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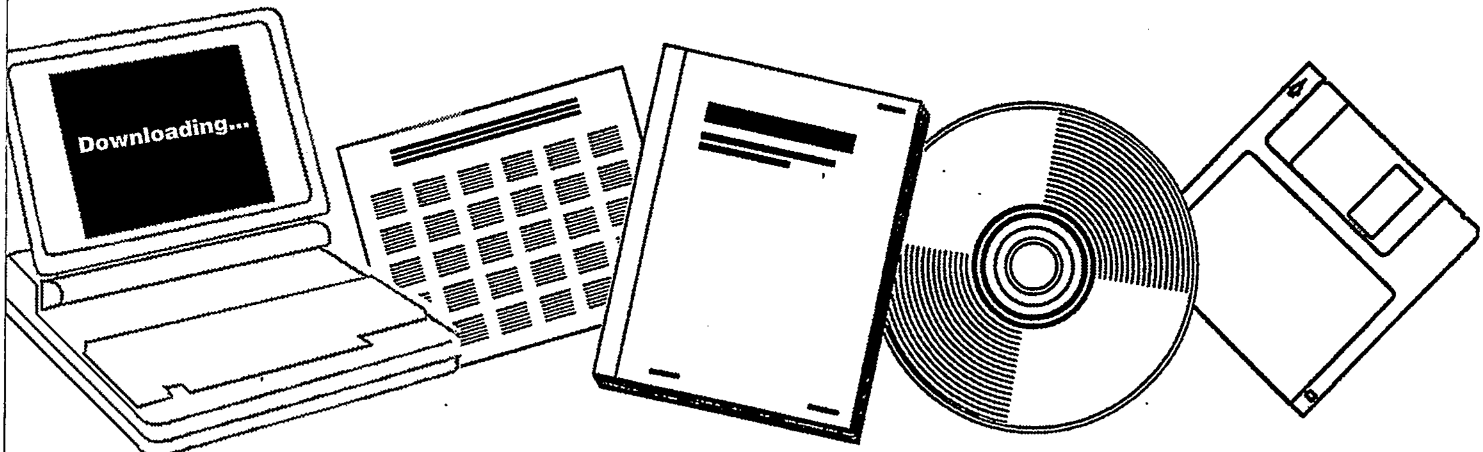
OPTIMUM CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS: SIXTH QUARTERLY TECHNICAL PROGRESS REPORT, APRIL-JUNE, 1988

UNION CARBIDE CORP., SOUTH CHARLESTON,
WV. SOLVENTS AND COATINGS MATERIALS DIV

29 JUL 1988



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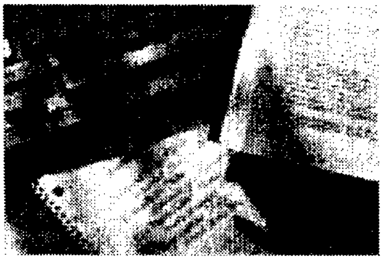

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SIXTH QUARTERLY TECHNICAL PROGRESS REPORT

DOE CONTRACT NO. DE-AC22-86PC90013

Optimum Catalytic Process for Alcohol Fuels from Syngas

Pittsburgh Energy Technology Center

July 29, 1988

Solvents and Coatings Materials Division

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

MASTER

TECHNICAL PROGRESS REPORT
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Don C. Best
D. C. Best
Program Manager

Patent Cleared by Chicago
OPC on August 15, 1988

Patent Hold

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OPC on August 15, 1988

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Appendixes

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, develop economic evaluations and process conceptualization, and evaluate catalysts in a bench-scale apparatus. 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 are also being 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 during the first year involved engineering support for the chemical investigations. Economic evaluations of a base case process for conversion of syngas to fuel alcohols were also pursued.

Current work in Task 3 involves experiments with selected catalytic systems and continuing economic and process conceptualization studies.

During the last 9 months of Task 3, our plan is to focus the work on catalyst stability studies, validations of models, and the synthesis of the best combination of catalyst and reactor systems.

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

We continued the study of additional additives to the homogeneous ruthenium catalyst in the search for improved activity. We have found that certain Mo and Ir compounds slightly increased the selectivity to higher alcohols. Platinum, copper, and palladium compounds tested are severe catalyst poisons. Phosphine compounds tested either retard the catalyst activity slightly or completely poison the system.

Chemical model studies have been carried out to investigate the mechanism of homogeneous hydrogenation of CO. The information gained could allow us to modify the system to enhance the rate of the rate-determining step. Results of these studies are consistent with the hypothesis that the first interaction between hydrogen and CO could be a reaction between a metal hydride and an activated carbon monoxide ligand bonded to a metal center.

Investigations into improving the performance of alkali-loaded molybdenum sulfide based catalysts have continued. We have completed a Plackett-Burman designed set of experiments to investigate the effect of eleven different metal additives on the performance of a potassium-molybdenum sulfide catalyst and found that the addition of three metal additives improves both the rate and selectivity to alcohols. One of these additives has a significantly greater effect than the others. Studies are continuing with these catalysts.

B. Task 3: Bench Scale Concept Evaluation

Experiments this quarter have tested a number of alternative procedures for the preparation of fuel alcohol catalysts. None of the catalysts tested has been superior to the standard catalyst.

MoS_2 with higher surface area has been prepared by changing the ammonium tetrathiomolybdate preparation procedure and stopping the H_2S feed sooner. The product of this procedure consists of uniform needle-like red crystals. The maximum surface area was 109.6 m^2/gram. Unfortunately, catalysts prepared from this material did not produce superior rate or selectivity.

Catalysts prepared by low temperature calcination to first produce MoS_3, then impregnating and calcining were little different from the standard except for a slower rate. Impregnation with potassium acetate from an ethanol solution did not improve performance.

Two catalysts were prepared from ammonium tetrathiomolybdate precipitated by a process yielding fine particles. Neither gave improved rate or selectivity.

A catalyst prepared from $(NH_4)_2MoO_2S_2$ was also not active enough and did not give improved selectivity.

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 will continue on homogeneous catalysts for the direct conversion of syngas to alcohols. Work on heterogeneous catalysts for alcohol production will also continue, with the emphasis on molybdenum-based catalysts.

Work on Task 3 will involve economic and engineering evaluations, as well as continuing engineering involvement in 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
A114:	A metal catalyst additive
A116-A125:	Metal catalyst additives

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.

Procedure B(g)

All catalysts are prepared by placing the indicated amounts of each of the 11 additives, 2.83 gm potassium acetate, and 10 gms of ammonium tetrathiomolybdate (ATM) into 100 cc of distilled water in a beaker, covering with a watch glass and stirring for 24 hrs. The mixture is then dried in a rotary evaporator with vacuum and a 80-90°C water bath for 4 hrs or until dry.

The dried catalyst is then calcined by placing it in a glass boat and inserting the boat into the horizontal tube furnace and then continuing as follows:

1) Purge at R.T. with 360 cc/min of nitrogen for 15 min.

2) Heat to 110°C and hold for one hour.

3) Start a 40cc/min flow of hydrogen to the furnace (in addition to the nitrogen flow) and heat to 400 °C at 10°C/min and then hold for 1 hr.

4) Turn off the hydrogen and the temperature controller, open the furnace and cool to RT.

Since the catalyst is pyrophoric at this stage, it should not be exposed to 100% air. When cooled to 23-25°C, it is passivated with air according to the following schedule:

cc/min		
N_2	Air	Hold time
360	120	15 min
360	240	15 min
360	360	15 min
240	360	15 min
120	360	15 min
0	360	15 min

The total time for the passivation is 1 hr and 15 min. However, if at any point the temperature rises more than one or two degrees, the current conditions are maintained until the temperature drops back to the original setting before making the next change.

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

We continued to investigate the direct conversion of syngas to alcohols using promoted ruthenium catalysts because of their good overall catalyst activities. Our objective is to improve the catalyst system so that fuel alcohols with substantial amounts of higher alcohols (C_2+ alcohols) can be produced at low pressure.

Earlier, we reported that with the addition of A16 and A92 or its derivatives, the activity of the ruthenium/I^- catalyst system and the production of C_2+ alcohols increased significantly. Also, the system is very selective for producing alcohols with only a small amount of undesirable products such as acetates. During this quarter we continued the search for other metallic and non-metallic additives which could substantially increase the activity of this catalyst system.

We also describe here some of the chemical model studies we have conducted to increase our basic understanding of the reaction mechanism for the conversion of syngas to oxygenates by homogeneous ruthenium catalysts. The first fundamental steps in the reaction mechanism are likely to involve the activation of carbon monoxide and hydrogen by metal centers forming reactive metal carbonyl species and reactive metal hydrido species, respectively. The interaction between these species would lead to the formation of a metal-formyl species. This formyl species would be subsequently transformed to methanol or other oxygenates via further hydrogenation (and carbonylation) and reductive elimination.

It is believed that the interaction between the reactive hydride and carbonyl species is a key step and perhaps the rate-limiting step in the catalytic cycle. An understanding in this fundamental catalytic step would gain important information on the nature of the interaction and would perhaps lead us to discover a more active catalyst.

2. Metallic and Non-Metallic Promoters for the Ruthenium System.

We continued the examination of additional metallic and non-metallic compounds in the hope that we would find some that would increase the activity of the catalyst system of Ru/A16/I^-/A92. We have found that Mo and Ir compounds have slight negative effects on the activity of the system but increased the selectivity to higher alcohols slightly.

Pt, Cu and Pd compounds are severe catalyst poisons since the presence of a small amount of them almost completely inhibited catalyst activity.

Phosphine compounds are known to be beneficial for carbonylation reactions, but they are also known to retard the catalyst activity of the Ru/I^- system. We hoped that A92 might have altered the catalyst characteristic so that phosphines could be beneficial to the Ru/A16/I-/A92 system. This however proved to be incorrect since we found that $P(n\text{-}Bu)_3$ retards the catalyst activity slightly while triphenylphosphine completely poisons the system.

Key to Tables 1 and 2.

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 Metal Complexes on the Ru/A16/I^-/A92 System

	TWL-#	13-31	13-37
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7
3	Solvent	1,3-DMEU	1,3-DMEU
4	mL	38	38
5	Additive	A16/KI/A92/$Mo(CO)_6$	A16/KI/A92/CuI
6	mmol	7.0/30/93/1.9	7.0/30/93/1.0
7	Press., psi	4000	4000
8	Temp.,°C	230	230
9	Time,hrs.	1.5	1.5
10	H_2/CO	1.0	1.0
11	MeOH, g	3.9	2.2
12	EtOH, g	3.8	3.3
13	n-PrOH, g	0.9	0.4
14	n-BuOH, g	0.3	0.1
15	Acetates, g	0.4	0.3
16	Tot. Prod., g	9.3	6.3
17	Rate, total, M/h	4.0	2.7
18	C_2+ alcohols %	44	52

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

Table 1. Effect of Metal Complexes on the Ru/A16/I^-/A92 System (cont'd)

	TWL-#	13-39	13-45
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7
3	Solvent	1,3-DMEU	1,3-DMEU
4	mL	38	38
5	Additive	A16/KI/A92/$[Ir(CO)_2Cl]_2$	A16/KI/A92/$Pt(acac)_2$
6	mmole	7.0/30/93/1.0	7.0/30/93/1.0
7	Press., psi	4000	4000
8	Temp.,°C	230	230
9	Time,hrs.	1.5	1.5
10	H_2/CO	1.0	1.0
11	MeOH, g	3.4	***
12	EtOH, g	3.8	
13	n-PrOH, g	0.6	
14	n-BuOH, g	0.2	
15	Acetates, g	0.6	
16	Tot. Prod., g	8.6	
17	Rate, total, M/h	3.6	
18	C_2+ alcohols %	44	

*** no analysis was carried out because very low activity was observed.

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

Table 2. Effect of Phosphines on the Ru/A16/I^-/A92 System

	TWL-#	13-43	13-41
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7
3	Solvent	1,3-DMEU	1,3-DMEU
4	mL	38	38
5	Additive	A16/KI/A92/P-n-Bu_3	A16/KI/A92/PPh_3
6	mmole	7.0/30/93/2.0	7.0/30/93/2.0
7	Press., psi	4000	4000
8	Temp.,°C	230	230
9	Time,hrs.	1.5	1.5
10	H_2/CO	1.0	1.0
11	MeOH, g	2.0	***
12	EtOH, g	3.7	
13	n-PrOH, g	0.2	
14	n-BuOH, g	0.0	
15	Acetates, g	0.3	
16	Tot. Prod., g	6.2	
17	Rate, total, M/h	2.6	
18	C_2+ alcohols %	54	

*** no analysis was carried out because very low activity was observed.
Experimental procedure: B(f); Analytical procedure: C(b); Key on page 17.

