



FE27293

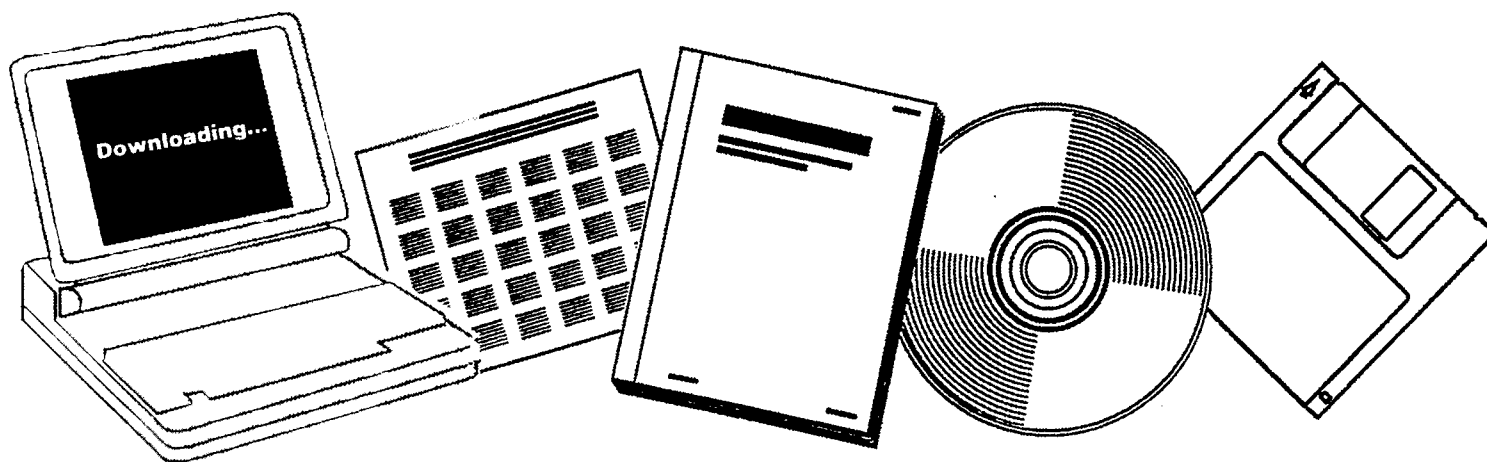
**NTIS**

**One Source. One Search. One Solution.**

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

**BRIGHAM YOUNG UNIV.  
PROVO, UT**

**05 JUL 1978**



U.S. Department of Commerce  
**National Technical Information Service**

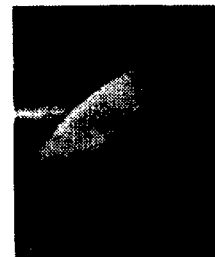
**One Source. One Search. One Solution.**

# NTIS



## **Providing Permanent, Easy Access to U.S. Government Information**

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.



### **Search the NTIS Database from 1990 forward**

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **[www.ntis.gov](http://www.ntis.gov)**. You now have access to information on more than 600,000 government research information products from this web site.

### **Link to Full Text Documents at Government Web Sites**

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

### **Download Publications (1997 - Present)**

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

**[www.ntis.gov](http://www.ntis.gov)**



U.S. DEPARTMENT OF COMMERCE  
Technology Administration  
National Technical Information Service  
Springfield, VA 22161

FE-2729-3

Distribution Category UC-90c

FE27293



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

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

Calvin H. Bartholomew  
Brigham Young University  
Provo, Utah 84602

Date Published -- July 5, 1978

PREPARED FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

Under Contract No. EF-77-S-01-2729

BIBLIOGRAPHIC DATA SHEET	1. Report No. FE-2729-3	2.	3. Recipient's Accession No.
	4. Title and Subtitle ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES		5. Report Date July 5, 1978
7. Author(s) Calvin H. Bartholomew		8. Performing Organization Rept. No.	
9. Performing Organization Name and Address Catalysis Laboratory Chemical Engineering Department Brigham Young University Provo, Utah 84602		10. Project/Task/Work Unit No.	
		11. Contract/Grant No. EF-77-S-01-2729	
12. Sponsoring Organization Name and Address Department of Energy Fossil Energy 20 Mass. Avenue N.W. Washington, D.C. 20545		13. Type of Report & Period Covered ATTN: Dr. Paul Scott Office of University Activities	
15. Supplementary Notes		14.	
16. Abstracts Evidence that monolithic supported catalysts are more active than pelleted catalysts on a rate/volume of catalyst basis was shown in support geometry tests at high conversions during this past quarter. Also, the per cent yield of methane was higher for the monolithic catalysts. H <sub>2</sub> S poisoning studies of alumina-supported Ni, Ni-Co, and Co powders showed that specific methanation rates were higher for Ni-Co before and after poisoning with 10 ppm H <sub>2</sub> S. These data provide indirect evidence for the presence of an alloy or bimetallic cluster in the Ni-Co catalyst. Five upper operating temperature limit tests were performed. These tests showed that our high loading catalysts are stable at high temperatures and under conditions similar to a commercial recycle methanation reactor. 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.			
17. Key Words and Document Analysis. 17a. Descriptors  Coal Gasification Methanation Catalysts Sulfur Poisoning  17b. Identifiers/Open-Ended Terms  17c. COSATI Field Group			
18. Availability Statement		19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages
		20. Security Class (This Page) UNCLASSIFIED	22. Price

## FOREWORD

This report summarizes technical progress during the third quarter (March 21, 1978 to June 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. Paul Scott was the technical representative for DOE.

The following students contributed to the technical accomplishments and to this report: Graduates - Erek Erekson, Ed Sughrue, and Gordon Weatherbee, and Undergraduates - Kevin Mayo, Don Mustard, and John Watkins. Elaine Alger and David Creer provided typing and drafting services. In this report data are reported in SI units.

## TABLE OF CONTENTS

FOREWORD . . . . .	iii
LIST OF TABLES . . . . .	v
LIST OF FIGURES . . . . .	vi
ABSTRACT . . . . .	1
I. OBJECTIVES AND SCOPE . . . . .	2
A. Background . . . . .	2
B. Objectives . . . . .	2
C. Technical Approach . . . . .	3
II. SUMMARY OF PROGRESS . . . . .	7
III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS . . . . .	9
IV. CONCLUSIONS . . . . .	34
V. REFERENCES . . . . .	36
APPENDICE	
A NTIS Bibliographic Data Sheet . . . . .	37

## LIST OF TABLES

1. Description of Reactor Tests for Task 2 . . . . .	5
2. Summary of Metal Surface Area Measurements Using $H_2$ Chemisorption at 25°C . . . . .	10
3. Particle Size Distribution for Ni-Co-A-100 Measured by Electron Microscopy . . . . .	13
4. Differential Reactor Data for Ni-Co-A-100 Before and After $H_2S$ Poisoning . . . . .	17
5. Specific Activity Data Before and After Exposure to 10 ppm $H_2S$ of Alumina-supported Ni, Ni-Co and Co in Powder Form . .	20
6. Comparison of Geometrical Surface Area and Conversion, Production and Selectivity . . . . .	21
7. Comparison of Geometrical Surface Area and Reaction Rates . . . . .	24
8. Experimental and Theoretical Mass Transfer Coefficients . . .	26

## LIST OF FIGURES

1. Project Progress Summary . . . . .	8
2. Electron Micrograph of BL-A-101 (blank alumina support) 295,000x . . . . .	14
3. Electron Micrograph of Ni-A-121 (6% Ni) 295,000x . . . . .	15
4. Electron Micrograph of Ni-Co-A-100 (10% Ni, 10% Co) 295,000x . . . . .	16
5. Fluidized Bed Reactor . . . . .	19
6. Enlarged Photograph Used for Determining GSA of $46.5 \text{ cm}^2$ Cordierite Monolith Coated with 10% Alumina . . . . .	23
7. Conversion of CO (overall) vs. Temperature for High Loading Catalysts at 2500 kPa, GHSV=30,000 $\text{hr}^{-1}$ , and Reaction Mixture Containing 64% $\text{CH}_4$ , 16% Ar, 14% $\text{H}_2$ , 4% CO, and 2% $\text{CO}_2$ . . . . .	28
8. Conversion of CO to $\text{CH}_4$ vs. Temperature for High Loading Catalysts at 2500 kPa, GHSV=30,000 $\text{hr}^{-1}$ and Reaction Mixture Containing 64% $\text{CH}_4$ , 16% Ar, 14% $\text{H}_2$ , 4% CO and 2% $\text{CO}_2$ . . . . .	29
9. Methanation Rates ( $\text{gmole/g-cat-sec} \times 10^7$ ) vs. Temperature for High Loading Catalysts at 2500 kPa, GHSV=30,000 $\text{hr}^{-1}$ , and Reaction Mixture Containing 64% $\text{CH}_4$ , 16% Ar, 14% $\text{H}_2$ , 4% CO and 2% $\text{CO}_2$ . . . . .	31



## ABSTRACT

Evidence that monolithic supported catalysts are more active than pelleted catalysts on a rate/volume of catalyst basis was shown in support geometry tests at high conversions during this past quarter. Also, the per cent yield of methane was higher for the monolithic catalysts.  $H_2S$  poisoning studies of alumina-supported Ni, Ni-Co, and Co powders showed that specific methanation rates were higher for Ni-Co before and after poisoning with 10 ppm  $H_2S$ . These data provide indirect evidence for the presence of an alloy or bimetallic cluster in the Ni-Co catalyst. Five upper operating temperature limit tests were performed. These tests showed that our high loading catalysts are stable at high temperatures and under conditions similar to a commercial recycle methanation reactor. 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-MoO<sub>3</sub>, 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 H<sub>2</sub>S tolerance tests, and (iv) support geometry comparisons.

