FE-1790-6
Distribution Category UC-90c

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

Phase 2

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

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Date Published--November 6, 1976

PREPARED FOR
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Under Contract No. E(49-18)-1790

FOREWORD

This report summarizes technical progress during the sixth quarter period (July 23, 1976 to October 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 - Richard Turner, George Jarvi and Gordon Weatherbee and Undergraduates - Kevin Mayo, Kenneth Atwood, and Glen Witt. Elaine Alger and Scott Folster provided typing and drafting services.

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ABSTRACT

This report details accomplishments during the sixth quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Alumina-supported Co (20 wt.% metal loading), Ni-MoO_3 (20%), and several Ni/Al_2O_3/monolith samples (10 and 20%) were prepared. Hydrogen adsorption data were obtained for alumina-supported Co, Ni-MoO_3,Ni-Ru, Ni-Rh, Ni-Pt, and Ni-Co before and after exposure to 10 ppm H_2S and for 2 fresh monolithic-supported nickel catalysts. Differential activity tests were conducted for pellet-supported Co, Ni-MoO_3, Ni-Ru and Ni-Rh (before and after poisoning) and for three monolithic nickel 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 pellet-supported nickel and cobalt catalysts in the absence and presence of water and on monolithic nickel catalysts at 2 different space velocities. A test to measure effects of carbon deposition was conducted for 3% Ni/Al_2O_3. The Principal Investigator attended the Centennial ACS Meeting in San Francisco and the ERDA Contractors Conference in Golden, Colorado, presented two invited papers and a seminar, visited three laboratories, received four visitors, and prepared several publications and proposals.

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 of 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 suport (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 the 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 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-continous 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 or 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 catlaysis 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 4, Catalyst Testing and Design, is well ahead of schedule. Tasks 2 and 3 have been essentially completed.

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

Task 1. Two pellet-supported catalysts were prepared: 20% Co/Al_2O_3 and 20% $Ni-MoO_3/Al_2O_3$. Several Ni/Al_2O_3/monolith catalysts were also prepared. Hydrogen chemisorptive uptakes were measured before and after exposure to 10 ppm H_2S (12 or more hours) for pellet-supported Co, $Ni-MoO_3$, Ni-Rh, and Ni-Co. Hydrogen uptakes were also determined for two monolithic-supported nickel catalysts.

Task 2. Reactor construction was completed during the fourth quarter. However, several minor additions and modifications were made during the past quarter.

Task 3. Measurements of methanation activity were carried out before and after exposure to 10 ppm H_2S for Co, $Ni-MoO_3$, Ni-Ru and Ni-Rh catalysts (pellet form) at 225 and 250°C, 20.5 psia, and a space velocity of 30,000 hr^{-1}. The fresh activity of three monolithic-supported nickel catalysts was measured under the same conditions.

Task 4. Conversion versus temperature measurements were carried out at 20.5 psia, 175-400°C, and a space velocity of 15,000 hr^{-1} for 20% Co/Al_2O_3, 3% Ni/Al_2O_3, and 14% Ni/Al_2O_3. Effects of 15 Vol.% water vapor on activity and selectively were determined for the two nickel catalysts. Conversion-temperature measurements were also made for three monolithic catalysts under similar conditions but at space velocities of 15,000 and 30,000 hr^{-1}.

Task 5. The principal investigator presented two invited papers at the Centennial ACS Meeting in San Francisco and a seminar at the University of Utah. He also visited catalysis laboratories at SRI, Stanford University, and the University of Utah and participated in the ERDA University Contractors' Conference in Golden, Colorado. Visitors to BYU included Professor Michel Boudart of Stanford University, Mr. Tony Lee of IGT, Mr. Bill Boyer of Corning Glass Works, and Mr. Robert Wade of the Ventron Corporation. A paper was published in the preprints of the ACS Fuel Chemistry Division and a proposal to continue this project an additional year was completed and submitted.

Miscellaneous. Mr. Scott Engstrom entered MIT for graduate work; Mr. Richard Turner initiated study at the University Utah Medical School. Mr. Gordon Weatherbee (Graduate - M.S.), Mr. Ken Atwood (Senior), and Mr. Glen Witt (Freshman) joined the research group in September.

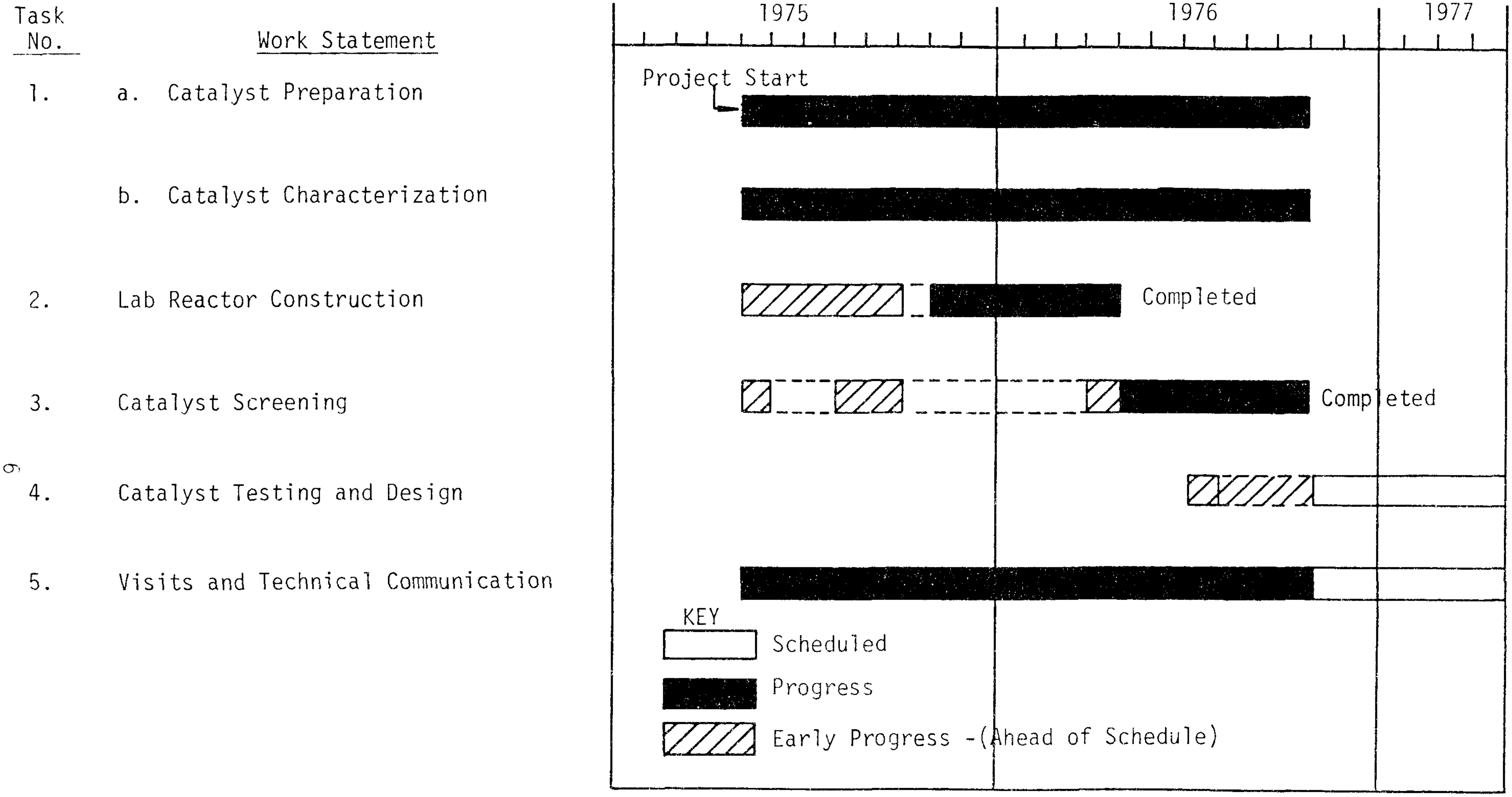

Figure 1. Project Progress Summary.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation: An alumina pellet-supported cobalt catalyst (20% Co/Al_2O_3) was prepared to provide a comparison with the Ni and Ni-Co catalysts previously tested. A 20% $NiMoO_3$ catalyst was prepared to compare against our 6% Ni-MoO_3 catalyst and to be used in sintering experiments as part of the companion NSF study. In addition several of the research size support monoliths from Corning Glass Works, 1" OD x 1.2", 200□/in^2, were prepared with Kaiser SA Medium alumina, calcined at 600°C, and coated with nickel nitrate solution. Various procedures for applying the alumina coating and impregnating with nickel nitrate were followed with varying degrees of success. The impregnation technique judged to be most useful involved dipping the coated monolith in Ni nitrate solution, blowing off the excess, drying with heat gun and heating at 200°C for no more than 90 minutes. More severe drying tended to cause nitrate decomposition in air. After the water of hydration was driven off, the monoliths were reduced in hydrogen using a previously described temperature schedule (3) to decompose the nitrate. A small temperature ramp prevents exothermic NH_3 formation and the associated temperature excursion, such as ocurred for Ni-M-107. Ni-M-113, -114, and -115 contain the desired 20% nickel metal and 20% alumina substrate. Various other samples were damaged in temperature excursions or in handling miscues. These production problems have been largely solved so that preparation of nickel alloys on monolith supports during the next quarter should proceed quite smoothly.

2. Characterization: Hydrogen chemisorption uptakes measured for six different pellet-type catalysts and two monolithic-types are summarized in Table 1. Two of the pellet type catalysts were poisoned with 10 ppm H_2S/H_2 for 12 hours and another four were poisoned with sufficient H_2S to cover 40% of all available metal sites. In all cases the uptake decreased after poisoning. Uptakes for two previously reduced monolithic nickel catalysts were measured after two hours of rereduction at 450°C and a GHSV of 2,000 hr^{-1}. Work is currently underway to determine if this time is sufficient for complete rereduction.

Hydrogen chemisorption isotherms before and after exposure to 10 ppm H_2S/H_2 (12 hours) are shown in Figure 2 for Co-A-100 (20% Co/Al_2O_3). The hydrogen uptake for the fresh catalyst of 43.4 moles/g is a factor of 4-5 less than typical values of 150-200 moles/g measured for 15-20% Ni/Al_2O_3 catalysts. The stoichiometry of hydrogen adsorption on cobalt and the extent of reduction to cobalt metal for these conditions is not known. However, experiments will be performed during the next quarter to determine the extent of reduction to the metal and the stoichiometry of H_2 adsorption on cobalt.

