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

Phase 2

Quarterly Technical Progress Report
For Period Jan. 23, 1977 to April 22,

Calvin H. Bartholomew

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PREPARED FOR THE
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Brigham Young University
Provo, Utah 84602

FOREWORD

This report summarizes technical progress during the eighth quarter period (January 23, 1977 to April 22, 1977) of a two-year study conducted for the Energy Research and Development Administration (ERDA) under Contract No. E(49-18)-1790 (new contract number EX-76-S-01-1790). This contract has been extended an additional 4 months pending review of the renewal proposal; hence the final report will be prepared at the end of August, 1977. 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 - George Jarvi, Gordon Weatherbee and Erek Erekson and Undergraduates - Kevin Mayo, Kenneth Atwood, and Glen Witt. Elaine Alger and Scott Folster provided typing and drafting services.

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ABSTRACT

This report details accomplishments during the eighth quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Monolithic-supported Ni, Ni-Co and Ni-MoO_3 catalysts were prepared. Hydrogen adsorption uptakes were measured for several pelleted and monolithic nickel and nickel alloy catalysts. Differential activity tests were conducted at 225 and 250°C, 20.5 psia, and 30,000 hr^{-1} for four commercial nickel and molybdenum containing catalysts. Conversion-temperature measurements were performed for pelleted Ni-Pt, Ni-Rh, Ni-Ru, and Co catalysts at high pressure (365 psia) and for several monolithic nickel catalysts at low pressure (20 psia). Steady state carbon deposition tests were performed for 3% Ni/Al_2O_3 and 14% Ni/Al_2O_3. The principal investigator attended the Rocky Mountain Fuel Symposium (with 6 students), the Spring Meeting of the California Catalysis Society, the North American Catalysis Society Meeting and the ASTM Catalyst Meeting, visited the University of Wisconsin and the Ventron Corporation and presented three seminars related to methanation research.

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 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: (i) sulfur poisoning, (ii) carbon deposition with associated plugging, and (iii) 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 (i) to study nickel and ruthenium alloy catalysts in the search for catalysts resistant to poisoning and carbon deposition and (ii) to investigate the effects on catalytic efficiency of support (monolith and pellet) geometry. The work has been divided into five tasks to be completed over a period of two years:

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

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

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

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

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

C. Technical Approach

The technical approach which will be used to accomplish the tasks outlined above is presented in the revised proposal dated May 17, 1974. The main features of that approach are reviewed here along with more specific details and modifications which have evolved as a result of progress. It is expected that various other aspects of this approach will be modified and improved as the project develops and as new data are made available. Nevertheless, the objectives, tasks and principle features of the approach will remain the substantially the same.

Task 1: Catalyst preparation and characterization. Alumina pellets and extruded monolithic ceramic supports (provided by Corning Glass Works) coated with high surface area alumina will be impregnated with nickel nitrate and an alloying metal salt. Metals which will be alloyed with nickel include cobalt, iron, molybdenum, rhodium, ruthenium, platinum, and palladium. Ruthenium will be used in combination with nickel, cobalt and palladium. Approximately equimolar quantities of base metals will be used in combination with nickel or other base metals; relatively small amounts of noble metal will be used in combination with 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 in 1974 as part of a previous methanation study supported by Corning Glass Works and Brigham Young University. The combination was found to be unworkable--unsatisfactory for pulse operation because of pulse broadening in the reactor and for continuous-flow operation due to high flow resistance in the small diameter tubing and sample valves. The reactor system was later modified for continuous-flow operation and collection of steady-state activity data, which were found to be more useful, realistic indicators of catalyst performance than the unsteady-state pulse measurements. Our continuous-flow reactor system was modified in 1976 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 4.0. Samples to be screened will include freshly-reduced catalysts and catalyst samples exposed in a separate poisoning system to 10 ppm H_2S over a period of 6-18 hours.