Task 3. Perform kinetic studies to find intrinsic rate data for alumina-supported Ni, Ni-Co, Ni-MoO<sub>3</sub>, 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. Effec-

tiveness 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  $H_2S$  poisoning rates, thermal deactivation rates, and operating temperature limits for Ni, Ni-Co, Ni-MoO<sub>3</sub>, 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-MoO<sub>3</sub>, 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-MoO<sub>3</sub>, 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-MoO<sub>3</sub>, 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-MoO<sub>3</sub>, 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 <sup>-1</sup> 1% CO, 4% H <sub>2</sub> , 95% N <sub>2</sub> (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 <sup>-1</sup> 1% CO, 4% H <sub>2</sub> , 95% N <sub>2</sub>
3. <u>Steady State (24 Hr.) Carbon Deposition Test:</u> Measure CO conversion and methane production at 500 and 525 K (250,000 hr <sup>-1</sup> ) before and after an exposure of 24 hours at 675 K.	675 K (24 hrs.) 140 kPa 200,000-250,000 hr <sup>-1</sup> 25% CO, 50% H <sub>2</sub> , 25% N <sub>2</sub> H <sub>2</sub> /CO = 2
4. <u>In situ H<sub>2</sub>S 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 <sub>2</sub> S using a glass reactor.	525 K 140 kPa 30,000 hr <sup>-1</sup> 1% CO, 4% H <sub>2</sub> , 95% N <sub>2</sub> 1 or 10 ppm H <sub>2</sub> S
5. <u>Support Geometry Tests:</u> Measure CO conversion and methane production as a function of temperature for the same Ni/Al <sub>2</sub> O <sub>3</sub> catalyst supported on monoliths and pellets of varying geometries.	575-675 K 140 kPa 30,000 hr <sup>-1</sup> 1% CO, 4% H <sub>2</sub> , 95% N <sub>2</sub>

#### 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. Three new pellet catalysts and several Torvex (DuPont Co.) monolith catalysts were prepared.  $H_2$  chemisorption measurements were performed on 24 monolithic, pelleted, or powdered catalysts. Electron micrographs were taken of Ni-A-121, Ni-Co-A-103 and blank alumina support. Comparison of the blank support micrographs with other micrographs taken in this laboratory showed that we have not had enough contrast between metal and support to give accurate particle size distributions.

Task 2. Fresh and  $H_2S$  poisoned Ni-Co-A-100 samples in powder form were differentially tested at 100 kPa,  $100,000\text{ hr}^{-1}$ , and 498, 523, 548 K. The results of these tests are consistent with a pore mouth or shell type  $H_2S$  poisoning model. Uniformly poisoned (in a fluidized bed) Ni, Ni-Co, and Co powders were also activity tested. Specific activities (turnover numbers) before and after exposure to 10 ppm  $H_2S/H_2$  were higher for Ni-Co relative to both nickel and cobalt; this synergistic effect provides evidence for the presence of an alloy in the Ni-Co catalyst. Conversion-temperature tests were carried out on several Torvex and cordierite monolithic catalysts and Ni-A-121 (3% Ni) pellets. The results from these tests showed that monoliths are clearly more active than pellets on a rate/volume of catalyst basis. Calculated mass transfer coefficients show that the tests were conducted in the mass transfer influencing regime.

Task 3. Construction on the Berty reactor system was completed and some operational tests were made.

Task 4. Upper operating temperature limit tests were performed on four different pelleted catalysts. These tests showed that the point of maximum conversion for these catalysts was near 723 K ( $450^\circ\text{C}$ ). Also, Ni-A-122 (20% Ni) did not rapidly deactivate until 823 K ( $550^\circ\text{C}$ ).

Task 5. The principal investigator visited and presented seminars at Los Alamos Scientific Laboratory, Norton Chemical Company, and Climax Molybdenum Company. Dr. Bartholomew also presented papers at the Conference on Catalyst Deactivation at Berkeley, California, and at the 85th National AIChE meeting. A science/technology concentrate concerning our work was published in Chemical and Engineering News. Preparation of several journal articles concerning our work is continuing.

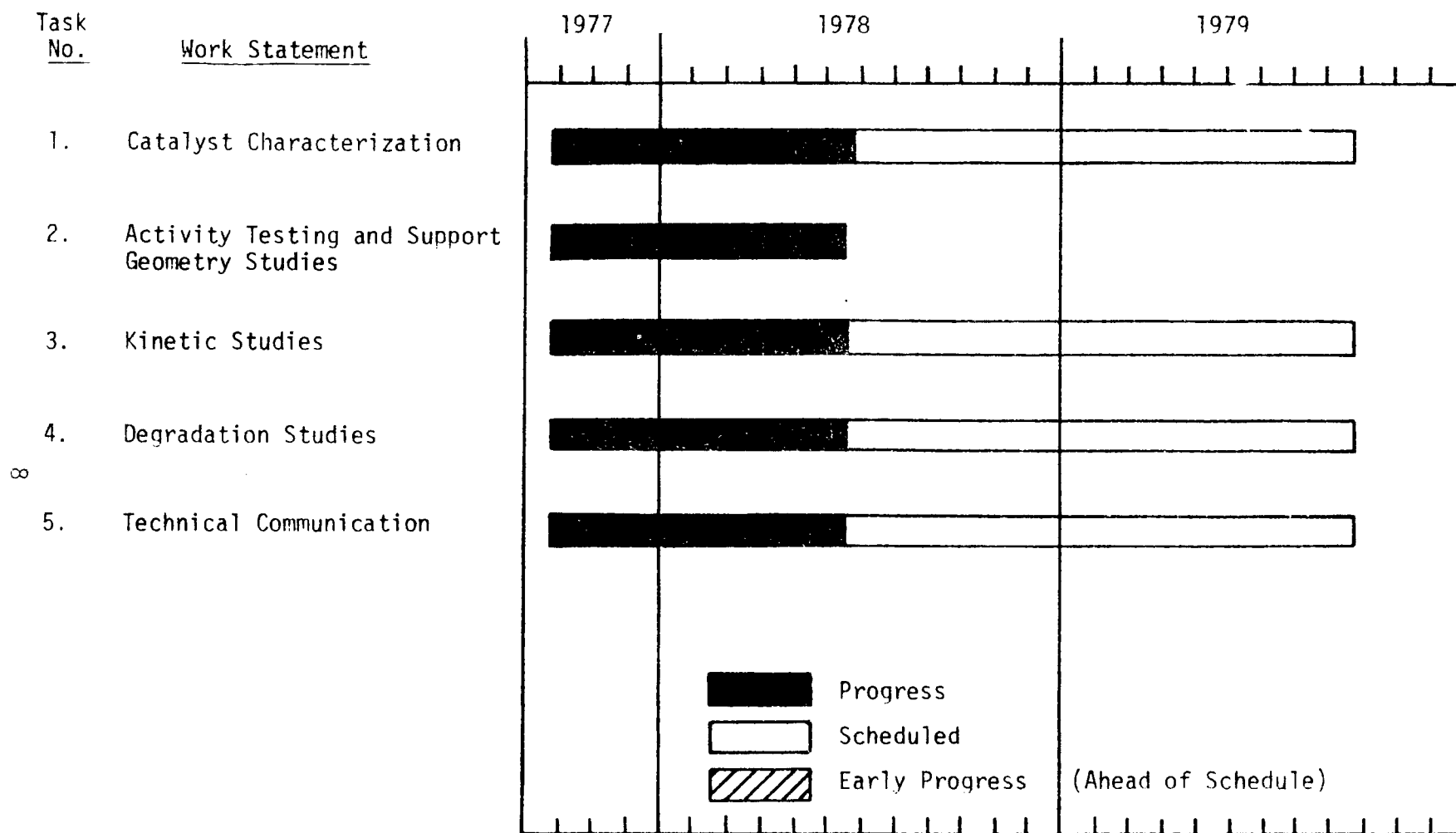


Figure 1. Project Progress Summary.



### III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

#### Task 1: Catalyst Characterization

##### 1. Catalyst Preparation

During this quarter two base metal pellet catalysts Ni-Co-A-103 (10% Ni, 10% Co on  $\text{Al}_2\text{O}_3$ ) and Ni-MoO<sub>3</sub>-A-105 (10% Ni, 10% MoO<sub>3</sub> on  $\text{Al}_2\text{O}_3$ ) 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 the nitrate salts.

Since chloride ions act to poison the methanation reaction, efforts were made to prepare ruthenium and platinum containing catalysts from chloride-free salts, ruthenium acetoacetate and platinum diamminodinitrite supplied by Matthey-Bishop. Ni-Ru (2.5% Ni - 0.5% Ru) and Ni Pt (15% Ni - 0.5% Pt) catalysts were prepared on Kaiser SAS  $\text{Al}_2\text{O}_3$  pellets. Since neither of these salts is soluble in  $\text{H}_2\text{O}$ , ethanol was used as the solvent for the Ru salt. The platinum diamminodinitrite was dissolved in concentrated  $\text{HNO}_3$ . After adding the nickel salt, the impregnating solution was neutralized with  $\text{NH}_4\text{OH}$ . The Ni-Pt catalyst, however, decomposed violently upon bulk reduction causing destruction of the pellets. The Ni-Pt catalyst will be prepared during the next quarter using a low temperature calcination to prevent such an explosion.

Several Ni/ $\text{Al}_2\text{O}_3$ /Torvex monolithic catalysts (3 wt. % nickel) were prepared for use in our geometry studies by adding an alumina washcoat and impregnating with nickel nitrate in a manner similar to that used for cordierite monolithic catalysts prepared earlier in this laboratory. Preparation of 20% Ni/ $\text{Al}_2\text{O}_3$ /cordierite monolithic catalysts for use in thermal stability tests was also initiated.