TABLE 1

Hydrogen Chemisorptive Uptake Data for Alumina Pellet and Monolith Supported Catalysts

Catalyst	Nominal Composition (wt.%)	H_2 Uptake (μ mole/gram) Before Poisoning	H_2 Uptake (μ mole/gram) After Poisoning
Pellets:			
Co-A-100 +	20% Co	43.4	34.5
Ni-MoO_3-A-102 +	10% Ni, 10% MoO_3	136.5	98.2
Ni-Rh-A-101 *	16.6% Ni, 3.4% Rh	168.8	113.1
Ni-Ru-A-106*	16.6% Ni, 3.4% Ru	185.4	109.3
Ni-Pt-A-100 *	15% Ni, 0.5% Pt	112.9	94.1
Ni-Co-A-100 *	10% Ni, 10% Co	116.3	65.0
Monoliths:			
Ni-M-107	8-9% Ni	25.6	
Ni-M-113	20% Ni	75.1	
Ni-M-114	20% Ni	65.4	

* 40% of metal sites were poisoned with H_2S

\+ poisoned for 12 hours with 10 ppm H_2S at a GHSV of 2,000 hr^{-1}

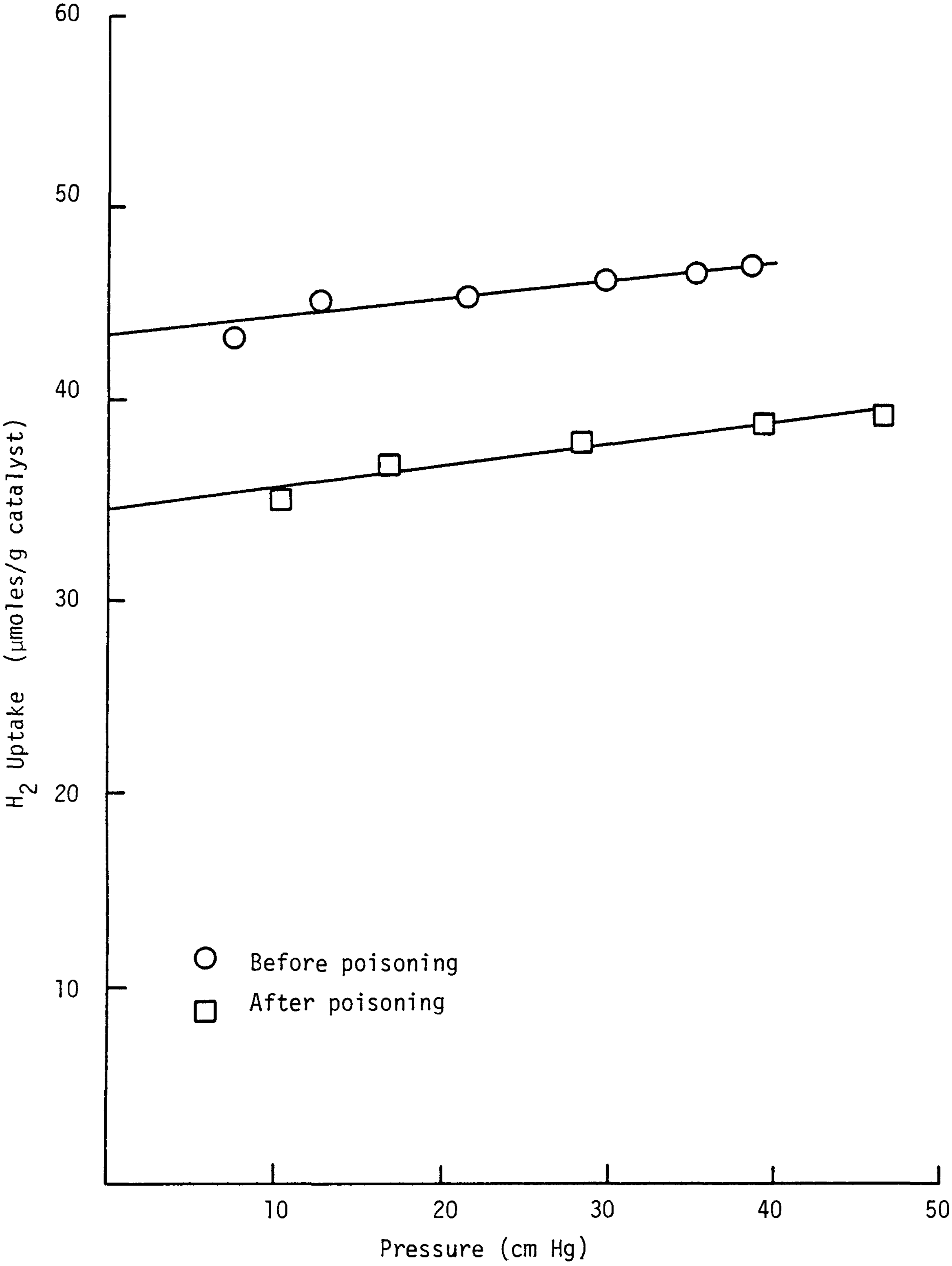

Figure 2. Hydrogen Chemisorption Isotherms for Co-A-100 (20% Co/Al_2O_3) Before and After Exposure to H_2S.

B. Task 2: Laboratory Reactor Construction.

Reactor construction was essentially completed during the fourth quarter. During the past quarter only minor modifications to the reactor system were made. In anticipation of running at high pressures and due to the initiation of the water addition studies, the sampling point for products was moved from just downstream of the reactor to downstream of both the condenser unit and the back pressure regulator. This was done to insure that the sampling line to the gas chromatograph would not be at high pressure, and also to eliminate water from the product sample line.

C. Task 3: Reactor Screening of Alloy Catalyst.

During this past quarter four pellet-supported catalysts and three monolithic-supported catalysts were screened in differential activity tests. The four pellet supported catalysts, Co-A-100, Ni-MoO_3-A-102, Ni-Ru-A-106 and Ni-Rh-A-101, each had an active metal loading of 20 wt.%. Two of the monolithic supported catalysts, Ni-M-113 and Ni-M-114, were also 20 wt. % active metal while the other monolithic suported catalyst, Ni-M-107, was about 8-10 wt.% active metal (part of this catalyst crumbled away leaving some uncertainty as to the metal loading). The catalyst samples of 1/8 inch pellets were approximately 4 to 6 ml in volume, giving a maximum bed depth of one centimeter. The monolithic catalysts were circular, one inch in diameter, approximately 1/2 inch in depth with 200 square channels per square inch. After the initial test the pellet supported catalysts were poisoned with 10 ppm H_2S in H_2 (GHSV = 2,000 hr^{-1}) for 12 hours at a temperature of 450°C, after which they were tested again.

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, reaction rates per gram of catalyst and turnover numbers 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, a pressure of 20.5 psia and a space velocity of 30,000 hr^{-1}, using a reactant gas mixture containing 1% CO, 4% H_2, and 95% N_2. Rates (per gram of catalyst) and turnover numbers at 250°C are shown graphically in Figures 3 and 4.

Comparison of rates on a mass basis (Tables 2 and 3 and Figure 3) shows Ni-MoO_3-A-102 (20% Ni-MoO_3/Al_2O_3) to have the highest activity. This high activity is a result of both a reasonably high surface area (see Table 1) and a very high turnover number, which is in very close agreement with the turnover number reported previously for 6% Ni-MoO_3 Al_2O_3 (4). Nevertheless, the turnover number for Co-A-100 (20% Co/al_2O_3) is higher, in fact the highest of any catalyst tested to date. Comparison of selectivities in Table 2 shows the nickel molybdate catalyst to be most selective at 250°C. All nickel containing-catalysts show higher selectivities to CH_4 at 250°C than at 225°C, in agreement with previously reported data (3,4). The cobalt catalyst, however

TABLE 2

Reactor Screening Data

225°C, GHSV = 30,000 hr^{-1}; 20.5 PSIA

Catalyst	% Conversion	% Production		% Selectivity	
	CO	CH_4	CO_2	CH_4	CO_2
Pellet Catalysts					
Co-A-100	5.17	4.32	0.12	84.3	2.3
Co-A-100 Poisoned	4.28	3.18	0.22	75.9	5.4
Ni-MoO_3-A-102	15.0	11.2	1.05	74.2	7.0
Ni-MoO_3-A-102 Poisoned	13.38	9.63	0.94	72.1	7.1
Ni-Rh-A-101	6.33	4.49	0.00	71.1	0.0
Ni-Rh-A-101 Poisoned	2.21	1.95	0.00	89.7	0.0
Ni-Ru-A-106	7.12	5.07	0.02	74.0	0.5
Ni-Ru-A-106 Poisoned	5.99	4.81	0.0	80.7	0.0
Monolithic catalysts					
Ni-M-107	6.61	4.98	0.00	75.6	0.0
Ni-M-113	11.57	8.72	0.05	75.4	0.4
Ni-M-114	13.52	10.2	0.14	75.4	1.1

Catalyst	Rate x 10^7 gMoles/gcat-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
Pellet Catalysts						
Co-A-100	3.2	2.7	3.7	3.1	--	--
Co-A-100 Poisoned	2.7	2.0	3.1	2.3	3.9	2.9
Ni-MoO_3-A-102	9.3	6.9	2.9	2.1	--	--
Ni-MoO_3-A-102 Poisoned	7.9	5.7	2.9	2.1	4.1	2.9
Ni-Rh-A-101	4.0	2.8	1.3	0.93	--	--
Ni-Rh-A-101 Poisoned	1.5	1.3	0.44	0.39	0.65	0.58
Ni-Ru-A-106	4.6	3.3	1.2	0.87	--	--
Ni-Ru-A-106 Poisoned	3.8	3.1	1.0	0.83	1.75	1.4
Monolithic Catalysts						
Ni-M-107	3.8	2.9	7.4	5.5		
Ni-M-113	6.3	4.8	4.2	3.2		
Ni-M-114	7.5	5.7	4.7	3.5		

TABLE 3

Reactor Screening Data
250°C; GHSV = 30,000 hr^{-1}; 20.5 PSIA

Catalyst	% Conversion	% Production		% Selectivity	
	CO	CH_4	CO_2	CH_4	CO_2
Pellet Catalysts					
Co-A-100	19.84	15.11	3.13	76.3	15.8
Co-A-100 Poisoned	12,59	9.3	1.0	73.9	8.1
Ni-MoO$_3$-A-102	34.38	27.64	3.01	80.4	8.8
Ni-MoO$_3$-A-102 Poisoned	34.0	28.23	2.99	83.1	8.8
Ni-Rh-A-101	11.28	8.31	0.00	73.7	0.0
Ni-Rh-A-101 Poisoned	4.06	3.15	0.00	78.0	0.0
Ni-Ru-A-106	12.95	9.90	0.02	76.5	0.2
Ni-Ru-A-106 Poisoned	11.58	9.52	0.03	82.3	0.3
Monolithic Catalysts					
Ni-M-107	14.62	11.38	0.17	77.9	1.2
Ni-M-113	27.95	24.60	0.49	88.0	1.8
Ni-M-114	31.7	27.82	0.55	87.8	1.7

Catalyst	Rate x 10^7 (Moles/gcat-sec)		Turnover Number x 10^3 Based on Fresh H_2 Uptake		Turnover Number x 10^3 Based on Poisoned H_2 Uptake	
	CO	CH_4	CO	CH_4	CO	CH_4
Pellet Catalysts						
Co-A-100	12.4	9.4	14.3	10.9	--	--
Co-A-100 Poisoned	8.0	5.9	9.2	6.8	11.6	8.6
Ni-MoO$_3$-A-102	21.3	17.1	7.8	6.3	--	--
Ni-MoO$_3$-A-102 Poisoned	20.2	16.8	7.4	6.1	10.3	8.5
Ni-Rh-A-101	7.1	5.3	2.3	1.7	--	--
Ni-Rh-A-101 Poisoned	2.75	2.10	0.81	0.63	1.2	0.93
Ni-Ru-A-106	8.3	6.3	2.25	1.70	--	--
Ni-Ru-A-106 Poisoned	7.2	6.4	1.95	1.70	3.3	2.9
Monolithic Catalysts						
Ni-M-107	8.4	6.5	16.3	12.7		
Ni-M-113	15.4	13.5	10.2	9.0		
Ni-M-114	17.6	15.5	11.0	9.6		

