OPTIMUM HIGHER ALCOHOL MIXTURES FOR FUELS FROM SYNGAS. SIXTH QUARTERLY TECHNICAL PROGRESS REPORT, JANUARY-MARCH 1986

UNION CARBIDE CORP., SOUTH CHARLESTON,
WV. RESEARCH AND DEVELOPMENT DEPT

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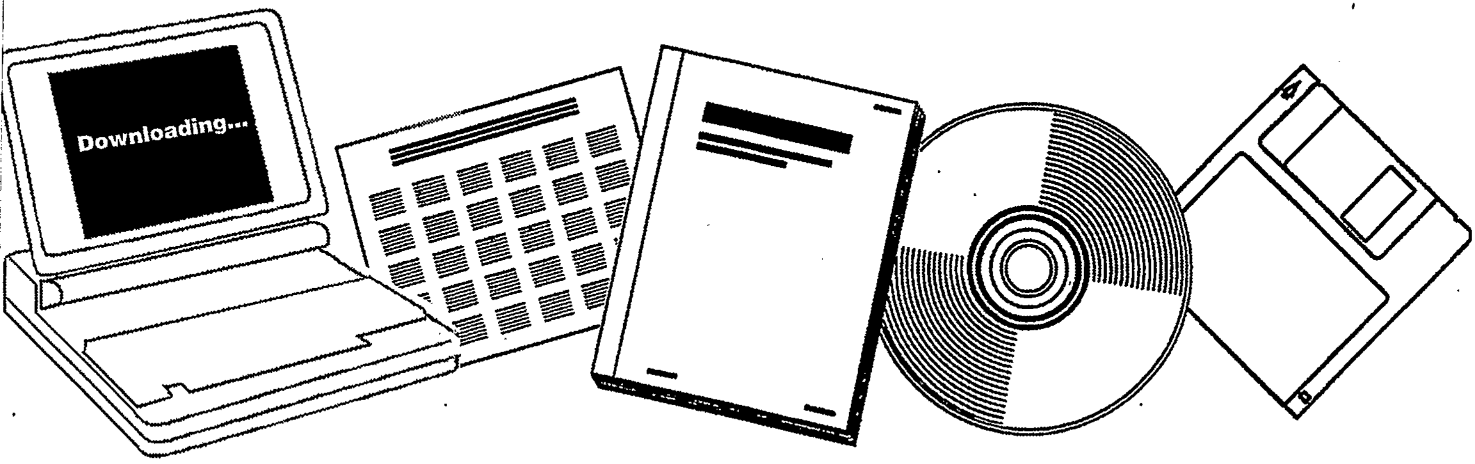

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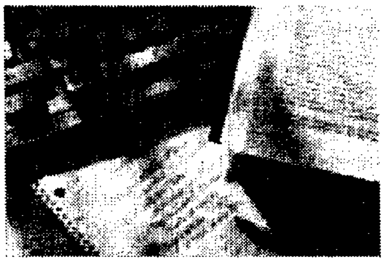

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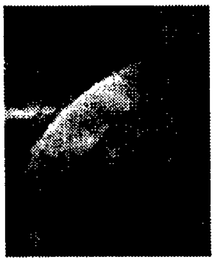

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SIXTH QUARTERLY TECHNICAL PROGRESS REPORT
DOE CONTRACT DE-AC22-84PC70022
OPTIMUM HIGHER ALCOHOL MIXTURES FOR FUELS FROM SYNGAS

APRIL 28, 1986

ENGINEERING, MANUFACTURING AND TECHNOLOGY SERVICES DIVISION
UNION CARBIDE CORPORATION
RESEARCH AND DEVELOPMENT DEPARTMENT
SOUTH CHARLESTON, WEST VIRGINIA

TECHNICAL PROGRESS REPORT
DE-AC22-84PC70022

Sixth Quarterly Report
January - March 1986

Optimum Higher Alcohol Mixtures for Fuels from Syngas

~~Patent Hold~~

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PATENT CLEARED BY CHICAGO OPC

ON MAY 12, 1986

Engineering, Manufacturing and Technology Services Division

Union Carbide Corporation
South Charleston Technical Center
South Charleston, West Virginia 25303

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ON MAY 12, 1986

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I. CONTRACT OBJECTIVE

The objective of the contract is to develop and evaluate novel homogeneous catalytic systems for the selective conversion of low H_2/CO-ratio syngas to alcohol fuel extenders.

II. SCHEDULE

The contract work was planned for the 24-month period beginning October 1, 1984.

Work on the project is divided into three tasks.

Task 1 is the study and development of a ruthenium-based catalytic system for alcohol production discovered at Union Carbide. The effects of reaction components, including additives, co-catalysts, and solvents, on catalyst productivity and selectivity are being investigated. Task 1 work will continue throughout the contract period.

Task 2 is the search for novel syngas conversion catalysts with improved performance. The major direction is toward metal systems not previously known to have significant catalytic activity in homogeneous CO hydrogenation reactions. Work on Task 2 will be pursued only at a minimal level during the remainder of the contract, being essentially complete.

Task 3 is a more detailed study of the most promising catalyst systems identified in Tasks 1 and 2. Investigations are to be carried out on both fundamental and process levels. Work in Task 3 is proceeding on the novel methanol homologation system discovered under this contract.

III. ORGANIZATION

The production of optimum higher alcohol mixtures for fuels from syngas by homogeneous catalysts is the goal of a research and development program conducted by the Engineering, Manufacturing and Technology Services Division of Union Carbide Corporation.

The work is performed at Union Carbide Corporation's South Charleston Technical Center, South Charleston, West Virginia 25303.

Principal investigator is Dr. B. Duane Dombek.

Program manager is Dr. Donald C. Best.

IV. SUMMARY OF PROGRESS

A. Task 1: Modification of Ruthenium Catalyst System

Because of their reactivity and selectivity in syngas-based reactions producing higher alcohols, ruthenium catalysts are being investigated more thoroughly in Task 1 of this contract. Research has been done on several ruthenium-based catalyst systems during this quarter.

