ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES. PHASE I. QUARTERLY TECHNICAL PROGRESS REPORT, JULY 23--OCTOBER 22, 1975

BRIGHAM YOUNG UNIV., PROVO, UTAH

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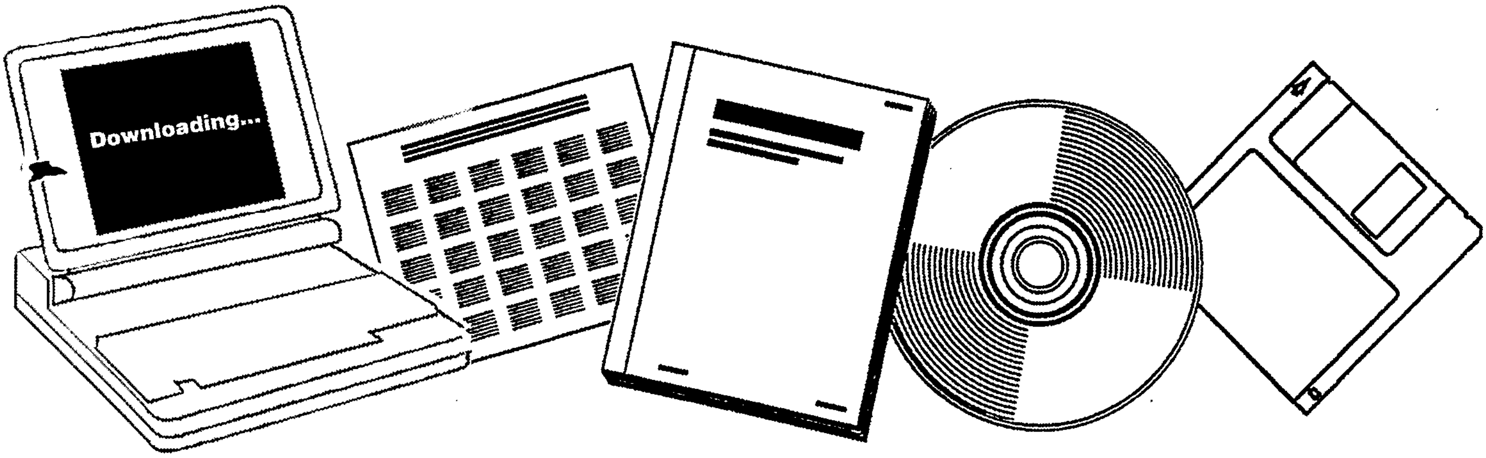

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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES

Phase I

Quarterly Technical Progress Report
For Period July 23-October 22, 1975

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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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DISCLAIMER

FOREWORD

This report summarizes technical progress during the second quarter period (July 23, 1975 to October 22, 1975) 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 - Kyung Sup Chung, Blaine Barton, Don Stowell and Richard Turner and Undergraduates - Norman Shipp, and Scott Engstrom. Michael King, Karen Weis and Scott Folster provided typing and drafting services.

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ABSTRACT

This report presents work accomplished during the second quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Alumina-supported alloys of nickel with ruthenium, rhodium, molybdenum, platinum, palladium, iron, and cobalt were characterized by surface area measurements and tested for methanation catalyst activity at ambient pressure, 225 and 250°C and at space velocities of 30,000 and 60,000 hr^{-1}. To determine effects of sulfur poisoning on surface area, the adsorption of hydrogen and carbon monoxide on most of these catalysts was measured before and after exposure to hydrogen sulfide. In addition, pellet-supported molybdate nickel-copper, ruthenium-cobalt and ruthenium-palladium alloy catalysts and monolithic-supported nickel catalysts were prepared. Reconstruction of a laboratory reactor to enable high pressure operation was eighty percent completed.

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. Hydrogen and carbon monoxide chemisorption uptakes will be measured before and after exposure to hydrogen sulfide. Metallic phases of these catalysts will be examined 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 at various time exposures to 10 ppm H_2S.

Task 4. The most promising catalysts based on the results of Tasks 1 and 3 will be compared 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. Close liaison shall be maintained 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 past 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 valve. 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 Bureau of Mines 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 2, Construction of Reactor System, and Task 3, Catalyst Screening, are well ahead of schedule.

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

Task 1. Alumina-supported Ni-Cu, MoO_3, Ru-Pd and Ru-Co catalysts were prepared in pellet form by impregnation, drying and reduction in hydrogen. Several monolithic-supported Ni-Al_2O_3 catalysts were prepared by special impregnations followed by drying and reduction. Hydrogen and carbon monoxide adsorption uptakes were measured for Ni-Fe and Ni-Co catalysts before and after exposure to 10 ppm H_2S in hydrogen. Adsorption of CO was also measured for pelleted Ni-Ru, Ni-Rh, and Ni-MoO_3 catalyst before and after treatment with H_2S. X-ray diffraction and fluoresence measurements for a 15 wt.% Ni/Al_2O_3 were initiated.

Task 2. An atmospheric laboratory reactor used for catalyst testing was reconstructed to allow for operation to 400 psia. A new 18-inch zone furnace, NDIR analyzer for CO and chromatographic accessories were added to the system. System upgrading and modifications are about 80% complete.

Task 3. Screening measurements of steady state methanation activity at 225, 250°C and space velocities of 30,000 and 60,000 hr^{-1} were carried out for alumina-supported Ni, Ni-Ru, Ni-Rh, Ni-Pt, Ni-Pd, Ni-Fe, Ni-Co, and Ni-MoO_3 catalysts.

Task 4. Work is scheduled to begin October 22, 1976.

Task 5. The principal investigator has established new technical communications with workers in methanation catalysis. He also participated in the University Contractors Conference (sponsored by ERDA/EPRI/NSF-RANN) held October 22-23 in Park City, Utah.

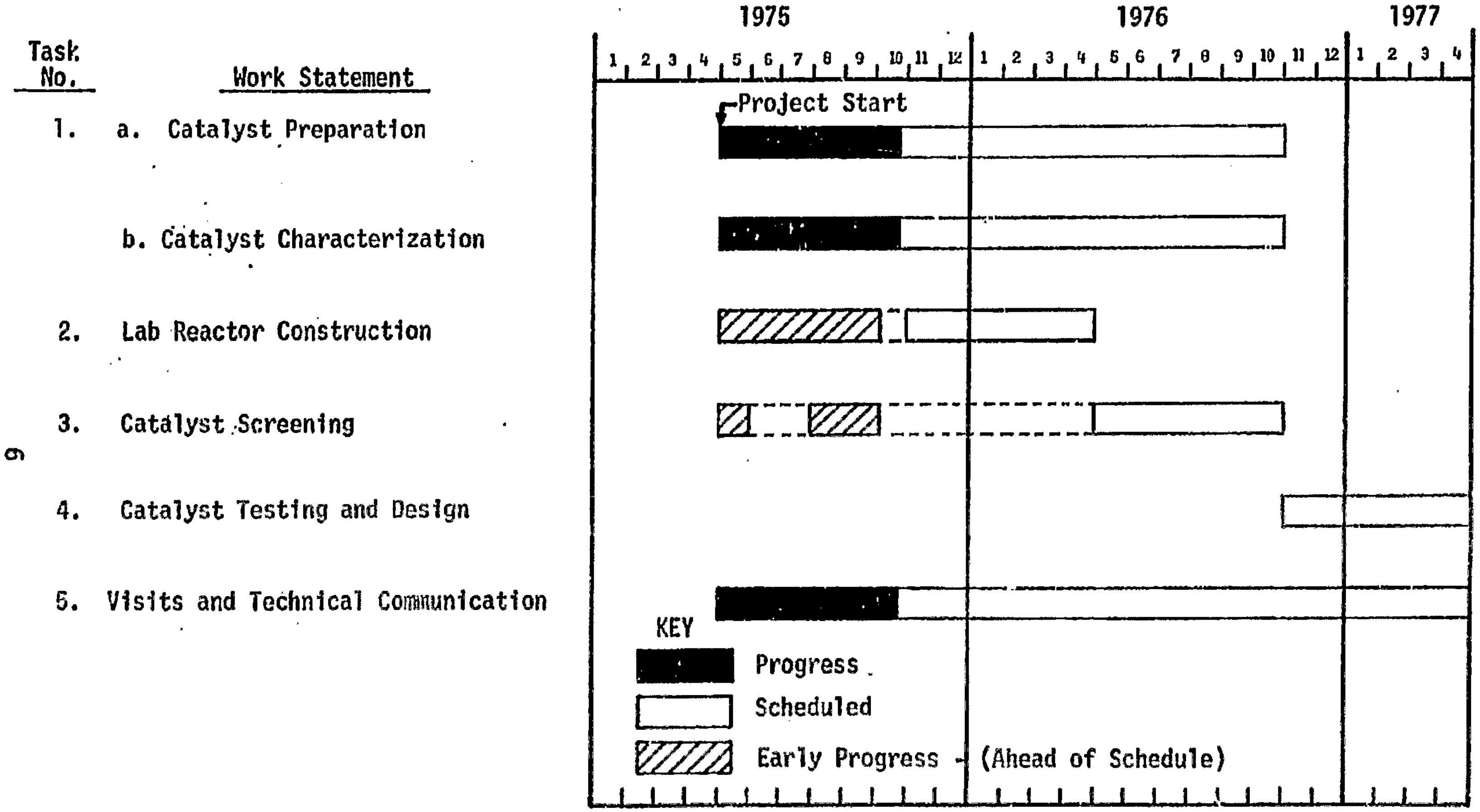

Figure 1. Project Progress Summary

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst preparation. Alumina pellet-supported Ni-Cu, Ru-Co, Ru-Pd, and MoO_3 catalysts were prepared according to the general procedure outlined in the first quarterly progress report[3] (QPR-1). The Ni-Cu catalyst was prepared by impregnation from a neutral solution of nickel and copper nitrates. The ruthenium alloys were prepared from slightly acidic impregnations of ruthenium chloride, palladium chloride, and cobalt nitrate salts. The molybdate catalyst was prepared from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ dissolved in ammonical solution. Kaiser SAS 5 x 8 mesh Alumina ($300 m^2/g$) was used in all pellet preparations. Nominal metal compositions are shown for these catalysts in Table 1. The purpose in preparing the alumina-supported molybdate was to compare its behavior for H_2 and CO adsorption with that of the $Ni-MoO_3/Al_2O_3$ in order to better understand the relative catalytic roles of nickel and molybdate sites in the bimetallic catalyst.

In order to explore various methods of monolithic catalyst preparation, six different monolithic-supported nickel catalysts were prepared, each with variations in the methods of application for either coating or impregnation. The Celcor EX-20 monolithic supports[4] (Corning Glass Works) consisting of a cordierite material (magnesium-alumina-silicate) were 2.54 cm diameter by 5.87 cm long. Al_2O_3 or $NiAl_2O_4$ coatings were applied by dipping in appropriate acidic collodial suspensions of Dispal-M Al_2O_3 (Continental Oil Co.), SA Medium Al_2O_3 (Kaiser), or aluminum and nickel nitrates followed by calcining at 600°C. Several dips were required in order to obtain sufficient coating on the monoliths. The details of wash-coat application for each sample are presented in Table 2. The results suggest that a 2.5:1 or 3:1 slurry of water and SA Medium gives the maximum amount of coating in the smallest number of dips. Following the application of a washcoat, each sample was impregnated with nickel nitrate by dipping in either a nickel nitrate melt or concentrated nickel nitrate solution. The details of impregnation for each sample are shown in Table 3. The impregnation of Dispal-M Al_2O_3 and $NiAl_2O_4$ coatings with $Ni(NO_3)_2 \cdot 6H_2O$ melt and the impregnation of SA Medium with 50% $Ni(NO_3)_2 \cdot 6H_2O$ in water were most successful in maximizing the nickel loading in a minimum number of applications.

2. Hydrogen and Carbon Monoxide Chemisorption on Nickel and Nickel Alloys and Effects of Hydrogen Sulfide on Adsorption. Procedures for measuring H_2 and CO chemisorptive uptakes were described in detail in QPR-1.[3] A brief review of the experimental method at this point is appropriate to aid the reader in understanding the significance of the data. The basic steps in pretreatment and surface area measurement are as follows:

a. The sample consisting of Al_2O_3 pellets impregnated with metal salts is dried at 100°C and reduced at 450-500°C at a hydrogen space velocity of $\approx 1500\ hr^{-1}$.