3. Chemical Model Studies

In recent publications concerning the reaction mechanism by which alcohols and other oxygenates are formed from the reaction of hydrogen and carbon monoxide, we and others have postulated that the first steps in the catalytic cycle are likely to be the activation of hydrogen and carbon monoxide to form active metal hydride and active metal carbonyl species. For the homogeneous ruthenium system, the active hydrido species that is possibly a species of the form $[HRu(CO)_4]^-$. On the other hand, the active carbonyl species may be $Ru(CO)_4I_2$. The reaction between these species was attempted and reaction was indeed observed. However, no formyl species could be observed as an intermediate. It is most likely that the formyl species is just too reactive to be detected.

It is well known that analogous complexes of the third row transition metals are usually more stable than those of the corresponding second row transition metal. We therefore decided to model the chemical reaction of $Ru(CO)_4I_2$ and $[HRu(CO)_4]^-$ using $Os(CO)_4I_2$ as the starting carbonyl species in the hope that the elusive metal formyl species coud be observed.

We first carried out the reaction between $Os(CO)_4I_2$ and a known strong hydride donor, $Li(HBEt_3)$. A reaction was observed to proceed very slowly at about -60°C and at a moderate rate at -30°C. The reaction did produce a species whose ^1H NMR spectrum was consistent with that of a metal formyl species. A characteristic resonance of the formyl proton was observed at 15.38 ppm (vs.TMS). This formyl is relatively stable at temperatures below 0°C but decomposed at room temperature.

We then proceeded to investigate the reaction between $Os(CO)_4I_2$ and $[HRu(CO)_4]^-$. We did not observe any reaction occurring at temperatures below 0°C. A slow reaction was apparent when the temperature was raised above 0°C as the disappearance of the hydride signal was noted, but no formyl species was detected.

This result is most likely because $[HRu(CO)_4]^-$ is less reactive than $Li(HBEt_3)$ at temperatures below 0°C. When the temperature was raised above 0°C and the reaction finally took place, the formyl species became more reactive and thus there was not a high [illegible] concentration of it formed before decomposition to allow detection by NMR.

Despite the fact that we did not observe the formyl intermediate in the latter reaction, we did demonstrate that a formyl species can be generated in the reaction between $Os(CO)_4I_2$, our model compound for $Ru(CO)_4I_2$, and the hydride $Li(HBEt_3)$. This is consistent with the hypothesis that the first interaction between hydrogen and CO could very well be a reaction between a metal hydride and an activated carbon monoxide ligand bonded to a metal center.

The experimental details for these studies are reecorded below.

Source of Chemicals

$Li(HBEt_3)$ and all the deuterated slovents were purchased from Aldrich Chemicals. $Os_3(CO)_{12}$ was obtained from Strem Chemicals.

Preparation of Complexes

$Os(CO)_4I_2$: 100 mmole of $Os_3(CO)_{12}$ and 100 mmole of I_2 were dissolved in 150 ml of benzene. The solution was charged into a Hastelloy autoclave under a nitrogen atmosphere. After the autoclave was sealed, it was purged with CO and then pressurized to 1000 psi of CO. It was then heated to 120°C for 6 hours. After cooling to room temperature and releasing the pressure, the autoclave was opened. A suspension of a cream-colored solid in benzene was obtained. The product was collected by filtration and washed with pentane thoroughly, then air dried. The yield was 90%.

$[PPN][HRu(CO)_4]$: In a 3-necked round-bottom flask equipped with a gas-inlet, about 150 ml of ammonia was condensed at -78°C using a dry-ice-acetone bath . Then 0.36 g of metallic sodium was carefully added in small pieces to the liquid ammonia. After all the sodium metal was added and dissolved, the solution became deep blue in color, and 1.32 g of $Ru_3(CO)_{12}$ was added in small portions. The solution turned green after the addition was completed The dry ice-acetone bath was removed and the solution was stirred and left to evaporate at a slow rate, through a buubbler to prevent entrance of air. After 3 hours, 95% of the ammonia was evaporated. The rest of the ammonia was removed under vacuum.

The residue was recooled to -78°C and 120 ml of methanol was added slowly followed by a solution of 3.8 g of [PPN]Cl in 80 ml of methanol and 0.50 g of acetic acid. A white precipitate of the product resulted. The product was collected by filtration at -78°C using a specially designed fritted filter. An off-white powder was obtained which was dried under vacuum at room temperature overnight. The product decomposes slowly at room temperature and was kept below 0°C for storage.

Proton NMR Studies

Reaction of $Os(CO)_4I_2$ with $Li(HBEt_3)$ in CD_3CN: The osmium complex (0.10 g) was dissolved in 1.0 ml of CD_3CN in an NMR sample tube sealed with a rubber stopper. The sample tube was then cooled to -198°C by submerging the bottom half of the tube in liquid nitrogen. An equimolar amount of the hydride in THF solution was injected into the sample tube. The tube was allowed to warm up to -80°C in the NMR probe. Spectra taken at this temperature indicated that no reaction had taken place. The sample was allowed to warm in the probe in 5°C increments and spectra were taken at each interval.

The reaction was similarly carried out in d_8-THF.

Attempted reaction of $Os(CO)_4I_2$ with $[PPN][HRu(CO)_4]$: The osmium complex (0.10 g) was dissolved in 1.0 ml of d_8-THF in an NMR sample tube sealed with a rubber stopper. The sample tube was then cooled to -198°C by submerging the bottom half of the tube in liquid nitrogen. An equimolar amount of the hydride in CD_3CN solution was injected into the sample tube. The tube was allowed to warmed up to -80°C in the NMR probe. A spectrum taken at this temperature indicated that no reaction had taken place. The sample was allowed to warm in the probe in 5 °C increments and spectra were taken at each interval.

The reaction was attempted in d_6-acetone similarly.

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 the potassium-molysulfide catalyst and specifically on the effect of metal additives.

2. Addition of Metals to MoS_2 Catalysts

We completed a Plackett-Burman designed set of experiments to evaluate the effect of eleven metal additives on the performance of the potassium molybdenum sulfide catalyst. The designed set, consisting of 12 experiments, is shown in Table 3, where the pluses indicate 0.1 weight percent of a particular additive (on a molybdenum sulfide basis) and the minuses, 0.01 weight percent. In addition to the eleven metal additives, the catalyst contains 10 gm of ammonium tetrathiomolybdate and 2.83 gm of potassium acetate, which is equivalent to 0.75 moles K / mole Mo. We modified our catalyst preparative method to allow us to introduce all eleven additives and potassium simultaneously because it would have been impossible to dissolve all of the additives into one pore volume of solution as our standard impregnation method requires. The method we used consisted of stirring ammonium tetrathiomolybdate and all the additives in a large amount of water, drying in a rotary evaporator and then calcining. The detailed catalyst preparative method can be found in Appendix B, Procedure B(g). Each catalyst was evaluated in a tubular reactor at 300°C, 1200 psig, and 6000 l/l/h of 1:1 H_2:CO as discussed in Appendix B, Procedure B(e).

The results of the twelve runs are shown in Table 4. There was excellent variation in the data with the selectivity to alcohols ranging from 42 to 75 % and the alcohol rate ranging from 9 to 16 lb/cf/h. The bar graphs of the contrast sums versus additives, in Figures 1 and 2, illustrate the effect of increasing the loading of each additive from 0.01 to 0.1 wt percent. Increasing the loading from 0.01 to 0.1 weight percent of those additives with positive contrast sums had a beneficial effect on performance, while increasing the loading of the additives with negative contrast sums was detrimental. While the bar graph analysis indicates the magnitude and direction of the effect of each of the additives, it does not indicate at what level of confidence these effects are significant. Regression analysis reveals that the effect on catalyst selectivity and productivity of several of the additives is significant at the 95% confidence level. Of particular interest is A116, which has a positive effect on both the rate and the selectivity to alcohols. The detrimental effect of some of the additives, A119, A122, and A123, is also significant at the 95% confidence level.

In order to determine how the method used for preparing the Plackett Burman designed set catalysts affects the performance of a catalyst containing only potassium and molybdenum sulfide, a catalyst was prepared via the method in Appendix B, Procedure B(g) and evaluated. The results are shown in the first entry in Table 5. This catalyst is not as active (13 vs. 18-20 lb/cf/h) as one of similar composition, but prepared by our standard prep, nor as selective to alcohols (67 vs 75-80%). Thus, those catalysts in the design (see Table 4) which exhibited rates of 15-16 lb/cf/h and alcohol selectivities of ≥70%, were actually performing better than a similarly prepared catalyst without any of the additives.

In order to confirm the effect of the additives which showed a positive effect on performance, two catalysts containing A116, A114 and A117 were prepared by the method in Appendix B, Procedure B(g). The results of the evaluations, shown in Table 5, differ little from the catalyst promoted by potassium only. A significant difference between these two catalysts and the catalyst without additives, as well as the twelve catalysts in the designed set, is their significantly lower densities, as shown in Table 6. When the productivity of the catalysts in Table 5 are compared on a weight basis rather than on a volume basis, there is a 50% increase in productivity to alcohols upon addition of the three additives. We do not know why the two catalysts containing A116, A114 and A117 have lower densities than the other catalysts prepared by the same method.

If we can obtain the same increase in productivity with catalysts prepared by our standard methods, we will be able to obtain the desired 30 lb/cf/h rate to alcohols. We are in the process of trying to prepare these catalysts. Our initial attempts were unsuccessful, in part because the potassium acetate and the A116 precursor mixtures are insoluble. We are modifying our preparative method and also investigating whether it is critical that the A116 be introduced into the ATM prior to decomposition to molybdenum sulfide, rather than directly onto the molybdenum sulfide. This work is continuing.

Figure 1. Effect of the various additives on the rate to alcohols (in lb/kg/hr).

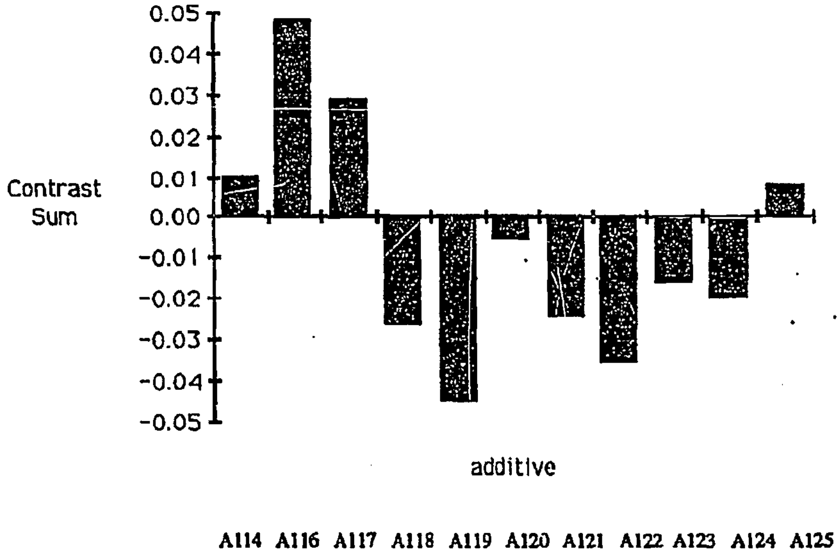


Figure 2. Effect of the various additives on the selectivity to alcohols.

