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SEVENTH QUARTERLY TECHNICAL PROGRESS REPORT

DOE CONTRACT NO. DE-AC22-86PC90013

Optimum Catalytic Process for Alcohol Fuels from Syngas

Pittsburgh Energy Technology Center

October 29, 1988

Solvents and Coatings Materials Division

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

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D. C. Best
Program Manager

DISCLAIMER

Patent Cleared by Chicago
OPC on November 29, 1988

PATENT STATUS

CONTENTS

I. CONTRACT OBJECTIVES

The objectives of this contract are to discover and evaluate the catalytic properties of novel homogeneous, heterogeneous, or combination catalytic systems for the production of alcohol fuel extenders from syngas, to evaluate analytically and on the bench scale novel reactor concepts for use in converting syngas to liquid fuel products, and to develop on the bench scale the best combination of chemistry, reactor, and total process configuration to achieve the minimum product cost for conversion of syngas to liquid fuel products.

II. SCHEDULE

This program is planned as a 33-month research and development effort, extending through September, 1989.

The contract work is composed of three tasks. Task 1, the preparation of a Project Work Plan, has been completed. Task 2 comprises the chemical investigation of novel and existing catalysts for the production of fuel alcohols from syngas, either directly or through a step-wise process. Task 3 consists of engineering activities which will support the chemical investigations and develop economic evaluations and process conceptualization. Tasks 2 and 3 will proceed for the entire duration of the program.

In current work under Task 2, catalyst systems identified in earlier work as having the best characteristics are being investigated in more detail. These studies include both homogeneous and heterogeneous systems. Engineering efforts under Task 3 have also been directed toward improving the catalytic characteristics of these systems.

In the final 9 months of Task 2, chemical investigations will largely serve to provide guidance to the engineering evaluations, and will include fundamental studies and process-related activities.

Task 3 work has involved engineering support for the chemical investigations. Economic evaluations of a base case process for conversion of syngas to fuel alcohols were also pursued. Task 3 work has also involved experiments with selected catalytic systems. Further work in Task 3 will include continuing economic and process conceptualization studies, as required.

III. ORGANIZATION

The development of an optimum process for alcohol fuels from syngas is the goal of a research and development program conducted by a group within the Solvents and Coatings Materials Division of Union Carbide Corporation. During the initial portion of the contract, this group was part of the Engineering, Manufacturing and Technology Services Division.

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 2: Catalyst Research

A statistically designed set of experiments with the homogeneous Ru-based catalyst system has helped to define the effects and significance of the three catalyst components studied. It has also pointed out that interactions among these components exist. General directions for optimum performance are indicated, but a more extensive experimental design would be required for further optimization. Such a study is not planned at the present time, but would be conducted if significant improvements in the activity of this system are developed in future work.

We have incorporated a novel metal additive and potassium into the heterogeneous molybdenum sulfide catalyst in such a way as to increase the activity of the material about 10% over that obtained with potassium only. In addition,we have found that the density of the catalyst is dependent on a combination of the following: the volume of ammonium tetrathiomolybdate (ATM) decomposed, the potassium loading, and the loading of the metal additive. We have characterized the catalysts by surface area, X-ray diffraction, and SEM/TEM. We observed differences in the X-ray diffraction pattern which were correlated with performance, but have been unable to identify the origin of the reflections not due to molybdenum sulfide. Surface area measurements of the samples varied dramatically even for several aliquots of the same catalyst and consequently did not help to differentiate between good and bad catalysts. Differences in SEM were noted, but were attributed to differences in the base material and did not correlate with catalyst performance.

B. Task 3: Engineering Evaluations

Different MoS_2 preparations differ in their stability when heated at 400°C in 10% hydrogen in nitrogen. A sample of MoS_2 obtained from ammonium tetrathiomolybdate prepared by reaction at 70°C was the most stable of those tested. The stability of MoS_2 prepared from ATM precipitated near the end of reaction appears to be poor and this may be due to coprecipitation of impurities.

Evaluation of catalysts prepared from MoS_2 which had been heated in nitrogen or 10% hydrogen did not show improved stability or selectivity. Since reaction rates were relatively high, the loss of surface area did not reduce catalyst activity. A catalyst prepared from ATM prepared at lower temperature gave unusually low rates and also showed deactivation. Selectivity was normal and hence the catalyst may have a lower

concentration of active sites.

Catalyst prepared after impregnating MoS_2 with a small amount of cobalt acetate required a longer time to reach a steady state selectivity but deactivation was similar to that of conventional MoS_2.

Cobalt-molybdenum catalyst was prepared by a novel procedure. The composition was approximately equimolar cobalt and molybdenum. The activity was only 12-13 lb alcohol /cubic ft/hr (after the density correction) but was still increasing slowly after 70 hours evaluation and hence no deactivation was observed. Carbon selectivity to hydrocarbons was about 20%. It is possible that this inefficiency may be reduced by increasing the potassium loading. Additional testing to check for stability at longer reaction times may be justified.

This phase of the program has been concluded because the catalyst preparations did not show potential for the magnitude of improvement required.

V. CHANGES

There were no contract changes during this quarter.

VI. FUTURE WORK

Work during the next quarter will continue on Tasks 2 and 3, as described in the schedule of Section II.

Task 2 work on heterogeneous catalysts for alcohol production will continue. This work will include a continuing investigation of molybdenum-based catalysts and the exploration of other types of heterogeneous catalysts. Work on ruthenium-based homogeneous catalysts for the direct conversion of syngas to alcohols has been concluded until alternative approaches are identified.

Work on Task 3 will involve economic and engineering evaluations as required to support the chemical investigations.

APPENDIXES

By K. E. Carmichael, N. E. Kinkade,

and T. W. Leung

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:

A16:	A metal-containing catalyst additive
A92:	A catalyst additive
A111:	A catalyst additive
A116:	A metal catalyst additive
A126, A127:	Compounds of metal additive A116

Appendix B. PROCEDURES FOR CATALYST TESTING

Catalyst tests carried out under this contract are assigned reference ID numbers which identify the appropriate researcher and the notebook reference of the experiment.

Procedure B(e)

A u-tube micro-reactor system is used for catalyst evaluation. The reactor system contains a manifold in which up to two gas feeds are mixed and then fed to two u-tubes, both of which are maintained at a constant temperature in a common sandbath. The system can be operated at up to 1200 psig, 400°C, and space velocities up to about 12000 l/l/h, and is equipped with an emergency shut-down system for unattended operation. The product analysis consists of collecting a liquid product from the water-cooled condenser, analyzing it on a GC and combining that analysis with on-line gas analyses for oxygenated compounds, hydrocarbons, hydrogen, carbon monoxide, and carbon dioxide.

The standard start-up procedure consists of charging the catalyst to a nitric acid (50/50 acid/water) washed 1/4 inch O.D. 316 stainless steel u-tube and installing it in the high pressure reactor system. The catalyst is charged either as a powder, mixed with two or three times its volume of 0.5mm glass beads, or as undiluted +10-20 mesh particles. In either case the inlet and outlet of the u-tube is filled with 0.5 mm glass beads and a glass fiber plug is placed in each end. The system is pressurized to the maximum anticipated reaction pressure and the u-tube fittings are tested for leaks with soap solution. The sandbath is then raised around the two u-tubes and the sand is fluidized with air. The sandbath temperature is increased with a temperature controller to the reaction temperature, the pressure is adjusted to the desired reaction pressure and the feed flows are established. The off-gas analysis is performed every two hours alternating between the two reactors. The liquid product is collected once a day at approximately 24 hour intervals or twice a day at approximately 8 hour and 16 hour intervals and subsequently analyzed.

Prior to discharging the catalyst, the reactor is cooled to ≤100°C, purged with nitrogen, and depressurized.

Procedure B(f)

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

Appendix C. PROCEDURES FOR PRODUCT ANALYSIS

Procedure C(b)

The organic products were analyzed by gas chromatographic methods. The analyses were carried out using a Hewlett-Packard Model HP-5880 equipped with a 10-ft Tenax column. The initial and final temperatures used were 40 and 200°C, respectively. Acetonitrile was used as an internal standard. Gas samples were analyzed using a Carle Analytical Gas Chromatograph, Series S.

Procedure C(e)

A Varian 3500 capillary gas chromatograph equipped with a Flame Ionization Detector and a Varian 8000 Autosampler was used for the liquid analysis. A 30 meter, 318 micron DB-1 capillary column was used for the analysis. A 100:1 split ratio is used along with a helium carrier gas flow rate of 0.8 cc/min. and 4.5 psig pressure. The column was temperature programmed by holding at 40°C for 4 minutes, heating to 180°C at 10°C/min. and holding for 2 minutes, and then heating to 240°C at 30°C/min and holding for 13 minutes. The injector temperature is 240°C and the detector temperature is 250°C. Prior to analysis of the liquid samples, approximately twenty percent diglyme is added and accurately weighed into the sample as an internal standard. Liquid standards are periodically run to determine chromatographic response factors.

Appendix D. TECHNICAL AND EXPERIMENTAL DATA

TABLE OF CONTENTS

I. TASK 2: Catalyst Research

A. Direct Syngas Conversion by Ruthenium Catalysts

1. Introduction

The good characteristics of the homogeneous Ru/A16/iodide/A92 catalyst system have been discussed in our earlier reports. This system can convert syngas to higher alcohols directly, producing only small amounts of undesirable products such as acetate esters. Furthermore, good rates to total products could be realized at relatively low pressures for homogeneous catalysts, less than 4000 psi. As reported earlier, we have modified this system to give us better results. Use of LiI as the iodide source and A111, a relative of additive A92, led to better catalyst activity.

Since there was some indication that the relative concentrations of each component in the catalyst system were important, we decided to carry out a statistically designed set of experiments to give an indication of the optimum combination of components. With the reaction conditions and the amount of ruthenium being held constant, we varied the amounts of A16, LiI and A111.

2. Statistically Designed Experiments

Since the discovery of the catalyst system of Ru/iodide/A16/A92, which shows good activity and selectivity to higher alcohols, we have noticed that there are certain interactions between the components of the system. In order to get some definite idea about the effects of the components as well as these interactions, we decided to perform a 3- variable statistically designed set of experiments.

To get meaningful results from a designed set of experiments, some prior knowledge on the useful ranges of the variables is useful. From our past experience, we knew that better results were obtained consistently when LiI was the iodide source and additive A111 was used. Also, we had some indication that the best results were usually obtained when the A16 concentration was between 0.05 M to 0.15 M. Thus, the A16 concentrations were chosen close to these limits. Likewise, the concentrations of LiI and A111 were chosen to include the most probable optimum.

