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

Phase 2

Quarterly Technical Progress Report
For Period May 23, 1976 to July 22, 1976

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DISCLAIMER

FOREWORD

This report summarizes technical progress during the fifth quarter period (May 23, 1976 to July 22, 1976) of a two-year study conducted for the Energy Research and Development Administration (ERDA) under Contract No. E(49-18)-1790. The principal investigator for this work is Dr. Calvin H. Bartholomew; Dr. Paul Scott is the technical representative for ERDA.

The following students contributed to the technical accomplishments and to this report: Graduates - Blaine Barton, Don Stowell, Richard Turner, and George Jarvi and Undergraduates - Richard Fowler and Scott Engstrom. Elaine Alger and Scott Folster provided typing and drafting services.

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ABSTRACT

This report details accomplishments during the fifth quarter of investigation of new pellet- and monolithic- supported alloy catalysts for methanation of coal synthesis gas. Hydrogen adsorption data were obtained for alumina supported Ni, Ru, alloys of ruthenium with Pd and Co, and alloys of nickel with Ru, Rh, MoO_3, Fe, Co, Pt, and Pd before and after exposure to low concentrations of H_2S in H_2. Differential activity tests were conducted for all the above mentioned catalysts at 225 and 250°C, 20.5 PSIA, and a space velocity of 30,000 Hr^{-1}. Conversion vs. temperature studies were conducted on six catalysts, namely, Ni, Ni-MoO_3, Ni-Pt, Ni-Co, Ni-Ru, and Ni-Rh. The Principal Investigator attended the ASTM Catalyst Committee Meeting in Washington, the Gordon Conference on Catalysis, and visited four methanation laboratories.

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, economical 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 methane or SNG. Although catalytic methanation of coal synthesis gas is an important cost item in the 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 appears to be important economical advantages in the development of more efficient, stable catalysts.

An extensive general review of the pertinent literature dealing with methanation catalysts was reported in the proposal, including reviews by Greyson(1) and Mills and Steffgen(2). From the literature, three major catalyst problems are apparent which relate to stability: (1) sulfur poisoning, (2) carbon deposition with associated plugging, and (3) sintering. These problems have received at best only modest attention. There has been very little research dealing with alloy catalysts for methanation, and there are no published investigations of the effects of catalyst support geometry on catalyst performance. 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 (1) to study nickel and ruthenium alloy catalysts in the search for catalysts resistant to poisoning and carbon deposition and (2) to investigate the effects on catalytic efficiency of support (monolith and pellet) geometry. The work has been divided into five tasks to be completed over a period of two years:

Task 1. Prepare pellet- and monolithic-supported nickel and ruthenium alloy methanation catalysts by impregnation with metal salts of nickel, ruthenium, iron, platinum, etc. followed by reduction in hydrogen. Measure hydrogen and carbon monoxide chemisorption uptakes before and after exposure to hydrogen sulfide. Examine metallic phases of these catalysts by x-ray diffraction for chemical composition and particle size.

Task 2. Design and construct a continuous flow laboratory reactor system capable of 25-1000°C and 1-25 atm. to be used for screening methanation catalysts and investigating effects of sulfur poisoning on methanation activity.

Task 3. Screen catalysts prepared in Task 1 using a reactor system constructed in Task 2 to determine methanation catalyst activity before and after exposure to 10 ppm H_2S.

Task 4. Compare the most promising catalysts based on the results of Tasks 1 and 3 for steady-state catalytic activity on different pellet and monolith supports of different hole sizes and geometries under various operating conditions, i.e., temperature, pressure, H_2/CO ratio and H_2S level.

Task 5. Maintain close liaison with organizations doing similar research such as the Bureau of Mines, Bituminous Coal Research, Institute of Gas Technology, and others.

C. Technical Approach

The technical approach which will be used to accomplish the tasks outlined above is presented in the revised proposal dated May 17, 1974. The main features of that approach are reviewed here along with more specific details and modifications which have evolved as a result of progress in related research over the past year. 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 substantially the same.

Task 1: Catalyst preparation and characterization. Alumina pellets and extruded monolithic ceramic supports (provided by Corning Glass Works) coated with high surface area alumina will be impregnated with nickel nitrate and an alloying metal salt. Metals which will be alloyed with nickel include cobalt, iron, molybdenum, rhodium, ruthenium, platinum, and palladium. Ruthenium will be used in combination with nickel, cobalt and palladium. Approximately equimolar quantities of base metals will be used in combination with nickel. Only very small amounts of noble metal will be used in combination with nickel or other base metals. Catalyst samples will be dried in vacuum at 70-100° C, reduced at 500° C in flowing hydrogen, and carefully passivated with 1% air in preparation for further testing. A dedicated reduction apparatus will be used to reduce and passivate large batches of pellets and monolithic catalysts. Alloy catalysts will be initially prepared in pellet form for chemisorption, x-ray diffraction, and reactor screening measurements. Only the more promising catalysts will be prepared in monolithic form.

Hydrogen and carbon monoxide chemisorption uptakes will be measured using a conventional volumetric apparatus before and after exposure of each catalyst to hydrogen sulfide. Catalysts will be exposed to 10 ppm H_2S over a period of several hours in a dedicated poisoning apparatus. 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 and perhaps ESCA) to determine carbon content and possible changes in phase composition or particle size. More extensive study of catalyst sintering or thermal degradation will be undertaken as part of a separate study supported by NSF and perhaps as an extension of this work, but is not intended to be within the scope of this two-year study.

Task 2: Laboratory reactor construction. It was initially proposed to construct a combination pulse-continuous flow reactor system for catalyst screening and testing. This apparatus was in fact constructed during the previous year as part of a previous methanation study supported by Corning Glass Works and Brigham Young University. The combination was found to be unworkable--unsatisfactory for pulse operation because of pulse broadening in the reactor and for continuous-flow operation due to high flow resistance in the small diameter tubing and sample valves.The reactor system was later modified for continuous-flow operation and collection of steady-state activity data, which were found to be more useful, realistic indicators of catalyst performance than the unsteady-state pulse measurements. Our continuous-flow reactor system, presently capable of 0-60 psig, will be modified for operation to 400 psig and significantly upgraded to enable convenient study of activity as a function of temperature, pressure, and feed composition.

Task 3: Reactor screening of alloy catalysts. Catalyst samples will be screened on the basis of steady-state methanation activity (reaction rate based upon catalyst surface area) measured in a differential flow reactor at atmospheric pressure and 225 or 250°C at a fixed H_2/CO ratio of 3.5-4.0. Samples to be screened will include freshly-reduced catalysts and catalyst samples exposed in a separate poisoning system to 10 ppm H_2S over a period of 6-18 hours.

Task 4: Catalyst geometry testing and design. The most promising catalysts based on the results of screening will be tested for activity and conversion as a function of pressure, temperature, H_2/CO ratio, and H_2S concentration. The conversion of carbon monoxide to methane as a function of temperature will be determined for various pellet and monolith geometries at both high and low pressures. The effects of water addition to the feed stream will also be investigated. Conversion of carbon monoxide to methane during in situ exposure to low levels of hydrogen sulfide and at low H_2/CO ratios will be used as a measure of stability toward sulfur poisoning and carbon deposition. A comparison of steady-state conversions at given temperature and pressure conditions for monolithic supports of different hole sizes and geometries will be used to optimize the geometry of the catalyst support.

Task 5: Technical visits and communication. Visits to other methanation laboratories such as the Pittsburgh Energy Research Center and the Institute of Gas Technology are planned. Close communication with other researchers working in methanation catalysis both in industrial and academic locations is also planned. The principal investigator will attend coal and catalysis meetings regularly to communicate with other workers regarding methanation catalysis.

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. Particularly Task 3, Catalyst Screening, and Task 4, Catalyst Testing and Design are well ahead of schedule.

Accomplishments during the last quarter are best summarized according to task:

Task 1. Preparation of monolithic-supported nickel and nickel alloys was initiated. Hydrogen chemisorptive uptakes were measured for fourteen different nickel and ruthenium catalysts before and after exposure to 10 ppm H_2S for 12 hours.

Task 2. The reactor construction was essentially completed during the previous quarter. However, several minor additions and modifications were made during this past quarter, including the final hookup for the steam generator and modifications in chromatographic analysis. New computer programs were written for analysis of kinetic data.

Task 3. Screening measurements of methanation activity were carried out before and after exposure to 10 ppm H_2S using; the newly constructed system for 14 different nickel and ruthenium catalysts at temperatures of 225 and 250°C, at 20.5 psia and a space velocity of 30,000 hr^{-1}. These catalysts included alumina-supported Ni (3 and 14%), Ni-Ru (3 and 20%), Ni-Rh, Ni-Pd, Ni-Pt, Ni-Fe, Ni-Co, Ni-MoO_3, Ru-Pd, Ru-Co, and commericial Ni (G-87, Girdler) and Ru (Engelhard).

Task 4. Integral (conversion versus temperature) tests were carried out at 20.5 psia for 6 catalysts: alumina-supported Ni, Ni-Ru, Ni-Rh, Ni-Pt, Ni-MoO_3, and Ni-Co.

Task 5. The principal investigator attended the ASTM catalyst committee meeting held May 17-18 in Washington, visited with Dr. Michael Biallis in Washington regarding the contract and made one day visits to each of the following Methanation Laboratories: 1) Carnegie-Mellon University (Professor Anthony Dent), 2) Pittsburgh Energy Research Center (Dr. Fred Steffgen, Dr. Bill Haynes and members of their research groups), and 3) Institute of Gas Technology (Mr. Tony Lee). The PI also attended the 1976 Gordon Research Conference on Catalysis in New Hampshire June 27 to July 2.

Miscellaneous. Mr. Blaine Barton and Mr. Donald Stowell each completed requirements for a masters degree in Chemical Engineering based on work performed as part of this contract. Mr. George Jarvi (graduate student) joined the research group June 15th and Mr. Kevin