Task 4: Catalyst geometry testing and design. The most promising catalysts based on the results of screening will be tested for activity and conversion as a function of pressure, temperature, H_2/CO ratio, and H_2S concentration. The conversion of carbon monoxide to methane as a function of temperature will be determined for various pellet and monolith geometries at both high and low pressures. The effects or water addition to the feed stream will also be investigated. Conversion of carbon monoxide to methane during in situ exposure to low levels of hydrogen sulfide and at low H_2/CO ratios will be used as a measure of stability toward sulfur poisoning and carbon deposition. A comparison of steady-state conversions at given temperature and pressure conditions for monolithic supports of different hole sizes and geometries will be used to optimize the geometry of the catalyst support. This task is not scheduled for completion until the end of 1977 (as outlined in the proposal).

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

II. SUMMARY OF PROGRESS

A project progress summary is presented in Figure 1 and accomplishments during the past quarter are summarized below. Figure 1 shows that task accomplishments are either on or ahead of schedule. Particularly Task 4, Catalyst Testing and Design, is well ahead of schedule. Tasks 2 and 3 have been essentially completed.

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

Task 1. Twenty-three Ni/Al_2O_3/monolith catalysts, six $Ni\text{-}Co/Al_2O_3$/monolith catalysts and six $NiMoO_3/Al_2O_3$/Monolith catalysts were prepared. Hydrogen uptakes were measured for ten pelleted nickel and nickel alloy catalysts and for eight monolith supported Ni and Ni-Co catalysts. The literature dealing with phase and surface compositions of alloys was reviewed, and calculations were made to estimate the phase uniformity and surface composition of supported nickel alloys of interest in this investigation (see Appendix A).

Task 2. Task was completed during the fourth quarter.

Task 3. Measurements of methanation activity at 225 and 250°C, 20.5 psia, and 30,000 hr^{-1} were carried out for four commercial nickel and molybdenum containing catalysts obtained from the Climax Molybdenum Co.

Task 4. Conversion-temperature measurements at a space velocity of 30,000 hr^{-1} were performed for alumina pellet-supported Ni-Pt, Ni-Rh, Ni-Ru and Co at high pressure (365 psia) and for four monolithic-supported (300 squares/square inch) Ni/Al_2O_3 catalysts at low pressure (20 psia). Several long term steady state carbon deposition tests at 400 or 450°C were carried out for samples of 3% Ni/Al_2O_3 and 14% Ni/Al_2O_3.

Task 5. The principal investigator attended the Second Rocky Mountain Fuel Symposium held February 17-18 in Salt Lake City (accompanied by 6 students), the Spring Meeting of the California Catalysis Society on March 31 and April 1 in Menlo Park, California, the North American Catalysis Society Meeting held April 26-28 in Pittsburgh (accompanied by Mr. Richard Pannell), and the ASTM D-32 Catalyst Committee Meeting held April 28-29 in Pittsburgh. He visited by invitation the Department of Chemical Engineering at the University of Wisconsin (Madison) and Ventron Corporation in Boston where he presented research seminars. In addition, the principal investigator and students made 4 technical presentations at the above mentioned meetings.

