DOE/PC/90013--T12

TWELFTH QUARTERLY TECHNICAL PROGRESS REPORT

DOE CONTRACT NO. DE-AC22-86PC90013

Optimum Catalytic Process for Alcohol Fuels from Syngas

Pittsburgh Energy Technology Center

February 20, 1989

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Solvents and Coatings Materials Division

Union Carbide Chemicals and Plastics Company Inc.
South Charleston Technical Center
South Charleston, West Virginia 25303

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Solvents and Coatings Materials Division

Union Carbide Chemicals and Plastics Company Inc.
South Charleston Technical Center
South Charleston, West Virginia 25303

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D. C. Best
Program Manager

Patent Cleared by Chicago
OPC on March 12, 1990

Patent Hold

DISCLAIMER

Patent Cleared by Chicago
OPC on March 12, 1990

PATENT STATUS

This Technical Report is being transmitted in advance of DOE patent clearance and no further dissemination or publication shall be made of the Report without prior approval of the DOE Patent Counsel.

CONTENTS

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 was 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, the effort has been mainly on heterogeneous catalysts. Novel systems which may exhibit superior behavior are being investigated.

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. Current work in Task 3 includes the evaluation of slurry-catalyzed processes for the production of fuel alcohols or their derivatives.

A ten-month no-cost extension of this contract has been applied for and granted.

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

Work continues on optimization of higher alcohol catalysts consisting of transition metals supported on metal oxides with the spinel structure. The majority of the recent work has been the execution of two statistically designed experiments to further define preparation procedures. Catalysts formulated this quarter had alcohol activities as great as 6 lb/ft^3/hr at 250°C and a GHSV of 6000 hr^{-1}. It was demonstrated that doubling the gas space velocity and increasing the temperature to 270°C could result in a 260% increase in activity along with an improvement in alcohol selectivity. The lower temperature had been used this quarter in the design to insure the absence of reactor hot-spots with all catalyst formulations.

With the two designed sets completed, the following variables were studied: the alkali promoter loading, the salt used to precipitate the spinel precursor, the concentration of spinel components, the sequence of the alkali impregnation step in the catalyst preparation, the spinel calcination temperature, and the spinel structural promoter.

Work planned for the next quarter is designed to complete the first round of optimization of the transition metal on spinel oxide support catalysts. In particular, a final 4x3 Hyper-Greco-Latin square designed set is planned to complete the bracketing of catalyst formulation, preparation, and pretreatment procedures. This will be followed by a five-variable factorial or face-centered cube designed set of experiments to further characterize the response surface and location of optimum levels.

B. Task 3: Engineering Studies

The slurry reaction system was successfully started up with non-reactive tests in November, 1989. The reactor ran for 100 hours with isopropanol and nitrogen feed at temperatures to 240°C and pressures to 800 psi. During this test, the reactor contained 30 grams of 75 to 150 micron alumina support. This test demonstrated that the catalyst filtering system (discussed in the previous quarterly report) would keep the catalyst out of the reactor effluent without clogging or the need for back-flushing. A material balance over the system was within two percent. The computer control system performed well.

A Plexiglas model of the slurry reactor was constructed in order to observe the gas-solid-liquid mixing patterns inside the reactor. It was found that the agitator must be running at least at 75% of capacity in order to pump any gas into the liquid. After a week of operation, there was no observable decrease in effectiveness of the agitation due to agglomeration of solids inside the impeller.

After being set up and calibrated, the gas chromatograph is now operational. The GC will simultaneously perform on-line analysis of the off-gas and automated analysis of the liquid collected.

The slurry reaction system has been recently started up using a commercial methanol catalyst. The catalyst was crushed, sieved to 75 – 150 microns, and activated in-situ using tetraethylene glycol dimethyl ether as the solvent. We are currently having problems with low productivity and high deactivation rates. We are working to determine the cause of these problems before operating with the spinel catalyst developed under Task 2.

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 the exploration of novel types of heterogeneous catalysts for the conversion of syngas to oxygenates.

Work on Task 3 will involve economic and engineering evaluations as required to support the chemical investigations. It will also involve the study of slurry-catalyzed systems for the production of fuel alcohols.

APPENDIXES

By J. G. Hippler and G. R. Sheffer

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:

A128 - A156: 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(i)

All catalyst evaluations are performed on a microreactor system designed to operate three 6-milliliter u-shaped fixed-bed reaction tubes simultaneously at pressures of 15-1500 psig, at temperatures between 25 and 400°C, and space velocities between 600 and 6000 hr^{-1} (STP). This reactor system was described in detail in our Eighth Quarterly Report. The system is capable of automated on-line gas-phase product analysis with post-sampling knock-out pots to collect product for future analysis. Pressure, feed gas composition and velocity, and off-gas sampling may be operated independently for each reaction tube. However, because the tubes utilize a common sandbath, they must be operated at the same reaction temperature. The microreactor system is equipped with an Emergency Shutdown System (ESD) for unattended, overnight operation.

The standard start-up procedure consists of charging the catalyst, generally in powder form, to the outlet leg of a u-shaped 1/4 in. O.D. 304 stainless steel tube. The catalyst is always diluted with an equal volume of 0.5mm glass beads to minimize the pressure drop across the bed. The inlet leg of the u-tube is filled with activated carbon to trap and decompose any metal carbonyl in the feed gas. Glass wool plugs are used to hold all solids in place. The inertness of all non-catalytic materials has been confirmed. The catalysts are activated using H_2/N_2 gas mixtures at atmospheric pressure in a modified gas chromatograph. The tubes are then placed into the microreactor system. The system is subsequently pressurized with feed gas. The absence of gas leaks is verified with soap solution. After reaction pressure is established, the feed gas flow rate is set and measured. The sandbath temperature is then increased to the desired setpoint. Finally, the off-gas analysis system is activated to provide sampling of the reactor effluent for each reactor tube every four hours.