TABLE 1

Composition of Alumina-supported Ruthenium and Molybdate Catalysts (Pellet form)

Catalyst Code	Nominal Composition (wt.%)
MoO_3-A-100	3% MoO_3
Ru-Co-A-100	0.52% Ru, 15.0% Co
Ru-Pd-A-100	0.49% Ru, 0.51% Pd
Ni-Cu-A-100	5% Ni, 0.6% Cu

TABLE 2

Preparation of Al_2O_3 and $NiAl_2O_4$ Washcoats on Corning Monoliths

	Wash Coat			
Catalyst Code	Type	# Washes	Wt. % Coating†	Comments
Ni-M-101	Dispal Al_2O_3 3:1 Slurry of $H_2O:Al_2O_3$	8	16.0	
Ni-M-102	Dispal Al_2O_3 2:1 Slurry	6	17.1	
Ni-M-103	SA Medium Al_2O_3 2:5.1 Slurry	3	15.3	SA Medium gives higher loading in fewer dips compared to Dispal-M
Ni-M-104	SA Medium Al_2O_3 3:1 Slurry Add Ni Nitrate	6	23.7	Ni nitrate and Al_2O_3 form $NiAl_2O_4$ at 600°C
Ni-M-105	Ni & Al Nitrate Slurry to give $NiAl_2O_4$	8	≈15	Sample broken during preparation. Composition is approximate
Ni-M-106	SA Medium Al_2O_3 3:1 Slurry	3	17.3	Also high loading in fewer dips

†Based upon wt. increase after heating at 600°C for ½ hour.

TABLE 3

Preparation of Monolithic-supported Nickel Catalysts

		Metal Application				
Catalyst Code	Wash Coat	Impreg. Medium	Drying Conditions	#Applications	Wt. % Ni*	Comments
Ni-M-101	Dispal Al_2O_3	$Ni(NO_3)_2 \cdot 6H_2O$ Melt	190°C, Vac.	6	15.7	Good method. Except channels plug if sample cools too fast.
Ni-M-102	Dispal	50 wt.% $Ni(NO_3)_2 \cdot 6H_2O$ in H_2O. Ppt. with NH_3. 10 min. wash in H_2O.	180-190°C	9	2.8	Poor method. Ni nitrate lost in wash.
Ni-M-103	SA Med. Al_2O_3	50 wt.% $(NO_3)_2 \cdot 6H_2O$ in H_2O. Ppt. with NH_3. 10 min. wash in H_2O.	100°C	11	13.7	Poor method. Too many applications.
Ni-M-104	$NiAl_2O_4$	$Ni(NO_3)_2 \cdot 6H_2O$ Melt	190°C	3	15.9	Good method. Plugging.
Ni-M-105	$NiAl_2O_4$	50 wt.% $Ni(NO_3)_2 \cdot 6H_2O$ in H_2O	200°C	15	≈16	Sample was dropped and broke. Composition is approximate.
Ni-M-106	SA Med.	50 wt.% $Ni(NO_3)_2 \cdot 6H_2O$ in H_2O	200°C	5	18.5	Good method. No plugging problems.

*Based upon wt. increase after reduction in H_2 at 500°C for 12-16 hours.

b. H_2 chemisorptive uptake is measured for the sample at 25°C and CO uptake at -83°C.

c. The sample is exposed to 10 ppm H_2S at 450°C for 6 hours.

d. H_2 and CO uptakes are again measured.

e. The sample is exposed to 10 ppm H_2S at 450°C for an additional 12 hours.

f. H_2 and CO uptake measurements are repeated.

Throughout the entire procedure the sample is contained in the same glass sample cell (described in QPR-1) to prevent exposure to the atmosphere.

A summary of hydrogen uptake data for catalysts investigated thus far is shown in Table 4. The uptake data for the 3% Ni, Ni-MoO_3, Ni-Ru, Ni-Rh, and 0.5% Ru catalysts were obtained during the first quarter and characteristic adsorption isotherms were included in QPR-1[3]; the remaining data were obtained during the second quarter.

Most of the hydrogen uptake data were determined for samples which had been previously reduced in the large reduction apparatus (described in QPR-1), passivated by exposure to less than 1% air, transferred to a small glass sample cell, and re-reduced in flowing hydrogen for at least 2 hours at 450-500°C. It was discovered, however, that prereduced and passivated Ni-Fe/Al_2O_3 was not completely reduced after two hours rereduction at 500°C in flowing hydrogen. In fact, approximately 6 hours were required to attain a stable, maximum state of reduction. This is illustrated by the data in Figure 2 showing that the H_2 uptake approaches very closely an asymptotic value of about 82μ moles/g after 6 hours. It was similarly observed that approximately 4 hours and 2 hours were required to completely reduce Ni-Co/Al_2O_3 and Ni-Pd/Al_2O_3 catalysts respectively. Since reduction of a passivated sample is directly related to removal of oxygen from the metal surface, there is a possible correlation between the heat of formation of the metal oxide and the difficulty of reduction. Indeed the $-\Delta H_f^\circ$ values for FeO, CoO and PdO are 64.6, 57.5, and 20.4 respectively. A similar correlation may also exist between the heats of formation for the nitrates and time for reduction of the supported nitrates; however, insufficient data are available to test the model in the latter case.

The magnitude of the hydrogen uptake in μmoles/gram of catalyst depends upon (1) the amount of active metal(s) in the sample and (2) the dispersion (or particle size) of the active component(s). Previous work[5] in this laboratory has established that metal dispersion decreases with increased nickel loading in the nickel-alumina system. This same effect is also apparent in the data for 3, 15 and 32 wt.% Ni in Table 4; in fact, the 15 wt.% Ni catalyst prepared in this laboratory has a higher surface area and significantly higher dispersion than the 32 wt.% commercial nickel (Girdler G-87). This can be explained in terms of differences in preparation and pretreatment. Commercial

TABLE 4

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

CATALYST	NOMINAL COMPOSITION	H_2 UPTAKE (µmoles/gram)	PERCENT DISPERSION
Ni-A-112	3 wt. % Ni on Al_2O_3	39.4	15.4
Ni-A-116	15 Wt. % Ni on Al_2O_3	187.8	14.7
G-87 (Girdler)	32 wt. % Ni on Al_2O_3	161.6	5.93
Ni-MoO_3-A-101	2.5 wt. % Ni - 3 wt. % MoO_3 on Al_2O_3	22.5	10.6*
MoO_3-A-101	3% MoO_3 on Al_2O_3	1.0	--
Ni-Ru-A-105	2.5 wt. % Ni - 0.5 wt. % Ru on Al_2O_3	44.6	18.76
Ni-Rh-A-100	2.5 wt. % Ni - 0.5 wt. % Rh on Al_2O_3	38.3	16.1
Ni-Co-A-100	10 wt. % Ni - 10 wt. % Co on Al_2O_3	114.9	6.76
Ni-Fe-A-100	10 wt. % Ni - 10 wt. % Fe on Al_2O_3	82.1	4.70
Ni-Pt-A-100	16 wt. % Ni - 0.5 wt. % Pt on Al_2O_3	115.4	8.94
Ni-Pd-A-100	16 wt. % Ni - 1.0 wt. % Pd on Al_2O_3	80.6	6.08

*Based upon nickel only.

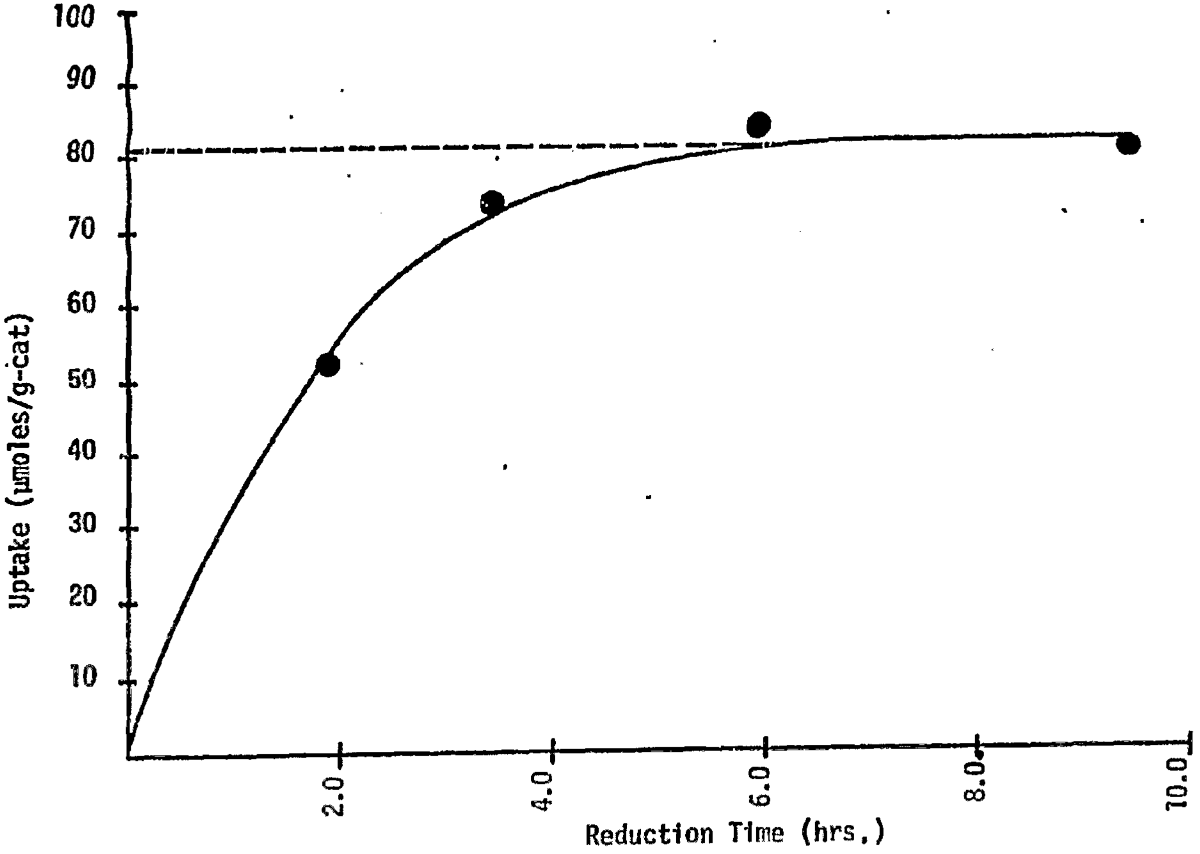

Figure 2. Effect of Reduction Time on H_2 Uptake for 20% Ni-Fe/Al_2O_3.

catalysts are normally prepared by calcination of the impregnated or precipitated supported metal salt followed by reduction in hydrogen. This high temperature calcination ultimately prevents complete reduction of nickel to the metallic state; in fact, a typical commercial nickel probably contains 30-50% NiO and/or $NiAl_2O_4$ even after reduction in flowing hydrogen at 500°C.[5] Our catalysts on the other hand are prepared by direct reduction of the supported metal salt in hydrogen to produce samples containing 80-90% of the metal in the metallic state and in a significantly higher state of dispersion compared to calcined samples.[5]

Comparison of surface areas and dispersions from Table 4 for nickel alloys compared to nickel catalysts show approximately the same surface areas for 3% Ni-Rh and 3% Ni-Ru compared to the 3% Ni catalyst. The 5.5% Ni-Mo catalyst, however, has approximately half the surface area of the 3% Ni, possibly because of interaction of part of the nickel with MoO_3 to form a complex which does not adsorb hydrogen. Moreover, the data for the 3% MoO_3/Al_2O_3 indicate that hydrogen adsorption on the molybdenum oxide is negligibly small. All of the alloys in the 15-20% range have 40-50% lower surface areas compared to the 15% Ni/Al_2O_3. At this point, it is of interest to note the following in regard to the effects of alloy composition on the CO and H_2 chemisorptions. In principle, it is possible that actual chemisorptive uptakes for alloys would be mole weighted averages of the individual metallic constituent uptakes; however, in practice this does not necessarily hold, and it is further likely that the surface compositions are not the same as the bulk compositions for many of these alloy catalysts.[6]

In QPR-1[3] data for chemisorption of CO on Ni and the effects of 10 ppm H_2S on H_2 chemisorption for Ni, $NiMoO_3$, Ni-Ru, and Ni-Rh catalysts were reported. Since that report, considerable data have been obtained in regard to CO chemisorption on Ni alloys and the effects of 10 ppm H_2S on both H_2 and CO adsorption.