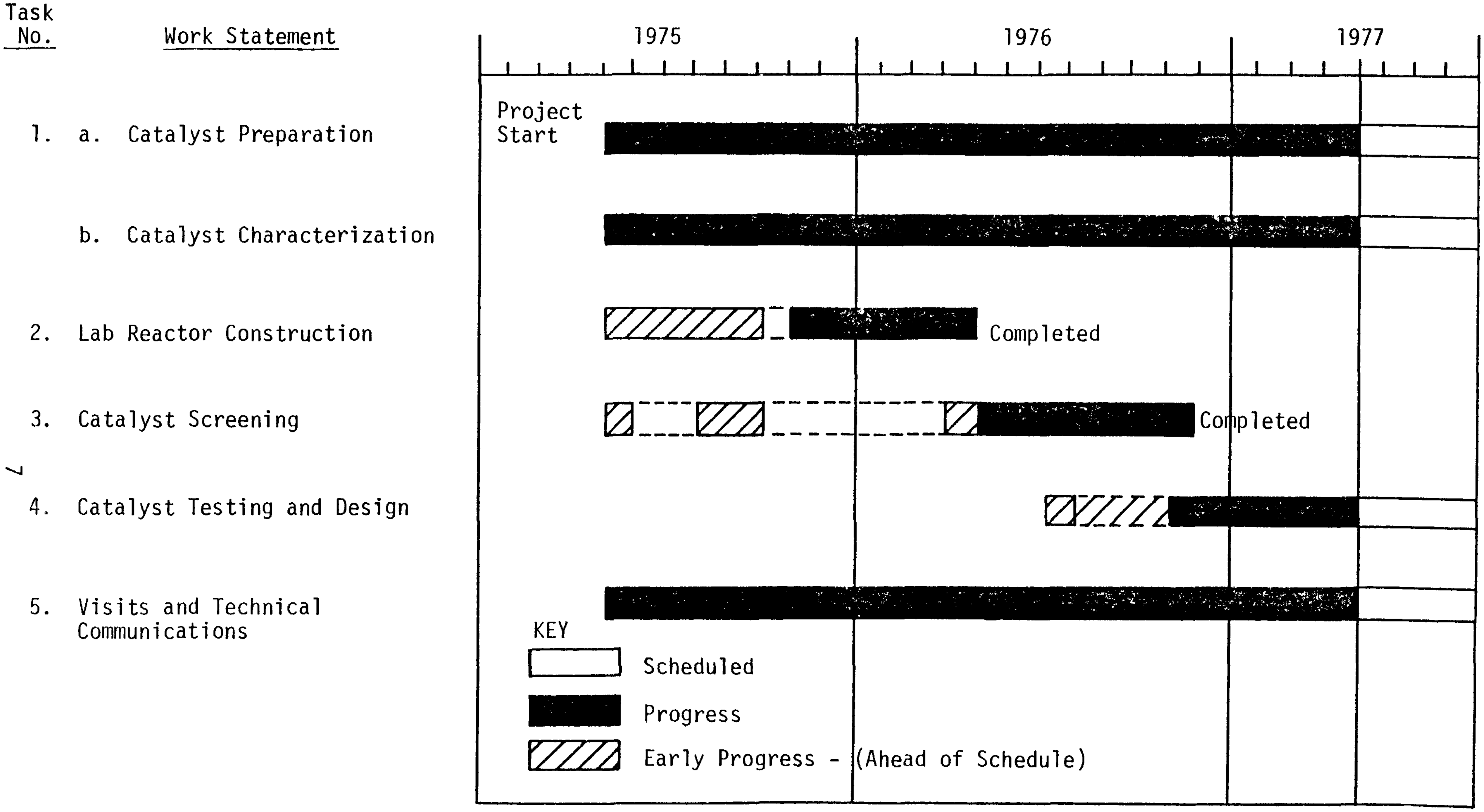

Figure 1. Project Progress Summary.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation: Four Ni/Al_2O_3 catalysts were prepared using 200 squares per square inch monolithic supports; metal loadings ranged from 5.9% to 11.2%. Nine Ni/Al_2O_3 catalysts were prepared using 300 squares per square inch monolithic supports. Six of these were found to contain 20% nickel metal after reduction. Ten Ni/Al_2O_3 catalysts were prepared using 236 triangles per square inch monoliths. Six of these were found to contain about 6% nickel metal after reduction. After the fifth dip into the nickel nitrate impregnation bath, these monoliths began to lose more alumina substrate than gain nickel nitrate. Whenever a monolith does not gain more weight following impregnation, we assume that the alumina cannot sustain any more dipping, and the impregnation is halted.

Six nickel cobalt alloy catalysts were prepared using 200 squares per square inch monoliths. The total metal loading after reduction varied from 9% to 13% of a 50-50 blend of nickel and cobalt. Again, problems in impregnation may account for the variations. The reduction step was carefully controlled to avoid temperature excursions experienced in the earlier preparation (3) of nickel-cobalt monoliths.

An attempt was made to impregnate six monoliths with a nickel and ammonium molybdate solution. The large volume of ammonia necessary to co-dissolve these substances prevents obtaining high loading even after four or five dips because the nickel nitrate is so dilute. Other preparation techniques are presently under investigation; for example, mixing the alumina with the nickel molybdate before coating on the monolith may give better results.