Appendix C. PROCEDURES FOR PRODUCT ANALYSIS

Procedure C(f)

All product analyses are completed in the gas phase using heated lines to transfer reactor effluent samples. A single Varian 3700 gas chromatograph equipped with two detectors is used for off-gas analysis. Inorganics (H_2, N_2, CO, and CO_2) are separated on a 1/8 in. x 10 ft. 80/100 mesh Carbosieve S-2 column purchased from Supelco and are measured by a thermal conductivity detector. All organic products are resolved on a 1/8 in. x 12 ft. 80/100 mesh Tenax column obtained from Alltech and are measured using a flame ionization detector. The Tenax column has been calibrated on an absolute weight basis using quantified mixtures of C_1-C_6 normal hydrocarbons, normal and branched alcohols, and normal aldehydes. Argon is used as the carrier gas for both columns. The following parameters are used for the GC oven and the two columns and detectors:

Temperature ramp: 50°C to 225°C at 8°C/min with a 10 minute hold at the upper temperature

Column	Flow Rate	Injector Temperature
Tenax	20 sccm	220°C
Carbosieve (sample)	20 sccm	170°C
Carbosieve (reference)	20 sccm	170°C

Detector	Temperature	Sensitivity	Attenuation	Other
TCD	200°C	5.0 mV	4X	Filament Temp. = 350°C
FID	250°C	10-10	8X	H_2 flow = 30 sccm Air flow = 300 sccm

Appendix D. TECHNICAL AND EXPERIMENTAL DATA

TABLE OF CONTENTS

I. TASK 2: Catalyst Research

A. Direct Syngas Conversion by Heterogeneous Catalysts

1. Introduction

Work continues on optimization of higher alcohol catalysts consisting of transition metals supported on metal oxides with the spinel structure. The majority of the work this quarter has been the execution of two statistically designed experiments, Latin Squares, to further define preparation procedures. Last quarter, it was reported that changes in the metal impregnation procedures resulted in catalysts with activity as great as 13 $lb/ft^3/hr$ and 46 wt% alcohol selectivity at 275°C, 1000 psig, and 6000 hr^{-1} GHSV with a hydrogen to carbon monoxide ratio of 2. Catalysts studied this quarter had alcohol activities as great as 6 $lb/ft^3/hr$ at 250°C with all other reaction conditions the same as previously mentioned. The lower temperature, 250°C, was used this quarter in the design to insure the absence of reactor hot-spots with all catalyst formulations.

Our goal remains to develop a catalyst with activity of greater than 20 lb alcohols/ft^3 catalyst/hr and alcohol selectivity of greater than 95 wt%, with C_2-C_6 alcohols comprising at least 30 wt% of the alcohol product.

2. Catalyst Preparation and Characterization

Catalyst Preparation: Except as noted, catalysts this quarter were prepared by coprecipitation and calcination of alkalinized spinel components followed by ammoniacal impregnation of the transition metal carbonate. Coprecipitation was performed by mixing an aqueous solution of metal nitrates with an aqueous solution of ammonium carbonate. The flow rate of each solution into the mixing beaker was adjusted to maintain a constant pH of 7. Precipitates were dried in a vacuum oven overnight, impregnated with alkali at a constant level of 9 mole %, and then calcined in air at 350°C for 4 hours. Transition metal compounds were added by incipient wetness impregnation using an ammonium hydroxide solution of the metal carbonate. The amount of metal impregnated was determined with respect to a desired surface layer coverage of the metal by calculating the moles of metal needed based on the metallic radius of the element and the surface area of the calcined catalyst precursor.

Catalyst Characterization: Surface areas of all calcined catalysts were measured using nitrogen adsorption isotherms. Catalyst densities were determined by measuring the volume in a graduated tube of a specified weight of catalyst.

3. Catalyst Testing

All catalysts were evaluated using Procedure B(i) of Appendix B, and products were analyzed using Procedure C(f) of Appendix C. Before syngas reaction, catalysts were activated by passing a 5% hydrogen in nitrogen gas mix over the catalyst at 250°C for 4 hours using a temperature ramp of 2°C/min. The system was then pressurized with syngas containing an equimolar concentration of carbon monoxide and hydrogen to 1000 psig. The temperature was adjusted to 250°C and the syngas flow rate set at 100 cc/g catalyst/min. The reaction product in most cases consisted exclusively of normal paraffins and alcohols.

4. Catalytic Results

The results of the Latin Square designed sets reported in our 11th Quarterly Report indicated that the best direction for further study was to look at A129/A132 bimetallics supported on a A139/A144 spinel oxide promoted with an alkali, A150. It was decided that the next set of experiments should focus on evaluating the effect of the alkali loading, the A129/A132 metal ratio, the salt used for spinel precursor precipitation, and the best oxide promoter and its method of introduction. A sixth (in terms of the transition metal on spinel oxide catalyst series), five-variable, four-level, Hyper-Greco-Latin Square was designed as the next step toward bracketing these variables; see Table 1 below.

Table 1. Hyper-Greco-Latin Square Design to Examine Catalyst Preparation and Formulation

	Method of Preparation	Spinel Ratio A139/A144	Oxide Promoter	Mole Fraction A132 in A129/A132 Mix	Alkali Promoter Concentration*
Level 1	A	0.5	none	0.00	0.00
Level 2	B	1.0	A147	0.33	0.03
Level 3	C	1.5	A138	0.67	0.06
Level 4	D	2.0	A154	1.00	0.09

* defined as A150 / (A150 + A139 + A144).

Preparation method A consisted of precipitating the aqueous solution of spinel element nitrates with $(NH_4)_2CO_3$, while preparation method B utilized Na_2CO_3 as the agent of precipitation. In preparation methods C and D, K_2CO_3 was used for the precipitation of the spinel precursor, but in method C the oxide promoter was added to the spinel precursor before calcination, while in method D the oxide promoter was added after calcination. Three mole percent of aluminum was added to all spinels to stabilize surface areas.

