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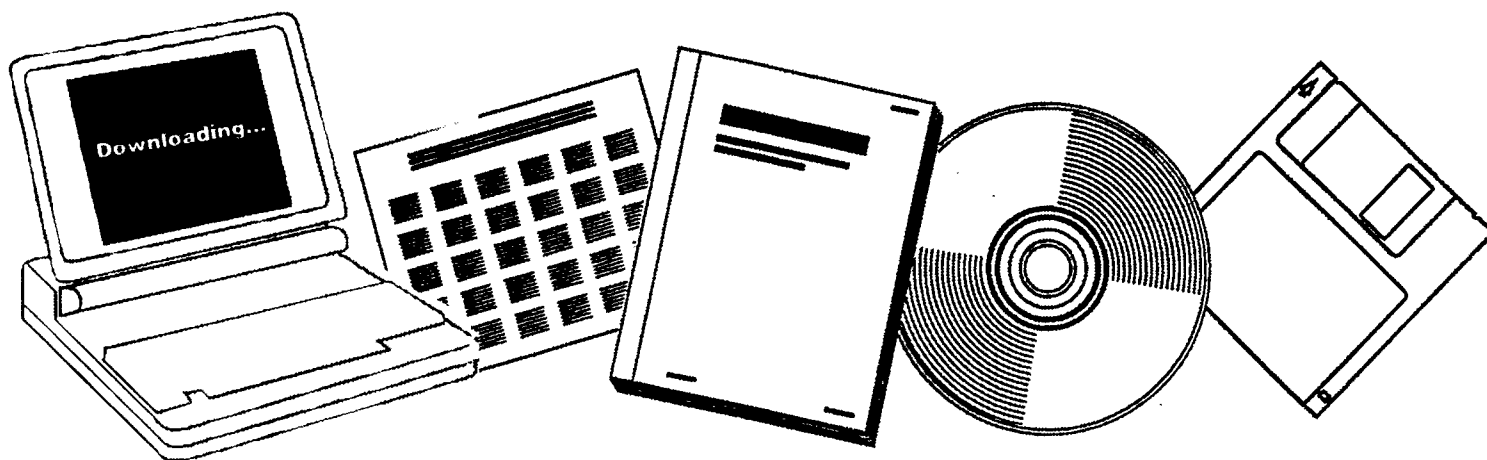
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**ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR
METHANATION OF COAL-DERIVED GASES.
QUARTERLY TECHNICAL PROGRESS REPORT,
DECEMBER 21, 1977--MARCH 20, 1978**

**BRIGHAM YOUNG UNIV.
PROVO, UT**

05 APR 1978



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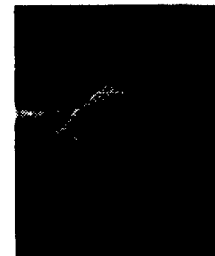
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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR
METHANATION OF COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period December 21, 1977 to March 20, 1978

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Date Published -- April 5, 1978

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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FOREWORD

This report summarizes technical progress during the second quarter (December 21, 1977 to March 20, 1978) of a study conducted for the Department of Energy (DOE) under Contract No. EF-77-S-01-2729. The principal investigator for this work was Dr. Calvin H. Bartholomew; Dr. Robert M. Wellek was the technical representative for DOE.

The following students contributed to the technical accomplishments and to this report: Graduates - Erek Erekson, George Jarvi, Ed Sughrue, and Gordon Weatherbee, and Undergraduates - Kevin Mayo, Don Mustard, and John Watkins. Elaine Alger and Scott Folster provided typing and drafting services. Beginning with this report data will henceforth be reported in SI units.

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ABSTRACT

During the second quarter several pelleted and monolithic nickel and nickel-cobalt catalysts were prepared and characterized by hydrogen adsorption. Differential reactor tests of powdered Ni-Co and Ni-Pd catalysts were carried out; the results show reasonably good agreement with results determined previously for pelleted catalysts. Electron micrographs were obtained for 20% Ni-MoO₃/Al₂O₃, the results of which when compared with H₂ chemisorption data suggest that nickel and molybdenum oxide may form a solid solution or intermetallic complex. Regeneration with CO and air of a high loading Ni-Co catalyst poisoned in a long term in situ H₂S run was shown to recover little of the H₂ chemisorptive uptake. Construction of the "Berty" reactor system is nearing completion, and all of the major equipment for the current contract have been received. These and other significant results obtained during this past quarter are presented and discussed. An account of technical communications with other workers and visits to other laboratories is also included.

I. OBJECTIVES AND SCOPE

A. Background

Natural gas is a highly desirable fuel because of its high heating value and nonpolluting combustion products. In view of the expanding demand for and depletion of domestic supplies of clean fuels, economic production of synthetic natural gas (SNG) from coal ranks high on the list of national priorities.

Presently there are several gasification processes under development directed toward the production of SNG. Although catalytic methanation of coal synthesis gas is an important cost item in each process, basic technological and design principles for this step are not well advanced. Extensive research and development are needed before the process can realize economical, reliable operation. Specifically, there appear to be important economical advantages in the development of more efficient, stable catalysts.

From the literature (1,2), three major catalyst problems are apparent which relate to stability: (i) sulfur poisoning, (ii) carbon deposition with associated plugging, and (iii) sintering. Our understanding of these problems is at best sorely inadequate, and the need to develop new and better catalyst technology is obvious. Nevertheless, there has been very little research dealing with new catalyst concepts such as bimetallic (alloy) or monolithic-supported catalysts for methanation. This study deals specifically with sulfur poisoning, carbon deposition, and the effects of support (monolith and pellet) geometry on the performance of alloy methanation catalysts.