Much of this work has focused on the direct conversion of syngas to higher alcohols in molten quaternary phosphonium salts as solvents; additional work has been done in neutral organic solvents. Several additives have been identified which alter the selectivity and/or the activity of the basic system. Most interesting is the observation that one of these additives allows the formation of alcohol products at good rates under significantly lower pressures than previously observed; substantial activity is observed at 3000 psi of syngas pressure.

Experiments in this portion of the project were carried out using Procedures B(a) and B(b) outlined in Appendix B, and product analyses were carried out according to Procedure C(a) of Appendix C. A more complete description of these experiments and tables of data are given in Appendix D.

B. Task 2: Development of Novel Catalysts

Earlier work performed as a part of this project has shown that catalyst systems composed of copper(I) salts and sodium methoxide can convert syngas to methanol and methyl formate at very high rates under extremely mild conditions (100°C, 1000 to 2000 psi). Higher alcohols are not produced and the catalyst has a limited lifetime, but the high activity and the mild conditions under which they operate prompted us to further investigate these systems with the goal of gaining a fuller understanding of the mechanism by which they operate. This information might then allow us to extend the catalyst lifetime and shift the products to higher alcohols.

During the past quarter work has continued on understanding the nature of the active copper species and on discovering the cause of the catalyst deactivation. The reactivity of the complex bis(triphenylphosphine)copper(I) tetrahydroborate in the presence of methoxide as well as the high activity of independently synthesized copper hydride in the presence of methoxide point to the involvement of both a copper hydride species and methoxide in the catalytic system. Copper hydride also showed some activity with sodium ethoxide, which is not normally a suitable base for this system.

Deactivation of the catalyst system seems to be closely tied to loss of methoxide and formation of formate. Water in the solvent was suspected to play a role in this transformation, but work in carefully dried diethyl carbitol and tetrahydrofuran has demonstrated that water is not the problem. A related catalyst system, CuCRA, containing copper(I) iodide, sodium hydride and sodium t-pentoxide, was investigated and found to be unreactive under the usual conditions.

Work on this copper-based system has been largely completed, but is continuing at a low level to gain understanding and prevent the loss of methoxide.

Experiments in this portion of the project were carried out following Procedure B(c) of Appendix B, and analyses were conducted according to Procedure C(b) of Appendix C. Further information and tables of data are given in Appendix D.

C. Task 3: Further Study of Superior Catalysts

Further investigations have been carried out in an effort to gain basic information on the catalytic chemistry involved in the novel methanol homologation system discovered earlier in this project. Logical extensions of this system are also under investigation, based on the knowledge already gathered. Experiments in this basic investigation of the homologation system were conducted following Procedure B(d) of Appendix B, and analytical determinations were carried out according to Procedure C(c) of Appendix C.

In preparation for statistically designed sets of experiments to be performed as part of Task 3, the methanol homologation system has been scaled up to a 300 mL autoclave, using 150 mL methanol rather than the previous 40 mL. No problems have been encountered in the scale-up. Results analogous to those obtained on the smaller scale have been seen on the larger scale under similar conditions. As soon as appropriate limits have been worked out, one or more sets of statistically designed experiments will be performed in order to optimize and learn more about the methanol homologation system.

Experiments involving catalyst scale-up were carried out according to Procedure B(e) of Appendix B. Analytical procedures are described in Procedure C(d) of Appendix C. Further experimental information and tables of data are presented in Appendix D.

V. CHANGES

There were no contract changes during this quarter.

VI. FUTURE WORK

Work during the next quarter will continue on Task 1, with the goal of improving ruthenium catalysts for the direct selective conversion of syngas to alcohols. Task 2 research involving other metal catalysts will be continued only at a low level.

Work on Task 3 will continue. This task involves the more thorough investigation of system(s) identified in Tasks 1 and 2 as the most deserving of further work. The system presently under investigation is the novel ruthenium-based methanol homologation system discovered under this contract.

Don C Best

D. C. Best

Program Manager

APPENDIXES

By S. L. Gipson, T. W. Leung, and R. W. Wegman

Appendix A. USE OF CODE SYSTEM

A code system is being 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 co-catalysts.

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.

The following coded information is included in this report:

A3: A catalyst additive
A9: A catalyst additive
A25: A catalyst additive
A28: A catalyst additive
A30-A37: Catalyst additives
A38-A39: Metal-containing catalyst additives
A40-A44: Nitrogen-containing catalyst additives
A45-A46: Catalyst additives
C7-C17: Metal-containing catalyst precursors

Appendix B. PROCEDURES FOR CATALYST TESTING

Catalyst tests carried out under this contract have been assigned reference numbers of the form SGHAM-X-y, where the character X identifies the appropriate researcher and the numeral y specifies the serial number of the experiment.

PROCEDURE B(a).

Into a specially designed glass liner, the catalyst and the additive(s) were charged along with 15.0g of $P(n\text{-}Bu)_4Br$. 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 and vented. The system was then pressurized to 1000 psig syngas and it was 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 vented and purged with nitrogen. The glass liner was taken out and the content analyzed by GC methods.

PROCEDURE B(b).

In experiments which used NMP as the solvent, 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 then 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(c).

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 further.

PROCEDURE B(d).

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(e).

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 was then raised to the desired operating temperature and the pressure raised to the desired operating pressure. 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 further.

Appendix C. PROCEDURES FOR PRODUCT ANALYSIS

PROCEDURE C(a).

Liquid organic product analyses were performed on a Hewlett Packard gas chromatographic instrument, model 5840A, equipped with a 30m x 0.32mm Durabond 1701 capillary column with initial temperature and final temperature set at 40 and 280°C, respectively.

PROCEDURE C(b).

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

PROCEDURE C(c).

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

PROCEDURE C(d).