Sixteen catalysts were prepared for this sixth designed set with compositions listed in Table 2. The total metal (A129 + A133) loading was maintained at 1/2 monolayer. Alkali was added to all catalysts by aqueous impregnation of the formate salt to coprecipitated catalyst precursors before calcination at a constant level of 9 mol%.

Table 2. Transition Metal On Spinel Oxide Catalyst Preparations: Designed Set 6

Preparation Notebook #	Method of Preparation	Spinel Ratio A139/A144	Oxide Promoter	Mole % A132 in A129/A132	A150 Mol %
5-GRS-126-1	A	0.5	none	0.00	0
5-GRS-126-2	A	1.0	A147	0.67	9
5-GRS-126-3	A	1.5	A138	1.00	3
5-GRS-126-4	A	2.0	A154	0.33	6
5-GRS-126-5	B	0.5	A147	0.33	3
5-GRS-126-6	B	1.0	none	1.00	6
5-GRS-126-7	B	1.5	A154	0.67	0
5-GRS-126-8	B	2.0	A138	0.00	9
5-GRS-126-9	C	0.5	A138	0.67	6
5-GRS-126-10	C	1.0	A154	0.00	3
5-GRS-126-11	C	1.5	none	0.33	9
5-GRS-126-12	C	2.0	A147	1.00	0
5-GRS-126-13	D	0.5	A154	1.00	9
5-GRS-126-14	D	1.0	A138	0.33	0
5-GRS-126-15	D	1.5	A147	0.00	6
5-GRS-126-16	D	2.0	none	0.67	3

The behavior of the individual catalysts is summarized in Table 3, while the analysis of the Latin Square is presented in Tables 4 and 5. A simple series of pluses and minuses has been used to indicate the magnitude of influence of each of the variables on the grand average of all responses. The grand average as well as the approximate magnitude of a single plus/minus sign is indicated for each category. Note that three was the maximum number of pluses or minuses given. The maximum result predicted for each category is also provided in the tables. A number of categories have been evaluated including physical properties (surface area, surface area to catalyst volume ratio) and catalytic performance (alcohol selectivities and yields).

Table 3. Transition Metal on Spinel Oxides Designed Set 6: Catalyst Performance Data.
Conditions: 250°C, 1000 psig, SV = 100 cc/g cat/min, H_2/CO = 2.0

	Surface	Alcohol Selec. (wt%)		Alcohol Yield	
Catalyst	area (m^2/g)	total	(C_2+)*	(lb/ft^3/hr)	(g/g cat/hr)
5-GRS-126-1	116	20	43	2.6	0.050
5-GRS-126-2	71	32	40	0.7	0.011
5-GRS-126-3	99	24	48	2.8	0.037
5-GRS-126-4	91	28	64	2.1	0.027
5-GRS-126-5	54	22	38	0.3	0.005
5-GRS-126-6	122	36	29	0.9	0.013
5-GRS-126-7	107	25	47	1.8	0.021
5-GRS-126-8	161	8	39	0.4	0.006
5-GRS-126-9	57	38	16	0.2	0.003
5-GRS-126-10	112	11	50	0.4	0.006
5-GRS-126-11	53	29	40	0.6	0.007
5-GRS-126-12	155	27	46	2.7	0.035
5-GRS-126-13	59	82	3	0.7	0.008
5-GRS-126-14	127	21	47	0.9	0.012
5-GRS-126-15	85	5	17	0.2	0.002
5-GRS-126-16	122	38	61	3.8	0.055
		(57	42	10.0	0.145)**

* Weight fraction of higher (C_2^+) alcohols in the overall alcohol product.

** Results observed when temperature was raised to 270°C and GHSV raised to 12000 hr^{-1}.

Table 5. Transition Metal on Spinel Oxides Designed Set 6: 5x4 Hyper-Greco-Latin Square Catalyst Physical Property Responses Relative to the Grand Average.

Variable	Level	Surface area (m^2/g)	Area/Volume (m^2/ml)
Method of Preparation	A	0	–
Method of Preparation	B	+	+
Method of Preparation	C	0	0
Method of Preparation	D	0	0
A139/A144 ratio in spinel	0.5	– – –	+ + +
A139/A144 ratio in spinel	1.0	+	0
A139/A144 ratio in spinel	1.5	–	–
A139/A144 ratio in spinel	2.0	+ + +	– –
Oxide Promoter	none	N/A	N/A
Oxide Promoter	A147	N/A	N/A
Oxide Promoter	A138	N/A	N/A
Oxide Promoter	A154	N/A	N/A
Mole % A132 in A129/A132	0.00	N/A	N/A
Mole % A132 in A129/A132	0.33	N/A	N/A
Mole % A132 in A129/A132	0.67	N/A	N/A
Mole % A132 in A129/A132	1.00	N/A	N/A
A150 Mole %	0	+ + +	+ + +
A150 Mole %	3	0	0
A150 Mole %	6	–	–
A150 Mole %	9	–	– –
Grand Average		99 (+/– = 8%)	113 (+/– = 7%)
Maximum Predicted		202	219

Table 4. Transition Metal on Spinel Oxides Designed Set 6: 5x4 Hyper-Greco-Latin Square Catalyst Chemical Reactivity Responses Relative to the Grand Average.