B. Objectives

The general objectives of this research program are (i) to study the kinetics of methanation for a few selected catalysts tested during the first two years, (ii) to investigate these catalysts for resistance to deactivation due to sulfur poisoning and thermal degradation. The work is divided into five tasks.

Task 1. Characterize the surface bulk, and phase compositions, surface areas, and metal crystallite sizes for alumina-supported Ni, Ni-Co, Ni-MoO₃, Ni-Pt, Ni-Ru and Ru catalysts.

Task 2. Continue activity testing and support geometry studies of Ni- and Ni bimetallic catalysts initiated during the first two years. The tests include (i) conversion vs. temperature runs at low and high pressures, (ii) steady-state carbon deposition tests, (iii) in situ H₂S tolerance tests, and (iv) support geometry comparisons.

Task 3. Perform kinetic studies to find intrinsic rate data for alumina-supported Ni, Ni-Co, Ni-MoO₃, Ni-Pt, Ni-Ru, and Ru catalysts over a range of pressures and feed compositions. Detailed rate expressions for each catalyst will be determined at low and high pressure.

Effectiveness factors for monolithic and pellet-supported nickel on alumina will be obtained by comparing specific rates to those of finely powdered nickel on alumina.

Task 4. Determine H₂S poisoning rates, thermal deactivation rates, and operating temperature limits for Ni, Ni-Co, Ni-MoO₃, Ni-Pt, Ni-Ru, and Ru catalysts.

Task 5. Continue laboratory visits and technical communications. Interact closely with industrial and governmental representatives to promote large scale testing and development of the two or three best monolithic or pelleted alloy catalysts from this study.

C. Technical Approach

The technical approach which will be used to accomplish the tasks outlined above is presented in the statement of work dated May 20, 1977. The main features of that approach are reviewed here along with more specific details and modifications which have evolved as a result of progress. It is expected that various other aspects of this approach will be modified and improved as the project develops and as new data are made available. Nevertheless, the objectives, tasks and principle features of the approach will remain the substantially the same.

Task 1: Catalyst Characterization

A comprehensive examination of alumina-supported Ni, Ni-Co, Ni-MoO₃, Ni-Pt, Ni-Ru, and Ru catalysts will be carried out to determine surface, bulk, and phase compositions, surface areas, and metal crystallite sizes using the following techniques: chemisorption, x-ray diffraction, chemical analysis, ESCA and SIMS spectroscopy, Auger spectroscopy and transmission electron microscopy.

Hydrogen chemisorption uptakes will be measured using a conventional volumetric apparatus before each reactor test and before and after deactivation tests. X-ray diffraction measurements will be carried out to determine the active metallic phases and metal crystallite size where possible. Selected "aged" samples from Task 4 will be analyzed (by x-ray, chemical analysis, and perhaps ESCA) to determine carbon content and possible changes in phase composition or particle size. Also, transmission electron micrographs will be made to determine particle size distributions for catalyst samples. A few samples will be analyzed by EDAX to determine composition.

Task 2: Activity Testing and Support Geometry Design

Methanation activity and sulfur tolerance measurements initiated during the previous two years of study (3) will be completed. Pellet and monolithic alumina-supported Ni, Ni-Co, Ni-MoO₃, Ni-Pt, Ni-Ru, and Ru catalysts, (both high and low metal loadings) will be activity

tested over a range of temperatures, pressures, and H_2S concentrations. A comparison of steady state conversions for nickel on different pellet and monolith supports of varying geometry will be made. Low pressure activity and sulfur tolerance tests will also be made for pelleted Co/Al_2O_3 and unsupported Ni-Co and Ni-Mo alloys. A summary of the five test procedures and corresponding experimental conditions is listed in Table 1.

Task 3: Kinetic Studies

In order to make more extensive kinetic studies of the six catalyst metal combinations a new mixed flow reactor system will be constructed. This system will be capable of operation to 7500 kPa and 775 K and over a range of reactant compositions. The reactor for this system will be a "Berty" type constant volume mixed flow Autoclave reactor.

Intrinsic rate data will be obtained for alumina-supported Ni, Ni-Co, Ni-MoO₃, Ni-Pt, Ni-Ru, and Ru catalysts over a range of pressures and feed compositions in order to obtain detailed rate expressions at low and high pressures. To insure gradientless operation in the reaction-limited regime the rates will be measured at low conversions (0-5%) and low temperatures (525-600 K) for samples which have been crushed to obtain small particles.

Isothermal effectiveness factors for monolithic and pellet-supported nickel on alumina will be obtained by comparing their specific rates to those of finely powdered nickel on alumina using the same mixed flow reactor.

Task 4: Degradation Studies

H_2S poisoning rates and thermal deactivation rates at low pressure will be studied using a new quartz reactor system. Quartz was selected as the material for the reactor because it must operate at high temperatures (750-1000 K) and in a corrosive (H_2S) environment. This reactor is also a constant volume mixed flow type reactor according to the design of Katzer (4). The quartz reactor system will be constructed during the early part of the contract period. Thermal deactivation at high pressures will be studied using a tubular stainless steel reactor previously discussed (3).

