# ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES. QUARTERLY TECHNICAL PROGRESS REPORT, DECEMBER 21, 1979-MARCH 20, 1980

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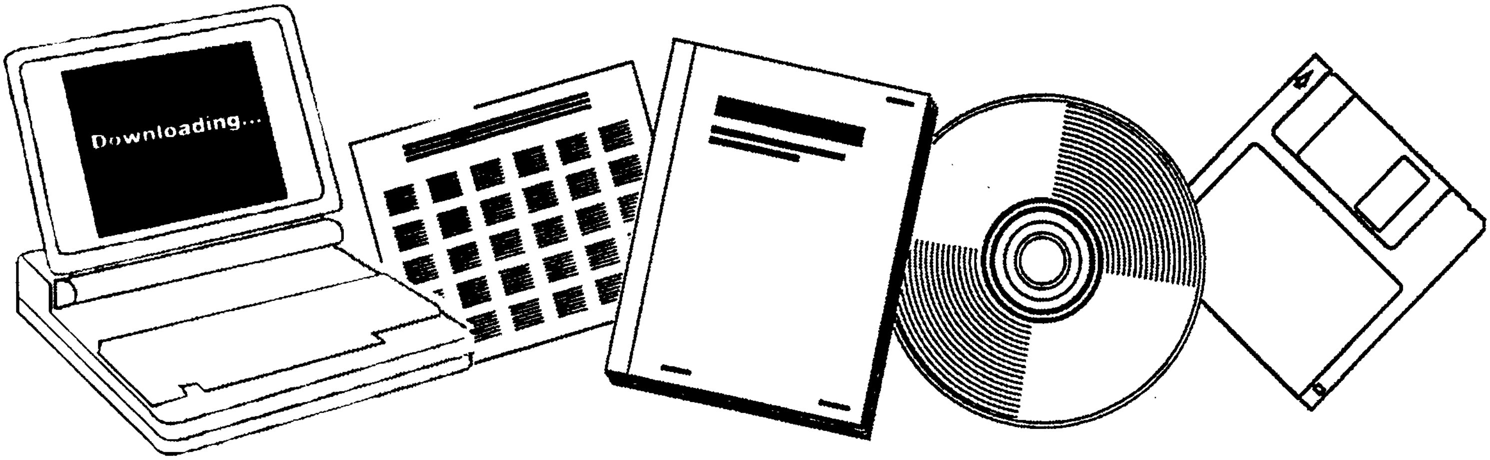

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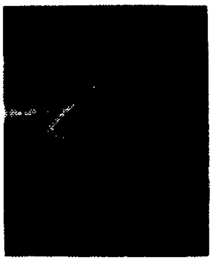

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# ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period December 21, 1979 to March 20, 1980

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

Date Prepared -- April 5, 1980

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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# FOREWORD

This report summarizes technical progress during the tenth quarter (December 21, 1979 to March 20, 1980) of a two and one-half year 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; Mr. Henry Pennline was the technical representative for DOE.

The following students contributed to the technical accomplishments and to this report: Erek Erekson, Ed Sughrue, Gordon Weatherbee, Don Mustard, Paul Moote, Clair James and Richard Bowman. Mr. Erekson and Dr. Bartholomew were the principal authors. Karen Barrett and Oscar Delgado provided typing and drafting services.

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# ABSTRACT

During CO adsorption at room temperature on nickel catalysts significant amounts of $Ni(CO)_4$ were observed to have formed. $H_2S$ poisoning increased $Ni(CO)_4$ formation. In methanation kinetic tests methane concentration had little effect on methanation rates, while $H_2O$ vapor severely inhibited the reaction. In some cases $H_2O$ vapor deactivated nickel catalysts. In poisoning studies it was determined that $H_2S$ adsorption on $Al_2O_3$ is very significant; thus $H_2S$ deactivation rates were measured on INCO nickel powder. Ruthenium has an apparent activation energy for methanation of 113 kJ/mol. Considerable deactivation is observed at 600 K and above. If deactivation of the catalyst is considered, there is no shift in apparent activation energy over a wide range of temperature as was seen on Ni. The principal investigator and students presented papers at the Fifth Rocky Mountain Fuel Symposium, the Spring Meeting of the California Catalysis Society Meeting and the 179th National ACS Meeting in Houston and entertained one visitor. The PI also presented a seminar at Cornell University and visited the University of Delaware.

# 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-$MoO_3$, 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 $H_2S$ tolerance tests, and (iv) support geometry comparisons.

Task 3. Perform kinetic studies to find intrinsic rate data for alumina-supported Ni 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 $H_2S$ poisoning rates, thermal deactivation rates, and operating temperature limits for Ni, Ni-Co, Ni-$MoO_3$, 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-$MoO_3$, 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-$MoO_3$, 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-$MoO_3$, 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) and thermal deactivation rates near the upper use temperature (in the presence and absence of steam) will be determined for Ni, Ni-Co, Ni-$MoO_3$, Ni-Pt, Ni-Ru, and Ru catalysts. $H_2S$ poisoning rates (at 525 K in the presence of 1 and 10 ppm $H_2S$ in $H_2$) will be measured over a range of temperatures for nickel 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

| | Test Procedures | Experimental Conditions |
|---|---|---|
| 1. | Temperature-Conversion Test: Measure CO conversion and methane production as a function of temperature, with and without 1% (by vol.) of steam present in the reactant mixtures. | 475-675 K<br>140 kPa<br>30,000 $hr^{-1}$<br>1% CO, 4% $H_2$, 95% $N_2$<br>(dry basis) |
| 2. | Temperature-Conversion Test (high pressure): Measure CO conversion and methane production as a function of temperature at 2500 kPa. | 475-675 K<br>2500 kPa<br>30,000 $hr^{-1}$<br>1% CO, 4% $H_2$, 95% $N_2$ |
| 3. | Steady State (24 Hr.) Carbon Deposition Test: 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.)<br>140 kPa<br>200,000-250,000 $hr^{-1}$<br>25% CO, 50% $H_2$, 25% $N_2$ |
| 4. | In situ $H_2S$ Tolerance Test: Measure intermittently the production of methane and hydrocarbons (by FID) during 24 hours exposure to feed containing 1 or 10 ppm $H_2S$ using a glass reactor. | 525 K<br>140 kPa<br>30,000 $hr^{-1}$<br>1% CO, 4% $H_2$, 95% $N_2$<br>1 or 10 ppm $H_2S$ |
| 5. | Support Geometry Tests: Measure CO conversion and methane production as a function of temperature for the same $Ni/Al_2O_3$ catalyst supported on monoliths and pellets of varying geometries. | 575-675 K<br>140 kPa<br>30,000 $hr^{-1}$<br>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 generally on schedule.

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

Task 1. Several catalysts were prepared and sent to other laboratories for industrial testing. An INCO powder/monolith was prepared. CO chemisorption studies showed that $Ni(CO)_4$ is made during room temperature adsorption. Sulfur poisoning enhances the formation of $Ni(CO)_4$ at even lower temperatures.

Task 2. No specific progress was made in this task during the past quarter. This task is essentially completed.

Task 3. During the past quarter the effects of $H_2O$ and $CH_4$ on methanation rates were studied. A high pressure water bubbler was designed and built. Studies to determine effects of $CH_4$ and $H_2O$ on the methanation kinetics were carried out. $CH_4$ has little effect, $H_2O$ a considerable effect. At high concentrations, water deactivates nickel catalysts. A ruthenium catalyst was tested for methanation activity in the Berty reactor. Ru deactivates rapidly at higher temperatures, probably due to formation of carbon, carbides, or high molecular weight hydrocarbons.

Task 4. In carbon deactivation studies in the Berty reactor it was observed that CO conversion had a large effect on the rate of deactivation. From Arrhenius plots of the deactivation rates on $E_{act}$ of 29.5 kJ/mol was determined. $H_2S$ adsorption studies showed that $H_2S$ adsorbs in very significant quantities on $Al_2O_3$ below 650 K. Several $H_2S$ deactivation tests are reported.

Task 5. Dr. Bartholomew and several students including Mr. Erekson and Mr. Sughrue attended the Fifth Rocky Mountain Fuel Symposium. Mr. Sughrue presented a paper on methanation kinetics. The PI also attended and presented papers at the Spring Meeting of the California Catalysis Society and the 179th National Meeting of the American Chemical Society. He also visited Professor Robert Merrill at Cornell University where he presented a seminar and Professor James Katzer of Delaware. Mr. Richard Pannell of Gulf Research visited our laboratory and presented an informal seminar.

