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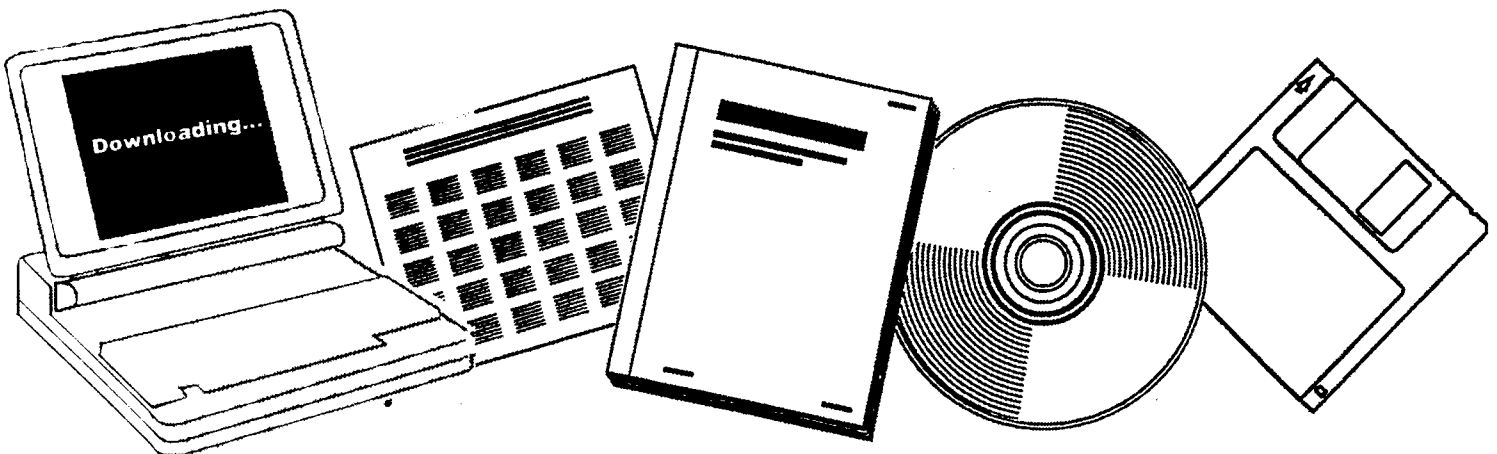
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**ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR
METHANATION OF COAL-DERIVED GASES. PHASE
I. QUARTERLY TECHNICAL PROGRESS REPORT,
OCTOBER 23, 1975--JANUARY 22, 1976**

BRIGHAM YOUNG UNIV., PROVO, UTAH

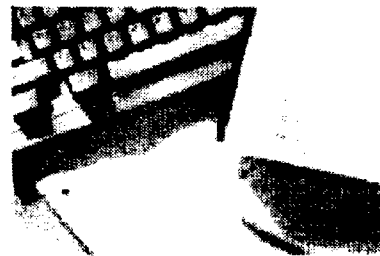
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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR
METHANATION OF COAL-DERIVED GASES

Phase 1

Quarterly Technical Progress Report
For Period October 23, 1975 to January 22, 1976

Calvin H. Bartholomew

MASTER

Brigham Young University
Provo, Utah 84602

Date Published--February 6, 1976

PREPARED FOR THE UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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

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Phase I .

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FOREWORD

This report summarizes technical progress during the third quarter period (October 23, 1975 to January 22, 1976) of a two-year study conducted for the Energy Research and Development Administration (ERDA) under Contract No. E(49-18)-1790. The principal investigator for this work is Dr. Calvin H. Bartholomew; Dr. Paul Scott is the technical representative for ERDA.

The following students contributed to the technical accomplishments and to this report: Graduates - Blaine Barton, Don Stowell, and Richard Turner and Undergraduates - Norman Shipp, and Scott Engstrom. Karen Weis and Scott Folster provided typing and drafting services.

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ABSTRACT

This report presents work accomplished during the third quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Hydrogen and carbon monoxide adsorption data for alumina-supported alloys of nickel with iron, cobalt, and platinum were obtained before and after samples had been exposed to 25 ppm H₂S. Hydrogen adsorption uptakes were measured for several monolithic-supported Ni/Al₂O₃ catalysts. In addition, chemical analysis and x-ray diffraction measurements were continued. Reconstruction of a laboratory reactor to enable high pressure operation was ninety percent completed. The principal investigator attended three meetings, a short course, presented one paper, and chaired a symposium on fuels, at which Mr. Blaine Barton also presented a paper.

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 H₂S.

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, H₂/CO ratio and H₂S 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 H₂S 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 H₂/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 H₂S 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, H₂/CO ratio, and H₂S 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 H₂/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 Ru-Pt was prepared in pellet form by impregnation, drying, and reduction in hydrogen. Hydrogen adsorption uptakes were measured for several monolithic-supported Ni/Al₂O₃ catalysts. Hydrogen and carbon monoxide adsorption uptakes were measured before and after exposure to 25 ppm H₂S for alumina-supported Ni-Fe, Ni-Co, and Ni-Pt. The procedures for poisoning catalysts with H₂S were refined and the concentration of H₂S/H₂ was determined analytically. Chemical analysis, x-ray diffraction and x-ray fluorescence measurements for Ni/Al₂O₃ catalysts were continued.

Task 2. Reconstruction of the low pressure laboratory reactor to allow for operation to 400 psi was continued. Mass flow meters were installed and calibrated; a new temperature programmer-controller was installed and tested. System upgrading and modifications are about 90% complete.

Task 3. No screening of catalysts was accomplished because the reactor was down. Work will continue however, during the next quarter.

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

Task 5. The principal investigator attended the California Catalysis Society meeting held November 7-8, presented a paper at the 68th annual AIChE meeting in Los Angeles (Nov. 16-22), attended a short course on Catalyst Deactivation (Nov. 17-18), and chaired The First Rocky Mountain Fuel Symposium held at BYU on January 30. Mr. Blaine Barton presented a paper on methanation at the Rocky Mountain Fuel Symposium.

Miscellaneous. Mr. Kyung Sup Chung completed his master's thesis dealing with "The Effects of H₂S Poisoning on H₂ and CO Chemisorption on Nickel and Nickel Alloys."