Operating temperature limits (and specific reaction rates within this range), thermal deactivation rates near the upper use temperature (in the presence and absence of steam), and H_2S poisoning rates (at 525 K in the presence of 1 and 10 ppm H_2S in H_2) will be determined for Ni, Ni-Co, Ni-MoO₃, Ni-Pt, Ni-Ru, and Ru catalysts. The extent of carbon-carbide deposited in the thermal deactivation runs will be determined by chemical analysis and x-ray diffraction.

TABLE 1

Description of Reactor Tests for Task 2

<u>Test Procedures</u>	<u>Experimental Conditions</u>
1. <u>Temperature-Conversion Test</u> : Measure CO conversion and methane production as a function of temperature, with and without 1% (by vol.) of steam present in the reactant mixture.	475-675 K 140 kPa 30,000 hr ⁻¹ 1% CO, 4% H ₂ , 95% N ₂ (dry basis)
2. <u>Temperature-Conversion Test (high pressure)</u> : Measure CO conversion and methane production as a function of temperature at 2500 kPa.	475-675 K 2500 kPa 30,000 hr ⁻¹ 1% CO, 4% H ₂ , 95% N ₂
3. <u>Steady State (24 Hr.) Carbon Deposition Test</u> : Measure CO conversion and methane production at 500 and 525 K (250,000 hr ⁻¹) before and after an exposure of 24 hours at 675 K.	675 K (24 hrs.) 140 kPa 200,000-250,000 hr ⁻¹ 25% CO, 50% H ₂ , 25% N ₂ H ₂ /CO = 2
4. <u>In situ H₂S Tolerance Test</u> : Measure intermittently the production of methane and hydrocarbons (by FID) during 24 hours exposure to feed containing 1 or 10 ppm H ₂ S using a glass reactor.	525 K 140 kPa 30,000 hr ⁻¹ 1% CO, 4% H ₂ , 95% N ₂ 1 or 10 ppm H ₂ S
5. <u>Support Geometry Tests</u> : Measure CO conversion and methane production as a function of temperature for the same Ni/Al ₂ O ₃ catalyst supported on monoliths and pellets of varying geometries.	575-675 K 140 kPa 30,000 hr ⁻¹ 1% CO, 4% H ₂ , 95% N ₂

Task 5: Technical Interaction and Technology Transfer

The principal investigator will continue to communicate closely with other workers in methanation catalysis, continue distribution of quarterly reports to selected laboratories to stimulate interest and feedback, attend important coal and catalysis meetings, and visit other methanation laboratories.

He will also interact closely with Mr. A.L. Lee at the Institute of Gas Technology, with personnel at the Pittsburgh Energy Research Center and with other coal gasification representatives to promote large scale testing and development of the two or three best catalysts from this study.

II. SUMMARY OF PROGRESS

A project progress summary is presented in Figure 1 and accomplishments during the past quarter are summarized below. Figure 1 shows that task accomplishments are either on or ahead of schedule.

Accomplishments and results from the last quarter are best summarized according to task:

Task 1. Four new pellet catalysts were prepared; H_2 chemisorption measurements of two monolithic catalysts and three pellet catalysts were performed. Electron micrographs were taken of Ni-MoO₃-A-103. The results show interaction at the crystallite level of nickel and molybdenum oxide. Samples of Ni, Ni-Co, and Ni-MoO₃ catalysts were sent to various labs for ESCA and x-ray analysis. Attempts to make Torvex monolith catalysts met with limited success.

Task 2. This task was essentially completed last quarter. However, during the second quarter differential activity measurements were conducted at 100 kPa, 498 and 523 K, and 100,000 hr⁻¹ for powdered samples of 20% Ni-Mo/Al₂O₃ and 16% Ni-Pd/Al₂O₃. The results of these tests agree favorably with those reported previously for pelleted catalysts.

Task 3. Construction of the "Berty" reactor system is near completion. All major equipment for Tasks 3 and 4 has been received including the Perkin-Elmer Sigma I gas chromatograph.

Task 4. An upper temperature limit test was made during this quarter. During the test large amounts of carbon were formed, and test conditions are being reevaluated.

Task 5. The principal investigator and 8 students attended the Third Rocky Mountain Fuel Symposium. Mr. Ed Sughrue visited the University of Idaho to discuss the design of "Berty" reactor systems. Dr. Robert Ference of Climax Molybdenum Co. visited our lab and present a seminar. Mr. George Jarvi completed his master's thesis. One paper was submitted for publication, and three other papers are being prepared for submission.