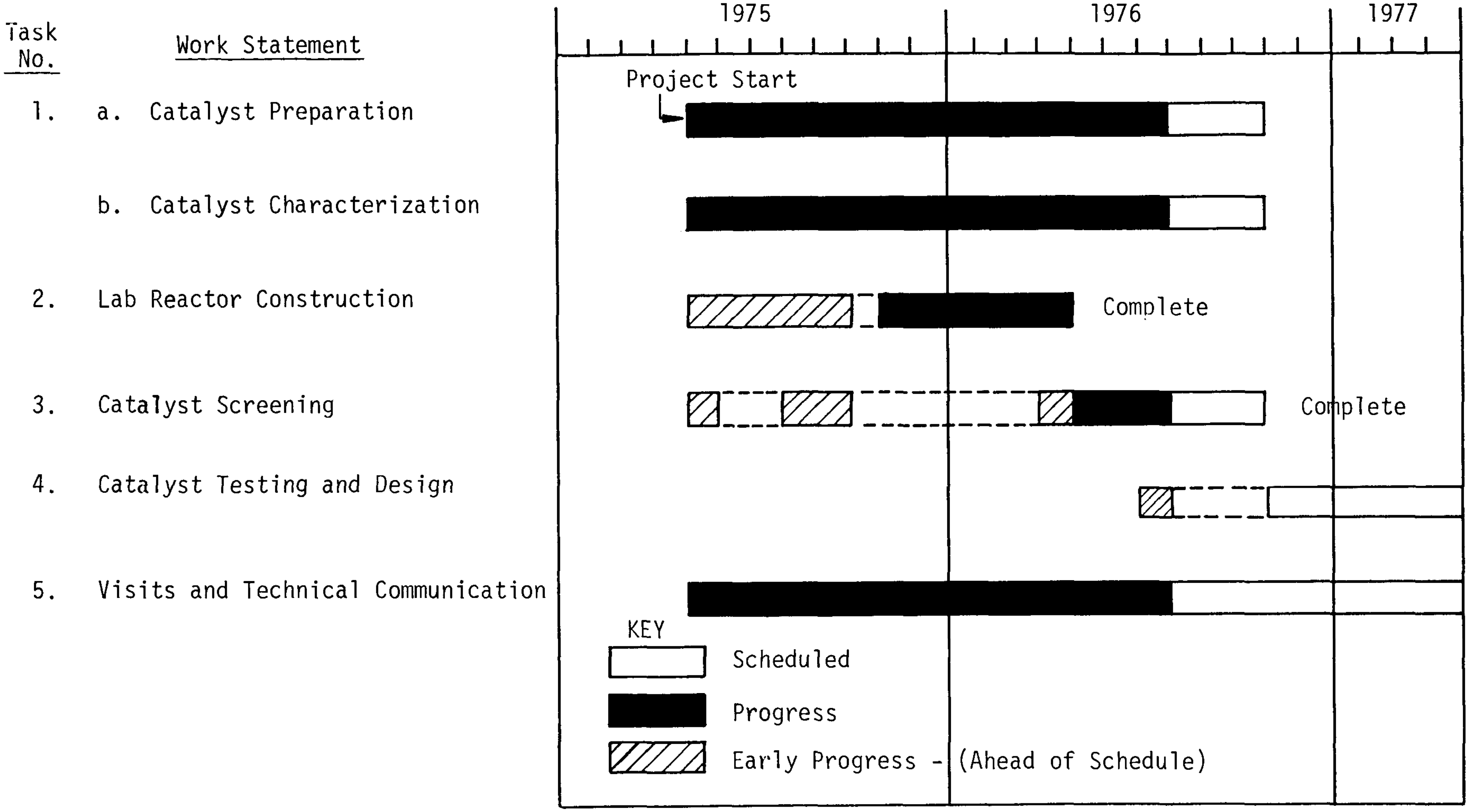

Figure 1. Project Progress Summary

Mayo (undergraduate) began work in late July.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation: Research size monoliths (Corning Glass Works) 1 inch OD by 3 inches long and having different geometries (200 □/in^2, 236 △/in^2, and 300 □/in^2) were cut into sections approximately 1/2 inch thick, acid washed and rinsed with distilled water to remove interfering ions and coated with SA Medium alumina to impart high surface area.

2. Characterization: Hydrogen chemisorption uptakes measured for 14 different nickel and ruthenium catalysts before and after exposure to 10 ppm H_2S for 12 hours are summarized in Table 1. The data show that H_2 adsorption generally decreases after exposure to H_2S; the decrease is greater for catalysts having a low metal loading as would be expected. However in three cases (Ni-A-116, Ni-Fe, and Ru-Co) an increase was observed. This may be explained as follows: Previous studies (3,4) indicate that nickel and iron supported on alumina are not completely reduced under typical reducing conditions to the metallic state, but rather only after many hours of exposure to H_2 at very high temperatures. The H_2S/H_2 exposure at 450°C for 12 hours may in fact increase the state of reduction to the metal and the metal surface area while at the same time blocking some metallic sites. The overall effect however could be an increase in metal surface area and H_2 adsorption.

The reason for repeating H_2 adsorption measurements on these catalysts, whose surface areas had been determined earlier in other experiments, arises out of the necessity of knowing the surface area at this particular point in the time-temperature-reduction history so that a meaningful basis is used for turnover numbers. The problem is that surface areas for a given sample can vary considerably with the time-temperature-reduction history and are very difficult to reproduce.

B. Task 2: Laboratory Reactor Construction.

During the previous quarter the reactor system was essentially completed. However, several modifications and additions were necessary during the past quarter; these included making final connections in the installation of the vaporizer system and alteration of the chromatographic column set up to include CO_2, H_2, N_2, CO, CH_4. Presently, during each run reactants and products are sampled alternately until 4 to 6 samples of each are obtained. The data are analyzed with new computer programs written during the past quarter to enable fast, error-free analysis of the kinetic data including statistical treatment. A PDP 10 computer is used because of the numerous, sophisticated calculations involved.

TABLE 1

Hydrogen Chemisorptive Uptake Data for Alumina-Supported Nickel Nickel Alloy and Ruthenium Alloy Catalysts

Catalyst	Nominal Composition (wt%)	H_2 Uptake (μ mole/gram) before Poisoning	After Poisoning
Ni-A-112	3% Ni	40.05	30.33
Ni-A-116	14% Ni	156.80	176.10
G-87 (Girdler)	32% Ni	149.15	147.46
Ni-MoO_3-A-101	2.5% Ni - 3% MoO_3	18.59	17.97
Ni-Ru-A-105	2.5% Ni - 0.5 wt% Ru	38.68	30.38
Ni-Ru-A-106	16.6% Ni - 3.4% Ru	157.0	
Ni-Rh-A-100	2.5% Ni - 0.5% Rh	37.74	25.52
Ni-Co-A-100	10% Ni - 10% Co	118.59	113.10
Ni-Fe-A-100	10% Ni - 10% Fe	91.37	92.25
Ni-Pt-A-100	15.7% Ni - 0.5% Pt	126.31	125.55
Ni-Pd-A-100	15% Ni - 1.0% Pd	85.44	85.77
Ru-Pd-A-100	0.49% Ru - 0.51% Pd	10.30	
Ru-Co-A-100	0.52% Ru - 15% Co	52.68	55.89
Engelhard Ru	0.50% Ru	8.78	4.44

C. Task 3: Reactor Screening of Alloy Catalysts.

During the previous quarter the catalysts shown in Table 1 were screened in differential activity tests. The catalysts can be classified in two groups according to the weight of active metal: 13 wt.% - 20 wt.% and 0.5-6 wt.%. This is a logical grouping as catalysts with a high metal loading display small but nevertheless significant mass transfer effects in the screening test. After their initial activity test most of these catalysts were poisoned with 10 ppm H_2S in H_2 (GHSV= 2000 hr^{-1}) for 12 hours at a temperature of 450°C, after which they were tested again.

In the activity screening tests measurements were made of the CO conversion, and CH_4 and CO_2 production. Methane and CO_2 production were based on the amount of CO converted to these products. From these data the selectivities of each catalyst to methane and carbon dioxide were calculated. In addition, the reaction rate per gram of catalyst and turnover number based on both CO conversion and CH_4 production were calculated. These results are shown in Tables 2 and 3 for temperatures of 225 and 250°C respectively and a space velocity of 30,000 per hour. Apparent activation energies calculated from the activities at 225 and 250°C for each catalyst are shown in Table 4.

A comparison of the data in Tables 2-4 shows significant absolute differences from activity data reported previously (5), although the general relative trends are similar in both sets of data. The earlier data was obtained in a Stainless Steel Catalytic Reactor described (5) in the annual report (pp. 53-55). The reaction zone of this reactor was placed in a clam shell furnace having a six inch heating zone. There was no preheater in the system; thus the gas entering the reaction zone was cooler than its surroundings and the six inch heating zone was insufficient to preheat the entering gas sufficiently to enable isothermal operation through the catalyst bed. These effects combined to cause significant (probably on the order of 10°C) thermal gradients both axially and radially within the reactor. The thermocouple in this system, placed in the center (radially) of the leading edge of the catalyst bed, sampled the lowest temperature portion of the bed. Thus, the activities reported previously were observed to be higher for a given measured temperature then are presently measured in our isothermal reactor with preheater. These observations do not invalidate the general trends which were reported previously but only affect the absolute magnitude of the numbers reported. The present reactor system with a more than adequately designed gas preheater and 22 inch heating zone is not subject to these thermal gradients and deviates from isothermal operation only in a small temperature change caused by the heat of reaction. This effect is minimized by maintaining shallow bed depths and low conversions for the screening test.

All catalysts were tested at 225 and 250°C (with the exception of Engelhard Ru and Ru-Pd-A-100 which showed no measurable activity at 225°C and were tested at 275°C) and a space velocity of 30,000 hr^{-1}, using a reactant mixture of 1% CO, 4% H_2 with the balance being

TABLE 2

Reactor Screening Data
225°C; GHSV = 30,000; 20.5 PSIA

Catalyst	% Conversion	% Production		% Selectivity	
	CO	CH_4	CO_2	CH_4	CO_2
Greater then 13% active metal					
G-87	13.7	10.9	0.3	79	2.2
G-87-Poisoned*	14.2	11.8	0.5	83	3.4
Ni-A-116	19.6	14.1	0.3	72	1.3
Ni-A-116-Poisoned	18.2	14.2	0.3	78	1.5
Ni-Co-A-100[+]	14.8	12.3	3.6	84	2.4
Ni-Co-A-100-Poisoned[+]	16.7	14.3	4.8	86	2.8
Ni-Pt-A-100[+]	12.3	9.6	0.0	79	0.0
Ni-Pt-A-100-Poisoned[+]	10.0	8.3	0.1	83	1.0
Ni-Pd-A-100[+]	5.5	4.4	0.0	80	0.0
Ni-Pd-A-100 Poisoned[+]	2.0	2.7	0.0	136	0.9
Ni-Ru-A-106	4.9	3.5	0.0	72	0.0
Less then 6 wt.% active metal					
Ni-A-112	1.96	1.34	0.0	68	0.0
Ni-A-112-Poisoned	1.96	1.25	0.0	64	0.0
Ni-MoO_3-A-101	1.36	0.80	0.0	59	0.0
Ni-MoO_3-A-101-Poisoned	0.58	0.32	0.0	56	0.0
Ni-Rh-A-100	2.55	1.72	0.0	68	0.0
Ni-Rh-A-100-Poisoned	1.13	0.82	0.0	75	0.0
Ruthenium containing catalysts					
Ni-Ru-A-105	2.34	1.62	0.0	70	0.0
Ni-Ru-A-105-Poisoned	1.26	0.94	0.0	77	0.0
Engelhard Ru**	0.78	0.29	0.0	37	0.0
Ru-Pd-A-100	4.71	2.85	0.0	61	0.0
Ru-Pd-A-100-Poisoned[‡]	1.41	0.13	0.0	20	0.0
Ru-Co-A-100	4.34	3.31	0.02	76	0.5
Ru-Co-A-100-Poisoned	2.83	2.17	0.02	81	0.6
Ru-Co-A-100[+]	4.56	3.66	0.06	80	1.3
Ru-Co-A-100-Poisoned[+]	4.94	3.19	0.04	65	0.8

* Data after exposure of the catalyst to 10 ppm (molar basis) H_2S for 12 hours at a temperature of 450°C.

[+] These catalysts were reduced for 10 hours at 450°C before the reactor test. All other catalysts were reduced for 2 hours at 450°C.

** Run at 275°C.
GHSV = 5000; 275°C

TABLE 2 (continued)

Reactor Screening Data
225°C; GHSV = 30,000; 20.5 PSIA

	Rate x 10^7		Turnover Number x 10^3			
	gMoles/gcat-sec		Based on Fresh H_2 Uptake		Based on Poisoned H_2 Uptake	
Catalyst	CO	CH_4	CO	CH_4	CO	CH_4
Greater then 13 wt.% active metal						
G-87	6.8	5.4	2.3	1.8		
G-87-Poisoned*	6.9	5.7	2.3	1.9	2.3	1.9
Ni-A-116	12.2	8.8	3.9	2.8		
Ni-A-116-Poisoned	11.4	8.9	3.6	2.8	3.2	2.5
Ni-Co-A-100+	8.4	7.0	3.6	3.0		
Ni-Co-A-100-Poisoned+	9.5	8.1	4.0	3.4	4.2	3.6
Ni-Pt-A-100+	7.4	5.8	2.9	2.3		
Ni-Pt-A-100-Poisoned+	6.0	5.0	2.4	2.0	2.4	2.0
Ni-Pd-A-100+	3.4	2.7	2.0	1.6		
Ni-Pd-A-100-Poisoned+	1.3	1.7	0.74	0.97	0.74	0.97
Ni-Ru-A-106	3.2	2.3	1.0	0.73		
Less then 6 wt.% active metal						
Ni-A-112	1.4	0.99	1.8	1.2		
Ni-A-112-Poisoned	1.4	0.92	1.8	1.1	2.4	1.5
Ni-MoO_3-A-101	1.0	0.60	2.8	1.6		
Ni-MoO_3-A-101-Poisoned	0.44	0.24	1.2	0.65	1.2	0.67
Ni-Rh-A-100	1.8	1.2	2.4	1.6		
Ni-Rh-A-100-Poisoned	0.8	0.6	1.1	0.8	1.7	1.2
Ruthenium containing catalysts						
Ni-Ru-A-105	1.7	1.2	2.2	1.5		
Ni-Ru-A-105-Poisoned	0.91	0.68	1.2	0.88	1.5	1.1
Engelhard Ru*	0.27	0.10	1.5	0.58		
Ru-Pd-A-100‡	0.69	0.42	3.4	2.0		
Ru-Pd-A-100-Poisoned‡	0.22	0.02	1.0	0.10		
Ru-Co-A-100	2.6	2.0	2.9	2.2		
Ru-Co-A-100-Poisoned	1.7	1.3	1.9	1.5		
Ru-Co-A-100+	2.8	2.2	2.6	2.1		
Ru-Co-A-100-Poisoned+	3.0	2.0	2.9	1.9	2.7	1.8

* Data after exposure fo the catalyst to 10 ppm (molar basis) H_2S for 12 hours at a temperature of 450°C.

