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Task 4.9 - Value-Added Products From Syn Gas

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TASK 4.9 - VALUE-ADDED PRODUCTS FROM SYN GAS

EXECUTIVE SUMMERY

The work on advanced fuel forms in 1996 is focused in part on the synthesis of higher alcohols from mixtures of hydrogen and carbon monooxide (syn gas) from coal gasification. This art has been practiced for many years in Germany, South Africa, and the United States. The conversion of coal gasification products to commercially valuable alcohols will provide an important new market for current and future gasification plants.

Initial work in this project utilized a novel molybdenum catalyst previously shown to be acitive for hydrodesulfurization reactions of coal liquids. This support for the active metal is a mixed oxide capable of interaction with the metal sites for catalysis of carbon monoxide reductions. A pressurized fixed-bed flow-through reactor was constructed and one catalyst was tested under a variety of conditions. Unfortunately, this catalyst with low metal loading was inactive. Therefore, a catalyst with a high metal loading and additional metal sites (cobalt, potassium) is now being tested.

1.0 INTRODUCTION

North Dakota has a large producer of syn gas from coal (Great Plains). Most of the syn gas is converted to methane; however, the methane produced has been and will continue to be uncompetitive with natural gas. The conversion of syn gas to chemicals or liquid fuel products (indirect liquefaction) has been extensively investigated in other laboratories for many years, but the commercialization of syn gas conversions has only occurred a few times in this country. Currently, it does not make much sense to convert the syn gas to a liquid fuel, since this will be uncompetitive with petroleum, at least for 10–20 years. It does make sense to convert it to chemical products that can compete with products currently produced from petroleum. The competitiveness is achieved by virtue of the selectiveness of the syn gas reactions for a product or type of product.

A very large market already exists for many kinds of alcohols and derivatives. Alcohols with 3–6 carbons are currently produced from petroleum via pathways that involve several steps. They are used extensively in solvents, esters, and monomers. Consequently the market prices range from \$0.50 to \$1.00/lb. Related compounds, such as aldehydes, acids, and esters are similarly priced. Diols are worth even more, i.e., 1,4-butanediol is currently \$1.16/lb. Several catalysts have been used for higher alcohol synthesis from syn gas, and Sasol produces alcohols in this way. Mixtures are generally obtained, and more efficient and selective catalysts are needed to improve the process. Some reactions may utilize locally produced ethanol as a feedstock for reaction with the syn gas.

Molybdenum sulfide has been investigated for syn gas reactions that produce alcohol products. Hydroxide is used with MoS_2 to produce alcohols in the Dow process. Conversions are frequently low, and the major product is methanol, but the system is tolerant to H_2S (found in syn gas from coal). The problem is how to increase the selectivity for larger alcohols.

2.0 OBJECTIVES

The objective of this task is to develop a process using an existing EERC layered catalyst (molybdenum sulfide hydrotalcite [MSH]) and its derivatives for conversion of syn gas to higher alcohols. This catalyst contains very small (nanoparticle) molybdenum sulfide clusters embedded in the layers of the hydrotalcite. The mixed oxide layers of the hydrotalcite contain both basic and acidic sites. Acidic groups are also present to promote C–O cleavage. Using the molybdenum sulfide in a bifunctional hydrotalcite matrix allows for the possibility of partially reduced intermediates to interact at the hydrotalcite sites and condense to larger species, which will reduce to alcohol products. Thus, the hydrotalcite matrix may increase the selectivity of the catalyst for alcohol products. The composition of the bimetallic component will be varied to study the chain growth characteristics of the reaction.

3.0 ACCOMPLISHMENTS

Bench-scale reactions of syn gas at moderate temperatures and pressures were conducted to determine products and yields of alcohol products using the EERC molybdenum sulfide catalysts. As described above, the MSH catalyst is unique, since it contains a "nanogrid" of molybdenum sulfide sandwiched between a bimetallic oxide.

3.1 Catalyst Preparations

The catalyst was prepared by exchanging ammonium tetrathiomolybdate (5 wt%) into an aluminum magnesium oxalate hydrotalcite in an aqueous slurry. The exchanged hydrotalcite was heated to 400°C to decompose the oxalate and convert the tetrathiomolybdate to the molybdenum sulfide.

A second catalyst was prepared by exchanging 30 wt% ammonium tetrathiomolybdate in the hydrotalcite. A catalyst was then prepared by adding cobalt and potassium to the molybdate-exchanged hydrotalcite.

The air-dried products were sized to separate +25-mesh particles from the fines. For the activation of these catalysts, 5 g of the catalyst was packed in a stainless steel tube and activated in flowing hydrogen for 12 hours at 400°C. The weight of the catalyst after activation was 4.8 g.

3.2 Apparatus

An apparatus was constructed to conduct the syn gas reactions over a fixed bed of the catalyst under pressurized flow conditions. The schematics of the apparatus are shown in Figure 1. A 6-in. tube reactor was packed with the desired catalyst (+25 mesh). The tube reactor was attached to a syn gas tank. The second end of the reactor was attached to two metal traps (100 mL). The first trap was cooled in ice and the second in dry ice–acetone slurry. The second metal trap was attached to a water displacement assembly via a needle valve for collecting the product gases. The reactor was placed in a vertical furnace.