A total of 8 experiments was carried out under the same conditions of 4000 psi of 1:1 syngas for a period of 1.5 h at 230 °C. The results are tabulated in Table 1.

The statistical analyses concerning the effects of each component and the interactions among them were conducted according to standard procedures as outlined by C. D. Hendrix in CHEMTECH, March, 1979 p. 167. These results can only tell whether

an interaction exists and cannot definitely indicate the lack of an interaction. However, major interactions should have been detected.

The results are summarized in Tables 2-4 and are elaborated below.

Effects of Variables on Total Rate to Products

LiI Concentration

As expected, the higher iodide concentration has a positive effect on the rate to total product in the range considered.

A16 Concentration

The rate to total product decreases as the concentration of A16 increases. It must be mentioned, however, that this may only be true for the range of concentrations used.

A111 Concentration

The number calculated for the effect of this component is near zero. Since previous experiments have shown that the addition of this substance does cause the product formation rate to increase, this result likely means that the amount of additive used has little effect on the rate within the range investigated.

LiI-A16 Interaction

The number calculated for the effect on rate is close to zero.

LiI-A111 Interaction

As the value calculated is -0.85 M/h, a significant number as compared even to the highest rate obtained in the set (which is 6.8 M/h), this certainly can be interpreted as supporting the existence of a (negative) interaction.

A16-A111 Interaction

As indicated by a relatively large value of 0.9 M/h, a positive interaction exists between these two components.

LiI-A16-A111 Interaction

Again, the calculated value seems to suggest interactions between these components.

Effects of Variables on the Rate to C_2+ Alcohols

LiI Concentration

As expected, the higher iodide concentration has a positive effect on the rate of C_2+ alcohols formation.

A16 Concentration

The rate to C_2+ product increases as the concentration of A16 increases despite the fact that higher A16 concentrations decrease the total rate of product formation.

A111 Concentration

A negative effect on the rate to C_2+ alcohols is suggested at the higher concentration of this component.

LiI-A16 Interaction

The number calculated for the effect on rate is close to zero and it can be interpreted as little or no interaction between these two components.

LiI-A111 Interaction

The value calculated is insignificant and does not support the existence on an interaction.

Co-A111 Interaction

A positive interaction affecting the rate is suggested between these two components.

LiI-A16-A111 Interaction

Even though the calculated value is close to zero, more data is needed for the determination since an interaction has been shown to exist between A16 and A111.

Effects of Variables on the Percentage of C_2+ Alcohols in the Products

It must be mentioned that the percentage of alcohols in the product is only important when the rate to product and/or the rate to C_2+ alcohols is high. The only significant variables we are able to define for this result are A16 and A111. As expected, A16 positively affects the percentage of C_2+ alcohols (+16%). This is a fact that we have suspected previously, which is now confirmed by this statistical analysis. On the other hand, A111, while increasing the rate to total product, is not directly involved in increasing the C_2+ alcohol yield, as suggested by the relatively large negative value (-11%).

Key to Table 1.

ID-#		
1	Catalyst	Catalyst precursor charged.
2	mmole	Amount of catalyst precursor charged.
3	Solvent	Solvent used.
4	mL	Amount of solvent used, in mL.
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, grams.
12	EtOH, g	Amount of ethanol produced, grams.
13	n-PrOH, g	Amount of n-propanol produced, grams.
14	n-BuOH, g	Amount of n-butanol produced.
15	Acetates	Amount of methyl and ethyl acetates produced.
16	Tot. Prod., g	Weight of total products analyzed.
17	Rate, total, M/h	Total rate in moles/l solution/hr.
18	C_2+ alcohols %	Mole % of C_2+ alcohols in total product.

Table 1. Effect of Additives on the Ru/A16/I^-/A111 System.

	TWL-#	13-79	13-67	13-71	13-69
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7	4.7	4.7
3	Solvent	1,3-DMEU	1,3-DMEU	1,3-DMEU	1,3-DMEU
4	mL	38	38	38	38
5	Additive	LiI/A16/A111	LiI/A16/A111	LiI/A16/A111	LiI/A16/A111
6	mmole	15/2.6/66	15/5.2/66	30/2.6/66	30/5.2/66
7	Press., psi	4000	4000	4000	4000
8	Temp.,°C	230	230	230	230
9	Time, hrs.	1.5	1.5	1.5	1.5
10	H_2/CO	1	1	1	1
11	MeOH, g	6.5	3.1	8	5
12	EtOH, g	4.7	3.4	5.4	5.3
13	n-PrOH, g	0.7	0.8	0.7	0.8
14	n-BuOH, g	0.2	0.2	0.3	0.4
15	Acetates	0.2	0.3	0.3	0.3
16	Tot. Prod., g	12.3	7.8	14.7	11.8
17	Rate, total, M/h	5.7	3.3	6.8	5.2
18	C_2+ alcohols %	36	47	34	46

Experimental procedure: B(f); Analytical procedure: C(b); Key on page 17.

Table 1. Effect of Additives on the Ru/A16/I⁻/A111 System (Cont'd.)

	TWL-#	13-73	13-75	13-77	13-81
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7	4.7	4.7
3	Solvent	1,3-DMEU	1,3-DMEU	1,3-DMEU	1,3-DMEU
4	mL	38	38	38	38
5	Additive	LiI/A16/A111	LiI/A16/A111	LiI/A16/A111	LiI/A16/A111
6	mmole	15/2.6/132	15/5.2/132	30/2.6/132	30/5.2/132
7	Press., psi	4000	4000	4000	4000
8	Temp.,°C	230	230	230	230
9	Time, hrs.	1.5	1.5	1.5	1.5
10	H_2/CO	1	1	1	1
11	MeOH, g	7	6.3	7.6	3.1
12	EtOH, g	1.6	4.1	2.8	3.4
13	n-PrOH, g	0.5	0.6	0.4	0.8
14	n-BuOH, g	0.4	0.2	0.1	0.2
15	Acetates	0.8	0.5	0.2	0.3
16	Tot. Prod., g	10.3	11.7	11.1	7.8
17	Rate, total, M/h	4.9	5.4	5.4	4.5
18	C_2+ alcohols %	18	33	22	47

Experimental procedure: B(f); Analytical procedure: C(b); Key on page 17.

Table 2. Rate to Total Product for the Catalyst System of Ru/LiI/A16/A111 with Different Amounts of the Variable Components

LiI (mmoles)	A16 (mmoles)	A111 (mmoles)	Total Rate, M/h
15	2.6	66	5.7
30	2.6	66	6.8
15	5.2	66	3.3
30	5.2	66	5.2
15	2.6	132	4.9
30	2.6	132	5.4
15	5.2	132	5.4
30	5.2	132	4.5

Table 3. Rate to C_2+ Alcohols for the Catalyst System of Ru/LiI/A16/A111 with Different Amounts of the Variable Components

LiI (mmoles)	A16 (mmoles)	A111 (mmoles)	C_2+ ROH Rate, M/h
15	2.6	66	2.05
30	2.6	66	2.31
15	5.2	66	1.55
30	5.2	66	2.39
15	2.6	132	0.88
30	2.6	132	1.19
15	5.2	132	1.78
30	5.2	132	2.11

Table 4. Mole Percentage of C_2+ Alcohols in Total Product for the Catalyst System of Ru/LiI/A16/A111 with Different Concentrations of the Variable Components.

LiI (mmoles)	A16 (mmoles)	A111 (mmoles)	% C_2+ ROH
15	2.6	66	36
30	2.6	66	34
15	5.2	66	47
30	5.2	66	46
15	2.6	132	18
30	2.6	132	22
15	5.2	132	33
30	5.2	132	47

Table 5. Statistical Analysis Table for Rate to Total Product.

	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Rate to Total Product, M/h
	-1	-1	-1	+1	+1	+1	-1	5.7
	+1	-1	-1	-1	-1	+1	+1	6.8
	-1	+1	-1	-1	+1	-1	+1	3.3
	+1	+1	-1	+1	-1	-1	-1	5.2
	-1	-1	+1	+1	-1	-1	+1	4.9
	+1	-1	+1	-1	+1	-1	-1	5.4
	-1	+1	+1	-1	-1	+1	-1	5.4
	+1	+1	+1	+1	+1	+1	+1	4.5
Effect, M/h	0.65	-1.1	-0.2	-0.15	-0.85	0.9	-0.55	

X_1, LiI
Effect = (-5.7+6.8-3.3+5.2-4.9+5.4-5.4+4.5)/4.0 = 0.65

X_2, A16
Effect = (-5.7-6.8+3.3+5.2-4.9-5.4+5.4+4.5)/4.0= -1.1

X_3, A111
Effect = (-5.7-6.8-3.3-5.2+4.9+5.4+5.4+4.5)/4.0 = -0.2

X_1X_2, LiI-A16 interaction
Effect = (+5.7-6.8-3.3+5.2+4.9-5.4-5.4+4.5)/4.0 = -0.15

X_1X_3, LiI-A111 interaction
Effect = (+5.7-6.8+3.3-5.2-4.9+5.4-5.4+4.5)/4.0 = -0.85

X_2X_3, A16-A111 interaction
Effect = (+5.7+6.8-3.3-5.2-4.9-5.4+5.4+4.5)/4.0 = 0.90

$X_1X_2X_3$, LiI-A16-A111 interaction
Effect = (-5.7+6.8+3.3-5.2+4.9-5.4-5.4+4.5)/4.0 = -0.55

Table 6. Statistical Analysis Table for Rate to C_2+ Alcohols

	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Rate to C_2+ ROH, M/h
	-1	-1	-1	+1	+1	+1	-1	2.05
	+1	-1	-1	-1	-1	+1	+1	2.31
	-1	+1	-1	-1	+1	-1	+1	1.55
	+1	+1	-1	+1	-1	-1	-1	2.39
	-1	-1	+1	+1	-1	-1	+1	0.88
	+1	-1	+1	-1	+1	-1	-1	1.19
	-1	+1	+1	-1	-1	+1	-1	1.78
	+1	+1	+1	+1	+1	+1	+1	2.11
Effect, M/h	0.44	0.35	-0.59	0.15	-0.12	0.56	-0.14	

X_1, LiI
Effect = (-2.05+2.31-1.55+2.39-0.88+1.19-1.78+2.11)/4.0 = 0.44

X_2, A16
Effect = (-2.05-2.31+1.55+2.39-0.88-1.19+1.78+2.11)/4.0 = 0.35

X_3, A111
Effect = (-2.05-2.31-1.55-2.39+0.88+1.19+1.78+2.11)/4.0 = -0.59

X_1X_2, LiI-A16 interaction
Effect = (+2.05-2.31-1.55+2.39+0.88-1.19-1.78+2.11)/4.0 = 0.15

X_1X_3, LiI-A111 interaction
Effect = (+2.05-2.31+1.55-2.39-0.88+1.19-1.78+2.11)/4.0 = -0.12

X_2X_3, A16-A111 interaction
Effect = (+2.05+2.31-1.55-2.39-0.88-1.19+1.78+2.11)/4.0 = 0.56

$X_1X_2X_3$, LiI-A16-A111 interaction
Effect = (-2.05+2.31+1.55-2.39+0.88-1.19-1.78+2.11)/4.0 = -0.14

Table 7. Statistical Analysis Table for Percentage of C_2+ Alcohols in the Product.