Variable	Level	Alcohol selectivity (wt%)	C_2+ alc. selectivity (wt%)	Alcohol rate ($lb/ft^3/hr$)	Alcohol rate (g/g/hr)
Preparation Method	A	0	+ + +	+ +	+ + +
Preparation Method	B	–	0	–	– –
Preparation Method	C	0	0	–	– –
Preparation Method	D	+ + +	– –	0	0
A139/A144 Ratio	0.5	+ + +	– – –	–	0
A139/A144 Ratio	1.0	–	0	– –	– –
A139/A144 Ratio	1.5	– –	0	0	0
A139/A144 Ratio	2.0	–	+ + +	+ + +	+ + +
Oxide Promoter	none	+	+	+ +	+ + +
Oxide Promoter	A147	– –	–	–	–
Oxide Promoter	A138	–	0	–	–
Oxide Promoter	A154	+ + +	0	0	–
Mole % A132	0	– – –	0	–	0
Mole % A132	0.33	–	+ +	–	–
Mole % A132	0.67	+ +	+	+	+
Mole % A132	1.0	+ + +	– –	+	+
A150 Mole %	0	–	+ +	+ +	+ + +
A150 Mole %	3	–	+ + +	+	+ +
A150 Mole %	6	0	– –	–	– –
A150 Mole %	9	+ + +	– – –	– –	– – –
Grand Average		28 (+/– = 10%)	39 (+/– = 8%)	1.3 (+/– = 13%)	0.02 (+/– = 15%)
Maximum Predicted		83	82	4.8	0.07

When the results are scrutinized, the following observations become apparent with respect to each of the variables examined:

1. Alkali (A150) concentration: Defined as A150 / (A150 + A139 +A144). The designed set indicates that the optimum A150 level is bracketed by:

   $$0 \text{ mol\%} \leq \text{level} \leq 3 \text{ mol\%}$$

   Increasing concentrations of alkali decreased the alcohol yield and the C_2+ selectivity with only a small increase in the overall alcohol selectivity. The data raise the question of whether it might be possible to design an alkali-free higher alcohol catalyst. In terms of catalyst physical properties, as expected, the addition of alkali resulted in a decrease in the spinel surface area per weight of catalyst.

2. Mole % A132 in A129/A132 bimetallic: Increasing amounts of A132 increase both the alcohol selectivity and the the alcohol yield while decreasing the C_2+ alcohol selectivity. The optimum A132 mole fraction is bounded by:

   $$0.67 \leq X(A132) \leq 1.00$$

3. A139/A144 ratio in spinel: Both the alcohol yield and the C_2+ selectivity increase with increasing A139 concentration. However, the overall alcohol selectivity decreases. An A139/A144 ratio of greater than 1.5 appears necessary for good catalytic behavior. Catalyst surface areas also increased substantially with increasing A139/A144 molar ratio.

4. Preparation method: In terms of the different carbonates (Na, K, and NH_4) used for spinel precursor precipitation, ammonium carbonate was superior to both potassium and sodium carbonates in alcohol yield, with similar selectivities observed among the three. Ammonium carbonate will be used in future preparations. Surprisingly, the preparation method had little impact on spinel surface areas.

5. Oxide promoters: None of the promoters examined (A147, A154, or A138) were superior to the case of using no promoter of all. These oxide promoters tend to be acidic in nature and other more basic oxide promoters should still be examined.

Overall, the maximum alcohol yield observed was 5 lb/ft^3/hr at 250°C and a GHSV of 6000 hr^{-1}. As shown in Table 3 for catalyst 5-GRS-126-16, however, the alcohol yield increases by 260% to 10.0 lb/ft^3/hr at 270°C and a GHSV of 12000 hr^{-1}. In addition, the alcohol selectivity increases, while the fraction of C_2+ alcohols decreases, with the change in reaction conditions. When the hydrocarbon and alcohol yields for catalyst 5-

GRS-126-16 are examined individually, the alcohol yield is directly proportional to the space velocity, but the hydrocarbon yield changes only slightly. This suggests that some of the hydrocarbons are being formed via secondary reactions (dehydration) of the alcohols and that perhaps the effect of the aluminum, used as a structural promoter, should be examined further.

In order to address some of the questions raised in the above paragraphs, a seventh series of transition metal on spinel oxide catalysts was formulated. In particular, a 4x3 Hyper-Greco-Latin Square designed set was constructed (Table 6) to further define preparation variables (including calcination and reduction procedures), to bracket the A132 loading, to determine whether the small amount of aluminum being added to increase surface areas is necessary, and to further bracket the A150 alkali loading. In addition to the 400°C calcination temperature utilized thus far in the catalyst preparations, it was decided to examine both lower, 250°C, and higher, 600°C, calcination temperatures. With any supported metal catalyst, reduction procedures can change metal dispersions; therefore a set of slower reduction conditions, namely a 0.5°C/min. temperature ramp using a 2% hydrogen in nitrogen reduction gas, was also examined. Two other preparation methods were examined to compare alkali addition to the spinel before calcination to that after calcination, and to compare incorporating the metal to be supported into the initial spinel precursor as opposed to impregnation afterwards. The compositions of the sixteen catalysts prepared for testing are given in Table 7.

Table 6. Hyper-Greco-Latin Square Designed Set 7: Examination of Catalyst Preparation and Formulation

	Calcin./Red. Procedures	Method of Preparation	A132 Loading	Alkali Promoter Concentration**	A139/A144/Al Molar Ratio
Level 1	250°C cal.	A	0.33 ML*	0.000	2.0/1.0/0.1
Level 2	600°C cal	B	0.67 ML	0.015	1.5/1.5/0.1
Level 3	0.5°C/min red.	C	1.33 ML	0.030	2.0/1.0/0.0
Level 4	2.0°C/min red.	D	2.00 ML	0.030***	1.5/1.5/0.0

* ML = monolayer coverage.

** Defined as A150 / (A150 + A139 + A144).

*** The 0.030 alkali promoter concentration was repeated as an internal check.

Preparation method A consisted of adding the A150 alkali promoter after calcination of the ammonium carbonate-precipitated spinel precursor, while preparation method B incorporated the alkali before calcination. Preparation methods C and D were identical to A and B with respect to the alkali incorporation but differed from A and B in that the A132 was incorporated into the spinel precursor before calcination.

Table 7. Transition Metal On Spinel Oxide Catalyst Preparations: Designed Set 7.