2. Characterization: Hydrogen chemisorption uptakes, measured for 19 different alumina supported catalysts, are reported in Table 1. Ten of the catalysts were pellet-types, eight were monoliths and one was a powdered sample.

Uptakes were measured on catalyst Ni-A-112 to study the effects of carbon deposition on the catalyst performance and surface area. The deposited carbon reduced the effective surface area by about 16%. After the carbon was removed through oxidation, the surface area was found to be about the same as the original value.

In the preceding quarter it was observed that steam in the reactant stream had a detrimental effect on catalyst surface area. Work done this quarter indicates that high pressure reactor testing also results in a decrease in surface area, to a greater extent, in fact, than does reactant steam

TABLE 1

Hydrogen Chemisorptive Uptake Data for Alumina Supported Pellet, Monolith and Powdered Catalysts

		H_2 Uptakes (μmoles/gram)	
Catalyst	Nominal Composition	Bulk Reduced Only	Reactor Tested
Pellets:			
Ni-MoO_3-A-101	2.5% Ni, 3% MoO_3	18.6[a]	14.2[b], 14.1[c]
Ni-Rh-A-100	2.5% Ni, 0.5% Rh	39.0[a,*]	34.3[b], 32.8[c]
Ni-Rh-A-101	16.6% Ni, 3.4% Rh	133.6	104.3[c]
Ni-Pt-A-100	15% Ni, 0.5% Pt	129.6	195.7[d,b],120.3[c]
Ni-Ru-A-105	2.5% Ni, 0.5% Ru	53.4[a]	43.5[b], 33.6[c]
Ni-Ru-A-106	16.6% Ni, 3.4% Ru		116.3[c]
Ni-Co-A-100	10% Ni, 10% Co		121.9[c], 102.5[c]
Co-A-100	20% Co		39.9[c]
Ni-A-116	14% Ni		158.6[e]
Ni-A-112	3% Ni	40.0[a], 34.9[d]	33.5[f], 42.8[g]
Monoliths:			
Ni-Co-M-101	4% Ni, 4% Co		30.3[e]
Ni-Co-M-102	5% Ni, 5% Co	34.7	
Ni-M-303	20% Ni		95.9[e], 102.8[e,h]
Ni-M-304	20% Ni		116.8[e]
Ni-M-305	20% Ni		113.6[e]
Ni-M-306	18% Ni		117.0[e]
Ni-M-307	19% Ni		103.7[e]
Ni-M-308	20% Ni		159.5[e]
Powdered:			
Ni-MoO_4-Al_2O_3	commercial- Climax Molybdenum Co.		31.2[e]

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[a] Data obtained in a previous quarter

[b] Steam in reactant stream

[c] High pressure reactor tested

[d] Sample not from same batch as others listed

[e] Regular differential or integral run

[f] Long term carbon deposition run

[g] Uptake after carbon had been removed via oxidation

[h] Sample was reduced several times before reactor testing

[*] This value was incorrectly reported as 30.0 in the last quarterly report.

as evidenced by surface areas for Ni-Ru-A-105 and Ni-Rh-A-100.

Work done this quarter to investigate the stoichiometry of hydrogen chemisorption on unsupported cobalt metal using a commercially prepared powder revealed that the powder was too coarse to provide accurately measureable H_2 uptakes. In order to obtain a more finely divided powder, a small sample of cobaltous hydroxide was precipitated from a cobaltous nitrate solution and reduced to the metal. Two preliminary measurements made on the precipitated sample are indicative of unexpectedly high surface area. In fact, the average uptake was 154 micromoles/gram, indicating crystallite diameters on the order of 50-70 nm. After further surface area measurements, i.e., BET and H_2 chemisorption, a larger sample will be prepared and studied.

3. Forecast. During the next quarter we will begin using x-ray diffraction, Electron microscopy, and ESCA (electron spectroscopy for chemical analysis) as well as chemisorption to better characterize our catalyst samples. We intend to discover more about bulk and surface compositions of the metal phases of our samples and to find if we have alloy formation in our bimetallic samples. Preparation of alloy monoliths will proceed with increased care to assure better reproducibility in metal and Al_2O_3 support loadings, reduction schedule, and surface area.