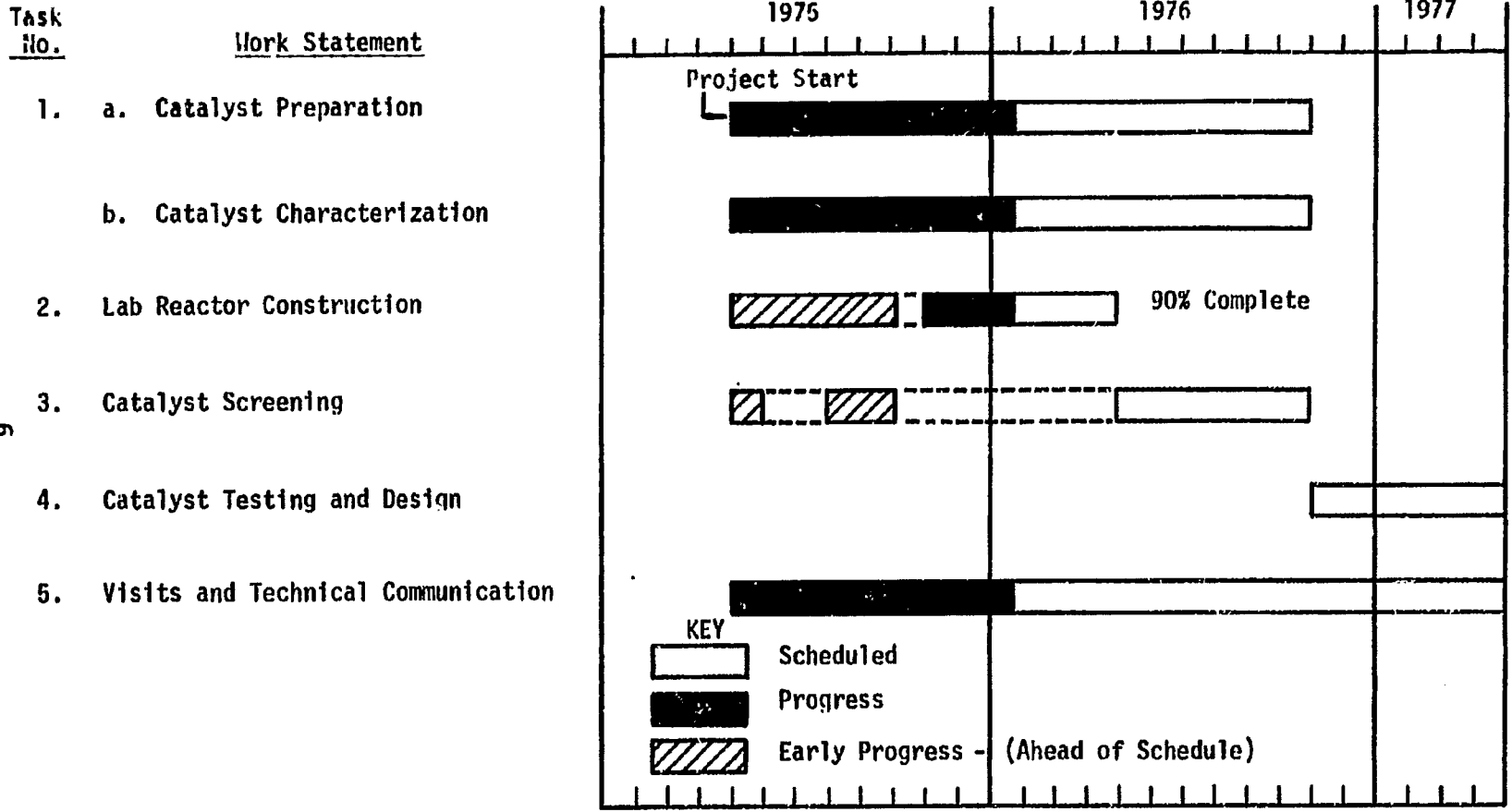


Figure 1. Project Progress Summary

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst preparation. Alumina pellet-supported Ru-Pt was prepared according to the general procedure outlined in the first quarterly progress report (QPR-1, Ref. 3). Ruthenium trichloride and chloroplatinic acid salts were used in the impregnation; the nominal composition was calculated to be 0.5 wt.% Ru and 0.5 wt.% Pt. The purpose in preparing this catalyst was to determine the result of alloying the most selective metal for methanation (platinum) with the least selective but probably most active metal (ruthenium).

This work tentatively concludes our preparation of pellet-supported alloy catalysts to be screened for the methanation reaction. Altogether, eleven different pellet-supported alloys of nickel and ruthenium have been prepared in this study. Approximately 20 different Ni/Al₂O₃ catalysts (pellet form) have been prepared in this and other studies (3-6), several of which have been or will be screened for methanation activity. In addition, several commercial nickel and ruthenium catalysts have been characterized and tested. During this past quarter, research samples of NiCoMo, NiMo, and NiMoO₄ supported on Al₂O₃ or Al₂O₃-SiO₂ have been obtained from the Climax Molybdenum Company for characterization and methanation screening.

2. Hydrogen chemisorption uptakes for monolithic supported nickel. An outline of the standard procedure used to measure chemisorptive uptakes of monolithic-supported nickel catalysts is presented in Table 1. This procedure for measuring uptakes differs from the one given previously in QPR-1 (3) in that reductions of previously reduced samples are done for 5 hours at 500°C (rather than 2 hours at 450°C) and subsequent evacuations are carried out 8-10 hours (rather than 1-2 hours). The change in reduction schedule is based on data from QPR-2 (4) and is designed to insure that all samples are uniformly and completely reduced. The change in evacuation time was necessitated by the difficulty in adequately evacuating large monolithic-supported catalyst samples.

In order to do chemisorptive work on monolithic-supported catalysts, a special chemisorption sample cell had to be designed and built. The monolithic sample cell is shown in Fig. 2. The purpose of the sealed glass bulb is to minimize the cell dead volume; the short uncoated monolith and the glass wool packing insure uniform flow through the monolithic-supported catalyst.

A summary of the hydrogen uptake data for the five monolithic-supported nickel catalysts is shown in Table 2, along with the data for Ni-A-116 (a pelletized alumina-supported 15 wt.% nickel catalyst). The Ni-M-102 catalyst was not tested due to its poor nickel loading (see QPR-2). A typical isotherm for the monolithic-supported catalysts (that of Ni-M-103) is shown in Figure 3.

TABLE 1

Standard Procedure for Measuring Uptake of
of Monolithic-supported Nickel Catalysts

Step	Procedure
Reduction	All samples reduced 12-16 hrs. at 450-500°C GHSV=1000 hr ⁻¹ . Reduce previously reduced catalysts 5 hrs. at 500°C, GHSV=1500 hr ⁻¹ .
Evacuation	Evacuate 8-10 hrs. (overnight) at 400-450°C and usually to about 2×10^{-5} torr.
Adsorption	1. Expose evacuated sample to measured amount of hydrogen at 25°C and 400 torr for 45 min. (if more than a single buret of gas is needed, time is measured from the moment the final measured buret of gas admitted). 2. Measure moles of hydrogen as a function of pressure from 0-400 torr.
Calculation	Plot hydrogen uptake versus pressure and extrapolate to zero pressure to determine uptake due to chemisorption.

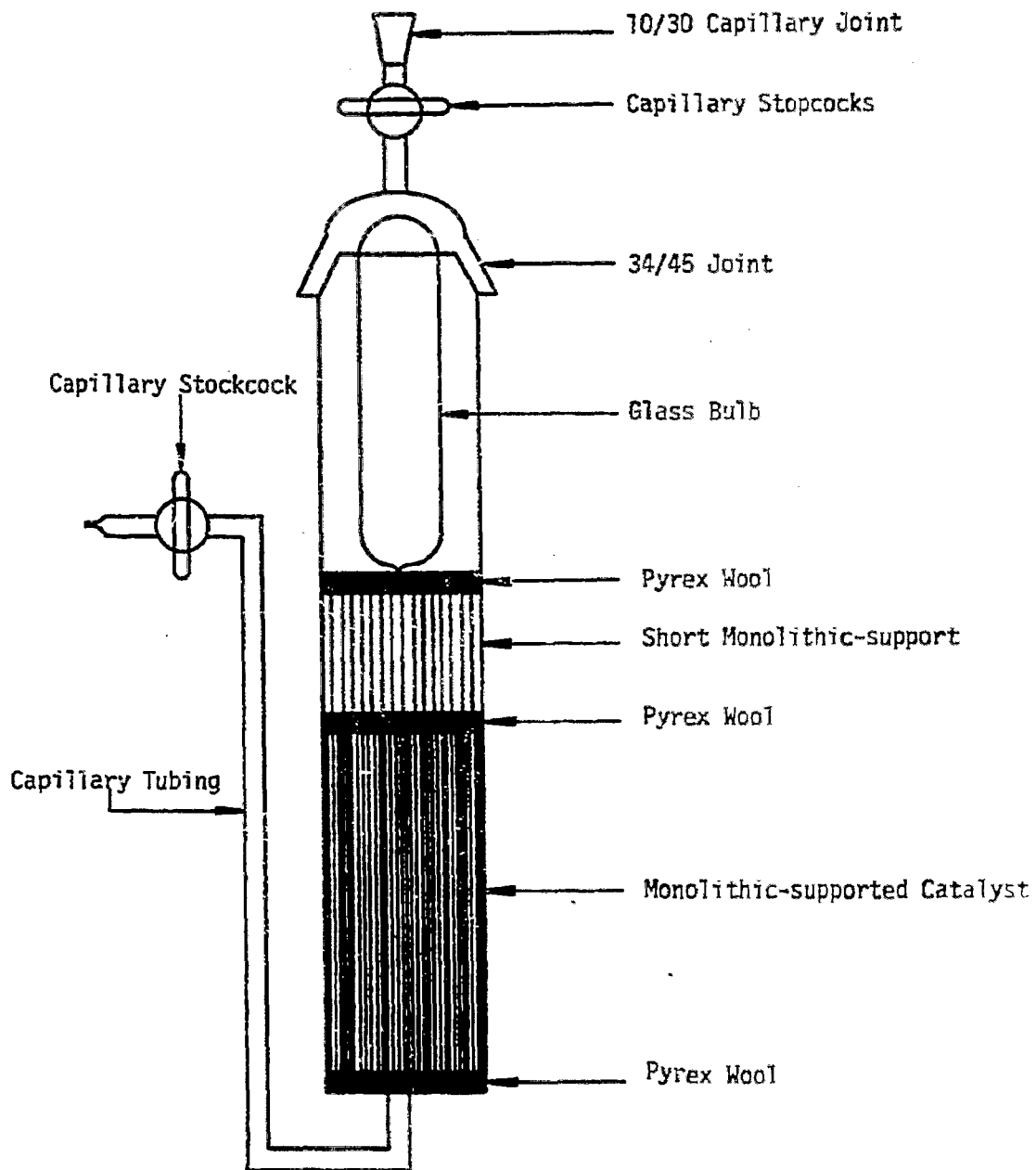


Figure 2. Chemisorption Sample Cell for Monolithic-supported Catalysts.