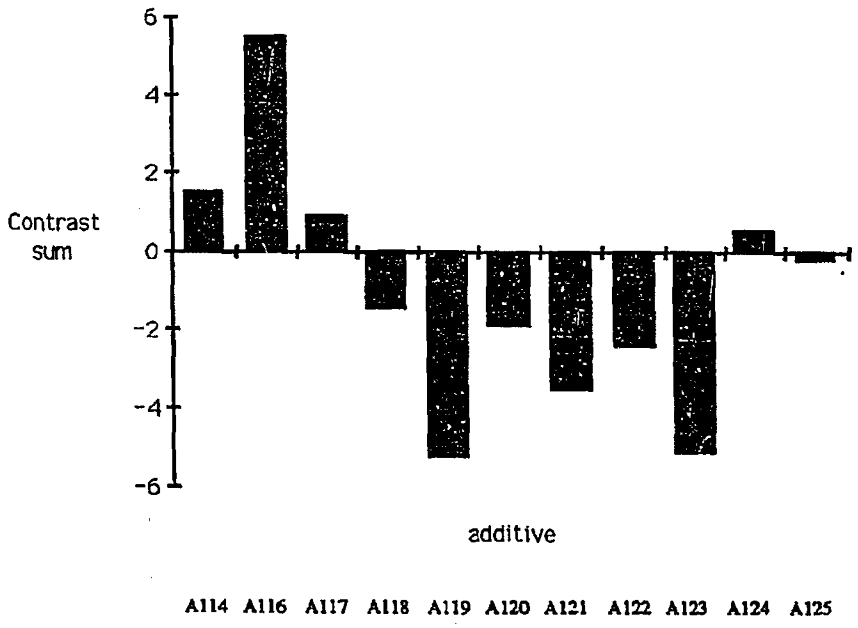


Table 3. Plackett Burman designed set of experiments for the evaluation of eleven metal additives.

Expt #	Metal Additive and Level*										
	A114	A116	A117	A118	A119	A120	A121	A122	A123	A124	A125
1	+	-	+	-	-	-	+	+	+	-	+
2	+	+	-	+	-	-	-	+	+	+	-
3	-	+	+	-	+	-	-	-	+	+	+
4	+	-	+	+	-	+	-	-	-	+	+
5	+	+	-	+	+	-	+	-	-	-	+
6	+	+	+	-	+	+	-	+	-	-	-
7	-	+	+	+	-	+	+	-	+	-	-
8	-	-	+	+	+	-	+	+	-	+	-
9	-	-	-	+	+	+	-	+	+	-	+
10	+	-	-	-	+	+	+	-	+	+	-
11	-	+	-	-	-	+	+	+	-	+	+
12	-	-	-	-	-	-	-	-	-	-	-

* + equals 0.1 weight percent and - equals 0.01 weight percent.

Table 4. Results of the Plackett Burman designed set of experiments.

Catalyst	C-molar Selectivity (%)				C_1-C_4	wt%	C_2/	RATE	% CO		Catalyst	Run
Number	MeOH	EtOH	nPrOH	nBuOH	H.C.	Alc.%	C_2+	C_2+	lb/cf/h	Conv.	Ref.	Ref.
1	27.55	20.92	6.50	1.27	33.23	57.31	42.77	73.66	13.97	17.59	26NEK99	26NEK116
2	36.45	24.68	8.48	1.10	17.00	72.12	40.20	72.42	15.69	13.98	26NEK102	26NEK118
3	32.04	24.56	8.55	1.17	24.66	67.67	43.30	72.19	14.91	14.17	26NEK104	26NEK132
4	36.52	26.32	8.45	1.09	19.60	73.71	41.21	73.94	15.28	13.59	26NEK105	26NEK134
5	32.53	25.24	7.55	1.39	26.78	68.05	42.94	74.26	12.93	13.37	26NEK114	28NEK104
6	32.50	28.03	8.59	1.20	20.20	71.77	45.43	74.50	16.40	15.79	26NEK115	28NEK6
7	34.34	21.56	5.70	1.02	31.61	63.78	37.31	76.26	10.50	11.40	26NEK129	28NEK12
8	23.11	21.68	5.87	0.94	44.21	52.65	47.21	76.40	9.69	14.48	26NEK131	28NEK40
9	18.92	14.99	6.17	0.96	52.80	42.15	46.12	68.04	10.69	20.81	28NEK2	28NEK20
10	20.72	18.93	5.92	0.90	48.32	47.43	47.40	74.04	9.62	15.13	28NEK3	28NEK22
11	34.06	25.44	8.40	1.39	22.50	70.90	42.60	72.39	15.05	12.57	28NEK17	28NEK32
12	40.01	23.62	9.06	1.12	15.58	75.37	37.67	70.21	13.87	11.77	28NEK18	28NEK34
Ave.	30.73	23.00	7.44	1.13	29.71	63.58	42.85	73.19	13.22	14.56		

Table 5. Results for catalyst containing only potassium and for two levels of A116, A114 and A117.

Additive	C-molar Selectivity (%)				C_1-C_4	wt%	C_2/	RATE	% CO		Catalyst	Run
loading	MeOH	EtOH	nPrOH	nBuOH	H.C.	Alc.%	C_2+	C_2+	lb/cf/h	Conv.	Ref.	Ref.
none	33.55	21.14	8.96	1.13	27.50	66.15	39.92	68.26	12.25	13.04	28NEK37	28NEK44
0.1wt%	36.60	22.98	6.56	0.80	21.13	68.60	37.66	74.72	11.02	10.49	28NEK50	28NEK56
1.0wt%	32.78	23.31	5.41	0.70	27.94	63.12	39.23	79.40	14.27	15.43	28NEK49	28NEK54

Table 6. Density of catalysts used in Plackett-Burman designed set of experiments and subsequent catalysts prepared by the same method.

Catalyst	Gm/cc
1	1.0691
2	1.2570
3	1.1340
4	1.2113
5	1.1528
6	1.1093
7	0.7954
8	1.25
9	1.3574
10	1.3448
11	1.151
12	1.072
Average	1.16±0.15

Loading*	gm/cc
0	1.182
0.1	0.757
1.0	0.671

* wt % of A116, A114, and A117

D. Task 2 Summary

We continued the study of additional additives to the homogeneous ruthenium catalyst in the search for improved activity. We have found that certain Mo and Ir compounds slightly increased the selectivity to higher alcohols . Platinum, copper, and palladium compounds tested are severe catalyst poisons. Phosphine compounds tested either retard the catalyst activity slightly or completely poison the system.

Chemical model studies have been carried out to investigate the mechanism of homogeneous hydrogenation of CO. The information gained could allow us to modify the system to enhance the rate of the rate-determining step. Results of these studies are consistent with the hypothesis that the first interaction between hydrogen and CO could be a reaction between a metal hydride and an activated carbon monoxide ligand bonded to a metal center.

Investigations into improving the performance of alkali-loaded molybdenum sulfide based catalysts have continued. We have completed a Plackett-Burman designed set of experiments to investigate the effect of eleven different metal additives on the performance of a potassium-molybdenum sulfide catalyst and found that the addition of A116 improves both the rate and selectivity to alcohols.

II. TASK 3: Bench Scale Concept Evaluation

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 is being 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 described in the previous quarterly report. The objective is to determine whether catalysts with improved rate and selectivity could be obtained by changing the preparation conditions or by changing the precursors. All of the evaluations have been of powdered catalysts, without depositing the active material on a support.

B. Experimental Program

Eleven catalyst preparations were evaluated this quarter. These evaluations were usually simultaneous runs with two different catalysts in two separate reactors heated in the same sand bath. The first experiments were generally made with two distinctly different catalysts or with several preparation variables changed simultaneously to screen for significant changes. Later experiments were generally direct comparisons with only one parameter changed.

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. Procedure B(e) of Appendix B was followed for the evaluations, and Procedure C(e) of Appendix C was used for the analytical determinations. The catalyst volume was always one cc as charged to the reactor. Different preparations produced different catalyst bulk densities and hence the actual weight charged varied from 0.791 to 1.266 g/cc in these experiments. 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/hr/cubic ft) 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/cc. This adjustment neglects the 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 3 through 14 (catalyst 1KEC21 is included in these figures although it was evaluated in the previous quarter). 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. For each catalyst, alcohol rate, total CO consumption rate, and selectivities to methanol, ethanol and methane are shown as a function of run time. The alcohol and hydrocarbon distributions are shown at two distinct times. For the shortest runs, these are the times of the first and last samples. The first sample is usually during the induction period when the rate is low. Part of this induction period may be due to slow purging of nitrogen from the reaction system. For the longer runs, the first distribution is from a sample at about 40 hours, which approximately coincides with the end of the shorter runs. A Schulz-Flory distribution would plot as a straight line on these figures. Best fit lines and the corresponding alpha values are given. This fitting included the single carbon products, methanol and ethanol, which are formed by slightly different reactions than the heavier products, and hence may not follow the Schulz-Flory distribution.

The units for alcohol rate and for total rate are different, and the vertical scales also change from figure to figure. When the total rate decreases while the alcohol rate increases, the selectivity to methane and hydrocarbons is decreasing.

1. Standard Catalyst Preparation

The molybdenum sulfide based catalyst tested during the previous quarter gave relatively low rates and selectivity. A demonstration was needed that we could produce catalyst comparable with those made in this program by N. E. Kinkade. Catalyst 1KEC62 was therefore prepared by following the standard procedure, except that the potassium loading was 0.35 moles/mole molybdenum (N. E. Kinkade obtained best results with 0.75 K/Mo).

The ATM used in this preparation was preparation 1KEC58, reaction was at 60°C and H_2S addition took 140 minutes. The product was calcined for one hour at 400°C in 10% H_2. During heatup the sample (10 grams) gave an exothermic decomposition starting abruptly at about 320°C and taking the sample over 400°C. This decomposition seems to be typical of good ATM. The section on calcination contains further discussion. Final weight loss was 37.9%, very close to the theoretical value of 38.5% for MoS_2 formation. Impregnation was with an aqueous solution of potassium acetate (0.71 cc/g MoS_2) and the sample was then calcined again at 400°C for 1 hour in 10% H_2. Surface area of the final catalyst was 3.2 m^2/gram.

Results of the catalyst evaluation by N. E. Kinkade (26NEK126) are shown in Figure 3 and Table 7. The maximum alcohol rate was 22.2 lb/hr/cubic ft after 23 hours. The rate had declined to 19.2 lb/hr/cubic ft when the evaluation was terminated after 45 hours. Selectivity at this time was 73% to alcohols and 20.9% to hydrocarbons. Wt% C_2+ alcohols was 41.4%.

Figure 3(b) shows that selectivity to methanol increased throughout the run; there was a corresponding drop in methane selectivity. Product distributions for the alcohols and hydrocarbons are also shown. These distributions do not change substantially over this time. Because both alcohol rate and total rate of CO consumption are decreasing at the end of the evaluation, this catalyst may be deactivating rapidly. This deactivation does not involve a selectivity change.