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

Appendix D. EXPERIMENTAL DATA

TABLE OF CONTENTS

I. TASK 1: Modification of Ruthenium Catalyst Systems

II. TASK 2: Development of Novel Catalysts

III. TASK 3: Further Study of Superior Catalysts

I. TASK 1: Modification of Ruthenium Catalyst Systems

A. Introduction

The good characteristics of ruthenium-based catalysts for syngas conversion were the basis for further investigation of these catalysts under Task 1 of this project. Ruthenium catalysts studied earlier in the contract have shown good activity, selectivity to higher alcohols, and catalyst stability at pressures of about 6000 psi. Efforts are continuing to improve the catalyst characteristics at lower pressures, both through catalyst screening studies and through a better understanding of the catalytic process.

The screening of additives to ruthenium catalyst systems for the direct conversion of syngas to alcohols has been continued. The system studied to the greatest extent during this quarter was that of ruthenium carbonyl in a molten phosphonium salt. An additive was found which can significantly enhance the formation of ethanol as well as other C_2+ products. In addition, this additive also increases the inherent activity of the catalyst system; substantial activity was observed at 3000 psi of syngas. The effect of the additive was also apparent in catalyst solutions of ruthenium carbonyl with an iodide promoter in N-methylpyrrolidone solvent.

B. Effects of Metal-Containing Additives in Ruthenium Systems

It has now been found that use of the novel metal-containing additive A38 in the catalyst system of ruthenium carbonyl/iodide in NMP causes the activity of the the system to increase substantially. More interestingly, the ratio of C_2+ products increased dramatically, and the major C_2+ product, amounting to about 33%, is ethanol. With longer reaction times, the methanol content is only about a few percent. The results are presented in Table I.

When A38 was used as an additive in the ruthenium carbonyl/$P(n\text{-}Bu)_4Br$ system, the results were similar to those carried out in NMP. The only difference may be the larger amount of other oxygenates being formed in the molten salt system. The activity of the catalyst system was also increased. Most significantly, it was found that even at 3000 psi, the system was reasonably active, as shown in Table II.

Tests were continued on a class of metal-containing additives earlier investigated in this project. It was found that when A39 was added to the catalyst system of ruthenium carbonyl/$P(n\text{-}Bu)_4Br$, it enhanced the formation of ethanol without much effect on the activity of the catalyst system.

However, further studies are needed before a definitive conclusion can be reached. Results are shown in Table III.

These experiments were carried out according to Procedures B(a) and B(b) of Appendix B. Product analyses were conducted using Procedure C(a) of Appendix C.

Key to Tables I-VI

SGHAM-L-#	
1 Catalyst	Catalyst precursor charged
2 mmole	Amount of catalyst precursor used
3 Solvent	Solvent used
4 mL/g	Amount of solvent used, in mL or grams
5 Additive	Additive employed
6 mmole	Amount of additive used
7 Press.,psi	Reaction pressure in psig
8 Temp.,°C	Reaction temperature
9 Time,hrs.	Reaction time in hours
10 H_2/CO	Syngas molar ratio
11 MeOH,g	Amount of methanol produced, in grams
12 EtOH,g	Amount of ethanol produced, in grams
13 CH_3CHO,g	Amount of acetaldehyde produced, grams
14 n-PrOH,g	Amount of n-propanol produced, grams
15 i-PrOH,g	Amount of i-propanol produced, grams
16 Other Ox.,g	Amount of other oxygenates produced, grams
17 Total Prod.,g	Weight of total products analyzed
18 % EtOH	Weight percent ethanol of products formed
19 C_2+/C_1 ratio	Wt. ratio of C_2 and higher products to C_1

Table I. Effects of Metal-Containing Additives

	SGHAM-L-#	3-33	2-41	2-49
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmole	1.25	1.25	1.25
3	Solvent	NMP	NMP	NMP
4	mL/g	50.0g	30.0g	30.0g
5	Additive	KI	KI/A38	KI/A38
6	mmole	11	11/1.5	11/3.0
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	3.4	2.3
12	EtOH,g	0.3	2.7	4.3
13	CH_3CHO,g	trace	1.4	2.0
14	n-PrOH,g	0.0	0.3	0.3
15	i-PrOH,g	0.0	0.2	0.4
16	Other Ox.,g	trace	0.2	1.2
17	Total Prod.,g	3.4	8.2	10.5
18	% EtOH	9.0	33	41
19	C_2+/C_1 ratio	0.1	1.4	3.6

See page 22 for key.

Table II. Effects of Metal-Containing Additives

SGHAM-L-#	2-55	2-63	2-67	1-115
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	1.25	1.25	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	15.0g	15.0g	15.0g
5 Additive	A38	A38	A38	A38
6 mmole	3.0	3.0	3.0	3.0
7 Press.,psi	5000	4000	4000	3000
8 Temp.,°C	230	230	230	230
9 Time,hrs.	3.0	3.0	6.0	3.0
10 H_2/CO	1.0	1.0	1.0	1.0
11 MeOH,g	2.8	1.3	1.7	2.0
12 EtOH,g	5.4	3.5	5.2	2.3
13 CH_3CHO,g	trace	0.2	0.3	0.1
14 n-PrOH,g	1.1	0.9	1.2	0.7
15 i-PrOH,g	0.1	0.1	0.2	trace
16 Other Ox.,g	6.9	4.5	6.6	2.9
17 Total Prod.,g	16.3	10.5	15.0	8.0
18 % EtOH	33	33	35	29
19 C_2+/C_1 ratio	4.8	7.1	7.8	3.0

See page 22 for key.

Table III. Effects of Metal-Containing Additives

	SGHAM-L-#	2-27	2-13
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmole	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	A39	A39
6	mmole	0.60	2.4
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	4.4	1.6
12	EtOH,g	1.3	3.4
13	CH_3CHO,g	-	-
14	n-PrOH,g	-	-
15	i-PrOH,g	-	-
16	Other Ox.,g	-	-
17	Total Prod.,g	5.7	5.0
18	% EtOH	23	68
19	C_2+/C_1 ratio	0.30	2.1

See page 22 for key.