	X1	X2	X3	X1X2	X1X3	X2X3	X1X2X3	C_2+ ROH %
	-1	-1	-1	1	1	1	-1	36
	1	-1	-1	-1	-1	1	1	34
	-1	1	-1	-1	1	-1	1	47
	1	1	-1	1	-1	-1	-1	46
	-1	-1	1	1	-1	-1	1	18
	1	-1	1	-1	1	-1	-1	22
	-1	1	1	-1	-1	1	-1	33
	1	1	1	1	1	1	1	47
Effect, in %	3.8	16	-11	2.8	5.3	4.3	2.3	

X_1, LiI
Effect = (-36+34-47+46-18+22-33+47)/4.0 = 3.8

X_2, A16
Effect = (-36-34+47+46-18-22+33+47)/4.0 = 16

X_3, A111
Effect = (-36-34-47-46+18+22+33+47)/4.0 = -11

X_1X_2, LiI-A16 interaction
Effect = (+36-34-47+46+18-22-33+47)/4.0 = 2.8

X_1X_3, LiI-A111 interaction
Effect = (+36-34+47-46-18+22-33+47)/4.0 = 5.3

X_2X_3, A16-A111 interaction
Effect = (+36+34-47-46-18-22+33+47)/4.0 = 4.3

$X_1X_2X_3$, LiI-A16-A111 interaction
Effect = (-36+34+47-46+18-22-33+47)/4.0 = 2.3

B. Direct Syngas Conversion by Heterogeneous Catalysts

1. Introduction

We have continued work on the heterogeneously catalyzed system based on alkali-loaded molybdenum sulfide and cobalt molybdenum sulfide catalysts. The work this quarter has been focused on improving the activity of potassium-molybdenum sulfide catalysts through the addition of A116 and determining the physical characteristics of different versions of these catalysts and potassium-molybdenum catalysts which perform either well or poorly. In addition we did some follow-up work on supported carbon catalysts.

All catalysts were evaluated using Procedure B(e) of Appendix B, and products were analyzed using Procedure C(e) of Appendix C.

2. Addition of A116 to MoS_2 Catalysts

Because the results of the Plackett-Burman designed set of experiments indicated that addition of A116 increased the activity of those catalysts by a significant amount, we have expended a considerable amount of effort trying to extend this result to our standard catalyst preparation. These standard catalysts are significantly more active than catalysts of a similar composition prepared by the method used in the Plackett-Burman experiments. If we can obtain the same increase in productivity with catalysts prepared by our standard methods, we may be able to obtain the desired 30 lb/cf/hr rate to alcohols.

We were surprised at the result mentioned in the last quarterly report, whereby a catalyst containing 0.75 moles K / mole Mo and prepared by the method used for the Plackett-Burman designed set catalysts exhibited a rate to alcohols of only 13 lb/cf/hr. In order to confirm that the low activity of this catalyst is due to something in the preparation and not due to a bad batch of ammonium tetrathiomolybdate (ATM), we prepared a catalyst using an incipient wetness impregnation of molybdenum sulfide produced from the same batch of ATM. This catalyst (30NEK100) exhibited similar performance (run 30NEK106) to that of previous standard preparations as shown below:

Rate, lb/cf/hr	17
% Alcohols	74
% Oxygenates	80

This demonstrates that there is nothing wrong with the batch of ATM used in the

Plackett-Burman designed set catalysts and thus, the cause of the lower activity of the catalysts studied in the Plackett-Burman designed experiments must lie in the method of their preparation.

The initial attempt to incorporate A116 into our standard catalyst preparative method was simply to simultaneously impregnate molybdenum sulfide with potassium and A116. However, we quickly discovered that potassium acetate and an aqueous solution of A126 (a compound containing A116) are insoluble.

We were able to incorporate A116 and potassium into the catalyst through a variety of ways as indicated below:

1) Stir-mixed one pore volume of aqueous solution of the A116 component (A126) with MoS_2, dried, added one pore volume of aqueous KOAc by stir-mix method, dried and decomposed.
2) Same as 1) except KOAc added first, then A116 component (A126).
3) Same as 1) except ATM was used in place of the MoS_2.
4) Same as 3) except that an alcoholic solution of A116 component (A127) was used in place of the aqueous A126.
5) Same as 3) except that the A116 solution was diluted and stirred overnight.
6) Same as 5 except A127 was used instead of A126.
7) Same as 6) except that a decomposition step was added prior to potassium addition.
8) Same as 3) except that a decomposition step was added prior to potassium addition.

The results are shown in Table 8. It should be noted that the table is divided into three sections. The first comprises catalysts containing A116, the second is standard catalysts prepared to validate different batches of ATM, and the third contains the results of catalysts prepared on a batch of ATM which was found to have low activity when converted to a standard catalyst. This batch of ATM was suspect immediately upon preparation because it was composed of dark powdery particles instead of the normal reddish needle-like crystalline material. X-ray diffraction, however, did not reveal the presence of any crystalline material other than ATM, so we proceeded with several catalyst preparations. When the standard preparation was evaluated we found it exhibited low activity, which we attribute to the ATM. No further catalysts were prepared on this ATM.

When we embarked on this investigation into the effects of additive A116, we were interested in its effect on the catalyst density and on catalyst activity on a volume basis (lb/cf/hr). We are interested in reducing the catalyst density while maintaining the catalyst activity on a volume basis, because we feel that such a catalyst would have a potential for a higher rate when compacted. Our standard potassium-molybdenum sulfide catalysts typically have a density of 1.0-1.1 gm/cc. We are also interested in the

effect on activity, because if A116 increases the activity on a volume basis then no compaction is necessary.

Thus, perusing Table 8 for catalysts with low density reveals a number of successes; however, all of the catalysts with a density between 0.6 and 0.8 gm/cc exhibit a rate to alcohols lower than typical of our standard catalysts. In order to express the rate on a weight basis, rather than on a volume basis, we divided the last rate by the density, resulting in mixed units (lb/(cf × gm/cc of catalyst)/hr) but a familiar standard of about 19-20. Now on perusing these values shown in the second to last column, we see that most of the catalysts with low density do indeed exhibit a rate on a weight basis which is higher than exhibited by the standard catalysts. Thus, the decrease in density is larger than the concurrent decrease in rate (on a volume basis) for a number of the A116 containing catalysts.

The next question is what sets these particular A116 containing catalysts apart from the rest. The most obvious factor is the preparative method: procedure seven, which requires decomposition of the A116 containing ATM prior to impregnation with potassium. There are a few catalysts which were prepared by this same method, but which did not exhibit the high rate on a weight basis. This may be due to a variety of factors, including differences in A116 loading, potassium loading and/or the volume of ATM used during its decomposition.

In order to eliminate variations in ATM preparation and in impregnation with A116, we prepared a large batch of ATM (obtaining 94% of the theoretical yield), loaded part of it with A116 and decomposed it to A116/MoS_2. This single preparation of A116/MoS_2 was used to investigate the effect of potassium loading. Three of the catalysts in Table 8, 30NEK70, 30NEK73 and 30NEK71, were prepared on aliquots from this batch of A116/MoS_2 and contain potassium loadings of 0.5, 0.75, and 1.0 moles K / mole Mo, respectively. The first result we noticed was that the density of the catalyst with the intermediate potassium loading, which has the same composition as several of our earlier low-density A116/K/MoS_2 catalysts, had a density of 0.95 gm/cc (i.e., not much lower than that of our standard K/MoS_2 catalysts). (This is the density measured immediately after preparation. When loaded into the reactor 6 days later, the density was measured to be 0.87 gm/cc.) The main difference between this preparation and the previous preparations of materials with similar compositions is the scale of the A116/MoS_2 preparation. It appears that the density may increase as the scale of the A116/ATM decomposition step increases. It also seems that the density of the catalysts may be changing with time or exposure to air/moisture.

In addition, the densities of the three preparations mentioned above decrease with increasing potassium loading. Evaluation of these preparations gave the results shown below:

Potassium	Density
0.5	1.11
0.75	0.87
1.0	0.69

The relationship between density and potassium loading may be partially due to simple dilution of the A116/MoS_2 material, which has a density of about 1.1 gm/cc, with the less dense potassium acetate (0.75 gm/cc), or it may be due to a more complicated reaction taking place between the two materials.

In order to investigate our hypothesis that catalysts of low density are useful because they may exhibit higher rates when compacted, we compacted a sample of 30NEK10 and obtained a density of 1.2 gm/cc after crushing to a powder. This compacted catalyst exhibits grossly different performance from the uncompacted material. The rate, on a volume basis, is indeed higher than for the uncompacted catalyst, but the increase in rate was significantly less than the increase in density. Perhaps even more surprising is that initially the selectivity to alcohols was only around 40%, although this improved with time to about 70%. Not only was the initial production of hydrocarbons very high, but the initial alcohols product distribution was skewed toward the higher alcohols. One possible explanation for above results may be the loss of very small pores due to the high pressure (8000 psi) used to compact the powder into a pellet.

We attempted to investigate the effect of pelleting pressure on the density of the ground pellet by pelletizing catalysts at pressures ranging from 3,000 to 8,000 psi. We found that in some cases liquid was squeezed out of the powder, and in all cases the resulting pellet was the consistency of lipstick rather than a hard pellet. We re-dried some material from one of these preparations and observed a 16% loss in weight. We have been aware that the K/MoS_2 catalysts are hygroscopic, but the time frame (a few days) in which these A116/K/MoS_2 catalysts became wet was much shorter than expected.

We did a thermogravimetric analysis (TGA) on the potassium acetate and found that it melts at 300°C (as indicated in the CRC handbook) and decomposes at about 450°C. Therefore, since we calcine our catalysts at 400°C, they probably contain potassium acetate (in accordance with our assumption based on the odor of acetic acid emitted from the catalysts), although this may or may not be true of the working catalyst. The presence of potassium acetate in the catalyst undoubtedly contributes to its hygroscopic nature.