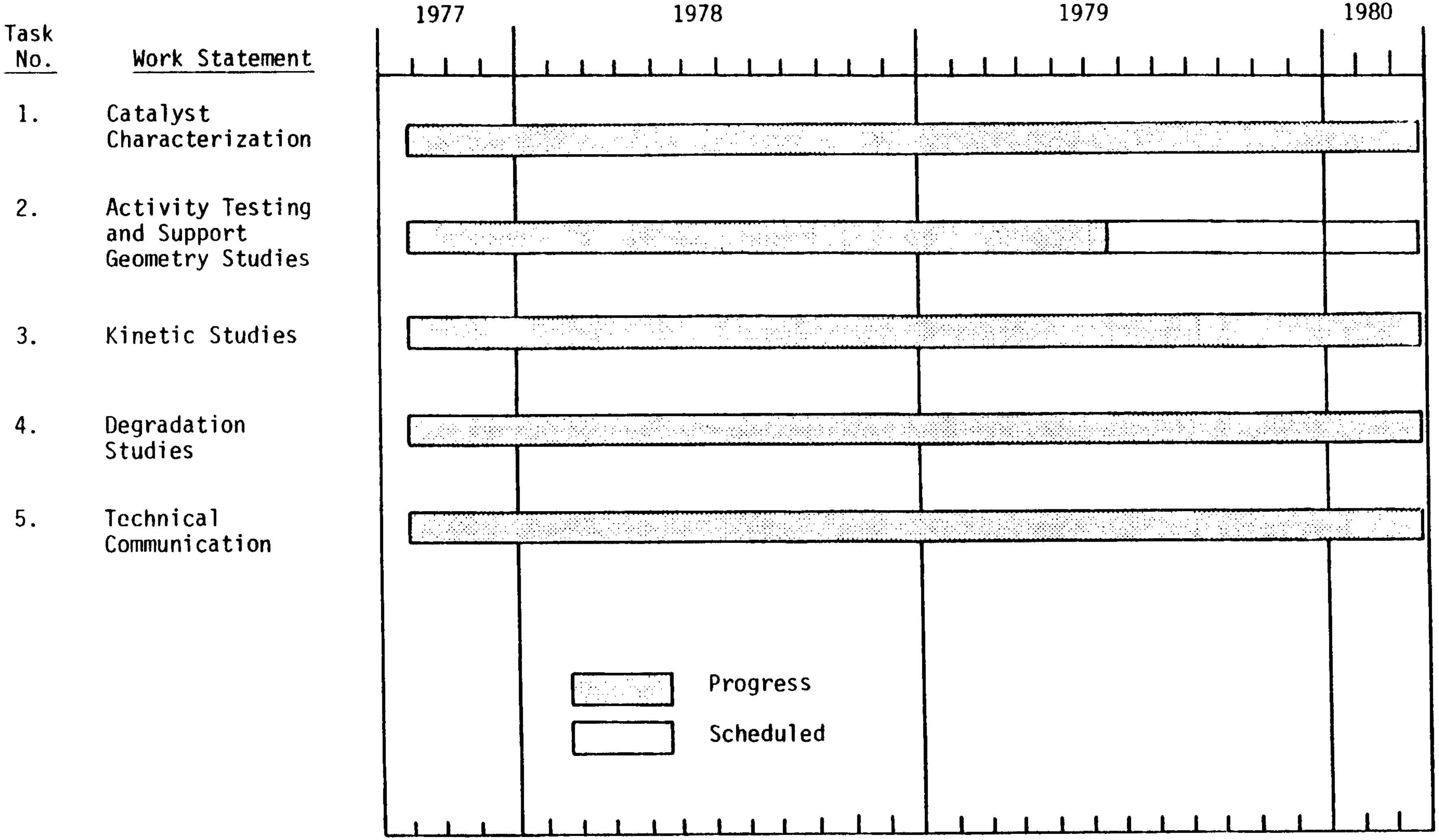

Figure 1. Project Progress Summary

# III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

## Task 1: Catalyst Characterization

### 1. Catalyst Preparation

Several catalyst samples were prepared during the last quarter. Some catalyst samples were sent to other laboratories as part of Task 5. These are listed in Table 2. Also listed are monoliths prepared for testing in this lab under Task 3. A new type of monolith catalyst was prepared for Task 4. A cordierite monolith was cut to 7 mm length. After the normal washing and drying, the monolith was dipped in a suspension of INCO nickel powder #287 in deionized water. The suspension contained 2 g of nickel powder/100 g of $H_2O$. The catalyst was placed on edge and allowed to dry slowly overnight in the hood, leaving about 0.8 g of nickel powder on each sample. These catalysts were given the number series Ni-PM-100.

### 2. Hydrogen Chemisorptions

Hydrogen chemisorption uptakes for three catalysts are listed in Table 3. Data for unsupported nickel powder (INCO) reduced at two different temperatures show that very little surface area is lost even after reduction at 675 K.

### 3. CO Chemisorption

During the past several quarters investigations have focused on the formation of nickel carbonyl during CO chemisorption on fresh and presulfided catalysts. Runs performed on Sample I of 3% $Ni/Al_2O_3$ (runs 34I-41I) constitute a full set of the data points on a single catalyst sample (see Table 4). Much of the data in Table 4 was reported previously (5). The fresh catalyst showed an initial uptake of 30.6 μmoles/g (Run 34I) and CO uptakes of 121 and 109 μmoles at 273 and 298 K respectively (Runs 35I and 36I). Run 37I was a 2 hour sulfiding treatment in a fluidized bed cell involving sufficient $H_2S$ in $H_2$ to poison approximately 50% of the metal surface area. As can be seen, the uptake did not decrease by 50%. Perhaps the previous measurements and pretreatments had the effect of further reducing the catalyst <u>or</u> changing its dispersion. Indeed, 0.81 mg and 1.06 mg of nickel was detected in the purge gas from the decomposition of $Ni(CO)_4$ formed during CO chemisorption.

From Run 39I a marked increase in the CO uptake was observed which can be attributed to the presence of sulfur on the catalyst. Sulfur apparently catalyzes the formation of $Ni(CO)_4$. After this run, the catalyst as seen in the reactor, appeared much whiter than before indicating loss of Ni. In this case six times the nickel was deposited on a heated glass tube as the gases from the chemisorption were evacuated. It appears that sulfur poisoning increases the rate of $Ni(CO)_4$ formation.

## Table 2

## Catalysts Prepared

| Recipient Laboratory | Configuration | Metal wt.% | Support wt.% | Catalyst ID |
|---|---|---|---|---|
| IGT | 31 □/cm$^2$<br>25 mm dia<br>76 mm length | 5% Ni | 10% $TiO_2$ | |
| | Extrudates | 10% Ni | 10% $CaAl_2O_4$ | |
| Conoco | 46.5 □/cm$^2$<br>12 mm dia<br>76 mm length | 5% Ni | 18% $NiAl_2O_4$ | |
| BYU | 31 □/cm$^2$<br>25 mm dia<br>12 mm length | 0.2% Ru | 4% $Al_2O_3$ | Ru-M-100 to 104 |
| | 31 □/cm$^2$<br>25 mm dia<br>12 mm length | 0.5% Ni | 10% $Al_2O_3$ | Ni-M-538 to 543 |
| | 31 □/cm$^2$<br>25 mm dia<br>12 mm length | 0.125% Ni | 2.5% $Al_2O_3$ | Ni-M-544 to 549 |

## Table 3

### Hydrogen Chemisorption Data

| Catalyst | $H_2$ Uptake (μmoles/g) |
|---|---|
| Ru-M-100 | 1.2[a] |
| INCO Powder #287 | 5.1[b] |
| INCO Powder #287 | 4.1[c] |

---

[a] Adsorption performed at 373 K.

[b] Previously reported, reduced at 573 K (5).

[c] Reduced at 673 K.

# Table 4

## Carbon Monoxide Chemisorption Measurements at 273 and 298 K Before and After Sulfur Poisoning (3% $Ni/Al_2O_3$)

| Run # | Temp K | Absorbate Gas | Uptake | CO/H | Sulfur poisoned[a] | Sulfur[b] Detected | Ni Detected |
|---|---|---|---|---|---|---|---|
| 34I[b] | 298 | $H_2$ | 30.6 | | | | |
| 35I | 273 | CO | 121 | 2.0 | | ND | 0.81 mg |
| 36I[c] | 298 | CO | 109 | 1.8 | | ND | 1.06 mg |
| 37I[b] | | | | | | | |
| 38I[c] | 298 | $H_2$ | 23.2 | | Yes | ND | |
| 39I | 273 | CO | 950 | 20.4 | Yes | ND | 6.66 mg |
| 40I[d] | 298 | CO | 314 | 6.8 | Yes | NA[f] | NA[f] |
| 41I[d] | 297 | $H_2$ | 8.0 | | | | |
| Remainder | | | | | | 210 µg | 8.0 mg |

---

[a] Sample poisoned in a fluidized bed at around 725 ± 5 K in 10 ppm $H_2S$ in $H_2$ until approximately 1/2 of the sites were covered. The flow rate of the 10 ppm $H_2S$ mix was 280-300 $cm^3$/min. The amount of sample was 1.0 g.

[b] According to wet chemical technique described earlier (3).

[c] Additional 2 h reduction before chemisorption.

[d] Additional 3 h reduction before chemisorption.

[e] Additional 1 h reduction before chemisorption.

[f] This sample was lost during the wet chemical sulfur determination.

Run 40I showed a large CO uptake, but not as large as in Run 39I. This decrease is undoubtedly due to the removal of Ni from the catalyst in the process of $Ni(CO)_4$ formation. A final $H_2$ uptake showed only 8 μmoles/g of surface area level. The catalyst at this point was a light grey color as a result of removal of Ni from the surface. The remainder of the sample contained only 8 mg (0.8%) nickel and 210 μg (8 μmoles) of sulfur, suggesting that 75% of the nickel had been lost but none of the sulfur had been lost.