\+ These catalysts were reduced for 10 hours at 450°C before the reactor test. All other catalysts were reduced for 2 hours at 450°C.

** Run at 275°C

‡ GHSV = 5000; 275°C

TABLE 3

Reactor Screening Data
250°C; GHSV = 30,000; 20.5 PSIA

Catalyst	% Conversion	% Production		% Selectivity	
	CO	CH_4	CO_2	CH_4	CO_2
Greater then 13% active metal					
G-87	30.4	27.2	0.85	89	2.8
G-87-Poisoned*	29.1	26.4	1.95	91	6.7
Ni-A-116	40.3	32.8	1.55	82	3.8
NI-A-116-Poisoned	37.3	31.7	1.31	85	3.5
Ni-Co-A-100[+]	35.5	28.5	2.27	80	6.4
Ni-Co-A-100-Poisoned[+]	38.4	30.9	3.69	81	9.6
Ni-Pt-A-100[+]	25.9	22.2	0.17	89	1.4
Ni-Pt-A-100-Poisoned[+]	21.8	19.5	0.30	88	0.9
Ni-Pd-A-100[+]	13.4	11.4	0.00	87	0.0
Ni-Pd-A-100-Poisoned[+]	8.3	8.2	0.13	98	1.5
Ni-Ru-A-106	10.3	8.9	0.00	87	0.0
Less then 6 wt.% active metal					
Ni-A-112	5.72	4.88	0.00	85	0.0
Ni-A-112-Poisoned	5.61	4.77	0.00	85	0.0
Ni-MoO_3-A-101	3.71	2.94	0.00	79	0.0
Ni-MoO_3-A-101-Poisoned	1.67	1.36	0.03	81	1.6
Ni-Rh-A-100	6.32	5.27	0.00	83	0.0
Ni-Rh-A-100-Poisoned	3.07	2.67	0.00	88	0.0
Ruthenium containing catalysts					
Ni-Ru-A-105	6.06	5.49	0.04	91	0.7
Ni-Ru-A-105-Poisoned	3.64	3.08	0.00	89	0.0
Engelhard 0.5 wt.% Ru	0.15	0.03	0.00	25	0.0
Ru-Pd-A-100 [‡]	2.35	1.08	0.00	47	0.0
Ru-Pd-A-100-Poisoned[‡]	0.48	0.04	0.00	10	0.0
Ru-Co-A-100[+]	11.1	9.52	0.37	86	3.2
Ru-Co-A-100-Poisoned[+]	8.67	6.60	0.16	76	1.9
*Ru-Co-A-100	10.9	9.29	0.28	86	2.6
*Ru-Co-A-100-Poisoned	10.9	8.78	0.24	81	2.2

[*] Data after exposure of the catalyst to 10 ppm (molar basis) in H_2 for 12 hours at a temperature of 450°C.

[+] These catalysts were reduced for 10 hours at 450°C before the reactor test. All other catalysts were reduced for 2 hours at 450°C.

[‡] GHSV = 5000

TABLE 3 (continued)

Reactor Screening Data -
250°C; GHSV = 30,000; 20.5 PSIA

Catalyst	Rate x 10^7 (Moles/gcal-sec)		Turnover Number x 10^3			
			Based on Fresh H_2 Uptake		Based on Poisoned H_2 Uptake	
	CO	CH_4	CO	CH_4	CO	CH_4
Greater then 13 wt.% active metal						
G-87	15.1	13.5	5.1	4.5		
G-87-Poisoned	14.2	12.9	4.8	4.3	4.8	4.4
Ni-A-116	25.1	20.5	8.0	6.5		
Ni-A-116-Poisoned	23.4	19.8	7.4	6.3	6.6	5.6
Ni-Co-A-100[+]	20.3	16.3	8.5	6.9		
Ni-Co-A-100-Poisoned[+]	21.7	17.5	9.2	7.4	9.6	7.7
Ni-Pt-A-100[+]	15.6	13.3	6.2	5.3		
Ni-Pt-A-100-Poisoned[+]	13.1	11.7	5.2	4.6	5.2	4.6
Ni-Pd-A-100[+]	8.2	6.9	4.8	4.1		
Ni-Pd-A-100-Poisoned[+]	5.2	5.1	3.1	3.0	3.04	2.98
Ni-Ru-A-106	6.7	5.8	2.1	1.8		
Less then 6 wt.% active metal						
Ni-A-112	5.0	4.5	6.3	5.7		
Ni-A-112-Poisoned	2.2	1.9	2.7	2.4	3.6	3.2
Ni-MoO_3-A-101	2.9	2.2	7.5	6.0		
Ni-MoO_3-A-101-Poisoned	1.3	1.0	3.4	2.8	3.5	2.9
Ni-Rh-A-100	4.5	3.8	6.0	5.0		
Ni-Rh-A-100-Poisoned	2.3	2.0	3.0	2.7	4.5	3.9
Ruthenium containing catalysts						
Ni-Ru-A-105	4.4	4.0	5.6	5.1		
Ni-Ru-A-105-Poisoned	2.6	2.3	3.4	3.0	4.3	3.8
Engelhard Ru	0.051	0.012	0.29	0.068		
Ru-Pd-A-100[‡]	0.35	0.16	1.7	0.77		
Ru-Pd-A-100-Poisoned[‡]	0.071	0.006	0.34	0.03		
Ru-Co-A-100	6.7	5.7	7.3	6.3		
Ru-Co-A-100-Poisoned	5.3	4.0	5.9	4.4		
Ru-Co-A-100[+]	6.6	5.6	6.3	5.4		
Ru-Co-A-100-Poisoned[+]	6.7	5.4	6.3	5.1	6.0	4.8

* Data after exposure of the catalyst to 10 ppm (molar basis) H_2S for 12 hours at a temperature of 450°C.

[+] These catalysts were reduced for 10 hours at 450°C before the reactor test. All other catalysts were reduced for 2 hours at 450°C.

[‡] GHSV = 5000

TABLE 4

Apparent Activation Energies for Methanation Catalysts
Based on measurements at 225-250°C and a space velocity of 30,000 hr^{-1}.

Catalyst	CO Conversion (kcal/mole)	CH_4 Production (kcal/mole)
G-87	16.5	19.0
G-87-Poisoned	14.9	16.8
Ni-A-116	15.0	17.5
Ni-A-116-Poisoned	14.9	16.7
Ni-Co-A-100	18.2	17.3
Ni-Co-A-100-Poisoned	17.2	16.0
Ni-Pt-A-100	20.5	12.3
Ni-Pt-A-100-Poisoned	16.1	17.7
Ni-Pd-A-100	18.1	19.4
Ni-Pd-A-100-Poisoned	29.5	23.2
Ni-Ru-A-106	20.6	23.7
Ni-A-112	22.2	26.8
Ni-A-112-Poisoned	21.8	27.8
Ni-MoO_3-A-101	20.8	27.0
Ni-MoO_3-A-101-Poisoned	21.9	30.0
Ni-Rh-A-100	18.8	20.7
Ni-Rh-A-100-Poisoned	23.2	24.6
Ni-Ru-A-105	19.7	25.3
Ni-Ru-A-105-Poisoned	22.0	25.5
Engelhard Ru*	37.7	48.8
Ru-Pd-A-100*	15.8	22.3
Ru-Pd-A-100-Poisoned*	25.5	27.0
Ru-Co-A-100	19.4	21.9
Ru-Co-A-100-Poisoned	23.2	23.0

* Based on 250-275°C

N_2. The catalyst samples of 1/8 inch beads were approximately 4 to 6 ml in volume, giving a maximum bed depth of one centimeter. Under these conditions CO conversions ranging from 0.15 to 40% were obtained. The higher values, obtained on the more heavy metal loading catalysts are admittedly much too high to realize differential kinetic data. However, these catalysts also gave the most consistent and reproducible results. The catalysts containing 13-20 wt.% active metal had confidence limits of ± 7% or better while the 0.5-6 wt.% catalysts showed variations in the data up to ± 15%. The selectivity data for Ni-MoO_3-A-101 in particular showed wide variations. This may be an effect of either a competing reaction, i.e., Fischer-Tropsch, or a change in the state of reduction from run to run. This catalyst will be studied further in Task 4 to determine the cause of these effects.

The selectivities to CH_4 for nickel containing catalysts as shown in Tables 2 and 3 are higher at 250°C than at 225°C. The ruthenium containing catalysts have lower selectivities to methanation than the nickel catalysts. Moreover, they do not show appreciable CO_2 formation except in the alloy containing cobalt, suggesting the formation of higher hydrocarbons on the ruthenium surface. As the percentage of ruthenium increases the selectivity decreases, the lowest selectivity being evidenced by the pure ruthenium catalyst. The selectivity of the ruthenium decreases with temperature and exposure to hydrogen sulfide (see Engelhard Ru and Ru-Pd-A-100).

Selectivity for carbon dioxide formation is exhibited to a significant extent only by the pure nickel and cobalt containing catalysts. The nickel-cobalt catalyst in particular exhibits CO_2 formation which is at least double that of any other catalyst. As nickel is alloyed with other metals the CO_2 production is significantly reduced. However, it should be noted that with the lower metal loading catalysts the CO_2 detection capacity of the chromatograph is pushed to the limit because of the initially very small CO conversions. Additional information on the selectivity of various catalysts has been and will be obtained in the integral catalyst tests scheduled as part of Task 4.

The methanation rates per gram of catalyst are shown in Tables 2 and 3 for 225 and 250°C, also in Figures 2 and 3 for 250°C. Figure 2 shows the catalysts with metal loading of 13 wt.% and higher. Of these catalysts Ni-A-116 has the highest activity while the Ni-Ru-A-106 has the lowest activity. Ni-Co and Ni-Pt catalysts also have activities which compare favorably with G-87 (Girdler), the commercial nickel catalyst, however, Ni-Pd, Ni-Ru, and Ru-Co do not.