B. Task 2: Laboratory Reactor Construction.

No accomplishments. This task was completed during the fourth quarter.

C. Task 3: Reactor Screening of Alloy Catalysts.

During this quarter we tested the methanation activity of four commercially prepared cobalt and molybdenum containing catalyst samples some of which were obtained from the Climax Molybdenum Co. Three of the samples, $FeMoO_4$, Ni-W on Al_2O_3-SiO_2, and Co-Mo on Al_2O_3 showed no measureable activity in differential tests (225 and 250°C). However, a $NiMoO_4$ on Al_2O_3 made by Climax Molybdenum Corporation showed reasonably good activity for methanation. The results from the differential test at 250°C are shown in Table 2. In comparison to our Ni-MoO_3-A-102 sample reported in QPR-6 (November 6, 1976) the commercial $NiMoO_4$ catalysts has significantly lower turnover numbers and overall rates. The differences in activity may be due to differences in preparation of the catalyst samples. The commercial catalyst was made from a solution of ammonium heptamolybdate, water, hydrogen peroxide, nitric acid and nickel nitrate,while our Ni-MoO_3-A-102 catalyst was made from a solution of ammonium heptamolybdate, water, ammonium hydroxide,

TABLE 2

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

Sample	% CO Conversion	% Production CH_4	% Production CO_2	% Selectivity CH_4	% Selectivity CO_2	Rate x 10^7 (Moles/gcat sec) CO	Rate x 10^7 (Moles/gcat sec) CH_4	Turnover No. x 10^3 N_{CO}	Turnover No. x 10^3 N_{CH_4}
$NiMoO_4$ on Al_2O_3-SiO_2 ∿8.1% Ni ∿14.6% Mo	4.77	3.77	1.03	79.0	21.6	1.399	1.105	2.24	1.77
Ni-MoO_3-A-102 ∿10% Ni ∿10% Mo	34.38	27.69	3.01	80.4	8.8	21.3	17.1	7.8	6.3

and nickel nitrate. Also, after drying overnight the commercial sample was calcined at 500°C for two hours. Our catalyst was reduced directly in hydrogen after drying at 80-100°C.

During the next quarter we will continue testing other commercial cobalt and molybdenum catalysts for comparison with our catalysts.

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

1. Accomplishments - Pellet-Supported Catalysts.

a. High Pressure Integral Runs. High pressure conversion versus temperature work was completed for pellet supported 16% Ni-Pt, 20% Ni-Ru, 20% Ni-Rh, and 20% Co catalysts. In every case the maximum conversion of CO is 99% or greater over a wide range of temperature. Therefore, comparisons are made at 50% and 90% CO conversion. Conversion vs. temperature plots for these catalysts are shown in Figures 2-5 and conversion data are summarized in Table 3.

The Ni-Ru and Ni-Rh have lower activity at low temperature than the other catalysts tested. The Ni-Pt and Co have conversion-temperature characteristics similar to the 14% Ni and 20% Ni-Co catalysts tested previously. Co, however, is a factor of two more active on a turnover number (active site) basis. The 20% Ni-MoO_3 was sintered during reduction and will be re-run this coming quarter. With its completion the high pressure tests on the pellet supported catalysts will be finished.

b. Steady State Carbon Deposition Tests. Progress in this area has been slower than expected due to the large number of problems encountered. The steady state runs are conducted at approximately 400°C since rates of carbon depsoition are not significant below 350-400°C (4). Differential tests at 250°C are made before and after each steady state run to determine the degree of deactivation of the catalysts. Because of the high concentration of H_2, and its nonlinear response in a He carrier gas to thermal conductivity, the absolute composition of the reaction mixture cannot be analyzed accurately. Nevertheless the measurements of CO and CH_4 are quite accurate, thus enabling good comparisons of catalytic activity.

To date, two catalysts have been tested, Ni-A-112 (3% Ni/Al_2O_3) and Ni-A-116 (14% Ni/Al_2O_3). The results are summarized in Table 4 and discussed below.