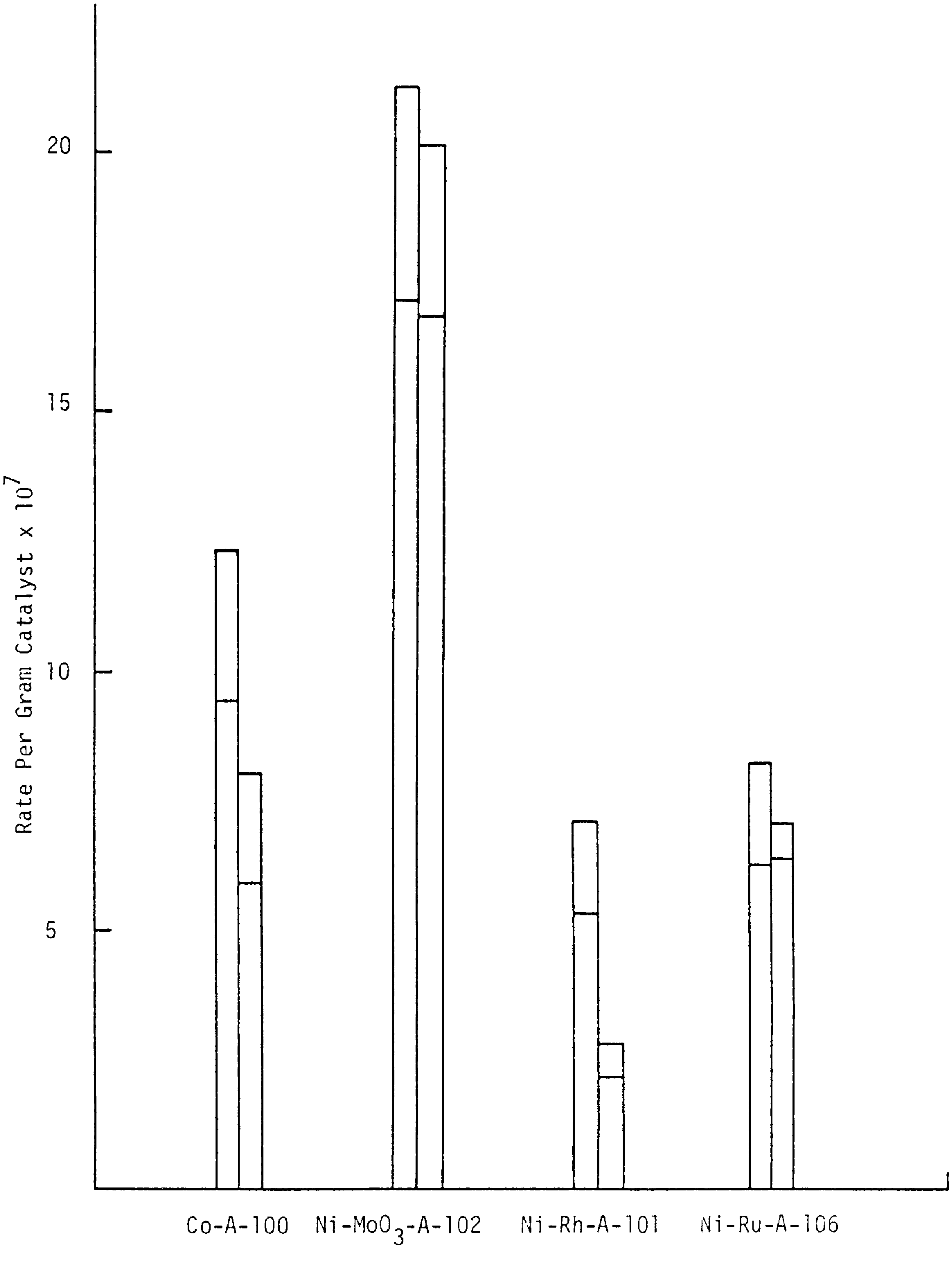

Figure 3. The Effect of H_2S on Methanation Activity at 250°C (GHSV = 30,000 hr^{-1}). The first bar of each pair represents the activity of the fresh catalyst; the second indicates the activity after exposure to 10 ppm (molar basis) H_2S in H_2 for 12 hours at a space velocity of 2,000 hr^{-1} and 450°C. The upper bar represents CO conversion while the lower bar represents methane production. The catalysts were reduced for 2 hours in flowing H_2 at 450°C.

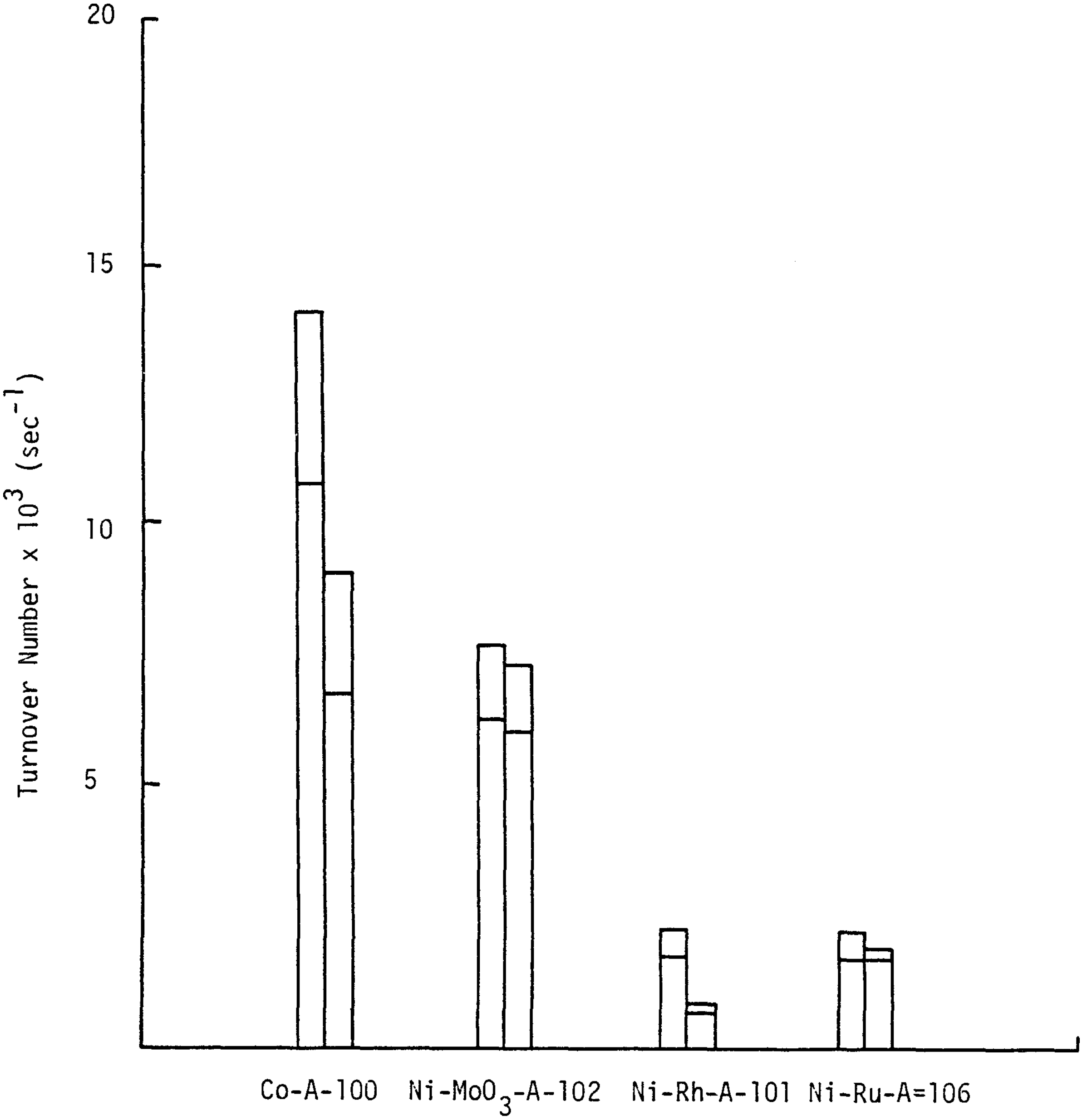

Figure 4. The Effect of H_2S on Turnover Number at 250°C (GHSV = 30,000 hr^{-1}). For explanation of the bars see Figure 2. The catalysts were reduced for 2 hours in flowing H_2 at 450°C.

shows a slightly lower selectivity to CH_4 at 250°C than at 225°C similar to the nickel-cobalt alloy for which data were reported in the last quarterly report (4). Moreover the cobalt catalyst shows a lower selectivity than did the nickel-cobalt alloy and a decrease in selectivity after exposure to H_2S poisoning, which effect was also seen for the nickel-cobalt alloy. These trends observed for the cobalt-containing catalysts were also evident for ruthenium catalysts discussed in the previous quarterly report (4).

Selectivity data in Tables 2 and 3 also show that significant amounts of carbon dioxide (2-16%) are formed by the cobalt and Ni-MoO_3 catalysts. Presumably the remainder of the products besides CH_4 include 10-20% C_{2+} hydrocarbons. The Ni-Ru and Ni-Rh alloys apparently form no CO_2 but presumably 20-25% C_{2+} hydrocarbons.

Table 4 shows the apparent activation energies, for the catalysts, calculated from the data in Tables 2 and 3. The value of 26.0 kcal/mole for the fresh cobalt is the highest of any catalysts tested thus far but is in excellent agreement with the value of 27.0 reported by Vannice (5). The value of 22.8 for the 20% Ni-MoO_3/Al_2O_3 is low relative to the value of 26.2 reported earlier (3) for the 6% Ni-MoO_3/Al_2O_3, presumably due to effects of pore diffusion because of the high conversions obtained for the higher loading catalyst. The values of 12.5 and 13.4 for the 20% Ni-Rh and Ni-Ru catalysts are approximately half the values of 20.7 and 25.3 observed previously (3) for the 3% catalysts. The larger conversions for the 20% catalysts might explain at least part of these differences.

In comparing the data for the monolithic supported catalysts with those previously reported for pellet-supported nickel catalysts (3,4), the monolithic catalysts have larger activation energies, even though the turnover numbers and conversions are higher for the monolithic catalysts. These larger activation energies are very likely a result of greater effectiveness (less pore resistance) for the monolithic catalysts. This hypothesis is reasonable since the average pore lengths are smaller for the Al_2O_3 monolith coating than for the 1/8 inch beads.