Table 5 summarizes chemisorption data for H_2 and CO before and after exposure to 10 ppm H_2S for 6 and 12 hours and shows the ratio of initial CO uptake to initial hydrogen atom uptake for each catalyst. Figures 3-10 are representative isotherms illustrating the effects of H_2S on CO adsorption for some of the samples described in Table 5 and the effects of H_2S on H_2 adsorption for the Ni-Fe and Ni-Co samples. Two very significant trends are apparent from the data in Table 5. First the effect of H_2S exposure is to decrease the H_2 uptake of the sample whereas CO chemisorption is generally increased (except for the ruthenium catalyst). The increase in CO adsorption after H_2S exposure is a most surprising result and one which we cannot yet explain. Secondly, the ratios of adsorbed carbon monoxide molecules to hydrogen atoms range from 1.5-2.0. These ratios indicate the possibility of multiple adsorption of CO molecules on metal atoms and are generally in agreement with studies of nickel, ruthenium, and rhodium catalysts but slightly higher than observed values for iron catalysts. Any large discrepancies between our CO adsorption

TABLE 6

Effects of H_2S on H_2 and CO Chemisorption
for Alumina-Supported Nickel and Nickel Alloys
(10ppm H_2S at 450°C)

CATALYST	NOMINAL COMPOSITION	H_2 Uptake (μmoles/g)			CO Uptake (μmoles/g)			$\frac{CO}{H}$
			H_2S Exposure			*H_2S Exposure*		
		INITIAL	6 HOURS	12 HOURS	INITIAL	6 HOURS	12 HOURS	
Kaiser Al_2O_3	Pure Al_2O_3	0.5	--	--	26.3	31.1	38.9	26.3
Inco Ni Powder	Pure Ni	3.47	--	--	5.3[c]	--	--	0.76
Ni-A-111	3% Ni	21.4[d]	16.8	14.0	80.0	243.9	373.6	1.87
Ni-MoO_3-A-101	2.5% Ni - 3% MoO_3	24.0[a] 21.1[b]	-- 13.57	-- 12.45*	107.3 --	260.8 --	257.6 --	2.23 --
MoO_3-A-101	3% MoO_3	1.0	--	--	8.0	8.0	--	4.0
Engelhard Ru	0.5% Ru	7.62	5.33	3.45	54.0	45.2	42.5	3.54
Ni-Ru-A-105	2.5% Ni - 0.5% Ru	47.6[a] 39.4[b]	-- 32.0	-- 25.8	148.2 --	283.1 --	295.6 --	1.56 --
Ni-Rh-A-100	2.5% Ni - 0.5% Ru	43.5[a] 38.3[b]	-- 33.5	-- 28.3	145.6 --	225.8 --	256.4 --	1.67 --
Ni-Fe-A-100	10% Ni - 10% Fe	82.13	49.60	42.71	255.1	305.6	393.4	1.55
Ni-Co-A-100	10% Ni - 10% Co	114.9	109.6	102.0	176.5	231.3	226.4	1.54

*After 24 hours H_2S

[a] & [b] Refer to different measurements for the same catalyst batch.

[b] Data reported in QPR-1

[c] Irreversibly chemisorbed at 25 and -83°C

[d] Reduced in small glass sample cell.

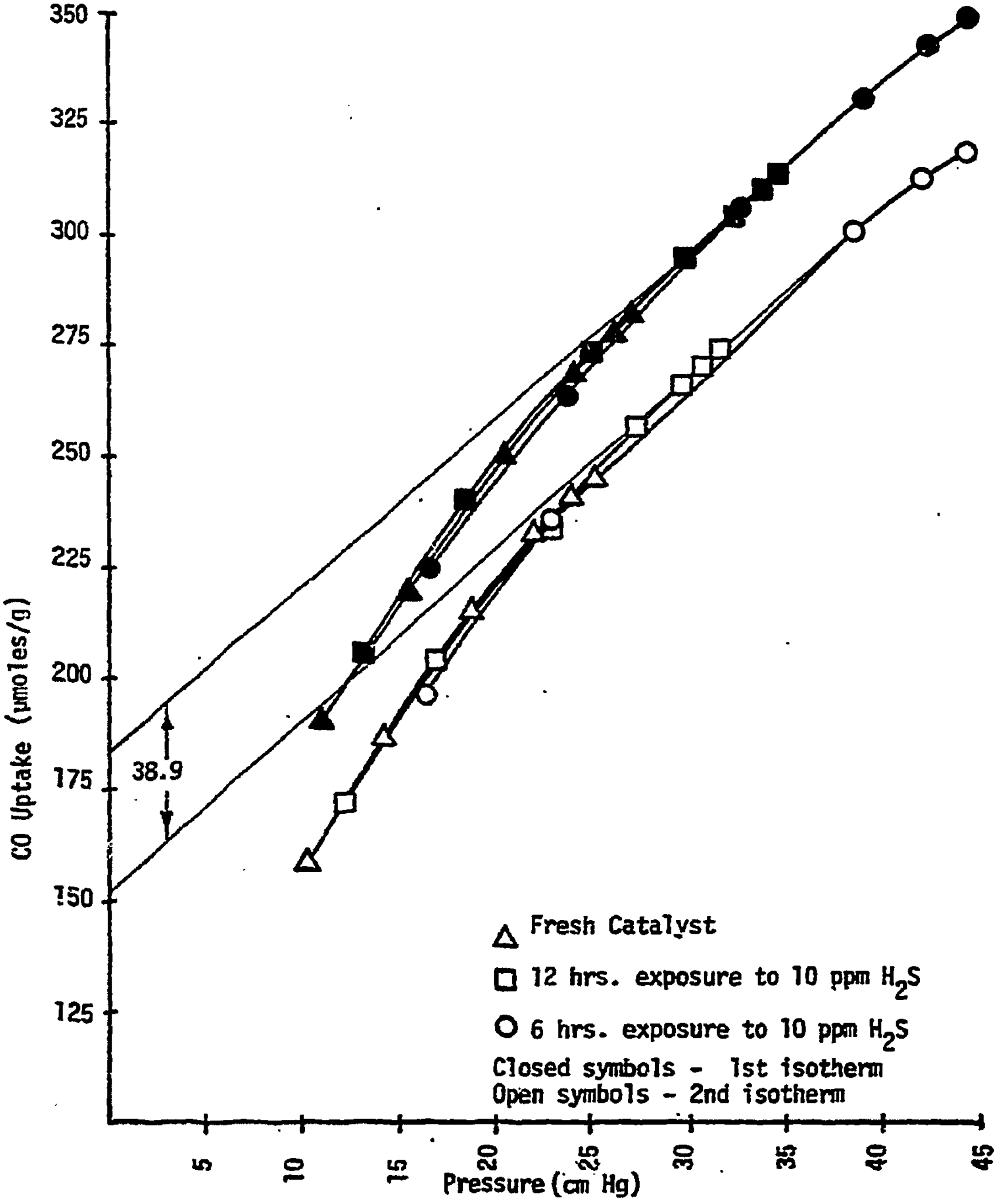

Figure 3. Effects of 10ppm H_2S Poisoning on CO Adsorption for Kaiser SAS Alumina Beads at -83°C

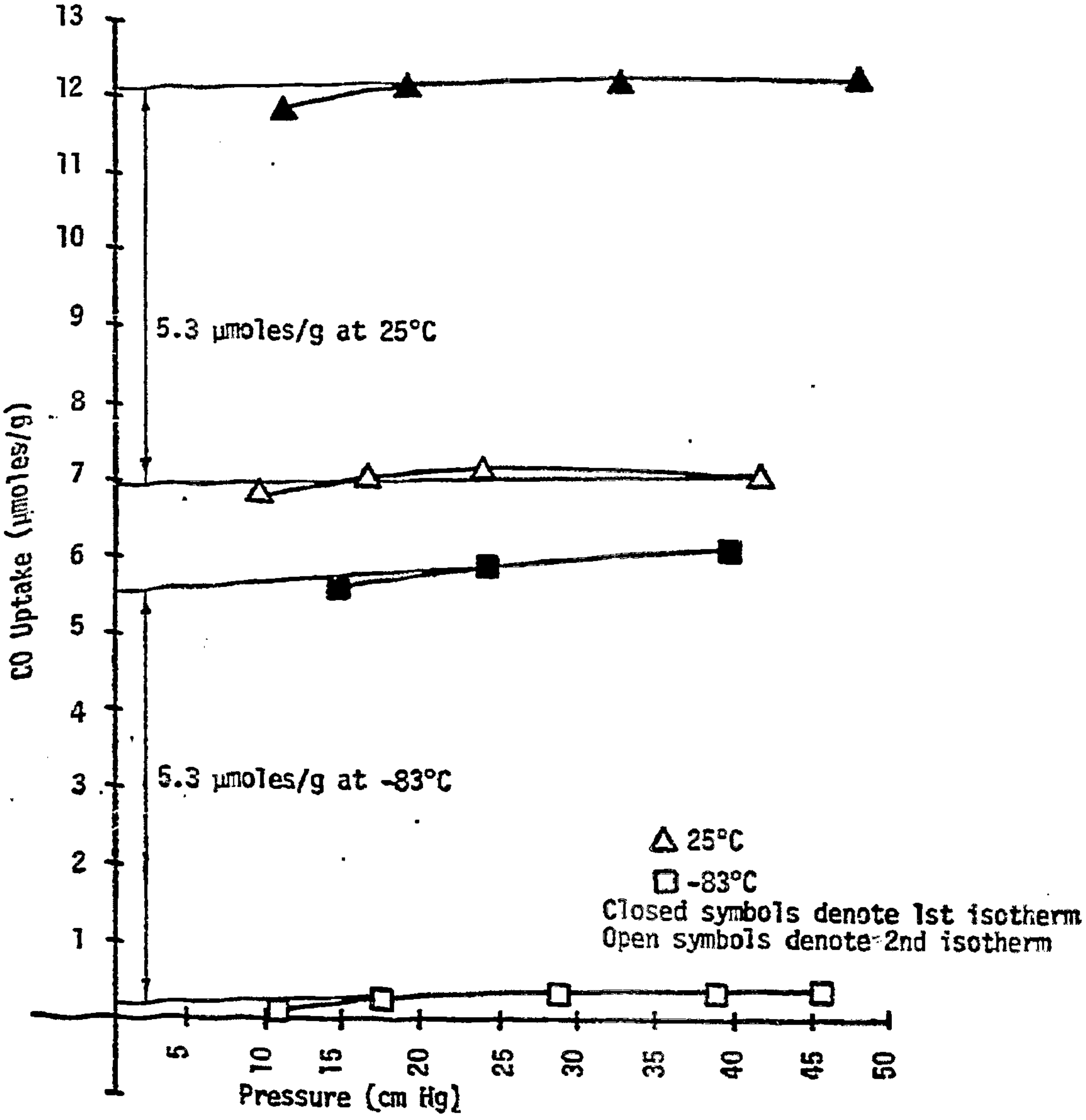

Figure 4. CO Adsorption on Inco Nickel Powder at 25 and -83°C.

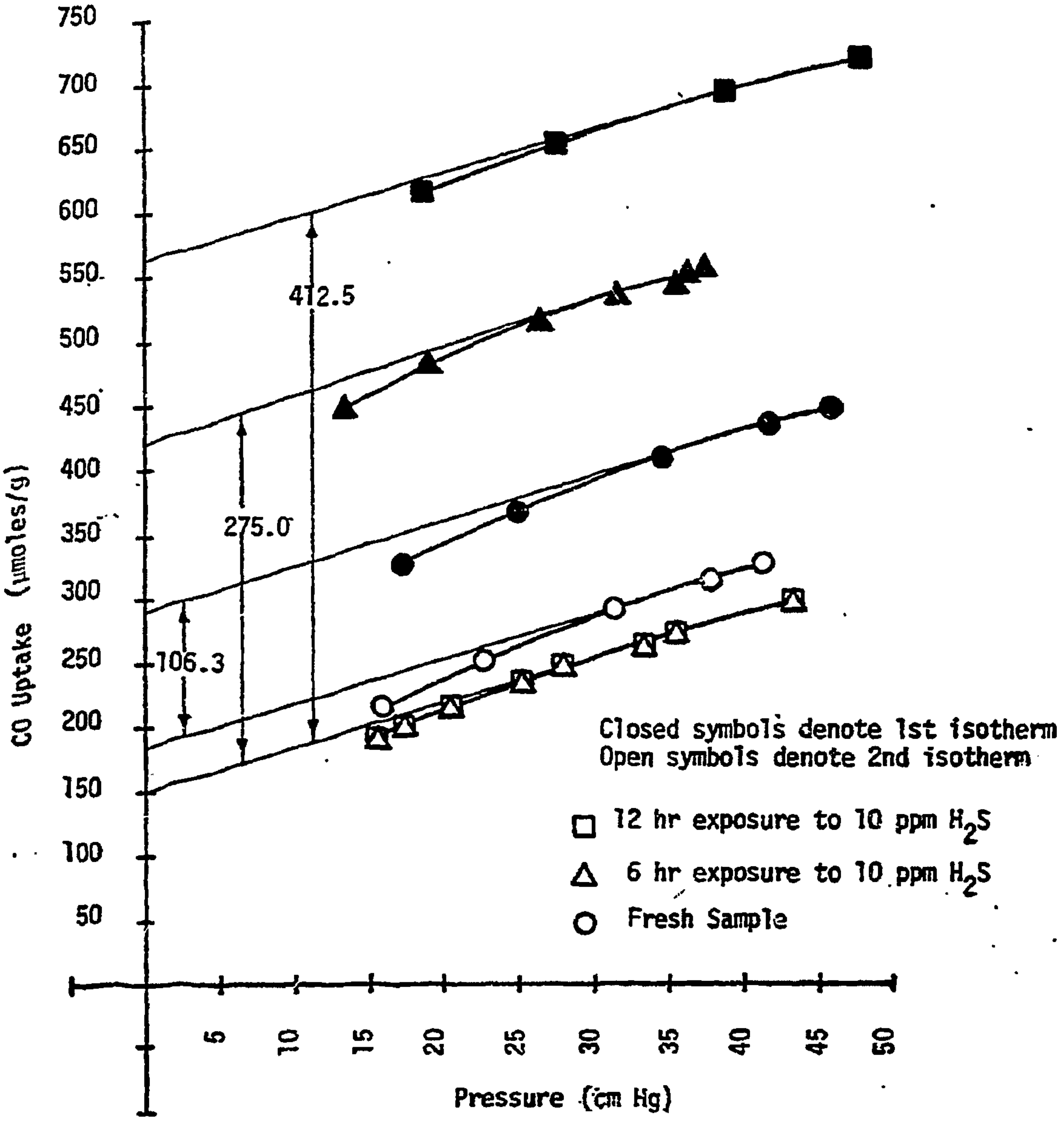

Figure 5. Effects of 10 ppm H_2S on CO Adsorption (-83°C) on Ni-A-111.