Hydrogen and carbon monoxide chemisorptions were performed on Ni-A-120 (3% $Ni/Al_2O_3$) before and after complete poisoning (see Table 5). $H_2$ uptake decreased to zero, CO uptake at 273 K increased by a factor of 2 after poisoning. In a repeat run, however, only 1/20th as much CO adsorbed and the sample was almost white, indicating severe loss of Ni. This loss was confirmed by chemical analysis of the gaseous effluent and the catalyst following CO adsorption.

In the fresh catalyst no loss of Ni was observed from the catalyst after CO adsorption at 273 K. There was also no Ni carbonyl found in the gaseous effluent after adsorption. After sulfur poisoning 50 and 100% of the catalyst and adsorbing CO at 273 K, about 50 and 95% of the nickel was removed. Significant amounts of Ni were found in the gas phase after adsorption.

### 4. Sulfur Analysis

Several INCO nickel powder catalysts tested in Task 4 were analyzed for sulfur. Data from this analysis is shown in Table 6. Because of the reactor configuration it was only possible to take random samples from the catalyst bed. Most of these samples were not completely poisoned. Nevertheless, for some samples more $H_2S$ was adsorbed on the sample than could be accounted for in a surface sulfide. This shows that multi-layered adsorption may well be occurring even at $H_2S$ concentration as low as 1 ppm.

## Task 2: Activity Testing

No specific progress was made under this task during the past quarter. However, plans have been made to finish activity tests of monolithic nickel catalysts of different geometries during the next quarter.

## Task 3: Kinetic Studies

The effects of the reaction products, $H_2O$ and $CH_4$, on the kinetics of methanation were examined this quarter. The addition of $CH_4$ in quantities up to 50% of the feed gas resulted in no significant changes in the reaction rate. Figure 2 shows this lack of change in reaction rates versus % $CH_4$ at 3 temperatures.

Table 5

$H_2$ and CO Uptakes for 3% Ni/$Al_2O_3$
Before and After Complete Sulfiding

| | $H_2$ Uptake (μmoles) | CO Uptake (μmoles) | CO/$Ni_s$ |
|---|---|---|---|
| Fresh | 41.5 | 316 | 3.8 |
| Poisoned (Run 1) | 0 | 563 | 6.8 |
| Poisoned (Run 2) | 0 | 35 | --- |

## Table 6

### Sulfur Analyses of Poisoned INCO Powder Catalysts

| Catalyst[a] | gm of Catalyst Sample | mg S | $S/Ni_s$[d] |
|---|---|---|---|
| 6.6 ppm, 525 K | 0.081 | 6.6 | 0.25 |
| | 0.099 | 35.5 | 1.10 |
| 1 ppm, 625 K | 0.1445 | 7.5 | 0.16 |
| | 0.1309 | 8.0 | 0.19 |
| | 0.0915 | 6.1 | 0.20 |
| | 0.1048 | 6.6 | 0.19 |
| 1 ppm, 525 K | 0.0971 | 3.2 | 0.10 |
| | 0.0908 | 1.8 | 0.06 |
| 1 ppm, 550 K | 0.0503 | 9.0 | 0.55 |
| 0.2 ppm, 600 K | 0.0527 | 3.2 | 0.19 |
| 1 ppm 575 K[b] | 0.1485[c] | 62.4 | 1.28 |
| | 0.1745[c] | 28.7 | 0.50 |
| | 0.2831 | 50.9 | 0.55 |
| | 0.1032 | 14.3 | 0.42 |

---

[a] All catalyst samples were unsupported INCO powder #287.

[b] These four samples constitute the complete catalyst sample.

[c] There was considerable glass wool contained in this sample. The weight of the actual nickel was probably closer to 0.16 gm. With this weight, $S/Ni_s = 0.55$.

[d] This ratio is the moles of S detected divided by the μmoles of Ni surface atoms using 5.1 μmoles of $H_2$/g of INCO powder reported previously (5).

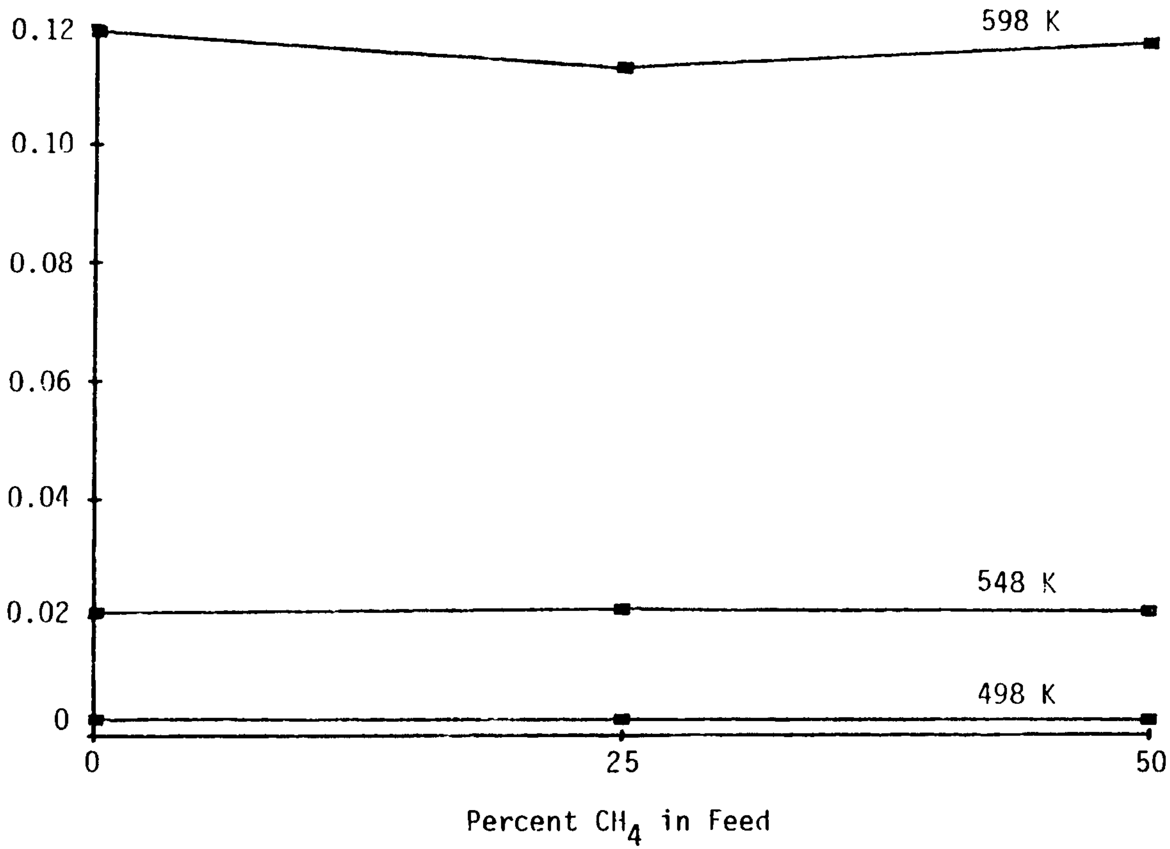

Figure 2. Effect of $CH_4$ concentration on methanation turnover numbers. Tests were made in the Berty reactor at the temperature listed and 690 kPa.

While the addition of $CH_4$ to the reactant gas was accomplished with little modification of the reactor system, the addition of water required the installation of a bubbler as shown in Figure 3. The $N_2$ diluent was diverted through the bubbler which consisted of a sampling cylinder filled with $H_2O$ and glass wool. The purpose of the glass wool was to break up gas bubbles and to reduce entrainment. To further reduce entrained droplets a trap was added behind the bubbler. Using this bubbling system complete saturation of the flowing gas was obtained. During the test, the level of $H_2O$ in th feed gas was controlled by raising the temperature of the bubbler unit.

Water had a significant inhibiting effect on the production of $CH_4$ as shown in Figure 4 where the rate of $CH_4$ formation at various percentages of $H_2O$ in the reactor are compared with the initial $CH_4$ production without $H_2O$. $H_2$ and CO concentrations were 3 and 1%. At 498 K there was approximately an 8% decrease in activity at 5% $H_2O$. At 523 K, the inhibition effect was stronger and the rate of $CH_4$ production at 3% $H_2O$ is only 65% of the initial without $H_2O$ rate. Finally at 573 K and 3% $H_2O$, only 45% of the initial rate was obtained.

The addition of $H_2O$ also produced increasing amounts of $CO_2$ indicating an increasing importance of the water gas shift. Irreversible deactivation of the catalyst was also noticed as the % $H_2O$ was increased. At 498 K after exposure to $H_2O$ percentages between 5 and 10 followed by, removal of the $H_2O$, no increase in $CH_4$ production occurred. Several hours of flowing pure $H_2$ across the catalyst resulted in recovery of much but not all of the original catalyst activity. A similar phenomenon was noticed at 523 K where addition of $H_2O$ in percentages of up to 2.0% was completely reversible whereas 3% $H_2O$ produced again the semi-irreversible behavior. At 573 K this threshold occurred at 0.5% $H_2O$. It is thought that the higher $H_2O$ concentration not only produced the $H_2O$ shift reaction in competition with methanation but also promoted an increased surface converage of adsorbed oxygen resulting in some NiO formation and loss of catalyst activity.