With regard to the second possible beneficial effect of A116, only two catalysts, 28NEK84 and 30NEK70, exhibit either an initial and/or last rate higher than exhibited by our standard catalysts. The first contained 1 wt% A116 and 0.75 moles K / mole Mo and was prepared by adding the A116 to a potassium-loaded molybdenum sulfide. The

other was prepared by decomposing the A116-impregnated ATM and then adding the potassium at a loading of 0.5 moles K / mole Mo. Both of these catalysts initially exhibited a rate higher than our standard catalysts, but only the first one ended up with a higher rate after our standard run duration of three days. We do not know why the second catalyst showed such a high degree of deactivation, but it initially looked very promising because its very high early rate was fairly constant through 40 hrs on stream. We did try to prepare this catalyst again and obtained a catalyst (30NEK93) with the same density, final rate and alcohol selectivity, but it did not exhibit the very high initial rate. We are not sure why we could not replicate this preparation.

We believe that A116 does indeed provide a beneficial effect on the activity of potassium-molybdenum sulfide catalysts for the production of alcohols; however, these catalysts are only 10-15% more active. We plan to conclude this line of experimentation in the near future.

3. Physical Characterization of Catalysts

We have chosen eight different catalysts - some high activity, some low; some high density, some low - for which we will obtain SEM/TEM, X-ray, surface area, and porosity data. Some of these catalysts are from the Plackett-Burman designed set of experiments and others contain only potassium or only potassium and A116 in addition to the molybdenum sulfide. We want to determine if we can detect any differences between catalysts having superior and inferior performance characteristics.

The surface area results are very confusing. The first series of surface area measurements showed two catalysts with surface areas greater than 10 m^2/gm. A second sample of the one with the highest surface area (38 m^2/gm) was submitted, and the surface area was found to be very low. We re-determined the surface areas on all eight samples after out-gassing at 400°C rather than 200°C, and found the change in surface areas ranged from 25% less to 30 times more! Three samples of one catalyst were evaluated after 400°C out-gassing and the surface areas obtained were 4.6, 10.2 and 26.1 m^2/gm. The surface area of two of these three samples was determined using a different instrument, and the results between instruments agreed very well. No difference between the three samples could be discerned by comparing them at seven times magnification.

Differences in SEM were attributable to differences in the MoS_2 starting material, and do not correlate with performance. Differences in X-ray may be correlated with performance, but we have been unable to identify the source of these differences.

4. Carbon Supported Catalysts

We evaluated two carbon supported catalysts. Both were the same composition, but one was decomposed prior to loading and the other was decomposed in situ and exposed to a reducing atmosphere only after reaching 400°C. The latter procedure as well as low temperature during drying are claimed to be necessary for high activity in a patent by Coal (Patents) Industry, Limited. Both catalysts performed almost identically, as shown in Table 9, and were about twice as active as one of a similar composition which had been examined during our previous Greco-Latin Square designed set of experiments on carbon supports. The major difference between the earlier catalysts and these more recent ones is the temperature of the drying steps. The Greco-Latin Square catalysts were dried in a rotary evaporator at about 80°C, while the recent preparations were dried at room temperature and using a vacuum pump rather than the house vacuum. This may be an important consideration and if we do further work on supported catalysts, we will explore it further. The activity of the carbon supported catalysts prepared most recently is about 1/3 that shown in the patent examples and of our unsupported catalysts.

Table 8. Results of Evaluation of Standard Catalysts and Catalysts Containing A116.

Catalyst ref	Prep Method	wt% A116	wt% K	Run ref	Density	Rate (lb/cf/hr) High	Rate (lb/cf/hr) Last	% Alc	Last Rate/ Density
28NEK067	1	10.00	0.75	28NEK76	1.32	24.0	21.0	70	15.9
28NEK084[a]	2	1.00	0.75	28NEK86	0.99	~25	~22		22.2
28NEK085[a]	2	5.00	0.75	28NEK88	1.10	~23	~20		18.2
30NEK15	4	0.93	0.75	30NEK30	0.85	16.0	15.0	77	17.6
28NEK124	4	0.93	1.22	30NEK4	0.99	15.0	14.6	71	14.7
28NEK127	5	4.85	0.73	30NEK6	1.20	19.0	17.0	75	14.2
28NEK126	5	1.00	0.73	30NEK16	1.27	17.0	15.0	72	11.8
30NEK14	6	0.93	0.75	30NEK28	0.90	13.0	12.0	68	13.3
30NEK10	7	0.93	0.75	30NEK22	0.72	19.5	17.0	78	23.6
30NEK10	7	0.93	0.75	30NEK34	0.71	19.0	18.0	80	25.4
30NEK10[b]	7	0.93	0.75	30NEK36	1.20	23.0	20.0	70	16.7
30NEK47	7	0.93	0.75	30NEK52	0.65	19.0	16.0	80	24.6
30NEK39	7	0.93	0.75	30NEK50	0.84	19.0	17.0	78	20.2
30NEK11	7	5.00	0.75	30NEK24	0.79	16.0	14.5	75	18.4
30NEK70	7	0.93	0.5	30NEK74	1.12	26.6	20.0	69	17.9
30NEK71	7	0.93	1.0	30NEK76	0.69	20.0	16.5	77	23.9
30NEK73	7	0.93	0.75	30NEK86	0.87	22.6	18.6	74	21.4
30NEK92[c]	7	0.93	0.5	30NEK96	0.86	23.0	19.6	73	22.8
30NEK93	7	0.93	0.5	30NEK104	1.15	23.5	19.2	67	16.7
30NEK84	8	0.93	0.75	30NEK94	0.90	21.5	17.7	72	19.7
28NEK117B	std	0.00	0.75	28NEK130	1.01	21.0	19.0	75	18.8
28NEK066	std	0.00	0.75	28NEK74	1.13	23.0	20.0	70	17.7
30NEK80	std	0.00	0.75	30NEK88	0.99	22.6	18.7	74	18.9
30NEK100[d]	std	0.00	0.75	30NEK106	0.82	22.0	17.0	74	20.7
28NEK098[e]	3	1.00	0.73	28NEK102	0.94	13.0	12.0	69	
28NEK099[e]	3	4.90	0.73	28NEK104	0.96	14.5	14.0	72	
28NEK107[e]	5	1.00	0.73	28NEK112	1.11	12.5	12.5	66	
28NEK108[e]	5	4.80	0.73	28NEK114	1.13	18.0	15.0	74	
28NEK117A[e]	std	0.00	0.75	28NEK128	1.10	16.0	13.0	79	

[a] No gas analysis

[b] Pelleted

[c] Not calcined

[d] ATM used in designed set.

[e] Made with same batch of questionable ATM.

Table 9. Results of Carbon Supported Catalysts

Catalyst Ref.	Run Ref.	% Alcohols	Rate, lb/cf/hr	CO Conv.	Comments
30NEK32	30NEK42	76	8.5	6.3	pre-reduced
30NEK33	30NEK44	77	7.8	5.8	reduced in-situ

D. Task 2 Summary

The statistically designed set of experiments with the homogeneous Ru-based catalyst system has helped to define the effects and significance of the three catalyst components studied: LiI, A16, and A111. It has also pointed out that interactions among these components exist. General directions for optimum performance are indicated, but a more extensive experimental design would be required for further optimization. Such a study is not planned at the present time, but would be conducted if significant improvements in the activity of this system are developed in future work.

We have incorporated A116 and potassium into a molybdenum sulfide catalyst in such a way as to increase the activity of the material about 10% over that obtained with potassium only. In addition,we have found that the density of the catalyst is dependent on a combination of the following: the volume of ammonium tetrathiomolybdate decomposed, the potassium loading, and the loading of A116. We have characterized the catalysts by surface area, X-ray diffraction, and SEM/TEM. We did observe differences in the X-ray diffraction pattern which were correlated with performance; however, we were unable to identify the origin of the reflections not due to molybdenum sulfide. Surface area measurements of the samples varied dramatically even for several aliquots of the same catalyst and consequently did not help to differentiate between good and bad catalysts. Differences in SEM were noted, but were attributed to differences in the base material and did not correlate with catalyst performance.

II. TASK 3: Engineering Evaluations

A. Introduction

In the planning for this contract, it was anticipated that the engineering activities in the second year of the program would involve the development of kinetic models for the performance of the best catalysts and the development of an improved process. However, since our evaluations indicate that further catalyst improvements are desirable before moving into process development, more engineering effort has been given to support the experimental program for catalyst preparation and improvement. The main aspects of catalyst performance to be improved are overall rate, selectivity to higher alcohols, and catalyst stability against deactivation. The objective for this particular part of the research program is to find ways of improving the K/Mo and K/Co/Mo catalysts. This is a separate activity from the investigation of effects of different additives on catalyst performance.

Work conducted this quarter is a continuation of the work reported in the previous quarterly. The objective is to find out whether catalyst with improved rate and selectivity could be obtained by changing the preparation conditions or by changing the precursors. The previous experiments were with molybdenum sulfide catalysts. Catalysts containing cobalt were tested in this quarter. The other main emphasis was on testing whether longer calcination times for molybdenum sulfide would produce a catalyst which did not deactivate as rapidly during reaction.

The experiments being pursued in this task, involving modifications on the existing MoS_2 and Co-MoS_2 catalysts, did not show as much promise as the approaches which involve the use of catalyst additives. Therefore, this part of the experimental program has been concluded.

B. Experimental Program

Six catalyst preparations were evaluated this quarter. Four of these were prepared from ATM and the remaining two were cobalt-molybdenum catalysts prepared by a novel route.

These evaluations were carried out with two different catalysts in two separate reactors heated in the same sand bath. The evaluation conditions, unless noted otherwise, were 300°C, 1200 psi, 1/1 H_2/CO ratio and a space velocity of 6000 reciprocal hours. The catalyst volume was always one cm^3 as charged to the reactor. Unless specified otherwise, all catalysts were evaluated using Procedure B(e) of Appendix B, and products were analyzed using Procedure C(e) of Appendix C.

Different preparations produced different catalyst bulk densities and the actual weight charged varied from 0.775 to 1.097 g/cm^3 in these six evaluations. This variation was assumed to be due to differences in particle size and size distribution and not to any fundamental catalyst property. The alcohol production rates (lb/cf/hr) were therefore normalized by dividing by the catalyst weight in grams. This gives the rate expected if all catalysts had a density of 1 g/cm^3. This adjustment neglects any additional correction to account for changes in gas conversion with the weight of catalyst.