TABLE 2

Nominal Composition and Hydrogen Chemisorptive Uptake Data for Monolithic-supported Nickel Catalysts

Catalyst	Nominal Composition	Preparation*	H ₂ Uptake ($\mu\text{moles/g-catalyst}$)	% Dispersion	Surface Area ($\text{m}^2/\text{g-cat.}$)
Ni-M-101	15.7 wt% Ni 13.5 wt% Al ₂ O ₃	Nickel - nickel melt (6) Washcoat - Dispal Al ₂ O ₃ slurry (8)	45.2	3.38	3.69
Ni-M-103	13.7 wt% Ni 13.2 wt% Al ₂ O ₃	Nickel - Aqueous nickel soln., ppt. with NH ₃ (11) Washcoat - SA Medium Al ₂ O ₃ slurry (3)	96.5	8.27	7.87
Ni-M-104	15.9 wt% Ni 19.9 wt% NiAl ₂ O ₄	Nickel - nickel melt (3) Washcoat - SA Medium Al ₂ O ₃ slurry plus Ni Nitrate to form NiAl ₂ O ₄ (6)	97.6	7.21	7.96
Ni-M-105	16 wt% Ni 12.6 wt% NiAl ₂ O ₄	Nickel - Aqueous nickel soln. (15) Washcoat - Ni & Al Nitrate slurry to give NiAl ₂ O ₄ (8)	70.2	5.15	5.72
Ni-M-106	18.5 wt% Ni 14.1 wt% Al ₂ O ₃	Nickel - Aqueous nickel soln. (5) Washcoat - SA Medium Al ₂ O ₃ slurry (3)	83.3	5.29	6.79
Ni-A-116	15 wt% Ni	Alumina pellets	187.8	14.7	15.39

* the number of metal applications or support washcoats is given in parentheses

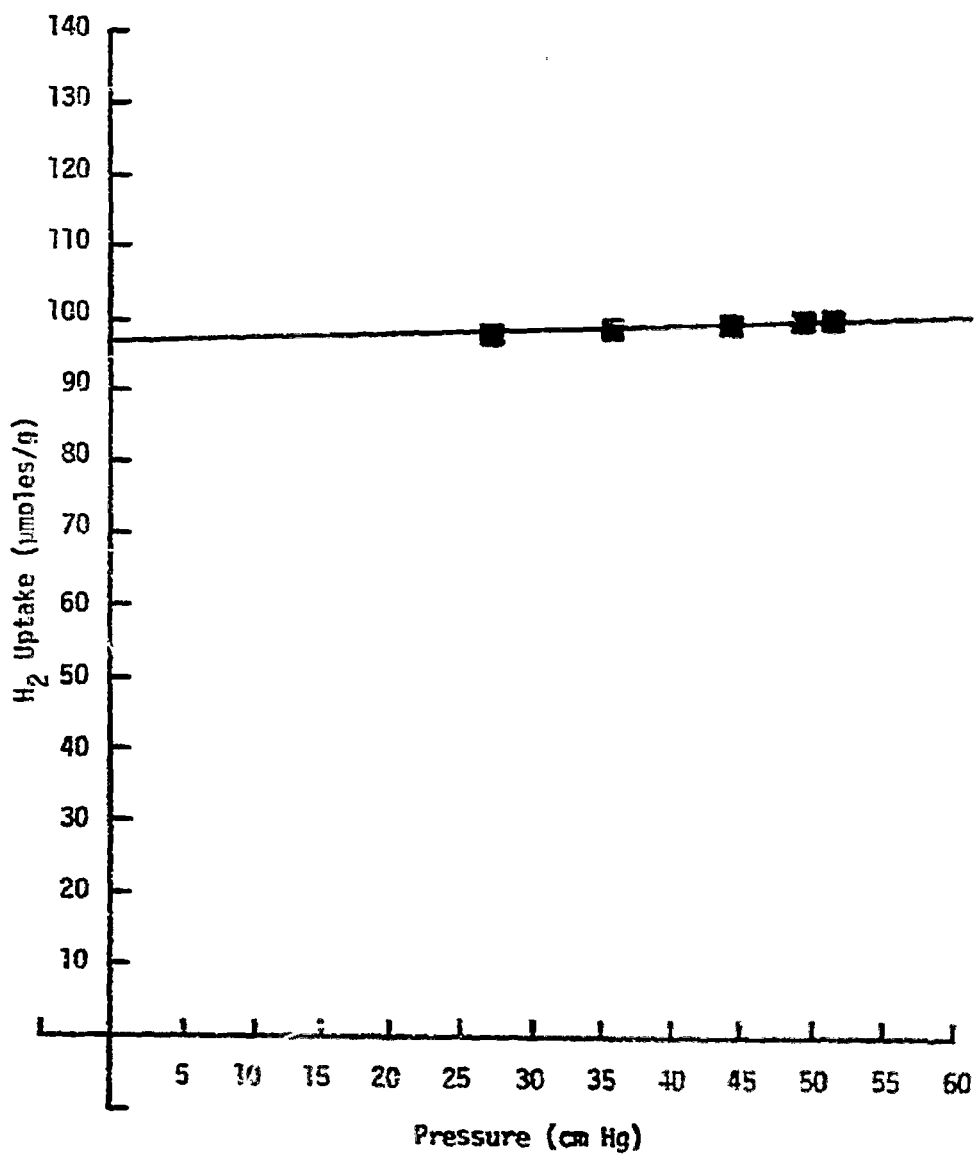


Figure 3. H₂ Chemisorption on Ni-M-103 at 25°C.

A comparison of the hydrogen uptake data for the different monolithic-supported catalysts shows Ni-M-103 and Ni-M-104 to have the highest uptakes, Ni-M-103 has the highest dispersion, while the Ni-M-104 catalyst, by virtue of its higher loading, has the highest surface area. Though these two catalysts are nearly equal in terms of uptake data, the Ni-M-104 catalyst requires far fewer impregnations to reach a reasonable nickel loading. This may be considered a significant advantage, as each impregnation requires several hours of additional preparation time. Ni-M-106 also requires few impregnations and has an uptake nearly as great as that of Ni-M-104. Therefore, the techniques used to prepare Ni-M-104 and Ni-M-106 (or some combination of these techniques) appear to be the most promising methods of monolithic-supported catalyst preparation thus far investigated. Details of these preparations are given in QPR-2 (3).

A comparison of the dispersions of the monolithic-supported catalysts with that of Ni-A-116 shows that the monoliths have roughly one-half the dispersion. This is to be expected as the monolithic catalysts have approximately a 50% loading of nickel on the alumina coating, as compared to 15% for Ni-A-116 (5).

3. Effect of H₂S on hydrogen and carbon monoxide chemisorption on pellet-supported alloy catalysts. Toward the end of the last quarter some of the nickel and nickel alloy catalysts were showing unexpectedly small decreases in H₂ chemisorption after H₂S poisoning. The results for Ni-Pt-A-100 (in Fig. 4), show that a decrease in H₂ uptake of only 3.2% was observed after 6 hours exposure to 10 ppm H₂S; earlier runs on nickel and nickel-iron catalysts showed larger decreases in H₂ uptake of 30-40% after 6 hours exposure to 10 ppm H₂S. The H₂ uptakes for Ni-Co-A-100 discussed in the last report also show less of a decrease in H₂ uptake after poisoning than expected, but this effect may be attributed in part to the higher metal loading on the catalyst compound (20%) to nickel catalysts of 3%. Since Ni-Pt-A-100 was the last catalyst to be tested and showed the lowest percentage decrease in H₂ uptake after 6 hours of H₂S exposure, it was suspected that something might be wrong with either the catalyst poisoning system or poisoning procedure. Because of the high reactivity of H₂S, it was thought that H₂S might react on the storage tank walls and over a period of time the actual concentration in the storage cylinder might be decreased significantly below the value originally certified by Matheson (109 ppm). To test the above hypothesis, an analytical method similar to the one used by Matheson was developed to determine the actual tank concentration.

Fig. 5 shows the experimental apparatus used to determine H₂S concentration. The wet test meter measures the volume of the gas passed from the system during a given amount of time. The procedure consists of bubbling a known volume of the H₂S/H₂ mixture through a fritted bubbler containing 25 ml of 0.1 M I₃ solution and then passing the same gas through a second bubbler containing 10 ml of 0.1 M S₂O₃ solution. The thiosulfate in the second bubbler reacts with any I₂ (g) carried over from the I₃ bubbler, and absorbs any H₂S not picked by the I₃ bubbler. After the known volume of gas has been passed through the bubblers the solutions