Of particular interest is the effect of exposure to H_2S on methanation activity. The cobalt containing catalysts, reduced over a period of 16 hours, passivated and rereduced for 10 hours show slightly increased activity after exposure to H_2S, i.e., these catalysts do not appear to be poisoned. However, samples rereduced only 2 hours after passivation exhibited the normal decrease in activity after H_2S exposure. This phenomenon may indicate that the cobalt requires a longer reduction period in order to form the alloy, desired state of reduction, and/or desired surface composition. The data in Tables

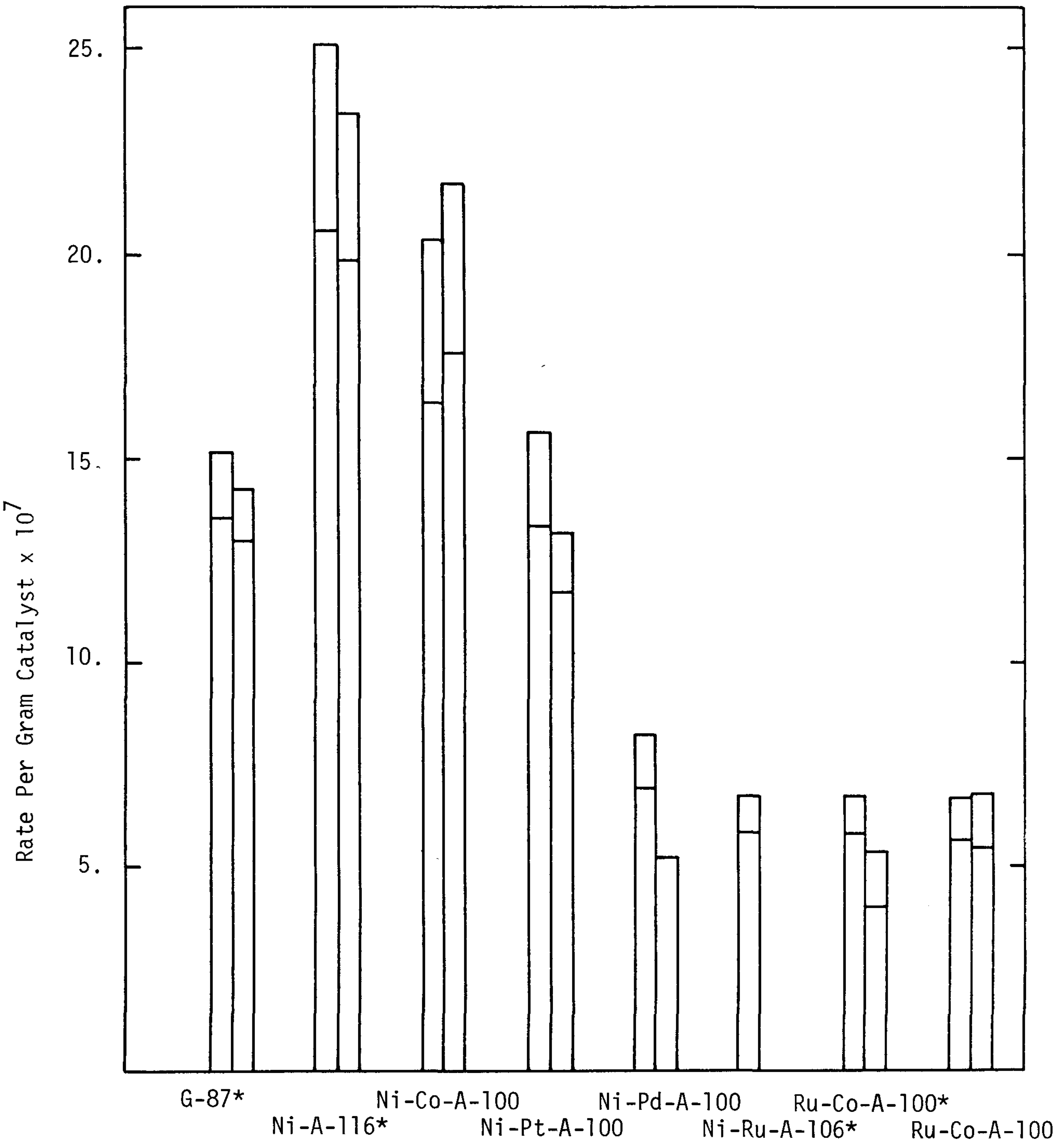

Figure 2. The Effect of H_2S on Methanation Activity at 250°C (GHSV = 30,000). The first bar of each pair represents the activity of the fresh catalyst; the second indicates the activity after exposure to 10 ppm (molar basis) H_2S in H_2 for 12 hours at a space velocity of 2,000 hr^{-1} and 450°C. The upper bar represents CO conversion while the lower bar represents methane production.

* These catalysts were reduced for 2 hours in flowing H_2 at 450 C. All others were reduced at least 10 hours at 450°C.

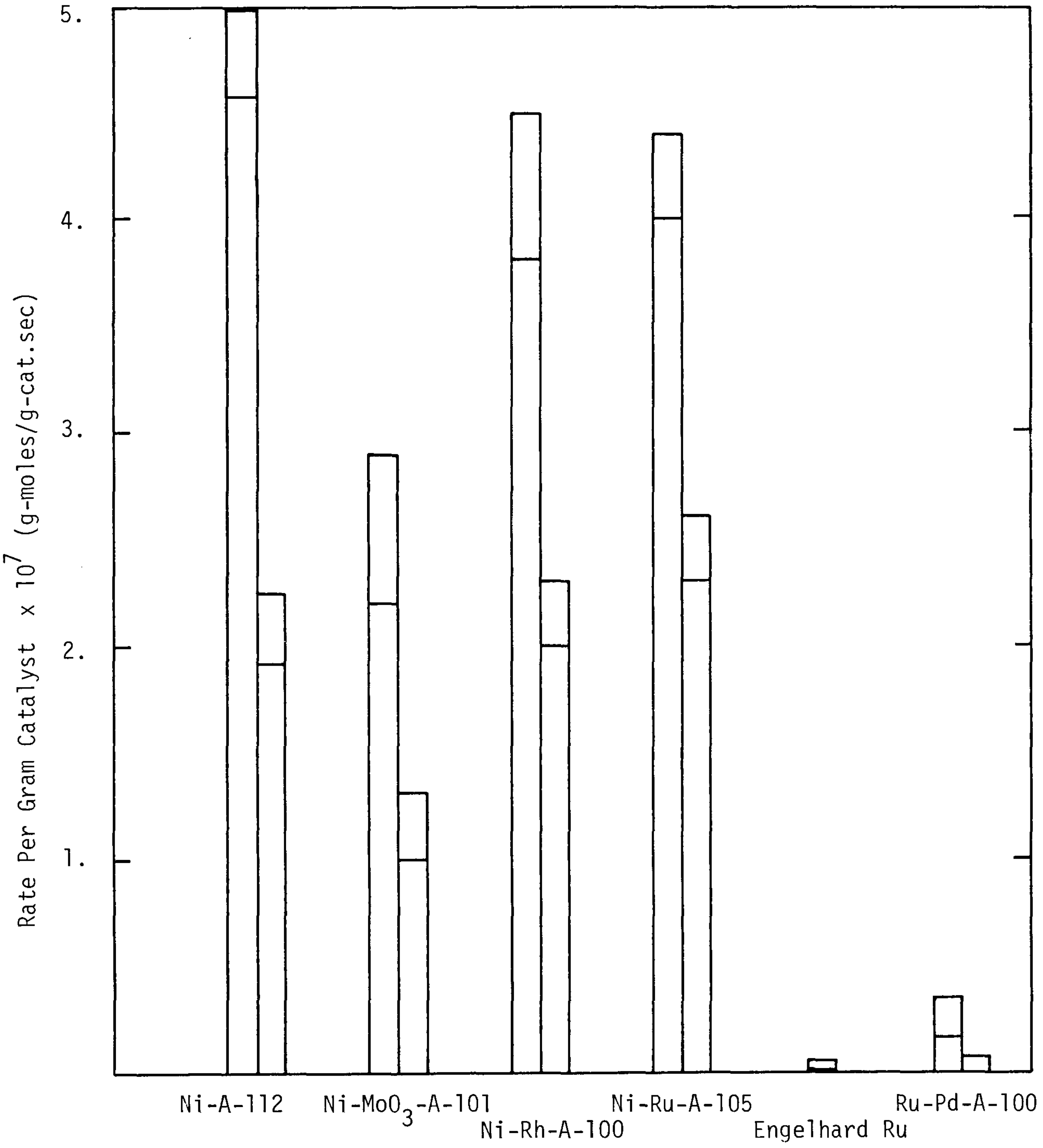

Figure 3. The Effect of H_2S on Methanation Activity at 250°C (GHSV = 30,000). For explanation of figure see Figure 2. The catalysts were reduced for 2 hours at 450°C in flowing H_2. Ru-Pd-A-100 was tested at a space velocity at 5,000 hr^{-1} because it had no detectable activity at 30,000 hr^{-1}.

2 and 3 show that generally a slight increase in selectivity was observed following exposure to H_2S; however the effect is most dramatic for the Ni-Pd catalyst.

Activity data for the 0.5-6 wt.% metal catalysts, shown in Figure 3, indicate, as would be expected, a much lower activity on a per mass basis than those with higher metal contents. Ni, Ni-Rh and Ni-Ru catalysts show about the same activity while the Ni-MoO_3 catalyst shows the lowest activity (per gram) of any Ni containing catalyst. The Engelhard Ru and Ru-Pd catalysts have by far the lowest activities of any tested.

The H_2S poisoning experiments in this study were purposely designed such that less sulfur would pass over the catalyst than necessary to completely saturate the surface. This, it was reasoned, would provide experimental leverage to compare residual metal areas and methanation activity for alloy catalysts exposed to just a "little bit" of H_2S. Recent experiments in this laboratory, however, have shown that poisoning of nickel catalysts by H_2S, even at 10 ppm and lower concentrations, is effectively irreversible, exhibiting a very steep breakthrough curve. Thus, the catalyst beads on the leading edge of the bed are heavily poisoned while those on the trailing edge "see" very little if any H_2S. Because of the nonuniform nature of the poisoned sample, it would not be meaningful to divide the sample and test only a portion for methanation activity or surface area. Hence the effects of poisoning on surface area and methanation activity reported here are the average values taken over non-uniform samples.

In a kinetic study of nickel, ruthenium, and rhenium methanation catalysts, Dalla Betta et al. (6) showed that exposure to H_2S effects an increase in selectivity to hydrocarbons (C_{2+}) and a decrease in selectivity for methane. Except for Ni-Pd the poisoning of the catalysts in this study causes very little change on the selectivity to methane. However, it effects a very strong decrease in the activity of the catalysts.

The turnover numbers, activity per H chemisorption site, for the catalysts having high metal contents are shown in Figure 4. The Ni-Co catalyst has the highest activity, while the Ni-Ru catalyst has the lowest activity; both Co containing catalysts compare favorably with the pure nickel catalysts. Calculations (7) made during the past quarter show that even at high conversions (10-30%) the kinetic data are not affected by heat transfer effects. These calculations, however, do show that the data are influenced to a small degree by pore diffusion. Nevertheless, the comparisons of specific activity are valid because the same support was used for all samples except the commercial catalyst.

Data are listed in Table 3 for two samples of the Ru-Co catalyst. These two samples received identical treatment except for the length of reduction prior to the activity tests. The first sample was reduced 2 hours while the second was reduced 10 hours. The length of reduction seemed to have a very significant effect on the catalyst's response