Much of the actual data from the evaluations is shown in Figures 2 through 7. One of the main features of these short duration runs is that the catalyst does not reach a true steady state and most measures of catalyst performance vary with time. Graphs A and B in each figure show alcohol rate, total CO consumption rate, and selectivities to methanol, ethanol and methane as a function of run time. The units for alcohol rate and for total rate are different, and the vertical scales also change from figure to figure.

Graphs C and D in each figure show the alcohol and hydrocarbon distributions at two distinct times. For the MoS_2 catalysts, these are the times of the first and last samples. The first sample is usually during the induction period when rate is low. Part of this induction period may be due to slow purging of nitrogen from the reaction system. For the cobalt-molybdenum catalysts, the first distribution shown is at a space velocity of 6000 hr^{-1} and the second is the last data point at a space velocity of 3000 hr^{-1}. Coordinates are chosen so that a Schulz-Flory distribution would plot as a straight line in these figures. Best fit lines and the corresponding alpha values are given. This fitting included the single carbon products, methanol and methane, which may be formed by different reactions than the heavier products, and hence need not follow the Schulz-Flory distribution.

1. Molybdenum Disulfide Surface Area

One of the features noticed in our previous work was that the surface area of the molybdenum disulfide varied in an uncontrolled manner with different preparations, even when a previous preparation was being duplicated. Another feature noticed in the catalyst evaluations has been a loss of reactivity with time. It seemed likely that the loss of activity with reaction time was due to rearrangement of the MoS_2 surface. It also seemed likely that different preparations of MoS_2 could differ in their stability. This is difficult to check from the samples used for evaluation because of the relatively short duration of the evaluations. Also, the actual catalyst contains potassium and this obscures the true surface area of the MoS_2.

Some experiments were therefore carried out to test the stability of the MoS_2 surface. Conditions were the same as for our standard calcination of ATM to produce MoS_2; 400°C, in 10% hydrogen in nitrogen. Holding times were 2 or 4 hours. After

cooling and passivating, so that a sample could be obtained for the surface area measurement, the residue could be reheated. Results are shown in Figure 1. The time axis in this figure is simply the time at 400°C and does not include any correction for heating and cooling times. The results shown at one hour are for MoS_2 after the standard calcination. ATM 2KEC25 was the first material treated in this way. Calcination was for only two hours. The first cycle produced significant loss in surface area but the second cycle produced little change. While the high temperature accelerated changes, the total duration of the experiment was too short.

All ATM samples were prepared by the standard procedure of feeding H_2S slowly to a solution of ammonium paramolybdate and ammonia. 2KEC25 was obtained by adding H_2S for one hour only. The yield was 35.6 grams of maroon crystals. For 2KEC6 the preparation was divided into stages. In the first stage, H_2S was added for one hour and after filtration 44.7 grams of maroon crystals was obtained. The reaction was continued with the filtrate until reaction became very slow; 17.2 grams of small black particles were obtained and designated 2KEC II. In the standard procedure, H_2S is added for about two hours, before the rate becomes too slow, and the yield is about 65 grams of ATM. This is presumably a mixture of the two slightly different products.

ATM 2KEC71 was prepared by adding H_2S for one hour while the liquid temperature was 70°C, instead of the normal 60°C. Yield was 19 grams. The low yield is presumably due to the higher temperature and the loss of ammonia from the solution. The product was maroon crystals, similar to the normal first stage product.

Figure 1 shows that 2KEC71 gives a more stable product MoS_2 than 2KEC6 II or 2KEC25, and also has a higher surface area. The curved line through these data points suggests that further calcination may have given a constant surface area of 30-40 m^2/g. 2KEC6 II is the most unstable material. The straight line fitted in Figure 1 corresponds to exponential decay to zero surface area.

From these few experiments it seems that different preparations do differ considerably in their stability. ATM prepared at higher temperature and shorter reaction time appears better than the other materials. It is possible that the ATM precipitated in the later stages of reaction is contaminated with more impurities than that precipitated initially. The precipitation of other components would explain the smaller particle size found in the second stage product. Additional experiments would be needed to confirm this conclusion. Also, there is no evidence that the loss in surface area in these experiments is related to loss in catalyst activity under reaction conditions.

The loss in surface area may be accelerated by the presence of hydrogen. ATM 2KEC44 was prepared similarly to 2KEC25. Two portions were calcined separately and gave surface areas of 86.9 and 89.3 m^2/g. After recalcining at 400°C for four hours in nitrogen only, the surface area was 78.7 m^2/g. Repeated heating and passivation do not cause rapid loss of area. ATM 2KEC25 calcined at 400°C gave 90.6 m^2/g. After

wetting with water (to simulate the final calcination step) and reheating successively for one hour and for four hours at 300°C the areas were 90.1 and 88.9 m^2/g respectively.

2. Reaction After Heat Treatment

These results showed that a combination of heating and hydrogen exposure decreased surface areas. If this heating procedure simply accelerates the changes occurring with time in the reactor, then the modified material would be more typical of MoS_2 after a long reaction time and perhaps more stable. The first experiment was the preparation and evaluation of catalyst 2KEC52B. The MoS_2 used was the material with 78.7m^2/g area described in the preceding section. Catalyst was prepared by impregnation with potassium acetate and calcining. Unfortunately the impregnation was done with the proportion of liquid appropriate to MoS_3 and K/Mo = 0.29 instead of 0.35 as in the standard catalyst used in this study.

Figure 2 shows the results. The maximum alcohol rate was below 20 lb/cf/hr. The rate shows a steady decline after the first day. The initial selectivity to methane is much better than expected with a standard catalyst (0.35 K/Mo) but the final value of about 15% carbon selectivity to methane is quite normal. The final value for alpha from the alcohol distribution is just below 0.2. This indicates that this catalyst is not very good at making the higher alcohols.

Heating in nitrogen may be too mild to produce a stable product. More severe treatment may be needed, even if this lowers the surface area substantially. Catalyst 2KEC80B was prepared in the standard procedure from ATM 2KEC6 II which had been heated in H_2 to reduce the surface area to 42.8 m^2/g. Results are shown in Figure 3. The maximum rate was 22.6 pounds of alcohol per cubic foot per hour, after correcting for the catalyst density of 0.953 g/cm^3. Unfortunately this rate was not maintained and the decline in rate was similar to that for 2KEC52B. Selectivities in the two evaluations were also similar, as are the product distributions shown in plots C and D.

The high rate was surprising and possibly indicates that the activity of MoS_2 is not directly related to BET surface area. It is also possible that the higher measured rate is due to random variation between evaluations. The selectivity and product distribution results show that these catalysts are very similar to each other and to the standard catalyst 1KEC62 evaluated previously. The different treatments therefore do not change the catalyst selectivity and definitely do not give greater stability. It would be desirable to test catalyst derived from 2KEC71 to find whether this also deactivates.

3. Catalyst from Low Temperature ATM

Before the surface area measurements on samples derived from 2KEC71 were

obtained, a catalyst, 2KEC57, was prepared and tested using ATM prepared in one hour reaction at a low temperature, 50°C. The preparation gave 20.8 g of orange powder, quite distinct from the maroon crystals normally formed at 60°C. While being calcined to produce MoS_2, the material gave a sudden exotherm from 400 to 465°C. A large exotherm has sometimes been associated with high activity and this seemed to be justification for testing further. Catalyst was prepared in the standard manner, but as before the K/Mo ratio was 0.29 instead of 0.35.

Results are shown in Figure 4. Both the alcohol rate and the total rates are about half of the normal values. Maximum rate is not reached until 40 hours, but after that there is a steady decline. The alcohol distribution is again rather steep, with little of the higher alcohols. Selectivity to methanol is much higher than to ethanol, but the resulting distribution fits the Schulz-Flory distribution almost exactly. The similarity of selectivity and product distribution to the results discussed above is an indication that the active sites are similar to those in a conventional catalyst. The low rate suggests that there were simply too few active sites.

If this evaluation has any value it is likely to be as further confirmation that a higher temperature preparation of ATM may be superior.

4. Cobalt Impregnated Catalyst

Another method considered for improving the surface stability of the MoS_2 catalyst was addition of cobalt by impregnation. ATM 2KEC70A, prepared in a one hour reaction at 60°C, was calcined for one hour at 200°C in 10% hydrogen to produce MoS_3. This solid was porous and a surface area measurement after evacuation at 275°C (to avoid formation of MoS_2) gave 40 m^2/g. This material was impregnated with a dilute solution of cobaltous acetate to give a mole ratio Co/Mo =0.035 and calcined for one hour at 300°C in 10% hydrogen. The evolution of heavy white fumes suggested that reaction occurred. The product was then impregnated with potassium acetate to give K/Mo = 0.35 and calcined at 400°C for one hour , to produce catalyst 2KEC80A.

Figure 5 shows the result of the evaluation. The catalyst bulk density was 1.089 g/cm^3 and this reduced the maximum measured rate from 25 lb/cf/hr to 23, as shown in plot A. Rate declined with time and selectivities were similar to those found in the previous evaluations. This shows that the presence of a small amount of cobalt makes very little difference to the performance. This obviously raises a question as to the distribution of the cobalt. One distinctive features of the evaluation results is the very high initial selectivity to methane and the low selectivity to methanol. This may indicate that the surface is initially modified by the presence of cobalt, but that as the reaction proceeds, cobalt migrates or is covered.

An interesting feature of the product distributions shown in plots C and D is that

methanol production is less than - and ethanol production is greater than - the best fit line for the Schulz-Flory distribution. The deviations are consistent in the different samples but difficult to explain from the reaction mechanism. Methanol can be formed without breaking the C=O bond and hence would be expected to be above the best fit line. Data from other evaluations show similar trends.

5. Cobalt-Molybdenum Catalysts

A novel method of forming a cobalt-molybdenum sulfide catalyst is described in some Japanese patents (Chemical Abstracts, vol 106, numbers 179672, 179673, and 216870). This was adapted and used to prepare two Co-Mo catalysts.

15 grams (0.0576 g moles) of ATM was dissolved in 40 ml of ethylene diamine (EDA) and cooled in ice. 7.178 grams (0.0288 g moles) of cobaltous acetate was dissolved in water and cooled. This solution was added dropwise to the EDA solution. The result was a milky red precipitate which was recovered by filtering under vacuum, washing with acetone, and drying overnight. The yield was 15.7 grams of orange powder. Analysis showed 9.63 wt% Co, 17.1 wt% Mo and 15.6 wt% S. The Co/Mo mole ratio was 0.917, showing that part of the molybdenum remained in solution and the precipitate was presumably mainly a compound with equimolar amounts of cobalt and molybdenum. A second preparation, using ethanol for washing, gave 11.4% Co, 18.5% Mo, and 16.4% S and a Co/Mo ratio of 1.003. This improvement was presumably due to better washing of the filter cake. In all cases the total analyzed was far below 100%, presumably because some EDA remained in the precipitate.