Table 5 shows the fractional changes in hydrogen uptake and turnover number with poisoning of the catalyst together with the ratio of these two numbers called the poisoning site activity ratio (PSAR). The PSAR is a measure of the change in activity of the the methanation sites as a result of partial poisoning. A value less than 1.0 indicates that either the most active sites are poisoned first or that H_2S interacts strongly with the remaining sites to decrease their activity. Conversely, a PSAR value greater than 1.0 indicates either the least active sites are poisoned first or that H_2S interacts with the remaining sites to enhance their activity. Thus the Ni-MoO_3 and Ni-Ru catalysts appear to be more resistant to low concentrations of H_2S than are the Ni-Rh and cobalt catalysts and in fact more resistant than any of the catalysts tested to date (4). These results are most encouraging. Nevertheless, it is not yet understood why the 20% Ni-MoO_3 catalyst is more resistant than the 6% Ni-MoO_3.

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)
Pellet Catalysts		
Co-A-100	28.0	26.0
Co-A-100 Poisoned	22.5	22.5
Ni-MoO_3-A-102	20.5	22.8
Ni-MoO_3 A 102 Poisoned	19.4	22.1
Ni-Rh-A-101	11.8	12.5
Ni-Rh-A-101 Poisoned	12.5	9.9
Ni-Ru-A-106	12.2	13.4
Ni-Ru-A-106 Poisoned	13.2	15.0
Ni-A-112 (3% Ni/Al_2O_3)*	15.5	19.2
Ni-A-116 (14% Ni/Al_2O_3)*	8.8	10.2
G-87 (32% Ni/Al_2O_3)*	13.7	14.2
Monolithic Catalysts		
Ni-M-107	16.4	17.1
Ni-M-113	18.3	21.5
Ni-M-114	17.6	20.8

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* Data determined for these catalysts during 4th and 5th quarters.

TABLE 5

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

Catalyst	$R_1 = H_2\ \text{Uptake}^f / H_2\ \text{Uptake}^I$	$R_2 = N^f_{CH_4} / N^I_{CH_4}$	Poisoned Site Activity Ratio = R_2/R_1
Co-A-100	0.795	0.624	0.785
Ni-MoO_3-A-102	0.719	0.968	1.350
Ni-Rh-A-101	0.670	0.371	0.554
Ni-Ru-A-106	0.590	1.000	1.695

Superscripts I = before poisoning
f = after poisoning

Forecast for Further Work. During the next quarter the recently poisoned Ni-Co catalysts will be tested. Otherwise, this task is essentially completed.

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

Planning of Experiments. This task involves a series of laboratory reactor tests of pellet and monolithic-supported Ni, Ni-Co, Ni-Ru, Ni-Rh, Ni-Pt, and Ni-MoO_3 catalysts as a function of temperature, pressure, H_2S concentration and geometry using the newly constructed reactor described previously (3). These particular catalysts have been chosen for further testing on the basis of promising results obtained in the screening tests (Task 3). This extensive program of testing was begun ahead of schedule during late Summer 1976 and is scheduled for completion by (earliest) October 1977; thus approximately half of this testing program will be completed during the first contract period (ending April 22, 1977).

During the past quarter preliminary experiments, discussions and planning efforts by the principal investigator and students associated with the project resulted in the development of a detailed experimental program for the testing of the methanation catalysts listed above. Altogether there are five different kinds of tests: (1) temperature versus conversion measurements at low pressure with and without steam in the feed gas, (2) temperature versus conversion measurements at high pressure, (3) 24 hour runs at 400°C and different H_2/CO ratios to determine resistance to carbon deposition, (4) measurement of activity at 250°C during in situ exposure to 1 and 10 ppm H_2S, and (5) high conversion measurements at low pressure for the same catalyst supported on monoliths of varying geometry. The detailed experimental conditions and basic procedures used in each of these tests are listed in Table 6. Experimental grids of the tests which are to be performed for each catalyst are shown in Tables 7 and 8 for pellet and monolithic-supported samples respectively.

The integral tests (Test 1 and 2) at high and low pressures will provide rate data over the range of conversion from 0 to 100% and conversion and selectivity data over the important range of temperature. From these data, turnover numbers, selectivities, conversion versus temperature curves, catalyst selectivities, and the effects of water on these parameters can be obtained. In order to determine turnover numbers, the metal surface area will be measured after each set of integral runs. From the steady state, 24-hr. runs (Test 3) the effect of carbon deposition on rate will be determined. Following these runs selected catalysts will be analyzed for carbon content to determine the extent of deposition; metal surface areas will be measured for each samples before and after the run to determine the effects of carbon deposition on hydrogen adsorption. Test 4 will provide data regarding the relative resistances to H_2S of nickel and nickel alloy catalysts (monolith and pellet supports), the rates of poisoning and the effects of H_2S concentration on the rate of poisoning. From the support geometry tests (Test 5) the effects of monolith and pellet geometry on CO conversion and selectivity to methane will be

TABLE 6

Description of Reactor Tests for Task 1

	Test and Procedures	Experimental Conditions
1.	Integral low pressure test: Measure CO conversion and methane production as a function of temperature, with and without 1 % (by vol.) of steam present in the reactants.	200-400°C 8 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2 (dry basis)
2.	Integral high pressure test: Measure CO conversion and methane production as a function of temperature.	200-400°C 350 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2
3.	Steady state (24 hr.) test: Measure intermittently CO conversion and methane production over a period of 24 hours for each value of H_2/CO while increasing temperature gradually to 400°C so that catalysts doesn't overheat.	Increase gradually from 250-400°C 8 psig 30,000-60,000 hr^{-1} 25-50% CO, 50-75% H_2 H_2/CO = 2, 3
4.	In situ H_2S poisoning 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 quartz reactor.	250°C 8 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2 1 or 10 ppm H_2S
5.	Support geometry tests: Measure CO conversion and methane production as a function of temperature for the same catalyst supported on monoliths and pellets of varying geometries.	300-400°C 8 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2

TABLE 7

Experimental Grid for Reactor Testing Pelleted Catalysts (Task 1)

Catalyst	Integral 8 psig 200-400°C 30,000 hr^{-1}		Integral 350 psig 200-400°C 30,000 hr^{-1}	24 hr. SS Run 8 psig, 400°C 30,000 hr^{-1} H_2/CO =		In Situ H_2S Glass Reactor 250°C, 8 psig 30,000 hr^{-1} FID detector	
	No H_2O	1 % H_2O		2	3	1 ppm	10 ppm
3% Ni/Al_2O_3	X	X	X		X		X
15% Ni/Al_2O_3	X	X	X	X	X	X	X
3% $Ni\text{-}Co/Al_2O_3$	X	X				X	X
20% $Ni\text{-}Co/Al_2O_3$	X	X	X	X	X		X
6% $Ni\text{-}MoO_3/Al_2O_3$	X	X	X		X	X	X
16% $Ni\text{-}Pt/Al_2O_3$	X	X	X		X		X
3% $Ni\text{-}Ru/Al_2O_3$	X	X	X	X	X		X
3% $Ni\text{-}Rh/Al_2O_3$	X	X	X		X		X

TABLE 8

Experimental Grid for Reaction Testing of Monolithic Catalysts (Task 1)

Catalyst*	Integral 8 psig 200-400°C 30,000 hr^{-1}		Integral 350 psig 200-400°C 30,000 hr^{-1}	24 hr. SS Runs 8 psig, 400°C 30,000 hr^{-1} $H_2/CO = 3$	In Situ H_2S Glass Reaction 250°C, 8 psig 30,000 hr^{-1}	Geometry✦ 8 psig 300-400°C 30,000 hr^{-1}
	No H_2O	1% H_2O				
15% Ni (3 inches long)	X					
15% Ni (200□/in^2)	X	X	X	X	X	X
(300□/in^2)						X
(236△/in^2)						X
15% Ni/Al_2O_3 Monolith	X	X	X	X	X	
Raney Ni Grid	X	X	X	X	X	
15% Ni-Co	X	X	X	X	X	
15% Ni-MoO_3	X	X	X	X	X	
15% Ni-Pt	X	X	X	X	X	
15% Ni-Ru	X	X	X	X	X	

*All catalysts (except the Raney Ni grid) will be supported on Al_2O_3-coated cordierite monoliths (200 squares/in^2) unless otherwise designated. Test samples are usually 1 inch O.D. by 1/2 inch thick.

✦Three samples of each catalyst, 3-4 runs for each sample determined. Since the methanation reaction is limited by mass transfer to the catalyst exterior at high conversions, the effects of different exterior surface areas should be moderately important in affecting conversion. It will also be important to measure metal surface areas before and after Test 4 and after Test 5.

Accomplishments - Pellet Supported Catalysts. During the last quarter, activity versus temperature tests were conducted on high loading nickel and cobalt catalysts. The results of these tests are shown in Figures 5 and 6. Important conversions parameters for these and other previously tested catalysts are given in Table 9. The Ni, Ni-Co, and Co catalysts have the highest conversions of the catalysts tested. The Ni catalyst has the highest conversion and reaches its maximum at the lowest temperature. The conversion for the Ni-Co catalyst is approxmately the same as the Ni catalyst but reaches its maximum at a slightly higher temperature. Conversion for the Co catalyst is not quite as high as the Ni or Ni-Co catalysts but does reach its maximum at the same temperature as the Ni catalyst. The Co catalyst has the highest CO_2 production of any of the catalysts tested, followed by the Ni-Co catalyst.

Table 10 shows the turnover numbers at high conversion for the Ni, Ni-Co, and Co catalysts along with other previously tested catalysts. The low metal content catalysts tend to have much higher activities on this basis than do the high loading catalysts. However the high loading Co catalyst has a much higher turnover number than the other catalysts in the latter group.

Activity versus temperature tests with steam injection in the feed were initiated for the same group of catalysts. Results for two Ni catalysts (Figures 7 and 8) show that water vapor has a large, detrimental effect on methane production. The overall conversion of CO is increased significantly at a given temperature by the presence of the water vapor. However, the methane production is reduced from 70-90% (no water) to 5-20% (with 15 vol.% water vapor); CO_2 is correspondingly increased by water. This undoubtedly results from an increase in the rate of the water gas shift reaction. The conversion to methane (in the presence of steam) is also found to decrease significantly with increases in temperature, as can be seen clearly in Figure 8. Consideration of the large observed effects of 15 vol.% water and the fact that industrial methanators involve much lower values of H_2O/CO suggests that realistically a lower concentration of steam should be used. Future tests will be carried out using 1-2% water vapor.

Preliminary runs indicate a slight decrease in the activity of the low loading Ni catalyst following the steam injection tests. This is illustrated in Figure 9 in which conversion versus temperature tests at 250-300°C without water were made immediately before and after the steam tests. Data for the high loading nickel (14% Ni/Al_2O_3) catalysts did not evidence measureable deactivation after testing with steam, except for a slight increase in selectivity to CO_2 production (Figure 10). Further tests are being carried out to determine the effects of the water vapor on catalyst composition and state of reduction.