Ni-A-112 LT #1 and LT #2

Steady state Run #1 was made on a pellet sample at a gas hourly space velocity (GHSV) of 15,000 hr^{-1} with a H_2 to CO ratio of 3.0 and 50% N_2 diluent. A 28% decrease in

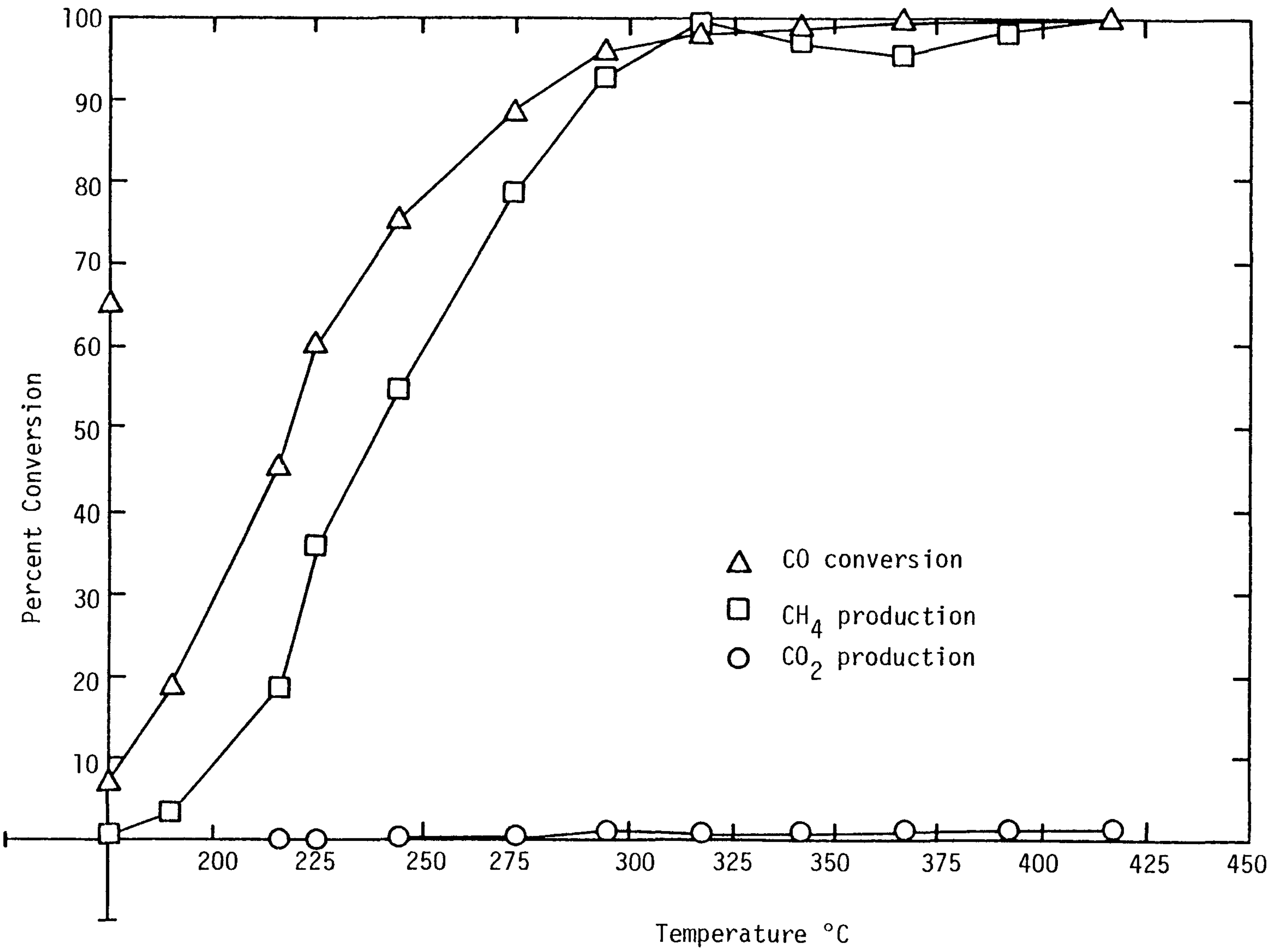

Figure 2. Conversion versus temperature Ni-Pt-A-100 (15.7% Ni, 0.5% Pt/Al_2O_3) (365 psia; GHSV = 30,000 hr^{-1}).