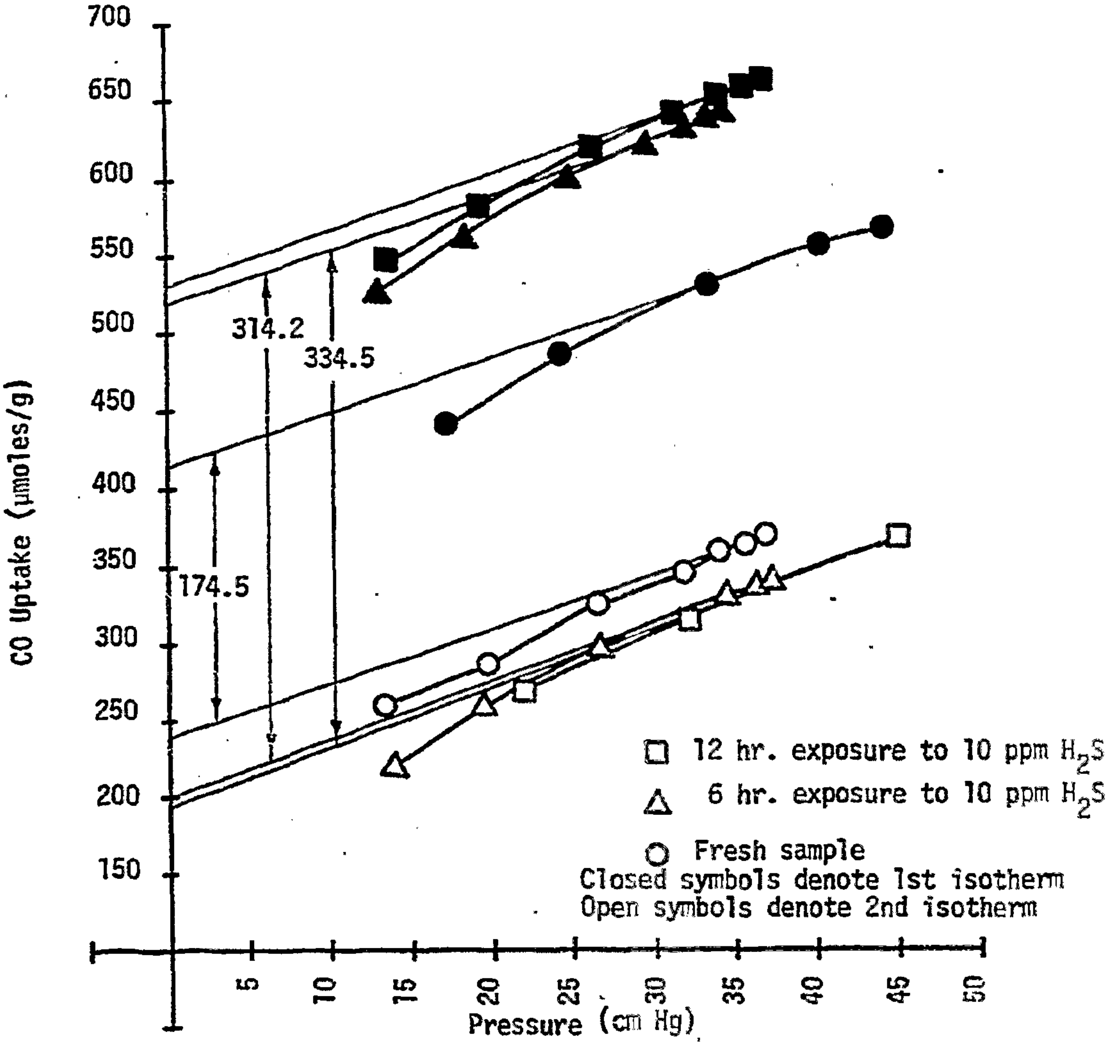

Figure 6. Effects of 10 ppm H_2S on CO Adsorption (-83°C) on Ni-Ru-A-105.

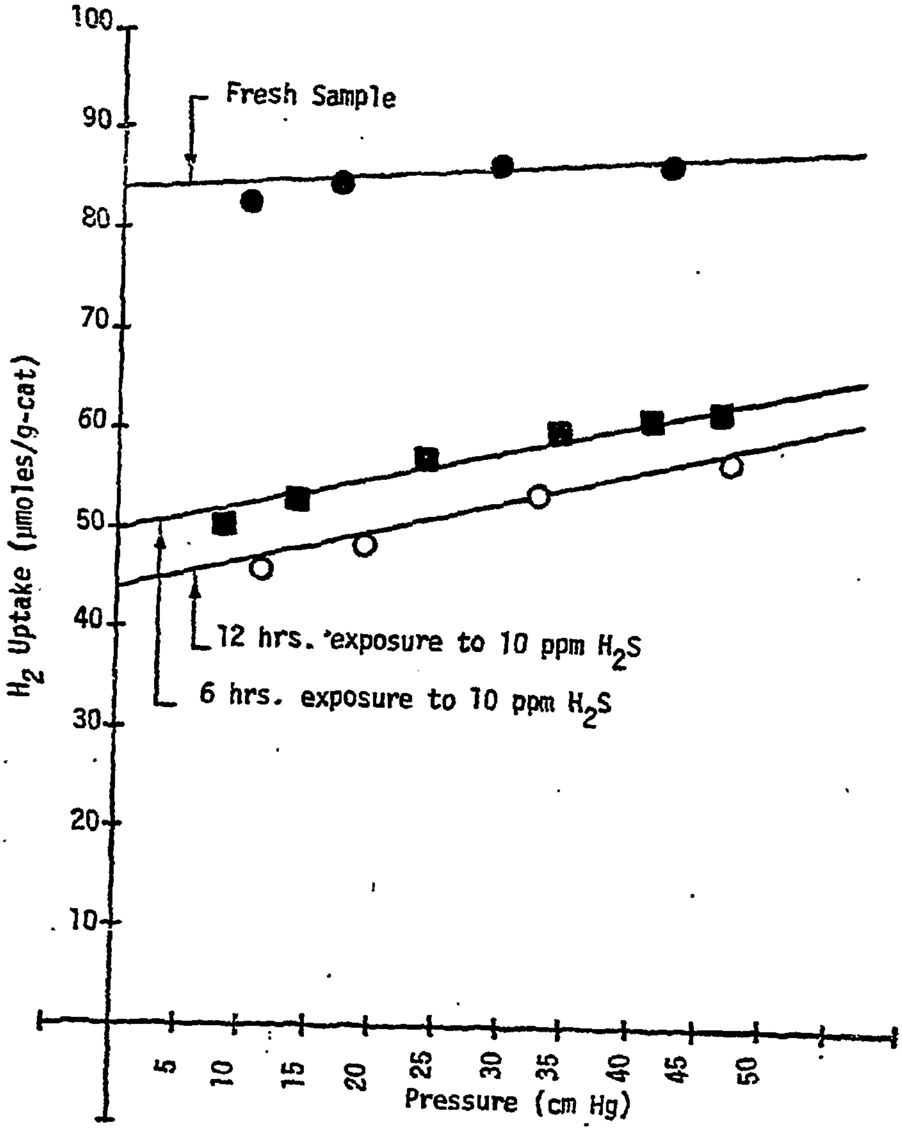

Figure 7. Effects of 10 ppm H_2S on H_2 Adsorption on Ni-Fe-A-100 (25°C).

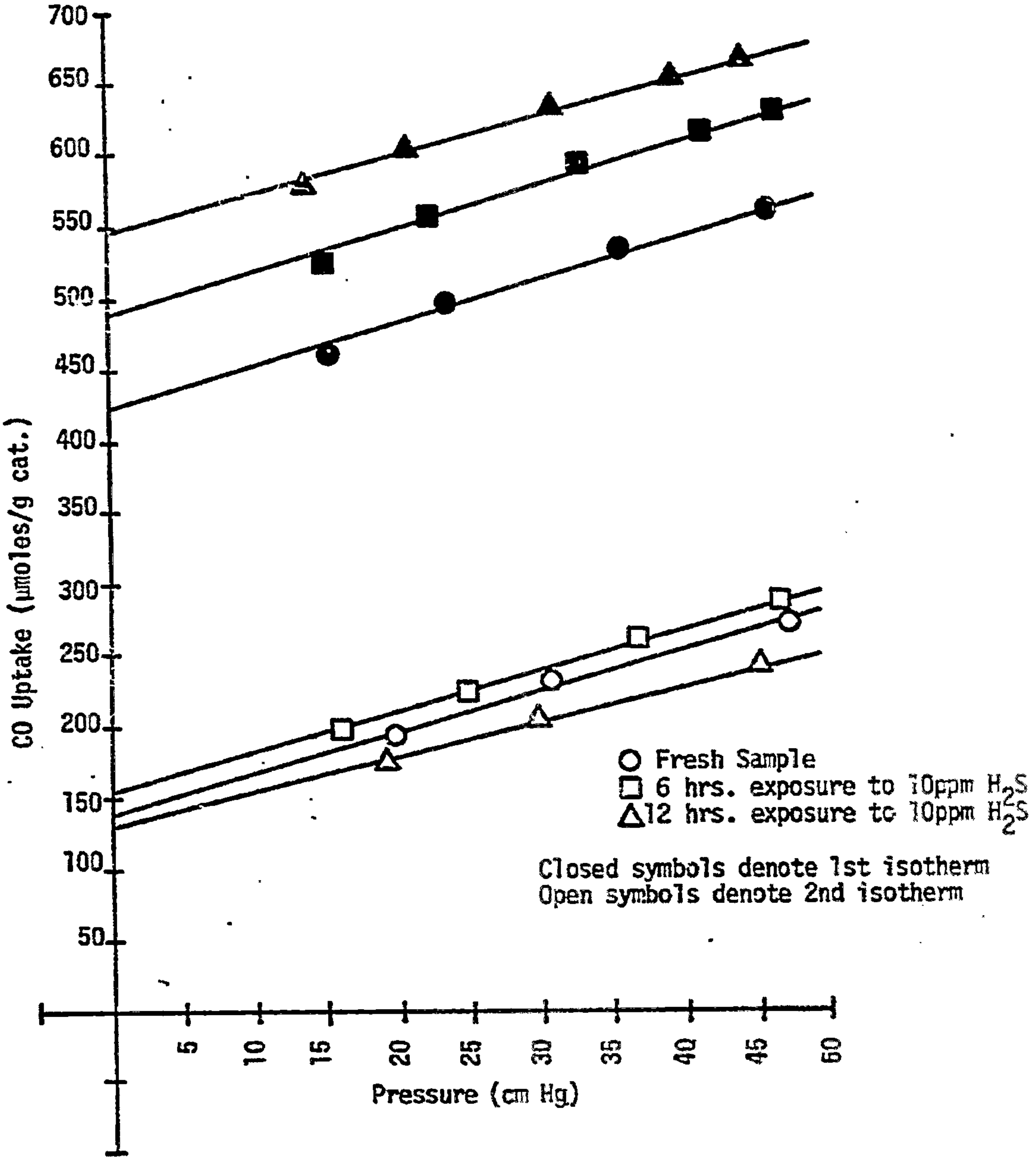

Figure 8. Effects of 10 ppm H_2S on CO Chemisorption on Ni-Fe-A-100 (-83°C).