A 0.2% Ru on alumina monolith catalyst was tested for methanation activity in the past quarter. Specific rates were obtained using the Berty recycle reactor at temperatures from 515 K to 615 K and 690 kPa (see Figure 5). Conversions were maintained below 10% by increasing space velocities as temperature increased. Methanation activity was found to be highly dependent on temperature over the entire temperature range studied with an apparent activation energy of 113 kJ/mol. Deactivation of the catalyst was temperature dependent with minimal deactivation occurring below 550 K. However, above 575 K extensive deactivation occurred within the first half hour of catalyst use (Figure 6). This shows that the true activation energy behavior is masked if steady state rates are used instead of initial rates.

## Task 4: Degradation Studies

Carbon deactivation studies to investigate temperature and conversion effects were continued this quarter using the Berty Recycle Reactor. Five tests at various temperatures from 523 to 623 K were

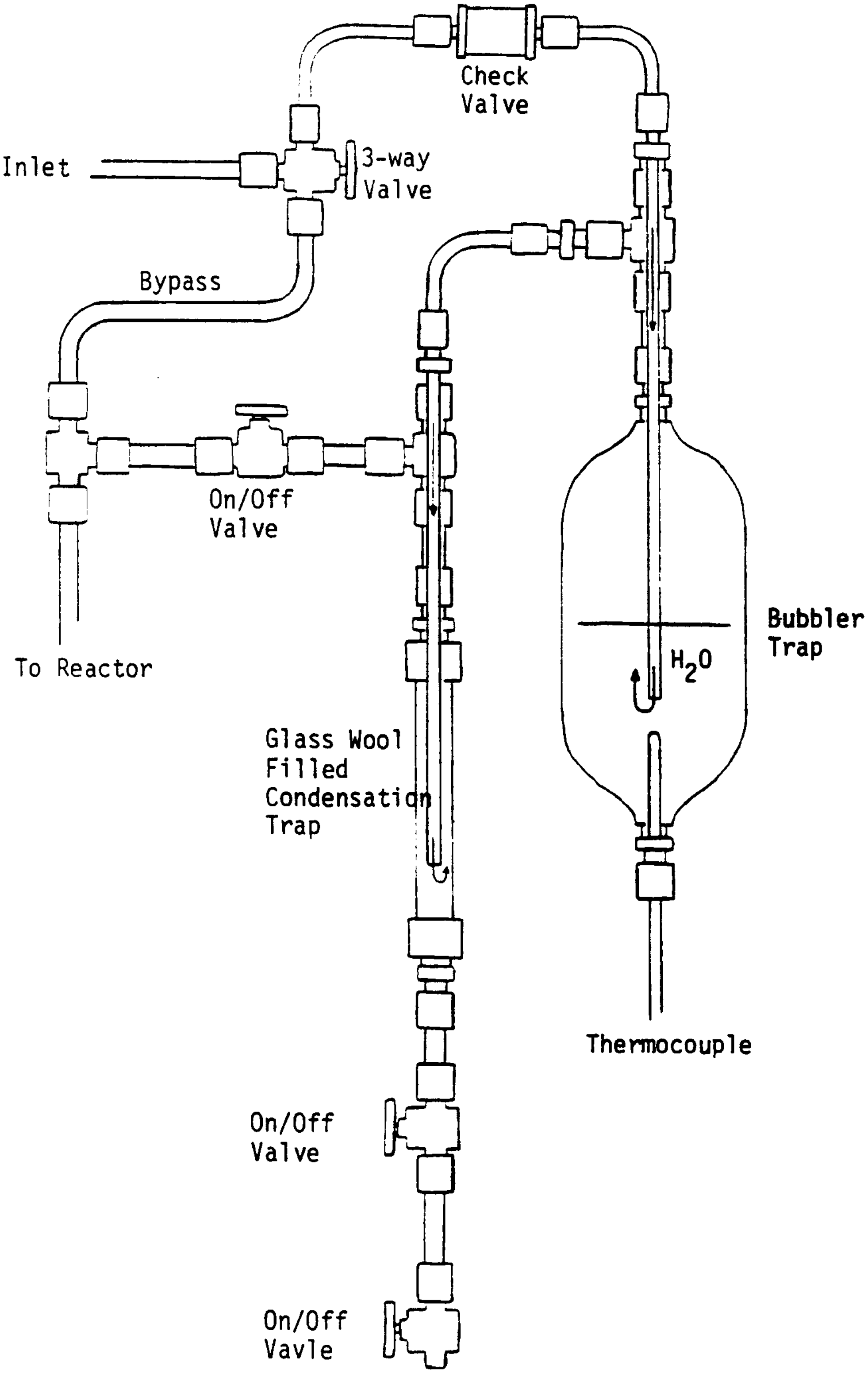

Figure 3. High Pressure Water Bubbler for Berty Reactor System.

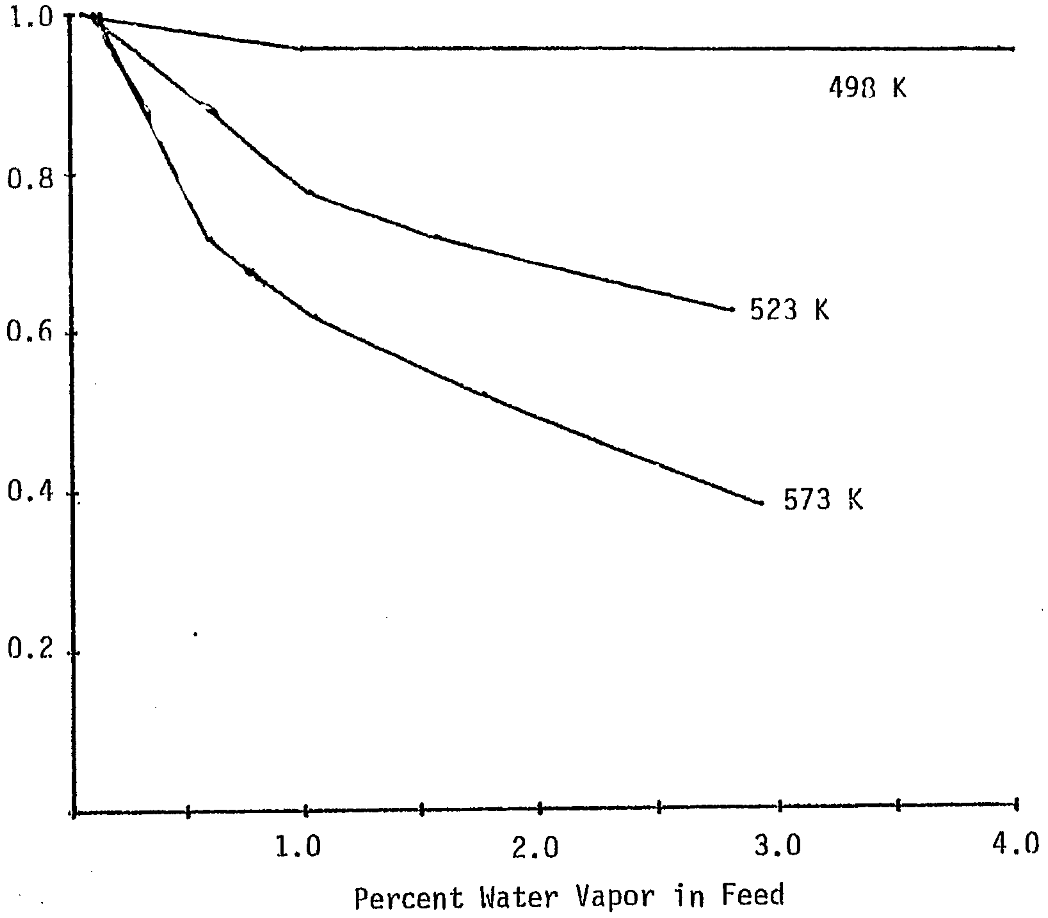

Figure 4. Effect of $H_2O$ concentration on methanation activity. Activity is defined as rate with $H_2O$/initial rate without $H_2O$.