Preparation Notebook #	Calcin./Red. Procedures	Method of Preparation	A132 Loading	A150 Concentration	A139/A144/Al Mole Ratio
7-GRS-5-1	250°C cal.	A	0.33 ML	0.000	2.0/1.0/0.1
7-GRS-5-2	250°C cal.	B	0.67 ML	0.030	1.5/1.5/0.0
7-GRS-5-3	250°C cal.	C	1.33 ML	0.030	1.5/1.5/0.1
7-GRS-5-4	250°C cal.	D	2.00 ML	0.015	2.0/1.0/0.0
7-GRS-5-5	600°C cal.	A	0.67 ML	0.015	1.5/1.5/0.1
7-GRS-5-6	600°C cal.	B	0.33 ML	0.030	2.0/1.0/0.0
7-GRS-5-7	600°C cal.	C	2.00 ML	0.030	2.0/1.0/0.1
7-GRS-5-8	600°C cal.	D	1.33 ML	0.000	1.5/1.5/0.0
7-GRS-5-9	0.5°C/min red.	A	1.33 ML	0.030	2.0/1.0/0.0
7-GRS-5-10	0.5°C/min red.	B	2.00 ML	0.000	1.5/1.5/0.1
7-GRS-5-11	0.5°C/min red.	C	0.33 ML	0.015	1.5/1.5/0.0
7-GRS-5-12	0.5°C/min red.	D	0.67 ML	0.030	2.0/1.0/0.1
7-GRS-5-13	2.0°C/min red.	A	2.00 ML	0.030	1.5/1.5/0.0
7-GRS-5-14	2.0°C/min red.	B	1.33 ML	0.015	2.0/1.0/0.1
7-GRS-5-15	2.0°C/min red.	C	0.67 ML	0.000	2.0/1.0/0.0
7-GRS-5-16	2.0°C/min red.	D	0.33 ML	0.030	1.5/1.5/0.1

For catalysts not calcined at 250 or 600°C, a 400°C calcination temperature was used. Except for the 0.5°C/min. reduction, a reduction rate of 2.0°C/min. was used. The 0.030 A150 promoter concentration was repeated as an internal check. The results for the individual catalysts are shown in Table 8, while the analysis of the Latin Square is summarized, using pluses and minuses as outlined previously, in Tables 9 and 10.

Table 8. Transition Metal on Spinel Oxides Designed Set 7: Catalyst Performance Data.
Conditions: 250°C, 1000 psig, SV = 100 cc/g cat/min, $H_2/CO = 2.0$

	Surface	Alcohol Selec. (wt%)		Alcohol Yield	
Catalyst	area (m^2/g)	total	(C_2+)*	($lb/ft^3/hr$)	(g/g cat/hr)
7-GRS-5-1	164	5	47	2.3	0.038
7-GRS-5-2	167	37	52	5.0	0.072
7-GRS-5-3	244	9	39	2.1	0.027
7-GRS-5-4	132	39	40	2.6	0.033
7-GRS-5-5	63	39	0	0.2	0.003
7-GRS-5-6	10	23	0	0.1	0.001
7-GRS-5-7	27	55	66	0.4	0.004
7-GRS-5-8	32	45	62	1.3	0.020
7-GRS-5-9	72	4	0	0.1	0.001
7-GRS-5-10	120	38	35	1.2	0.022
7-GRS-5-11	87	4	9	0.1	0.001
7-GRS-5-12	133	24	64	3.8	0.047
7-GRS-5-13	45	0	0	0.0	0.000
7-GRS-5-14	72	17	52	2.6	0.058
7-GRS-5-15	28	0	0	0.0	0.000
7-GRS-5-16	107	14	53	1.4	0.022

* Weight fraction of higher (C_2^+) alcohols in the overall alcohol product.

Table 9. Transition Metal on Spinel Oxides Designed Set 7: 4x3 Hyper-Greco-Latin Square Catalyst Physical Property Responses Relative to the Grand Average.

Variable	Level	Surface area (m^2/g)	Area/Volume (m^2/ml)
Calcin./Red. Procedures	250°C cal.	+ + +	+ + +
Calcin./Red. Procedures	600°C cal.	– – –	– – –
Calcin./Red. Procedures	0.5°C/min. red.	0	0
Calcin./Red. Procedures	2.0°C/min. red.	–	–
Method of Preparation	A	0	0
Method of Preparation	B	0	–
Method of Preparation	C	0	0
Method of Preparation	D	0	+
A132 Loading	0.33 ML	N/A	N/A
A132 Loading	0.67 ML	N/A	N/A
A132 Loading	1.33 ML	N/A	N/A
A132 Loading	2.00 ML	N/A	N/A
Alkali (A150) Conc.	0.000	0	–
Alkali (A150) Conc.	0.015	0	–
Alkali (A150) Conc.	0.030	0	+
Alkali (A150) Conc.	0.030	0	+
A139/A144/Al Ratio	2.0/1.0/0.1	+	+
A139/A144/Al Ratio	1.5/1.5/0.1	+ +	+ +
A139/A144/Al Ratio	2.0/1.0/0.0	– –	– –
A139/A144/Al Ratio	1.5/1.5/0.0	–	–
Grand Average		94 (+/– = 15%)	105 (+/– = 14%)
Maximum Predicted		256	316

Table 10. Transition Metal on Spinel Oxides Design Set 7: 4x3 Hyper-Greco-Latin Square Catalyst Chemical Reactivity Responses Relative to the Grand Average.