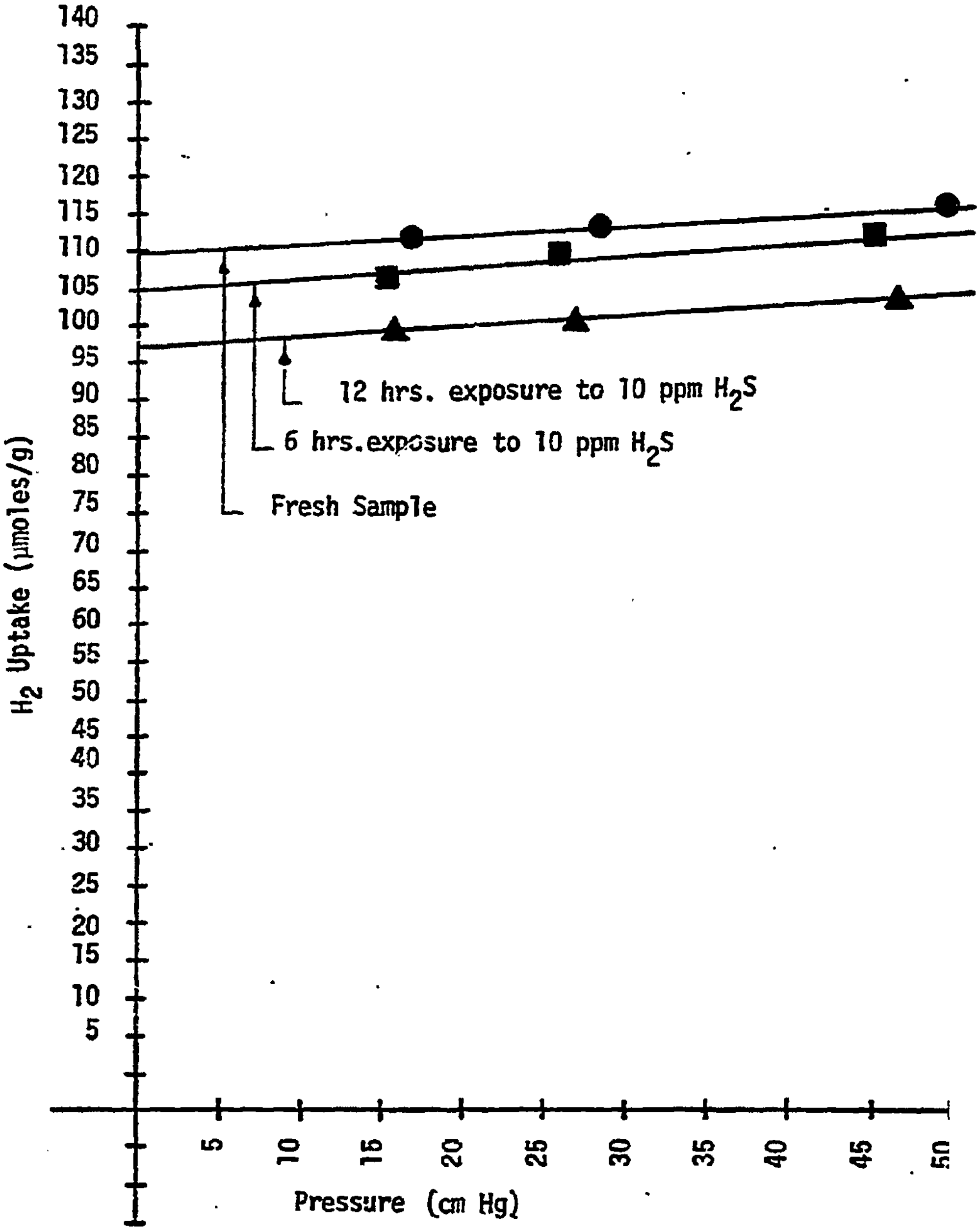

Figure 9. Effects of 10 ppm H_2S on H_2 Adsorption on Ni-Co-A-100 (25°C).

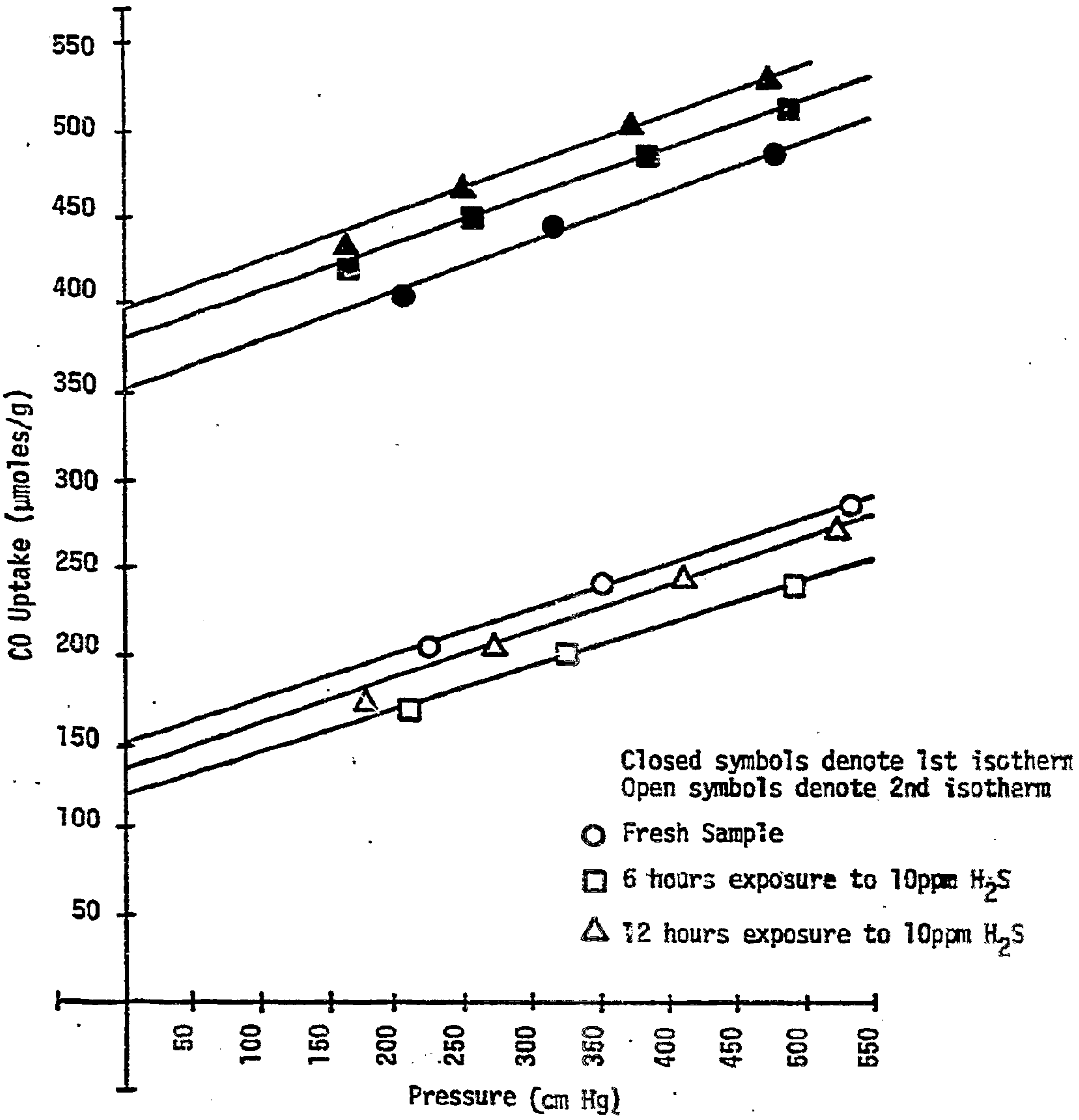

Figure 10. Effects of 10ppm H_2S on CO Adsorption on Ni-Co-A-100. (-83°C)

data and those reported by others are very likely due to differences in equilibration pressure. Data from our last report[3], for a nickel catalyst show that CO uptake can vary significantly as a function of equilibration pressure; in other words the monolayer coverage of CO is not well defined. Nevertheless there is evidence from the literature and from our data which suggests metal carbonyl formation at the surface during exposure to CO for many catalyst systems. Since these and other details vary significantly from catalyst to catalyst, additional observations in regard to Table 5 are discussed separately (below) in some depth for each catalyst.

a. <u>Al_2O_3, Ni Powder, and Ni/Al_2O_3</u>. Data from Table 5 for Kaiser SAS Al_2O_3 show that CO uptake increases with increasing exposure to H_2S. These support uptake data were used to correct for chemisorption on the support in determining CO uptake for the alumina-supported catalysts listed in Table 5; in each case the appropriate correction was applied for exposure to 10 ppm H_2S for 0, 6, or 12 hours.

Isotherms for CO adsorption on an Inco nickel powder (a high purity nickel having particles in the 1-3μ range) are shown in Figure 4. The first isotherm at 25°C corresponds to the CO uptake of the sample obtained after evacuation at 400°C; the CO adsorption extrapolated to zero pressure is 12.1 μmoles/g of nickel and corresponds to a value of CO/H of 1.74. Recent nitrogen BET and H_2 chemisorption measurements[7] (this laboratory) for the same nickel powder and previous data by O'Neill[8] using Argon BET and H_2 chemisorption on a nickel powder show that hydrogen chemisorbs dissociatively on nickel with a surface stoichiometry of $H/Ni_s = 1$. These H_2 and CO chemisorption data together provide strong evidence for the existence at 25°C of surface complexes such as $Ni(CO)_1$ and $Ni(CO)_2$, where the latter species, a surface carbonyl, predominates.

After evacuation at 25°C of the CO covered nickel powder, the second isotherm (at 25°C) was obtained--corresponding to carbon monoxide (or possibly nickel carbonyl) removed by evacuation at room temperature. The difference between the first and second isotherm, 5.3 μmoles/g corresponds to irreversibly held CO, and the corresponding CO/H value is 0.76. Brooks and Christopher[9] report a CO/H value of 0.6 at 25°C for an NRC nickel powder. It is not known whether their data included reversibly adsorbed CO, and their pretreatment of the powder is questionable.

CO uptake data for the Inco nickel powder at -83°C show the same amount of irreversibly adsorbed CO as compared to 25°C but a negligible uptake for the second isotherm. In other words, at -83°C the initial CO/H value is 0.76 and there is no reversibly adsorbed CO (or nickel carbonyl) which can be pumped off at -83°C. The results, by the way, are consistent with various proposed bridged structures for CO adsorption which account for the CO/Ni_s value of less than one.

In summary, our data for the nickel powder combined with earlier observations[3] of nickel loss for Ni/Al_2O_3 samples strongly suggest nickel carbonyl formation at 25°C whereas at -85°C no easily evacuated carbonyl is formed. Hence, our procedure involving CO adsorption at -83°C avoids the problem of carbonyl formation and loss of nickel metal or alternatively loss of reversibly adsorbed CO.

The data in Table 5 for 3% Ni/Al_2O_3 show a value of CO/H of 1.87 suggesting that twice as many CO molecules are adsorbed on the nickel catalyst as hydrogen atoms. Recent studies in our laboratory[5] have shown that in alumina-supported nickel catalysts prepared according to our techniques, 60-90% of the surface nickel is reduced to nickel metal; unreduced nickel is presumably NiO. Since very recent measurements in our laboratory indicate negligible CO adsorption on NiO, our CO chemisorption results suggest that either $CO/Ni_s = 2$ or that there is CO "spillover" from the nickel crystallites on to the support. Since the CO/H value is 0.76 for the same conditions on nickel powder and the results for Ni/Al_2O_3 have been corrected for CO adsorption on Al_2O_3 in the absence of nickel, the spillover effect may be a reasonable possibility.

Brooks and Christopher[9] have observed ratios of CO/H ranging from 0.8 to 1.8 for nickel-alumina catalysts using CO chemisorption at 25°C and H_2 chemisorption at 250°C. The variation in their results can be explained in part due to variations in equilibration pressures. Unfortunately their results may have been affected by carbonyl formation at 25°C resulting in loss of nickel and by the unusually high temperature selected for H_2 chemisorption for which the surface stoichiometry is unknown. Nevertheless, their observation of CO/H = 1.8 agrees closely with our results. Brooks and Christopher[9] observed CO/H values of 3.4 to 30 for nickel exchanged zeolites. The unusually high CO uptakes were attributed to CO adsorption on Ni^{2+} sites, since large CO uptakes were also observed for the unreduced catalyst. For Ni/Al_2O_3, however, we observed an uptake of only 26 μmoles/g for a passivated (air exposed) sample, the value of which is identical to the uptake for the Al_2O_3 support alone. In other words, CO does not adsorb on NiO or any other nickel species in our catalyst besides nickel metal.

Gardner[10] has studied the chemisorption of CO on nickel, chromium, and platinum using infrared spectroscopy. He classifies the species resulting from chemisorption of carbon monoxide on these metals as intermedians and carbonyls. The latter designation may be important with respect to our results, since carbonyl formation corresponds to $Ni(CO)_x$ where x = 1-4. Indeed, formation of $Ni(CO)_2$ at the surface could also explain the CO/H value of 1.87 for 3% Ni/Al_2O_3.

b. Molybdate Catalysts. As seen from Table 5, there are two sets of H_2 chemisorption data shown for the $Ni\text{-}MoO_3$-A-101 catalyst; both sets of data were obtained by rereduction of two small samples selected from a large sample reduced in our large reduction apparatus.[3] The difference in the initial H_2 uptake is indicative of the reproducibility obtained in rereduction and surface area measurements for two different samples of the same catalyst.