2. Potassium Loading

Most evaluations have been carried out with a potassium loading of 0.35 moles per mole of molybdenum. This was an arbitrary value chosen because higher loadings reduce the surface area even more significantly. Catalyst 1KEC27, with a K/Mo ratio of 0.2 (evaluation 26NEK96) was prepared by impregnating MoS_3 with aqueous potassium acetate and then calcining for one hour at 400°C in 10% H_2. The preparation was similar to that of catalyst 1KEC21 reported previously.

Catalyst 1KEC54 was prepared as a standard catalyst with the exception that a lower potassium loading was used. The actual loading was 0.09 K / Mo. Results from this catalyst can be compared directly with results from 1KEC62. Table 7 summarizes the main points. Values given are experimental results obtained after about 45 hours operation with each catalyst. Detailed results are contained in Figures 4, 5 and 6.

Increased potassium loading causes a progressive reduction in hydrocarbon formation. Alcohol production rate also increases, but only slowly from 0.2 to 0.35 K/Mo (although this may be misleading because the two catalysts was prepared differently). At higher loadings, C_2/C_2+ increases. This is because the proportion of higher alcohols in the product decreases. The last two columns show the product distributions in terms of the Schulz-Flory alpha value. These values were obtained by a simple curve fitting routine in which the C_1 compounds (methanol and methane) were included in the data. This may give misleading values because the C_1 products do not require C-C bond formation in their production. In this case the values do show less heavy products as the potassium loading increases. The alpha values for both alcohols and hydrocarbons are very similar as if both are affected in the same way by potassium loading.

The two lowest potassium loadings show distinctly different results for alcohol rate. Catalyst 1KEC54 produced alcohols at essentially a constant rate while catalyst 1KEC21 shows a pronounced increase in rate with time. This suggests that the catalyst prepared by impregnation of MoS_3 does not have the correct active sites for alcohol production, but these develop slowly during reaction. Figure 6 shows the normal pattern of alcohol rate versus time. Thus with higher potassium loadings there seems to be little difference in the results of these two preparation procedures. In all cases the catalysts may also be deactivating since the total rates of CO consumption were decreasing. For all catalysts except 1KEC21, a steady state selectivity pattern seemed to be achieved.

Comparison of these results shows a more favorable alcohol distribution at the lower potassium loading, but with unacceptably high hydrocarbon formation. Although alcohol production increases slowly with time for catalyst 1KEC21 there is no evidence that selectivity would ever become satisfactory. In all cases the total rate decreases as if deactivation is relatively unaffected by potassium loading.

For catalyst preparations from MoS_2 samples of different surface areas, or in preparations of catalysts from other precursors, we do not know the best potassium loading. One single potassium loading was used in all tests because the experimental time did not allow for systematic variation of loading.

Table 7. The Effects of Potassium Loading

Catalyst	K / Mo	Alcohol Rate *	Select to HC	C_2 / C_2+	Schulz-Flory alpha alcohols	Schulz-Flory alpha hydrocarbons
1KEC54	0.09	4.93	87.9	50.6	0.356	0.405
1KEC21	0.1	7.75	78.3	59.	0.405	0.376
1KEC27	0.2	18.4	25.7	71.9	0.228	0.223
1KEC62	0.35	19.1	20.9	78.6	0.210	0.141

* Alcohol rate is in lb/hr/cubic foot but the experimental values have been normalized to a catalyst bulk density of 1 g/cc. For the catalysts 1KEC54, 1KEC27, and 1KEC62, the densities, as charged to the reactor, were 1.19, 0.883 and 1.005 g/cc respectively.

3. Ammonium Oxythiomolybdate Catalyst Precursor

Dow Chemical Co. has a Japanese patent (JP 62 34,986, see Chemical Abstracts 107:219459) on the preparation of catalyst from $(NH_4)_2MoS_2O_2$ (AOTM). This is interesting because during calcination this compound cannot form MoS_3 as an intermediate before MoS_2 formation. AOTM was prepared by reaction of H_2S with ammonium paramolybdate (APM) solution cooled in ice (instead of the Dow procedure which used $(NH_4)_2S$). The result was thick needle-like yellow crystals. Yield was 29.5 grams from 32 grams APM. This product was calcined for 1 hour at 200°C in nitrogen. This produced 18.4% weight loss and yielded a metallic grey-colored powder. Catalyst 1KEC100 was prepared from this material by impregnating with potassium acetate solution in ethanol (0.5 cc/gram solid) and recalcining for 1 hour at 400°C in 10% H_2. The K/Mo ratio was approximately 0.35.

This catalyst was evaluated by N. E. Kinkade (28NEK28) and results are shown graphically in Figure 7. Comparison with the standard catalyst, Figure 3, shows a great deal of similarity in all trends. Although the preparation is different, there is little difference in the results. Also, both the total rate and the alcohol rate decrease in the later part of the evaluation, showing the same deactivation pattern. Because 1KEC100 did not give better results than the standard catalyst, no further work was done with AOTM precursor.

4. Ammonium Tetrathiomolybdate Calcination

The standard procedure for production of MoS_2 has been to heat in a stream of 10% H_2 in nitrogen. The heating rate is about 10°C per minute until the furnace reaches 400°C. The sample is held at 400°C for one hour, before cooling and passivating. During the heating procedure, the ATM undergoes reaction. Reaction begins when the sample is at about 200°C. The first reaction is endothermic and the sample temperature increases more slowly than the furnace temperature. Since MoS_3 can be prepared at this temperature, it is natural to assume that the main reactions are loss of $(NH_4)_2S$ (or further decomposition products) to produce the trisulfide. When the sample reaches about 300°C, it seems that most of the endothermic decomposition has been completed. The sample temperature now rises more rapidly than the furnace temperature.

At a temperature between 320°C and 375°C, the temperature measured by the sample thermocouple rises rapidly. The temperature shoots above the furnace temperature and then quickly falls. This is due to an exothermic reaction which releases sulfur (yellow deposits form on the outlet tube) and leaves MoS_2. Previous observation was that good catalyst was made when the exotherm was most energetic.

Observation of the exotherm in most cases simply shows an abrupt temperature rise. A few cases have shown sample temperatures escalating before the actual exotherm. The explanation is probably that the severe exotherm is triggered when the reaction begins to run away. This need be started in only one place in the sample but propagates quickly through the remainder of the sample. Heating MoS_3 under the same conditions also gives the exotherm.

Over the range of conditions tested here, the exotherm does not appear necessary for catalyst preparation. Catalyst 1KEC95 was prepared by impregnation of MoS_3, followed by slow calcination to avoid the rapid exotherm. This catalyst gave an alcohol formation rate of about 15 lb/hr/cubic foot. Unfortunately, the initial selectivity was poor. This seems to demonstrate that the presence of potassium during decomposition does not produce a better initial surface structure.

The severity of the exotherm must be partly determined by the depth of ATM around the thermocouple and the location of the thermocouple in the sample. The data collected to date do not show a relationship between catalyst performance and the occurrence or severity of the exotherm.

5. Impregnation From Ethanol Solution

It seemed possible that the initial catalyst performance could be improved by changing the initial distribution of potassium. Some catalysts were prepared by impregnation with potassium acetate solutions in ethanol. In all cases a small amount of water was also present to give the required solubility. It was hoped that impregnation with solutions near saturation would promote surface adsorption of potassium to give a uniform coverage of the surface before drying the impregnated catalyst.

An initial test of this option was included in the testing of catalyst from AOTM. Because the results were encouraging, a direct comparison was made of impregnation from aqueous solution with impregnation from ethanol. The ATM used (1KEC135) was prepared by the standard procedure, but with H_2S feed stopped after one hour. Ethanol wash was used only after the filter cake was relatively dry. ATM (15g) was calcined for one hour at 400°C in 10% H_2. During calcination the sample temperature jumped suddenly from 340°C to 362°C but this was much less severe than the normal exotherm. Weight loss was 37.9%. Surface area of the MoS_2 was 109.6 m^2/g.

Impregnation was with 0.4 cc/gram, to give K/Mo of 0.35. Both samples were then calcined simultaneously for one hour at 400°C in 10% H_2. Catalyst 2KEC18A was prepared from aqueous solution and 1KEC18B from the ethanol solution. Evaluations were 28NEK60 and 28NEK62 respectively. Both catalysts gave very similar results (Figures 10 and 11). The catalyst prepared with ethanol gave the highest alcohol rate, 21.9 lb/hr/cubic ft, but because the catalyst density was 1.266 c/cc, this reduces to a normalized rate of 17.3 lb/hr/cubic ft. On this basis aqueous impregnation gave slightly better rate.

The most disturbing feature of these results was that neither catalyst gave good reaction rate despite the high surface area. The problem does not appear to be simply too much surface area and not enough potassium because the total rate and the selectivity to hydrocarbons was reasonable. There is a distinct possibility that the emphasis on using MoS_2 with a high surface area may be the wrong direction for improvement. A future study will test catalyst made from ATM which is less crystalline but which gives lower surface area.

6. Preparation of Catalyst From Smaller Particles

Some results from the previous quarter showed that the surface area of MoS_2 depended on the particle size of the ATM before calcination. This was surprising because most of the surface area should be formed within particles rather than being external. Some experiments were carried out to prepare ATM with smaller particle size by rapid precipitation. The assumption was that more rapid precipitation may produce a structure with more internal defects which might change the catalyst performance.

A number of different precipitation procedures were tried. The first used an entirely nonaqueous system. ATM dissolved in dimethylformamide (DMF) was precipitated as very fine particles, not visibly crystalline under an optical microscope, by dropwise addition to cooled agitated diethyl ether. Catalyst 1KEC50 was prepared from this by the standard procedure of calcining to MoS_2 (no exotherm was observed with 1.9 gram sample), impregnating from aqueous solution and recalcining. The second procedure used ATM dissolved in water and precipitated by dropwise addition to agitated chilled ethanol. This sequence gave fine particles with a surface area of 53.9 m^2/g after calcination. Very small red crystals of ATM were prepared by a similar procedure using acetone for precipitation. This was used to prepare catalyst 1KEC124. The ATM was calcined for one hour at 200°C in N_2, (24.2% wt loss), impregnated with aqueous solution (0.5 cc/g) to give 0.35 K/Mo, and calcined for one hour at 400°C in 10% H_2. The evaluation was 28NEK46.

Results are shown in Figures 11 and 12. In the evaluation of 1KEC50 there was a leak in the gas supply upstream of the reactor, reducing the actual flow rate and increasing conversion to over 70%. This probably accounts for the low rate and the increased selectivity to heavier products. Better results were obtained with catalyst 1KEC124, Figure 12. This catalyst had the lowest bulk density, (0.791 g/cc) as charged to the reactor. After normalizing to a density of 1 g/cc, the maximum rate to alcohols was 20.3 lb/hr/cubic ft, after 41 hours. The alcohol rate then declined to 18 lb/hr/cubic ft at 71 hours but appeared to be almost stable at that value. Methane selectivity began at 33.9% but decreased to 17.3% at 71 hours. Methanol selectivity increased steadily from 12.9% to 40.7% in the same time. The alpha values for alcohol and hydrocarbons also decreased during the run. Again, the alpha values for alcohols and hydrocarbons are approximately equal. Although the alcohol rate appeared to be stable at the end of the evaluation, the total rate of CO reaction appeared to be on a continued downward trend. The activity decay was about 25% per day. It is impossible to tell whether this decline in rate would continue or would stop when hydrocarbon selectivity reached a steady state.

These catalysts did not show any clear advantage over the standard preparation and this direction was abandoned. It would be desirable to repeat the water/ethanol precipitation procedure, followed by the standard calcination/impregnation procedure to see whether this improves results.

7. Molybdenum Trisulfide vs Disulfide

One of the modifications to the standard catalyst which has been tried several times has been impregnation of the trisulfide rather than the disulfide. The reason that this was considered was that potassium is then present while the final stage of decomposition takes place. Since potassium acetate melts at 292°C, and decomposition of the trisulfide occurs above 300°C, it seemed very likely that the presence of potassium during decomposition could modify the surface structure of the final catalyst.