Variable	Level	Alcohol selectivity (wt%)	C_2+ alc. selectivity (wt%)	Alcohol rate ($lb/ft^3/hr$)	Total rate ($lb/ft^3/hr$)
Calcin./Red. Proc.	250°C cal.	0	+ +	+ + +	+ + +
Calcin./Red. Proc.	600°C cal.	+ + +	0	– –	–
Calcin./Red. Proc.	0.5°C/min red.	–	–	0	–
Calcin./Red. Proc.	2.0°C/min red.	– – –	–	–	+
Preparation Method	A	– – –	– – –	– –	+ +
Preparation Method	B	+ +	+	+ +	–
Preparation Method	C	–	–	– –	0
Preparation Method	D	+ +	+ + +	+ +	–
A132 Loading	0.33 ML	– – –	–	–	+
A132 Loading	0.67 ML	+	0	+ +	0
A132 Loading	1.33 ML	–	+	0	0
A132 Loading	2.00 ML	+ + +	+	–	0
A150 Conc.	0.000	0	0	0	+
A150 Conc.	0.015	+	–	0	0
A150 Conc.	0.030	0	+	0	–
A150 Conc.	0.030	0	+	0	–
A139/A144/Al Ratio	2.0/1.0/0.1	+	+ + +	+ + +	+ +
A139/A144/Al Ratio	1.5/1.5/0.1	+	0	0	0
A139/A144/Al Ratio	2.0/1.0/0.0	–	– – –	– –	–
A139/A144/Al Ratio	1.5/1.5/0.0	0	0	0	0
Grand Average		22 (+/– = 15%)	32 (+/– = 16%)	1.5 (+/– = 25%)	11.5 (+/– = 25%)
Maximum Predicted		67	107	5.7	46.0

Examining the results listed in Tables 9 and 10, the following observations become apparent with respect to each of the variables studied:

1. Calcination/reduction procedures: The calcination temperature of the spinel has a large effect on both the physical characteristics of the catalyst as well as its catalytic behavior. The lower the calcination temperature the greater the alcohol yield, but there is some decrease in the alcohol selectivity. The influence of reduction conditions was much less than for calcination temperature, with the slower reduction procedure resulting in slightly improved alcohol selectivity and yield compared with the standard reduction.

2. Preparation method: The impregnation of the alkali promoter before calcination of the spinel precursor, as in methods B and D, was clearly superior in both alcohol selectivity and yield to alkali impregnation following precursor calcination, as in methods A and C. The incorporation of the transition metal, A132, by impregnation of the spinel precursor (method B) after calcination resulted in catalytic performance superior to introduction of the transition metal to the spinel precursor before calcination.

3. A132 loading: An A132 loading of greater than 0.33 monolayers appears to be necessary for best catalytic performance. Although the alcohol yield declines at a loading of 2.0 monolayers, this may be a phenomenon of the method of impregnation and may not necessarily represent the upper A132 monolayer boundary. This parameter should be further investigated.

4. Alkali concentration: The concentration of the A150 alkali promoter did not play a major role in altering the catalytic behavior of the catalyst. The higher loadings only slightly improved the alcohol selectivity. The optimum alkali loading still appears to be between 0.00 and 0.03 as was indicated by the data in designed set 6. The internal check, repetition of the 0.03 concentration, was successful as indicated by the similar results for the two sets of data, helping to insure that the differences in catalytic performance resulting from the designed set are much greater than the error associated with micro-reactor data repeatability.

5. A139/A144/Al spinel molar ratio: The incorporation of aluminum as a structural promoter in the spinel has a positive influence on the surface area and appears to have only a positive influence on catalytic performance, suggesting

that it does not play a role in the secondary reaction of alcohol dehydration. The aluminum does amplify the difference in catalytic behavior between the catalysts with an A139/A144 ratio of 2 as compared to a A139/A144 ratio of 1.

Overall, the results of the seventh experimental designed set indicate that the variables having major effects on the final catalytic performance are spinel precursor calcination temperature, the position in the preparation sequence of alkali addition, and the A139/A144 ratio in the spinel. The alkali loading is properly bracketed, but the loading of A132 is not and must be further examined. The maximum alcohol yield predicted by designed set 7 is 5.7 lb/ft^3/hr, which is only 20% better than designed set 6, but considering the wide variety of variables examined this result is not too surprising. The 5.7 lb/ft^3/hr alcohol yield may be translated, with the change in reactor conditions as in 5-GRS-126-16, to an alcohol yield of 15 lb/ft^3/hr or 75% of our 20 lb/ft^3/hr goal.

5. Future Work

In order to finish the bracketing or choosing of catalyst formulation and preparation variables in the upcoming quarter, an eighth 4x3 Hyper-Greco-Latin Square designed set has been constructed. It is anticipated that this designed set will be followed by a 5-variable factorial or face-centered cube designed set to map the response surface and expose the nature of the interactions of the primary variables. The eighth Latin square is intended to further bracket the optimum calcination temperature, further bracket the A132 loading, study the effect of spinel precursor pH and temperature of precipitation, examine the influence of reaction temperatures over the range of 250 to 290°C, examine other methods of A132 impregnation, and evaluate other basic elements in addition to the alkalis as suggested by designed set 6. The actual structure of the Latin square is provided in Table 10 and the results will be reported in the next quarterly.

Table 10. Hyper-Greco-Latin Square Designed Set 8: Examination of Catalyst Preparation and Formulation

	A132 Impreg. Method	A132 Loading	Other	Calcination Temperature	Base Promoter
Level 1	A	0.67 ML*	T rxn.=270°C	150°C	A150
Level 2	B	1.33 ML	pH ppt.=11	225°C	A155
Level 3	C	2.00 ML	T rxn.=290°C	300°C	A156
Level 4	D	4.00 ML	T ppt.=100°C	400°C	A136

* ML = monolayer coverage.

Impregnation method A consists of impregnating an ammoniacal solution of the A132 carbonate onto the spinel support (*1*). Method B involves the preparation and impregnation of reverse A132 micelles as in the UOP patent literature (2). Ion exchange impregnations will be attempted in method C (*3,4*). Finally, method D will involve preparing A132 colloids (*5*) in ethanol solutions and impregnating those onto the spinel surface. More details on these impregnation methods will be provided in the next quarterly report.