##### 2. Chemisorption

During the last quarter hydrogen chemisorption measurements were carried out on 24 different catalysts, 16 Torvex Honeycomb (DuPont Co.) monoliths (3% Ni), 6 Ni or Ru containing pellet catalysts, and 2 powdered catalysts. These results reported in Table 2 show the hydrogen uptakes of the 3 wt. % Ni monolithic catalysts to be comparable with the pellet catalysts containing 3 and 6 wt. % nickel.

##### 3. Transmission Electron Microscopy

Transmission electron microscopy measurements of 6% nickel on alumina, 10% nickel - 10% cobalt on alumina and the Kaiser SAS medium alumina support were carried out during the contract period. A slight modification to the procedure recorded in previous reports was made. A holey formvar coated grid was implemented in place of the non-hole formvar coated grid, i.e., the formvar was prepared in the same manner as before stated, with one exception; when the

Table 2  
Summary of Metal Surface Area  
Measurements Using H<sub>2</sub> Chemisorption  
at 25°C

<u>Monolithic Catalysts:</u>	<u>Nominal Composition (wt.%)</u>	<u>Uptake (μmoles/gram)</u>
Ni-TM-110	3.0% Ni	36.8 <sup>a</sup>
Ni-TM-111	3.0% Ni	38.5 <sup>a</sup>
Ni-TM-310	3.0% Ni	29.6 <sup>a</sup>
Ni-TM-311	3.0% Ni	31.5 <sup>a</sup>
Ni-TM-312	3.0% Ni	33.9
Ni-TM-112	3.0% Ni	34.2 <sup>a</sup>
Ni-TM-150	3.0% Ni	46.1 <sup>a</sup>
Ni-TM-151	3.0% Ni	46.8 <sup>a</sup>
Ni-TM 152	3.0% Ni	42.2 <sup>a</sup>
Ni-TM-350	3.0% Ni	45.2 <sup>a</sup>
Ni-TM-352	3.0% Ni	49.0 <sup>a</sup>
Ni-TM-356	3.0% NI	26.1 <sup>a</sup>
Ni-TM-357	3.0% Ni	31.5 <sup>a</sup>
Ni-TM-113	3.0% Ni	36.9
Ni-TM-314	3.0% Ni	29.7
Ni-TM-315	3.0% Ni	30.2
<u>Pellet Catalysts:</u>		
Ni-A-120	3% Ni	31.0 <sup>a</sup>
Ni-A-121	6% Ni	73.9
Ni-A-122	20% Ni	212.7

Table 2 cont.

<u>Pellet Catalysts:</u>	<u>Nominal Composition (wt.%)</u>	<u>Uptake (<math>\mu</math>moles/gram)</u>
Ru-A-100	.5% Ru	1.6
Ni-MoO <sub>3</sub> -A-105	10% Ni 10% MoO <sub>3</sub>	52.8
Ni-Co-A-103	10% Ni 10% Co	117.4
<u>Powders</u>		
Ni-Co-A-100 before poisoning		148.2 <sup>b</sup>
Ni-Co-A-100 after poisoning		69.7 <sup>b</sup>

---

<sup>a</sup>Temperature-Conversion tested @ 8 psig

<sup>b</sup>Differentially tested

liquid formvar coat was set aside to dry a fine water mist (from human breath) was placed on the formvar coat. This caused minute holes to form in the hardened formvar. The purpose of this grid support modification is to provide better resolution of the catalyst. When the ground catalyst is placed on the holey formvar coated grids a good percentage of the catalyst particles will appear above a hole. This method eliminates any inconsistencies that may arise due to the support, such as variable thickness of the support causing resolution problems or contamination on the support which could affect also the micrograph.

A particle size distribution was completed from several micrographs of the prepared nickel-cobalt sample (see Table 3). Micrographs of the alumina support, however, provided some cause for concern because of the closeness in structural appearance of some areas of the support to that of a metal impregnated support (see Area 1 of Figure 3 as compared to Figure 2). However, many areas of the alumina-supported nickel show a contrast between the support and metal particles (Area 2 of Figure 3) and in these areas we feel confident that an accurate metal crystallite size can be determined (see Figure 4). We are, therefore, investigating procedures to increase the contrast between the support and the metal and we are confident that the contrast problem will be resolved. Unfortunately, we will need to re-evaluate our previously obtained micrographs for several alumina-supported samples to be sure that the contrast allows unambiguous choice between metal particles and support structure.

## Task 2: Activity and Support Geometry Tests

Both fresh and partially sulfided samples (treated in 10 ppm  $\text{H}_2\text{S}/\text{H}_2$  at  $450^\circ\text{C}$ ) of Ni-Co-A-100 (powdered form) were differentially tested at 498, 523 and 548 K at a space velocity of  $100,000 \text{ hr}^{-1}$ . The results are compared in Table 4. Previously reported data on Ni-Co-A-100 pellets is also included. The sample was tested in the powdered form to decrease the effects of diffusional resistance and pore mouth poisoning thought possible in pellets. CO turnover numbers for the fresh powder were 2-3 times larger than those previously reported for a pelleted sample; however, the methane turnover numbers were about the same. The high percentage of CO conversion without corresponding methane or carbon dioxide production for the powder suggest that there may be some problem with the analysis or that the surface composition of the powdered sample is significantly different and such as to produce a significant amount of heavy hydrocarbons. The nickel-cobalt powder was prepared from the same batch as the pelleted sample, but it was bulk reduced at a different time possibly under slightly different conditions. The higher  $\text{H}_2$  uptake suggests that its surface properties could be much different from the earlier batch. This renders the comparison between the pellets and powder difficult and perhaps inconclusive. Also some  $\text{CO}_2$  was found to be in the reactant stream during the differential test of the sulfided powder which alters the test conditions somewhat and accounts for the negative values of  $\text{CO}_2$  production, mainly artifacts of the calculation.

Table 3  
Particle Size Distribution for Ni-Co-A-100  
Measured by Electron Microscopy

<u>Sample</u>	<u>Treatment</u>	Per cent Particles <sup>a</sup> in each Size Range <sup>b</sup>					
		<u>&lt;2.28</u>	<u>2.29-2.73</u>	<u>2.74-3.19</u>	<u>3.20-3.64</u>	<u>3.65-4.10</u>	<u>4.11-4.55</u>
Ni-Co-A-100	Reduced and Passivated	3.0	1.7	6.7	12.2	20.2	32.8
		<u>4.56-5.01</u>	<u>5.02-5.46</u>	<u>5.47-5.92</u>	<u>5.93-6.38</u>	<u>6.39-6.83</u>	<u>6.84&gt;</u>
		14.3	3.8	0.8	0.8	0.8	2.9

Surface averaged mean diameter = 5.1 nm.

<sup>a</sup>According to number average diameters of particles

<sup>b</sup>Size Ranges are in nm (1nm = 10Å)



Figure 2. Electron Micrograph of BL-A-101 (blank alumina support) 295,000x.



Figure 3. Electron Micrograph of Ni-A-121 (6% Ni) 295,000x.



Figure 4. Electron Micrograph of Ni-Co-A-100 (10% Ni, 10% Co) 295,000x.



Table 4

Differential Reactor Data  
for Ni-Co-A-100 Before and After H<sub>2</sub>S Poisoning  
(100 kPa, 100,000 hr<sup>-1</sup>, 95% N<sub>2</sub>, 4% H<sub>2</sub>, 1% CO)

Catalyst	$\mu\text{moles/g}$ <u>H<sub>2</sub> uptake</u>	H <sub>2</sub> S poisoned <u>uptake</u>	% CO <u>conversion</u>	% Production		% Yield		Rate X10 <sup>7</sup> g moles/ g cat-sec		Turnover # X10 <sup>3</sup>	
				CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	CO	CH <sub>4</sub>
<u>at 498 K</u>											
Ni-Co-A-100 before poisoning	148.2		15.6	4.7	0.0	0.03	0.00	33.8	10.1	11.4	3.42
Ni-Co-A-100 Pellets	114.9		14.8	12.3	3.6	.84	.024	8.4	7.0	3.6	3.0
Ni-Co-A-100 after poisoning <sup>a,b</sup>	148.2	69.7	1.7	1.7	-0.3	1.02	-0.16	3.6	3.6	2.5	2.6
<u>at 523 K</u>											
Ni-Co-A-100 before poisoning	148.2		26.0	14.1	0.9	.54	.04	56.5	30.6	19.0	10.3
Ni-Co-A-100 pellets	114.9		35.5	28.5	2.27	.80	.064	20.3	16.3	8.5	6.9
Ni-Co-A-100 after poisoning	148.2	69.7	6.2	4.2	-0.1	.87	-0.02	13.3	8.9	9.5	6.4
<u>at 548 K</u>											
Ni-Co-A-100 before poisoning	148.2		50.0	30.5	7.3	0.61	0.15	108.4	66.2	36.6	22.4
Ni-Co-A-100 pellets				Not Available							
Ni-Co-A-100 after poisoning	148.2	69.7	9.9	8.3	0.7	.84	.07	21.2	17.84	15.2	12.8

<sup>a</sup>poisoned in fixed bed in flowing H<sub>2</sub> and 10 ppm H<sub>2</sub>S until approximately 50% poisoned

<sup>b</sup>reactant stream contained approximately .01% CO<sub>2</sub>

Nevertheless, the methane turnover number data for the powdered catalyst before and after poisoning reveal a significant decrease in specific activity of the remaining sites after poisoning, in contrast to the increase observed previously for the pellet supported catalyst (3). Hence, the data suggest that catalyst geometry plays an important role in the poisoning process and these data are indeed consistent with a pore mouth or shell type poisoning model.