A direct comparison of this procedure with the standard preparation was made using the same ATM preparation (1KEC131A) for both catalysts. This was believed to be necessary because catalyst made from different ATM batches gives different results. In this ATM preparation H_2S feed was stopped after one hour and the product consisted of large red crystals. The surface area of MoS_2 after the standard 400°C calcination was 88.5 m^2/g. MoS_3 was prepared by calcining for 90 minutes at 200°C in nitrogen. Some previous MoS_3 samples had been made at 275°C for one hour. The lower temperature was tried in order to minimize the extent of surface rearrangement and the longer time was necessary to complete the decomposition. Weight loss was 24.0% for MoS_3 formation.

Impregnation was with an ethanol solution of potassium acetate, containing a small proportion of water. For MoS_3, the liquid loading was 0.37 cc/g and $0.37 \times 192 / 160 =$ 0.444 cc/g for MoS_2. Both impregnated samples were calcined again for one hour at 400°C in 10% H_2. Evaluations were 28NEK68 and 28NEK70; they were extended to four days to give a little more data on the deactivation rate. Some of the results are shown in Table 8 for 38 and 86 hours; for comparison the data for 1KEC62 at 39 hours is also shown. Catalyst 2KEC2A was prepared from MoS_2 and 2KEC2B from MoS_3.

Figures 13 and 14 show the detailed results. The product distributions are relatively similar at the end of the run. The catalyst from MoS_3 (2KEC2B) gave the highest rate but also showed serious deactivation. Both catalysts required 40 hours or more to reach their maximum rate. Both catalysts also showed increased selectivity to methanol for the first 70 hours of operation. These similarities suggest that these results are due to the ATM itself and not to the particular preparation procedure.

Table 8. The Effects of Potassium Loading

Catalyst	K / Mo	Alcohol Rate *	Select to HC	C_2 / C_2+	Schulz-Flory alpha alcohols	Schulz-Flory alpha hydrocarbons
2KEC2A (MoS_2)						
38 hr	16.9	11.8	46.6	57.7	0.345	0.245
86 hr	30.7	12.3	35.2	73.5	0.219	0.222
2KEC2B (MoS_3)						
39 hr	34.7	16.6	28.9	62.2	0.264	0.266
85 hr	41.9	13.8	23.0	72.0	0.211	0.228
1KEC62 (Standard)						
45 hr	35.6	20.9	19.5	79.7	0.210	0.141

* Alcohol rate is in lb/hr/cubic foot but the experimental values have been normalized to a catalyst bulk density of 1 g/cc.

8. Ammonium Tetrathiomolybdate Preparation

As stated in the previous quarterly report, different batches of ATM have different particle size distributions and these seemed to correlate with catalyst performance. The ATM preparation used here was essentially isothermal, with the H_2S flow continuing for about two hours until reaction was very slow. In the later stage of reaction the H_2S feed was decreased as the reaction slowed. It seemed likely that the particle size, and perhaps the product composition, changed with time during the preparation.

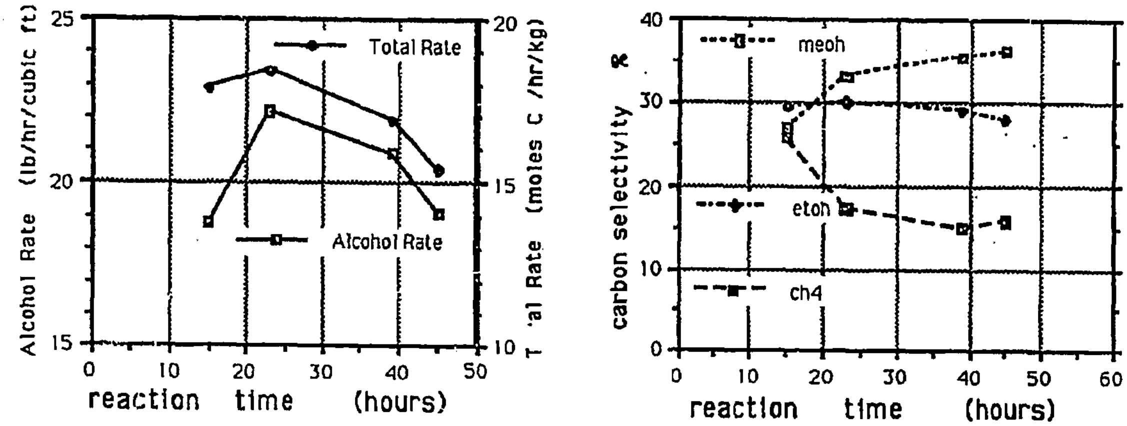
Therefore the preparation was divided into two stages. The first stage lasted one hour and H_2S feed was maintained at a constant high rate. ATM begins to precipitate during the last 10 minutes of this time. The flask is then cooled and the contents filtered. No ethanol wash is used until all the filtrate has been collected and reaction restarted in a clean flask. Reaction is continued at the original temperature (60°C) until the rate slows substantially. The second stage product is collected in a second filtration.

The first stage product consists of well defined deep red crystals. The second stage product is always finer. Some red crystals are present but most of the product is finer and darker. The particles are more irregular and may be agglomerates.

First stage and second stage products were calcined separately under the standard conditions to produce MoS_2. Measurement shows consistently that the first stage product produces disulfide with the highest surface area. It was this finding which resulted in the production of several catalysts from first stage material. As discussed above in presenting the results of the evaluations of 2KEC2A and 2KEC2B, this high surface area material does not seem to generate good catalyst.

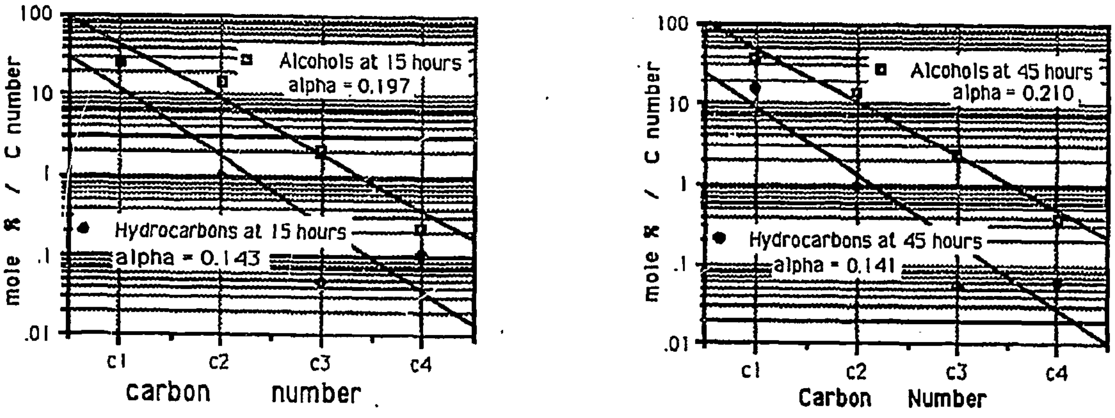
The poor performance of all catalysts made from this material suggests a systematic variation in the properties of the ATM. The high surface areas may have been misleading. Evaluation of catalyst from second stage product will be covered in the next report.

Figure 3. Catalyst 1KEC62, Evaluation 26NEK126. Standard Catalyst from MoS_2, K/Mo = 0.35. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, $H_2/CO = 1$; Procedure B(e).



(A) Rate vs. Time

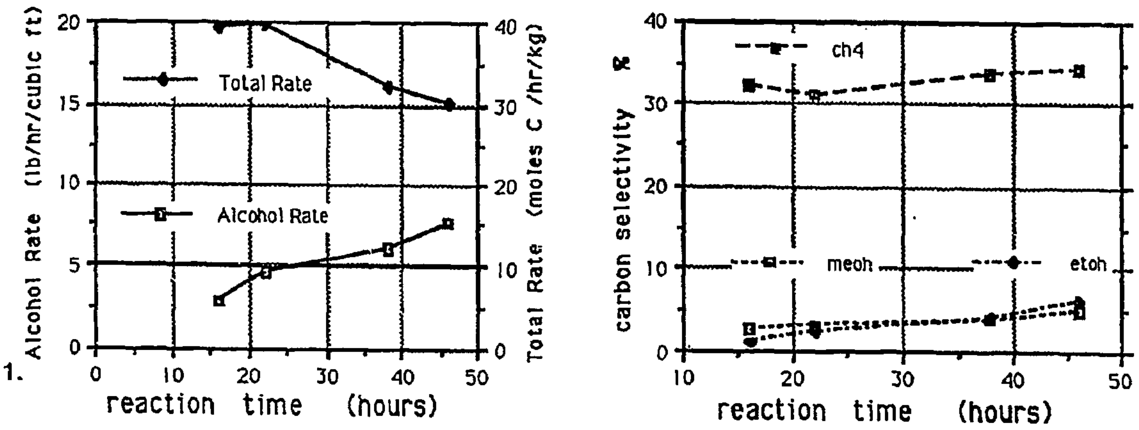
(B) Selectivity vs. Time



(C) Product Distribution

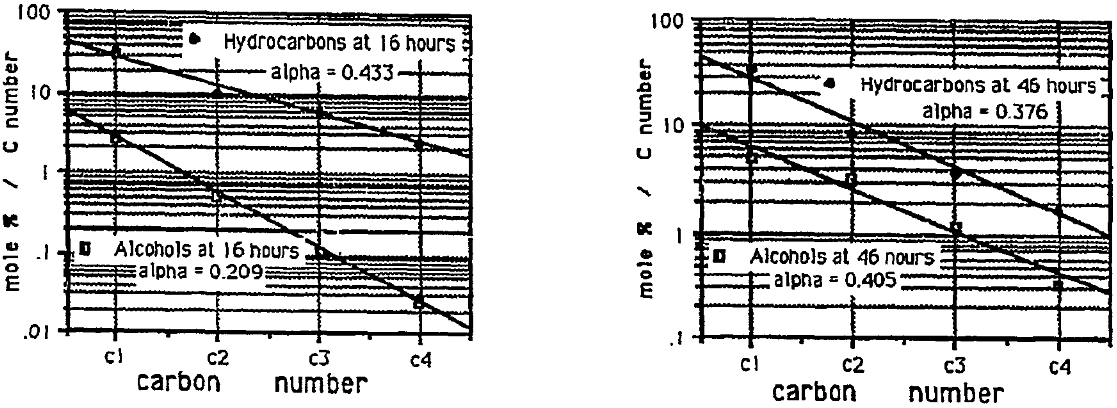
(D) Product Distribution

Figure 4. Catalyst 1KEC21, Evaluation 26NEK124. Catalyst from MoS_3 (275°C), K/Mo = 0.1 from aq soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, H_2/CO =1; Procedure B(e).