C. Effects of Organic Additives in Ruthenium Systems

When the nitrogen-containing organic additive A40 was used in a ruthenium/iodide catalyst system, significant changes were noted. Relatively small amounts of A40 added to the ruthenium carbonyl/$P(n\text{-}Bu)_4Br$ system cause an increased amount of ethanol product, as shown in Table IV. When a larger amount of A40 was used, the amount of ethanol decreased but that of other oxygenates increased dramatically. Interestingly, when A40 was replaced by A41, 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 V. The related compounds A42 and A43 were also tested as promoters, but they had a negative effect on the catalyst system, as shown in Table VI.

These experiments were carried out according to Procedures B(a) and B(b) of Appendix B. Product analyses were conducted using Procedure C(a) of Appendix C.

Table IV. 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	mmole	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	A40	A40	A40	A40/Rh(acac)$_3$
6	mmole	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	CH_3CHO,g	0.3	trace	0.1	0.0
14	n-PrOH,g	trace	trace	0.2	trace
15	i-PrOH,g	trace	trace	0.2	trace
16	Other Ox.,g	0.3	0.9	3.5	1.4
17	Total 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

See page 22 for key.

Table V. Effects of Organic Additives.

	SGHAM-L-#	1-67	1-71	1-73
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmole	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	A41	A41/A44	A41
6	mmole	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	CH_3CHO,g	0.50	0.3	-
14	n-PrOH,g	0.3	trace	-
15	i-PrOH,g	trace	trace	-
16	Other Ox.,g	trace	trace	-
17	Total Prod.,g	8.4	5.5	trace
18	% EtOH	39	51	-
19	C_2+/C_1 ratio	0.95	1.3	-

See page 22 for key.

Table VI. Effects of Organic Additives.

	SGHAM-L-#	1-55	1-75
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmole	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	A42	A43
6	mmole	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	CH_3CHO,g	trace	trace
14	n-PrOH,g	-	-
15	i-PrOH,g	-	-
16	Other Ox.,g	-	-
17	Total Prod.,g	5.3	3.9
18	% EtOH	26	46
19	C_2+/C_1 ratio	0.36	0.86

See page 22 for key.

D. Task 1 Summary

Several catalyst additives have been observed to have beneficial effects on ruthenium catalysts in homogeneous solutions. The presence of a novel metal-containing additive has been found to significantly enhance both the rate of syngas conversion and the yield of higher alcohols. Additionally, the use of this additive has been found to allow operation at pressures lower than previously used; an experiment at 3000 psi gave better performance than some runs at 5000 psi not using the additive.

Other additives have been tested which change the selectivity to higher alcohols without affecting the total reaction rate significantly. Work is continuing in an attempt to further improve the performance of this system at low pressures.

II. TASK 2: Development of Novel Catalysts

A. Introduction

The goal of Task 2 is to discover novel catalysts for the conversion of synthesis gas to higher mixed alcohols. Some of the potentially catalytic systems studied are based on metals not previously known to exhibit significant catalytic activity in homogeneous syngas conversion reactions. Most of the research on Task 2 during this quarter has been carried out on the novel, liquid-phase catalytic system based on copper, which converts syngas to oxygenated products under low pressures and at low temperatures. Research on this system has now been essentially completed because of the present limitations of the system.

B. The Involvement of Copper Hydride in the Copper/Methoxide System

Earlier work on this project has demonstrated the hydrogenation of CO under exceptionally mild conditions, 80-120°C and 1000-2000 psi, by the copper/methoxide system. This system is composed of a Cu(I) salt and sodium methoxide in a solvent, usually diethyl carbitol or tetrahydrofuran. The system catalyzes the hydrogenation of CO to methanol and methyl formate, but as yet does not produce significant amounts of higher oxygenates. The copper/methoxide system also suffers from rapid catalyst deactivation, which is still under investigation.

Earlier work had suggested that the active copper species might be a copper hydride. The copper hydride would be formed by β-hydride elimination from cuprous methoxide. Hydrogenation of CO has also been observed with a system composed of copper(I) iodide and sodium 3-pentoxide. Cuprous 3-pentoxide has been proposed to undergo thermal decomposition to form copper hydride.

In order to further explore the involvement of copper hydride in the copper/methoxide system, other methods of introducing copper hydride into the reaction were sought. One alternative to cuprous alkoxides is the use of copper(I) tetrahydroborates. It has been reported [1] that some copper tetrahydroborates may decompose thermally to form copper hydride according to equation (1).

$$CuBH_4 \quad \text{------>} \quad CuH + BH_3 \qquad (1)$$

With phosphine ligands, copper tetrahydroborate complexes are stable at room temperature, but can decompose on heating. Therefore the complex bis(triphenylphosphine)copper(I) tetrahydroborate was synthesized and its activity for CO hydrogenation tested. The experiments were performed using Procedure B(c) described in Appendix B and analyzed following Procedure C(b) from Appendix C. Results of the experiments are summarized in Table VII.

In the presence of the usual 110 mmol sodium methoxide, the copper tetrahydroborate complex was moderately active. However, in the absence of sodium methoxide, no gas uptake occurred and no products were produced. The gas uptake with sodium methoxide, 1600 psi, was considerably lower than a typical experiment with CuI. However, an experiment with the standard CuI/NaOMe system run immediately after the copper tetrahydroborate experiments also consumed only 1600 psi of syngas. Investigation showed that the apparent low gas uptake was caused by a leak in the gas inlet valve to the autoclave. In the absence of the leak both experiments would have displayed higher uptakes. Therefore it can be concluded that the copper tetrahydroborate system is approximately as active as the CuI system for CO hydrogenation.

However, it cannot be said with certainty that the reactivity of the copper tetrahydroborate system resulted from thermal decomposition to copper hydride. Since the copper tetrahydroborate complex was only reactive in the presence of sodium methoxide, it is possible that the methoxide simply displaced the tetrahydroborate and produced the usual copper methoxide catalyst. If the copper tetrahydroborate complex did decompose to copper hydride, then the sodium methoxide must still be involved in the CO hydrogenation even after formation of copper hydride.