Partly because of these unusual results and the obviously nonuniform nature of  $H_2S$  poisoning, a further series of tests was conducted for alumina supported Ni, Ni-Co, and Co Catalysts of high metal loading (14-20%) in powder form in which the samples were poisoned in a uniform manner by 24 hour exposure to 10 ppm  $H_2S/H_2$  in a fluidized bed reactor. A schematic of the fluidized bed reactor is shown in Figure 5. The methane turnover number data obtained before and after poisoning at high space velocities and low conversions are shown in Table 5. Poisoned site activity ratios (PSAR values), ratios of the turnover number of the poisoned to that of the fresh catalyst, are also listed. That the PSAR values for the uniformly poisoned catalysts are significantly less than one (on the order of 0.5) suggests that adsorbed  $H_2S$  interacts with the nickel surface to deactivate more than one nickel site for every adsorbed sulfur atom and/or restructures the surface such that the remaining sites are less active. The larger methane turnover numbers and PSAR values for Ni-Co compared to Ni and Co, an obvious synergistic effect, provide indirect evidence of an intimate bimetallic interaction or perhaps an alloying effect.

It should be mentioned here that the nickel and nickel-cobalt catalysts were observed to be relatively stable over a period of 30-60 minutes during which time 5-6 chromatographic samples were obtained. The  $Co/Al_2O_3$  powder, however, was observed to lose activity with time particularly at the higher temperature (525 K) and especially after exposure to  $H_2S$ . For example, the poisoned sample lost 45% of its initial activity at 525 K over a period of about 45 minutes. This deactivation is possibly a result of high molecular weight hydrocarbons depositing on the surface, since supported Co is known to be active for Fischer-Tropsch Synthesis. Because this deactivation was not observed in the testing of the same catalyst in pellet form at lower space velocities, the deactivation phenomenon may be dependent upon catalyst geometry and upon space velocity.

As part of the support geometry testing under Task 2, several monolithic and beaded catalysts were tested under high temperature and hopefully mass transfer limiting conditions to see if support geometry had an effect in these reaction regimes.

Each of the catalysts tested (see Table 6) was characterized by determination of geometrical surface area (GSA). This catalyst characteristic is the criterion by which monolithic and pelleted catalysts can be compared in mass transfer limiting regimes. The geometrical surface area (GSA) is the exterior surface area of the catalyst implied by the geometry of the catalyst support and is reported as  $cm^2$  surface area/ $cm^3$  catalyst volume.

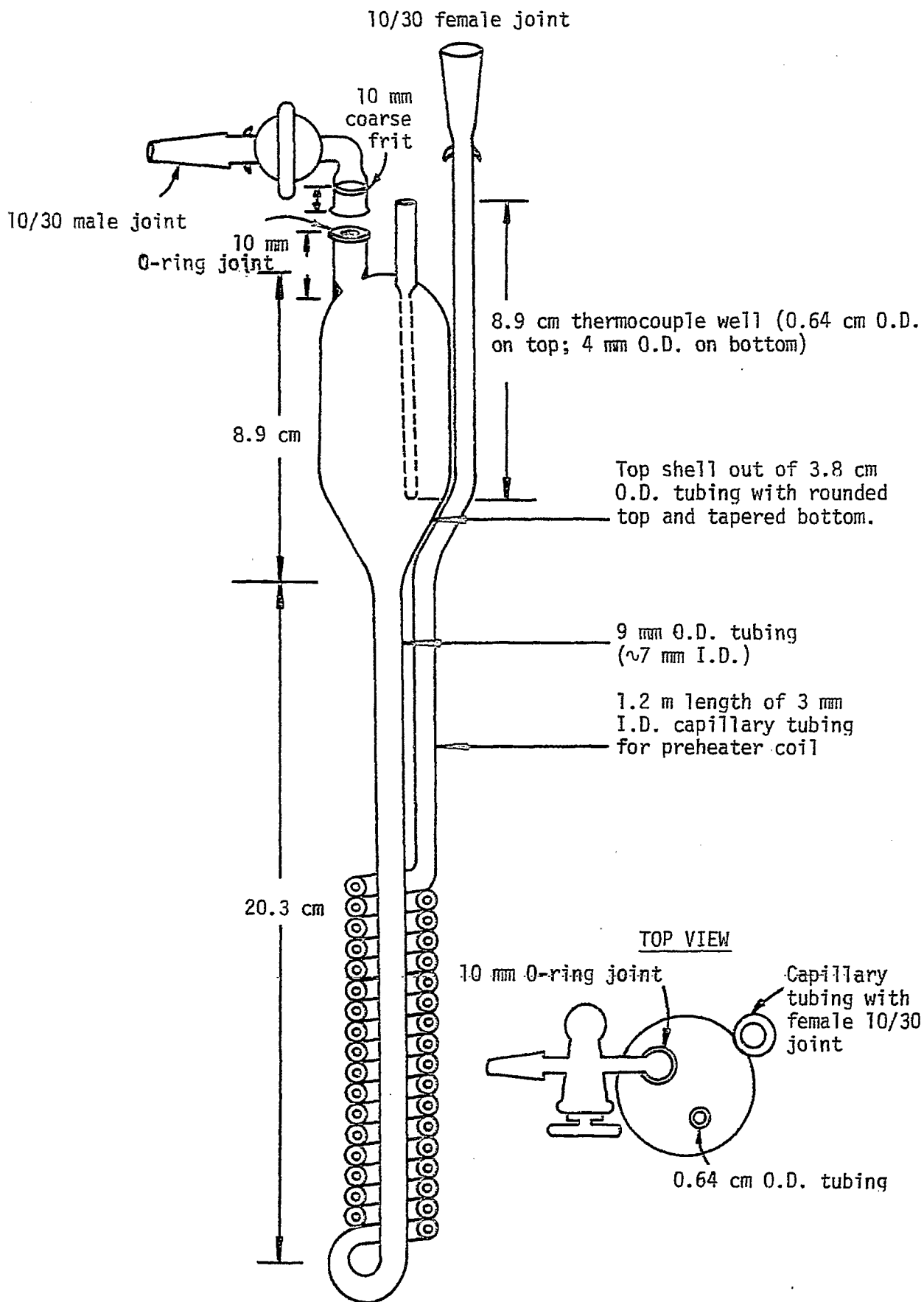


Figure 5. Fluidized Bed Reactor.

Table 5

Specific Activity Data<sup>a</sup> Before and After Exposure<sup>b</sup> to 10ppm H<sub>2</sub>S  
of Alumina-Supported Ni, Ni-Co and Co in Powder Form

<u>Catalyst</u>	<u>% CO Conversion</u>	<u>% CH<sub>4</sub> Yield<sup>c</sup></u>	<u>CH<sub>4</sub> Turnover No. X10<sup>3</sup> (sec<sup>-1</sup>)</u>	<u>Poisoned Site Activity Ratio<sup>d</sup></u>
<u>At 500 K</u>				
<u>Ni-A-116 (14% Ni)</u>				
fresh	4.04	71.5	2.4	
poisoned	2.69	61.4	1.0	0.42
<u>Ni-Co-A-100 (10% Ni, 10% Co)</u>				
fresh	4.46	61.2	6.0	
poisoned	2.80	81.8	4.1	0.68
<u>Co-A-100 (20% Co)</u>				
fresh	2.01 <sup>e</sup>	61.2	3.8	
poisoned	2.26 <sup>f</sup>	55.8	2.0	0.53
<u>At 525 K</u>				
<u>Ni-A-116 (14% Ni)</u>				
fresh	9.85	83.6	6.9	
poisoned	6.28	74.2	2.8	0.40
<u>Ni-Co-A-100 (10% Ni, 10% Co)</u>				
fresh	8.60	85.6	16.1	
poisoned	8.44	89.7	13.4	0.83
<u>Co-A-100 (20% Co)</u>				
fresh	5.81 <sup>e</sup>	56.9	10.3	
poisoned	3.25 <sup>f</sup>	65.2	3.5	0.34

<sup>a</sup>At 140 kPa, a space velocity of about 100,000 hr<sup>-1</sup> in a gas mixture containing 1% CO, 4% H<sub>2</sub>, 95% N<sub>2</sub>.

<sup>b</sup>Exposure to 10ppm H<sub>2</sub>S in a fluidized bed over a period of several hours sufficient to poison about 50% of the surface.

<sup>c</sup>Methane yield is the fraction of converted CO which is transformed to methane.

<sup>d</sup>Turnover number for the poisoned divided by that for the fresh catalyst.

<sup>e</sup>Space velocity = 100,000 hr<sup>-1</sup>

<sup>f</sup>Space velocity = 38,000 hr<sup>-1</sup>

Table 6

Comparison of Geometrical Surface Area and Conversion,

Production and Selectivity

[140 kPa, GHSV = 50,000 hr<sup>-1</sup>, 700 K, 1% CO, 4% H<sub>2</sub>, 95% N<sub>2</sub>]

Catalyst	GSA	% Conversion CO	% Production		% Yield	
			CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
Beads (0.32 cm diam.)	8.7	58.9	37.4	14.0	63.5	23.8
Celcor monoliths						
46.5 □/cm <sup>2</sup>	17.8	92.9	64.1	17.8	69.0	19.1
Torvex monoliths						
40.8 ○/cm <sup>2</sup> DuPont Alumina Coat	16.6	96.2	65.5	18.9	68.1	19.7
40.8 ○/cm <sup>2</sup> Cat. Lab. Alumina Coat	16.3	96.6	67.6	18.0	69.9	18.6
10.7 ○/cm <sup>2</sup> DuPont Alumina Coat	8.9	86.3	57.6	17.8	66.8	20.7
10.7 ○/cm <sup>2</sup> Cat. Lab. Alumina Coat	9.2	88.9	59.3	16.6	66.7	18.7

The GSA of the catalyst beads was determined by multiplying the surface area of a single catalyst sphere by the number of beads in the reactor sample and then dividing by the reactor sample volume ( $6.3 \text{ cm}^3$ ). The GSA of the monolithic catalysts was determined by measuring the circumference of a single monolith channel, multiplying by the length of a monolith, multiplying by the number of channels per monolith, and dividing by the volume of a monolith. The circumference of a monolith channel was determined by photographing a monolith through a magnifying lense, then blowing up the photograph. Figure 6 is a representative enlarged photograph of a coated, impregnated, reduced monolithic catalyst. This method gave results comparable to those reported by Corning Glass Works for uncoated monoliths.