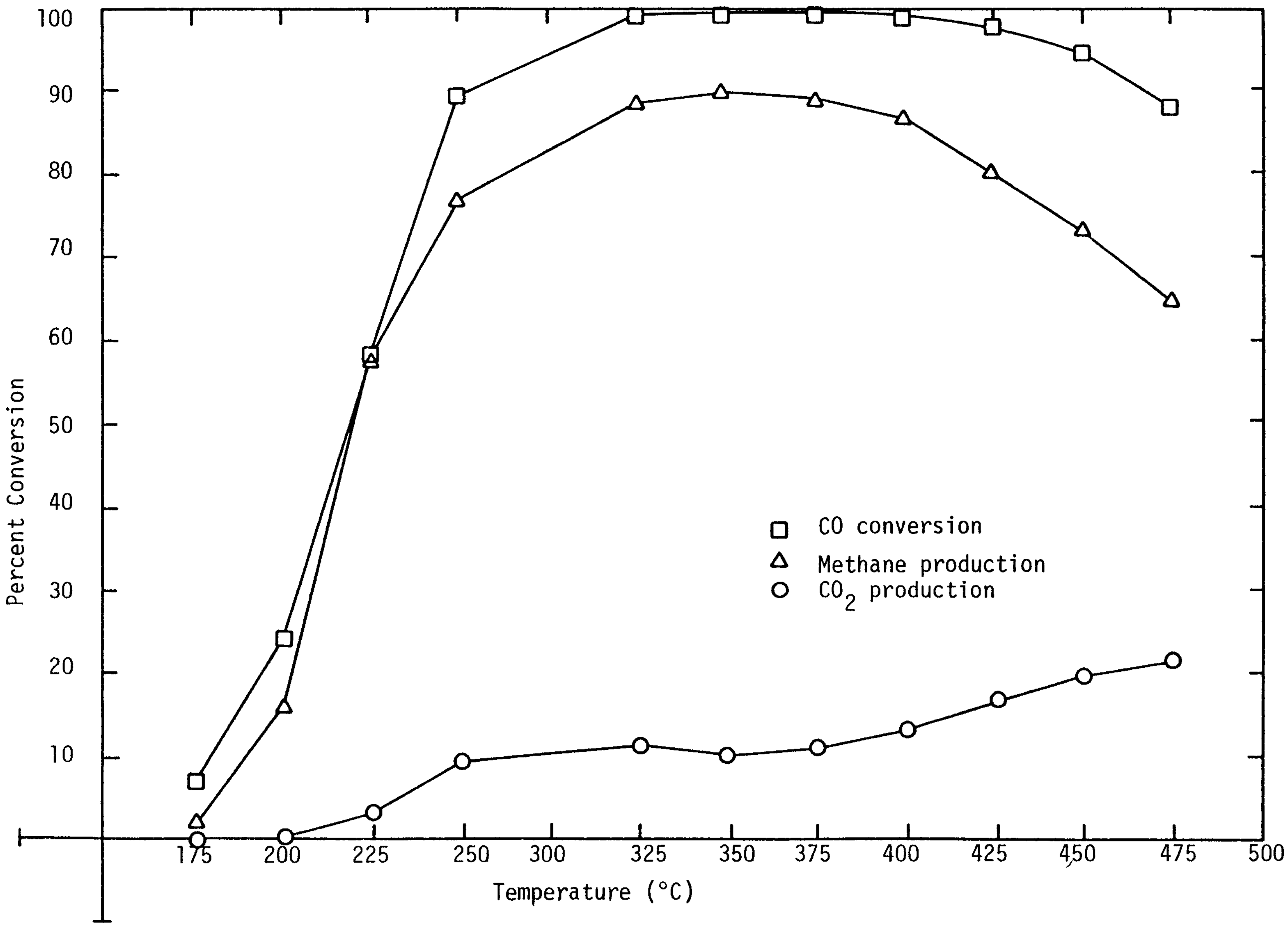

Figure 5. Conversion versus Temperature for Ni-A-116 (14.0 wt.% Ni/Al_2O_3) (20.5 psia; GHSV = 15,000 hr^{-1}).

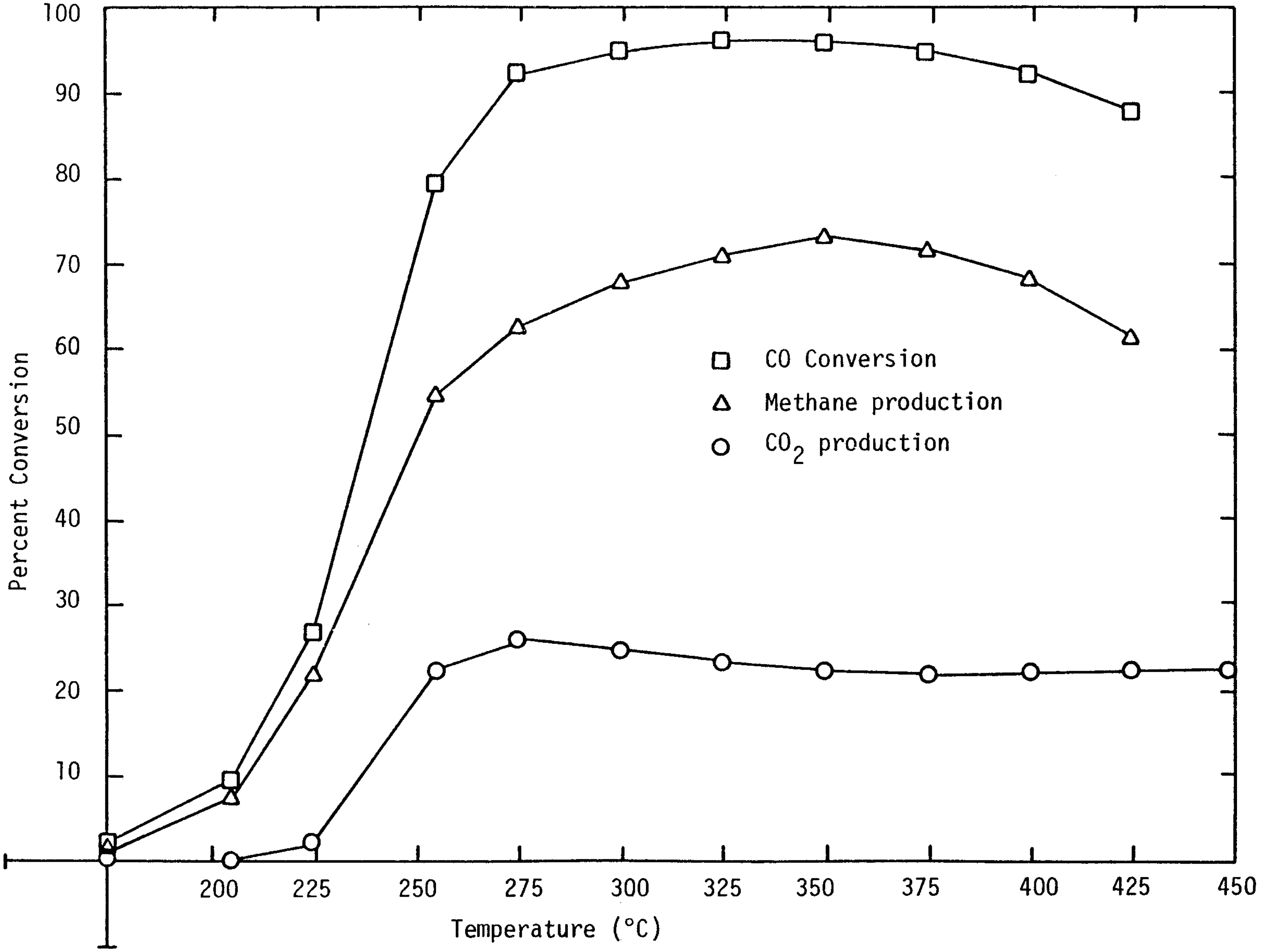

Figure 6. Conversion versus Temperature for Co-A-100 (20% Co/Al_2O_3)
(20.5 psia; GHSV = 15,000 hr^{-1})

TABLE 9

Summary of Integral Test Results
(20.5 psia; GHSV = 15,000 hr^{-1})

Catalyst	Temperature of CO Conversion		Maximum CO Conversion	At Maximum CO Conversion	
	50% (°C)	Maximum (°C)		CH_4 Produc.	CO_2 Produc.
Low Loading Catalysts					
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%
High Loading Catalysts					
Ni-A-116	220	325	99%	89%	10%
Ni-Co-A-100	210	329	99%	84%	16%
Ni-Pt-A-100	237	375	84%	70%	13%
Co-A-100	235	325	96%	71%	23%
Integral Tests with Steam Injection					
Ni-A-112	285	400	96%	3%	86%
Ni-A-116	245	350	99%	19%	75%
Monolithic Catalysts					
Ni-M-113	255	325	100%	96%	4%

TABLE 10

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}
Low Loading Catalysts				
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
High Loading Catalysts				
Ni-A-116	10.1	9.1	10.1	9.0
Ni-Co-A-100	13.0	11.1	13.0	11.1
Ni-Pt-A-100	10.9	10.0	11.5	9.6
Co-A-100	35.7	26.4	35.7	26.4

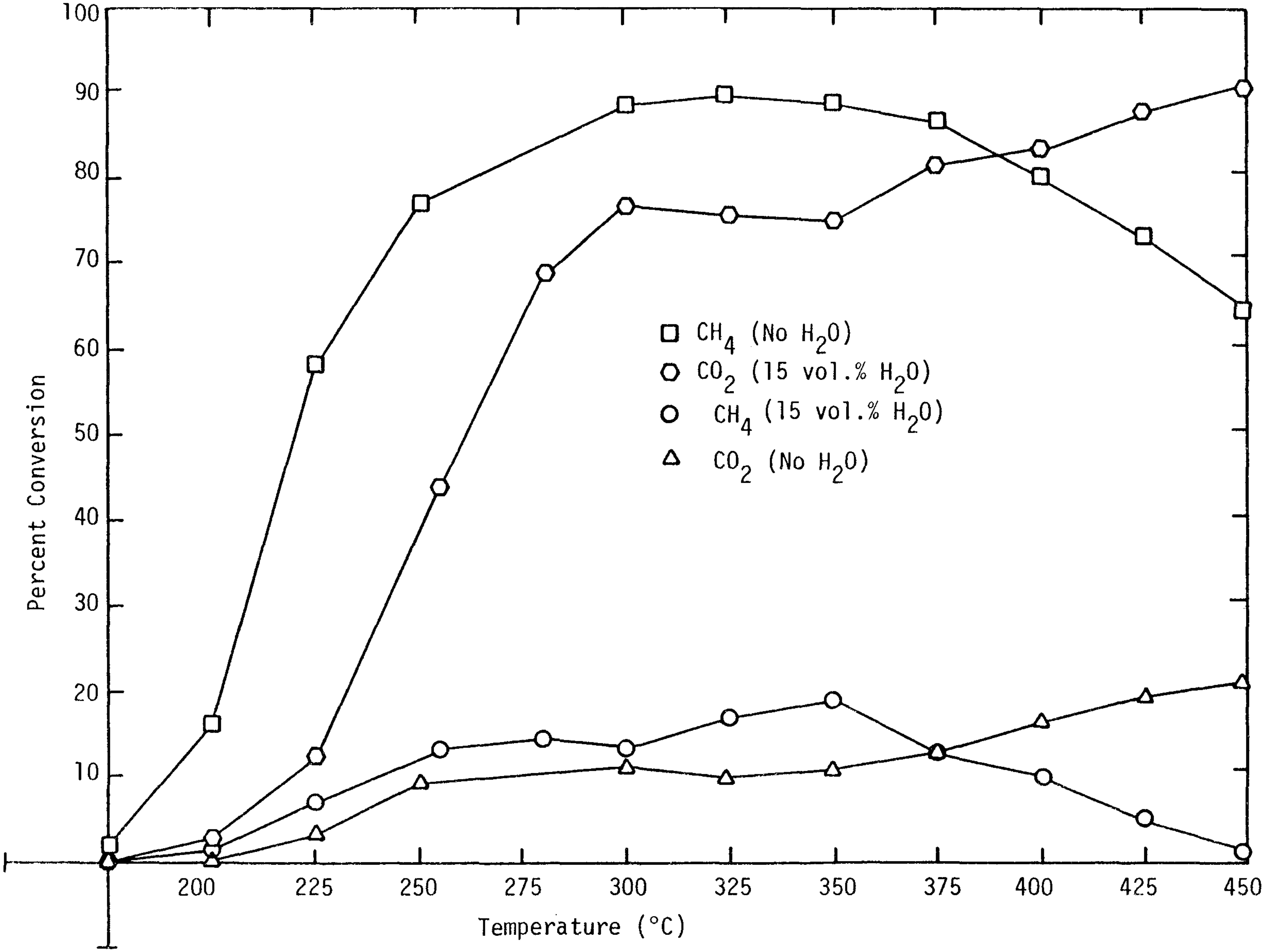

Figure 7. Effects of Steam (15 vol.%) on Conversion Versus Temperature for Ni-A-116 (14.0% Ni/Al_2O_3) (20.5 psia; GHSV - 15,000 hr^{-1}).