It is important to note that the H_2 uptakes for the $Ni\text{-}MoO_3$ catalyst are approximately the same as for the 3% Ni/Al_2O_3 reduced in a small glass cell. Moreover, the data in Table 5 also indicate that chemisorption of H_2 on MoO_3 is negligible (1 µmole/g) and chemisorption of CO on MoO_3 is very small (8 µmole/g). These observations suggest that the nickel sites do and the MoO_3 sites do not chemisorb H_2 and CO. Effects of H_2S poisoning are not observed to be the same for Ni and Ni-MoO_3 catalysts nor are they expected to be the same since the interaction of H_2S with MoO_3 is clearly of importance in hydrodesulphurization.[11]

c. Ruthenium Catalysts. In order to compare the behavior of the nickel-ruthenium alloy with that of ruthenium metal, an Engelhard catalyst (0.5 wt.% Ru) and our own alloy catalyst, Ni-Ru-A-105, were studied under the same conditions. First, it is interesting to note that the value of CO/H is 3.54 for the industrial ruthenium catalyst. Sinfelt and Yates[12] obtained a value of 1.15 for a 5% Ru/SiO_2. However, the experimental method used by the latter differed from the method used in this laboratory. In particular their equilibration pressures were much lower and their temperature for CO adsorption was 25°C. In a very recent study, Dalla Betta[13] has shown that CO/H values for Ru/Al_2O_3 vary from 0.5 to 3.8 and that the ratio increases with increasing ruthenium dispersion. He reports a value of 3.8 for CO/H on 0.5% Ru/Al_2O_3 in good agreement with our data. Thus, CO adsorption on ruthenium may result in formation of $Ru(CO)_3$ or $Ru(CO)_4$. The value of CO/H for ruthenium is the highest for any catalyst in Table 5, whereas the value for the Ni-Ru alloy is essentially the same as for Ni and other catalysts (see Table 5).

It is interesting to note that the effect of H_2S poisoning on CO chemisorption for ruthenium is different than for all other catalysts shown in Table 5. Namely there is a decrease rather than increase in CO uptake..

d. Ni-Rh/Al_2O_3. The data in Table 5 show a relatively small increase in the CO uptake after exposure to 10 ppm H_2S for 12 hours. This suggests the important possibility that Ni-Rh may have a higher resistance to sulfur poisoning than nickel or ruthenium catalysts. This possibility must of course be verified with activity measurements after H_2S exposure.

The value of CO/H for Ni-Rh is 1.67 suggesting the possibility of $Ni(CO)_2$ and $Rh(CO)_2$ formation at the surface. Yates and Sinfelt,[14] however, observed values of CO/H for rhodium catalysts ranging from 0.83 to 1.47; Wanke and Dougherty[15] observed values as high as 1.8 to 2.3 for 0.5 wt% Rh/Al_2O_3. Rhodium is known[16] to form carbonyls $[Rh(CO)_3]_n$, $Rh_2(CO)_8$ and $[Rh_4(CO)_{11}]_n$; moreover, from IR studies with supported rhodium[17] the occurrence of $Rh(CO)_2$, RhCO and Rh_2CO surface species was inferred. Wanke and Dougherty[15] suggested on the basis of geometrical considerations that high CO/Rh ratios should likely occur at sites with low coordination number.

e. Ni-Fe/Al_2O_3. The effects of H_2S on H_2 and CO chemisorption are similar to those observed for other catalysts--namely 40 and 48% decreases in H_2 adsorption after 6 and 12 hours exposure to 10 ppm

H_2S; 20 and 54% increases in CO adsorption for 6 and 12 hours exposure respectively. The value of 1.55 for CO/H is not unreasonable in view of values of 1.25 observed for reduced magnetite of high purity.[18] Values of 0.58 and 0.65 reported by Bayer et al.[18] for promoted iron catalysts are understandably lower because of the presence of alumina and alkali promoters at the surface. Nevertheless, Bayer et al.[18] observe 50-75% decreases in CO adsorption after exposure of iron-containing ammonia synthesis catalysts to concentrated H_2S at 25°C followed by reduction in hydrogen at 450°C. Since our catalysts were exposed to very dilute H_2S (10 ppm) at 450°C we are not certain whether a comparison of the data of Bayers et al. with ours is reasonable. For example, in the presence of concentrated H_2S at 25°C a nickel catalyst will form bulk nickel sulfide.[18] Nevertheless, we are not yet able to explain why the adsorption of CO is increased for our catalysts after exposure to H_2S.

f. Ni-Co/Al_2O_3. The effects of H_2S on H_2 and CO chemisorption are of surprisingly small magnitude--only an 11% decrease in H_2 adsorption and a 28% increase in CO adsorption after 12 hours exposure to 10 ppm H_2S. These data suggest that Ni-Co/Al_2O_3 may have a high resistance to H_2S poisoning; however, it should be noted that the available surface for poisoning is relatively large for Ni-Co and Ni-Fe catalysts which contain 20 wt.% metal compared to 3% in other catalysts. Nevertheless, the apparent poisoning resistance of Ni-Co is much larger than Ni-Fe--a somewhat surprising result. It is of further interest that the CO/H values for the Ni-Fe and Ni-Co (1.55 and 1.54 respectively) are so very nearly identical--a reasonable expectation in view of the chemical similarities of Fe and Co.

3. X-ray Diffraction and Fluorescence Measurements. The purpose of X-ray diffraction measurements is two-fold: (1) measurement of metal crystallite size and (2) determination of metallic phases. X-ray diffraction measurements for 15 wt.% Ni/Al_2O_3 were carried out during this last quarter using a Debye-Scherrer camera. The results summarized in Table 6 show that both Al_2O_3 and nickel metal are observed in the sample. Unfortunately, the lines for both the Kaiser Al_2O_3 and nickel metal were broad, diffuse and especially weak in the case of nickel. The photographic approach is clearly not satisfactory for determination of particle size. Arrangements have been made, however, to use another instrument at the University featuring a diffractometer and strip chart recorder.

X-ray fluorescence measurements have been initiated for Ni/Al_2O_3 catalysts to determine more quantitatively the chemical composition of our samples. Thus far we have learned how to use the University spectrometer and have prepared and run a standard for Ni and Al.

4. Work Forecast. During the next quarter we will continue characterization of pelleted catalysts and begin characterization of monolithic-supported nickel catalysts. Hydrogen and carbon monoxide

TABLE 6

Observed X-ray Diffraction Lattice Parameters
For Ni-A-114 (15% Ni/Al_2O_3)

d VALUE(A^o)	DESCRIPTION	ASSIGNMENT
2.85	weak, diffuse	Al_2O_3
2.42	broad, diffuse	"
2.27	weak	"
1.98	strong, very broad	Al_2O_3, Ni
1.78	very weak, diffuse	Ni
1.52	"	Al_2O_3
1.39	strong, broad	Al_2O_3
1.25	very weak, diffuse	Ni
1.14	"	Al_2O_3
.808	"	Al_2O_3

adsorption will be measured for Ni-Pd, Ni-Pt, Ru-Pd and Ru-Co catalysts and possibly nickel powder before and after exposure to 10 ppm H_2S. H_2 chemisorptive uptakes will be measured for three or four of the monolithic-supported nickel catalysts. In addition, X-ray diffraction and fluorescence measurements will be carried out for Ni/Al_2O_3, and two or three nickel alloy catalysts to determine phase and chemical composition as well as metal crystallite size.

B. Task 2: Laboratory Reactor Construction

Details of the proposed reactor system for testing catalysts up to 400 psig and 1000°C were presented in QPR-1.[3] A schematic of the completed reactor system will be included in the next report. Most of the purchased equipment including a new 18-inch-zone furnace, NDIR CO detector, and chromatographic accessories has now been received and installed; in fact, construction of the system is roughly 80% complete. Only the new mass flow meter system and temperature programmer for the furnace have not been delivered; however, delivery of both items within the next month is assured. Even so, the system is presently operational with limited temperature programming capabilities.

The forecast for the next period includes completion of the construction and testing of the reactor system.

C. Task 3: Reactor Screening of Alloy Catalysts

1. Screening Results. Both differential (low conversion) and integral (high conversion) test procedures were outlined previously.[3] In previous differential screening tests[3] at 275°C, CO conversions of 15-35% were observed. In order to achieve more completely kinetic-limited results (e.g. lower conversions) reaction temperatures of 225 and 250°C were selected for differential tests, all other conditions being held the same.

Reactor screening data in the form of conversions, specific rates per gram of catalyst, turnover numbers (rates per site per second), and selectivities are presented in Tables 7-10 for 225 and 250°C at space velocities of 30,000 and 60,000 hr^{-1}. At 250°C conversions for the 3 wt.% catalysts (Ni-A-112, Ni-Ru, Ni-Rh, and $Ni-MoO_3$) range from 4 to 14% depending upon the space velocity, whereas conversions for the 15 to 20 wt.% catalysts (all other catalysts) range from 11 to 53%. At 225°C the conversion ranges are 4 to 7% and 6 to 35% for low and high metal loadings respectively. Thus, it is apparent that truly differential (low conversion) conditions can be approached at 225°C for the low (3%) metal loading catalysts but not for the 15-20 wt.% catalysts. Apparently then, for our reactor system and for typical methanation catalysts low conversion rate data can only be obtained for catalysts with a low metal loading (3-5 wt. %). Accordingly it

TABLE 7 Reactor Screening Data for Nickel and Nickel Alloy Catalysts

225°C, GHSV = 30,000 hr^{-1}, 16 psia

Catalyst	% Conversion CO	% Production CH_4	% Production Other	Rate x 10^7 ($\frac{mole}{g\ sec}$) CH_4	Rate x 10^7 ($\frac{mole}{g\ sec}$) CO	Turnover # x 10^3(sec^{-1}) CH_4	Turnover # x 10^3(sec^{-1}) CO	Selectivity to CH_4
Ni-Co-A-100								
Ni-Pd-A-100	16.77	15.20	1.60	9.91	10.95	4.77	5.27	0.906
Ni-Ru-A-105	5.18	3.48	1.73	2.79	4.17	3.12	4.68	0.672
Ni-Rh-A-100								
Ni-Pd-A-100	6.9	6.67	0.267	4.62	4.79	2.87	2.97	0.97
Ni-MoO_3-A-101	2.9	2.5	0.4	1.83	2.11	4.07	4.69	0.87
Ni-Fe-A-100	De-activates under reactor conditions							
G-87	22.45	19.55	2.88	9.81	11.25	3.04	3.49	0.871
Ni-A-112	6.63	4.47	2.13	3.62	5.35	4.60	6.80	0.674
Ni-A-116	34.63	28.08	6.55	19.23	23.74	5.13	6.32	0.815

TABLE 8 Reactor Screening Data for Nickel and Nickel Alloy Catalysts
225°C, GHSV = 60,000 hr^{-1}, 20 psia

	% Conversion	% Production		Rate x 10^7 (mole/g sec)		Turnover # x 10^3 (sec^{-1})		
Catalyst	**CO**	**CH_4**	**Other**	**CH_4**	**CO**	**CH_4**	**CO**	**Selectivity to CH_4**
Ni-Co-A-100								
Ni-Pt-A-100	15.53	14.03	1.43	18.47	20.33	8.88	9.80	0.903
Ni-Ru-A-105	4.15	3.25	0.88	5.23	6.63	5.87	7.44	0.788
Ni-Rh-A-100								
Ni-Pd-A-100	6.63	5.43	1.23	7.76	9.49	4.81	5.89	0.817
Ni-MoO_3-A-101	3.70	3.03	0.67	4.84	5.86	10.74	13.03	0.827
Ni-Fe-A-100		De-activates under reactor conditions						
G-87	20.37	17.43	2.93	18.53	21.63	5.75	6.72	0.856
Ni-A-112	5.70	4.63	1.03	7.12	8.71	9.04	11.05	0.812
Ni-A-116	24.05	21.98	2.05	30.88	33.76	8.47	8.99	0.914

TABLE 9 Reactor Screening Data for Nickel and Nickel Alloy Catalysts
250°C, GHSV = 30,000 hr^{-1}, 16 psia

	% Conversion	% Production		Rate x 10^7 (mole/g sec)		Turnover # x 10^3 (sec^{-1})		
Catalyst	CO	CH_4	Other	CH_4	CO	CH_4	CO	Selectivity to CH_4
Ni-Co-A-100	46.08	35.73	10.38	22.38	28.90	10.95	14.15	0.775
Ni-Pt-A-100	30.8	30.5	0.27	19.73	19.93	9.50	9.58	0.990
Ni-Ru-A-105	10.60	8.68	1.95	6.97	8.53	7.81	9.56	0.819
Ni-Rh-A-100	9.13	8.40	0.73	6.63	7.20	8.68	9.42	0.920
Ni-Pd-A-100	15.53	13.43	2.10	9.49	10.96	5.89	6.80	0.865
Ni-MoO_3-A-101	10.2	8.8	1.35	6.50	7.50	14.40	16.65	0.863
Ni-Fe-A-100			De-activates under normal reactor conditions					
G-87	43.53	38.88	4.65	19.60	21.8	6.05	6.77	0.893
Ni-A-112	14.00	11.33	2.60	9.18	11.31	11.65	14.35	0.810
Ni-A-116	52.75	45.63	7.13	31.44	36.35	8.38	9.68	0.870

TABLE 10 Reactor Screening Data for Nickel and Nickel Alloy Catalysts
250°C, GHSV = 60,000 hr^{-1}, 20 psia

	% Conversion	% Production		Rate x 10^7 (mole/g sec)		Turnover # x 10^3 (sec^{-1})		
Catalyst	CO	CH_4	Other	CH_4	CO	CH_4	CO	Selectivity to CH_4
Ni-Co-A-100	38.7	30.43	8.27	38.03	48.3	18.6	23.7	0.787
Ni-Pt-A-100								
Ni-Ru-A-105	9.47	8.03	1.47	12.70	14.97	14.20	16.80	0.848
Ni-Rh-A-100								
Ni-Pd-A-100	11.2	10.3	0.9	14.67	15.93	9.09	9.85	0.92
Ni-MoO_3-A-101	9.3	8.7	0.65	13.56	14.58	30.14	32.41	0.93
Ni-Fe-A-100			De-activates under reactor conditions					
G-87								
Ni-A-112	14.43	13.58	0.88	20.64	21.99	26.19	27.91	0.941
Ni-A-116	43.53	38.17	5.43	53.38	60.94	14.21	16.22	0.877

would be desirable in obtaining accurate kinetic rate data to prepare all of the catalysts with metal loadings in the 3-5% range. Nevertheless, for purposes of screening, the data obtained at moderate conversions are adequate for comparative purposes and satisfy the objectives of this study.