In order to establish with some certainty the involvement of copper hydride in the copper/methoxide system, it was decided to synthesize copper hydride directly. Copper hydride was prepared by reaction of copper(I) iodide and diisobutylaluminum hydride in pyridine at -50°C [2]. The copper hydride was precipitated with ether and washed several times with ether at -78°C. Since in its pure form copper hydride is not very stable at room temperature, the copper hydride and diethyl carbitol to be used as solvent were kept at -78°C until just before use. The DEC was then thawed and the solid and liquid added to the autoclave. The experiments were performed according to Procedure B(c) of Appendix B and analyzed by Procedure C(b) from Appendix C. The results of the experiments are reported in Table VIII.

As with the copper tetrahydroborate system, no reactivity was observed in the absence of sodium methoxide. However, in the presence of 110 mmol sodium methoxide, the system was the most active one ever observed in the 150 mL autoclave. The gas uptake was 4480 psi and 7.0% methanol and 12.6% methyl formate were produced. A standard run using copper(I) iodide run immediately afterwards consumed 3270 psi syngas and produced 5.8% methanol and 10.5% methyl formate. The copper hydride system was also examined at 1000 psi in an attempt to extend its lifetime, but the opposite effect was noted. Copper hydride also hydrogenated CO in the presence of sodium ethoxide. The activity was considerably lower than with methoxide, but CuI displays no activity with ethoxide. This is presumably because copper(I) ethoxide decomposes through a radical mechanism, producing copper metal rather than copper hydride. The ethanol and ethyl formate produced by the copper hydride/sodium ethoxide system were derived from the ethoxide, but the methanol and methyl formate could have come only from hydrogenation of CO.

Unlike the copper tetrahydroborate system, it is highly unlikely that methoxide displaced hydride from copper hydride to produce the usual copper methoxide catalyst. Also, if that were the case the sodium ethoxide system should have been inactive. Thus these results point very strongly to the involvement of copper hydride in the copper/methoxide system. But these results also clearly point to the importance of methoxide, or other alkoxide, in these systems since even copper hydride is inactive in the absence of alkoxide. The results agree with previous indications that it is loss of methoxide that is deactivating the copper/methoxide system. The exact role of the alkoxide and the mechanism of its loss are subjects under continuing investigation at a low level of activity.

1. Bianchini, C.; Ghilardi, C.A.; Meli, A.; Midollini, S.; Orlandini, A. Inorg. Chem., 1985, 24, 924.

2. Whitesides, G.M.; San Filippo, J. Jr. J. Am. Chem. Soc., 1970, 92, 6611.

Key to Tables VII-IX

SGHAM-G-#	
1 Catalyst	Copper species used as catalyst precursor.
2 mmoles	Amount of copper species in mmoles.
3 NaOMe, mmoles	Amount of sodium methoxide in mmoles.
4 Solvent	Solvent used for reaction.
5 mL	Volume of solvent.
6 Additive	Additive employed.
7 mmoles	Amount of additive in mmoles.
8 Pressure, psi	Reaction pressure, psi.
9 H_2/CO	Synthesis gas molar (volume) ratio.
10 Temp, °C	Reaction temperature.
11 Time, hrs	Reaction time in hours.
12 Uptake, psi	Gas uptake in psi.
13 Wt.% MeOH	Amount of methanol observed in final solution.
14 Wt.% MeOF	Amt. of methyl formate obs. in final solution.
15 Other Prods	Other products observed in final solution.

Table VII. CO Hydrogenation by Bis(triphenylphosphine)copper(I) Tetrahydroborate

SGHAM-G-#	79	81	82
1 Catalyst[a]	P_2CuBH_4	P_2CuBH_4	CuI
2 mmoles	5	5	5
3 NaOMe, mmoles	110	0	110
4 Solvent[b]	DEC	DEC	DEC
5 mL	75	75	75
6 Additive	none	none	none
7 mmoles	0	0	0
8 Pressure, psi	2000	2000	2000
9 H_2/CO	1:1	1:1	1:1
10 Temp, °C	110	110	110
11 Time, hrs	3	3	3
12 Uptake, psi	1600	0	1600
13 Wt.% MeOH	3.4	0	5.3
14 Wt.% MeOF	4.1	0	8.8
15 Other Prods	none	none	none

P_2CuBH_4 = bis(triphenylphosphine)copper(I) tetrahydroborate.

[b] DEC = Diethyl carbitol.

See page 37 for key.

Table VIII. Reactivity of Copper Hydride Systems

SGHAM-G-#	85	86	87	89	88	90
1 Catalyst	CuH	CuH	CuI	CuH	CuH	CuH
2 mmoles	5	5	5	5	5	5
3 NaOMe, mmol	0	110	110	110	0	0
4 Solvent[a]	DEC	DEC	DEC	DEC	DEC	DEC
5 mL	75	75	75	75	75	75
6 Additive[b]	none	none	none	none	NaOEt	NaOEt
7 mmoles	0	0	0	0	110	110
8 Press, psi	2000	2000	2000	1000	2000	1000
9 H_2/CO	1:1	1:1	1:1	1:1	1:1	1:1
10 Temp,°C	110	110	110	110	110	110
11 Time, hrs	3	3	3	3	3	3
12 Uptake, psi	0	4480	3270	2980	280	720
13 Wt.% MeOH	0	7.0	5.8	3.6	1.0	2.0
14 Wt.% MeOF	0	12.6	10.5	5.1	1.2	1.5
15 Other Prods	none	none	none	none	none[c]	none[c]

[a] DEC = Diethyl carbitol.

[b] NaOEt = sodium ethoxide.

[c] Products included ethanol and ethyl formate derived from ethoxide.

See page 37 for key.