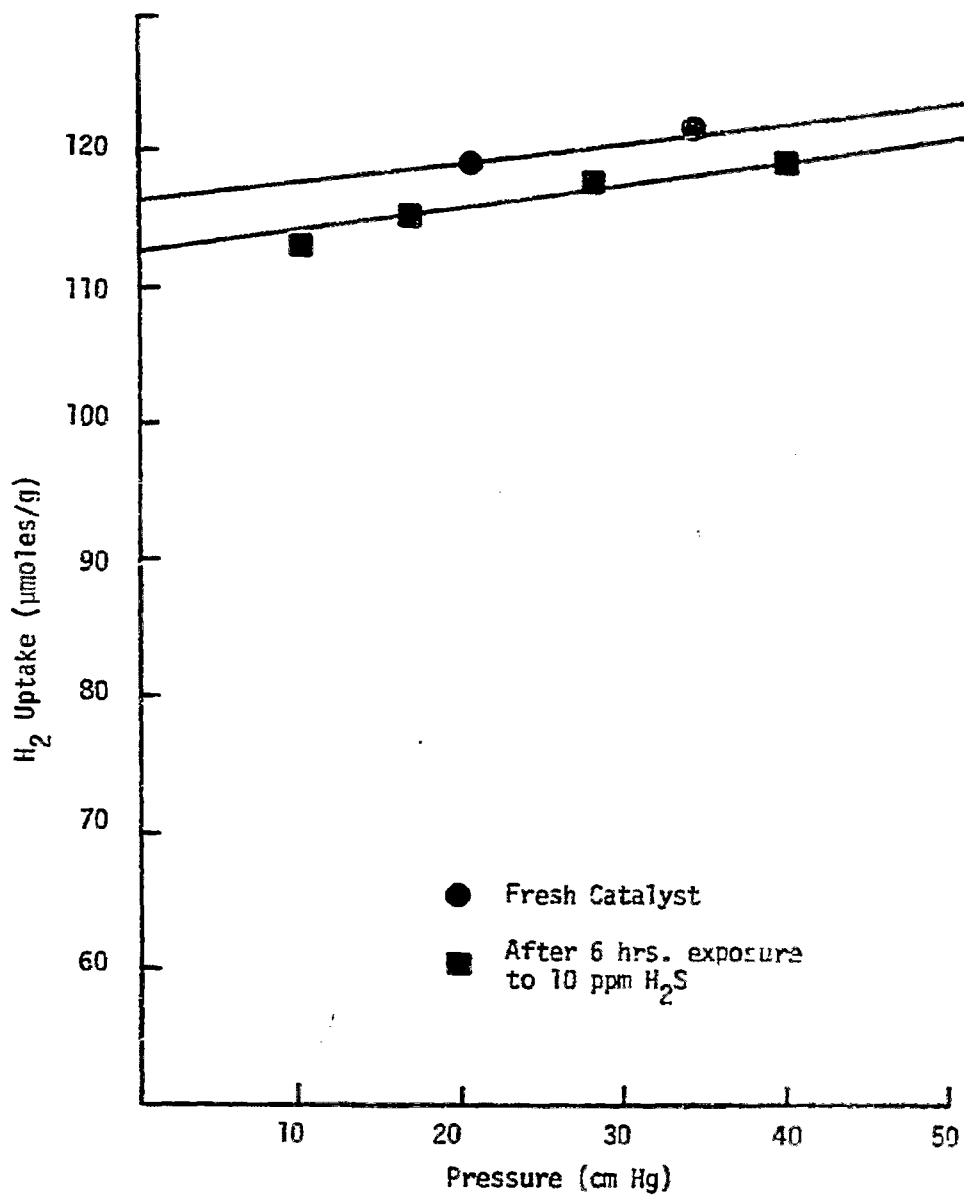


Figure 4. Effect of H₂S on Hydrogen Chemisorption (25°C) for Ni-Pt-A-100.

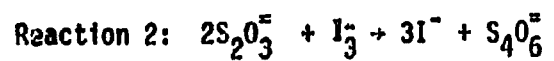
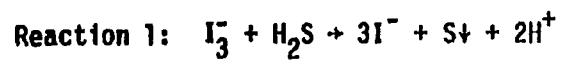
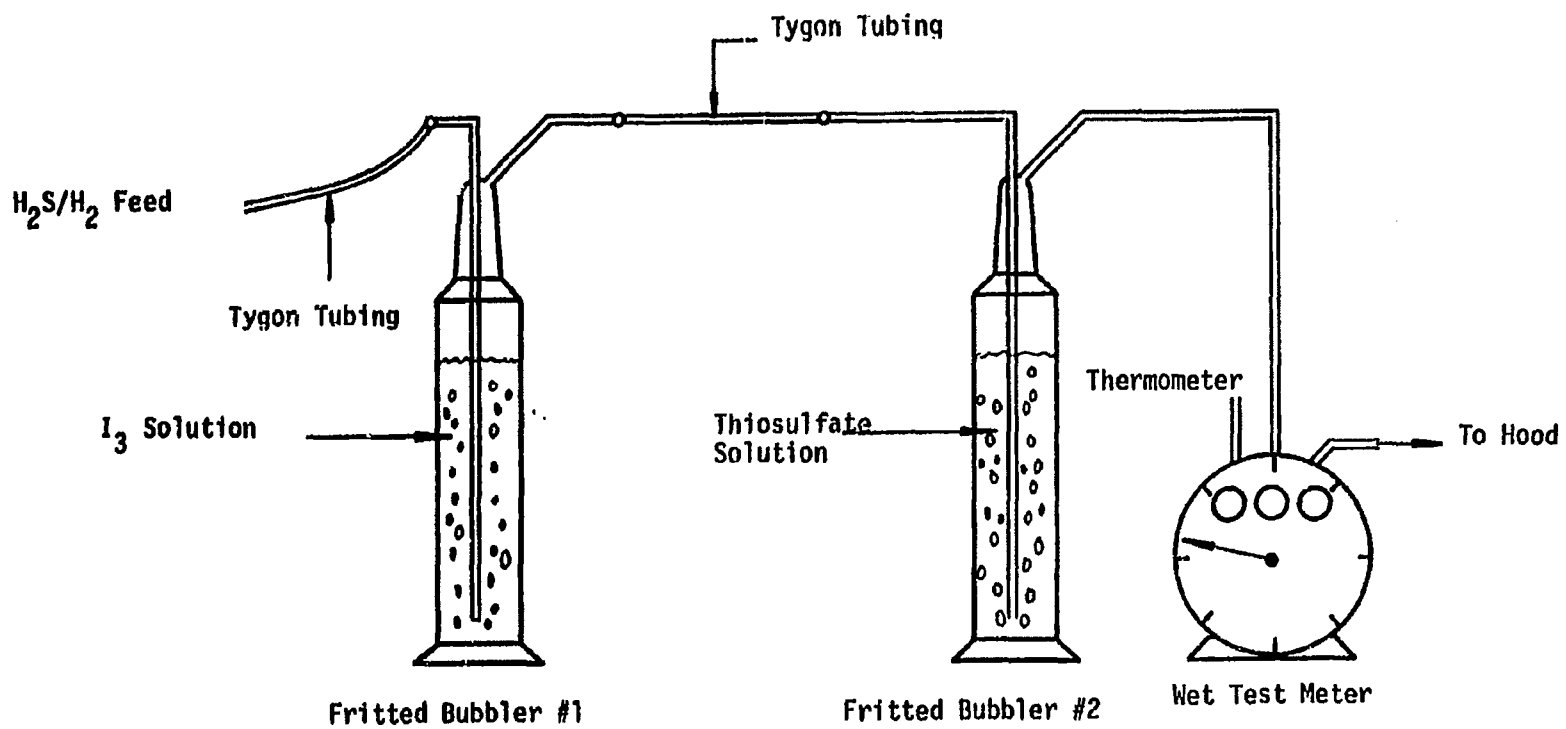


Figure 5. Experimental Apparatus for H₂S/H₂ Analysis.

in the bubblers are mixed together and the remaining I_3^- is titrated with standard thiosulfate to determine the unreacted I_3^- . The standard thiosulfate solution is standardized with NBS quality potassium dichromate. Knowing the amount of I_3^- that reacts with the H_2S , it is then possible to calculate the concentration of H_2S in the standard volume of gas passed through the bubblers.

Two consecutive runs yielded 120.1 and 120.9 ppm for the concentration of H_2S in the tank. In discussing the results with Matheson, it was found that the previous owner of our tank used a more concentrated mixture of H_2S some of which presumably adsorbed on the walls and then later desorbed, after the partial pressure of H_2S was lowered to meet our requirements. This additional information still didn't explain the recently observed and smaller than expected decreases in H_2 adsorption after H_2S poisoning. To determine whether the poisoning system was actually delivering the calculated concentrations of H_2S , another experiment was performed using the same apparatus as described above; however, in this case a calculated mixture of 30 ppm H_2S in H_2 was used, produced by mixing the tank mixture (120 ppm H_2S in H_2) with pure hydrogen. The results from this analytical method showed the concentration to be 32 ppm; hence, it appears the poisoning system does deliver the correct concentration of H_2 based on the bubble flow meter prediction.

To eliminate any other possible mechanical imperfections which might result in analytical errors, several modifications were made in the poisoning system: (1) the line (pressure) regulators were balanced using a differential water manometer, (2) the rotameters for both streams were matched and adjusted to give the same maximum flow readings, and (3) a new high capacity, bubble flow meter was fabricated and installed to give more accurate flow rates.

Even though, the above experimentation did not explain the smaller than expected effects observed in recent poisoning studies, it is felt the poisoning system is not the cause of the anomalies; the modifications and calculations increase our confidence in the apparatus.