Conversion and selectivity data at 700K and 140 kPa (1 atm) for the catalyst monoliths and beads are listed in Table 6. Conversion vs. temperature tests were conducted at 140 kPa and  $50,000 \text{ hr}^{-1}$ , using a reactant gas containing 1% CO, 4%  $\text{H}_2$ , and 95%  $\text{N}_2$ . The temperature varied from 450 to 750 K, however, the catalysts were compared at 700 K since that temperature was nearest the maximum CO conversion for all the catalysts. Each data value in Table 6 represents the average of data obtained for 3-4 identical samples of each geometry. Comparison of the CO conversion data for different monoliths shows significantly higher conversions for the monoliths having the larger GSA. The beaded catalyst compared to the monolith catalysts of about the same GSA achieves substantially lower conversion to CO. Moreover its methane yield is also significantly less relative to the monolithic catalysts.

Rates per gram and per volume catalyst at 700 K, 140 kPa, and  $50,000 \text{ hr}^{-1}$  are shown in Table 7. On the basis of moles of CO converted per gram of catalyst per second, a comparison of the data for the Torvex monoliths shows that the catalysts with the higher GSA also have the higher reaction rate. This indicates that for monoliths the higher the GSA the higher the reaction rate that can be expected. In comparison to the Celcor monoliths the  $263 \text{ O/in}^2$  Torvex monoliths have slightly but significantly higher rates of reaction although these two catalysts have nearly the same GSA. This difference in activity is accounted for by Hegedus (5) who shows that according to mass transfer considerations the hexagonal monolith channels should give better activity than the square monolith channels. On a rate/gram basis a comparison of the monoliths and beads shows a different result. Even though the beads have a smaller GSA than the monoliths, the rate of CO conversion in the pellets is as high as the best rate seen for the monoliths. This means that on a rate per gram basis the pellets are better than some of the monoliths with about the same GSA and as good as the others with greater GSA. We expect, however, that the new monoliths developed by Corning Glass Works with a GSA of  $28 \text{ cm}^2/\text{cm}^3$  will perform better than the 0.32 cm pellets on a mass basis.

Table 7 indicates that the weight difference between the monoliths and pellets is substantial and since all catalyst samples had the same volume, comparison on a volume basis should be more meaningful.

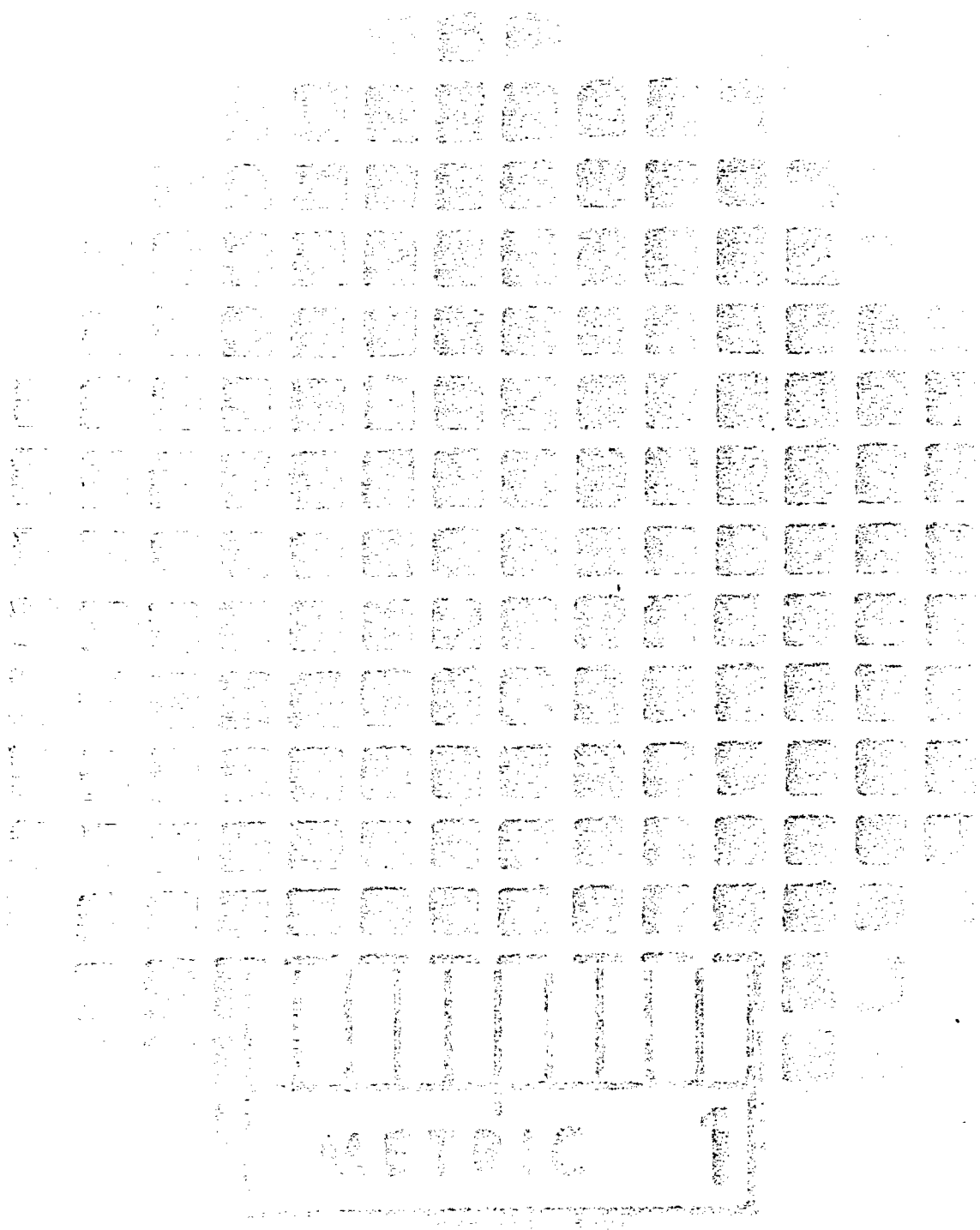


Figure 6. Enlarged Photograph Used for Determining GSA of  $46.5 \text{ cm}^2$   
Cordierite Monolith Coated with 10% Alumina.

Table 7

Comparison of Geometrical Surface Area and Reaction Rates  
 [140 kPa, GHSV = 50,000 hr<sup>-1</sup>, 700 K, 1% CO, 4% H<sub>2</sub>, 95% N<sub>2</sub>]

<u>Catalyst</u>	<u>GSA</u> <sup>1</sup>	<u>wt.</u>	Rate per gram x10 <sup>7</sup> (mole/g-cat.-sec.)		Rate per volume x10 <sup>7</sup> (moles/cm <sup>3</sup> -cat.-sec.)	
			<u>CO</u>	<u>CH<sub>4</sub></u>	<u>CO</u>	<u>CH<sub>4</sub></u>
Beads (0.32 cm diam.)	8.7	2.451	94.3	59.9	36.6	23.3
Celcor 46.5 □/cm <sup>2</sup> 10 % Alumina	17.8	4.620	79.7	54.9	58.1	40.1
Torvex 40.8 ○/cm <sup>2</sup> Dupont Alumina Coat	16.6	4.048	94.7	64.5	60.8	41.4
40.8 ○/cm <sup>2</sup> Cat. Lab. Alumina Coat	16.3	4.159	91.2	63.7	60.2	42.1
10.7 ○/cm <sup>2</sup> DuPont Alumina Coat	8.9	5.079	67.9	45.3	54.7	36.5
10.7 ○/cm <sup>2</sup> Cat. Lab. Alumina Coat	9.2	5.322	66.6	44.4	56.3	37.5

<sup>1</sup>GSA is cm<sup>2</sup> exterior surface area/cm<sup>3</sup> bulk volume of catalyst.



On the basis of moles of CO converted per volume of catalyst per second, a comparison of the data for monoliths in Table 7 shows the same trends as discussed above, though the differences are not as profound. However, a comparison of the monoliths and beads shows significantly different results. That is monolithic supported catalysts evidence substantially higher rates/volume than the beaded catalyst. In fact, the monoliths with high-GSA show rates of CO conversion nearly twice those of the beads. Table 7 shows that the same trends that are seen in the rate of CO conversion are also seen in the rate of CH<sub>4</sub> production. These results indicate that it would take nearly twice the volume of beads (or pellets) to convert a given amount of CO to CH<sub>4</sub> as it would monoliths. Thus, the use of monolith supported catalysts would enable the size of methanation reactors to be reduced significantly. Moreover, a monolithic reactor could be operated efficiently at substantially higher space velocities than beads or pellets at a fraction of the pressure drop.