References

1. U. S. Patent 4,677,234 (assigned to Union Carbide).

2. U. S. Patent 4,714,693 (assigned to Universal Oil Products).

3. H. A. Benesi, R. M. Curtis, and H. P. Studer *J. Catal.* **10**, 328, (1968).

4. S. Ichikawa, *J. Chem. Soc., Chem. Comm.*, 403 (1989).

5. E. R. Savinova, A. L. Chuvilin, and V. N. Parmon, *J. Mol. Catal.*, **48**, 217 (1988).

B. Task 2 Summary

Work continues on optimization of higher alcohol catalysts consisting of transition metals supported on metal oxides with the spinel structure. The majority of the work has been the execution of two statistically designed experiments, Latin Squares, to further define preparation procedures. Catalysts formulated this quarter had alcohol activities as great as 6 $lb/ft^3/hr$ at 250°C and a GHSV of 6000 hr^{-1}. It was demonstrated that doubling the gas space velocity and increasing the temperature to 270°C could result in a 260% increase in activity along with an improvement in alcohol selectivity. The lower temperature had been used this quarter in the design to insure the absence of reactor hot-spots with all catalyst formulations. A number of variables were addressed in the two designed sets completed: the bracketing of the optimum alkali promoter loading, determination of the best spinel precursor precipitation salt, bracketing of the concentration of spinel components, determination of the best place to incorporate the alkali impregnation step in the catalyst preparation, the importance of spinel calcination temperature, and the effect of the spinel structural promoter on catalytic behavior. Work planned for the next quarter is designed to complete the first round of optimization of the transition metal on spinel oxide support catalysts. In particular, a final 4x3 Hyper-Greco-Latin square experimental designed set to complete the bracketing of catalyst formulation, preparation, and pretreatment procedures is planned. This will be followed by a five-variable factorial or face-centered cube designed set of experiments to further characterize the response surface and location of optimum levels.

II. TASK 3: Engineering Research

A. Reaction Engineering Studies

1. Introduction

Work this quarter on the reaction engineering slurry facility has involved pre-start-up tests of individual elements of the system. These elements included the physical equipment (leak testing and calibration), computer control system, agitation, filtering system, and analytical methods. After successfully completing these tests, the system was started up using methanol catalyst CCI #6341 in order to evaluate the reactor using a "standard catalyst". After these tests are complete, a rigorous set of tests is planned on the best catalyst developed under Task 2.

2. Laboratory Facilities and Results

The slurry reaction system was pressure tested to check for leaks and the liquid pumps, mass flow meters, and wet test meter were all calibrated. The system started up with non-reactive tests in November in order to test the control system and the filters and to demonstrate that a material balance can be closed over the system. During this test with isopropanol and nitrogen feed and the reactor containing 30 grams of 75 to 150 micron alumina support, the reactor ran continuously for 100 hours at temperatures to 240°C and pressures to 800 psi. This test demonstrated that the catalyst filtering system would keep the catalyst out of the reactor effluent without clogging or the need for back-flushing. The material balance over the system was within two percent, and the computer control system performed as expected.

A Plexiglas model of the slurry reactor was constructed in order to observe the gas-solid-liquid mixing patterns inside the reactor. The most important result of these tests was that we learned that the agitator must be running at least at 75% of capacity in order to pump any gas into the liquid phase. With the agitator operating at capacity (2000 rpm) the liquid phase exhibited a five percent expansion due to gas hold-up under test conditions (water and air at atmospheric pressure). The hold-up is expected to increase at the higher operating pressure of the reactor. After a week of operation, there was no observable decrease in effectiveness of the agitation due to agglomeration of solids inside the impeller. A steady increase in the amount of solids attached to the reactor walls was observed during the course of the tests. This will be accounted for by incorporating a time-dependent catalyst deactivation factor into any kinetics developed with the reactor.

The gas chromatograph was set up, calibrated, and shown to be operational. The GC will simultaneously perform on-line analysis of the off-gas and automated analysis of the liquid collected. The following section discusses the GC method used to analyze the gas and liquid samples.

The slurry reaction system has been recently started up using methanol catalyst CCI #6341. The catalyst was sieved to 75 - 150 microns and around 25 grams were placed in the reactor using tetraethylene glycol dimethyl ether (tetraglyme) as the solvent. The catalyst was activated in-situ at 750 psi by feeding 50 sccm hydrogen and 150 sccm nitrogen to the reactor while the reactor temperature was increased from 150°C to 250°C over twenty hours. The nitrogen was then turned off and 200 sccm of hydrogen was fed to the reactor at 240°C for four hours. After this time, carbon monoxide was fed to the reactor to initiate the reaction.

Initial results with the methanol catalyst show a productivity of about one gram of methanol per hour with 25.9 grams of catalyst. The production rate dropped to less than 0.05 grams of methanol per hour after less than a week of operation, indicating a rapid deactivation rate under these conditions. These results were obtained with a 2:1 H_2:CO ratio (450 sccm total flow) at 240°C, 750 psi. We are currently investigating the causes for the low productivity and high deactivation rate. This catalyst has been shown to produce methanol at a rate of about one gram per gram catalyst per hour with little deactivation in a gas-phase reaction. After reconciling the differences between the slurry and the gas-phase reactions, we expect to start-up with the spinel catalysts developed under Task 2.