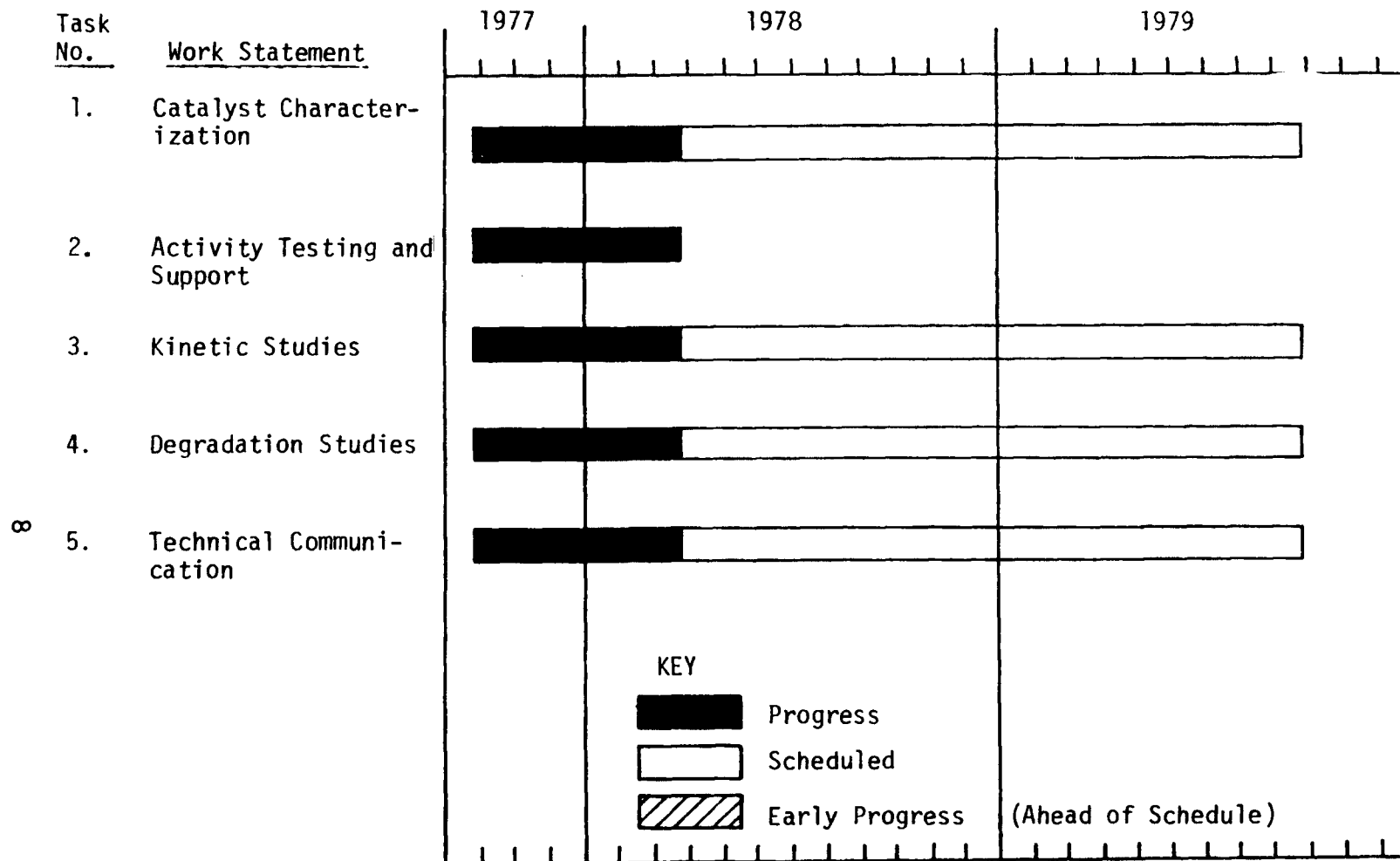


Figure 1. Project Progress Summary.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1: Catalyst Characterization

1. Catalyst Preparation

During this quarter four pellet catalysts (Ni-A-120 (3% Ni on Al_2O_3), Ni-A-121 (6% Ni on Al_2O_3), Ni-A-122 (20% Ni on Al_2O_3) and Ni-Co-A-102 (3% Ni, 3% Co on Al_2O_3)) were prepared for the kinetic and degradation studies in Tasks 3 and 4. These catalysts were prepared using impregnation techniques similar to those previously reported (3). However, since these catalysts will be tested at high temperatures, the Kaiser SAS 5x8 mesh alumina pellets were calcined 3 hours at 1075 K, before impregnating with aqueous solutions of nitrate salts.

During the past quarter attempts were made at preparing two dozen monolithic supported catalysts using Torvex Ceramic Honeycomb (DuPont Co.) monolithic supports, coated by the manufacturer with an activated alumina wash coat. The catalyst preparation was the same as that previously reported for monolithic catalysts (3), but due to two major problems all of the catalysts were unsuitable for activity testing.

The first of these two problems was that if more than one impregnation was used in preparing the catalysts a significant amount of alumina was lost to the metal salt solution into which the monolith was dipped. This made the monoliths unsuitable for testing because their metal loadings could not be accurately determined. It is hypothesized that the formation of metal salt crystals in the alumina weaken the wash coat when the catalysts were dried in between impregnations. This results in some of the alumina being sloughed off during the next impregnation. This problem was solved by first calcining the monoliths for two hours at 873 K before impregnating them just once or twice in a super-saturated solution of metal salt.

However, a second problem arose when the catalysts prepared by the latter method were bulk reduced in flowing hydrogen at 723 K. The alumina wash coat separated from the Torvex monoliths and disintegrated. It is suspected that either the dehydrated alumina coated adheres poorly to the monolith or more likely that the high loading nickel (Al_2O_3) created by impregnation and drying has low mechanical integrity or poor adherence.

Nickel/ Al_2O_3 /Torvex monolith catalysts will be prepared again during the next quarter, and it is expected that these problems will be overcome by first calcining the alumina coated monoliths at 873 K for two hours and then by allowing just one impregnation in metal salt solution. Also, to help alleviate the second problem the catalyst will be prepared with low metal loadings rather than high metal loadings as previously attempted.

2. Chemisorption

During the last quarter hydrogen chemisorption measurements were carried out on four different catalysts, two nickel on alumina monolithic catalysts Ni-AM-203, Ni-AM-204, and two nickel-cobalt pellet catalysts, one that had been H_2S in situ poisoned and then CO and air regenerated, Ni-Co-A-100, and one newly prepared, Ni-Co-A-102. These results are reported in Table 2.