Mass transfer coefficients were calculated for monoliths and pellets to see if the experiments were actually in the mass transfer limiting regime (see Table 8). The experimental values were calculated according to:

$$k_m = r_p M / a C_A$$

where  $k_m$  is the mass transfer in cm/sec,  $r$  is the rate in g-moles/g-cat-sec,  $\rho$  is the bulk density,  $M$  is the molecular weight of carbon monoxide,  $a$  is the GSA in cm<sup>2</sup>/cm<sup>3</sup>, and  $C_A$  is the log mean concentration of CO in g/cm<sup>3</sup>. The theoretical values of  $k_m$  were calculated according to the method of Hegedus (5):

$$k_m = (D/2R) B (1 + .095 (4R^2 G / \rho D L))^{0.45}$$

where  $D$  is the diffusivity of CO,  $R$  is the hydraulic radius,  $B$  is the limiting Sherwood number for fully developed laminar flow,  $G$  is the feed flux in g/cm<sup>2</sup>-sec,  $\rho$  is the bulk density and  $L$  is the monolith channel length.

From Table 8 one can see that these experiments were carried out in the mass transfer influenced regime, but that mass transfer was not the rate limiting step. Since diffusivity and hence the mass transfer coefficient are inversely dependent upon pressure, the calculated mass transfer coefficient should be about a factor of 10 less at 10 atm, suggesting that truly mass-transfer-limiting conditions will obtain under these conditions. During the next quarter, we will test several monolith and pelleted catalysts at 10 atm in the mass transfer limiting regime. Nevertheless, in the tests just completed the monolithic catalysts are clearly better than pelleted catalysts on a rate per volume basis, even though mass transfer does not clearly limit the rate.

Table 8

Experimental and Theoretical Mass Transfer  
Coefficients(140 kPa, GHSV = 50,000 hr<sup>-1</sup>, 700 K, 1% CO, 4% H<sub>2</sub>, 95% N<sub>2</sub>)

	Experimental <u><math>k_m</math> (cm/sec)</u>	Theoretical <u><math>k_m</math> (cm/sec)</u>
Beads (0.32 cm diam.)	2.71	14.8
Celcor 46.5 □/cm <sup>2</sup> 10% Alumina	6.43	20.1
Torvex 40.8 ○/cm <sup>2</sup> Dupont Alumina Coated	8.09	21.1
40.8 ○/cm <sup>2</sup> Cat. Lab Alumina Coat	8.52	21.8
10.7 ○/cm <sup>2</sup> Dupont Alumina Coat	6.94	10.6
10.7 ○/cm <sup>2</sup> Cat. Lab Alumina Coat	7.61	10.5

### Task 3: Kinetic Studies

Construction of the high pressure mixed flow system has been completed. Five runs have been made to check the equipment. Temperature control and equilibration have proven to be the main concerns. The temperature inside the Berty reactor and the heating rate have been found to be functions of reactor pressure, impeller speed and flow rate. Higher flow rates give a more uniform temperature in reactor, while increasing reactor pressure and impeller speed increases temperature equilibration and heating rates.

Several reactor tests with catalyst pellets in the reactor are scheduled early in the next quarter after which the system should be ready for beginning kinetic studies.

### Task 4: Degradation Studies

During the past quarter upper operating temperature limit (thermal degradation) tests were performed on high loading alumina-supported Ni, Ni-Co, Ni-MoO<sub>3</sub>, and Ni on nickel aluminate catalysts. The tests were performed at 2500 kPa and a space velocity of 30,000 hr<sup>-1</sup>. The reactant gas was 64% CH<sub>4</sub>, 16% Ar, 14% H<sub>2</sub>, 4% CO, 2% CO<sub>2</sub>.

In Figure 7 the conversion of CO (overall, i.e. to all products) is shown with respect to temperature. The equilibrium conversion as calculated by the Edward's Thermochemical Program is higher than the actual conversions experienced in the upper temperature limit runs. At peak conversion the order of catalyst activity was Ni=Ni-Co>Ni/NiAl<sub>2</sub>O<sub>4</sub>>Ni-MoO<sub>3</sub>. A second run on Ni-A-122 (20% Ni) was made to investigate the deactivation at higher temperatures. Deactivation did not become rapid until ~823 K (1022°F). The catalyst still converted 50% of the reactant CO at 886 K (1135°F). These catalyst did better than those reported by Lee (6) where most of the commercial catalysts deactivated at 783 K (950°F). It may be possible that the catalysts tested in our laboratory performed better at high temperatures because of differences in pressure or gas purification although in Lee's work and ours the reactants were passed through an active carbon filter. It is more likely, however, that the catalysts developed in this laboratory by a rather unique preparation are actually more thermally stable or more resistant to carbon deposition than commercial methanation catalysts, especially in view of the superior performance of the Ni/Al<sub>2</sub>O<sub>3</sub> relative to Ni/NiAl<sub>2</sub>O<sub>4</sub> more representative of commercial preparations. This will be verified, however, by running 1 or 2 of the best commercial catalysts under the same conditions during the next quarter.

The mole percent conversion of CO to CH<sub>4</sub> versus temperature is shown in Figure 8. The equilibrium production of methane is much lower than the actual production for all of the catalysts tested above 600 K. This anomalous result can be explained by the observations that (1) at equilibrium large amounts of graphitic carbon are predicted, (2) at equilibrium, decomposition of CH<sub>4</sub> is important above 600 K, whereas the actual rate of decomposition may be negligible at these temperatures and (3) the Edward's Thermochemical Program assumes ideal

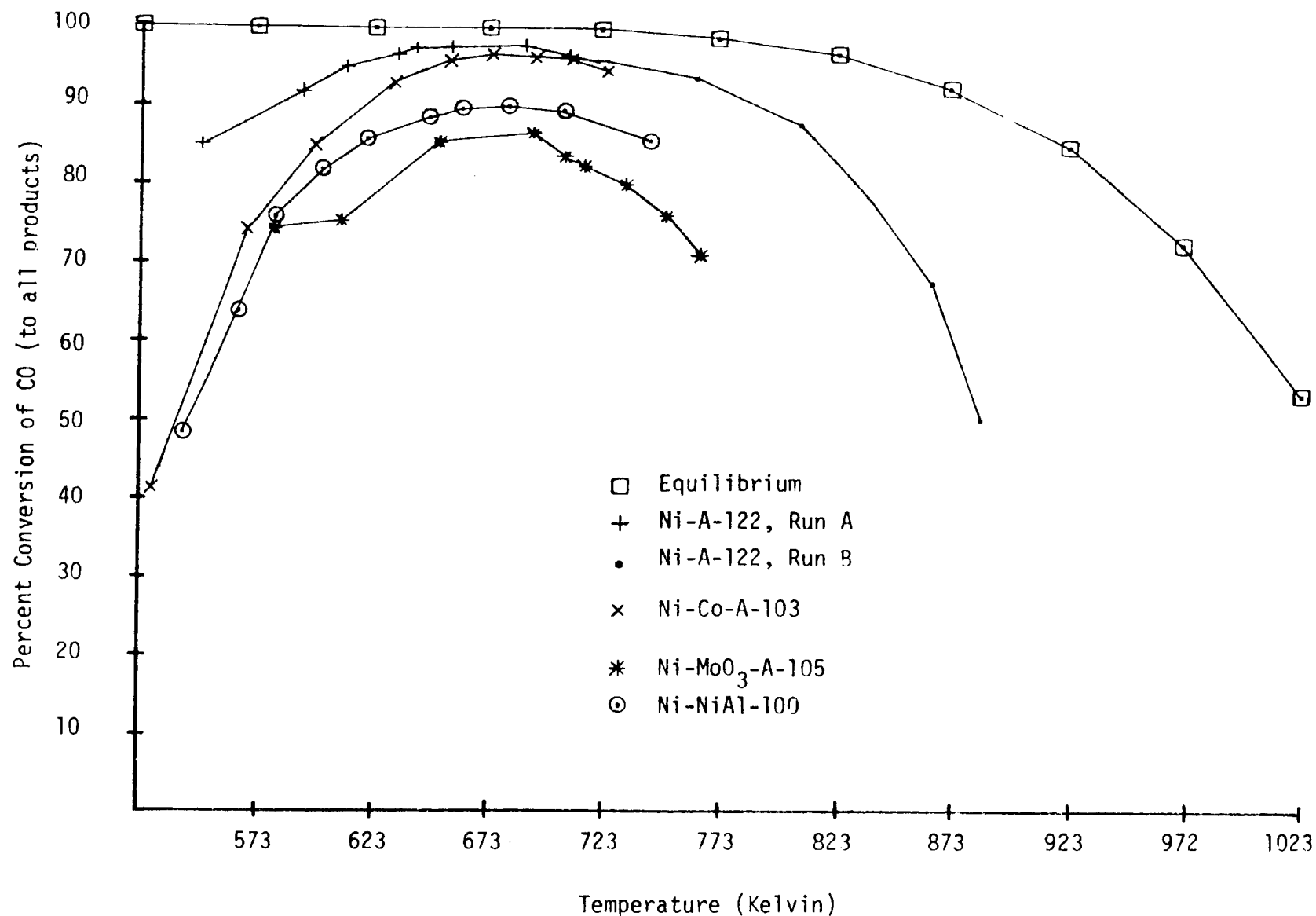


Figure 7. Conversion of CO (overall) vs. Temperature for High Loading Catalysts at 2500 kPa, GHSV=30,000 hr<sup>-1</sup>, and Reaction Mixture Containing 64% CH<sub>4</sub>, 16% Ar, 14% H<sub>2</sub>, 4% CO, and 2% CO<sub>2</sub>.