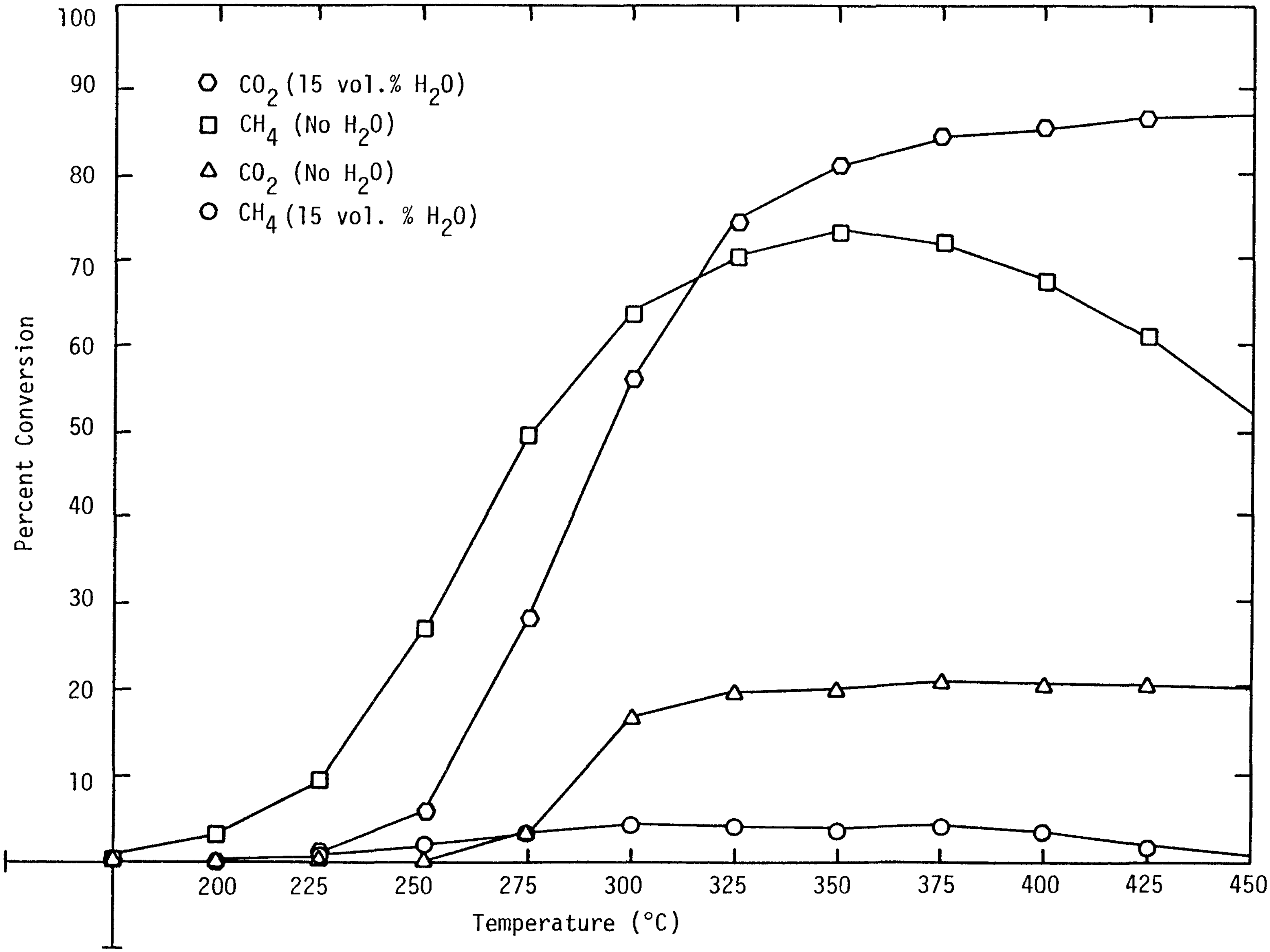

Figure 8. Effects of Steam (15 vol.%) on Comversion versus Temperature for Ni-A-112. (3% Ni/Al_2O_3) (20.5 psia; GHSV = 15,000 hr^{-1}).

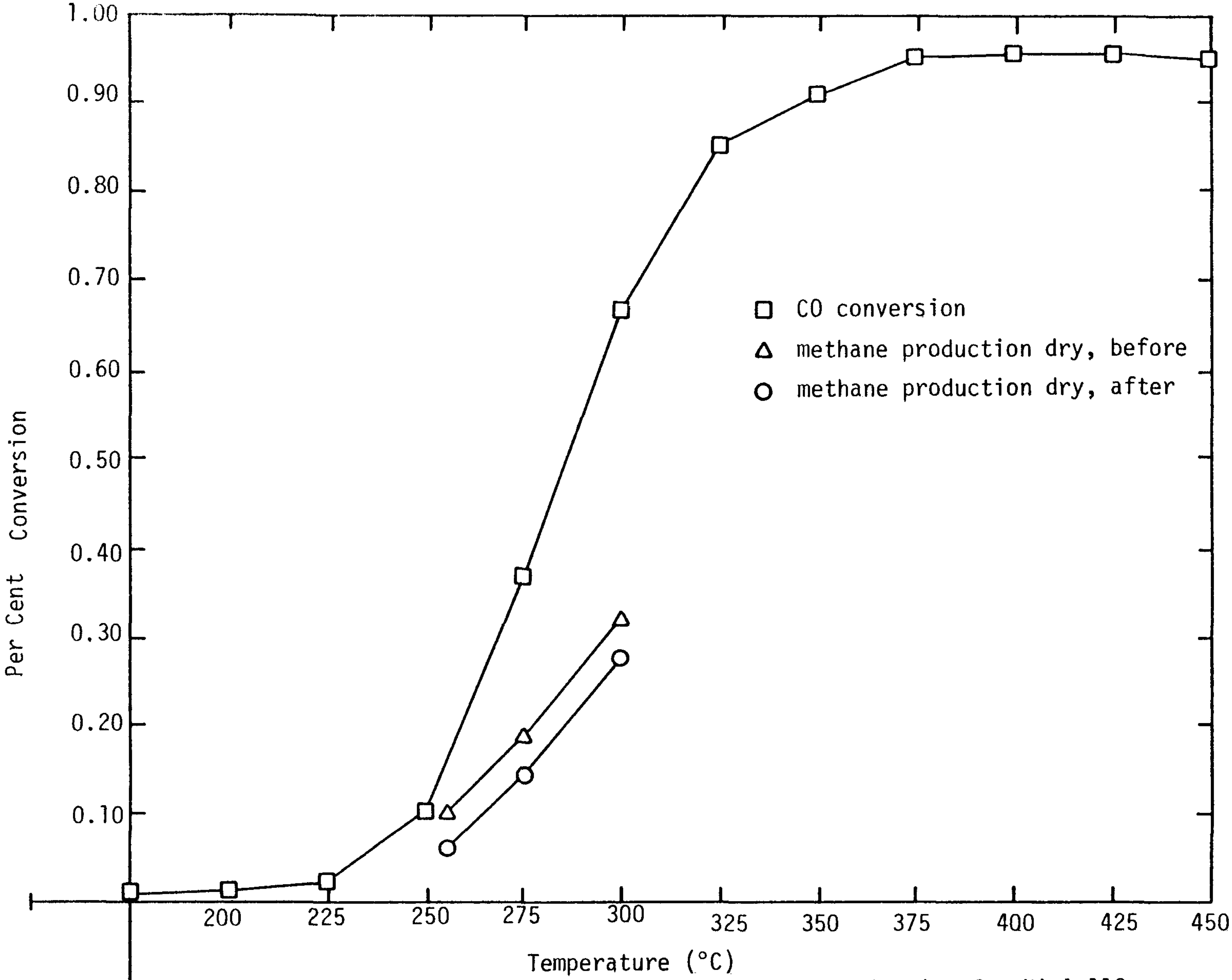

Figure 9. Methane production Before and After Steam Injection for Ni-A-112 (3% Ni/Al_2O_3) (20.5 psia; GHSV = 15,000 hr^{-1}).