From examination of the data for Ni-Co-A-100 pellets it can be seen that CO and air regeneration of nickel-cobalt catalysts following long term H_2S in situ poisoning results in very little recovery of metal surface area as measured by hydrogen chemisorption.

Examination of the data for monolithic catalysts shows that the hydrogen chemisorption for Ni-AM-204 is comparable to that previously reported for other nickel on alumina monolith catalysts. In comparison to the other monoliths, the hydrogen chemisorption of Ni-AM-203 would appear to be somewhat low. Since these catalysts were all prepared at the same time and according to the same conditions and methods, the reason for the lower uptake of Ni-AM-203 is not obvious.

3. Electron Microscopy

Electron micrographs were taken of the catalyst, Ni-MoO₃-A-103, using an Hitachi HU-11E electron microscope (3). A particle size distribution was determined from several micrographs; the data are listed in Tables 3 and plotted in Figure 2. Figure 3 shows a sample micrograph of Ni-MoO₃-A-103 (x 310,000). The small dark spherical shaped particles were assumed to be Ni crystallites. The dark needle like structures may be Al₂O₃ pores which have been filled with nickel crystallites, although these were not observed as distinctly in micrographs of Ni/Al₂O₃ (no Mo present).

In earlier work involving nickel catalysts (3) relatively good agreement was observed between mean particle diameters calculated by H_2 chemisorption and by transmission electron microscopy, the mean diameter calculated by TEM being slightly higher. However, for Ni-MoO₃-A-103 the chemisorptive mean diameter is 8.95 nm, while the mean diameter from TEM was only 4.06 nm. These are both surface averaged means. Since hydrogen does not chemisorb on MoO₃ catalysts (3), H_2 chemisorption on Ni only was considered in calculating the chemisorptive mean diameter. The significant disagreement between the TEM data and the chemisorptive data suggests that either significant amounts of MoO₃ are on the surface of the Ni crystallites, MoO₃ is in solid solution with nickel, or a nickel-molybdenum complex oxide is formed. This is the best evidence so far for interaction at the molecular level between two catalytic compounds on one of our bimetallic catalysts. We will continue TEM studies of other bimetallic catalysts in the next quarter.

Some electron microscope work was also conducted on a Co-Cu catalysts prepared by Dr. F. Massoth and co-workers at the University of Utah. The results of this work will be presented by Dr. Massoth

Table 2
 Summary of Metal Surface Area
 Measurements Using H₂ Chemisorption
 at 25°C

<u>Catalyst</u>	<u>Nominal Composition (wt.%)</u>	<u>Uptake (μmoles/gram)</u>
<u>Pellet Catalysts:</u>		
Ni-Co-A-100	10% Ni, 10% Co	107 ^{a,d}
Ni-Co-A-100	10% Ni, 10% Co	0 ^{b,d}
Ni-Co-A-100	10% Ni, 10% Co	4 ^c
Ni-Co-A-100	10% Ni, 10% Co	80 ^{a,e}
Ni-Co-A-100	10% Ni, 10% Co	134 ^{a,f}
Ni-Co-A-102	3% Ni, 3% Co	37.6 ^a
Ni-Pd-A-100	15% Ni, 1% Pd	105 ^{a,g}
Ni-Pd-A-100	15% Ni, 1% Pd	99 ^{a,g}
Ni-Pd-A-100	15% Ni, 1% Pd	112 ^{a,g}
<u>Monolithic Catalysts:</u>		
Ni-AM-201	25.5% Ni	201.1 ^{a,d}
Ni-AM-203	25.5% Ni	179 ^a
Ni-AM-204	27.5% Ni	204.5 ^a

^aBulk reduced

^bLong term H₂S in situ poisoning tested

^cLong term H₂S in situ poisoning followed by CO and air regeneration

^dPreviously reported

^eReduced an additional 2 hrs

^fReduced an additional 10 hrs

^gReduced an additional 15 hrs

Table 3

Particle Size Distribution for Ni-MoO₃-A-103 Measured by Electron Microscopy

<u>Sample</u>		<u>Percent Particles in Each Size Range¹</u>									
<u>Sample</u>	<u>Treatment</u>	<u><1.93</u>	<u>1.93-2.26</u>	<u>2.27-2.58</u>	<u>2.59-2.90</u>	<u>2.91-3.22</u>	<u>3.23-3.54</u>	<u>3.55-4.99</u>	<u>5.00-6.61</u>	<u>6.62-8.22</u>	<u><8.22</u>
Ni-MoO ₃ -A-103	Reduced and Passivated	2.1	2.8	5.0	23.4	19.2	31.2	11.7	2.5	1.4	0.7

Surfaced averaged mean diameter was 4.06 nm.