Two portions of this material were calcined in 10% hydrogen for one hour. White fumes evolved when the samples reached about 200°C and in each case appeared to stop before the end of calcination. This was believed to be EDA vapor condensing to a mist as the gas left the furnace. Weight loss was 42% after calcining at 300°C and 46% at 400°C. The calcined powders were black. Both samples were impregnated (0.215 g potassium acetate/gram powder) and calcined for one hour at 400°C. White fumes were still evolving at the end of this period and so the samples were reheated and calcined for a further hour to eliminate all trace of EDA or other volatiles. The potassium loading was chosen to give a molar ratio K/(Co + Mo) = 0.3, assuming the solids were $(MoS_2)_2CoS$. The ratio would be 0.275 if the solids were MoS_2CoS, and higher in any sample containing residual EDA or other impurity.

Catalyst 2KEC37A (bulk density 0.854 g/cm^3) was produced from the sample calcined at 400°C and 2KEC37B (0.775 g/cm^3) from the sample calcined at 300°C. Evaluation results are shown in Figures 6 and 7 respectively. In each case the first two data points were obtained at a space velocity of 6000 hr^{-1} and then the gas flow was reduced to 3000 hr^{-1} to raise the conversion. Both catalysts show a continued increase in rate with time and even after 70 hours the rate and selectivity continue to change.

Catalyst 2KEC37A shows a very pronounced drop in selectivity to methanol and an increase in the selectivity to ethanol. In both cases, the initial selectivity to methane was low and declined further. Reduction in gas feed rate increased the conversion to methane but unlike the selectivity to alcohols, methane selectivity lines out relatively quickly.

Figure 1. Surface Areas of MoS_2 Derived from Different ATM Samples as a Function of Time Held at 400°C.

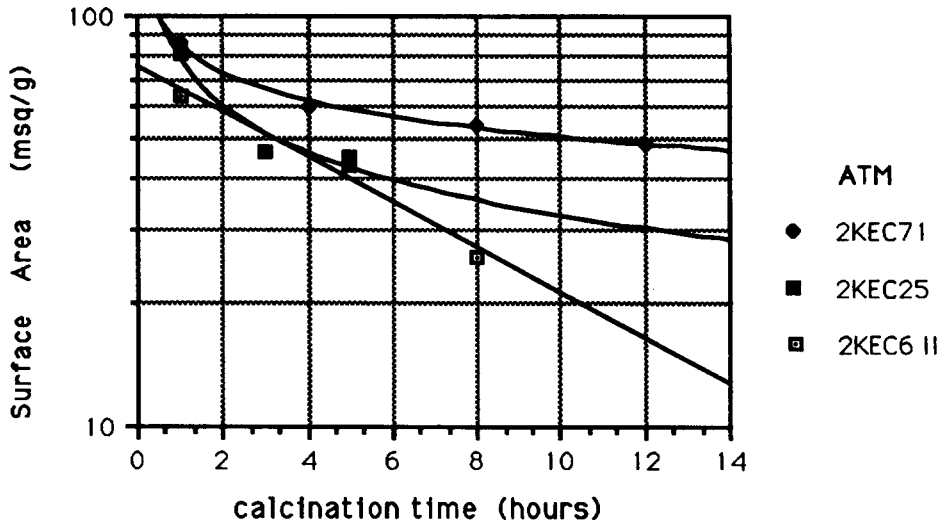
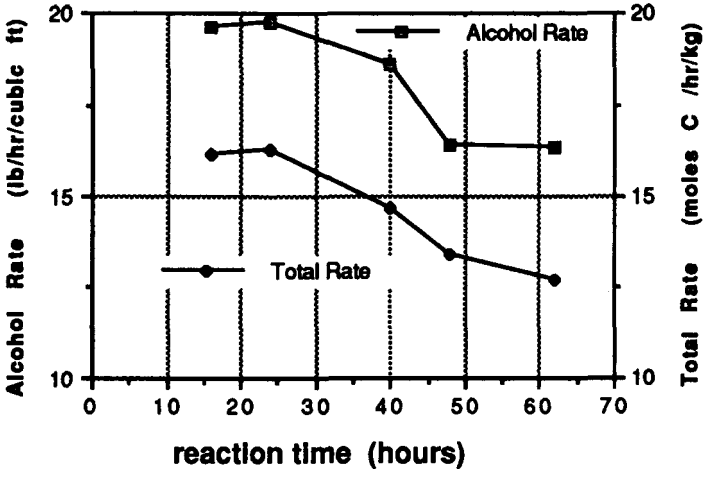
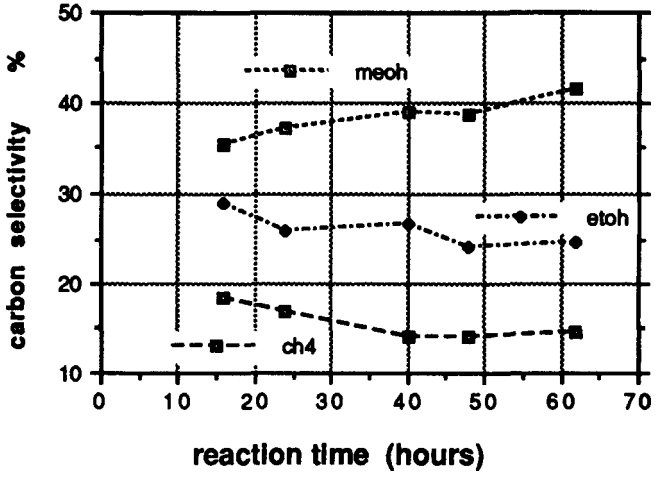


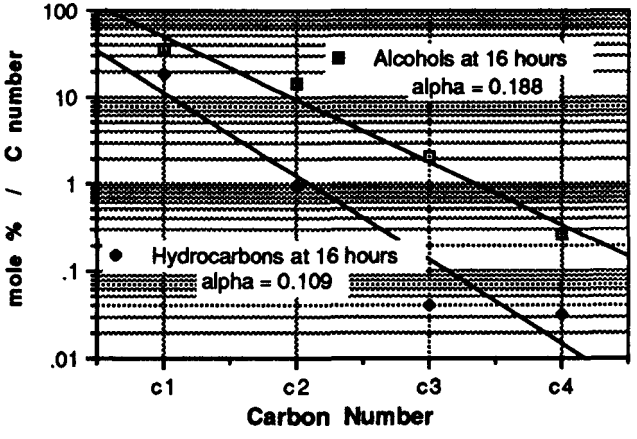
Figure 2. Catalyst 2KEC52B; ATM prep 60°C; MoS_2 prep 400°C (5 hours); impreg 0.29 K/Mo; calcine 400°C.
Evaluation 28NEK94; 300°C; 1200 psig; H_2/CO = 1/1; SV = 6000hr^{-1}



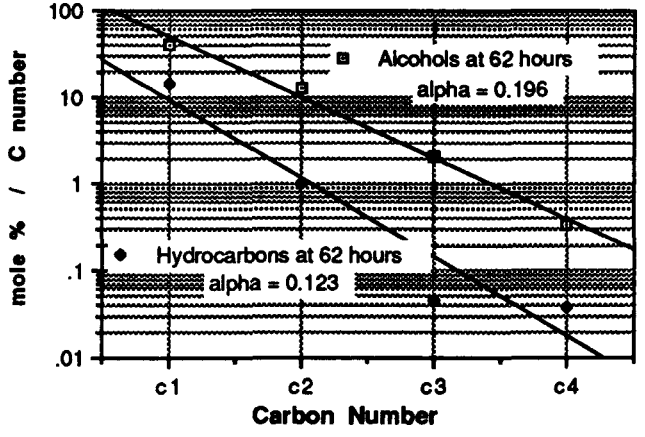
(A) Rate vs. Time



(B) Selectivity vs. Time

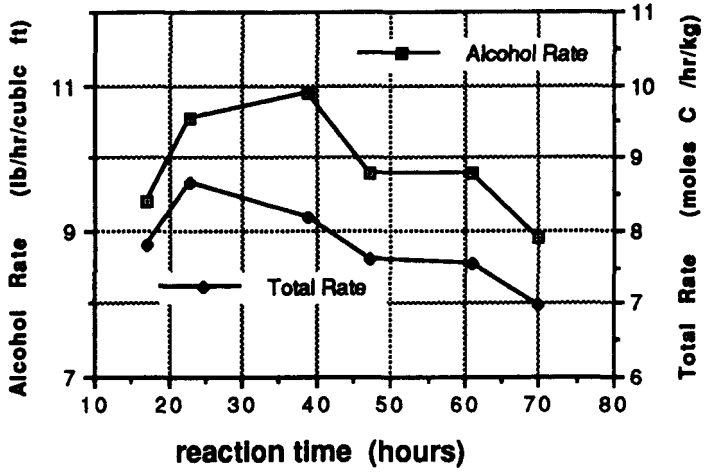


(C) Product Distribution

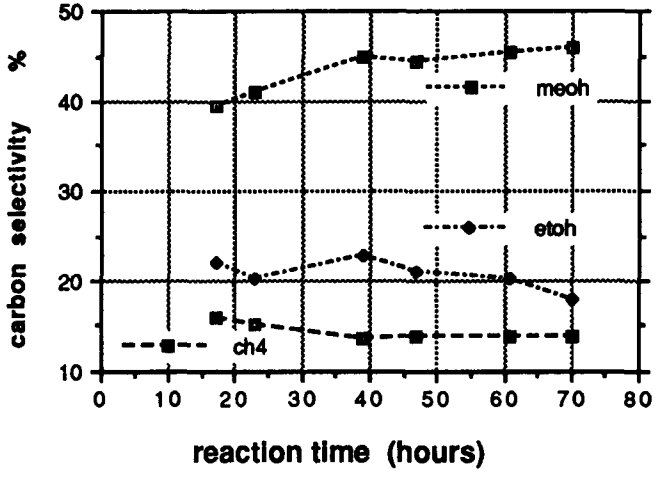


(D) Product Distribution

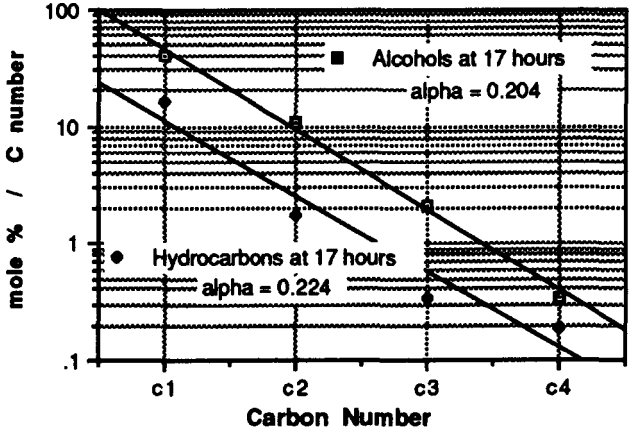
Figure 3. Catalyst 2KEC57; ATM prep 50°C; MoS_2 prep 400°C; impreg 0.35 K/Mo; calcine 400°C.
Evaluation 28NEK96; 300°C; 1200 psig; H_2/CO = 1/1; SV = 6000 hr^{-1}