C. The Copper/Methoxide System in Dry Solvents

The solvent most commonly used in the work with the copper/ methoxide system, diethyl carbitol, is very hygroscopic. It was felt that water in the solvent could be causing the loss of methoxide and the formation of sodium formate. Reaction of methoxide with water produces hydroxide and methanol and reaction of hydroxide with CO could produce formate. Therefore, it was decided to examine the reactivity of the copper/methoxide system in carefully dried solvents. The reactions were performed using Procedure B(c) described in Appendix B and analyzed using Procedure C(b) found in Appendix C. The results of these experiments are summarized in Table IX.

In DEC dried by refluxing several days over sodium, the gas uptake was lower than expected, but the products were normal, including the usual brown solids containing sodium formate. It was felt that the low activity might be due to solvent decomposition so a milder drying procedure was tried. The DEC was predried over 4A molecular sieves and then refluxed over calcium hydride. The results were about the same, except that the selectivity to methyl formate was unusally high. Gas chromatographic analysis showed that the dried DEC contained no detectable water and that undried DEC contained about 0.1% water, so an experiment was tried with 0.1% water as an additive, but full activity was not restored. Since drying the DEC also removed dissolved oxygen, an experiment was tried in which the dry DEC was saturated with oxygen before reaction, but no difference in reactivity was observed. Finally, a standard experiment with undried DEC was run and it too showed lower than usual activity. One experiment in tetrahydrofuran dried over sodium/benzophenone showed the same results as the DEC experiments. The cause of the lower than usual activity is unknown. However, these experiments clearly demonstrate that water is not causing the loss of methoxide and/or formation of formate. Completely dry solvents produce the same formate-containing solids as are produced with undried solvent.

Table IX. The Copper/Methoxide System in Dry Solvents

SGHAM-G-#	91	93	94	96	97	95
1 Catalyst	CuI	CuI	CuI	CuI	CuI	CuI
2 mmoles	5	5	5	5	5	5
3 NaOMe, mmol	110	110	110	110	110	110
4 Solvent[a]	DEC[b]	DEC[c]	DEC[c]	DEC[c]	DEC	THF[d]
5 mL	75	75	75	75	75	75
6 Additive	none	none	H_2O	O_2	none	none
7 mmoles[e]	0	0	2	Sat.	0	0
8 Press, psi	2000	2000	2000	2000	2000	2000
9 H_2/CO	1:1	1:1	1:1	1:1	1:1	1:1
10 Temp, °C	110	110	110	110	110	110
11 Time, hrs	3	3	3	3	3	3
12 Uptake, psi	1620	1420	1800	1720	1600	1840
13 Wt.% MeOH	4.0	0.1	2.2	2.3	NA[f]	3.0
14 Wt.% MeOF	7.7	8.5	7.3	6.4	NA[f]	8.4
15 Other Prods	none	none	none	none	none	none

[a] DEC = Diethyl carbitol; THF = tetrahydrofuran.

[b] Dried by refluxing over sodium.

[c] Dried with 4A mol. sieves, then refluxing over CaH_2.

[d] Dried by refluxing over sodium/benzophenone.

[e] Sat. = saturated.

[f] Not Analyzed.

See page 37 for key.

C. Investigation of a Complex Reducing Agent

It was noted that the copper/methoxide system has some features in common with a class of heterogeneous reducing agents known as the complex reducing agents, or CRA's. CRA's are prepared from a transition metal salt, sodium hydride and an alcohol which reacts with part of the sodium hydride to form the sodium alkoxide [3]. Thus the CRA's contain a transition metal, hydride and alkoxide, similar to the systems containing copper hydride and sodium methoxide. CRA's have been reported to reduce substrates such as alkyl and aryl halides [4], aldehydes, ketones [5], alkenes and alkynes [6]. In the presence of CO, CRA's will carbonylate aryl halides [7]. The similarity of CRA's to the copper methoxide system prompted an experiment in which the CRA prepared from copper(I) iodide, sodium hydride and tert-amyl alcohol was used as a catalyst for CO hydrogenation. Although this material did reduce bromobenzene to benzene as reported in the literature, it did not catalyze the hydrogenation of CO in diethyl carbitol. No other work was done with the CRA's.

[3] Brunet, J.J.; Vanderesse, R.; Caubere, P. J. Organomet. Chem., 1978, 157, 125.

[4] Vanderesse, R.; Brunet, J.J.; Caubere, P. J. Org. Chem., 1981, 46, 1270.

5. Brunet, J.J.; Mordenti, L.; Caubere, P. *J. Org. Chem.*, 1978, **43**, 4804.

6. Brunet, J.J.; Mordenti, L.; Loubinoux, B.; Caubere, P. *Tet. Lett.*, 1977, 1069.

7. Brunet, J.J.; Sidot, C.; Loubinoux, B.; Caubere, P. *J. Org. Chem.*, 1979, **44**, 2199.

D. Task 2 Summary

Research during this quarter has been devoted to a further investigation of the liquid-phase copper catalyst system which produces oxygenates from syngas at low pressures. The goal of this research has been to better understand the nature of the catalyst species and determine the causes of catalyst deactivation. Experimental results have been obtained which support the involvement of a copper hydride intermediate in the syngas conversion process. The necessity of methoxide has also been demonstrated. Deactivation of the catalyst system appears to be closely tied to the loss of methoxide and the generation of formate during the catalytic process. Experiments with carefully dried solvents indicate that water is not causing this problem.

Because of the present practical limitations of this system, any further work on it will be minimal and would involve new approaches to overcoming the problems of deactivation and low yields of higher alcohols.

III. TASK 3: Further Study of Superior Catalysts

A. Introduction

The objective of Task 3 is to investigate in more detail the characteristics and chemistry of catalyst systems identified in Tasks 1 and 2 as having the most potential for further development. The activities included in this task are both of a fundamental chemical nature and a process-oriented nature.

Work which has been done this quarter in Task 3 falls into both categories. The system presently under study is the novel low-pressure homologation system which converts methanol to ethanol upon reaction with syngas. Fundamental chemical studies are being directed toward a better understanding of the chemical steps involved. At the same time, studies are being carried out to characterize the system by studying its responses to various process variables. A series of statistically designed experiments is planned, and preparations are being made for these studies.