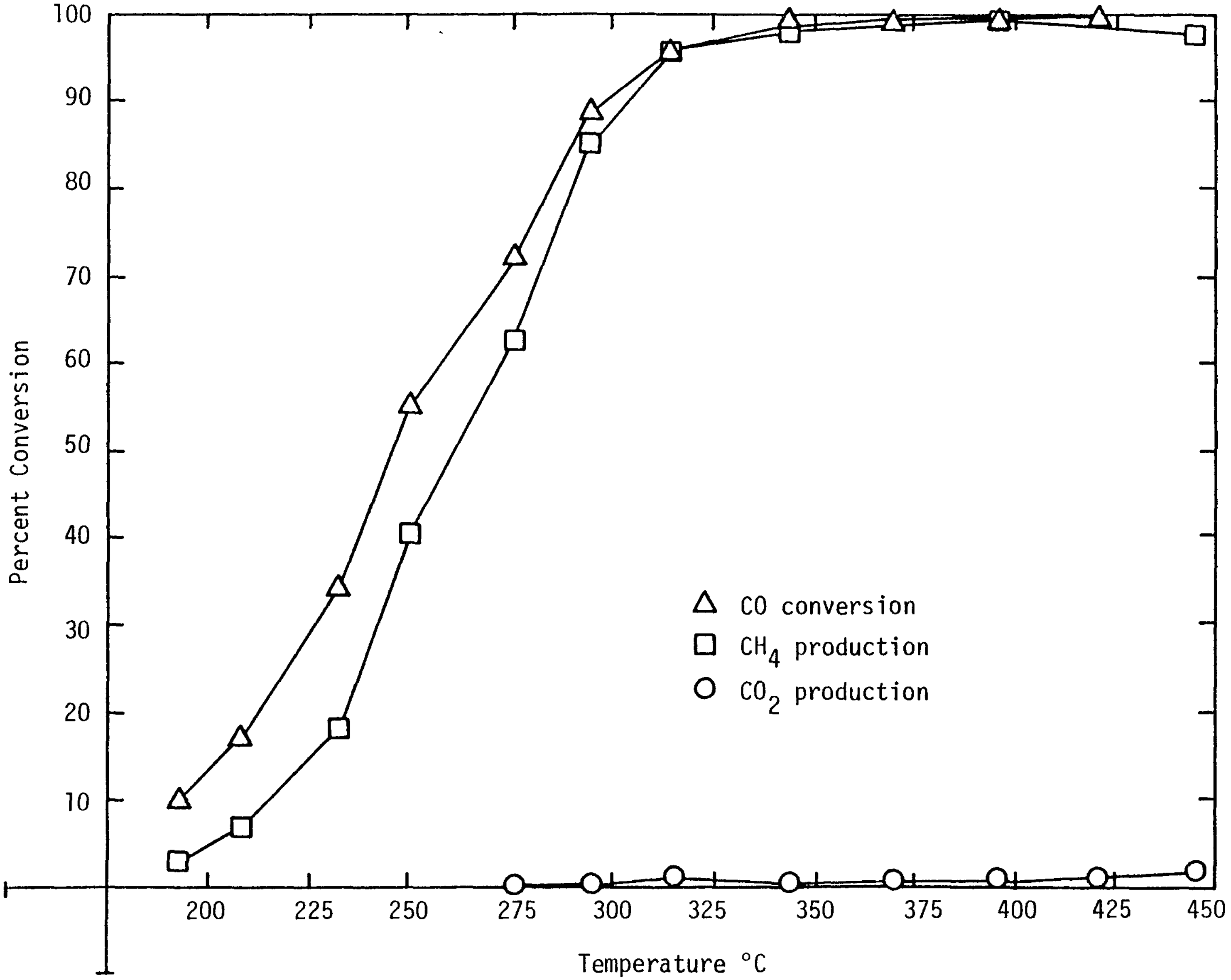

Figure 3. Conversion versus temperature Ni-Rh-A-101 (16.6% Ni, 3.4% Rh/Al_2O_3) (365 psia; GHSV = 30,000 hr^{-1}).