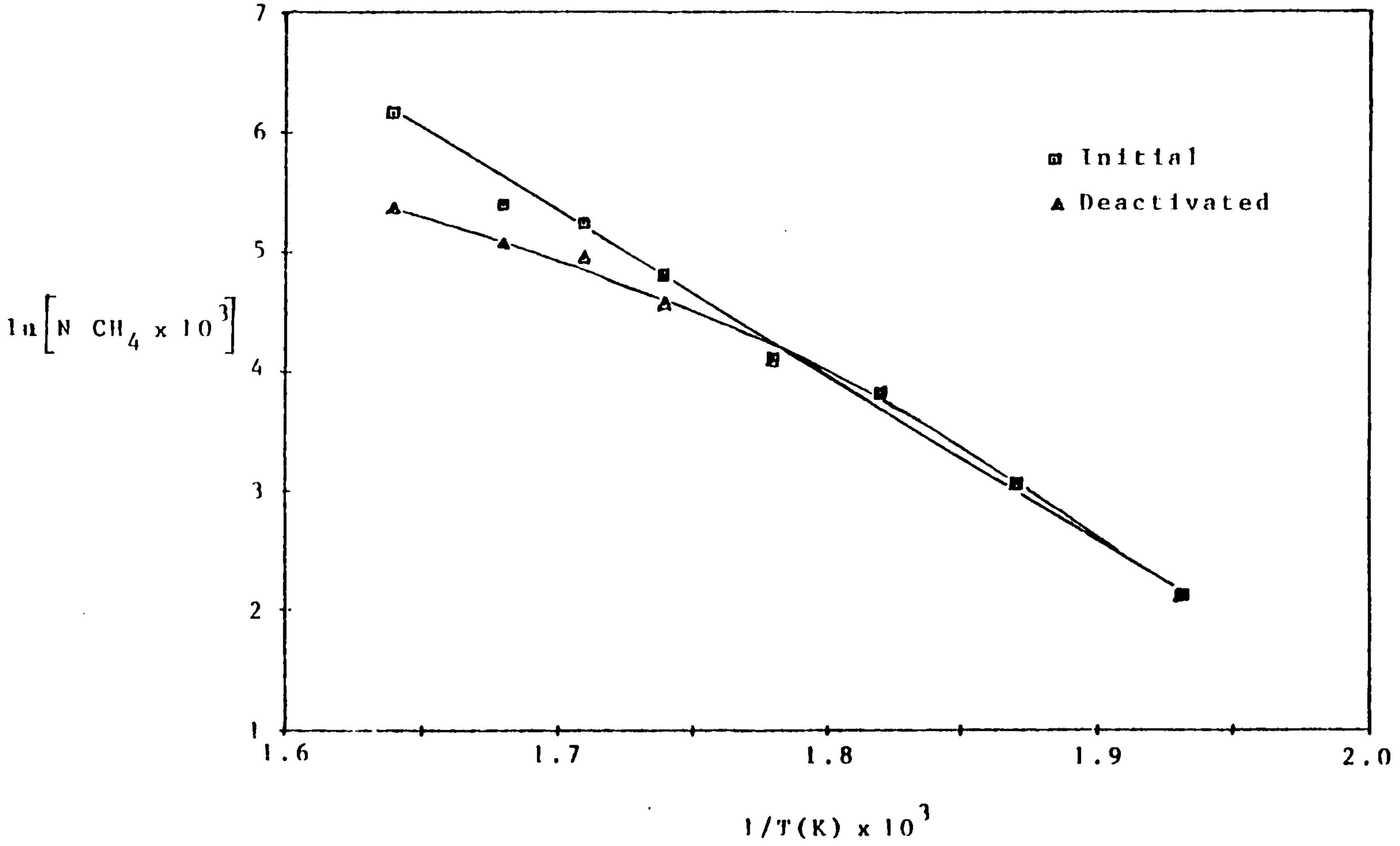

Figure 5. Arrhenius Plot of Catalyst Activity versus Reciprocal Temperature for Ru-M-100 at 690 kPa.

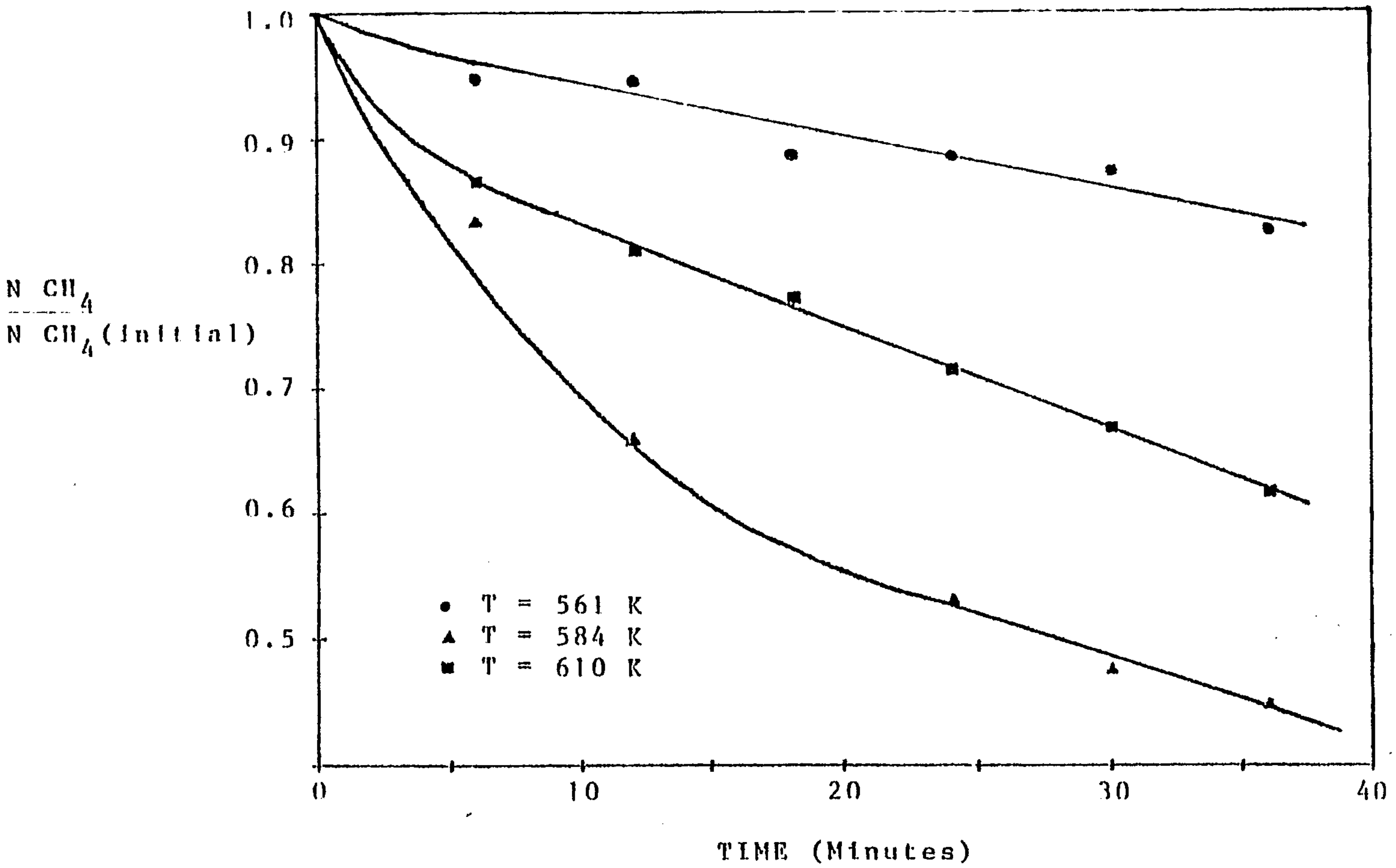

Figure 6. Carbon deactivation of monoliths, comparing three temperatures. Tests were performed in the Berty reactor at 690 kPa.

made. Figure 7 shows the results of two tests at 548 and 598 K indicating that the rate of deactivation increased with temperature. Figure 8 reports the natural logarithm of the rate of deactivation versus the inverse temperature. The slope of this curve produces an activation energy of approximately 29.5 kJ for the rate of deactivation. This number is close to the activation energy reported by SRI for the transformation of $C_\alpha$ to $C_\beta$.

Figure 9 compares the effect of reactor conversion on the deactivation of the catalyst. As conversion increases in the reactor from 0.1 to 0.92, the deactivation decreases to almost insignificant values. This indicates that the deactivation is not due to an impurity but to reactor conditions favoring carbon formation on the catalyst. High conversions caused a marked decrease in the partial pressure of CO. Conversely, there is a sharp increse in $H_2O$ partial pressure which results not only in higher $H_2/CO$ ratios due to the water-gas-shift reaction but also in considerable $H_2O$ gasification of the carbon on the catalyst. Decreasing the rate of carbon formation on the catalyst in turn decreases the rate of carbon deactivation.

It was shown previously (6) that good mixing is obtained in the quartz CFSTR. However, it remained to be shown that $H_2S$ did not adsorb on the reactor walls in appreciable amounts. Sulfur adsorption tests in the quartz CFSTR were performed initially by Fitzharris (7). These tests were repeated in the present study and several additional tests were performed.

In order to test the adsorption of $H_2S$ the reactor was purged with flowing $H_2$. Then, at time zero the flow was switched from pure $H_2$ to 2.1 ppm $H_2S$ at the same volumetric rate. The response of the outlet stream is plotted in Figure 10. Also plotted is the ideal response assuming perfect mixing and no $H_2S$ adsorption. The actual response deviates from ideality; thus piecewise integration of the area between the curves yields the total adsorption, i.e. 0.05 μmoles $H_2S$. This amount was negligible compared to the catalyst uptakes measured in all the tests performed with this reactor.