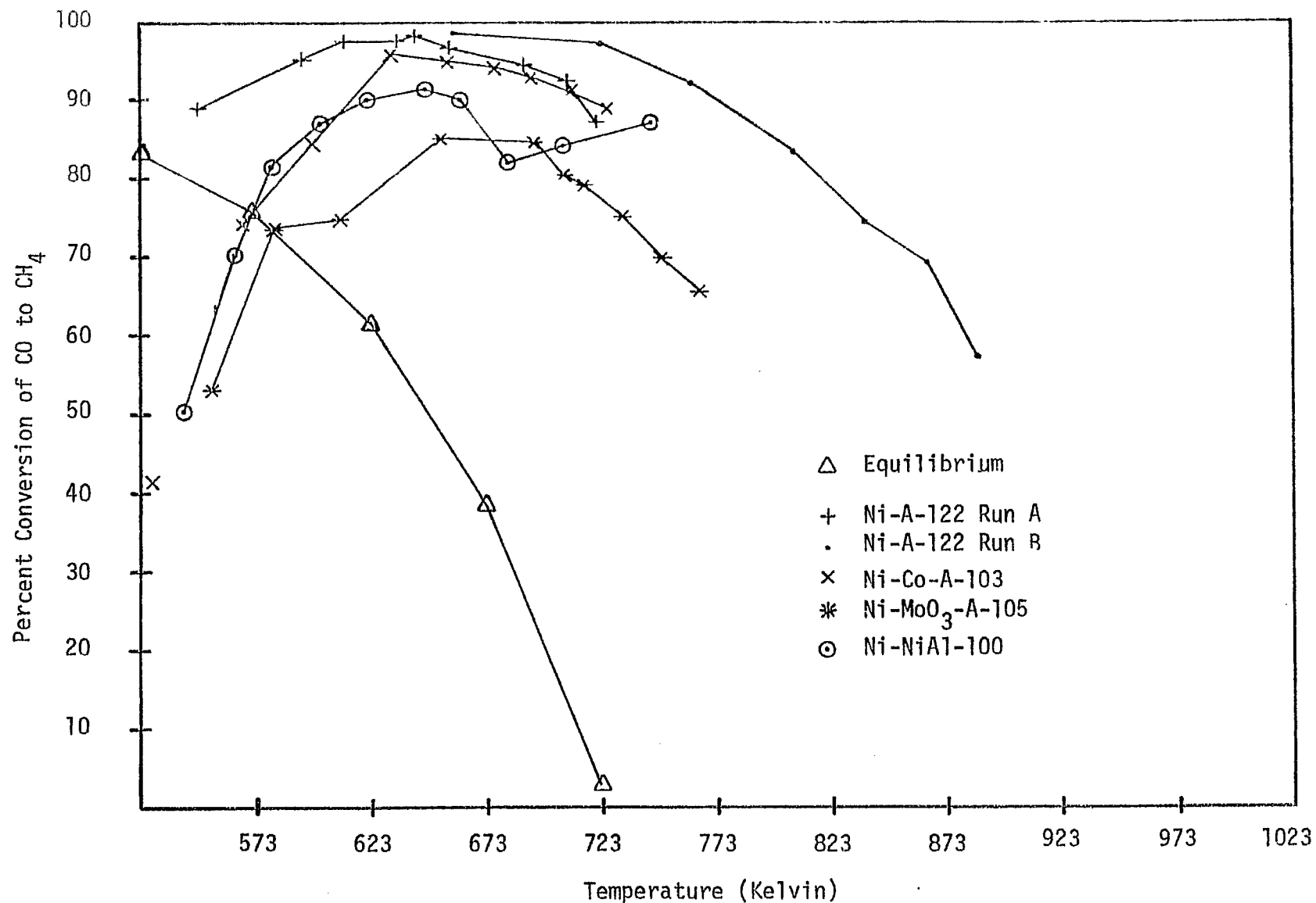


Figure 8. Conversion of CO to CH<sub>4</sub> vs. Temperature for High Loading Catalysts at 2500 kPa, GHSV=30,000 hr<sup>-1</sup> and Reaction Mixture Containing 64% CH<sub>4</sub>, 16% Ar, 14% H<sub>2</sub>, 4% CO and 2% CO<sub>2</sub>.

gas behavior. However, since our tests were conducted at 2500 kPa (365 psia), the errors associated with the ideal gas assumption should be small. The first two observations are probably more significant since most of our catalysts did not appear to have deposited large amounts of carbon. Nevertheless, these catalysts will be chemically analyzed for carbon during the next quarter; selected samples will be submitted for Auger analysis. The presence or absence of surface carbon will help to establish the cause of deactivation.

The apparent increase in methane production of the Ni/NiAl<sub>2</sub>O<sub>4</sub> above 700 K while the CO conversion dropped off (Figure 8) is very interesting. This catalyst will be tested at higher temperatures during the next period. It may be that the Ni/NiAl<sub>2</sub>O<sub>4</sub> catalyst is more active and/or selective at higher temperatures or perhaps it was not totally reduced.

In Figure 9 the rate of CH<sub>4</sub> production per gram catalyst-sec is shown versus temperature. These results are similar to those in Figure 7. However, the Ni/NiAl<sub>2</sub>O<sub>4</sub> catalyst was much more dense and thus showed a lower rate/gram.

It may be worthwhile to mention that rather than using preheater coils, either uncatalyzed monoliths or low surface area alumina balls were placed above the catalyst bed to act as preheaters. This was done to minimize iron carbonyl formation which may cause rapid carbon deposition (3). This possibility is supported by data for Ni-A-122 (Run C) obtained with the normal stainless steel preheater coils in place and without an active carbon filter present for the reactants. The CH<sub>4</sub> rate/gram on this run decreased rapidly above 650 K but then increased above 700 K. Physical examination of the catalyst after the run proved that the samples was extremely carbon fouled. In fact, almost all of the catalyst pellets had disintegrated from the carbon deposition! The increase in methane production above 700 K suggests a separate catalytic mechanism may become rate limiting at the high temperature.

#### Task 5: Technical Interaction and Technology Transfer

On May 3 the principal investigator, Dr. Bartholomew, visited by invitation the Division of Applied Photochemistry at Los Alamos Scientific Laboratory (New Mexico), toured selected laboratories and presented a seminar "The Future of Catalysis." Several stimulating discussions with scientists of the AP Division focused on the possible applications of Laser Technology to the study of catalysts and catalytic reactions.

On May 15th he visited the Norton Chemical Company in Akron, Ohio where he presented a seminar on CO and H<sub>2</sub> adsorption on nickel and toured the company's R & D facilities. The following day he attended a meeting of the D-32 Catalyst Committee of the American Society for Testing and Materials and participated in the preparation of standard techniques for measuring metal areas of Ni/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts using hydrogen adsorption. Discussions with Dr. Robert Farrauto (Engelhard)

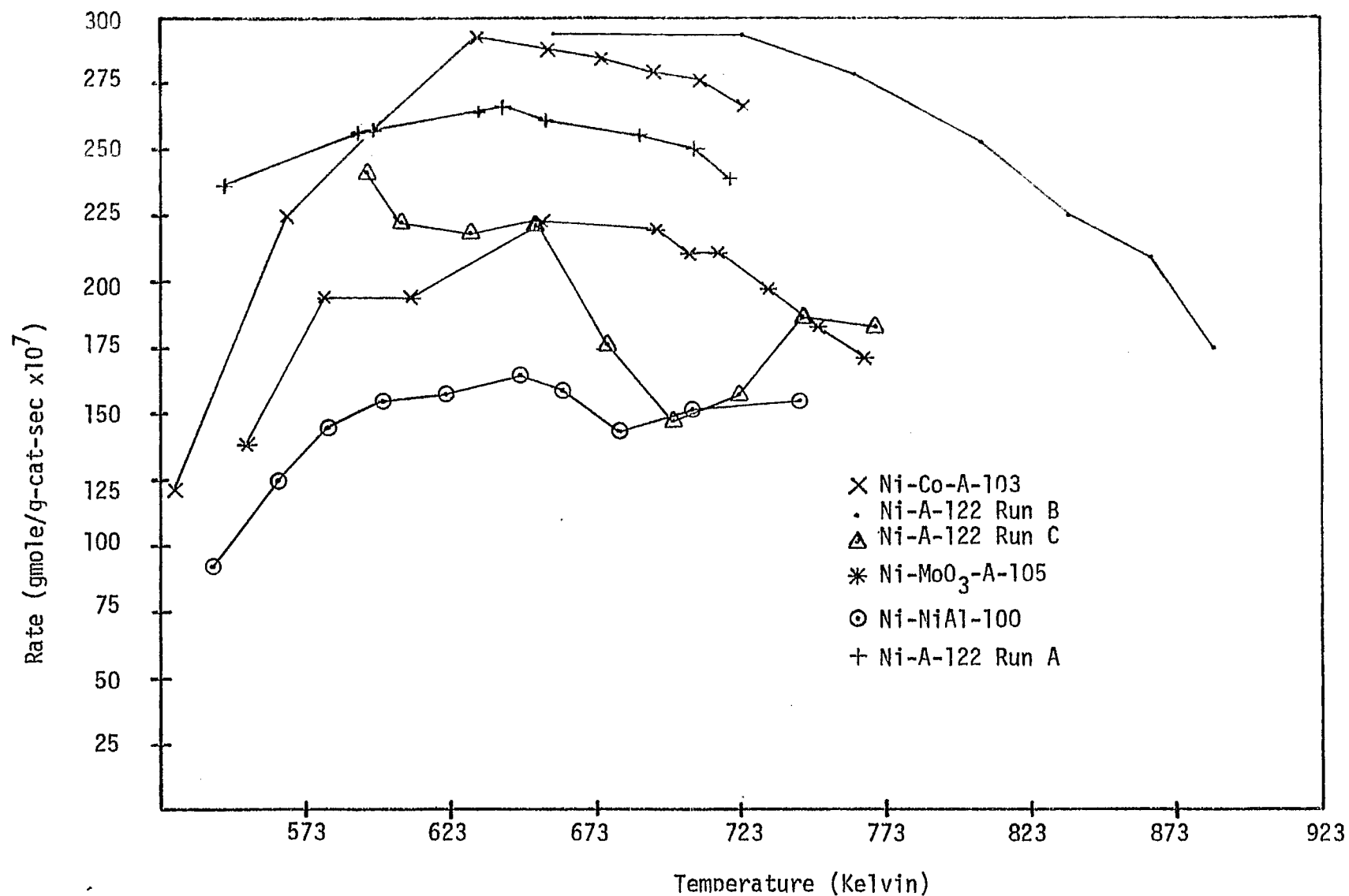


Figure 9. Methanation Rates (g-mole/g-cat-sec  $\times 10^7$ ) vs. Temperature for High Loading Catalysts at 2500 kPa, GHSV=30,000 hr<sup>-1</sup>, and Reaction Mixture Containing 64% CH<sub>4</sub>, 16% Ar, 14% H<sub>2</sub>, 4% CO and 2% CO<sub>2</sub>.

and Dr. Ruth Haines (NBS) provided useful feedback on several catalyst characterization problems.

