols was tested by addition of SnI_2 , ZnCl_2 , and $\text{ZnCl}_2\text{-Rh}(\text{CO})_2(\text{acac})$ to the system. Results are shown in Table 10. The activity was inhibited and solvent decomposition enhanced in all cases. Similar results were obtained in sulfolane solvent, but an increase in the amount of other oxygenates was noted. These results may be a consequence of enhanced formaldehyde condensation due to the added promoters. The activity of these mixtures and the stability of the veratrole and 2-methoxyphenol solvents, however, are less than desirable.

The examination of formalin (30% aqueous formaldehyde) as an added reagent or solvent for catalytic reactions directed toward fuel alcohol production was suggested by the results above. Methanol was the only alcohol detected in large amounts with Ru-NaI- ZnCl_2 or - HfCl_4 mixtures containing formalin. A large weight loss (ca. 50%) was noted in the presence of HfCl_4 , which appears to result from the active operation of the water-gas shift reaction and from the conversion of formaldehyde into non-alcohol products.

Table 10. Effects of Lewis Acids on Ruthenium Catalysts

SGHAM-V-#	3-51	3-61	3-78	3-86
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	Ru_3/Rh
2 mmol	2.0	6.0	6.0	6.0/3.0
3 Solvent	Veratrole	Sulfolane	2-Methoxyphenol	2-Methoxyphenol
4 mL	75	75	75	75
5 Promoter	NaI/SnI_2	NaI/SnI_2	NaI/ZnCl_2	NaI/ZnCl_2
6 mmol	20/4.5	20/4.5	20/33	20/33
7 Pressure, psi	3000	6000	6000	6000
8 H_2/CO	1:1	1:1	1:1	1:1
9 Temp, °C	240	240	240	240
10 Time, hrs.	5.5	2.0	3.0	3.0
11 Wt.% MeOH	0.30	0.60	0.30	trace
12 Wt.% EtOH	0.70	0.10	0.60	0.20
13 Solids	none	none	none	much
14 Solv. Decomp.	21.0	5.0	65	80

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 50.

Table 10. Effects of Lewis Acids on Ruthenium Catalysts (Cont'd)

SGHAM-V-#	3-90	3-97	3-101
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	6.0	6.0	6.0
3 Solvent	Formalin	Formalin	H_2O
4 mL	75	75	75
5 Promoter	NaI/ZnCl_2	NaI/HfCl_4	NaI/HfCl_4
6 mmol	20/33	20/20	20/20
7 Pressure, psi	6000	6000	6000
8 H_2/CO	1:1	1:1	1:1
9 Temp, °C	240	240	240
10 Time, hrs	2.5	2.0	2.0
11 Wt.% MeOH	22.8 ^a	10.0 ^a	-
12 Wt.% EtOH	0.5	-	0.5
13 Solids	none	much	much
14 Solv. Decomp.	-	42	7

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 50.

^a Formed mainly as a result of solvent decomposition.

4.1.1.13 Lanthanide Promoters in Phosphonium Salt Solvent

In catalytic systems for conversion of syngas to alcohols and polyols using ruthenium catalysts, the solvents used are usually polar organic solvents which are inert to hydrogenation. Recently, there have been reports of using molten tertiary phosphonium salts as solvents for these systems [1]. There are certain advantages which may be possible in using these molten salts as solvents. Polar solvents are particularly good reaction solvents for the above mentioned catalytic systems, and molten phosphonium salts certainly are polar media. Further, since these salts are non-volatile and are solids at ambient temperature, the separation of organic products from the reaction medium could be easier than when using other organic solvents.

It was observed earlier that the addition of certain lanthanide complexes to ruthenium catalytic systems increased the C_2+ content of the organic product. In certain cases, the rate of alcohol formation also increased. Therefore it was decided to carry out screening experiments to examine the effects of adding these catalyst components to ruthenium catalytic systems in the molten phosphonium salts as solvent(s).

The major organic products from the catalytic conversion of syngas to alcohols using ruthenium catalysts in molten $P(n-Bu)_4Br$ are methanol and ethanol. Together, they account for greater than 95% by weight of the products. The ratio of ethanol to methanol is 0.57.

When additive $LaCl_3$ was added to the catalytic system, the rate of formation of both methanol and ethanol decreased, but the ratio of ethanol to methanol increased. Since the amount of ethanol produced also decreased, the addition of $LaCl_3$ did not enhance the formation of ethanol. It was thought that the alcohol formation rate decrease might be due to the possible increase in acidity of the solution. Therefore, experiments with added bases

were carried out. Indeed, the results (see Table 11) showed that with the addition of either proton sponge or potassium carbonate, the alcohol formation rates are better than with no additive. More importantly, the ratio of ethanol to methanol is also better, as it increased from 0.57 to 1.2 in both experiments with an added base.

Additive LuCl_3 seemed to have the effect of enhancing the rate as well as the ratio of ethanol to methanol (see Table 12), even in the absence of an added base.

1. Knifton, J.F. *Platinum Metals Rev.*, 1985, **29**, 63; and references therein.

Key to Tables 11 and 12

SGHAM-L-#

1 Catalyst	Catalyst precursor.
2 mmol	Amount of precursor in mmoles.
3 Solvent	Solvent employed.
4 mL/g	Amount of solvent in mL or grams.
5 Additive	Additive employed.
6 mmol	Amount of additive used.
7 Base added	Basic promoter used.
8 mmol	Amount of base added.
9 Press., psi	Reaction pressure.
10 H ₂ /CO	Synthesis gas volume (molar) ratio.
11 Temp., °C	Reaction temperature.
12 Time, hr	Reaction time in hours.
13 MeOH, g	Weight of methanol produced, in grams.
14 EtOH, g	Weight of ethanol produced, in grams.
15 EtOH/MeOH	Ethanol/methanol weight ratio.

Table 11. Effects of LaCl₃ Catalyst Additive

SGHAM-L-#	1-47	1-43	1-45	1-41
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	1.25	1.25	1.25	0.63
3 Solvent	PBu ₄ Br	PBu ₄ Br	PBu ₄ Br	PBu ₄ Br
4 mL/g	15.0g	15.0g	15.0g	15.0g
5 Additive	none	LaCl ₃	LaCl ₃	LaCl ₃
6 mmol	-	0.70	0.70	0.40
7 Base added	none	none	Proton sponge	K ₂ CO ₃
8 mmol	-	-	2.1	1.5
9 Press.,psi	5000	5000	5000	5000
10 H ₂ /CO	1.0	1.0	1.0	1.0
11 Temp.,°C	230	230	230	230
12 Time,hr	3.0	3.0	3.0	3.5
13 MeOH,g	3.0	0.56	2.6	1.9
14 EtOH,g	1.7	1.2	3.2	2.2
15 EtOH/MeOH	0.57	2.1	1.2	1.2

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 57.

Table 12. Effects of LuCl_3 Catalyst Additive

SGHAM-L-#	1-47	1-27	1-22
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	0.33
3 Solvent	PBu_4Br	PBu_4Br	PBu_4Br
4 mL/g	15.0g	15.0g	15.0g
5 Additive	none	LuCl_3	LuCl_3
6 mmol	-	0.70	0.70
7 Base added	none	none	none
8 mmol	-	-	-
9 Press., psi	5000	5000	5000
10 H_2/CO	1.0	1.0	1.0
11 Temp., °C	230	230	230
12 Time, hr	3.0	6.0	3.0
13 MeOH, g	3.0	3.2	0.40
14 EtOH, g	1.7	4.0	0.81
15 EtOH/MeOH	0.57	1.3	2.0

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 57.