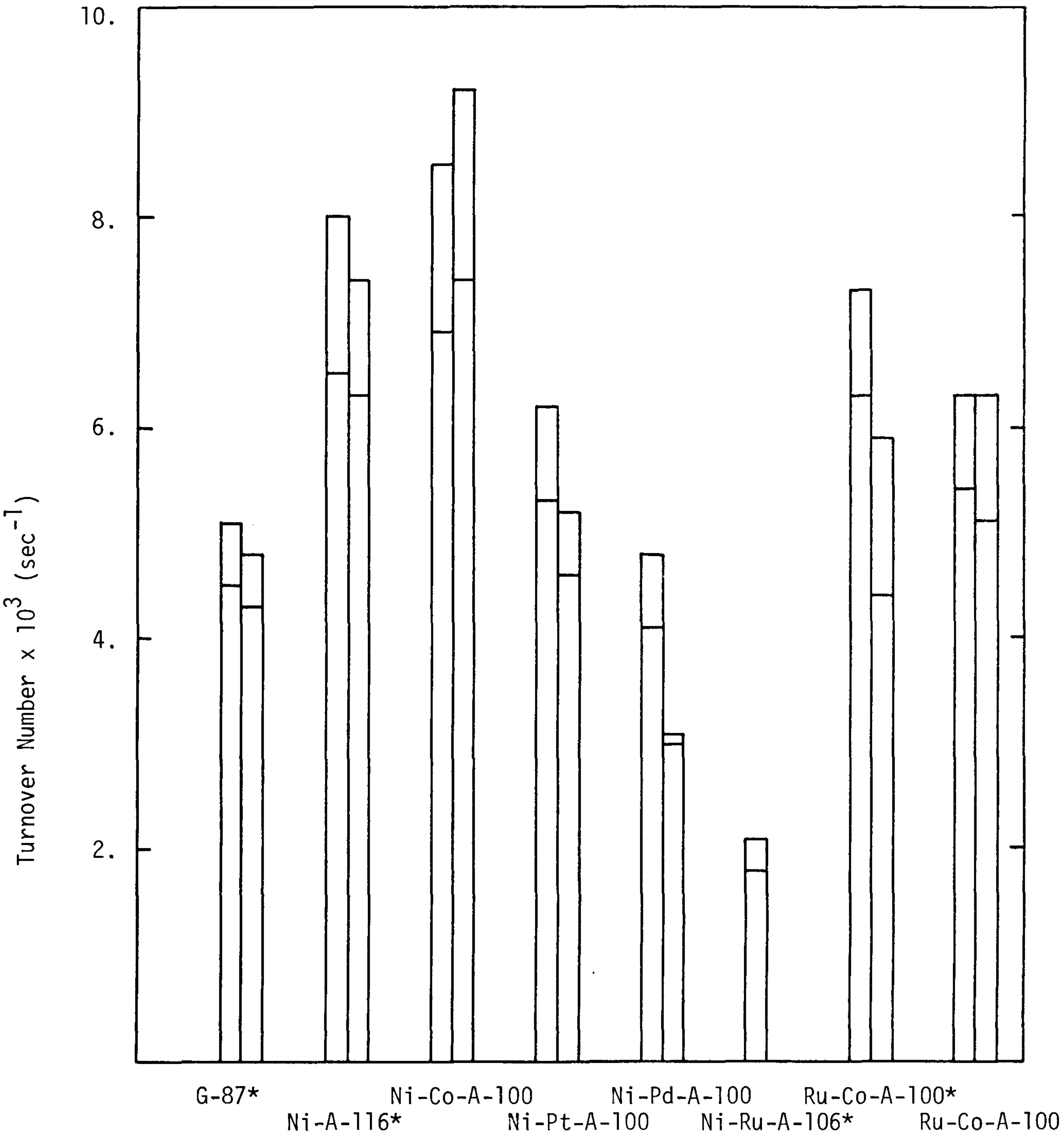

Figure 4. The Effect of H_2S on Turnover Number at 250°C (GHSV = 30,000). For explanation of the bars see Figure 2. The catalysts with * were reduced for 2 hours in flowing H_2 at 450°C. All other catalyst were reduced at least 10 hours at 450°C.

to partial poisoning by H_2S; that is, the sample which was reduced longer appeared unaffected by H_2S. The Ni-Pt catalyst exhibited large variations in selectivity to methane depending upon the reduction time: for example, 99% selectivity to methane was measured after 2 hours reduction as compared to 85% for 10 hours reduction. This catalyst also showed variations in H_2 uptake with length of reduction; this is consistant with observations (8) that Ni-Pt catalysts reduce more quickly than nickel catalysts. These effects are probably due to: 1) the state of reduction of the surface, i.e., the different metals reach different reduction states and/or 2) changing surface metal composition of the catalyst due to induced surface reconstruction by the reducing hydrogen environment. This might come about because the Ni-H bond is stronger than the Pt-H bond, causing Ni enrichment on the surface. Since Ni has a lower selectivity for methane than Pt (9), the increased nickel content of the surface would bring about a decrease in selectivity.

Figure 5 shows the turnover numbers for the catalysts having low metal contents. These data show no effects of heat or mass transfer and negligible pore resistance effects. The turnover numbers obtained for these nickel catalysts are slightly lower then for those having a heavy metal loading, suggesting that a metal-support interaction affects the rate. The noble metal (Ru) catalysts show much lower turnover numbers; this result is in disagreement with the work of Vannice (9).

The fractional changes in hydrogen uptake and turnover number with poisoning of the catalyst together with the ratio of these two numbers called the poisoned site activity ratio (PSAR) are shown in Table 5. The PSAR is a measure of the change in activity of the methanation sites as a result of partial poisoning. A value less then 1.0 indicates that either the most active sites are poisoned first or that the H_2S interacts strongly with the remaining sites to decrease their activity. Conversely, a PSAR value greater then 1.0 indicates either the least active sites are poisoned first or that the H_2S interacts with the remaining sites to enhance their activity. Thus, cobalt containing catalysts are less susceptible to the effects of low concentrations of H_2S since the least active sites are poisoned first. Ni-A-112 (3% Ni/Al_2O_3) and $Ni\text{-}MoO_3$-A-101 appear to be least resistant to sulfur and exhibit extensive differentiation in the activity of various sites. Ni-Ru and Ni-Rh appear to have greater resistance to H_2S than Ni.

Table 5 shows the apparent activation energies calculated from the data in Tables 2 and 3. The high metal loading catalysts exhibit values 2-5 kcal/mole lower then the low metal loading catalysts. This effect is due to the presence of pore resistance in the case of the former catalysts. It is informative to compare the values for the pure nickel catalysts with the alloys. The variations from catalyst to catalyst are strong evidence of alloy formation in the bi-metallic catalysts. Especially interesting is Ni-Pt which before

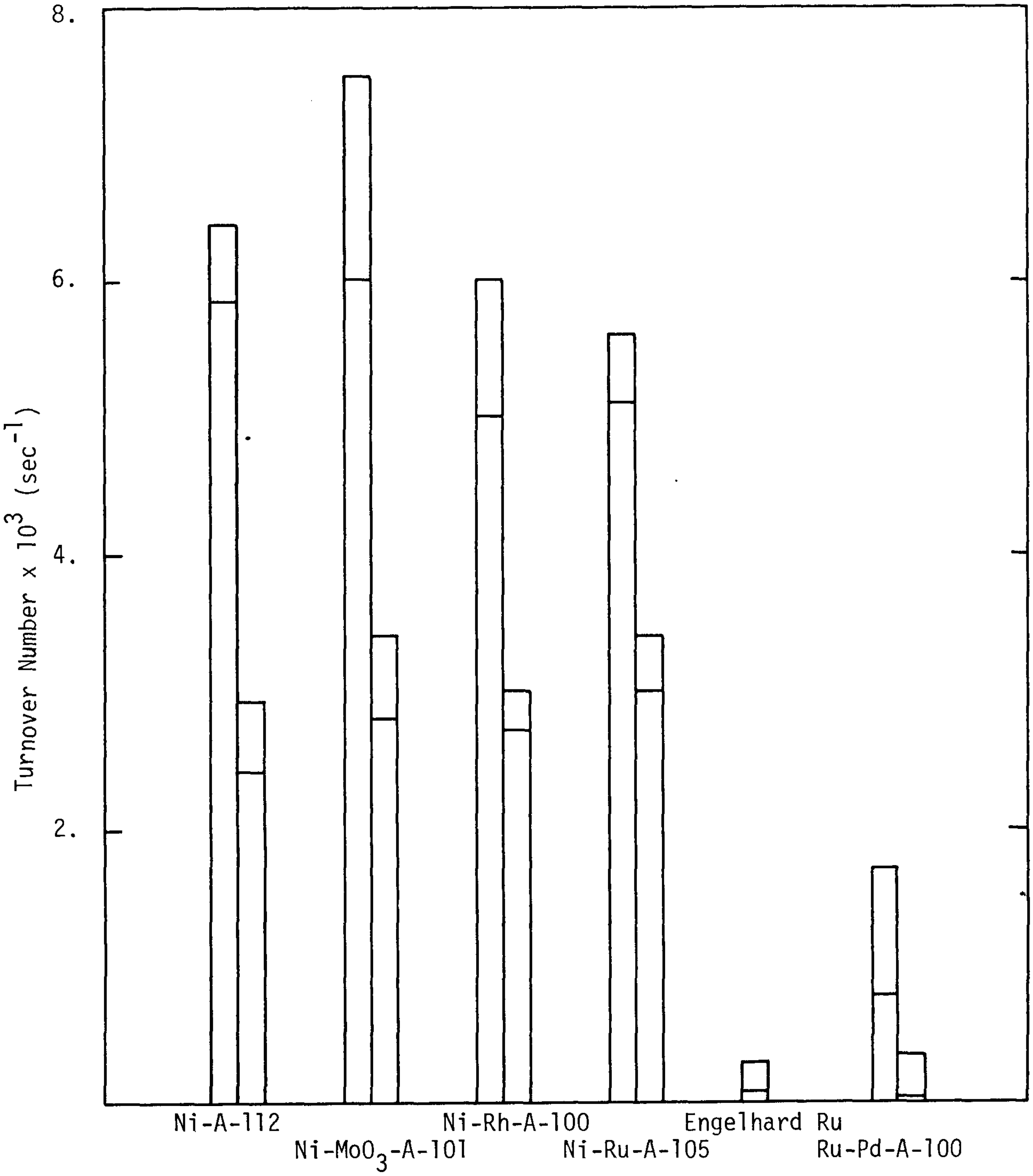

Figure 5. The Effect of H_2S on Turnover Number at 250°C.(GHSV = 30,000). For explanation of the bars see Figure 2. The catalysts were reduced for 2 hours at 450°C in flowing H_2. Ru-Pd-A-100 was tested at a space velocity of 5,000 hr^{-1} because it had no detectable activity at 30,000 hr^{-1}.

TABLE 5

Changes in H_2 Uptake and Turnover Number Due to Poisoning.
250°C; GHSV = 30,000

Catalyst	$R_1 = H_2Uptake^f/H_2Uptake^I$	$R_2 = N_{CH_4}^f/N_{CH_4}^I$	Poisoned Site Activity Ratio = R_2/R_1
G-87	0.989	0.954	0.965
Ni-A-116	1.12	0.969	0.865
Ni-Co-A-100	0.954	1.08	1.13
Ni-Pt-A-100	0.994	0.874	0.879
Ni-MoO_3-A-101	0.967	0.465	0.481
Ni-Rh-A-100	0.676	0.530	0.784
Ni-Ru-A-105	0.785	0.586	0.746
Ni-A-112	0.757	0.420	0.555
Ru-Co-A-100	1.06	1.06	1.00

Superscripts I = before poisoning
f = after poisoning

poisoning shows a very low activation energy for methane production. After poisoning the activation energy more closely approaches that of pure nickel, suggesting that the most active methanation sites on this catalyst are the first sites to be poisoned, or that the surface concentration of nickel is increased by a further exposure to the H_2 reducing environment.

Since chemisorption work with Ni-Fe-A-100 has shown that this catalyst takes about 10 hours to reach maximum reduction, differential tests with this catalyst were performed after 12 hours reduction to determine if this catalyst would be more stable after a long reduction. Figure 6 shows that the catalyst continues to exhibit serious deactivation with time. This catalyst also exhibits very low selectivity toward methane and high CO_2 production.

Task 4: Catalyst Life and Geometry: Testing and Design.

Accomplishments. During the last quarter activity vs. temperature tests were conducted on 6 nickel and nickel alloy catalysts. The results of these tests are shown in Figures 7 through 12 with a summary of some of the important conversion parameters in Table 6. The Ni-Co catalyst has the highest CO conversion and reaches its maximum at the lowest temperature of any catalyst tested. This catalyst also has the highest overall CO_2 production. Ni-Pt-A-100 has a surprisingly low maximum conversion considering its high metal content. However, it has extremely high selectivity for methane over the range 200-275°C. The least active catalyst is Ni-Ru-A-105. Ni, Ni-Co, and Ni-MoO_3 exhibit curves characteristic of nickel with a very steep rising slope. Ni-Rh and Ni-Ru exhibit comparatively shallow rising slopes and a later and sharper maximum. Ni-Pt fall about midway between these two types of curve. The variations of these catalysts give direct evidence of bi-metallic interaction in modifying the characteristics of the nickel catalyst. Table 7 shows the approximate turnover number for these catalysts at 325°C and at maximum conversion. The four low metal content catalysts exhibit much higher activity on this basis compared to the heavy loading catalysts. Ni-MoO_3-A-101 especially and to a lesser extent Ni-A-112 exhibit turnover numbers much higher then might be expected from the differential screening results. Of course, the turnover numbers at 325°C are strongly influenced by pore diffusion and mass transfer effects. Nevertheless these activities are useful for comparing performance under actual reaction conditions at high conversions.

Task 5: Technical Visits and Communication.