Apparent activation energies for some of these catalysts are shown in Table 11. With the exception of Ni-MoC$_3$-A-101, the catalysts appear to have activation energies of 12-18 k cal/mole for both CO conversion and methane formation. Ni-MoO$_3$-A-101 has a significantly higher value of 26 kcal/mole which is close to the value of 25 kcal/mole for nickel reported by Vannice.[19] The far right column lists the activation energies for various metals as reported by Vannice and measured under kinetic-limited (low conversion) conditions. Considerably lower activation energies for alloys compared to those of either alloy component very likely result at least in part from mass transfer (or diffusional) limitations. In addition, the variations are partly the result of alloy formation, the alloy having catalytic properties different from either of the pure metals.

Vannice[19] has reported selectivities for the methanation reaction over the group VIII metals to be in the following decreasing order: Pd>Pt>Ir>Ni>Rh>Co>Fe>Ru. This order correlates well with measured selectivities for alloys of these same metals with nickel as shown in Table 12. Of special interest is Ni-Pt-A-100 which shows the highest selectivity, 99% for 250°C and higher temperatures. Changes in space velocity and temperature have appreciable effects on the selectivity as can be seen for example in the data for Ni-A-112, Ni-Pd-A-100 and Ni-Ru-A-105. Generally the selectivity increases with increasing temperature for a given space velocity and with increasing space velocity for a given temperature.

Figures 11 and 12 illustrate the magnitude of the rates per gram of catalyst, the turnover numbers, and selectivities at 250°C and a space velocity of 30,000 hr^{-1}. Nominal compositions and hydrogen uptakes used to calculate turnover numbers are listed in Table 4. It should be noted that the active metal loadings which vary significantly between catalysts have an obviously marked effect on the activity of the catalyst per unit catalyst weight as can be seen in Figure 11 where the listed order corresponds to the order of wt.% active metal. A comparison of these rates with the hydrogen uptake data shows that the rate is strongly influenced by the available surface area. For example, Ni-A-116 (15 wt.% Nickel) is more active (per unit mass) than G-87 (32 wt.% nickel) mainly because the surface area of the former catalyst is larger.

Turnover numbers for 250°C and a space velocity of 30,000 hr^{-1} are shown in decreasing order of activity in Figure 12. Ni-MoO$_3$-A-101, Ni-A-112 (3% nickel) and Ni-Co-A-100 are the most active and G-87 the least active. The details of these results are discussed below for each catalyst.

TABLE 11 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	CH_4 Production	Metal*	CH_4* Production
Ni-Co-A-100			Co	27.0±4.4
Ni-Pt-A-100	12.4	14.3	Pt	16.3±0.8
Ni-Ru-A-105	14.8	19.0	Ru	24.2±1.2
Ni-Rh-A-100			Rh	24.0±0.4
Ni-Pd-A-100	17.1	14.8	Pd	19.7±1.6
Ni-MoO_3-A-100	26.2	26.2		
Ni-Fe-A-100			Fe	21.3±0.9
G-87	13.7	14.2	Ni	25.0±1.2
Ni-A-112				
Ni-A-116				

*Data of Al Vannice (Exxon) Ref. 19

TABLE 12 Selectivities to Methane

Catalyst	250°C		225°C	
	30,000 hr^{-1}	60,000 hr^{-1}	30,000 hr^{-1}	60,000 hr^{-1}
Ni-Co-A-100	0.775	0.787		
Ni-Pt-A-100	0.990		0.906	0.903
Ni-Ru-A-105	0.819	0.848	0.672	0.788
Ni-Rh-A-100	0.920			
Ni-Pd-A-100	0.865	0.92	0.97	0.817
Ni-MoO_3-A-101	0.863	0.93	0.87	0.827
Ni-Fe-A-100	De-activates under reactor conditions			
G-87	0.893		0.871	0.856
Ni-A-112	0.810	0.941	0.674	0.812
Ni-A-116	0.870	0.877	0.815	0.914

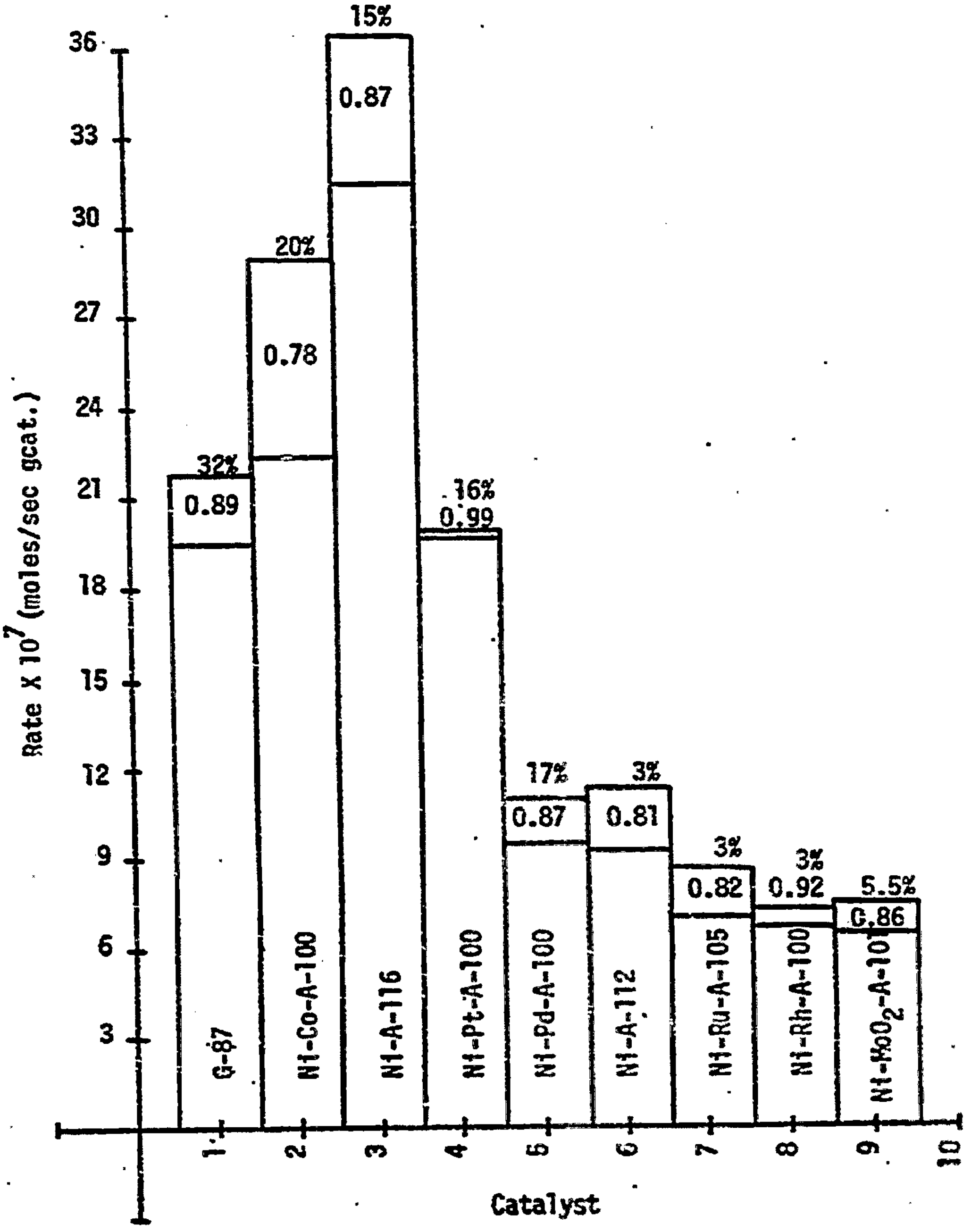

Figure 11. Specific Methanation Rates (mass basis) for Nickel and Nickel Alloy Catalysts. (Percentages are active metal loadings. Fractions represent selectivity to methane.)

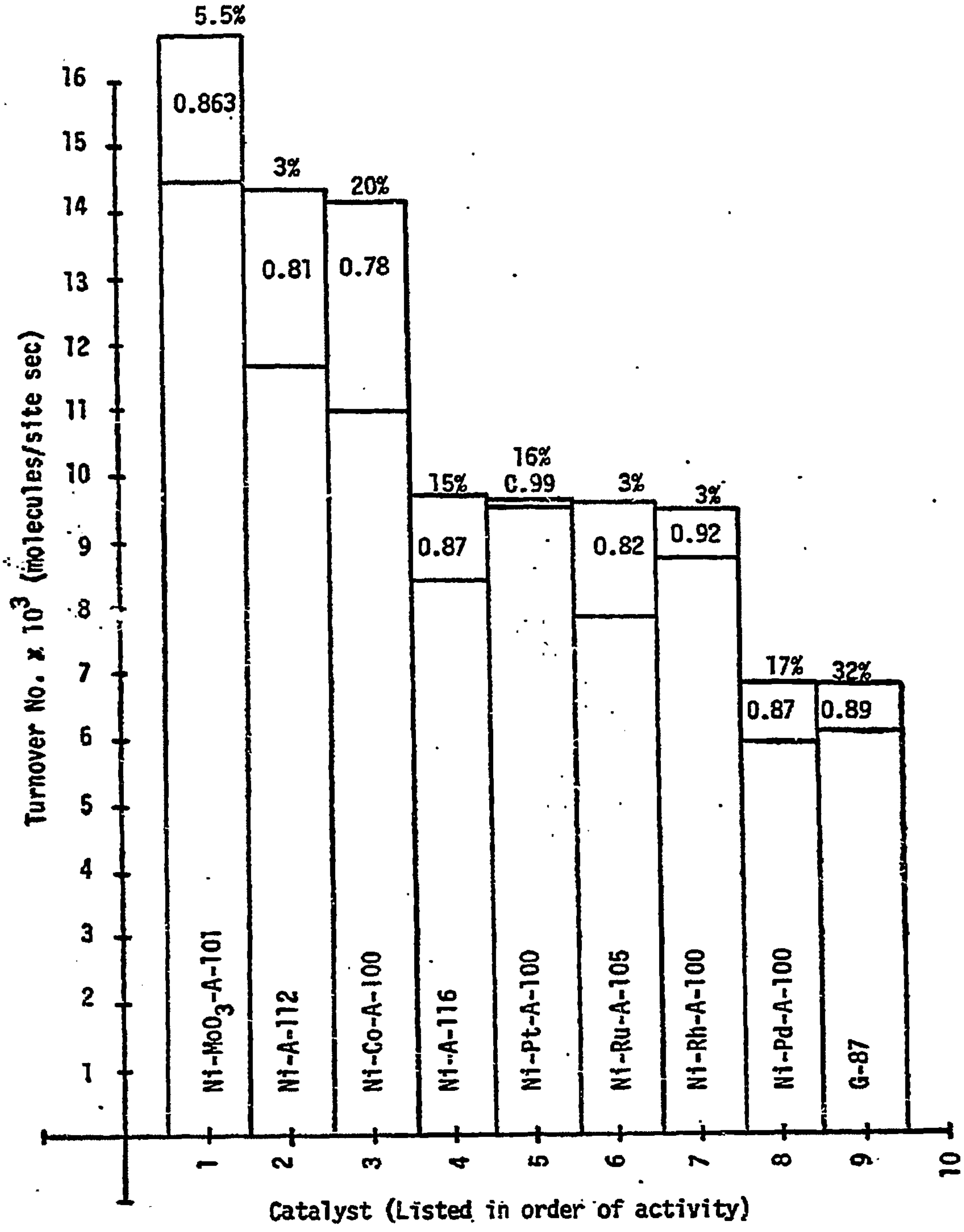

Figure 12. Turnover Numbers (molecules product/site sec) for Methanation on Nickel and Nickel Alloy Catalysts. (Percentages are active metal loadings. Fractions represent selectivity to methane.)