Further $H_2S$ adsorption tests were performed on catalyst supports and Ni catalysts. $H_2S$ uptakes are shown in Table 7, at various temperatures and $H_2S$ concentrations. Both cordierite monoliths without an alumina washcoat and the empty reactor, showed little change in uptake with temperature. At 678 K the cordierite monolith with a 2% $Al_2O_3$ washcoat adsorbed 0.2 μmoles $H_2S$ g, but at 525 K a similar monolith took up about 12 μmoles $H_2S$/g. This test was terminated long before the $H_2S$ capacity was reached. This suggests that the high surface area alumina washcoat is the material adsorbing the $H_2S$ at the lower temperature. Below 670 K the adsorption capacity rapidly increases to values which interfere with measurements of $H_2S$ adsorption on the nickel surface of catalysts. The addition of one percent $H_2O$ vapor greatly reduced $H_2S$ adsorption on the support at 589 K, but was still too large to be neglected. A monolith impregnated with 0.1% Ni and 2% $Al_2O_3$ was tested at 678 K. The uptake was 3.3 μmoles of $H_2S$.

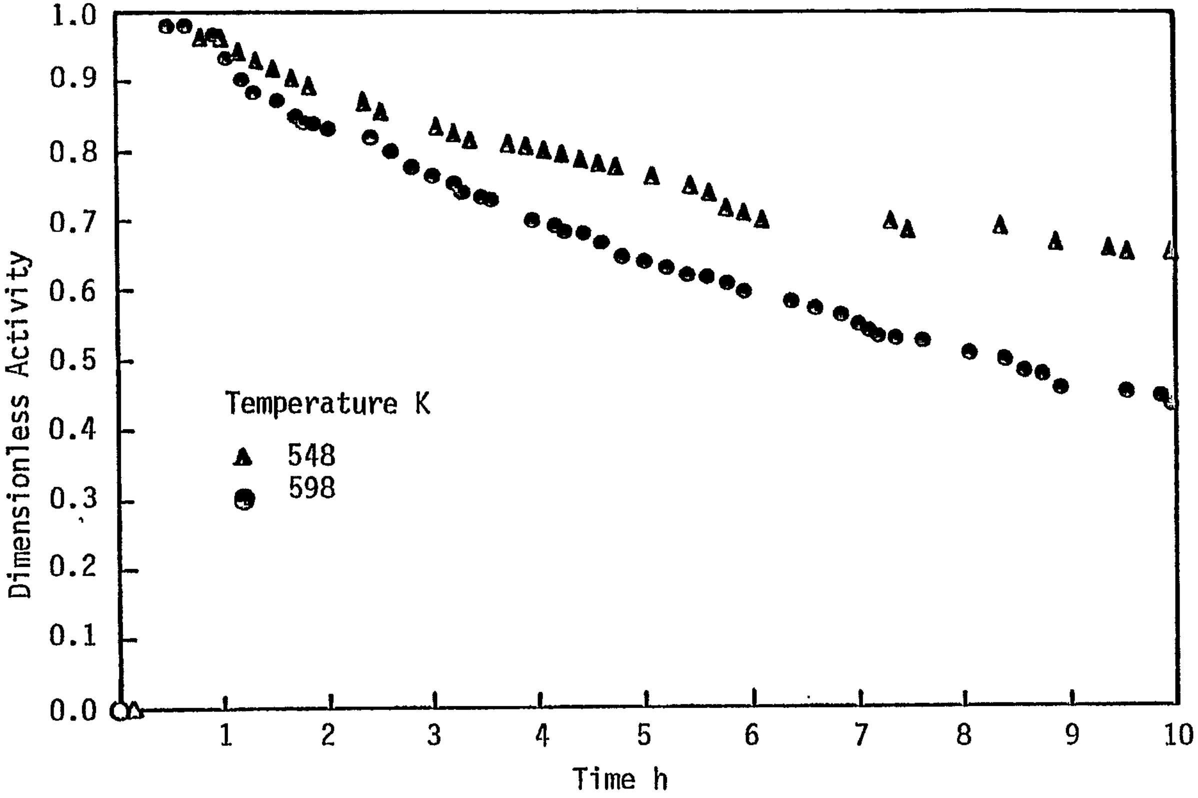

Figure 7. Carbon deactivation of Ni monoliths, comparing two temperatures. Tests were performed in the Berty reactor at 690 kPa.

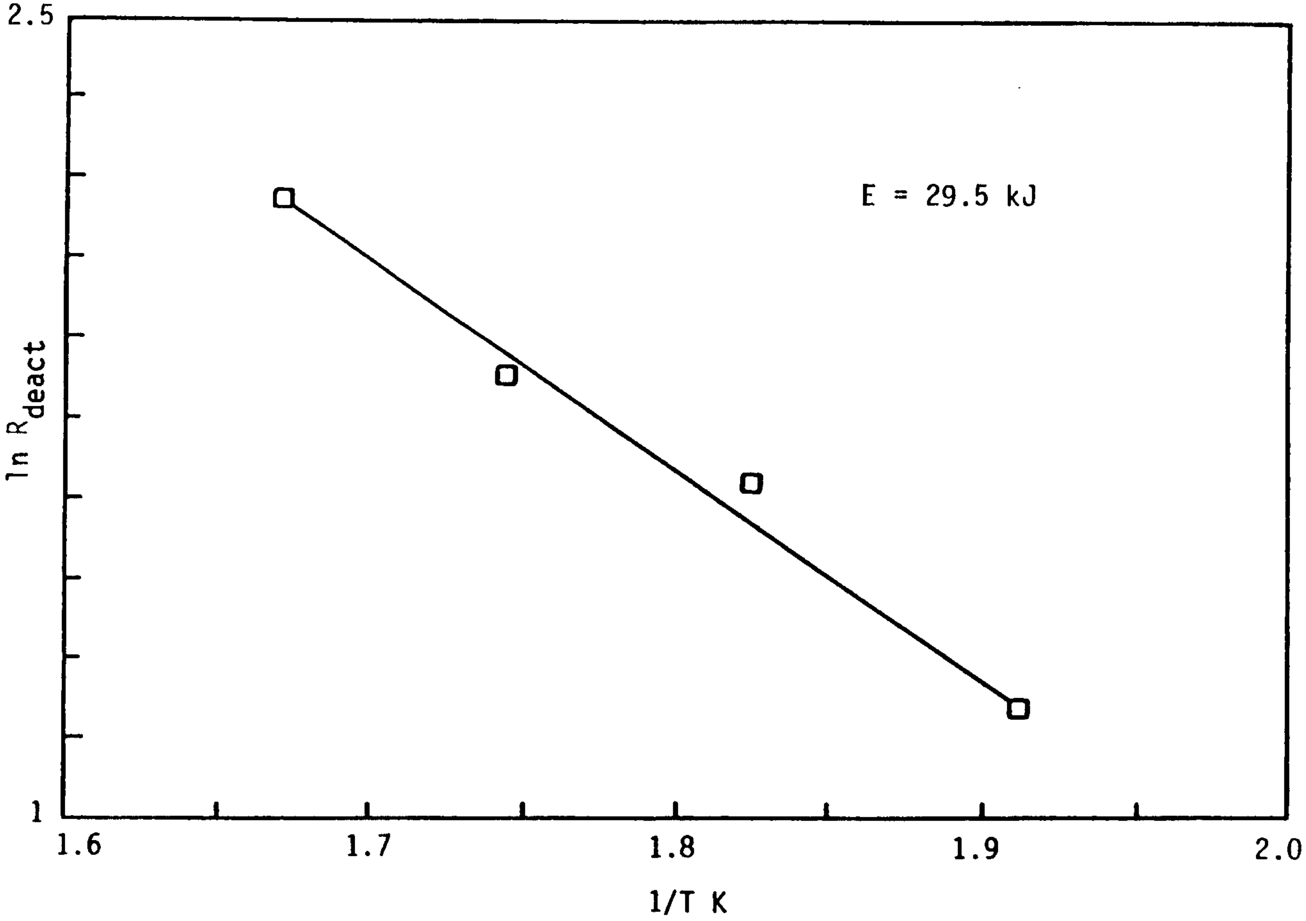

Figure 8. Arrhenius plot of carbon deactivation rates, assuming $R_{deact} = k$ where k is a function of T only.