The principal investigator Dr. Bartholomew, attended the ASTM catalyst committee meeting held May 17-18 at the National Bureau of Standards in Washington D.C. The primary involvement of the PI at this meeting was in committee discussions to establish standards for measuring Pt and Ni metal surface areas. A procedure was proposed

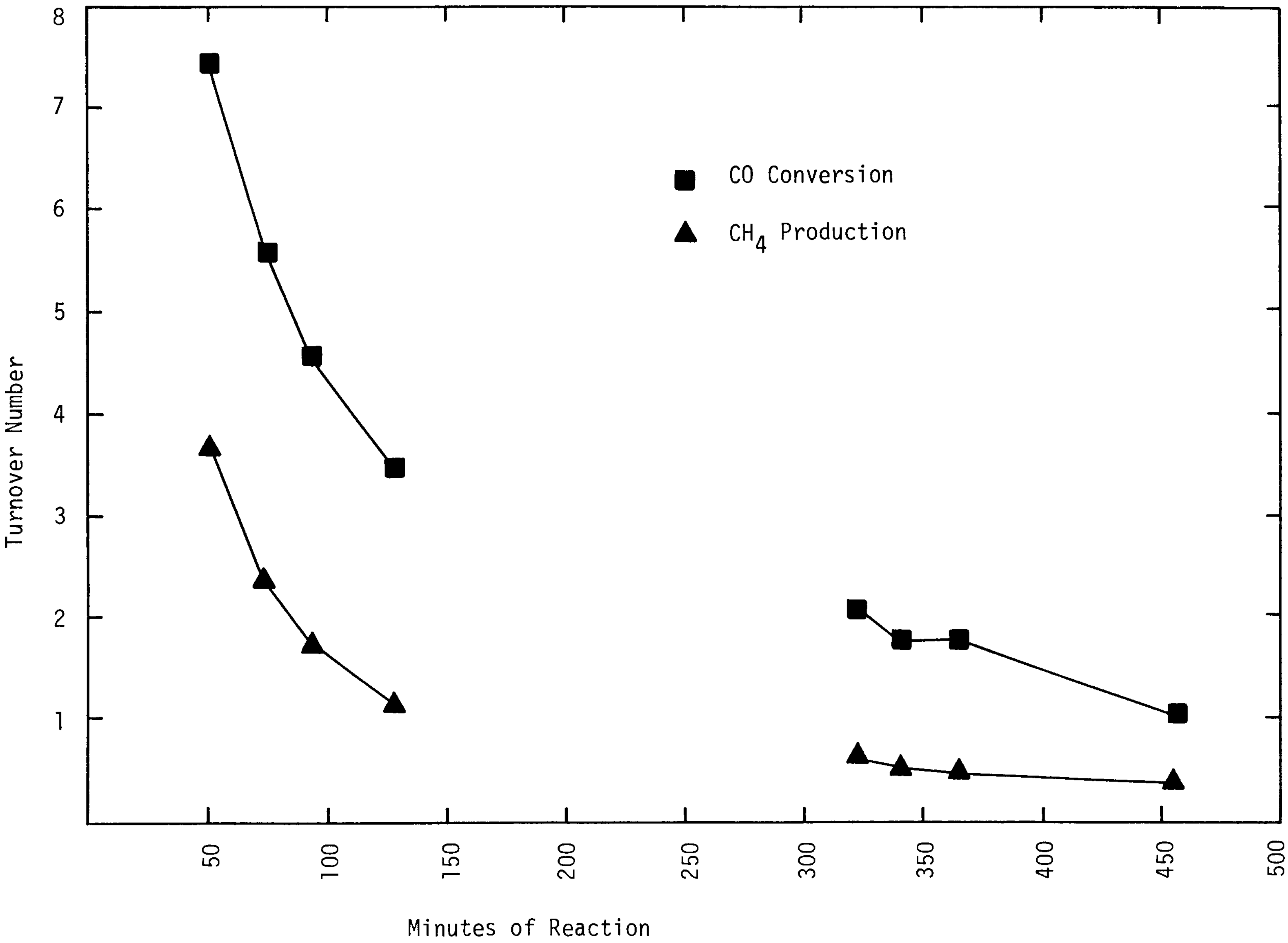

Figure 6. Activity vs. Time for Ni-Fe-A-100 measured at 250°C. During the break the temperature was lowered to 225°C. Then raised back to 250°C. $H_2/CO = 4$; GHSV = 30,000; 20.5 PSIA.

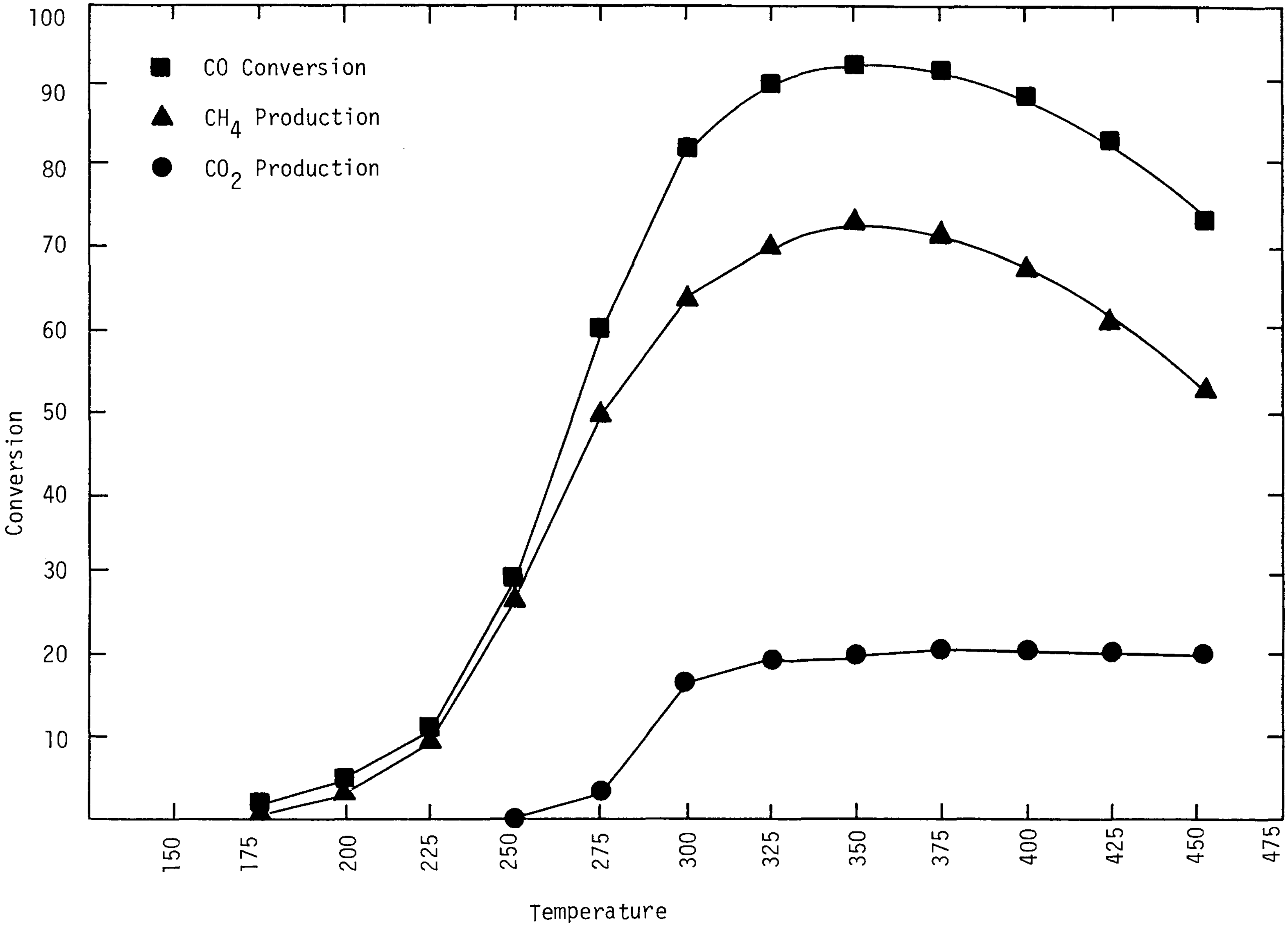

Figure 7. Conversion vs. Temperature for Ni-A-112. GHSV = 15,000; 20.5 PSIA; 1% CO, 4% H_2 in N_2.

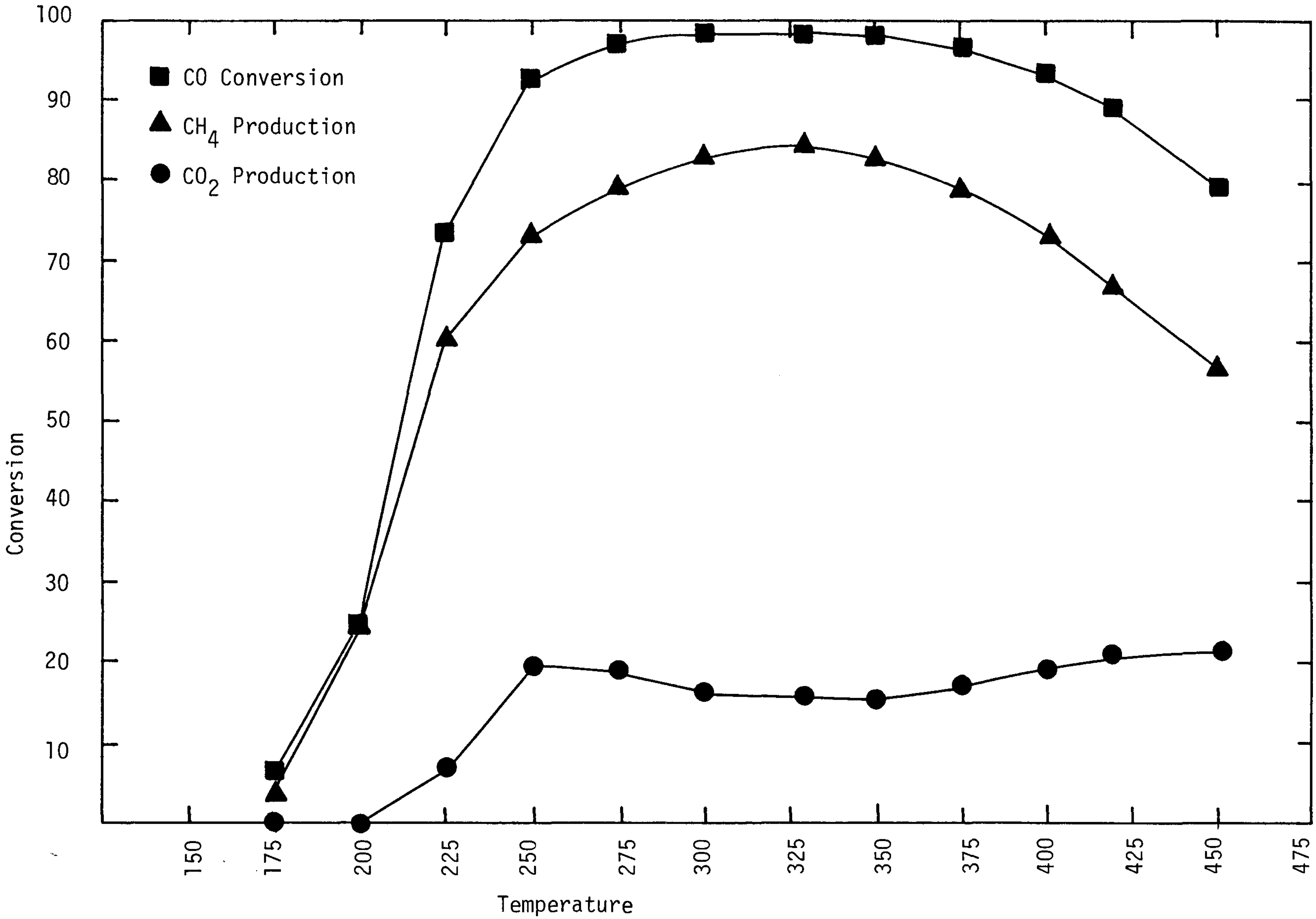

Figure 8. Conversion vs. Temperature for Ni-Co-A-100. GHSV = 15,000; 20.5 PSIA; 1% CO, 4% CH_4 in N_2.