(A) Rate vs. Time

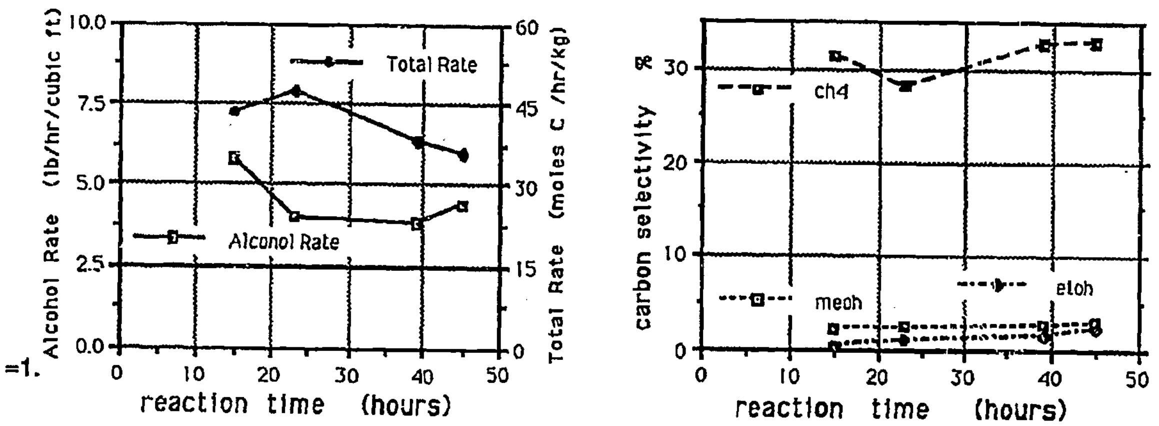
(B) Selectivity vs. Time



(C) Product Distribution

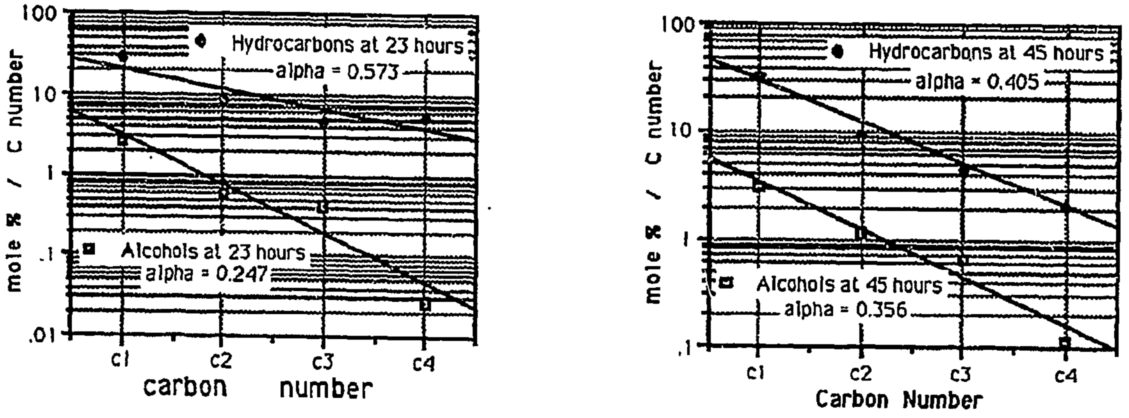
(D) Product Distribution

Figure 5. Catalyst 1KEC54, Evaluation 26NEK110. Catalyst from MoS_2, K/Mo = 0.09 from aq soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, H_2/CO = 1; Procedure B(e).



(A) Rate vs. Time

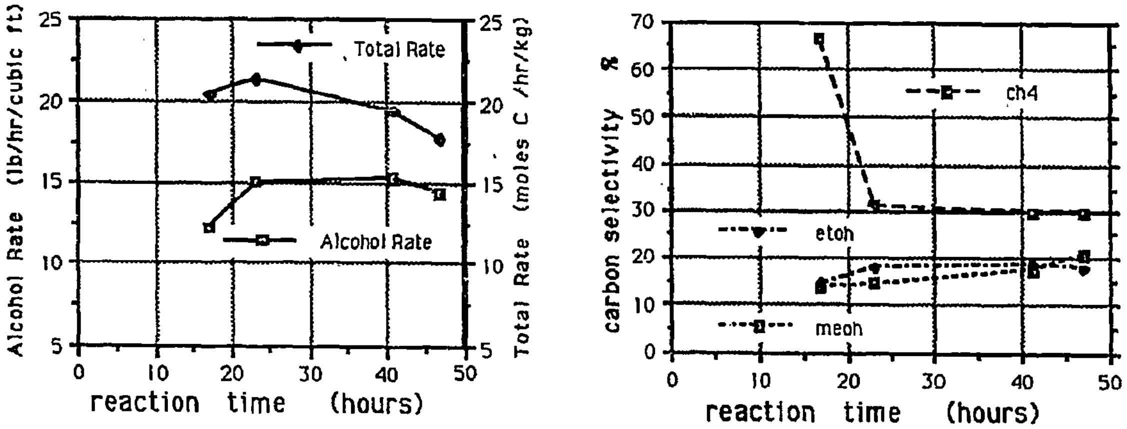
(B) Selectivity vs. Time



(C) Product Distribution

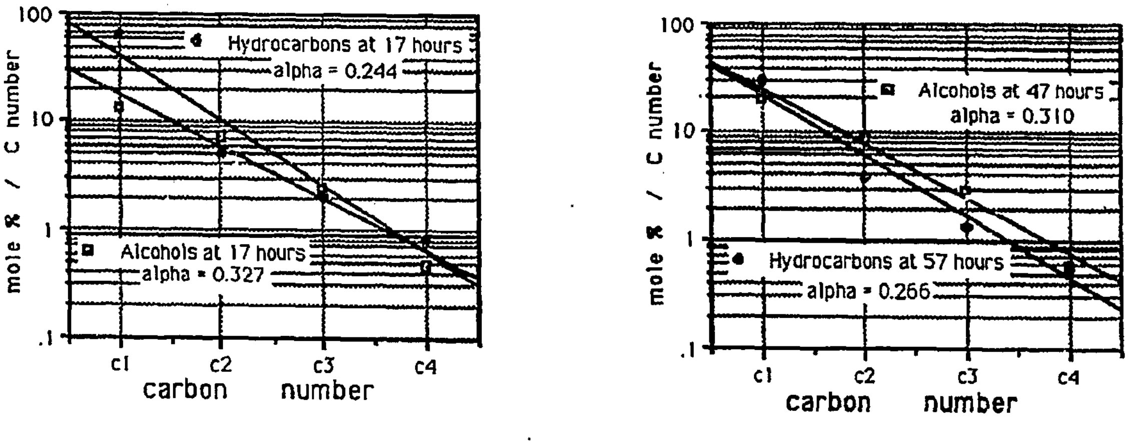
(D) Product Distribution

Figure 6. Catalyst 1KEC27, Evaluation 26NEK96. Catalyst from MoS_3 (275°C), K/Mo = 0.2 from aq soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, $H_2/CO = 1$; Procedure B(e).



(A) Rate vs. Time

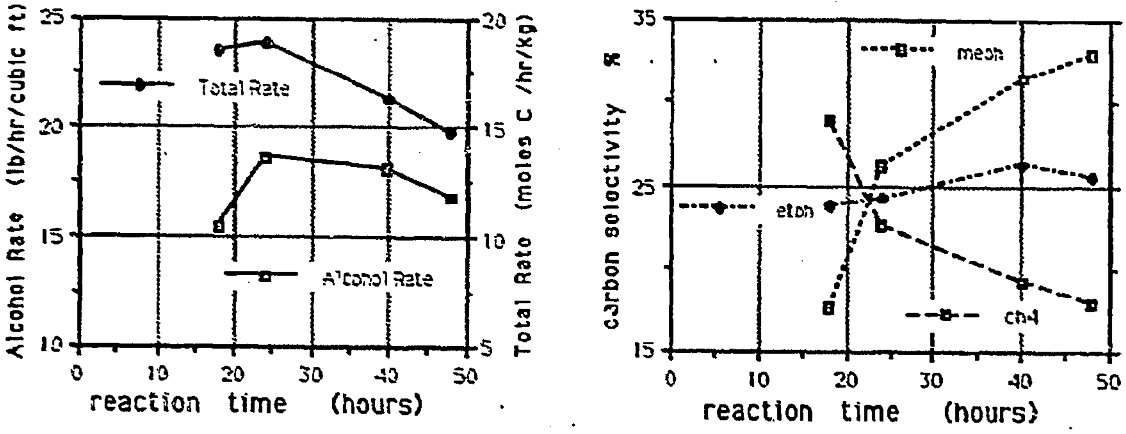
(B) Selectivity vs. Time



(C) Product Distribution

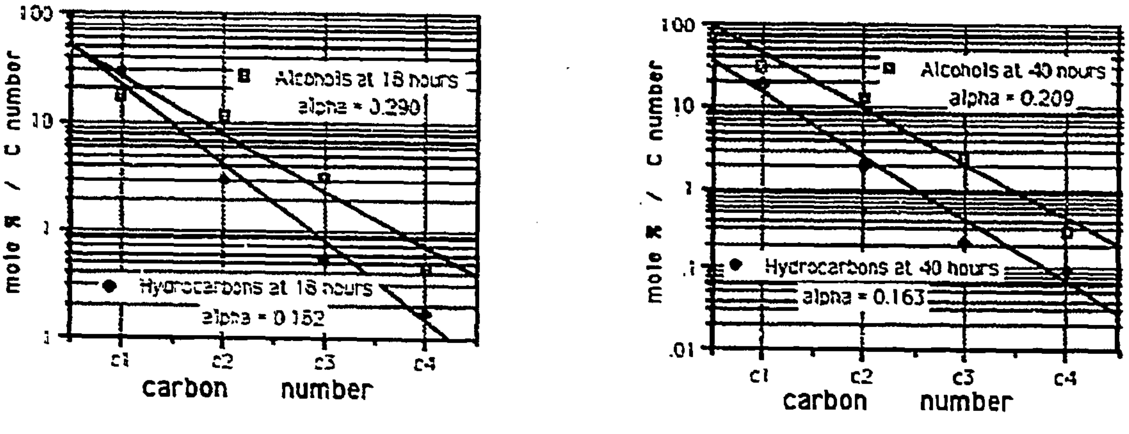
(D) Product Distribution

Figure 7. Catalyst 1KEC100, Evaluation 28NEK28. Catalyst from AOTM (200°C), K/Mo = 0.35 from EtOH soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, $H_2/CO = 1$; Procedure B(e).



(A) Rate vs. Time

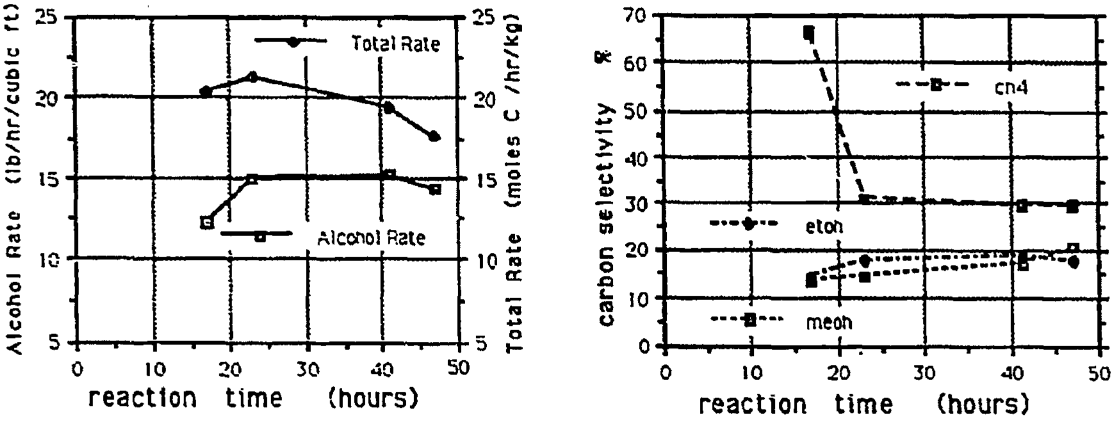
(B) Selectivity vs. Time



(C) Product Distribution

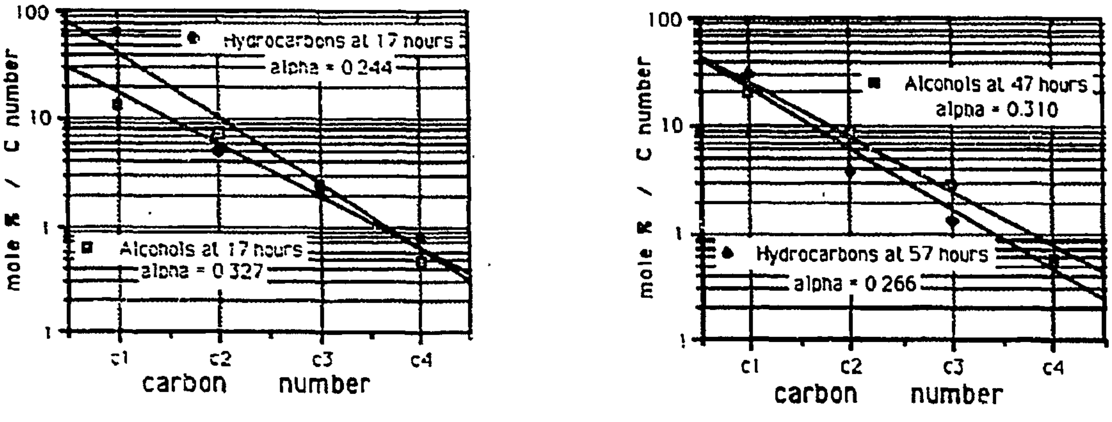
(D) Product Distribution

Figure 8. Catalyst 1KEC95, Evaluation 28NEK26. Catalyst from MoS_3 (220°C), K/Mo = 0.35 from aq soln , no exotherm. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, $H_2/CO = 1$; Procedure B(e).