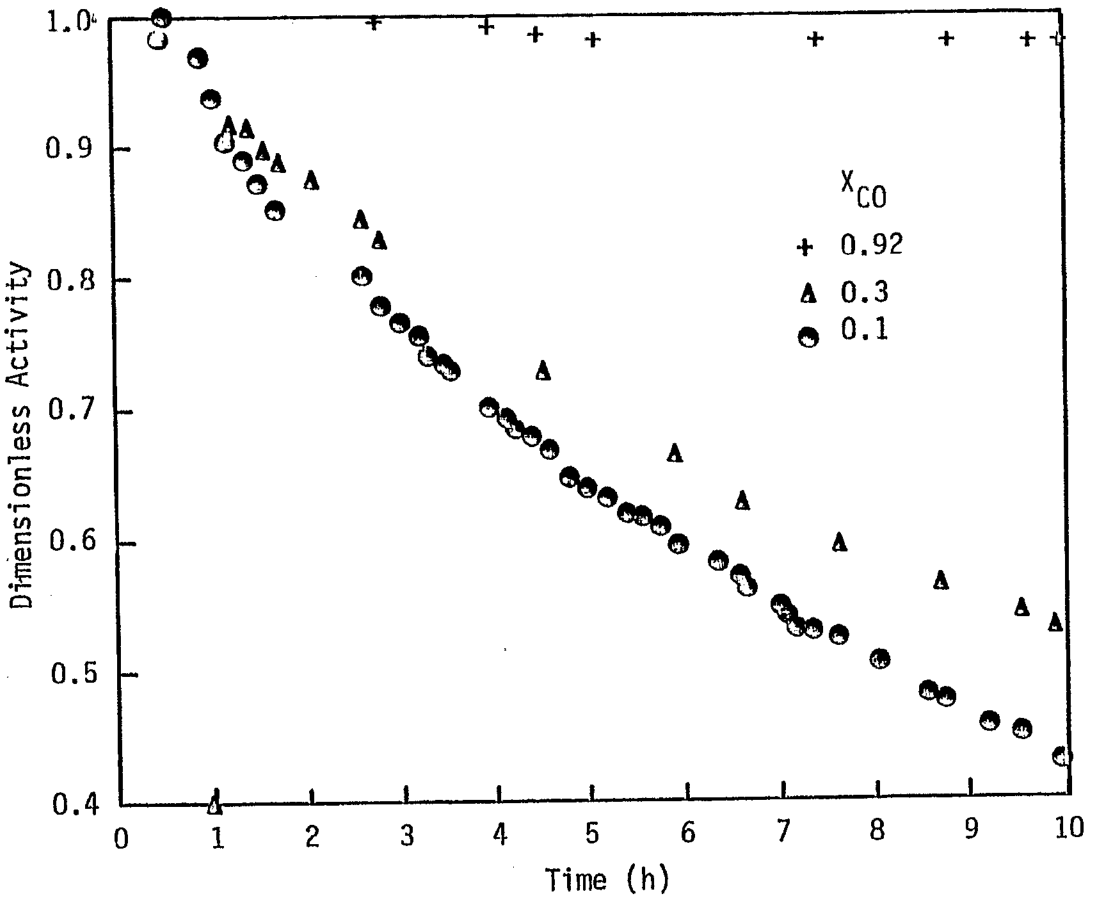

Figure 9. Effect of CO conversion on carbon deactivation. Three separate conversions are shown. Temperature = 598 K and pressure = 690 kPa.

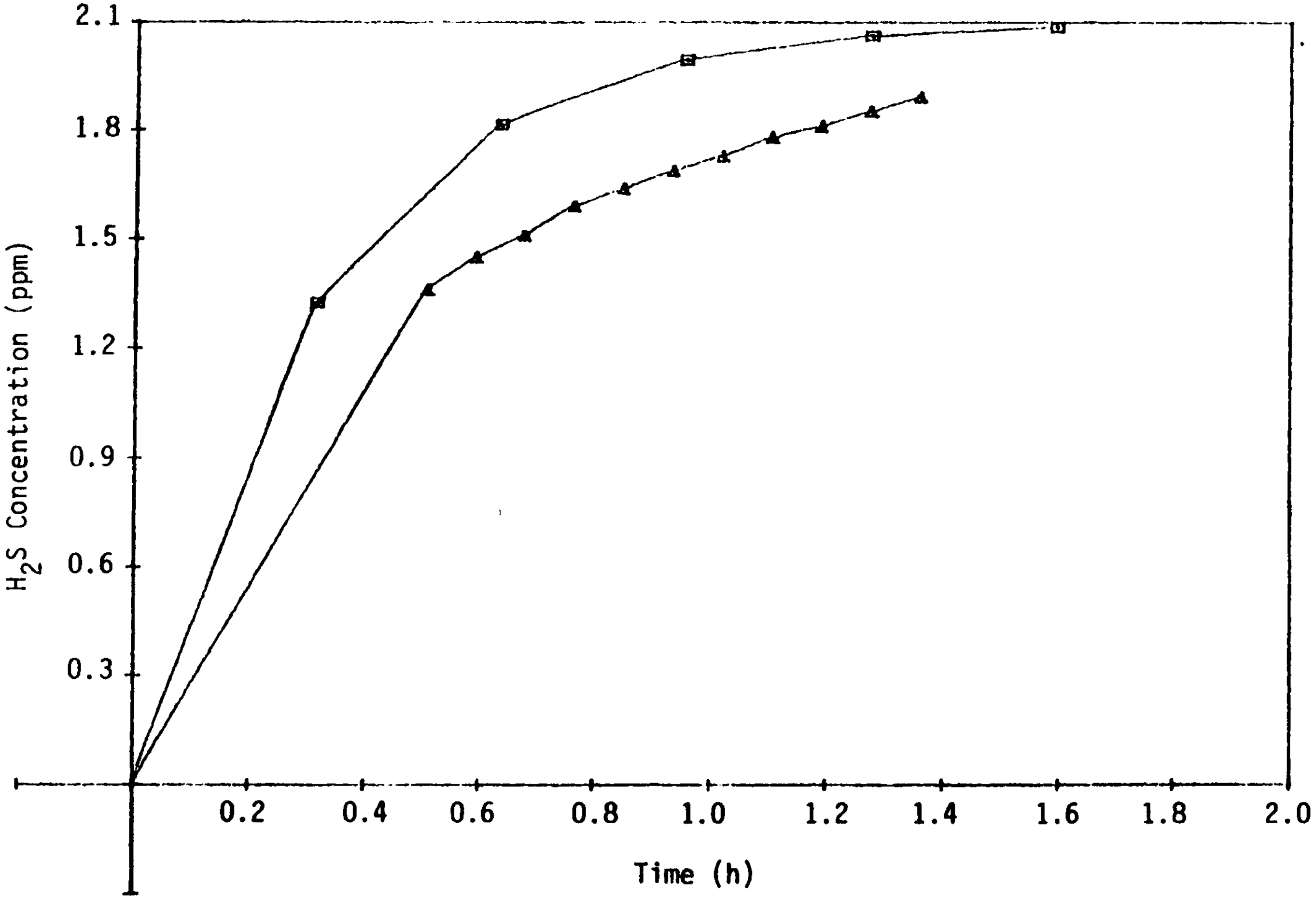

Figure 10. Response of quartz CFSTR with cordierite monolith to a step increase (2.1 ppm) in $H_2S$ concentration. Temperature = 678 K and flow rate was 68 ml/min.

## Table 7

## $H_2S$ Adsorption Uptakes

| Catalyst | Temperature (K) | $H_2S$ Concentration (ppm) | Uptake (μmoles/g) | Uptake μmoles/g $Al_2O_3$ |
|---|---|---|---|---|
| None (reactor only) | 678 | 2.1 | 0.05 | |
| | 525 | 10 | 0.15 | |
| Cordierite Monolith (no $Al_2O_3$) | 678 | 2.1 | 0.23 | |
| | 525 | 10 | 0.73 | |
| Cordierite Monolith (with $Al_2O_3$) | 678 | 2.1 | 0.20 | 10 |
| | 650 | 2.1 | 1.1 | 55 |
| | 525 | 10 | >12 | >600 |
| | 589 | 7.3 | 1.5[a] | 55[a] |

NOTE: All runs were performed in a Quartz mixed-flow reactor.

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[a] For this run 1% $H_2O$ vapor was added to the inlet stream.

Several $H_2S$ deactivation tests were made on INCO powder in glass fixed-bed reactor cells. The conditions for these tests were 525 K, 100 kPa, 1% CO and space velocities from 40,000 to 80,000 $h^{-1}$. Data from these tests are shown in Table 8. Data from Uken's work (8) is added for comparison. $k_d$ is the deactivation rate constant as calculated by the Bartholomew and Fowler deactivation model (9). $\theta_f$ represents the number of $H_2S$ molecules required to deactivate each nickel surface atom. It is calculated by finding the intersection of the activity vs. $\theta$ ($H_2S$ molecule/initial H adsorption site) curve with the abscissa. Generally, the value $k_d$ increases and $\theta_f$ decreases with decreasing $H_2S$ concentration showing that $H_2S$ deactivates more nickel sites/$H_2S$ molecule at lower concentrations.

While 525 K was chosen for most $H_2S$ deactivation tests because it closely corresponds to the temperature at the entrance of a commercial recycle methanator. In addition, several runs were made over the temperature range of 525 to 625 K to determine the dependence of temperature on the rate of deactivation. In Table 9 the $k_d$ values and $\theta_f$ values for their runs are compared. At 1 ppm $H_2S$ $k_d$ increased and $\theta_f$ decreased from 525 to 625 K showing that nickel was poisoned by $H_2S$ more rapidly at the higher temperature. For the runs at 0.2 ppm $H_2$, $k_d$ did not change significantly and $\theta_f$ decreased only slightly from 525 to 575 K. At 1 ppm the apparent activation energy for $k_d$ is 18.4 kJ/mol, while the activation energy is 2.4 kJ/mol at 0.2 ppm. This suggests that at very low concentrations temperature has little effect on the rate of deactivation.

The effect of CO concentration on $H_2S$ deactivation was studied by making four tests with different CO concentrations while keeping the $H_2S$ concentration constant. Table 10 shows the $k_d$ and $\theta_f$ values. During these tests $H_2S$ appeared in the exit stream when the CO concentration was 5% or above. For the 20% CO run only 1/4th of the reactant $H_2S$ adsorbed on the catalyst while the rest passed through to the product stream. This probably means that at higher CO concentrations adsorbed CO or carbon inhibited $H_2S$ adsorption on the nickel surface lowering the sticking coefficient of $H_2S$.