B. Methanol Homologation

The reductive carbonylation of methanol, i.e., the reaction of methanol with synthesis gas to yield acetaldehyde (equation 2), is normally carried out with a cobalt-iodide catalyst at 160-180°C and 3000-6000 psig.

$$CH_3OH + H_2 + CO \xrightarrow{\quad} CH_3C(O)H + H_2O \qquad (2)$$

In most cases the acetaldehyde selectivities are 55 to 80%. It is known that addition of ruthenium to a cobalt-iodide catalyst results in the formation of ethanol. It is thought that Ru hydrogenates acetaldehyde with the net reaction being homologation of methanol (equation 3).

$$CH_3OH + 2H_2 + CO \xrightarrow{\quad} CH_3CH_2OH + H_2O \qquad (3)$$

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%.

Earlier work in this project has shown that the homologation reaction can be carried out at significantly lower pressure with a novel ruthenium-containing catalyst. Some of the earlier results are reported in Table X.

All of the homologation experiments reported here were carried out at pressures below 3000 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 reduced reaction pressure made possible by this catalyst is a significant breakthrough in methanol homologation technology. Since methanol is readily obtained from synthesis gas this catalyst may provide a low pressure route to ethanol and possibly other higher alcohols. A more detailed discussion of the catalytic approach and experiments is presented in the following sections.

Table X. Earlier Results with the Methanol Homologation System

SGHAM-W-#	Molar Ratio				Temp.,°C	EtOH Sel.,%
	A9	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
17-75	1	3	2	20	130	80.1

C. Catalyst Studies

In our initial studies we found that Ru and additives A9, A25, and A28 are critical components of the catalyst. The homologation catalyst is normally charged as a mixture of Ru, A9, A25 and A28 to a reactor containing methanol. Ru is typically charged as C7, which is very soluble in methanol. C7 is converted to C16 under reaction conditions. When mixed together in methanol at 22°C, A9 rapidily 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 XI. 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 X). The lower ethanol selectivity in 13-111 may be a result of the reduced ruthenium solubility. C15 is similiar to C7 and the activity and ethanol selectivity are similar to run 17-60 (Table X). C9 and C10 are ruthenium complexes containing the elements of A25. In both cases the ethanol selectivity is less than 30%.

Various compounds containing A9 were examined as catalyst precursors. In run 17-87, A9 was replaced with C11 which does not readily react with A25. The catalyst activity was very low. C12 and C13 are compounds containing the elemtns of A9 and A25 but in different molar amounts. The ethanol selectivity is somewhat lower with C12 than with A9 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 X, in the absence of A25 very little ethanol is obtained. Other additives similiar to A25 were obtained and examined in the homologation reaction. The results are reported in Table XI. In these experiments Ru was charged as C7. 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 A9 prior to catalysis. Therefore, C14, a compound derived from A9 and A36, was prepared. C14 is chemically similiar to C13. Run 18-26 utilizing C14 can be compared with 18-24 where a mixture of A9 and A36 was charged. The ethanol selectivity increased by 16% with C14. Although A32-A37 are chemically similiar 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 XI indicates that markedly different results can be obtained depending on the compounds utilized in the catalyst charge. The catalyst consisting of A9, C7, A25 and A28 can give ethanol selectivities of 80%. It appears that A9 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 X) 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 X). 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). At this time the identity of A31 is not known. Note that the temperature is 140°C and 130°C for runs 17-60 and 17-74, respectively. At 140°C the conversion of A25 to A30 is complete whereas at 130°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 3000 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.

A comprehensive list of the experiments carried out in this part of the project during the quarter is given in Table XII. All of these experiments, as well as those in Tables X and XI, were carried out according to Procedure B(d) of Appendix B and analyzed according to Procedure C(c) of Appendix C.

Table XI. Effects of Catalyst Composition Changes.

SGHAM-W-#	Catalyst, molar ratio	Temp., °C	EtOH Sel.,%
13-111	A9:C8:A25:A28 = 1:1:1:20	140	31.4
18-9	A9:C15:A25:A28 = 1:2:1:20	140	74.2
17-101	A9:C9:A28 = 1:2:20	140	23.0
17-99	A9:C10:A28 = 1:1:20	140	22.9
17-87	C11:C7:A25:A28 = 1:3:2:20	140	16.5
17-95	C12:C7:A28 = 1:3:20	140	69.6
17-82	C13:C7:A28 = 1:3:20	140	80.1
18-1	C13:C7:A28 = 1:3:20	130	76.9
18-12	C13:C7:A28 = 1:3:20	150	no analysis
17-108	A9:C7:A32:A28 = 1:2:1:20	140	13.6
17-112	A9:C7:A33:A28 = 1:2:1:20	140	34.3
17-126	A9:C7:A33:A28 = 1:2:1:20	155	47.3
18-4	A9:C7:A34:A28 = 1:2:1:20	140	28.1
18-10	A9:C7:A35:A28 = 1:2:1.5:20	140	25.5
18-24	A9:C7:A36:A28 = 1:2:1:20	140	35.2
18-28	A9:C7:A37:A28 = 1:2:1:20	140	24.1
18-26	C14:C7:A28 = 1:2:1	140	51.7
18-3	A9:C7:A25:A3 = 1:2:1:20	140	74.6
18-20	A9:C7:A25:A45 = 1:2:1:15	140	50.2
18-32	A9:C7:A25:A45 = 1:2:2:15	140	68.5
18-38	A9:C7:A25:A46 = 1:2:1:20	140	49.2

Key to Table XII.

SGHAM-W-#

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

Table XII. Comprehensive Table of Homologation Experiments

	SGHAM-W-#	17-82	17-87	17-95	17-99
1	Catalyst	C13	C11	C12	A9
2	mmole	2.00	2.00	2.00	2.00
3	Ru	C7	C7	C7	C10
4	mmole	6.00	6.00	6.00	2.00
5	Additive	none	A25	none	none
6	mmole	0.0	4.00	0.0	0.0
7	Promoter	A28	A28	A28	A28
8	mmole	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_2/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

See page 55 for key.