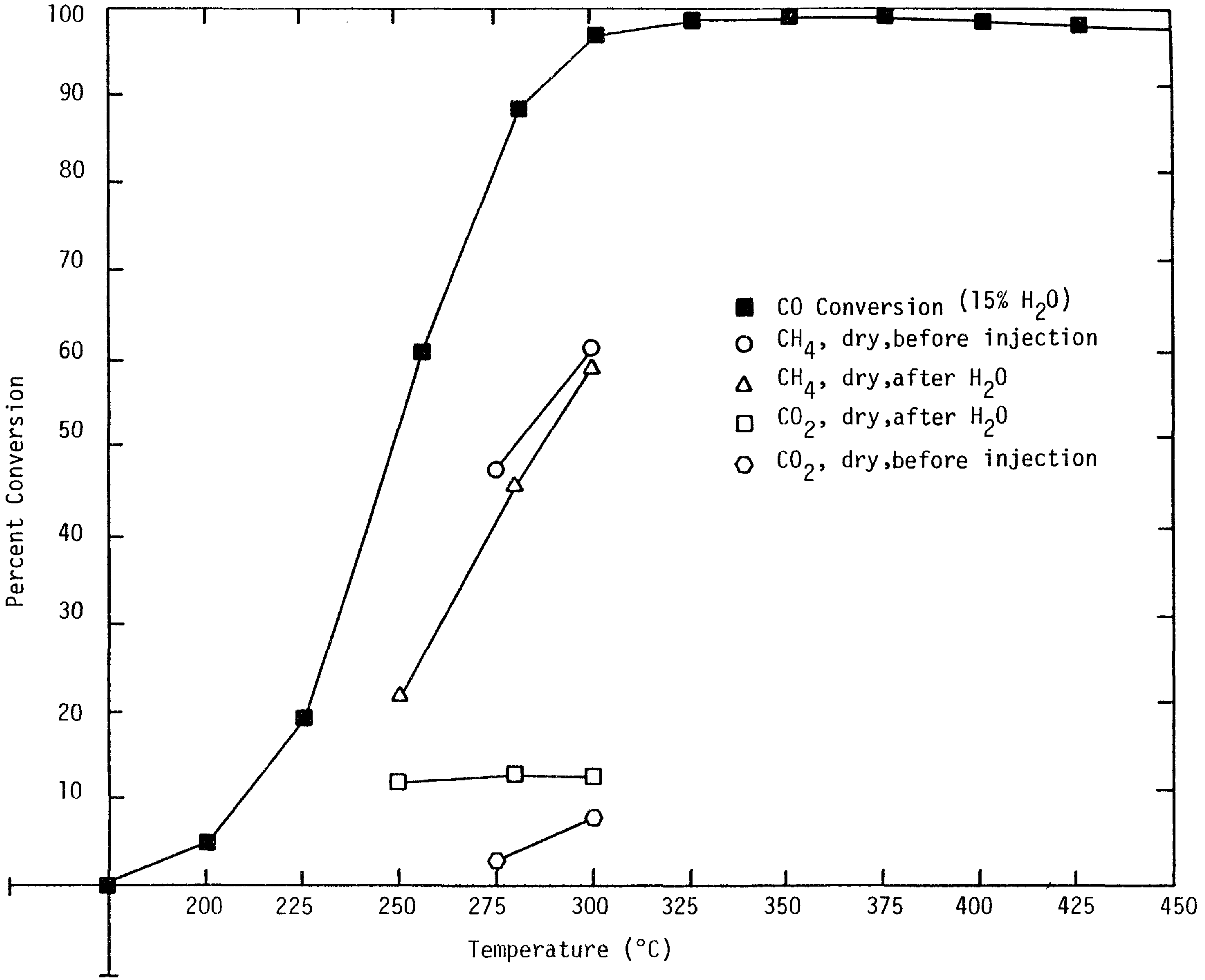

Figure 10. Methane Production Before and After Steam Injection for Ni-A-116 (14.0% Ni/Al_2O_3) (20.5 psia; GHSV = 15,000 hr^{-1}).

During the past quarter 24 hour reaction experiments were carried out to measure the effects of carbon deposition on activity for Ni-A-112 (3% Ni/Al_2O_3) at three H_2/CO ratios. While the activity was indeed slightly different for each H_2/CO ratio the decrease in activity after operation at 400°C for nearly 24 hours was not measureable. These results were most puzzling in view of the large decreases in activity observed by Dalla Betta (6) after running his catalysts for 24 hours at 25°C. Nevertheless, our reactant gas containing 1% CO, 4% H_2, and 95% N_2 was considerably more dilute than that used by Dalla Betta (75% H_2, 25% CO). In future long term deactivation test experiments we will use 20-50% CO and 80-50% H_2 in the reactant mixture.

Accomplishments - Monolithic-supported Catalysts. Selectivity and activity vs. temperature tests at 20 psia were performed on three monolith-supported nickel catalysts. Ni-M-107, one of the damaged pieces, was included for comparison. Not only was it sintered to some degree in the reduction step, but pieces of it were broken off, preventing accurate gravimetric determination of nickel loading. It contains approximately 10% Ni metal. Figure 11 shows the temperature conversion behavior for Ni-M-107. The high temperatures at which maximum conversions of CO to CO_2 and CH_4 are obtained suggests the effects of thermal damage. While the degree to which CO_2 was produced is comparable to other catalysts, the sum of CO_2 and CH_4 production does not equal CO conversion, suggesting hydrocarbon formation and perhaps carbon deposition.

Ni-M-113 was run at the same space velocity as the previous integral runs in this study, 15,000 hr^{-1}. Figure 12 shows high methanation selectivity at 250°C and complete CO conversion at 300°C, very similar in performance to the pellet-supported Ni. However, the selectivity for the monolithic catalyst reaches a maximum of 96% at about 325°C compared to 89% for pellet supported Ni. This result is most exciting. The CO_2 production (evidence of water-gas-shift) increases with increasing temperature and the selectivity to methane decreases with increasing temperature at temperatures higher than 350°C in very similar manner to Ni/Al_2O_3 pellets (see Figure 5 and Table 9), except that CO_2 production is less for the monolith.

To test the effects of space velocity on conversion, Ni-M-114 (a catalyst prepared in identical manner to Ni-M-113) was run with a space velocity of 30,000 hr^{-1}, double that used for Ni-M-113. Figure 13 shows that with twice the reactant flow, the percent conversion of CO to methane is about 10% less and the maxima occur at temperatures 25 degrees higher. CO_2 production is increased.

Forecast for Next Quarter. Generally, testing will continue on pellet and monolith catalysts according to the experimental plan outlined in Tables 7 and 8. During this next quarter integral tests wil be performed at high and low pressure with and without steam in the reactant mixture.

E. Task 5: Technical Visits and Communications.

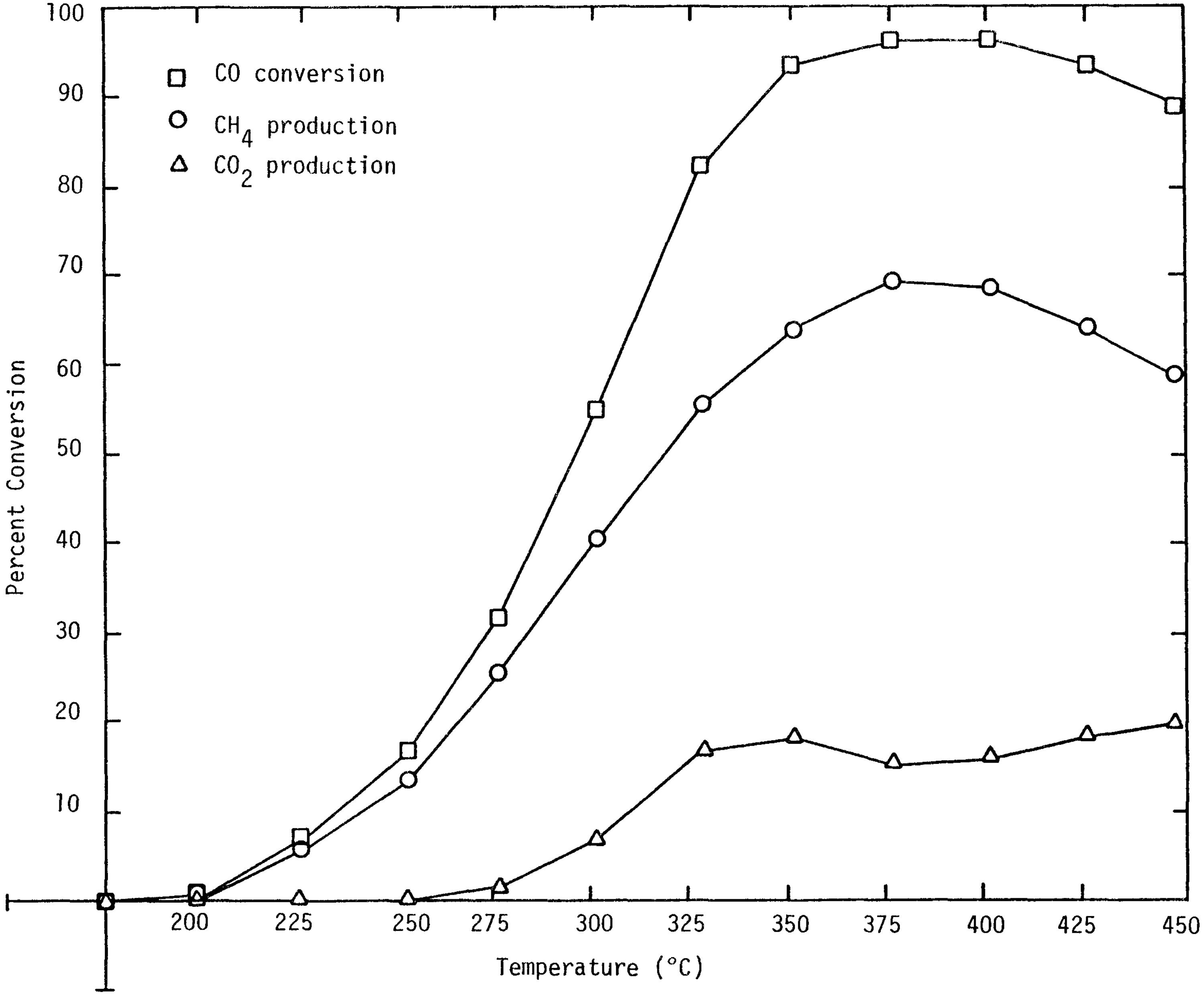

Figure 11. Conversion versus Temperature for Ni-M-107 (10% Ni/Al_2O_3/Monolith) (20.5 psia; GHSV = 30,000 hr^{-1}).

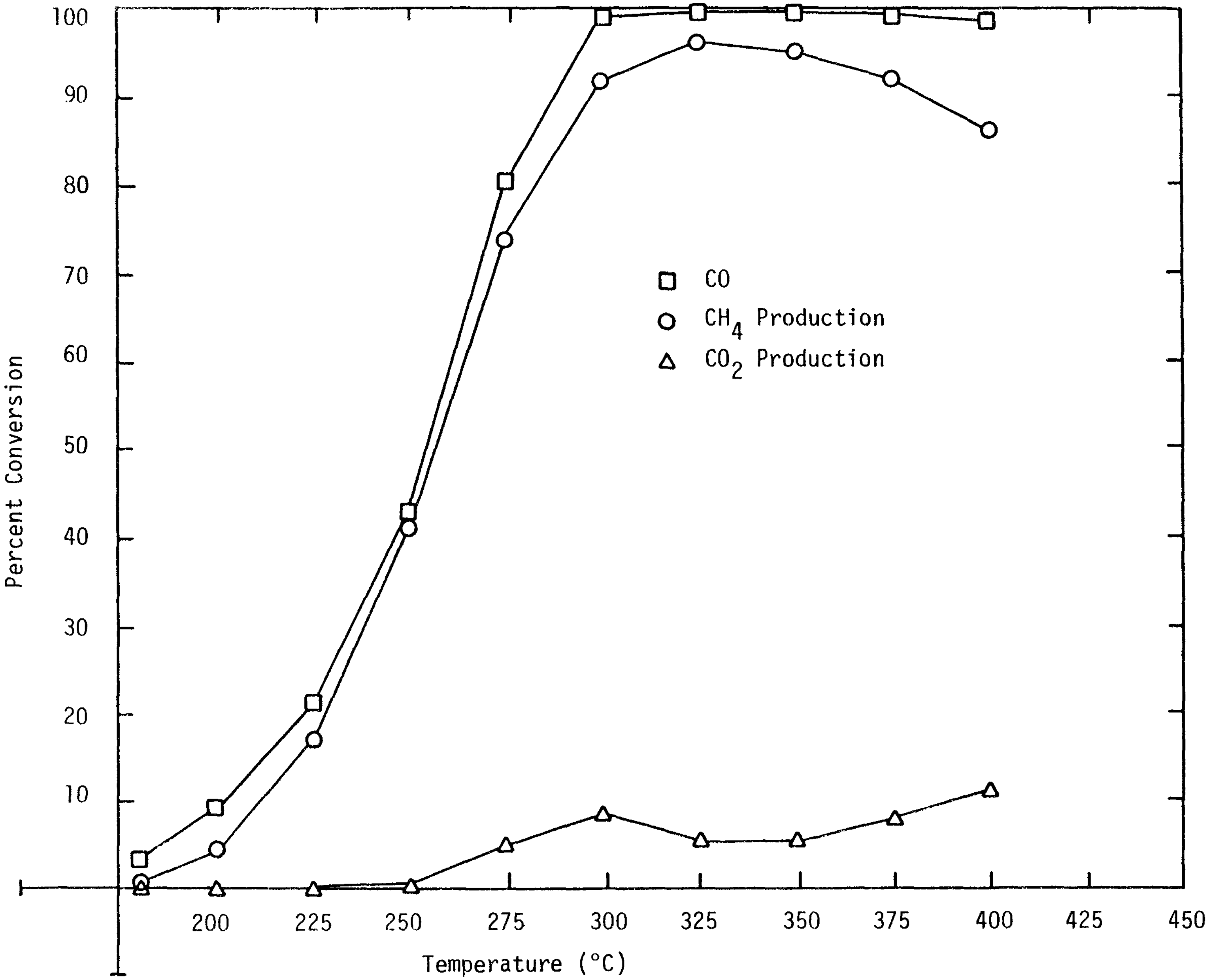

Figure 12. Conversion versus Temperature for Ni-M-113 (20% Ni/Al_2O_3/Monolith) (20.5 psia; GHSV = 15,000 hr^{-1}).