(A) Rate vs. Time

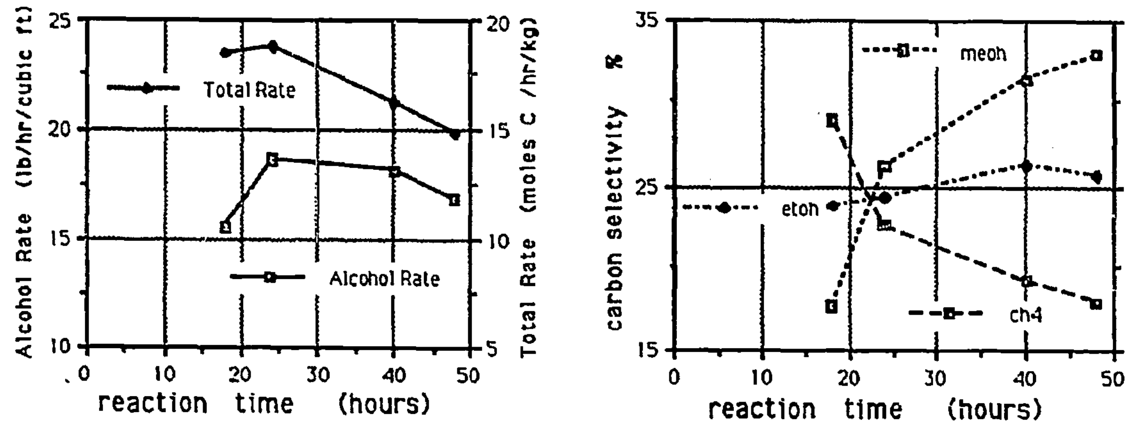
(B) Selectivity vs. Time



(C) Product Distribution

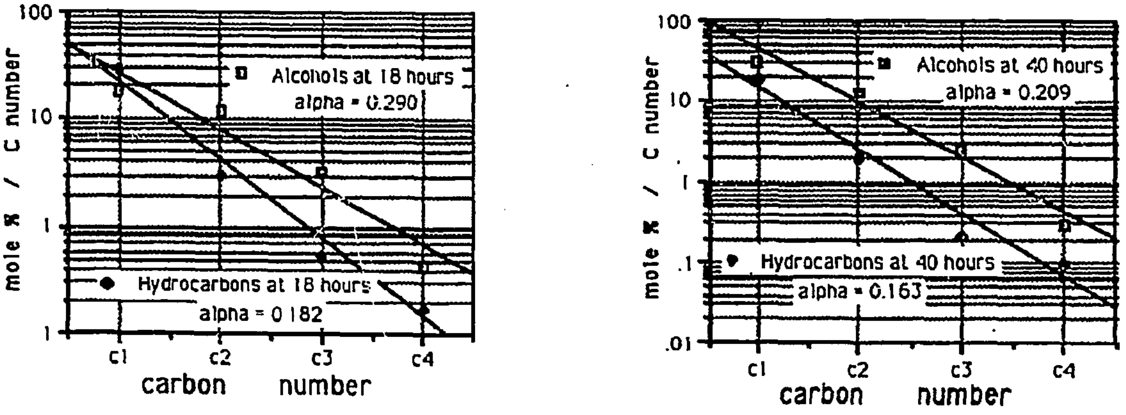
(D) Product Distribution

Figure 9. Catalyst 2KEC18A, Evaluation 28NEK60. Catalyst from MoS_2 , K/Mo = 0.35 from aq soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, H_2/CO = 1; Procedure B(e).



(A) Rate vs. Time

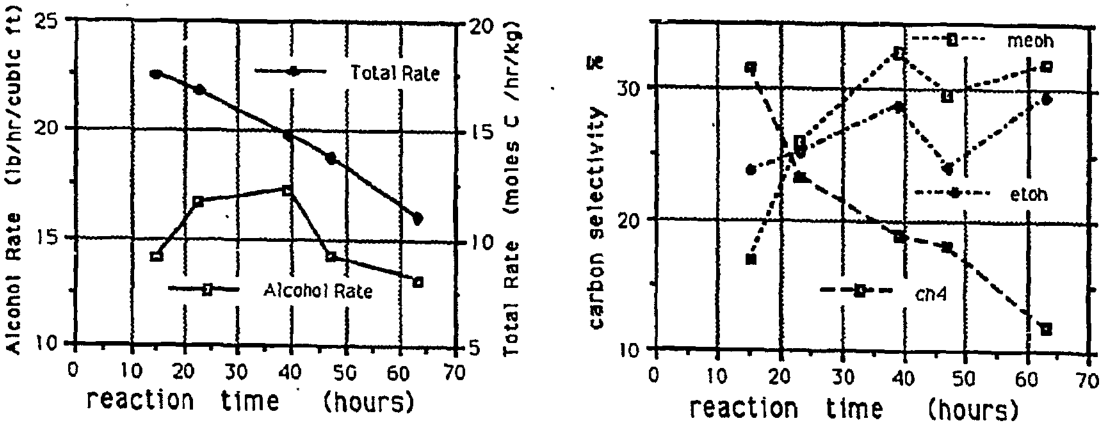
(B) Selectivity vs. Time



(C) Product Distribution

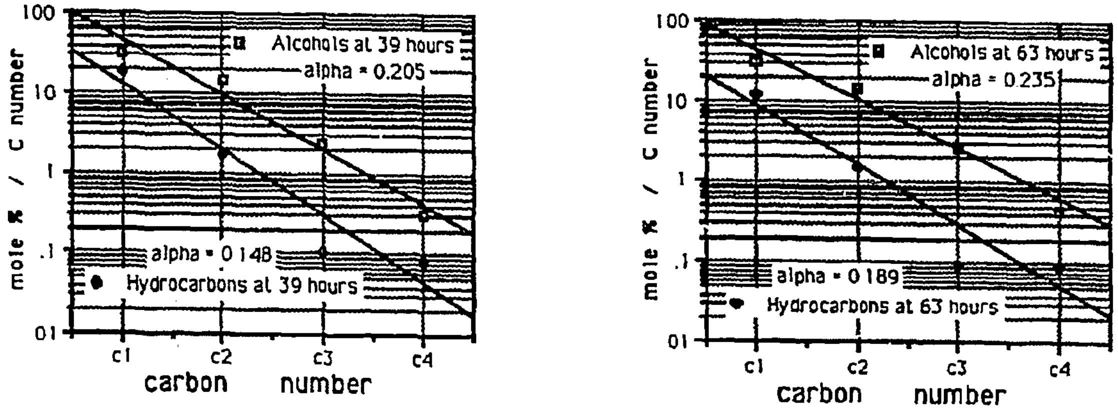
(D) Product Distribution

Figure 10. Catalyst 2KEC18B, Evaluation 28NEK62. Catalyst from MoS_2, K/Mo = 0.35 from EtOH soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, H_2/CO = 1; Procedure B(e).



(A) Rate vs. Time

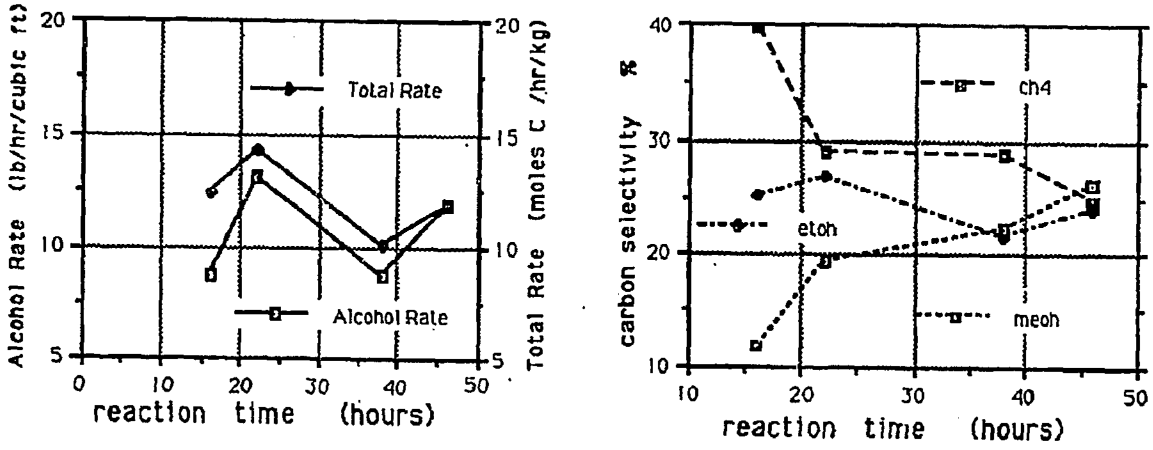
(B) Selectivity vs. Time



(C) Product Distribution

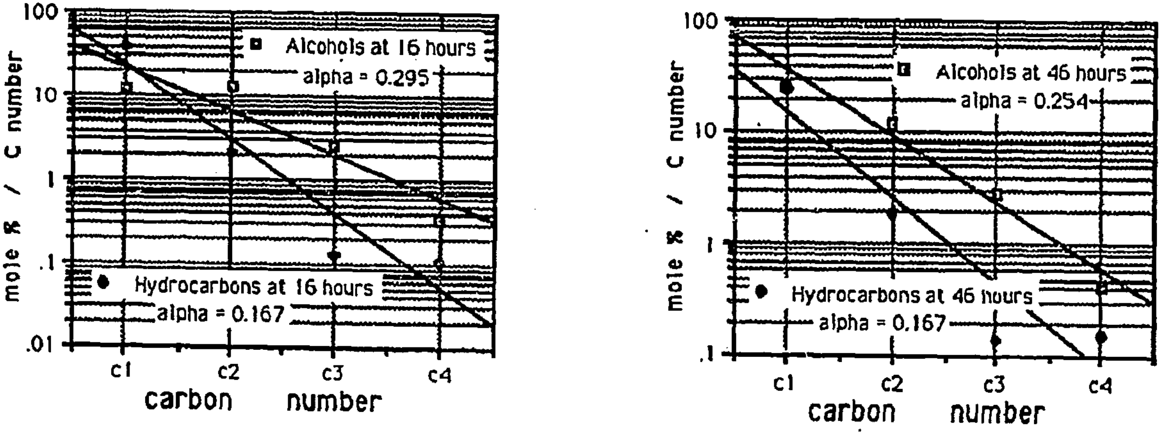
(D) Product Distribution

Figure 11. Catalyst 1KEC50, Evaluation 26NEK108. Catalyst from ATM precipitated DMF/Ether, MoS_2, K/Mo = 0.35 from aq soln. Evaluation at 300°C, 1200 psi, **S V = 4600 hr^{-1}**, H_2/CO = 1; Procedure B(e).