3. Analytical Facilities and Procedures

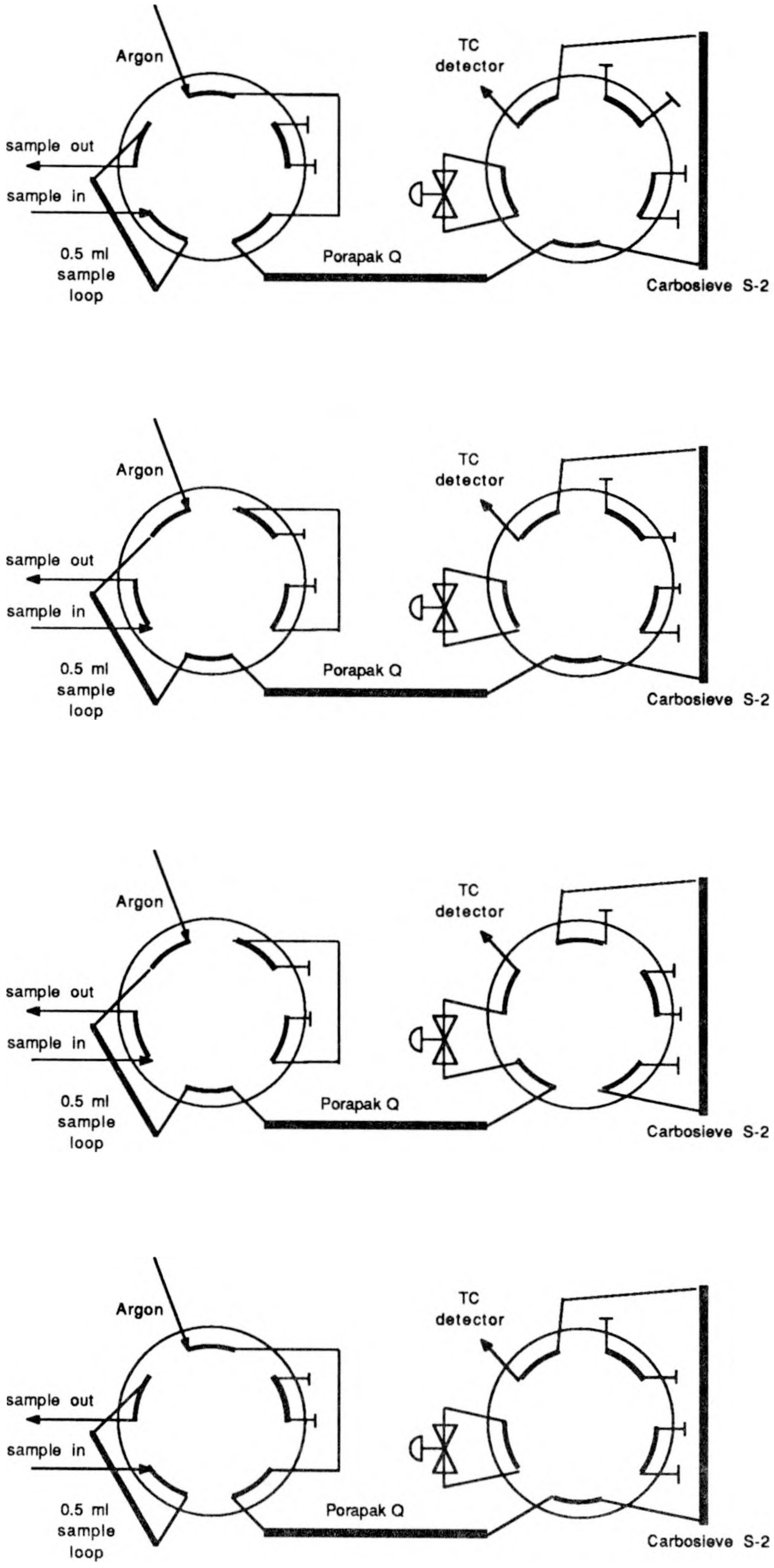
A single Hewlett-Packard HP5890 Series II gas chromatograph is used for simultaneous gas and liquid analysis. The liquid product is collected in a two-liter product receiver. This product is periodically collected, weighed, and injected into the GC using an HP7673A automatic sampler. The off-gas is transferred from the product receiver to the GC through a heated vapor line. The gas phase is sampled using a 0.5 milliliter sample loop in the GC.

The liquid phase is separated on a 30 meter, DB1701 capillary column with a 0.25 m film thickness which was obtained from J&W Scientific. The effluent from the capillary column is measured with flame ionization detector. The column is operated with a head pressure of 60KPa which gives an elution time of 2.000 minutes for methane. The split vent flow and the septum purge flow are 72.5 ml/min and 5.9 ml/min, respectively. The injector temperature is 200°C and the detector is at 250°C. The detector is operated with 360 ml/min air, 29.7 ml/min H_2 and 30 ml/min argon make-up.

The gas phase is separated using a 1/8 in. x 10 ft. 80/100 mesh Porapak Q column and a 1/8 in. x 6 ft Carbosieve S-2 column and is measured using a thermal conductivity detector. The Carbosieve S-2 column is used to separate H_2, N_2, CO, and CH_4 and the Porapak Q column separates the other gases. Figure 1 shows the switching scheme used to sample the gas phase and switch between the two columns. The valve box temperature is maintained at 135°C. The detector is held at 250°C, set on low sensitivity, and the signal is inverted. The flow rate through the column is 27 ml/min.

The oven temperature is ramped from 50°C to 210°C at 8°C/min and then held at 210°C for seven minutes. Argon is used as a carrier gas in both columns.

FIGURE 1
VALVE SWITCHING SCHEME FOR GAS ANALYSIS



Fill/Purge Sample loop.

Feed sample to both colums.
Time = 0.0 minutes.

Isolate gases in Carbosieve column, separate gases using Porapak Q.
Time = 2.1 minutes.

Separate gases in Carbosieve column.
Purge/fill sample loop.
Time = 21.0 minutes

B. Task 3 Summary

Evaluation of the slurry reaction system is underway. We have demonstrated that a methanol catalyst can produce methanol in a continuous slurry reactor, although at a rate lower than expected. Work is underway to identify the causes of the low production rate. Testing of the spinel catalysts developed under Task 2 will commence after testing with the methanol catalyst is complete. The computer control system, the catalyst filters, and the gas-solid-liquid agitation have all been tested and shown to work as expected. The ability to close a material balance under operation conditions has been demonstrated. The gas chromatograph has proven to give reproducible and reliable results for both on-line gas analysis and liquid analysis.