The problem was finally resolved when some rough calculations were made which showed that the amount of H_2S passed through the catalyst is small compared to the amount of catalyst present on a molar basis. Hence, space velocity and catalyst loading coupled with dispersion are very important considerations which cannot be ignored in comparing catalyst poisoning rates. The high loadings of Ni-Pt and Ni-Co catalysts also explain why smaller than expected decreases in surface area were observed after H_2S exposure. All subsequent work will be done with a H_2S concentration of 25 ppm, a GHSV of 2000 hr^{-1} , and at a temperature of 450°C (as before). Space velocities will be based on the bulk specific volume of the catalyst as measured with a 1" diameter cylinder filled with 50 ml of catalyst.

The correct space velocity for poisoning is now obtained by first running H_2 through the sample cell until the desired space velocity has been obtained, then channeling the flow through the bubble flow meter and determining the flow rate at the lower pressure drop. After the new flow rate has been obtained, the H_2 flow is cut back and the H_2S flow increased until the same total flow has been obtained and the concentration of H_2S is 25 ppm. The mixture is then channeled back through the sample cell and the flow rate rechecked.

Several runs have been made with the new procedure and modified poisoning system discussed previously. Figures 6 through 8 show the decreases in H_2 adsorption for Ni-Fe-A-100, Ni-Co-A-100, and Ni-Pt-A-100 after 6 hours and 12 hours of exposure to 25 ppm H_2S in H_2 . Table 3 summarizes the hydrogen adsorption data obtained for these catalysts after exposure to 10 and 25 ppm H_2S/H_2 . Measurements of chemisorbed CO after 12 hours exposure to 25 ppm H_2S are almost complete, except for support corrections, so that CO chemisorption results on the above catalysts will be covered in the next report.

It is interesting to note that for Ni-Fe-A-100, the percentage decrease in hydrogen uptake is larger for the catalyst poisoned in 10 ppm H_2S than for the run with 25 ppm; however, in view of the earlier discussion on space velocity and loading effects this result is reasonable because the 25 ppm run started with a catalyst with a considerably higher surface area. Because the space velocity was the same for each run, the amount of H_2S which passed through the catalyst was the same; and since the initial surface area was larger for the 25 ppm run, not as much surface could be poisoned with a given amount of H_2S .

The data for Ni-Pt-A-100 indicate that, for a given initial surface area, a catalyst poisoned with 25 ppm shows a larger decrease in surface area than the same catalyst poisoned with 10 ppm. However, the decrease in surface area is considerably less than corresponding decrease for an equivalent nickel catalyst of the same initial surface area.

The data for Ni-Co-A-100 indicate that this catalyst is also quite resistant to H_2S exposure. Because no experimental upsets were observed during the 25 ppm run, it is difficult to explain why this catalyst would be more resistant to a 25 ppm H_2S stream than a 10 ppm H_2S stream. Unless the reactor data show the same trends for this catalyst, the 25 ppm run will have to be repeated.

4. Discussion of effects of H_2S on carbon monoxide chemisorption.
In the last quarterly report (QPR-2, Ref 4) measurements of carbon monoxide uptakes at $-83^\circ C$ were reported for a number of nickel alloy catalysts before exposure, after 6 hours, and 12 hours exposure with 10 ppm H_2S at $450^\circ C$. Uptakes of carbon monoxide for all catalysts containing nickel and its alloys increased rather than decreased after H_2S poisoning. This surprising result was not discussed or explained in the last report (4). In order to understand this unexpected phenomenon and to evaluate the effect of poisoned alumina support on carbon monoxide uptake, carbon monoxide chemisorption uptakes on the alumina support were also measured

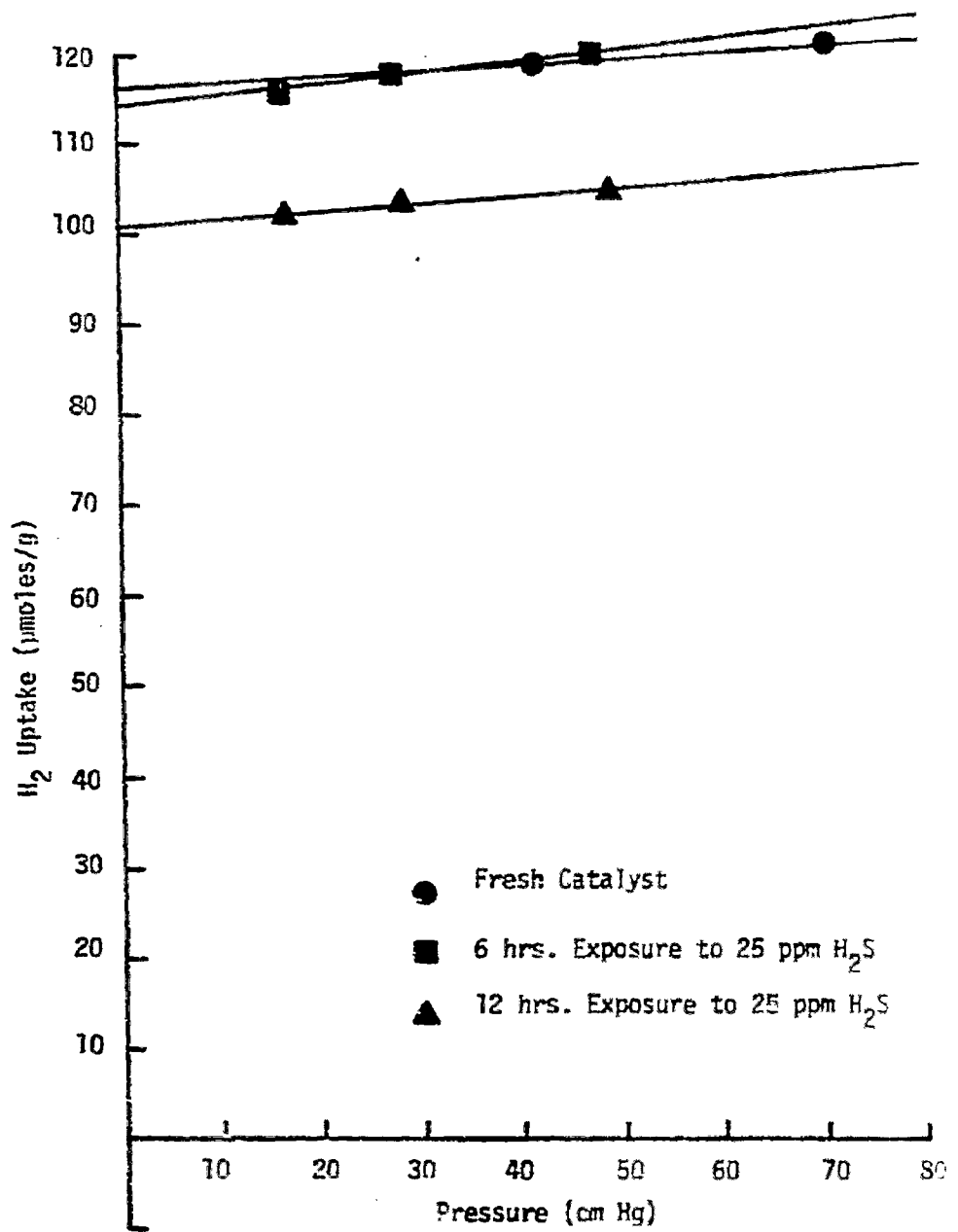


Figure 6. Effect of H₂S on Hydrogen Chemisorption (25°C) for Ni-Co-A₁₀₀.