¹Size ranges are in nm (1 nm = 10⁰Å)

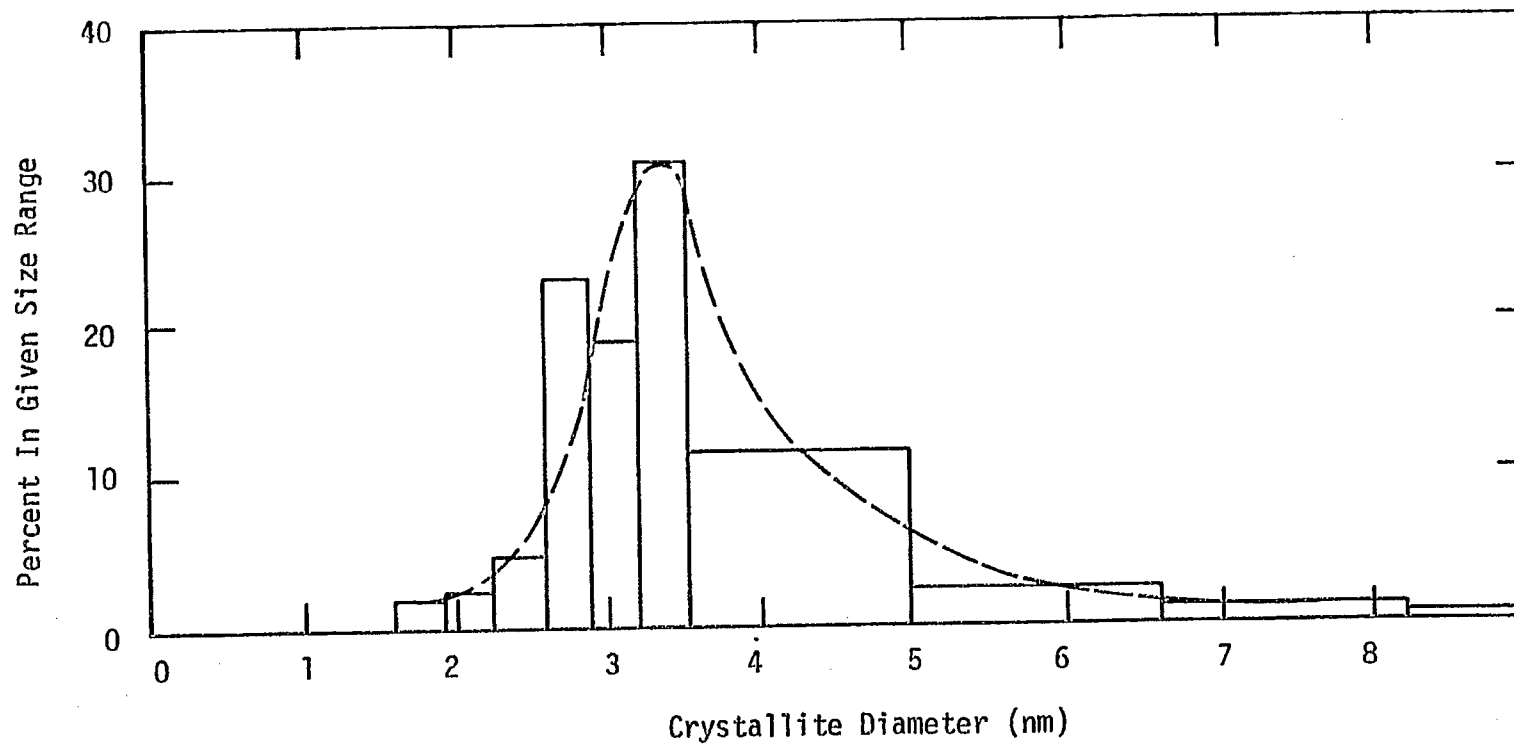


Figure 2. Crystallite Size Distribution for 20% Ni-MoO₃/Al₂O₃ Measured by TEM.



Figure 3. Electron Micrograph of Ni-MoO₃-103 (10% Ni, 10% MoO₃/Al₂O₃)
x 310,000.

under a separate DOE contract.

Energy Dispersive X-Ray Analysis (EDAX) work was performed on Ni-Co-A-100. The sample area studied showed approximate concentrations of Ni and Co to be 9.8 wt.% and 8.2 wt.% respectively. The nominal composition was previously assumed to be 10% Ni and 10% Co.

4. ESCA Analysis

A sample of our Ni-MoO₃-103 (10% Ni, 10% MoO₃/Al₂O₃) was submitted to Dr. Robert Lewis of Chevron Research for ESCA analysis.

Samples of Ni-A-116, (14% Ni/Al₂O₃), Ni-Co-100 (10% Ni, 10% Co/Al₂O₃), and Ni-MoO₃-103, were submitted to the Institute for Mining and Metallurgical Research in Lexington, Kentucky (through Dr. Phil Reucroft of the University of Kentucky) for ESCA and X-ray analysis.

We are hopeful these ESCA data will provide us with surface composition, chemical states of the surface, and perhaps evidence of alloy or cluster formation. The x-ray analysis of the nickel catalyst will provide particle size data for comparison with our H₂ chemisorption and electron microscopy data.

Task 2: Activity Testing and Support Geometry Design

This task was essentially completed during the first contract period (3) and the first quarter of the present contract (5). Nevertheless, some of the previously reported activity data for high metal loading nickel catalysts in pellet form (e.g., Ni-Co, Ni-Pd, and Ni-Pt) were felt to have been influenced by pore diffusional resistance and/or a temperature gradient across the bed since CO conversions were on the order of 15-35%. Hence differential activity tests were carried out during this past quarter for finely powdered samples of Ni-Co and Ni-Pd catalysts at 498, 523, and 548 K, 100 kPa, and 100,000 hr⁻¹. By increasing the space velocity by factor of three over the previous measurements the conversion were decreased for the two lowest temperatures to less than 3-7%. These data are reported in Table 4 and compared with the previously determined data for pelleted catalysts at 498 and 523 K, 140 kPa, and 30,000 hr⁻¹. The turnover number for Ni-Co powder and pellets are in fairly good agreement although the rates for the pellets are larger; the turnover numbers for Ni-Pd powders and pellets agree very well. That larger turnover numbers are observed for the Ni-Co pellets compared to the powders tested at a much higher space velocity suggests the lowering of the rate due to pore diffusional resistance in the pellets was more than offset by the increase in rate due to an increasing temperature gradient across the bed. The very good agreement for the turnover numbers over powdered and pelleted Ni-Pd/Al₂O₃ suggest that diffusional and temperature effects had minimal influence on the previously reported rate data for the pellets. It is remarkable that such good agreement is obtained for the turnover numbers in different tests run in different reactors, over different samples of the same catalyst, and tested by different personnel.