The following week Dr. Bartholomew attended a conference on Catalyst Deactivation and Poisoning held May 24-26 at the Lawrence Berkeley Laboratory in Berkeley, California and presented a paper on "H<sub>2</sub>S Poisoning of Supported Nickel and Nickel Bimetallic Catalysts," based on our ERDA-DOE supported research. In discussions following the talk quite specific feedback was obtained in regard to our sulfur poisoning work. Bob Lewis of Chevron questioned whether our PH<sub>2</sub>S/PH<sub>2</sub> ratio was high enough to cause bulk sulfide formation. Although the chemical analysis of our samples suggests only monolayer coverage, his comment certainly has stimulated us to conduct some further experiments to check this out. There were quite a number of other interesting papers presented dealing with sintering, metal support interactions, poisoning, and effects of additives. Discussions with other workers during and in between sessions were quite fruitful in terms of stimulating ideas for future work while obtaining feedback on several of our ongoing studies.

Dr. Bartholomew also visited with scientists and engineers at the Climax Molybdenum Company of Michigan on June 5th, presented a seminar on "Molybdenum Based Methanation Catalysts" and toured their research and development facilities. Discussions focused on the NiMoO<sub>3</sub> catalysts prepared at BYU and at Climax which are more active and sulfur resistant than nickel catalysts and the results of our tests on several fluidized methanation catalysts (some prepared at Climax) for Bituminous Coal Research.

The following day (June 6) he met with Paul Scott and Mike Biallis of DOE-Fossil energy to review progress on the current project and to discuss ideas for possible follow on work. In the afternoon he visited Dee Stevenson of DOE-Office of Energy Research to obtain feedback on concepts for a new proposal.

On June 7th, Dr. Bartholomew presented a paper "Bimetallic Methanation Catalysts" at the 85th National Meeting of the American Institute of Chemical Engineers in Philadelphia. This presentation was a summary of activity and deactivation studies conducted over the past year in behalf of ERDA and DOE. There were two other very interesting papers presented at the same session--a paper by Professor John Butt of Northwestern dealing with hydrocarbon synthesis (characterization, activity and selectivity studies) on Fe and Ni-Fe alloys and a paper by Professor Albert Vannice of Penn State on metal support interactions in the Ni/TiO<sub>2</sub> system and their effects on methanation activity and selectivity.

Professor Butt has been able to verify by Moessbauer Spectroscopy what we suspected early in our ERDA-supported work (7) namely, that Ni-Fe deactivates via formation of an Fe carbide. His works also shows that Fe carbide is the active species in a reduced iron catalyst.



The work of Vannice with Ni/TiO<sub>2</sub> shows that metal support interactions can have a marked effect upon activity and selectivity in hydrocarbon synthesis. The apparent strong interaction between Ni and TiO<sub>2</sub> which lowers H<sub>2</sub> adsorption on nickel sites but increases their activity is very much akin to the observations reported in our last report (8) of an interaction between Ni and molybdenum oxide which lowers H<sub>2</sub> adsorption and likewise increases methanation activity.

Just at the end of this quarter, Dr. Bartholomew was invited to participate in a workshop sponsored by the National Science Foundation held June 22 and 23 at the University of Maryland. The purpose of the workshop was to assess the current status of fundamental research in catalysis and to define future basic research needs, priorities, and promising directions. Dr. Bartholomew assisted in the formulation of guidelines and directives in metal catalysis and catalyst degradation.

Our research effort with monolithic catalysts recently received national attention in a science/technology concentrate appearing in the June 19th issue of Chemical and Engineering News. This article refers to our recent work which shows that monolithic catalysts are more active and possibly more cost effective than pellet catalysts for methanation.

During this past quarter we have continued our preparation of several manuscripts for journal publication. We have delayed submitting them for publication while we tie up one or two loose ends experimental-wise. For example, we are waiting to get better data on bulk and surface compositions of our bimetallics before we publish the activity data. We anticipate, however, submitting at least 2 manuscripts during the next quarter.

#### IV. CONCLUSIONS

1. Support geometry tests of several monolithic and pelleted catalysts showed that monolithic catalysts are clearly more active than pellets on a rate/volume of catalyst basis. Also, the per cent yield of methane was higher for the monolithic catalysts. These tests were conducted at high conversions under conditions similar to those in a commercial reactor.

2. Uniform  $H_2S$  poisoning of alumina-supported Ni, Ni-Co, and Co powders in a fluidized cell and subsequent activity testing showed that specific activities were significantly higher for Ni-Co. This synergistic effect supports the hypothesis that the activity of the Ni-Co catalyst is due to the presence of an alloy. Other  $H_2S$  poisoning tests of Ni-Co/ $Al_2O_3$  powders compared with pellets provides evidence for a shell type poisoning model.

3. High temperature tests with a reactant stream similar to a commercial methanation recycle reactor showed that high loading Ni-A-122 retained activity to 823 K (550°C). The temperature of maximum conversion for high loading Ni, Ni-Co, Ni-MoO<sub>3</sub>, and Ni on nickel aluminate in similar tests was near 723 K (450°C).

4. Electron micrographs of an alumina support blank showed that in some cases there has not been sufficient contrast between the support and metal particles to enable unambiguous determination of metal crystallite size distributions. Our techniques are being re-evaluated.

5. In discussing and presenting the research supported by this contract we have encountered considerable interest in three main aspects of our work. These three areas appear to have the greatest potential at this point for contributing to either the science or technology of catalysis and fossil fuel conversion:

a. Monolithic-supported catalysts: Monolithic catalysts are significantly more active and selective for methane production at high space velocities. We believe it would be possible to maintain high conversions of CO at space velocities as high as 50,000-100,000  $hr^{-1}$ , 2-3 times the allowable throughput for fixed pellet beds because of pressure drop considerations. We are currently working with industrial representatives to have these tested on a larger scale.

b. Ni-Co and Ni-MoO<sub>3</sub> Bimetallics: Both our Ni-Co and Ni-MoO<sub>3</sub> catalysts are more active and sulfur tolerant than nickel in methanation of CO. We have at least indirect evidence at this point of bimetallic interactions which account for this synergistic behavior. Commercial Ni-Co and Ni-MoO<sub>3</sub> catalysts are now under development, and in at least one instance, we know that our work has influenced

this development.

c. Poisoning and Carbon Deposition Studies: There is considerable interest in our studies of poisoning by  $H_2S$  and fouling by carbon deposition during reaction of nickel and nickel bimetallics because these same problems are encountered on the very similar catalysts in a number of other important catalytic processes including numerous hydrogenation reactions, fuel cell catalysis, and hydrocarbon synthesis.

## V. REFERENCES

1. M. Greyson, "Methanation" in "Catalysts" Vol. IV., ed. P.H. Emmett, Rheinhold Pub. Corp., New York, 1956.
2. G.A. Mills and F.W. Steffgen, "Catalytic Methanation", Catalysis Reviews 8, 159 (1973).
3. C.H. Bartholomew, "Alloy Catalysts with Monolith Supports for Methanation of Coal-Derived Gases", Final Technical Progress Report FE-1790-9 (ERDA), Sept. 6, 1977.
4. J.R. Katzer, private communication.
5. L.L. Hegedus, "Effects of Channel Geometry On the Performance of Catalytic Monoliths", Symposium on Catalytic Approaches to Environmental Control, American Chemical Society, Division of Petroleum Chemistry, Chicago Meeting, August 26, 1973.
6. IGT Process Research Division, "Hygas: 1972 to 1974, Pipeline Gas from Coal-Hydrogenation", Interim report No. 1, ERDA, July 1975.
7. C.H. Bartholomew, "Alloy Catalysts with Monolith Supports for Methanation of Coal-Derived Gases", Quarterly Technical Progress Report FE-1790-2 (ERDA), Nov. 6, 1975.
8. C.H. Bartholomew, "Alloy Catalysts with Monolith Supports for Methanation of Coal-Derived Gases", Quarterly Technical Progress Report FE-2729-2 (ERDA), April 5, 1978.

## **SATISFACTION GUARANTEED**

**NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.**

▲ **E-mail: [info@ntis.gov](mailto:info@ntis.gov)**

▲ **Phone: 1-888-584-8332 or (703)605-6050**

# **Reproduced by NTIS**

National Technical Information Service  
Springfield, VA 22161

***This report was printed specifically for your order  
from nearly 3 million titles available in our collection.***

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

## **About NTIS**

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at  
**<http://www.ntis.gov>**.

# **NTIS**

**Ensuring Permanent, Easy Access to  
U.S. Government Information Assets**



U.S. DEPARTMENT OF COMMERCE  
Technology Administration  
National Technical Information Service  
Springfield, VA 22161 (703) 605-6000

---