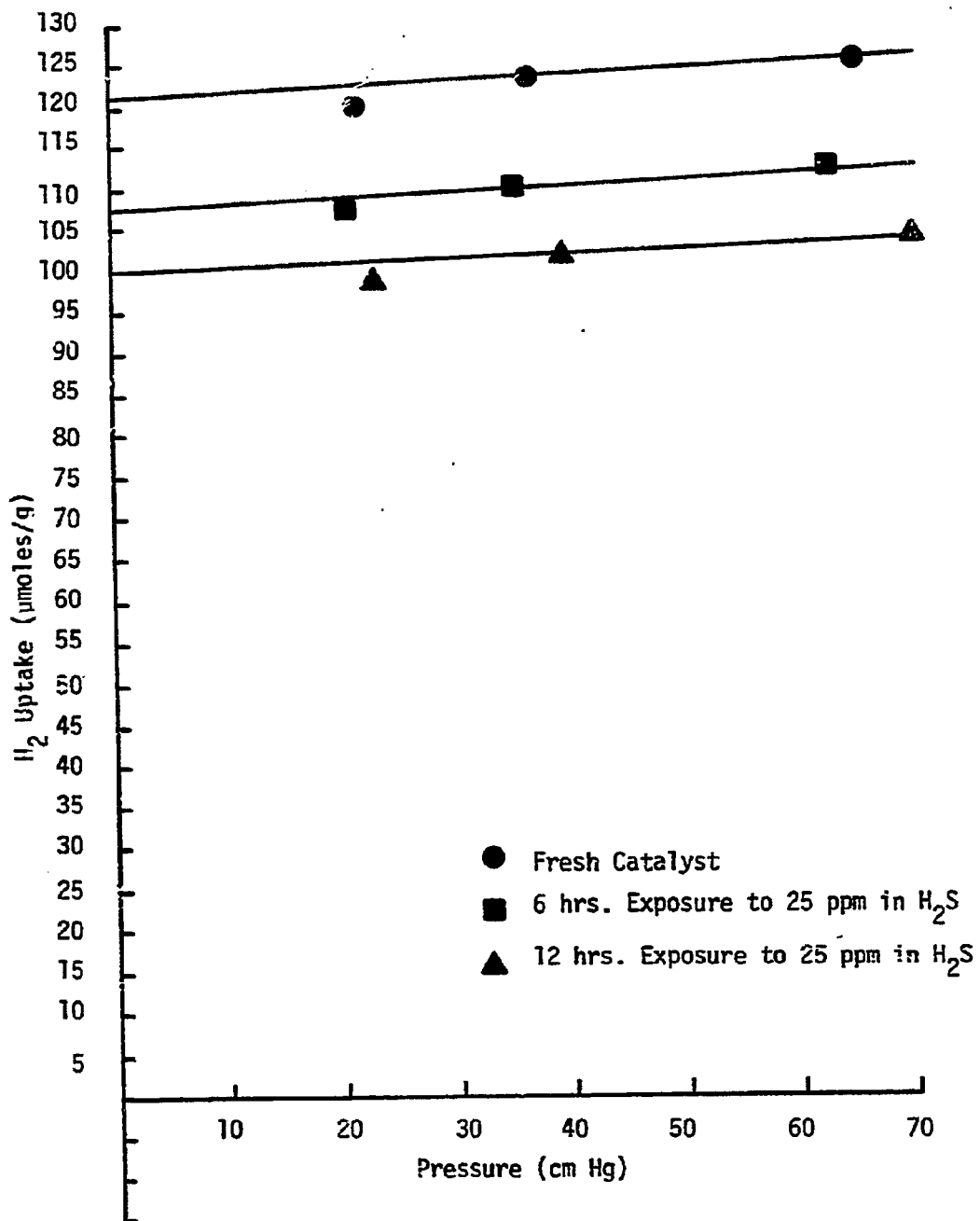


Figure 7. Effect of H₂S on Hydrogen Chemisorption (25°C) for Ni-Pt-A=100.

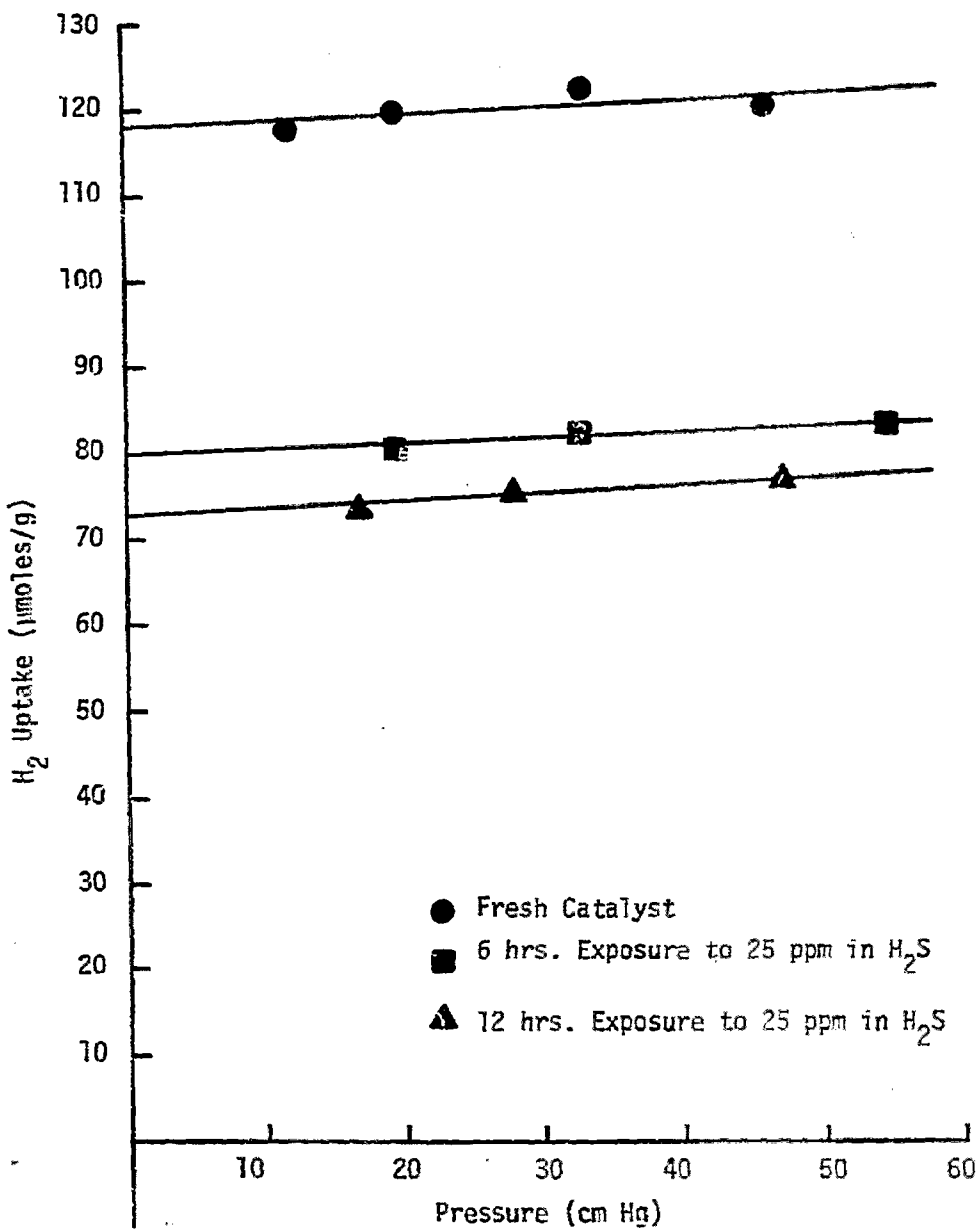


Figure 8. Effect of H₂S on Hydrogen Chemisorption (25°C) for Ni-Fe-A-100.

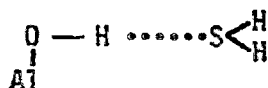
Table 3. Effect of 10 and 25 ppm H₂S on Hydrogen Adsorption

<u>Catalyst</u>	<u>10 ppm H₂S</u>			<u>25 ppm H₂S</u>		
	<u>Initial</u>	<u>6 hrs.</u>	<u>12 hrs.</u>	<u>Initial</u>	<u>6 hrs.</u>	<u>12 hrs.</u>
Ni-Fe-A-100	80.6	49.6(38)*	42.7(8.5)	118	80.0(32)	72.5(6.35)
Ni-Pt-A-100	116.2	112.5(3.2)	---	121.5	107.6(11.4)	100.0(6.2)
Ni-Co-A-100	114.93	109.63(4.6)	102.04(11.2)	116.0	114.6(1.2)	100.5(13.4)

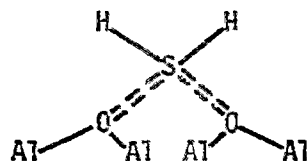
* Percent decreases in adsorption are indicated in parenthesis.

before and after exposure to H₂S under the same conditions as the nickel catalysts. After 6 hours of poisoning with 10 ppm H₂S, carbon monoxide uptake on alumina increased from 26.3 to 31.11 μmoles/g, and after 12 hours uptake increased to 38.9 μmoles/g. This increase in carbon monoxide uptake on alumina after poisoning can be explained by considering H₂S adsorption mechanisms on alumina.

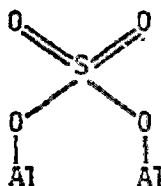
Dalla Lana et al. (7) studied adsorption of H₂S, SO₂ and their mixtures on aluminas and zeolites using infrared spectroscopy. Their proposed surface structure of adsorbed H₂S on γ-alumina is shown below:



However, this structure is inadequate to explain the color change of the catalyst on H₂S adsorption they observed. They also proposed the following surface structure of adsorbed H₂S on NaOH doped γ-alumina which indicates reaction with the oxide ions of the alumina lattice:



Massoth (8) presented the following model for the surface structure of sulfated-alumina:



which is analogous to a molybdena catalyst where S is replaced by Mo. It has been also reported (9) that the effect of sulfate incorporation is to appreciably lower the surface OH concentration and raise the Lewis acid site concentration from that of the pure alumina. Thus, the new Lewis acid sites produced by sulfidation can adsorb an amount of carbon monoxide which depends on their concentration.

In order to correctly determine the amount of carbon monoxide chemisorbed on the metal components of each catalyst, carbon monoxide uptakes after poisoning were corrected by subtracting the corresponding amount adsorbed on the alumina support for the same length of exposure. However, in spite of the support correction carbon monoxide uptakes

increased by the factor of 2-3 after 12 hours of poisoning with 10 ppm H₂S in the following decreasing order: Ni>Ni-MoO₃>Ni-Ru>Ni-Rh (see QPR-2). This is almost the same decreasing order for the loss of surface area measured by hydrogen chemisorption after 12 hours of poisoning with 10 ppm H₂S, except that Ni and Ni-MoO₃ are in reverse order. This suggests a correlation between the decrease in hydrogen uptake after poisoning and the increase in carbon monoxide uptake after poisoning.