3.3 Catalytic Reactions

As described above, the catalyst was activated by heating in a flow of hydrogen (8–10 mL/min) at 400°C for 12 hours. The reactor was heated to the desired temperature (250°–350°C) and then pressurized with 1000 psi of syn gas. The outflow of the gaseous product from the reactor was set at 100 cm^3/min. After the desired reaction time, the flow of the gas was stopped, and residual gas was allowed to bleed out from the system. The products from the traps were transferred into a 100-mL volumetric flask by washing with methylene chloride, and the volume was made up to 100 mL. A 10-mL aliquot of the solution was mixed with 1 mL of internal standard (2,2,4-trimethylpentane) in methylene chloride and analyzed by gas chromatography (GC). The gas was not collected, but in future runs will be collected into a gas bag and analyzed by GC and Fourier transform infrared (FT-IR) analyses.

4.0 RESULTS AND DISCUSSION

Reactions of syn gas were carried out in a flow reactor under the following reaction conditions:

Reaction temperature: 250°, 300° and 330°C
Syn gas pressure: 400 and 1000 psi
Reaction time: 1 hr
Gas flow: 100 cm^3/min
Catalyst: MSH (5 wt% ammonium tetrathiomolybdate on hydrotalcite, 1.85 wt% Mo)

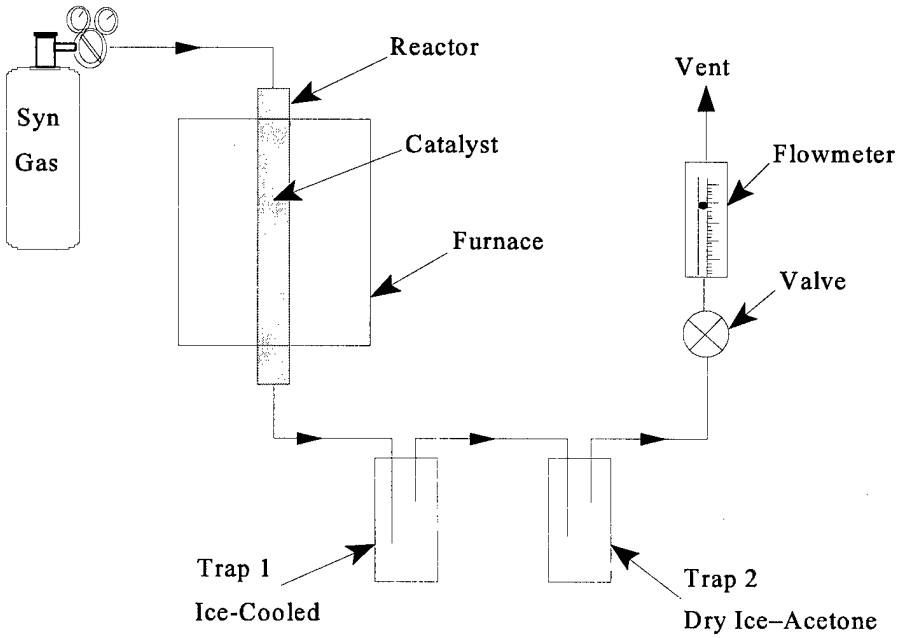

Figure 1. Apparatus for syn gas reactions.

Contents of the two traps were extracted with dichloromethane. An aliquot of the product was mixed with standard and analyzed by GC. The chromatograms from all these runs showed the absence of any volatile alcohol, hydrocarbon product, or water. It is concluded that the catalyst used in these tests did not catalyze the conversion of syn gas to higher alcohols. The catalyst had a low loading of molybdenum, and the molybdenum may have been imbedded too deeply in the oxide layers. Tests with the catalyst with higher concentrations of molybdenum and the Co- and K-impregnated MSH are in progress.

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(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 0127

1. Program/Project Identification No.	2. Program/Project Title	3. Reporting Period
DE-FC21-93MC30097	TASK 4.0 ADVANCED FUEL FORMS	4-1-96 through 6-30-96
4. Name and Address: Energy & Environmental Research Center, University of North Dakota, PO Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000		5. Program/Project Start Date: 1-12-93
		6. Completion Date: 12-31-97

7. FY: 96/97

8. Months or Quarters: Quarters

9. Cost Status — a. Dollars Expressed In Thousands — b. Dollar Scale

10. Cost Chart

Fund Source		Quarter 1st	Quarter 2nd	Quarter 3rd	Quarter 4th	Cum. to Date	Tot. Plan
DOE	P	0	14	13	13	14	40
	A	0	10			10	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		0	14	13	13	14	40
Total A		0	10			10	
Variance		0	4			4	

P = Planned A = Actual

Total Planned Costs for Program/Project: $40

	1st JAN	1st FEB	1st MAR	2nd APR	2nd MAY	2nd JUN	3rd JUL	3rd AUG	3rd SEP	4th OCT	4th NOV	4th DEC
80												
40												
c. Cumulative Accrued Costs												
Planned			0			14			27			40
Actual			0			10						
Variance			0			4						

11. Major Milestone Status	Units Planned / Units Complete	av	bv	cv
4.9 Value-Added Products from Syngas	P			
	C			
	P			
	C			
	P			
	C			
	P			
	C			
	P			
	C			
	P			
	C			
	P			
	C			
	P			
	C			

12. Remarks

13. Signature of Recipient and Date: Ramesh K. Sharma

14. Signature of DOE Reviewing Representative and Date

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Energy & Environmental Research Center University of North Dakota PO Box 9018 Grand Forks, ND 58202-9018 (701) 777-5000	1-12-93	12-31-97

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Subtask 4.9	Value-Added Products from Syngas			
a	Complete matrix of conditions for syngas batch reactions with MoTPHT catalyst	9/96		
b	Optimize composition of catalyst	12/96		
c	Determine conditions for fixed bed flow-through reactions of syngas	12/96		

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