Table XII. Comprehensive Table of Homologation Experiments (Cont'd.)

SGHAM-W-#	17-101	17-108	17-112	17-126
1 Catalyst	A9	A9	A9	A9
2 mmole	2.00	2.00	2.00	2.00
3 Ru	C9	C7	C7	C7
4 mmole	4.00	4.00	4.00	4.00
5 Additive	none	A32	A33	A33
6 mmole	0.0	2.00	2.00	2.00
7 Promoter	A28	A28	A28	A28
8 mmole	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_2/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

See page 55 for key.

Table XII. Comprehensive Table of Homologation Experiments (Cont'd.)

	SGHAM-W-#	18-1	18-3	18-4	18-9
1	Catalyst	C13	A9	A9	A9
2	mmole	2.00	2.00	2.00	2.00
3	Ru	C7	C7	C7	C15
4	mmole	6.00	4.00	4.00	4.00
5	Additive	none	A25	A34	A25
6	mmole	0.0	2.00	2.00	2.00
7	Promoter	A28	A3	A28	A28
8	mmole	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_2/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

See page 55 for key.

Table XII. Comprehensive Table of Homologation Experiments (Cont'd.)

SGHAM-W-#	18-10	18-12	18-20	18-24
1 Catalyst	A9	C13	A9	A9
2 mmole	2.00	2.00	2.00	2.00
3 Ru	C7	C7	C7	C7
4 mmole	4.00	6.00	4.00	4.00
5 Additive	A35	none	A25	A36
6 mmole	3.00	0.0	2.00	2.00
7 Promoter	A28	A28	A45	A28
8 mmole	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_2/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

See page 55 for key.

Table XII. Comprehensive Table of Homologation Experiments (Cont'd.)

SGHAM-W-#	18-26	18-28	18-32	18-38
1 Catalyst	C14	A9	A9	A9
2 mmole	1.00	2.00	2.00	2.00
3 Ru	C7	C7	C7	C7
4 mmole	4.00	4.00	4.00	4.00
5 Additive	none	A37	A25	A25
6 mmole	0.0	2.00	4.00	2.00
7 Promoter	A28	A28	A45	A46
8 mmole	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_2/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

See page 55 for key.

D. Scale-up of the Methanol Homologation System

In preparation for performing designed sets of experiments with the ruthenium-based methanol homologation system, a number of experiments have been performed in a 300 mL autoclave, probing various aspects of the reactivity of the scaled-up system. These experiments were performed according to Procedure B(e) found in Appendix B and the products were analyzed by Procedure C(d) from Appendix C. The results of the experiments are summarized in Table XIII.

In the larger volume system the rates to ethanol and its equivalents generally total about 1 M/hr and the selectivities are in the 70 to 80 percent range. There is some indication, run G-103, that high catalyst concentrations can reduce selectivity. In run G-106 the effect of low temperature on reactivity was investigated. The reaction was begun at 100°C and the temperature increased in 10° increments. The catalyst activity was very low at 100 and 110°C, but moderate activity began at 120°C. At 130 and 140°C maximum activity was observed. This suggested a lower practical limit of 125°C. Run G-107 was performed at 125°C and did show good activity, but the selectivity was lower than in run G-106, perhaps because of differences in the catalyst concentration.

Key to Table XIII.

SGHAM-G-#	
1 Catalyst	Cat. system; C5 includes Ru, A9, A28.
2 mmol Ru	Amount of Ru added.
3 Additive	Additive used in reaction.
4 MeOH, mL	Amount of methanol used, mL.
5 H_2/CO	Synthesis gas volume (molar) ratio.
6 Temp.,°C	Reaction temperature.
7 Time, hr	Reaction time in hours.
8 Uptake, psi	Gas uptake in psi.
9 Rate to EtOH	Rate to ethanol, M/hr.
10 Rate to EtOH Eq.	Rate to ethanol equivalents, M/hr.
11 Rate to Other Ox.	Rate to other oxygenates, M/hr.
12 Tot.EtOH Sel., wt.%	Weight percent selectivity to ethanol plus equivalents.

Table XIII. Scale-up of the Methanol Homologation System

	SGHAM-G-#	102	103	104
1	Catalyst	C5	C5	C5
2	mmol Ru	4	12	12
3	Additive	A25	A25	A25
4	MeOH, mL	150	150	150
5	H_2/CO	2:1	2:1	2:1
6	Temp., °C	140	140	140
7	Time, hr	2.77	0.92	3.77
8	Uptake, psi	3500	870	5240
9	Rate to EtOH	0.71	0.23	0.66
10	Rate to EtOH Eq.	0.52	0.36	0.33
11	Rate to Other Ox.	0.28	1.13	0.24
12	Tot EtOH Sel.,wt.%	70.8	25.8	74.2

See page 62 for key.

Table XIII. Scale-up of the Methanol Homologation System (Cont'd).

SHGAM-G-#	105	106	107
1 Catalyst	C5	C5	C5
2 mmol Ru	12	12	9
3 Additive	A25	A25	A25
4 MeOH, mL	150	150	150
5 H_2/CO	2:1	2:1	2:1
6 Temp., °C	140	140a	125
7 Time, hr	2.50	2.80	3.13
8 Uptake, psi	3380	3200	3410
9 Rate to EtOH	0.74	0.67	0.47
10 Rate to EtOH Eq.	0.37	0.40	0.45
11 Rate to Other Ox.	0.35	0.10	0.09
12 Tot EtOH Sel., wt.%	67.9	81.1	73.5

[a] Temperature increased in 10° increments from 100°C to 140°C.

See page 62 for key.

E. 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 precursors in the catalytic chemistry. The effects of using related and different catalyst precursors have been investigated, and these studies are continuing.

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

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