Table 4

Methanation Activity Data at Low Pressure and Low Temperatures
For Nickel Bimetallic Catalysts in Powder and Pellet Form

Catalysts	H ₂ Uptake (moles/g)	% Conversion CO	% Production		% Selectivity		Turnover # x 10 ³	
			CH ₄	CO ₂	CH ₄	CO ₂	CO	CH ₄
At 498 K								
Ni-Co-A-100 ^a	134	2.7	1.1	0.0	40.4	0.7	1.9	0.8
Ni-Co-A-100 ^b	115	14.8	12.3	3.6	84	2.4	3.6	3.0
Ni-Pd-A-100 ^a	112	1.6	0.8	0.1	49.1	0.1	1.4	0.7
Ni-Pd-A-100 ^a	105	3.1	1.6	0.0	51.8	0.0	2.8	1.5
Ni-Pd-A-100 ^b	107	5.5	4.4	0.0	80.0	0.0	2.0	1.6
At 523 K								
Ni-Co-A-100 ^a	134	6.7	4.6	0.0	68.3	0.4	4.8	3.3
Ni-Co-A-100 ^b	115	35.5	28.5	2.27	80.0	6.4	8.5	6.9
Ni-Pd-A-100 ^a	112	3.5	2.6	0.1	76.4	2.6	3.1	2.3
Ni-Pd-A-100 ^a	105	6.4	4.9	0.0	77.0	0.0	5.8	4.5
Ni-Pd-A-100 ^b	107	13.4	11.4	0.0	87	0.0	4.8	4.1
At 548 K								
Ni-Co-A-100 ^a	134	16.3	13.1	0.8	80.6	5.1	11.7	9.4
Ni-Pd-A-100 ^a	112	7.6	6.6	0.0	86.9	0.7	6.7	5.8
Ni-Pd-A-100 ^a	105	12.3	10.1	0.0	82.9	0.0	11.2	9.3

^aPowders tested at 100 kPa and 100,000 hr⁻¹.^bPellets tested at 140 kPa and 30,000 hr⁻¹.

During the next quarter, additional differential test are planned for Ni-Co and Ni-MoO₃ catalysts in powder form to determine specific rates at low conversions and high space velocities before and after exposure to H₂S in a fluidized bed (which will provide more uniform poisoning of the samples). Further activity testing of commercial cobalt and molybdenum containing catalysts are also planned for this summer.

Task 3: Kinetic Studies

Significant progress was made in the construction of the high pressure mixed flow system. All major equipment purchases, including the Berty reactor, high pressure mass flow meters, CO and H₂S detectors, and the Haskell compressor have been received. A 0.64 cm thick x 122 cm x 153 cm, steel panel was erected in order to serve the dual purposes of control panel and high pressure explosion barrier. Installation of this control panel was completed and work is presently in progress to complete plumbing of valves and meters and to connect the panel with the Berty reactor.

The Berty reactor has been modified with the insertion of a new inner sleeve which replaces reactor and catalyst volume requirements. This sleeve is also designed to allow 2.5 cm diameter monolith catalysts to be tested. An electronic temperature controller was constructed to allow simultaneous control of the three separate heaters in the Berty heater bonnet. Construction and testing of the new reactor system should be completed during the next quarter.

Task 4: Degradation Studies

During this quarter a Perkin-Elmer Sigma I gas chromatograph was received and preliminary tests have been made to check its operation. This system has the capability of analyzing fixed gases, hydrocarbons, and sulfur compounds. Also, it can analyze samples repetitively without manually starting each run. This feature will be most useful during long term degradation studies and H₂S poisoning studies. At present the gas sampling valve is plumbed for either gas sampling or column switching. Since the Sigma I is able to analyze data from more than one detector, we will be changing the plumbing so the valve will perform column switching and gas sampling in the same chromatograph run.

In setting up the quartz reactor system, it was found that the quartz impeller was out of balance. This was returned to the manufacturer for repair. Also, a catalyst basket for holding pellets and monoliths was designed and arrangements made for its construction.

An upper temperature limit test was performed during the last quarter. However, it did not prove as successful as hoped. The reaction conditions were 365 psia, reactant gas composition: 79% CH₄, 15% H₂, 4% CO, 2% CO₂ and initial temperature 573 K. The temperature was increased on a slow ramp (1"/min). The run was ended at 923 K when it was noticed that more H₂ was in the product gas than in the reactant

gas. Pyrex wool was used to support the catalyst pellets which melts above 773 K. In the future quartz wool will be used for this test. When the reactor was opened after the run, a large amount of carbonaceous material had formed on the reactor walls and in the catalyst bed. The catalyst pellets had broken up into a fine powder. We are not sure whether the carbon formation was a function of the reactant gas composition or the melting of the glass wool.