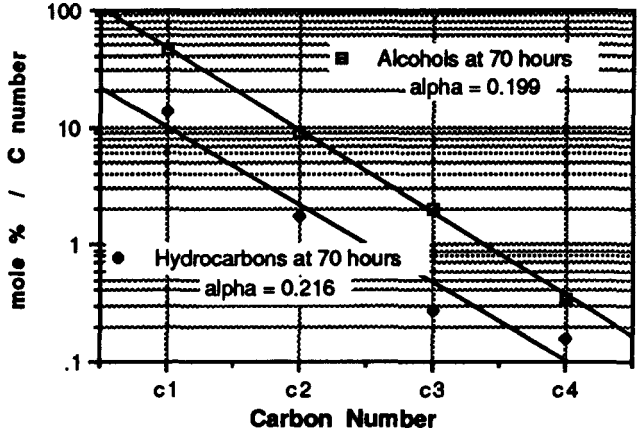
(A) Rate vs. Time



(B) Selectivity vs. Time

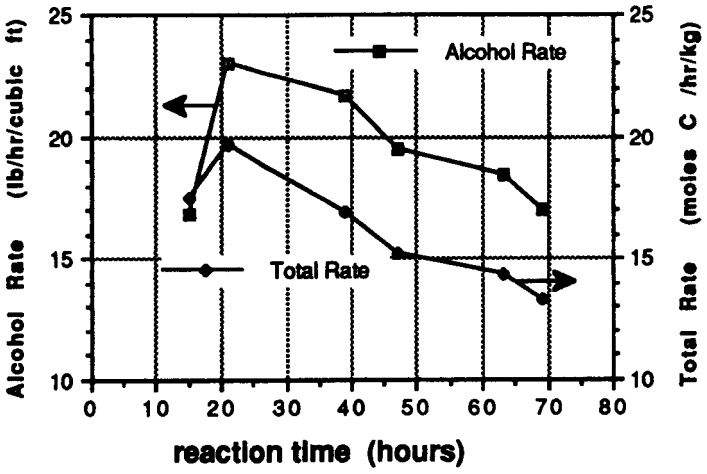


(C) Product Distribution

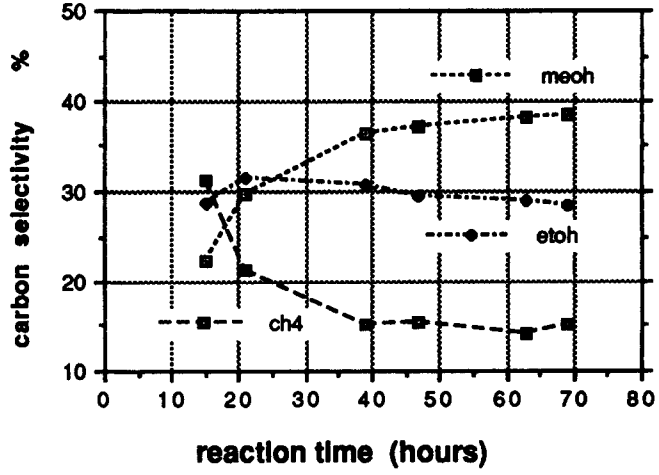


(D) Product Distribution

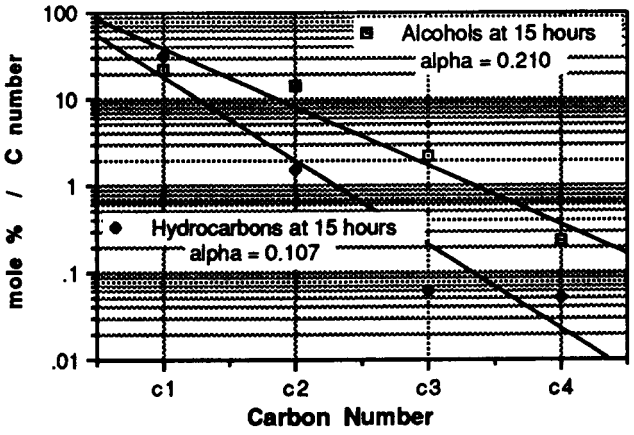
Figure 4. Catalyst 2KEC80A; ATM prep 60°C; MoS_2 prep 400°C (5 hours); impreg 0.35 K/Mo; calcine 400°C.
Evaluation 28NEK118; 300°C; 1200 psig; H_2/CO = 1/1



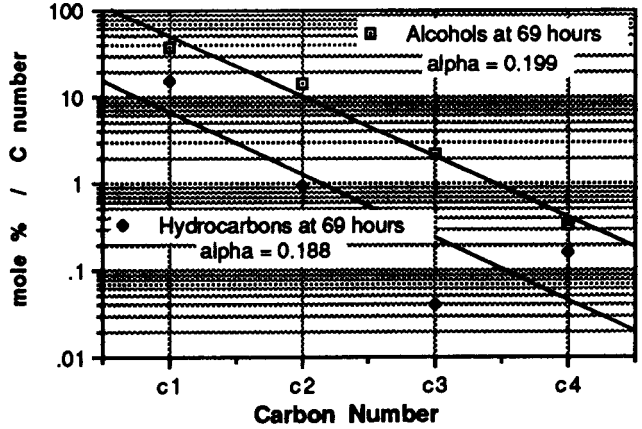
(A) Rate vs. Time



(B) Selectivity vs. Time

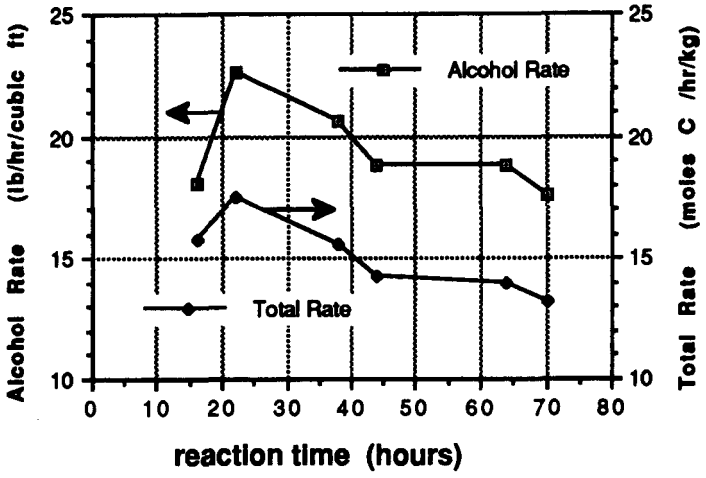


(C) Product Distribution

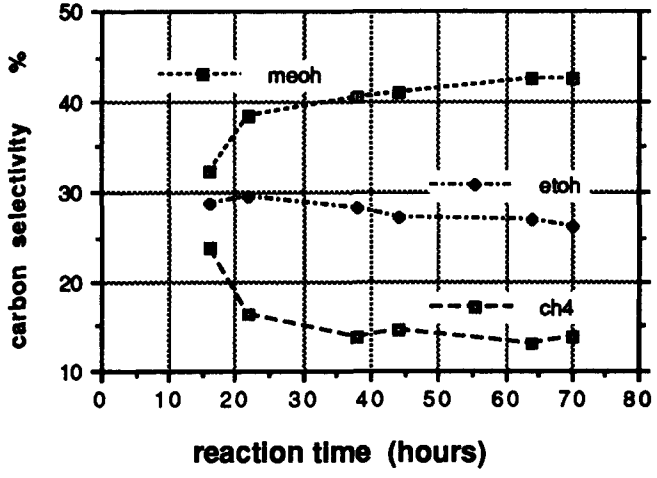


(D) Product Distribution

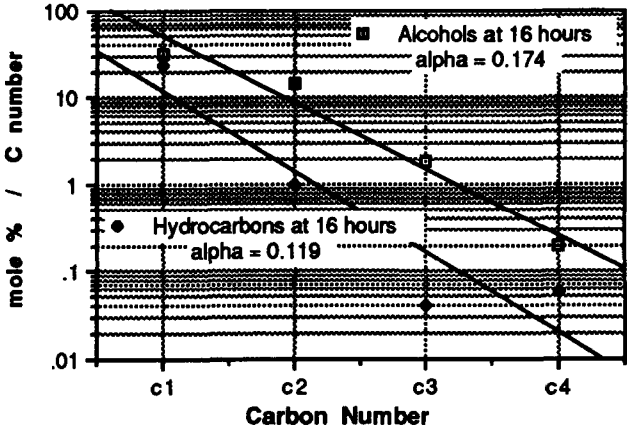
Figure 5. Catalyst 2KEC80B ; ATM prep 60°C; MoS_3 prep 200°C; impreg 0.35 K/Mo; calcine 400°C.
Evaluation 28NEK120; 300°C; 1200 psig; H_2/CO = 1/1