Unland (10) observed a decreasing adsorption of carbon monoxide uptake on alumina-supported ruthenium and rhodium poisoned with SO₂. Bayer et al. (11) studied the effect of preadsorbed sulfur compounds at -195°C and 1 atm. on carbon monoxide adsorption on iron catalysts and observed a decrease in adsorption as sulfur content was increased. However, for catalysts promoted with magnesia the uptake decreased slightly with increasing H₂S, then increased, passed through a maximum, and decreased. Several explanations were proposed for this maximum: (1) the penetration of sulfur atoms into the iron crystallites after a certain concentration of sulfur on the surface has been achieved, (2) polysulfide nucleation of iron crystals with migration of sulfur atoms to the nuclei occurring after a critical concentration of sulfur has been achieved, and (3) migration of the alkali promoter or mixtures thereof with alkali sulfides at -195°C uncovering fresh iron surface.

In comparing the results of Bayer et al. (11) with those of this study, it should be emphasized that Bayer et al. exposed their samples to concentrated (1 atm) H₂S at 25°C; such conditions are likely to result in formation of bulk as well as surface sulfides. Since the catalysts in this study were exposed to very dilute H₂S (10 ppm) at 450°C to ensure only formation of surface sulfides, a comparison of results from this study and Bayer et al. may not be meaningful.

In our experiment a reversible color change from black and grey to light blue and grey for poisoned Ni-A-111 and poisoned Ni-MoO₃-A-101 was observed upon admission of carbon monoxide. The original color was recovered upon evacuation of the carbon monoxide. However, the intensity of color change was greater at 25°C than -83°C. No color change was observed for all fresh catalysts and for poisoned ruthenium, poisoned molybdate, and poisoned Kaiser alumina. Thus, this color change was mainly due to interaction between adsorbed sulfur on nickel and carbon monoxide providing evidence that some kind of weakly adsorbed surface complex of carbon monoxide with preadsorbed sulfur is formed on the nickel surface which could possibly migrate to the alumina support. The most likely complex of adsorbed sulfur with carbon monoxide is the well known carbonyl sulfide (COS) or possibly a related complex such as (CO)_xS. An alternative explanation is that the adsorbed sulfur changes the surface structure and promotes carbon monoxide spillover to the alumina support. It is also possible that adsorbed sulfur on nickel acts as an electron donor adsorbing carbon monoxide, but preventing hydrogen adsorption.

5. Chemical analysis, x-ray fluorescence and diffraction experiments.
Two alumina-supported nickel catalysts, Ni-A-113 and Ni-A-114, having nominal compositions of 9 and 15 wt.% respectively, were submitted to

Gulf Research for chemical analysis. The analysis revealed 7.55 and 13.53 wt.% nickel. Thus, these nickel catalysts actually contain 10-15% less nickel than expected by assuming that all of the nickel nitrate originally present in the impregnating solution had been transferred to the alumina pellets. This assumption is clearly approximate since in each preparation a small portion of the nickel nitrate is left on the bottom and walls of the breaker after impregnation and drying; indeed, this small portion might account for the 10-15% nickel lost in the preparation.

X-ray fluorescence measurements were initiated during the past quarter for the purpose of running routine chemical analysis on each of our catalysts. The spectrometer at BYU is capable of analyzing for low as well as high atomic numbered elements. Thus, we can determine the relative percentages of metals and Al_2O_3 support. Several man-days effort was spent in learning the method, sample preparation techniques, and determining a calibration curve for nickel and alumina. The calibration is necessary because of interaction between nickel and alumina fluorescence causing non-linear response of the instrument. A calibration curve for known compositions of nickel and alumina powders is shown in Figure 9. This curve will be used in determining the composition of alumina-supported nickel and nickel alloy catalysts.

X-ray diffraction measurements are needed for (1) estimation of metal crystallite size and (2) determination of metallic phases for selected catalysts. It is especially important to be able to show if our bimetallic catalysts contain alloys rather than separate metals or oxide phases. X-ray camera measurements for a Ni/ Al_2O_3 catalyst were reported in QPR-2 (4). The results showed both Al_2O_3 and nickel metal to be present, but because of diffuse broadlines the photograph was not suitable for estimating particle size. It was hoped that other diffractometers at the University could be used to obtain better resolution.

X-ray diffraction measurements were carried out during the third quarter using a General Electric diffractometer located in Geology and a Phillips diffractometer located in Metallurgy. Both instruments are equipped with goniometers, counting electronics, and chart output. Unfortunately the G.E. instrument is somewhat dated and the detector is simply not sensitive enough for our purposes. In fact, we were unable to separate alumina or nickel peaks from the unstable background. Our experience with the newer Phillips instrument was better. Although the principal (111) peak of nickel was obscured by a broad (400) alumina peak we were able to observe the secondary (200) peak for nickel metal. The background-to-noise ratio was nevertheless poor for the $2^\circ C/min$ scan, but it was apparent from this experiment that we would be able to improve our signal-to-noise ratio by decreasing the scan rate to $0.12^\circ/min$ or by counting over long period of time at fixed angles. In other words, the experiment demonstrated that it is feasible to use the Phillips instrument to determine phase composition and particle size for nickel-alumina catalysts. Unfortunately the Phillips instrument will be dedicated solely for metallurgical work during the next few months. We are presently negotiating with the University of Utah for part-time use of one of their diffractometers.

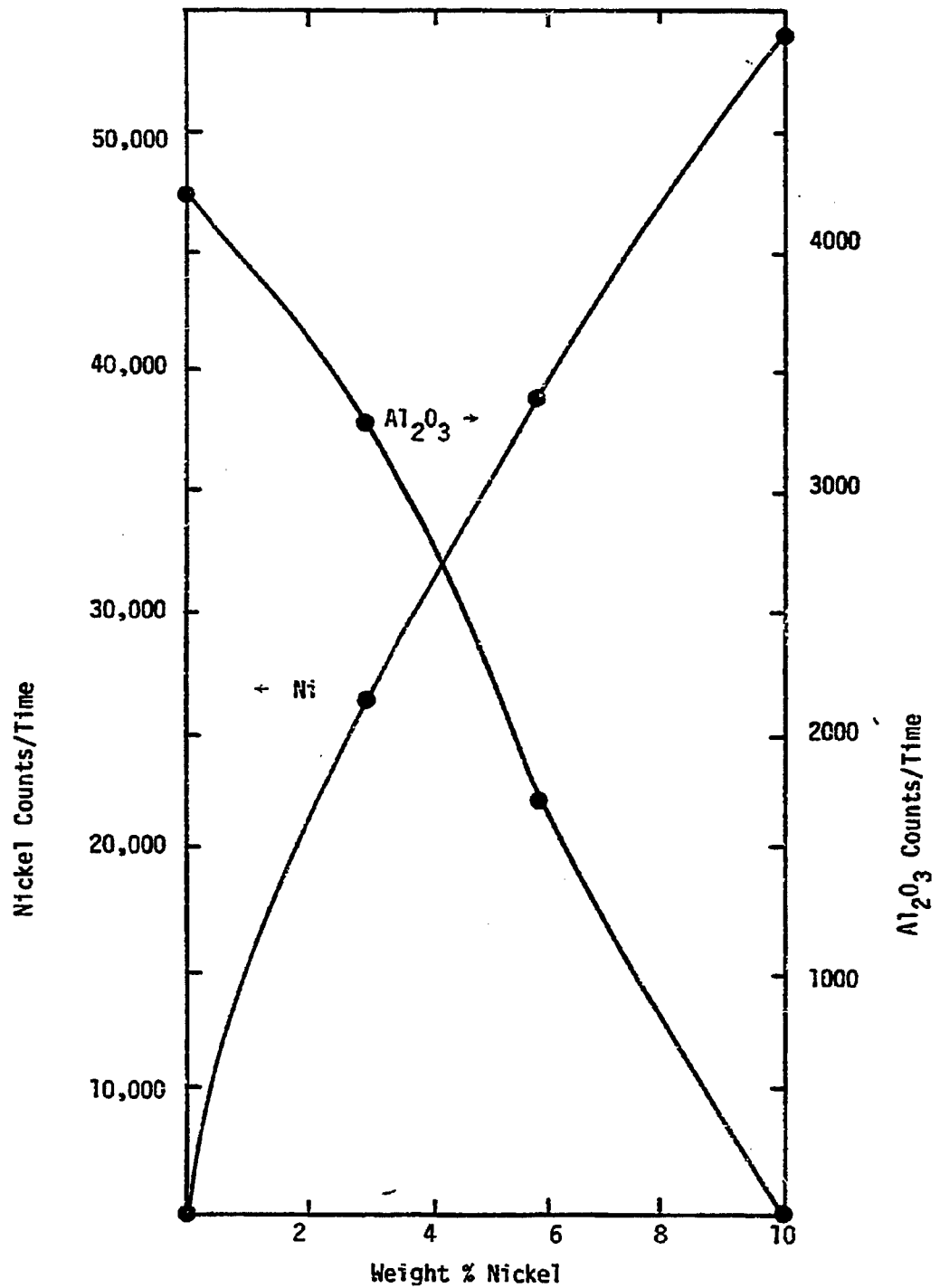


Figure 9. Calibration of Nickel-Alumina System for X-ray Fluorescence Using Pure Alumina and Nickel Powders.