(A) Rate vs. Time

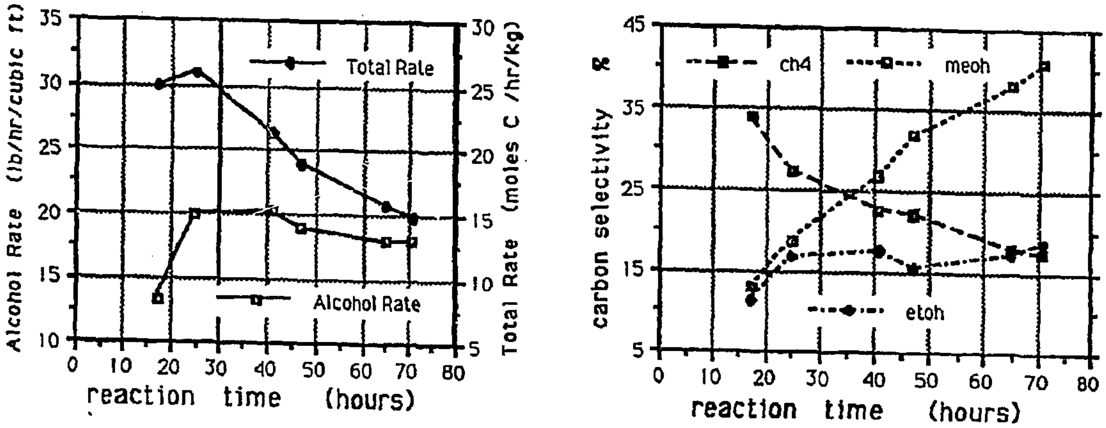
(B) Selectivity vs. Time



(C) Product Distribution

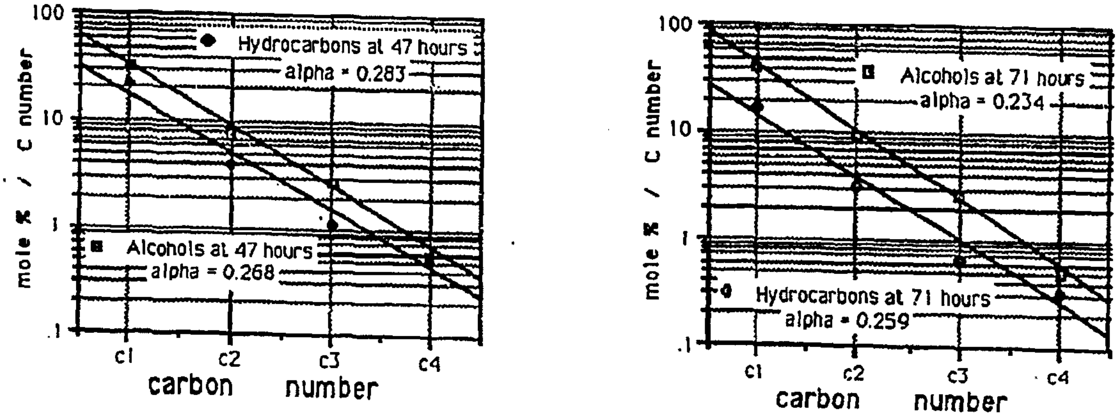
(D) Product Distribution

Figure 12. Catalyst 1KEC124, Evaluation 28NEK46. Catalyst from precipitated ATM, MoS_3 (200°C), K/Mo = 0.1 from aq soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, H_2/CO = 1; Procedure B(e).



(A) Rate vs. Time

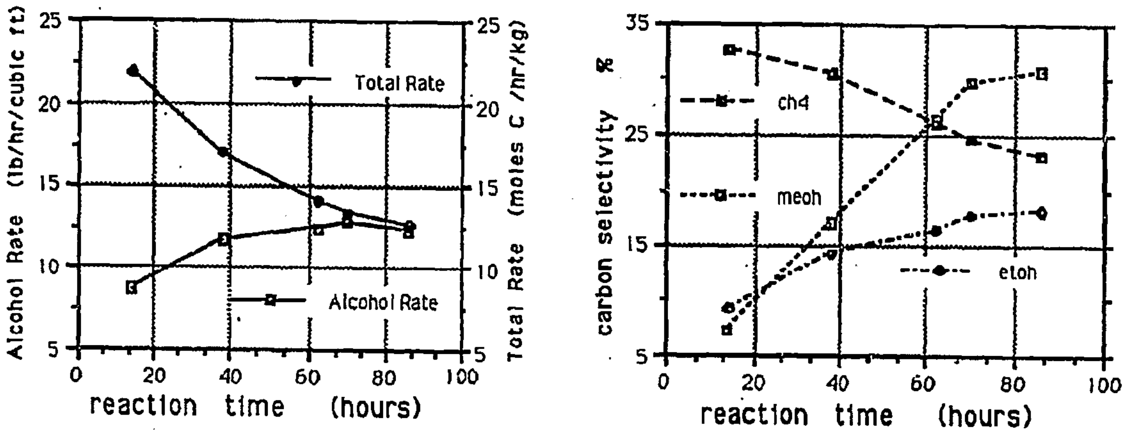
(B) Selectivity vs. Time



(C) Product Distribution

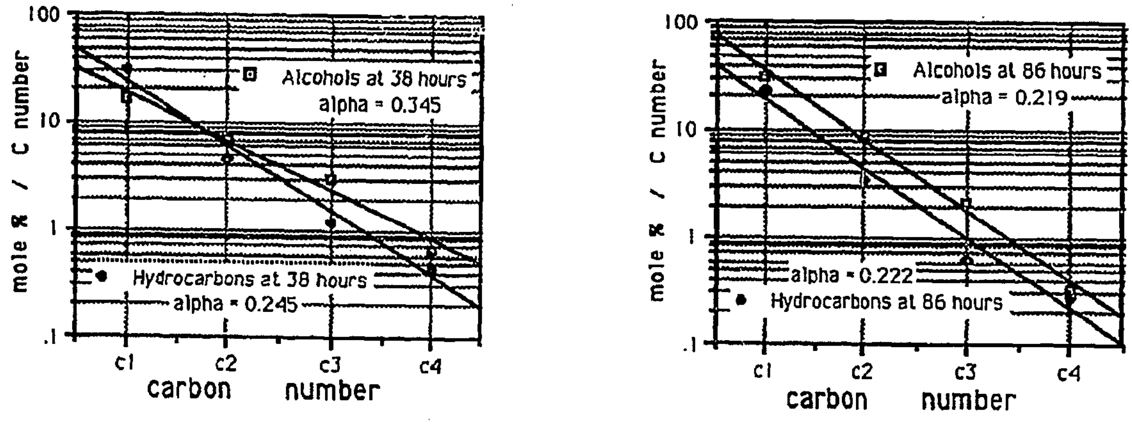
(D) Product Distribution

Figure 13. Catalyst 2KEC2A, Evaluation 28NEK68. Catalyst from ATM 1KEC131A, MoS_2, K/Mo = 0.35 from EtOH soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, $H_2/CO = 1$; Procedure B(e).



(A) Rate vs. Time

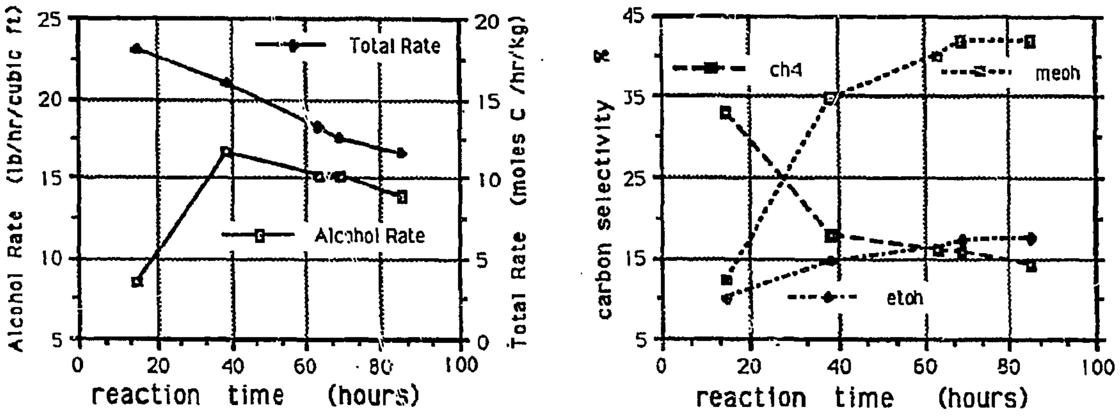
(B) Selectivity vs. Time



(C) Product Distribution

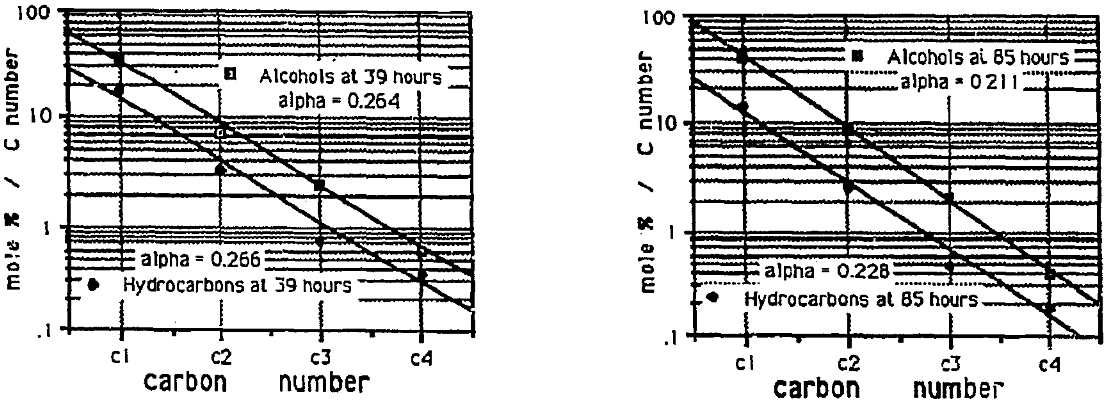
(D) Product Distribution

Figure 14. Catalyst 2KEC2B, Evaluation 28NEK70. Catalyst from ATM 1KEC131A, MoS$_3$ (200°C), K/Mo = 0.35 from EtOH soln. Evaluation at 300°C, 1200 psi, S V = 6000 hr^{-1}, H$_2$/CO = 1; Procedure B(e).



(A) Rate vs. Time

(B) Selectivity vs. Time



(C) Product Distribution

(D) Product Distribution

D. Task 3 Summary

These experiments have tested a number of alternative procedures for the preparation of fuel alcohol catalysts. None of the catalysts tested has been superior to the standard catalyst.

MoS_2 with higher surface area has been prepared by changing the ATM preparation procedure and stopping the H_2S feed sooner. The product is then uniform needlelike red crystals. The maximum surface area was 109.6 m^2/gram. Unfortunately, catalysts prepared from this material did not produce superior rate or selectivity.

Catalysts prepared by low temperature calcination to first produce MoS_3, then impregnating and calcining were little different from the standard except for a slower rate. Impregnation with potassium acetate from an ethanol solution did not improve performance.

Two catalysts were prepared from ATM precipitated to give fine particles. Neither gave improved rate or selectivity.

Catalyst prepared from $(NH_4)_2MoO_2S_2$ was also not active enough and did not give improved selectivity.

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