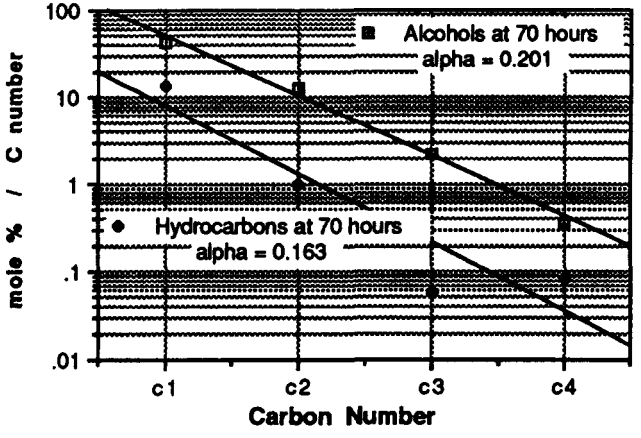
(A) Rate vs. Time



(B) Selectivity vs. Time

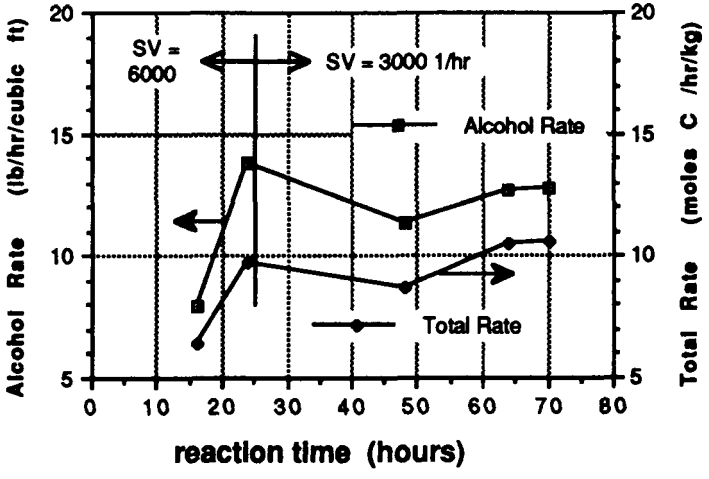


(C) Product Distribution

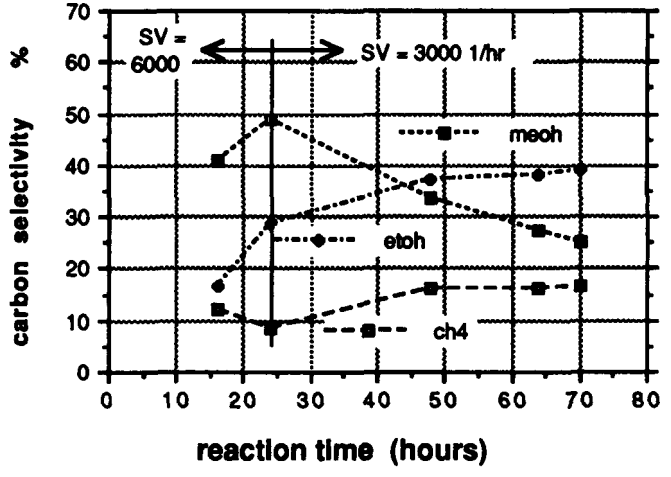


(D) Product Distribution

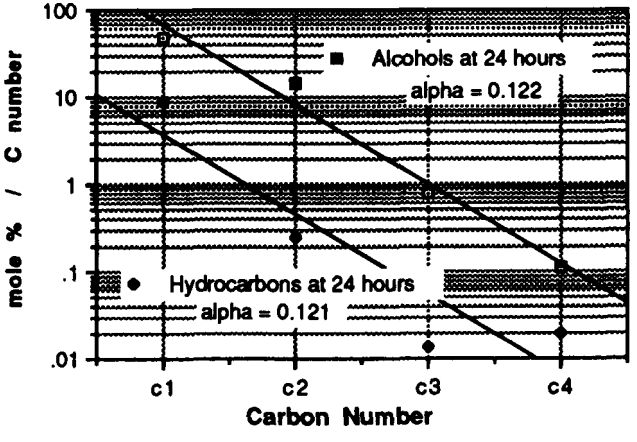
Figure 6. Catalyst 2KEC37A; CoMo (EDA); calcine 400°C; impreg 0.3 K/M; calcine 400°C.
Evaluation 28NEK80; 300°C; 1200 psig; H_2/CO = 1/1



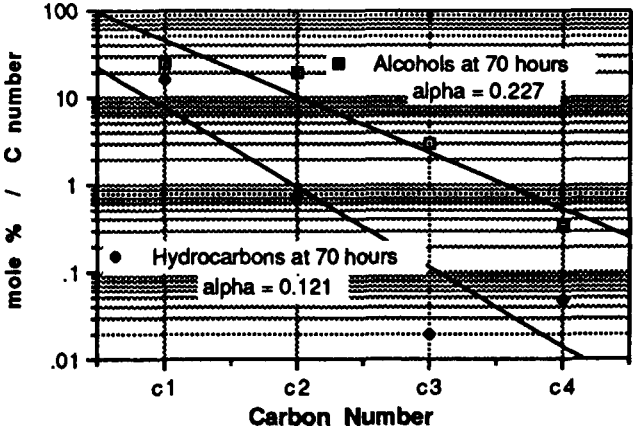
(A) Rate vs. Time



(B) Selectivity vs. Time

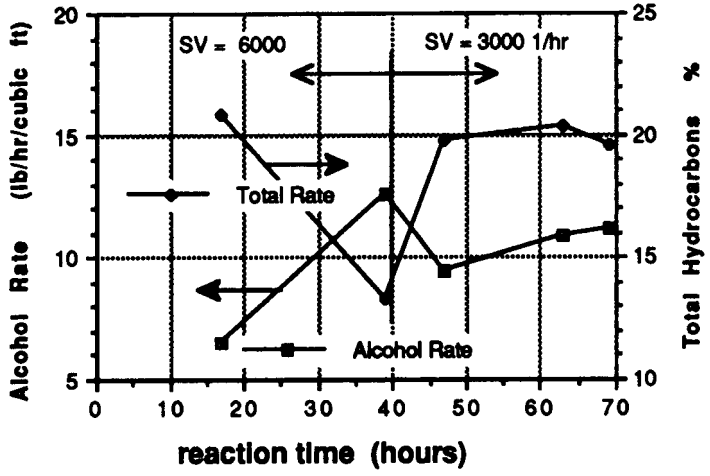


(C) Product Distribution

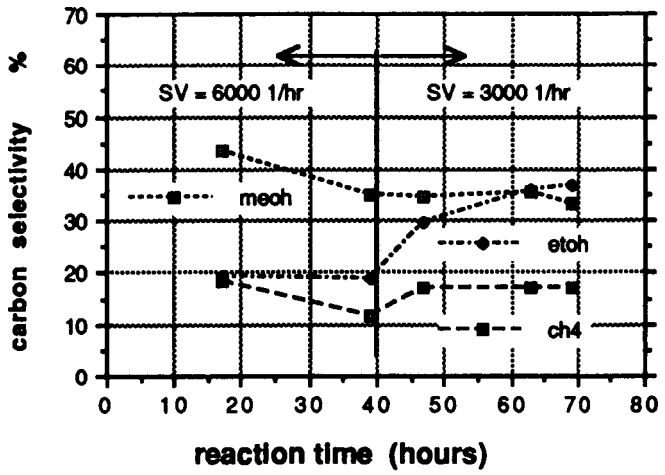


(D) Product Distribution

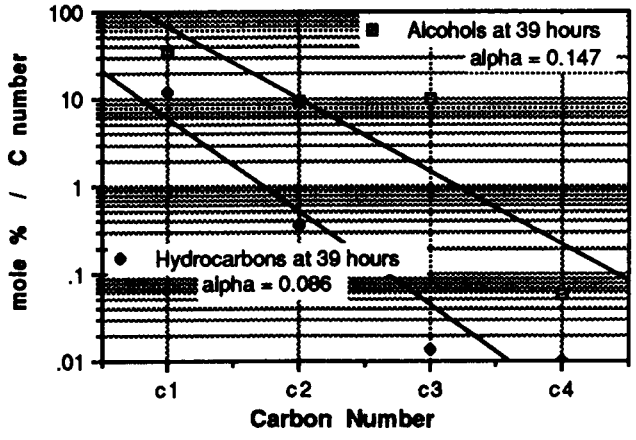
Figure 7. Catalyst 2KEC37B; CoMo (EDA); calcine 300°C; impreg 0.3 K/M ; calcine 400°C.
Evaluation 28NEK82; 300°C; 1200 psig; H_2/CO = 1/1



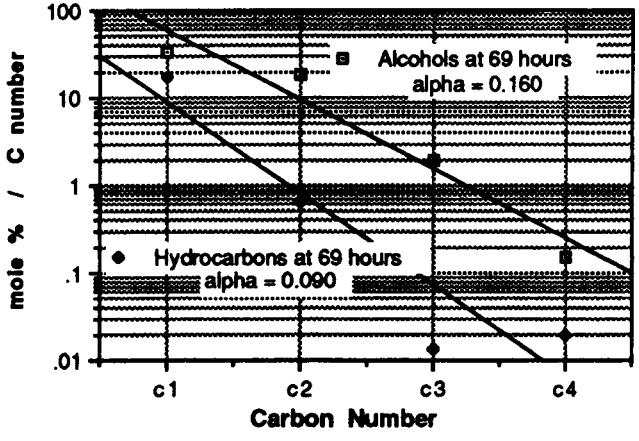
(A) Rate vs. Time



(B) Selectivity vs. Time



(C) Product Distribution



(D) Product Distribution

D. Task 3 Summary

Different MoS_2 preparations differ in their stability when heated at 400°C in 10% hydrogen in nitrogen. A sample of MoS_2 obtained from ATM prepared by reaction at 70°C was the most stable of those tested. The stability of MoS_2 prepared from ATM precipitated near the end of reaction appears to be poor and this may be due to coprecipitation of impurities.

Evaluation of catalysts prepared from MoS_2 which had been heated in nitrogen or 10% hydrogen did not show improved stability or selectivity. Since reaction rates were relatively high, the loss of surface area did not reduce catalyst activity. A catalyst prepared from ATM prepared at lower temperature gave unusually low rates and also showed deactivation. Selectivity was normal and hence the catalyst may have a lower concentration of active sites.

Catalyst prepared after impregnating MoS_3 with a small amount of cobalt acetate required a longer time to reach a steady state selectivity but deactivation was similar to that of conventional MoS_2.

Cobalt-molybdenum catalyst was prepared by a novel procedure. The composition was approximately equimolar cobalt and molybdenum. The activity was only 12-13 lb alcohol/cf/hr (after the density correction) but was still increasing slowly after 70 hours evaluation and hence no deactivation was observed. Carbon selectivity to hydrocarbons was about 20%. This may be reduced by increasing the potassium loading. Additional testing to check for stability at longer reaction times may be justified.

This phase of the program has been concluded because the catalyst preparations did not show potential for the magnitude of improvement required. If further work is pursued on these approaches in other parts of the program, the cobalt-molybdenum catalyst should be tested for a longer time, and a catalyst obtained from ATM prepared at higher temperatures should be investigated further.