In Table 10, $\theta_f$ values were calculated according to $H_2S$ adsorbed and not total $H_2S$ entering the reactor. For the 20% CO run $\theta_f$ was much lower than any run at 2% CO. This test was performed at 525 K and well below CO partial pressures that would cause carbon deactivation according to recent work from this laboratory (10). However, since $H_2S$ poisons the hydrogenating ability of catalysts (11), these catalysts may accumulate carbonaceous material at lower temperatures and CO pressures than in sulfur-free streams.

Two tests were made with reactant $H_2O$ vapor added to the feed. These tests are compared with a similar dry test in Table 11. With $H_2O$ vapor present $k_d$ increases for the unsupported catalyst. For the supported catalyst $H_2S$ adsorption capacity greatly increased since the alumina adsorbed large amounts of $H_2S$. Thus, $k_d$ is smaller as not all the $H_2S$ deactivated the metal surface. Thus, a supported catalyst maintains activity longer in the presence of $H_2S$ since the support adsorbs some of the $H_2S$.

Table 8

Deactivation Rate Constants For Several $H_2S$ Concentrations

| $H_2S$ Concentration ppm | $P_{H_2S}/P_{H_2}$ $x\ 10^6$ | $k_d$ [a] | $\theta_f$ [b] |
|---|---|---|---|
| 10 | 12 | 2.0[c] | 2.0[c] |
| 6.6 | 33 | 1.3 | 5.9 |
| 1.0 | 5.0 | 2.0 | 2.8 |
| 1.0 | 1.0 | 2.0 | 3.0 |
| 0.5 | 0.5 | 2.3 | 1.8 |
| 0.2 | 0.2 | 4.8 | 1.0 |

NOTE: All runs were made on INCO nickel powder at 525 K, 100 kPa, and with large $H_2$/CO ratios. The space velocity was between 40,000 and 80,000 $h^{-1}$.

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[a] $k_d$ is the deactivation rate constant from the Bartholomew model (9).

[b] $\theta_f$ is the number of adsorbed $H_2S$ molecules required to deactivate each surface nickel site.

[c] From Uken (8).

Table 9

Temperature Effects on Deactivation Rate Constants

| Temperature (K) | $k_d$[a] | $\theta_f$[b] |
|---|---|---|
| | 1 ppm $H_2S$ | |
| 525 | 2.0 | 3.0 |
| 575 | 2.3 | 2.1 |
| 625 | 4.0 | 1.6 |
| | 0.2 ppm $H_2S$ | |
| 525 | 4.8 | 1.0 |
| 575 | 4.8 | 0.85 |
| 600 | 5.2 | 0.87 |

NOTE: All runs were performed on INCO nickel powder at 100 kPa and 1 to 2% CO with hydrogen diluent. Thus, the ppm $H_2S$ and the $P_{H_2S}/P_{H_2}$ ratio were the same.

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[a] $k_d$ is the deactivation rate constant from the Bartholomew model.

[b] $\theta_f$ is the number of adsorbed $H_2S$ molecules required to deactivate each surface nickel site.

Table 10

Deactivation Rate Constants for a Range of CO Concentrations

| Mole % CO | $H_2S$ Concentration ppm | $P_{H_2S}/P_{H_2}$ x $10^6$ | $k_d$[a] | $\theta_f$[b] |
|---|---|---|---|---|
| 2 | 0.2 | 0.2 | 4.8 | 1.0 |
| 5 | 0.2 | 0.21 | 6.3 | 0.79 |
| 10 | 0.2 | 0.22 | 9.0 | 0.59 |
| 20 | 0.2 | 0.25 | 22 | 0.44 |

NOTE: All runs were made on INCO nickel powder samples at 525 K, 100 kPa, and with a hydrogen diluent. The space velocity was 80,000 $h^{-1}$.

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[a] $k_d$ is the deactivation rate constant from the Bartholomew model

[b] $\theta_f$ is the number of adsorbed $H_2S$ molecules required to deactivate each surface nickel site.

## Table 11

### Effects of $H_2O$ Vapor on $H_2S$ Deactivation Rate Constants

| Catalyst | Mole % $H_2O$ | $k_d$[a] | $\theta_f$[b] |
|---|---|---|---|
| INCO Powder | 0 | 4.8 | 1.0 |
| INCO Powder | 1 | 6.7 | 1.4 |
| 3% $Ni/Al_2O_3$ | 1 | 4.4[c] | 1.4[c] |

NOTE: All runs were made at 525 K, 100 kPa, 2% CO in Hydrogen and 0.2 ppm $H_2S$.

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[a] $k_d$ is the deactivation rate constant from the Bartholomew model (9).

[b] $\theta_f$ is the number of adsorbed $H_2S$ molecules required to deactivate each surface nickel site.

[c] These values were calculated assuming that $H_2S$ adsorbs only on the nickel metal surface.

Fitzharris (7) in his studies on nickel showed that the methanation activity of their catalyst was proportional to the square of the unsulfided surface area, suggesting that the stoichiometry of $H_2S$ deactivation was on S atom adsorbed per 2Ni surface sites (at $H_2S$ concentrations of 13-80 ppb and 661 K in 4% CO in $H_2$ in a quartz CFSTR). Similar runs were made in this study using special INCO powder monoliths at 525, 575 and 625 K. The conditions for the test were 2% CO in $H_2$, 0.2 ppm $H_2S$, and total flow rate equal to 150 ml/min. Activity vs. functions of the unsulfided surface area were plotted. Ideally, if the stoichiometry of $H_2S$ adsorption is $2Ni_s$ per $S_{ads}$, then the curves should fit a straight line when plotted against the square of unsulfided surface area. For the runs at 525 and 575 K the best fit of the activity data is to a stoichiometry of 1 $Ni_s/S_{ads}$. For the run at 625 K a plot of activity vs. "sulfur-free" area to the 1.5 power corresponding to 1.5 $Ni_s/S_{ads}$, was the best fit of the data. These data show that the stoichiometry of deactivation may change with temperature.

## Task 5: Technical Interaction and Technology Transfer

During the past quarter, the principal investigator, Dr. Bartholomew, and several students attended and participated in several technical meetings, communicated with other workers regarding research problems related to $CO/H_2$ synthesis; and visited other laboratories. On February 14th, Dr. Bartholomew visited with Professor Robert Merrill at Cornell University and pesented a Surface Science Seminar dealing with "Adsorbed Species in CO Hydrogenation on Nickel." He also visited with Professor James Katzer at the University of Delaware the following two days (February 15 and 16th) to work with him on a literature review of sulfur poisoning. On February 21-22 the principal investigator and several students attended the Fifth Rocky Mountain Fuel Symposium. The meeting featured a presentation by Dr. Heinz Heineman of the Lawrence Berkeley Laboratory on Liquid Fuels from Coal (including indirect liquefaction). Mr. Edward L. Sughrue of our group presented a paper on "Kinetic Studies of Nickel Methanation Catalysts."

Dr. Richard Pannell of Gulf Research visited us on February 26 and presented an informal seminar on CO hydrogenation on cobalt and iron. On March 13-14 Dr. Bartholomew attended the Spring meeting of the California Society and presented a paper on "Determination of Metal Cryustallite Size in Supported Nickel Catalysts." He also attended the 179th meeting of the American Chemical Society in Houston on March 25-27 and presented two papers: "Nickel-Support Interactions: Their Effects on Particle Morphology, Adsorption and Activity Selectivity Properties," and "Sulfur Poisoning of CO and $H_2$ Adsorption on Supported Nickel." Mr.A. Douglas Moeller, a recent M.S. graduate from our group presented a paper dealing with "Deactivation by Carbon and Regeneration of Nickel and Nickel Molybdenum Methanation Catalysts."

## IV. CONCLUSIONS

1. Nickel carbonyl is formed in measureable amounts during room temperature adsorption of CO. Sulfur poisoning of the catalyst increases $Ni(CO)_4$ formation.

2. The concentration of $CH_4$ in the feed has little effect on methanation turnover numbers in the range of 498 to 598 K. However, water vapor inhibits methanation rates by both increasing the water-gas shift reaction and deactivating the catalyst. The deactivation is probably caused by surface oxidation reversible at low temperatures, but irreversible at 573 K (in the presence of flowing hydrogen over the catalyst at that temperature).

3. Ruthenium catalysts deactivate quite rapidly during methanation at temperatures above 600 K. Taking this into account, there is no shift in apparent activation energy over a wide range of temperature. The $E_{act}$ is 113 kJ/mol.

4. $Al_2O_3$ adsorbs relatively significant quantities of $H_2S$ below 650 K. $H_2O$ vapor reduces the amount adsorbed.

5. Deactivation rates due to sulfur poisoning of nickel during methanation depend on temperature, $H_2S$ concentration and reactant composition. The higher the temperature and the lower the concentration, the greater the deactivation per $H_2S$ molecule. As CO concentration increases, $H_2S$ breakthrough increases. $H_2O$ vapor increases the rate of deactivation.

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