6. Work forecast. Hydrogen chemisorption uptakes will be measured for Ni-Cu, Ru-Pd, Ru-Pt, and Ru-Co catalysts. Measurements of CO chemisorption before and after exposure to 25 ppm H₂S will be completed for Ni-Co, Ni-Fe, and Ni-Pt catalysts. In addition, x-ray diffraction and fluorescence measurements will continue for Ni/Al₂O₃ and two or three nickel alloy catalysts to determine phase and chemical composition as well as metal crystallite size.

8. Task 2: Laboratory Reactor Construction

During the past quarter, all but three of the proposed modifications discussed in QPR-1 and QPR-2 have been completed. The following is a discussion of the status of these modifications and an explanation of one further change to be made during the first month of this quarter.

The Matheson mass flow meters and flow controller which enable flow measurement at high pressures have been installed. Presently the calibration of these instruments is being investigated by examining four parameters: absolute accuracy, reproducibility, pressure effects, and time dependent stability. A temperature controller-programmer constructed by the Chemistry Instrument Shop at BYU for the reactor furnace is operational and is currently being monitored to assure its dependability. Construction of a steam generator is complete but the unit has not been inserted into the reactor system. A column switching apparatus for the gas chromatograph has also arrived and will soon be installed to make possible analysis of H₂S, CO₂ and C₂⁺ hydrocarbons in the product gas stream.

The further modification to be made early in this quarter is to alter the method of sampling the gas streams before and after passing over the catalyst bed in the reactor. Presently a bypass line shown in Figure 19, page 45, QPR-2 is being used to route the gas stream around the reactor to the gas chromatograph for analysis. The difference in pressure drop between the reactor and bypass lines causes flow rate fluctuations of the various reactant gases. Thus, the actual reactant gas stream is not analyzed in the bypass mode, but rather a perturbation thereof.

To rectify this situation small 1/8 or 1/16 in. OD sampling tubes with rotometer controls will be attached just before the entrance and just following the exit of the reactor (Figure). A constant flow of 30-50 ml/min will be maintained in both these tubes during experimental runs. Appropriate valves will allow either of these two bleed streams to be shunted to the gas chromatograph for analysis. Continuous operation and sampling before and after the reactor without perturbation of the system will then be possible.

These modifications are scheduled to be completed within the first month of the fourth quarter. High pressure testing of the system is also scheduled for this next quarter.

C. Task 3: Reactor Screening of Alloy Catalysts

No screening of alloy catalysts been performed during this quarter due to fairly extensive modifications of the reactor system and several

systematic failures of the gas chromatograph. The gas chromatograph has been serviced and the cause of systematic failures, a bad thermocouple, discovered and repaired. It is expected that catalyst screening will be in full progress by the middle of the upcoming quarter. During the next quarter, screening tests for alumina-supported Ru, Ru-Pt, Ru-Pd, Ru-Co, and Ni-Cu will be carried out at 225 and 250°C. Alumina-supported Ni-MoO₃, Ni-Ru, Ni-Rh, Ni-Fe, Ni-Co, Ni-Pt, Ni-Pd, and selected industrial methanation catalysts will be screened after exposure to either 10 ppm or 25 ppm H₂S.

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 were made with technical and sales representatives of Corning Glass Works to send us pure Al₂O₃ monolithic supports of various geometries and these were received approximately 2 months ago. The performance of these pure alumina supports will be compared with that of coated cordierite monoliths in the geometry studies.

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 attended the California Catalysis Society Meeting held November 7-8 in Pasadena where he engaged in fruitful discussions with other investigators in regard to hydrogen and carbon monoxide chemisorption on nickel. The PI also presented a paper "Chemistry of Nickel-Alumina" catalysts at the 68th Annual AIChE meeting in Los Angeles held November 16-22 and attended a short course dealing with "Catalyst Deactivation." The short course was rigorous, informative and very pertinent to our present poisoning work.

Dr. Bartholomew was symposium chairman for the First Rocky Mountain Fuel Symposium held January 30 at Brigham Young University. Approximately 170 professionals and students attended the all-day meeting

which was split into two technical sessions for most of the day. The symposium featured 24 different speakers in discussions of coal gasification, oil shale, and tar sand research and development. Mr. Blaine Barton presented some of our recent kinetic data in a talk entitled "Alloy Catalysts for Methanation of Coal Synthesis Gas." Our luncheon speaker, Senator Frank Moss of Utah, discussed the political aspects of fuel development in the West. Feedback in regard to the symposium has been quite favorable and the prospects are very good for a 2nd Rocky Mountain Fuel Symposium next year.

F. New Publications and Personnel

Mr. Kyung Sup Chung completed work on his master's thesis entitled, "The Effects of H₂S Poisoning on Hydrogen and Carbon Monoxide Chemisorption on Nickel and Nickel Alloys." Mr. Chung has already begun work at the University of Utah (Department of Mining, Metallurgical, and Fuels Engineering) toward a PhD and will take his master's oral examination on February 19. Mr. Richard Fowler, a junior in Chemical Engineering joined our research group in January and will participate in this ERDA study.

IV. CONCLUSIONS

- A. Measurement of hydrogen adsorption on monolithic-supported Ni/Al₂O₃ shows that catalysts prepared by impregnation from the nickel nitrate melt or aqueous nickel nitrate on SA Medium Alumina or Ni/Al₂O₄ supports have the highest dispersions and surface areas. Monolithic catalysts have roughly half the nickel metal dispersion as do pellet catalyst. This is to be expected since the monolithic catalysts have a much higher loading of nickel on alumina (5).
- B. The effects of H₂S poisoning on a catalyst depend upon catalyst loading, H₂S/H₂ space velocity and concentration and temperature of exposure. If poisoning effects are to be compared between catalysts, these parameters must be fixed.
- C. In comparing the effects of H₂S poisoning on hydrogen chemisorption for alumina supported alloys of nickel with iron, cobalt, and platinum, the order of magnitude of decrease in H₂ adsorption is Ni-Fe>Ni-Pt>Ni-Co-- in other words, Ni-Pt and Ni-Co are more resistant to H₂S poisoning than Ni-Fe (and Ni).
- D. The increase in carbon monoxide adsorption after exposure to H₂S may be explained by the formation of a COS or (CO)_xS complex which after formation migrates to the support.
- E. Ni/Al₂O₃ catalysts contain 10-15% less actual nickel (by chemical analysis) than expected if none were lost in the impregnation step.
- F. X-ray diffraction measurements to determine phase composition and crystallite sizes of alumina-supported nickel and nickel alloys are feasible, if a sensitive instrument is available and if the signal-to-noise ratio is increased by running at very slow rate, or by counting at fixed angles.

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APPENDICES

- A. REPORT DISTRIBUTION LIST
- B. BIBLIOGRAPHIC DATA SHEET

BIBLIOGRAPHIC DATA SHEET		1. Report No. OPR No. 3	2.	3. Recipient's Accession No.
4. Title and Subtitle ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES				5. Report Date January 1976
7. Author(s) Calvin H. Bartholomew				6.
9. Performing Organization Name and Address Catalysis Laboratory Chemical Engineering Science Brigham Young University Provo, Utah 84602				8. Performing Organization Rept. No.
12. Sponsoring Organization Name and Address Energy Research and Development Administration Fossil Energy 20th Mass. Ave., N.W. Washington, D.C. 20545				10. Project/Task/Work Unit No.
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15. Supplementary Notes				13. Type of Report & Period Covered 23 Oct. 1975-22 Jan. 1976
16. Abstracts <p>This report presents work accomplished during the third quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Hydrogen and carbon monoxide adsorption data for alumina-supported alloys of nickel with iron, cobalt, and platinum were obtained before and after samples had been exposed to 25 ppm H₂S. Hydrogen adsorption uptakes were measured for several monolithic supported Ni/Al₂O₃ catalysts. In addition, chemical and x-ray measurements were continued. Reconstruction of a laboratory reactor to enable high pressure operation was ninety percent completed. The principal investigator attended three meetings, a short course, presented one paper, and chaired a symposium on fuels, at which Mr. Blaine Barton also presented a paper.</p>				14.
17. Key Words and Document Analysis. 17a. Descriptors Coal Gasification Methanation Catalyst(s)				
17b. Identifiers/Open-Ended Terms				
17c. COSATI Field/Group				
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