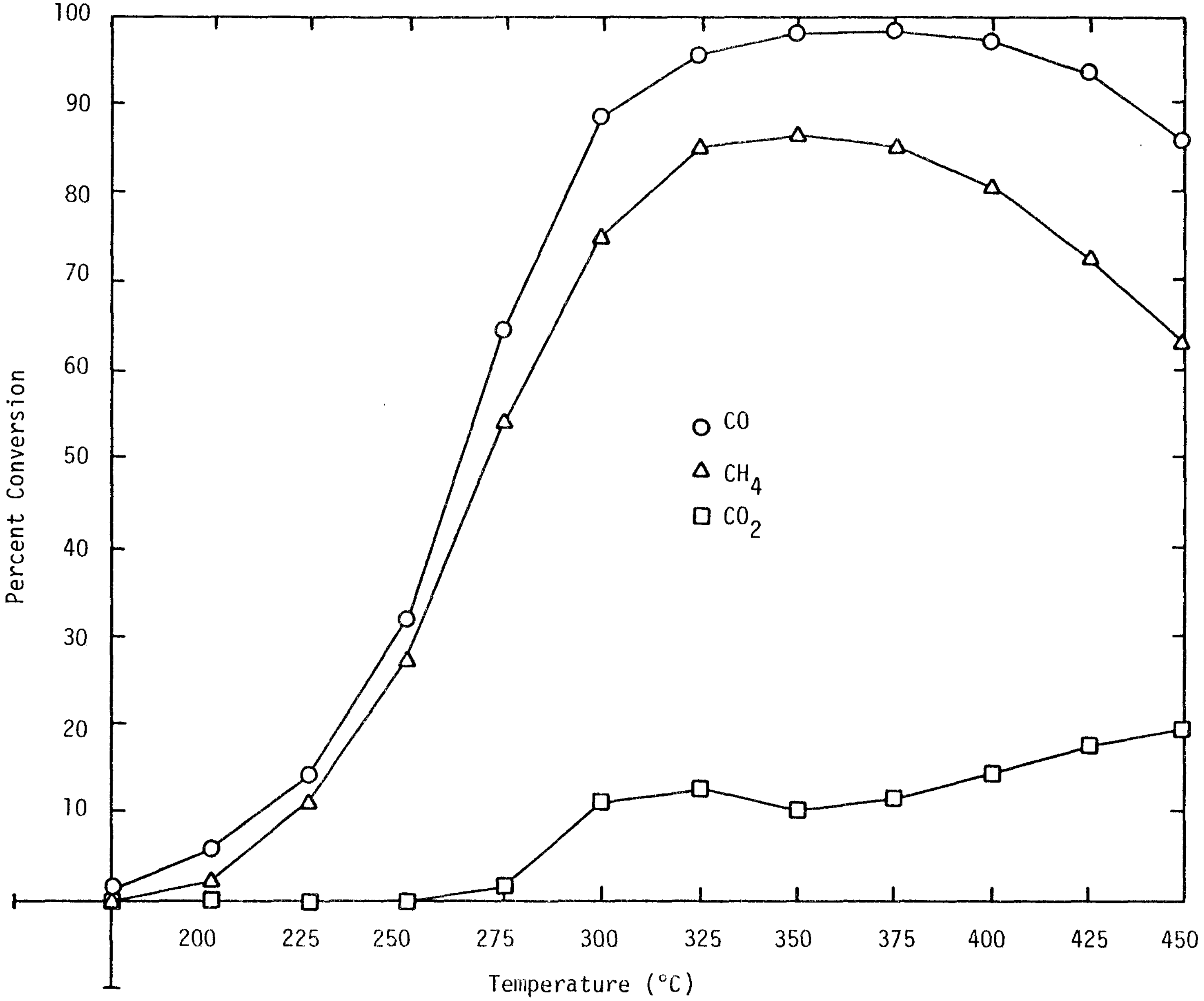

Figure 13. Conversion versus Temperature for Ni-M-114 (20% Ni/Al_2O_3/Monolith) (20.5 psia; GHSV = 30,000 hr^{-1}).

Accomplishments. The principal investigator, Dr. Bartholomew, presented two invited papers dealing with activities and kinetics of nickel and nickel alloys methanation catalysts at the Centennial Meeting of the American Chemical Society held August 30 - September 3 in San Francisco. One of these papers presented at the methanation symposium in the Division of Fuel Chemistry, summarized results of activity tests performed under this contract. On September 2, he visited with Henry Wise, Jon McCarty, Kenneth Sancier, and Bernard Wood at SRI in Menlo Park regarding various aspects of methanation catalysis and toured their laboratories. This was followed with a short visit to Stanford University to discuss alloy catalysis with members of Professor Boudart's research group. On September 3 and 4 Dr. Bartholomew participated in the ERDA sponsored University Contractors' Conference in Golden, Colorado.

On October 14, Dr. Bartholomew was invited by the Department of Fuels Engineering at the University of Utah to present a seminar on Methanation Studies performed at BYU. While at the University of Utah he also visited with Professors Massoth and Oblad, toured the catalysis research laboratories of Professor Oblad, discussed plans for the 2nd Rocky Mt. Fuel Symposium with Professors Massoth and Wood, and attended a Seminar given in the Chemistry Dept. by Professor Michel Boudart of Stanford. The following day Professor Boudart visited BYU; an informal seminar was held in which recent studies at both BYU and Stanford were discussed.

Other visitors to BYU included Mr. Tony Lee of IGT (September 22), Mr. Bill Boyer of Corning Glass Works (October 27) and Mr. Robert Wade of Ventron Corporation (October 28). Mr. Lee presented a seminar in which he discussed testing of methanation and water-gas-shift catalysts. Possible testing at IGT of catalysts developed at BYU was also discussed. The visit with Mr. Boyer focused on continued cooperative efforts between Corning Glass Works and BYU. Arrangements were made to obtain additional monolithic supports. The discussion with Mr. Wade focused on sulphur-resistant catalysts such as nickel and cobalt borohydrides. The possibility of a symposium on borohydride catalysts was discussed, and Dr. Bartholomew was introduced by phone to Prof. Tom Russell at the University of Eastern New Mexico who is currently investigating borohydride catalysts for methanation. Arrangements were made between Professors Russell and Bartholomew to exchange technical information.

Altogether the visits, meetings, presentations, and interactions with other workers have stimulated many useful interchanges of up-to-date, pertinant information regarding the project. In fact, the principal investigator is presently in close communication with more then 20 other laboratories in methanation catalysts in the United States and Europe.

During the past quarter, a publication based on work performed during the 2nd quarter, "Methanation Activity of Suported Nickel Alloys" was published in the Preprints of the ACS Divsion of Fuel Chemistry (Vol. 21, No. 4). Two large publications dealing with effects of H_2S on CO and H_2 adsorption and with methanation activities of alloy catalysts (and effects of H_2S thereon) are in preparation. A proposal to continue this contract work an additional two years was completed and submitted during this past quarter. The preparation of the proposal involved extensive searches of the literature dealing with methanation catalysis, sulphur poisoning, carbon deposition, and sintering.

Forecast. During the next quarter preparation of two new publications will continue. The Principal Investigator will attend the ASTM D-32 Catalyst Committee Meeting in Oakridge, Tenn. and will visit and present Seminars at Engelhard Industries, Continental Oil Co, and the University of Idaho.

Miscellaneous.

During the past quarter, Mr. Scott Engstrom graduated with a B.S. in Chemical Engineering and entered MIT to begin graduate study toward a masters. Mr. Richard Turner (M.S. candidate) was accepted at the University of Utah Medical School and began study there during late September. Mr. Gordon Weatherbee (M.S. candidate), Mr. Kenneth Atwood (Senior), and Mr. Glen Witt (Freshman) joined the research group in September, are already trained and performing productively.

IV. CONCLUSIONS

1. Surface areas measured by H_2 adsorption for 20% Co/Al_2O_3 are 4-5 times smaller than typical values for 15% Ni/Al_2O_3.

2. A 20% Ni-MoO_3/Al_2O_3 catalyst prepared in this laboratory evidences very high activity on a mass or surface area basis because of its reasonably high surface area and high activity per catalytic site.

3. The turnover number for a 20% Co/Al_2O_3 catalyst (prepared in this laboratory) is the highest observed of any catalyst tested thus far. Its activation energy is also relatively large so that its rate increases more rapidly with increasing temperature than other catalysts containing nickel and nickel alloys as active phases. Its production of CO_2 is larger and its selectivity to methane smaller then Ni/Al_2O_3.

4. Higher activation energies are observed for monolithic-supported nickel compared to pellet-supported. This effect is very likely a result of greater catalyst effectiveness for a monolithic catalysts compared to pellet catalysts due to the shorter diffusion paths in monolithic catalysts. These data suggest that monolith-supported catalysts may be more efficient than pellet-supported catalysts for production of methane.

5. A higher selectivity to methane is observed for monolithic-supported nickel compared to pellet-supported nickel.

6. Recently prepared Ni-MoO_3 and Ni-Ru catalysts (each 20 wt.% metal loading) appear to be more resistant to sulfur poisoning than all other catalysts tested thus far including 6% Ni-MoO_3/Al_2O_3.

7. The presence of water vapor (15 vol.%) in the reactant mixture results in a large decrease in selectivity to CH_4 and a large increase in selectivity to CO_2 for nickel catalysts. This is undoubtedly due to an increase in the rate of the water gas shift reaction.

8. The effect of increasing the space velocity over monolithic-supported nickel is to decrease the conversion of CO and the selectivity to CH_4.

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APPENDICES

APPENDIX A

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