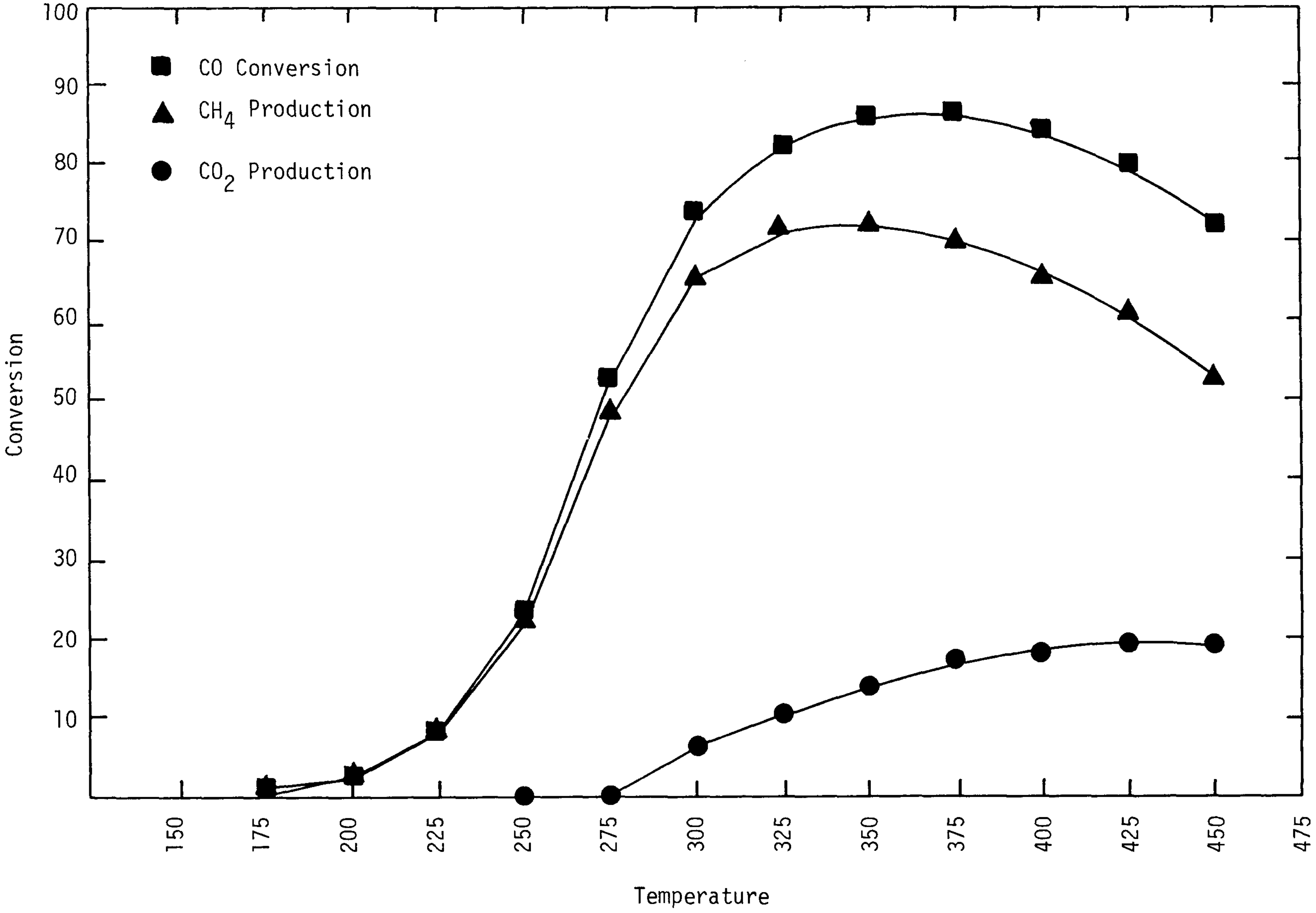

Figure 9. Conversion vs. Temperature for Ni-MoO_3-A-101
GHSV = 15,000; 20.5 PSIA; 1% CO, 4% H_2 in N_2

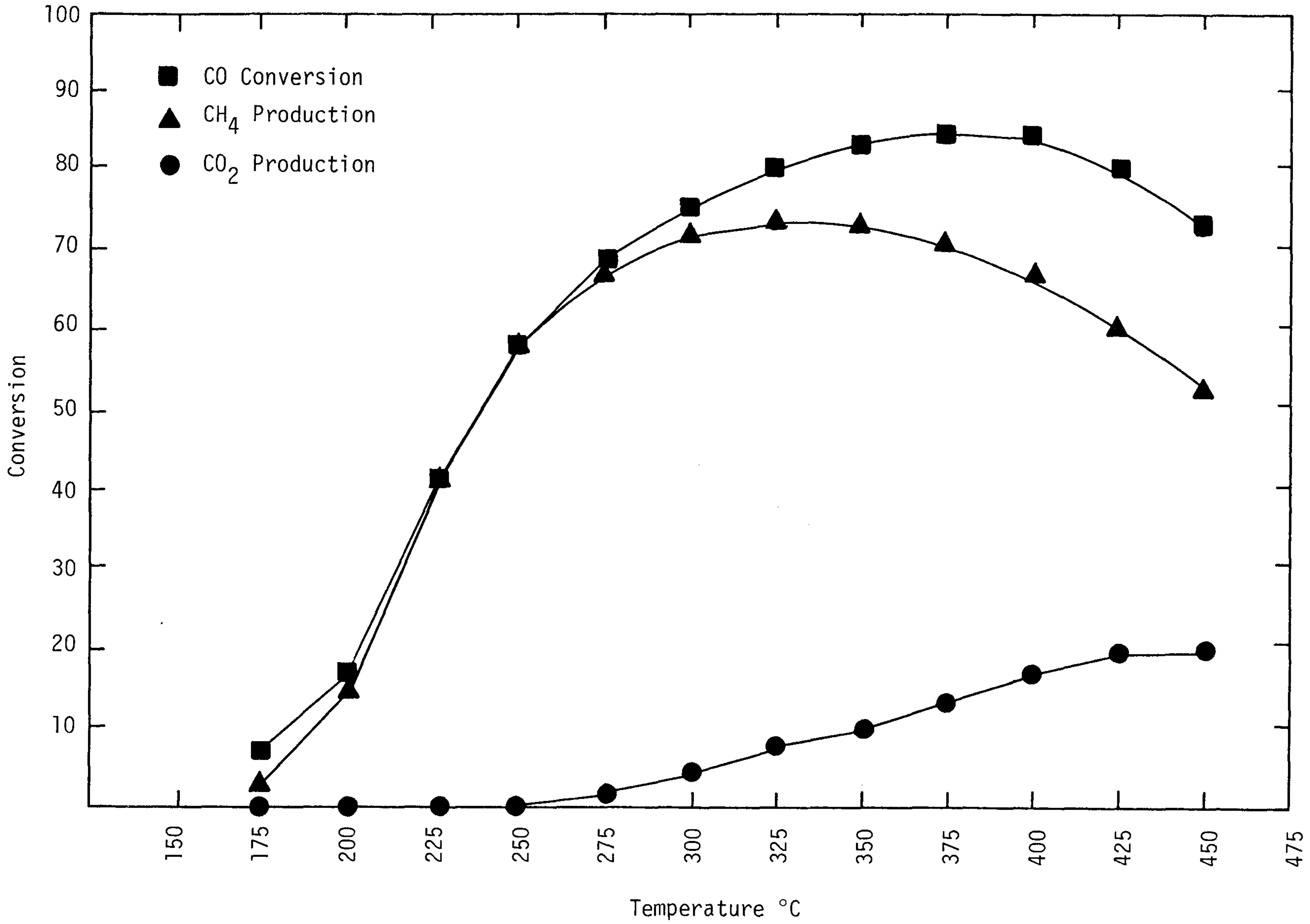

Figure 10. Conversion vs. Temperature for Ni-Pt-A-100
GHSV = 15,000; 20.5 PSIA; 1% CO, 4% CH_4 in N_2

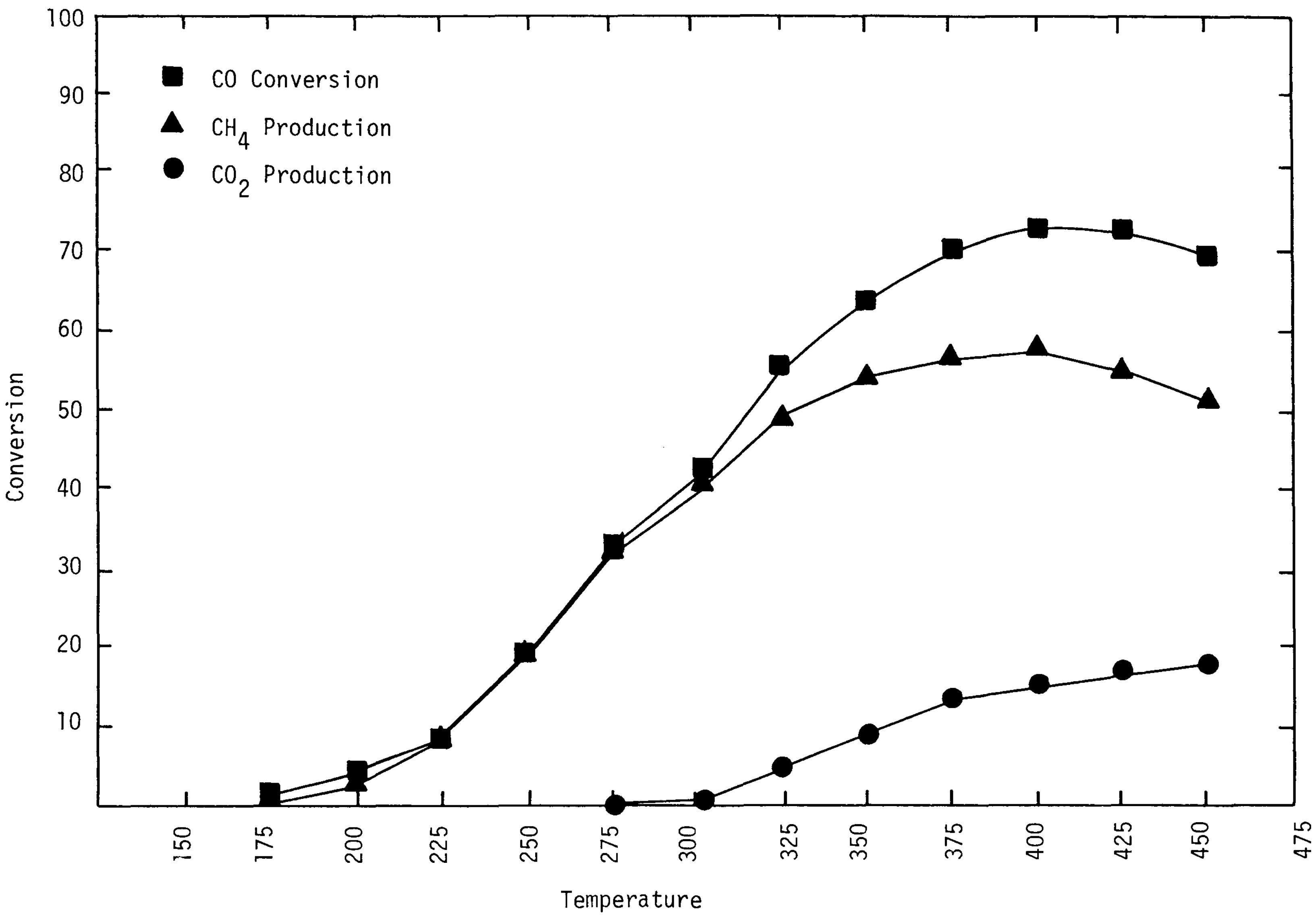

Figure 11. Conversion vs. Temperature for Ni-Ru-A-105. GHSV = 15,000; 20.5 PSIA 1% CO, 4% H_2 in N_2