We plan to investigate the reasons for carbon formation and alter the test to avoid this problem. In addition, we will have the catalyst powder chemically analyzed for carbon content. Also, we will develop a computer program to calculate activity data when CH_4 is used as a diluent and CO_2 is a reactant.

Task 5: Technical Interaction and Technology Transfer

Dr. Bartholomew and 8 students, Jay Butler, Erik Erekson, Mark Jeffery, Donald Mustard, Edward Sughrue, John Watkins, Art Uken and Gordon Weatherbee attended the 3rd Rocky Mountain Fuel Symposium held Feb. 10-11 in Albuquerque. Dr. Bartholomew participated as symposium chairman while Mr. Weatherbee presented a paper entitled, "In situ Poisoning by Sulfur of Nickel and Nickel Bimetallic Methanation Catalysts". There were 22 other presentations dealing with various aspects of coal, tar sands, and oil shale development. The Rocky Mountain Fuel Society was successfully organized and officers for the new organization were elected. Dr. Bartholomew was elected to the Board of Directors.

On December 30, Mr. Ed. Sughrue visited the research lab of Dr. William Thompson at the University of Idaho at Moscow. The purpose of the visit was to examine the "Berty" high pressure constant volume mixed flow systems built by Dr. Thompson. Instruction concerning installation, maintenance, and application of the "Berty" system for university lab research was received. Safety measures were also discussed in depth.

On March 17, Dr. Robert Ference, of the Climax Molybdenum Co. of Michigan visited our laboratory where he presented a seminar dealing with applications of Molybdenum catalysts and toured our facilities. We are currently in close communication with Dr. Ference regarding the preparation and testing of Ni-MoO_3 catalysts.

Much of the effort of the principal investigator and students during this quarter was directed towards the preparation of theses and publications. Mr. George Jarvi completed his Master's Thesis entitled: "Methanation Catalysts: Activity, Adsorption and Degradation Studies of Nickel and Nickel Bimetallic Catalysts for Methanation". Mr. Gordon Weatherbee completed most of the work on his thesis dealing with similar studies of pellet supported catalysts. A publication based on Mr. Jarvi's work with monolithic and pellet catalysts was prepared for journal publication and is almost ready for submission. A publication based on Mr. Jarvi and Mr. Weatherbee's work, "Nickel Bimetallic Catalysts for Methanation of CO : The Effects of Pressure, H_2O , H_2S , and Carbon Deposition on Activity," was submitted to AIChE in preparation

for the June meeting in Philadelphia. Two other publications based on the ERDA-DOE work were prepared and are almost ready for submission. Our writing activities, visits, meetings, and other communications by phone and mail have been helpful in keeping us up-to-date while letting others benefit from our research.

During the coming quarter Dr. Bartholomew will attend and present papers at a conference in Berkeley May 24-26 dealing with catalyst deactivation and the 85th National AIChE meeting in Philadelphia (June 4-8). He has also been invited to present a short talk on catalysis at Los Alamos in early May. We anticipate submitting at least 2 journal publications for review during the next quarter.

Miscellaneous

In late February Mr. George Jarvi successfully completed work towards an M.S. degree and left BYU to pursue research with IGT in Chicago. Mr. Gordon Weatherbee has nearly completed his M.S. work and has expressed a strong interest in pursuing Ph.D. work. The research performed by both of these students was under the previous ERDA contract. In view of his rich experience and demonstrated productivity we are hopeful of continuing Mr. Weatherbee on the present contract in connection with some important problems dealing with sulfur poisoning, carbon deposition, and CO-CO₂ kinetics. Accordingly, Dr. Bartholomew has recently prepared and submitted a proposal for contract revision in order to make this possible.

IV. CONCLUSIONS

1. Electron micrographs of Ni-MoO₃-A-103 showed that the mean particle diameters as calculated by H₂ chemisorption and by electron microscopy for this sample were in significant disagreement. This suggests that there is nickel-molybdenum oxide interaction at the molecular level. Most likely a solid solution of the two catalytic compounds or a nickel-molybdenum oxide complex is formed.

2. Regeneration with CO and air of high loading Ni-Co-A-100 poisoned in a long term in situ H₂S deactivation run recovered very little of the H₂ chemisorptive uptake.

3. Reasonably good agreement is obtained for turnover numbers determined in differential activity tests for pellet and powdered samples of alumina-supported Ni-Co and Ni-Pt, even though the powdered samples were run at a much higher space velocity and lower conversions than the pellets.

4. Carbon formation appears to be a serious problem in our high temperature degradation tests. The procedure and particularly the gas composition need careful reconsideration.

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16. Abstracts During the second quarter several pelleted and monolithic nickel and nickel-cobalt catalysts were prepared and characterized by hydrogen adsorption. Differential reactor tests of powdered Ni-Co and Ni-Pd catalysts were carried out; the results show reasonably good agreement with results determined previously for pelleted catalysts. Electron micrographs were obtained for 20% Ni-MoO ₃ /Al ₂ O ₃ , the results of which when compared with H ₂ chemisorption data suggest that nickel and molybdenum oxide may form a solid solution ² or intermetallic complex. Regeneration with CO and air of a high loading Ni-Co catalyst poisoned in a long term in situ H ₂ S run was shown to recover little of the H ₂ chemisorptive uptake. Construction of the "Berty" reactor system is nearing completion, and all of the major equipment for the current contract have been received. These and other significant results obtained during this past quarter are presented and discussed. An account of technical communication with other workers and visits to other laboratories is also included.					
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