G-87 is a commercial nickel catalyst manufactured by Girdler Catalyst Corp. and is included as a comparison against other nickel catalysts. It is unique, however, from the other catalysts tested because it contains a different support of unknown composition which may influence the diffusional and mass transfer characteristics of the catalyst. Because of its high nickel loading (32 wt.%) it is expected that its rate per unit weight should be high. However, its turnover number is the lowest measured. This may be due to the effect of unreduced NiO present in the catalyst which is known[20] to be an effective catalyst for the decomposition of methane: $CH_4 + H_2O \longrightarrow CO + 3H_2$, thus retarding the ultimate conversion to methane. Indeed the conversion versus temperature data plotted in Figure 13 show a maximum methane production of about 80% compared to 90%[5] for our Ni-A-114 which was prepared in such a manner as to maximize nickel metal formation and minimize formation of NiO.

Ni-Co-A-100 contains a high loading of metal with equal weight percents of nickel and cobalt. It is of special interest in that both the rate per unit weight and the turnover number are high. The selectivity of this catalyst for the methanation reaction (78% at 250°C and GHSV = 30,000) is the lowest of any tested. Vannice[19] has likewise reported cobalt to have a selectivity of 78% under similar reaction conditions and the selectivity for nickel to be 90% also in good agreement with our data. Thus, cobalt has a strong effect on the selectivity of the Ni-Co catalyst.

Ni-Fe-A-100 was found to completely deactivate within two hours under normal reactor operating conditions. When the catalyst was removed from the reactor some of the beads showed a brown (rust) color as compared to the normal black. The observations suggest that the iron may scavange the oxygen from the CO to form various iron oxides and thus effectively poison the catalyst. It is also possible that the Ni-Fe catalysts was not completely reduced at the beginning of the test (see Figure 2). Additional reactor and X-ray tests are planned to investigate these possibilities.

Ni-Pd-A-100 was found to be the least active of the alloys tested thus far with a turnover number about the same as G-87.

Ni-Pt-A-100 has rate characteristics which are not outstandingly different from the other catalysts. The selectivity, however, is significantly improved. Vannice[19] has shown platinum to be one of the most selective catalysts for methane--namely about 98% to CH_4. As an alloy with nickel in the amount of only one atomic percent platinum continues to effect a 99% selectivity to methane.

Ni-A-116 is a high loading (15 wt.%) nickel catalyst used to compare against other catalysts containing 15-20 wt.% alloy. It has the highest rate per unit weight but has a turnover number the same as Ni-Pt-A-100 and somewhat lower than the cobalt alloy.

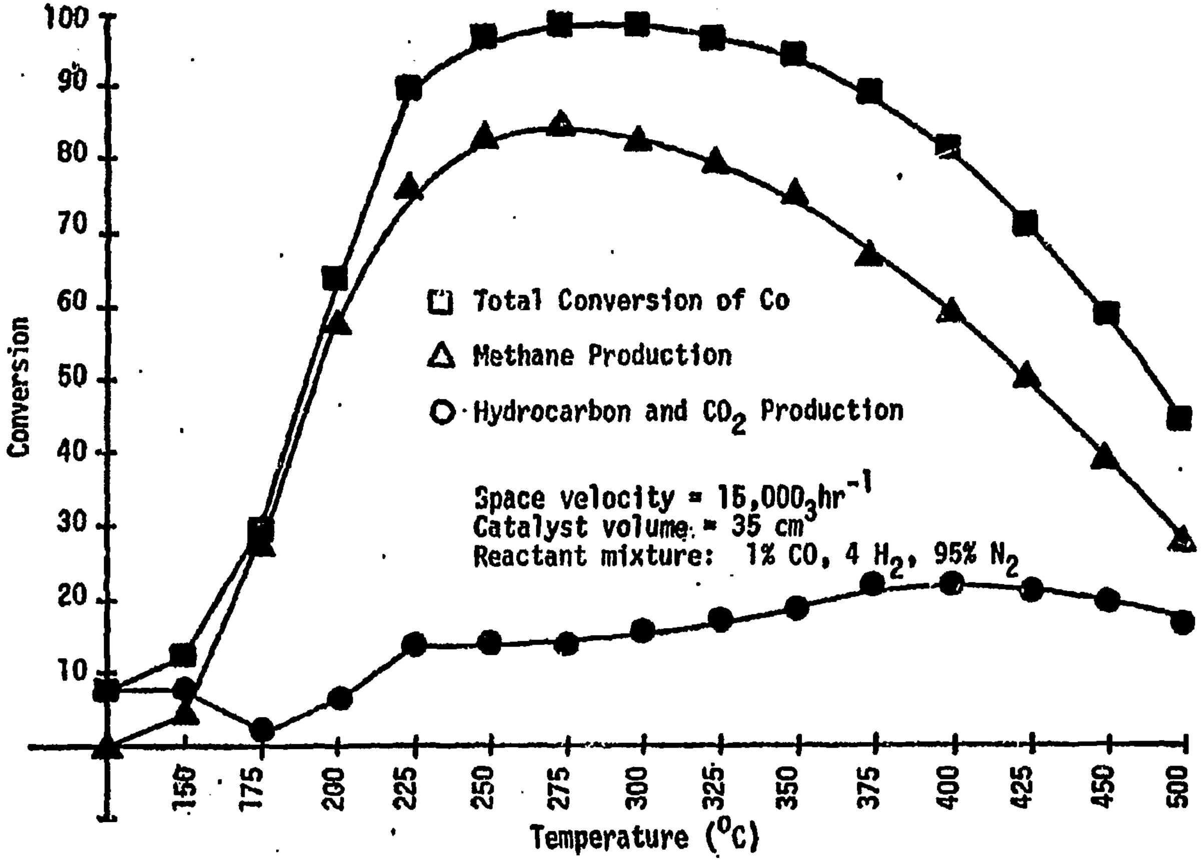

Figure 13. Integral Activity Test for G-87 (Girdler) Nickel Catalyst

$Ni\text{-}MoO_3$-A-101 has a relatively low active surface area. Thus, its rate per unit weight is among the lowest tested. However, its turnover number is the highest of any catalyst tested. Assuming a method to increase the active surface area can be found, this catalyst is a most promising candidate for further study.

Ni-Ru-A-105 and Ni-Rh-A-100 behave typically as nickel catalysts showing comparitively little effects of alloying although both are slightly less active then Ni-A-112, a nickel catalyst of comparable weight loading. The Rh does cause some increased selectivity to methane but not as pronounced as for platinum.

2. Work Forecast. During the next quarter screening tests for alumina-supported Ru will be repeated at 225 and 250°C. Alumina-supported $Ni\text{-}MoO_3$, Ni-Ru, Ni-Rh, Ni-Fe, Ni-Co, Ni-Pt, Ni-Pd and selected industrial methanation catalysts will also be screened according to the same procedure after exposure to 10 ppm H_2S. Conversion versus temperature behavior will be measured for most of these catalysts and compared with corresponding results for selected commercial catalysts.

D. Task 4: Catalyst Geometry Testing and Design

This task is scheduled to begin 18 months after initiation of the project or in other words October 22, 1976. No experimental work was completed during the past quarter nor is any work scheduled for the next quarter in connection with this task. Arrangements have been made with technical and sales representatives of Corning Glass Works in which they will send us additional monolithic supports of various geometries. The possibility of testing one or two samples of sprayed-Raney-nickel catalyst of the parallel plate configuration has also been discussed further with technical representatives at the Bureau of Mines in Pittsburgh.

E. Task 5: Technical Visits and Communication

1. Accomplishments. During the past quarter the principal investigator has continued technical communications with other workers active in methanation catalysis, many of whom are listed on the Report Distribution List in Appendix B. Private communications in the form of letters, phone calls, exchange of preprints, and informal discussions at meetings have been very helpful in keeping up-to-date and comparing important results while avoiding unnecessary duplication of other's research.

The principal investigator is presently Secretary-Treasurer of the California Catalysis Society and the Task Force Leader for Metal Surface Areas on the ASTM D-32 Committee. These professional duties bring the principal investigator directly in contact with others working in catalyst characterization, surface area measurement, and methanation catalysis, all pertinent to this present investigation.

The principal investigator and Mr. Kyung Sup Chung attended the ERDA/EPRI/NSF-RANN Contractors Conference held October 22-23, 1975 in Park City, Utah. The experience was very profitable both in terms of direct private conversations with other workers in coal conversion catalysis and in very informative presentations dealing with coal conversion. Preliminary arrangements to visit other laboratories were initiated during this meeting.

2. Work Forecast. During the next quarter the principal investigator will attend the Fall meeting of the California Catalysis Society and will also present a paper on "Chemistry of Ni/Al_2O_3 Catalysts" at the 68th Annual AIChE meeting in Los Angeles in November. Attendance at these meetings will provide additional opportunities for the principal investigator to build and continue communications with other workers in methanation catalysis.

IV. CONCLUSIONS

A. In preparation of monolithic catalysts, a 2.5:1 or 3:1 slurry of water and SA Medium Al_2O_3 gives the maximum coating in the smallest number of dips. Impregnation with a $Ni(NO_3)_2 \cdot 6H_2O$ melt or with a 50 wt.% aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ maximizes the nickel loading with a minimum number of applications.

B. In a 3% $Ni\text{-}Mo/Al_2O_3$ catalyst, the nickel sites adsorb both H_2 and CO, whereas the MoO_3 sites do not.

C. Values of CO/H generally range from 1.5-2.0 for alumina-supported nickel alloy catalysts suggesting the formation of surface metal carbonyls during CO adsorption or possibly CO spillover to the support.

D. The uptake of carbon monoxide for alumina-supported nickel alloys is observed to <u>increase</u> after exposure to 10 ppm H_2S at 450°C for 6 or 12 hours. The reason for this behavior is not yet understood.

E. Hydrogen uptake after 12 hours exposure to 10 ppm H_2S (at 450°C) is decreased only 11% for 20 wt.% $Ni\text{-}Co/Al_2O_3$ compared to 54% for 20% $Ni\text{-}Fe/Al_2O_3$. These data suggest that Ni-Co may have a high resistance to sulfur poisoning.

F. Data for CO adsorption on a nickel powder at 25°C show a CO/H value of 1.74 suggesting surface carbonyl formation. After evacuation at 25°C, however, the ratio decreases to 0.76, showing that reversible adsorption-desorption occurs. A value of CO/H of 0.76 is also obtained at -83°C before and after pumping at the low temperature indicating no reversible adsorption. The number of CO molecules irreversibly adsorbed per surface nickel atom is 0.76 suggesting the existence of bridged structures for CO on nickel. Our procedure of measuring CO adsorption at -83°C avoids complications due to either carbonyl formation or reversible CO adsorption.

G. Steady state conversion measured at 225 and 250°C, 1 atm, and for space velocities of 30,000 and 60,000 hr^{-1} indicate that very nearly differential (low conversion) conditions obtain only for low (3-6 wt.%) metal loading catalysts. Screening data for 15-20 wt.% $metal/Al_2O_3$ catalysts are influenced by mass transfer or diffusional limitations.

H. $Ni\text{-}MoO_3/Al_2O_3$ is the most active catalyst on a per surface area basis. $Ni\text{-}Pt/Al_2O_3$ has the highest selectivity for methane production--namely 99% (250°C 30,000 hr^{-1}). A 15 wt.% Ni/Al_2O_3 is the most active catalyst on a per mass basis--even more active than a commerical 32 wt.% Ni/Al_2O_3 simply because the 15% catalyst has a high nickel surface area.

I. Conversion versus temperature data indicate that a commerical nickel catalyst attains a maximum methane production of 80% at 250-300°C compared to a production of 90% for a 15 wt.% Ni/Al_2O_3 prepared in this laboratory. The higher selectivity for the latter catalyst is possibly a result of its higher state of reduction to metallic nickel.

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B. BIBLIOGRAPHIC DATA SHEET

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7. Author(s) Calvin H. Bartholomew

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15. Supplementary Notes

16. Abstracts

This report presents work accomplished during the second quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Alumina-supported alloys of nickel with ruthenium, rhodium, molybdenum, platinum, palladium, iron, and cobalt were characterized by surface area measurements and tested for methanation catalyst activity at ambient pressure, 225 and 250°C and at space velocities of 30,000 and 60,000 hr^{-1}. To determine effects of sulfur poisoning on surface area, the adsorption of hydrogen and carbon monoxide on most of these catalysts was measured before and after exposure to hydrogen sulfide. In addition, pellet-supported nickel-copper, molybdate, ruthenium-cobalt and ruthenium-palladium alloy catalysts and monolithic-supported nickel catalysts were prepared. Reconstruction of a laboratory reactor to enable high pressure operation was eighty percent completed.

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