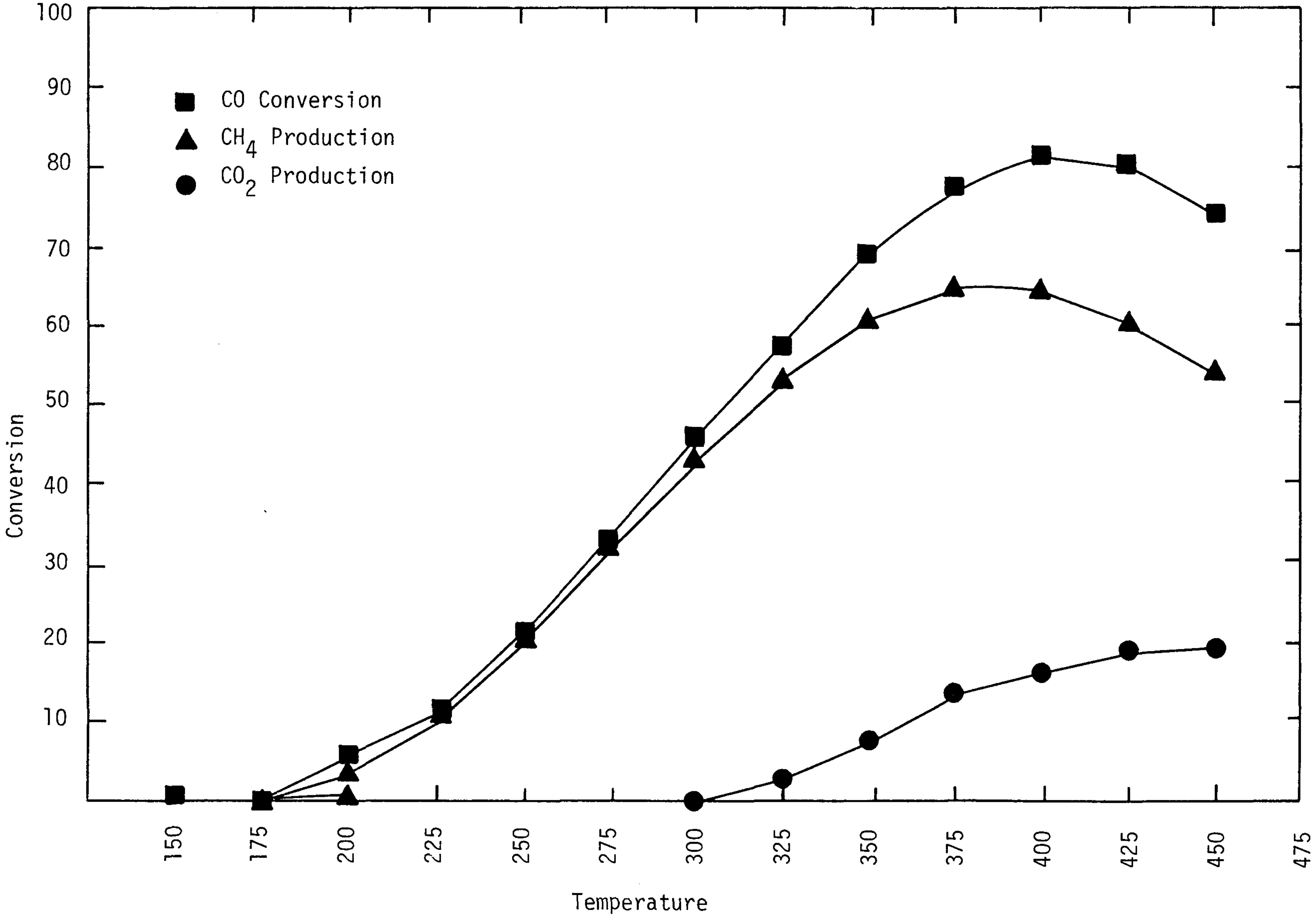

Figure 12. Conversion vs. Temperature for Ni-Rh-A-100
GHSV = 15,000; 20.5 PSIA; 1% CO, 4% H_2 in N_2

TABLE 6

Summary of Integral Test Results.

	Temperature of CO Conversion		Maximum	At Maximum CO Conversion	
Catalyst	50%(°C)	Maximum (°C)	CO Conversion	CH_4 Production	CO_2 Production
Ni-Co-A-100	210	329	99%	84%	16%
Ni-Pt-A-100	237	375	84%	70%	13%
Ni-A-112	265	350	93%	74%	20%
Ni-MoO_3-A-101	270	375	86%	70%	17%
Ni-Rh-A-100	310	400	81%	64%	16%
Ni-Ru-A-105	312	414	73%	56%	16%

Tests were conducted at GHSV = 15,000; temperature increasing at 2°C per minute; 1% CO, 4% H, balance N_2; 20.5 PSIA.

TABLE 7

Approximate Turnover Numbers from Integral Tests.

Catalyst	325°C N_{CO}	325°C N_{CH_4}	At Maximum Conversion N_{CO}	At Maximum Conversion N_{CH_4}
Ni-Co-A-100	13	11.1	13	11.1
Ni-Pt-A-100	10.9	10.0	11.5	9.6
Ni-A-112	44.9	35.0	46.0	36.5
Ni-MoO_3-A-101	84.6	73.5	88.4	72.1
Ni-Rh-A-100	24.2	22.5	34.3	27.2
Ni-Ru-A-105	24.1	21.3	32.0	25.0

for measuring Ni areas, based on work performed in this study and the related NSF study. While at NBS Dr. Bartholomew toured the surface chemistry facilities and discussed methanation research with Dr. John Yates of NBS. The NBS researchers have measured rates on clean polycrystalline nickel ribbon (1.8 x 10^{15} sites/cm^2) in a static reactor at 115 Torr and 740 K (H_2/CO = 5) to obtain a turnover number of 0.9 sec^{-1}. This, according to Dr. Yates, compares favorably with the value of 0.22 sec^{-1} (E_a = 17.4 k cal/mole) obtained by Harriot and Fontaine under similar conditions using a pulse-flow differential reactor.

While in Washington, Dr. Bartholomew visited with Dr. Mike Biallis of ERDA to discuss progress during the past year and ideas for a follow-on proposal. A similar, brief visit was made with Dr. Raffi Turian at NSF regarding our NSF research.

During the same trip the PI made one day visits to three other methanation laboratories: (1) Carnegie-Mellon University, (2) The Pittsburgh Energy Research Center, and (3) The Institute of Gas Technology (IGT).

At Carnegie-Mellon University Dr. Bartholomew discussed in detail with Professor Anthony Dent his ERDA-supported investigation of catalytic hydrocarbon synthesis (methane included) and toured Professor Dent's laboratory, getting a close look at his reactor systems and other experimental apparatus. The day's agenda also included interchange of ideas on methods of catalyst characterization, comparison of equipment design, and discussion regarding possible cooperative efforts.

The visits to the Pittsburgh Energy Research Center (PERC) was equally stimulating and fruitful. During the morning Dr. Bartholomew visited with Dr. Fred Steffgen, supervisor of chemical research and two members of his group, Dr. Charles Kibby and Dr. Richard Wiffenbach. Dr. Kibby is involved in basic methanation research using a pulse reactor, adsorption apparatus, and a new ESCA system. Dr. Wiffenbach is testing Fischer-Tropsch catalysts using a nicely designed laboratory reactor system with a "Berty" autoclave mixed flow reactor. In discussing data on Fischer-Tropsch catalysts, it was concluded that ruthenium containing alloys (such as those in this study) would be of interest in Fischer-Tropsch synthesis.

The afternoon was spent in visiting with Dr. Michael Baird and Dr. Richard Schehl of Dr. Bill Hayne's group and in touring screening, bench scale, and pilot plant facilities for testing methanation catalysts (mainly of the sprayed Raney-nickel variety). Catalyst testing procedures were emphasized in discussions with Dr. Baird; the discussion with Dr. Schehl focused on catalyst deactivation. Apparently the catalyst at PERC are experiencing several types of degradation including sulfur poisoning, carbon deposition, and sintering. Because of the obvious similarity of the parallel plate configuration used at PERC to the monolithic catalysts in this study, arrangements were made with Dr. Baird and Dr. Haynes to spray Raney Ni on a parallel plate configuration to be constructed and subsequently tested at BYU.

At IGT Dr. Bartholomew enjoyed a most worthwhile visit with Mr. Tony Lee, the principal researcher in methanation. The discussion was centered on procedures for testing catalysts and on evaluations to qualify catalysts for industrial use, particularly in the Hygas process. Mr. Lee has a well-designed laboratory reactor system for testing catalysts at high pressures and over long periods of time. The tests of IGT include using mixed flow and fixed bed reactors to determine activity at 1000 psig and 575°F, the upper use temperature limit, the lower use temperature limit, the deactivation rate at the upper temperature limit and the effects of H_2/CO ratio, H_2O concentration, and poisons such as H_2S, C_6H_6, and NH_3. The possibility of having catalysts from this study tested at IGT was discussed; to qualify a catalyst for testing we would need to determine activity data at 400 psig, the upper and lower temperature limits, and the activity as a function of time for three days at the upper temperature limit using a mixture of 4% CO, 15% H_2, 2% CO_2, and the remainder CH_4.

Mr. Lee observed that the two most important areas of catalyst research and development in methanation are (1) developing a sulfur resistant catalyst and (2) increasing the upper use-temperature-limit. All poison resistant catalysts he has tested thus far contained neither nickel or ruthenium. H_2S poisoning is the principal problem in the Hygas methanation plant, where H_2S levels should not but somtimes do exceed 1 ppm. The order of toxicity for various sulfur compounds is $H_2S > CO_3 > CH_3SH > C_2H_5SH > C_4H_4S$.

The Gordon Research Conference on Catalysis held June 28 to July 2 was as usual top quality. The talks and discussions were generally very good and some quite pertinent to coal research. Although the attendees at these conferences are constrained from making formal reference to the proceedings, the PI took copious notes, which have already proven useful. In addition the PI had ample opportunity to discuss methanation catalysis with other attendees, including about a dozen who are doing methanation-related research. Arrangements were made with several of these researchers to exchange reports, papers and data. Dr. Bartholomew also presented a minitalk (10-15 min.) dealing with adsorption stoichiometries on Ni based on the NSF work and obtained feed back which will be useful in both the NSF and ERDA studies.

Miscellaneous

Mr. Blaine Barton and Mr. Donald Stowell have completed requirements for a masters degree in chemical engineering based on work performed as part of this contract. Both will take industrial jobs during the very near future. Their theses deal respectively with kinetics of alloy methanation catalysts and effects of H_2S on adsorption and methanation activity. Mr. George Jarvi, (gradute student) joined our research group June 15th and is presently pursuing masters research in methanation catalyst testing involving monoliths and pellets; he is assisted by Mr. Kevin Mayo (undergraduate) who began work in late July.

IV. CONCLUSIONS

A. Most catalysts show decreased hydrogen uptake after exposure to H_2S. Increases in hydrogen uptake after exposure to 10 ppm H_2S in H_2 at 450°C are possibly the result of further reduction of the metal by hydrogen. In this case the increased metal surface due to further reduction more then offsets the loss of surface sites due to H_2S adsorption.

B. Previously reported activity data were affected by non-isothermal conditions in the old reactor and are 20-50% greater than data determined in the new reactor in which isothermal operation is assured for low conversions; nevertheless, the general trends reported previously are still valid.

C. Ni and Ni alloys are more active then Ru and Ru alloys.

D. Ni-Co is the most active catalyst on a per hydrogen adsorption site basis. A 14 wt% Ni/Al_2O_3 is the most active catalyst on a per mass basis.

E. The selectivity to methane for Ni-Pt, Ni-Co, and Ru-Co changes with length of reduction time possibly due to changes in surface composition. A similar effect may also explain the large change in selectivity of Ni-Pd upon poisoning.

F. Catalysts with high metal content exhibit higher turnover numbers than do catalysts with low metal content. This is evidence for a metal support interaction, as there are no appreciable differences in metal particle size between the two groups.

G. Cobalt containing catalysts exhibit the greatest resistance to partial poisoning by H_2S. Ni/Al_2O_3 and $Ni\text{-}MoO_3/Al_2O_3$ exhibit the least resistance to poisoning.

H. The activity data for high metal content catalysts are influenced by pore resistance. This is evident in a 2-5 kcal/mole lower apparent activation energy for the high metal catalysts compared to catalysts with low metal loadings.

I. Conversion vs. temperature data are considerably different for bi-metallic catalysts compared to the pure metals. $Ni\text{-}MoO_3/Al_2O_3$ shows an unexpectedly high activity (on a per site basis) at 325°C.

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APPENDICES

APPENDIX A

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