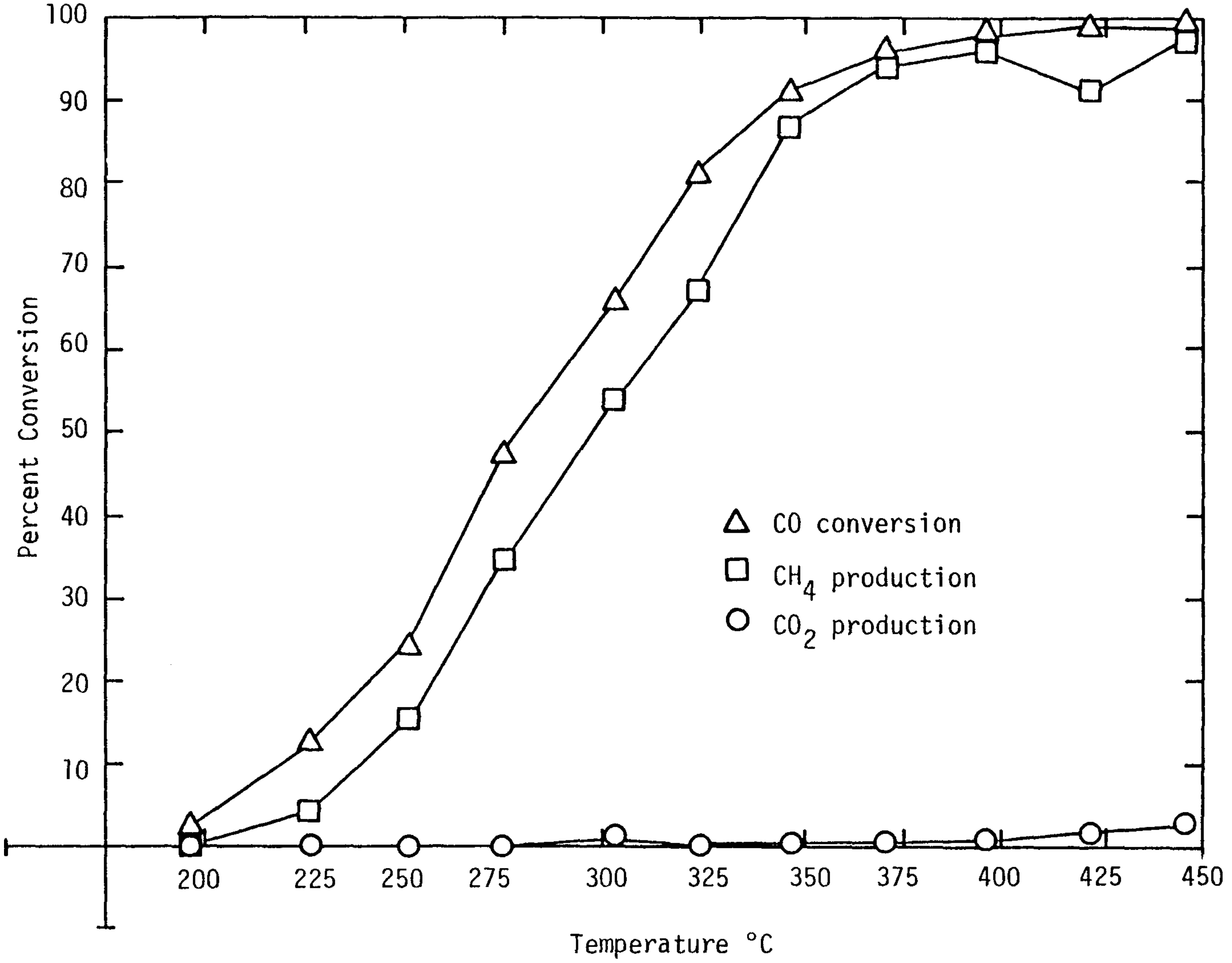

Figure 4. Conversion versus temperature for Ni-Ru-A-106 (16.6% Ni, 3.4% Ru/Al_2O_3) (365 psia; GHSV = 30,000 hr^{-1}).

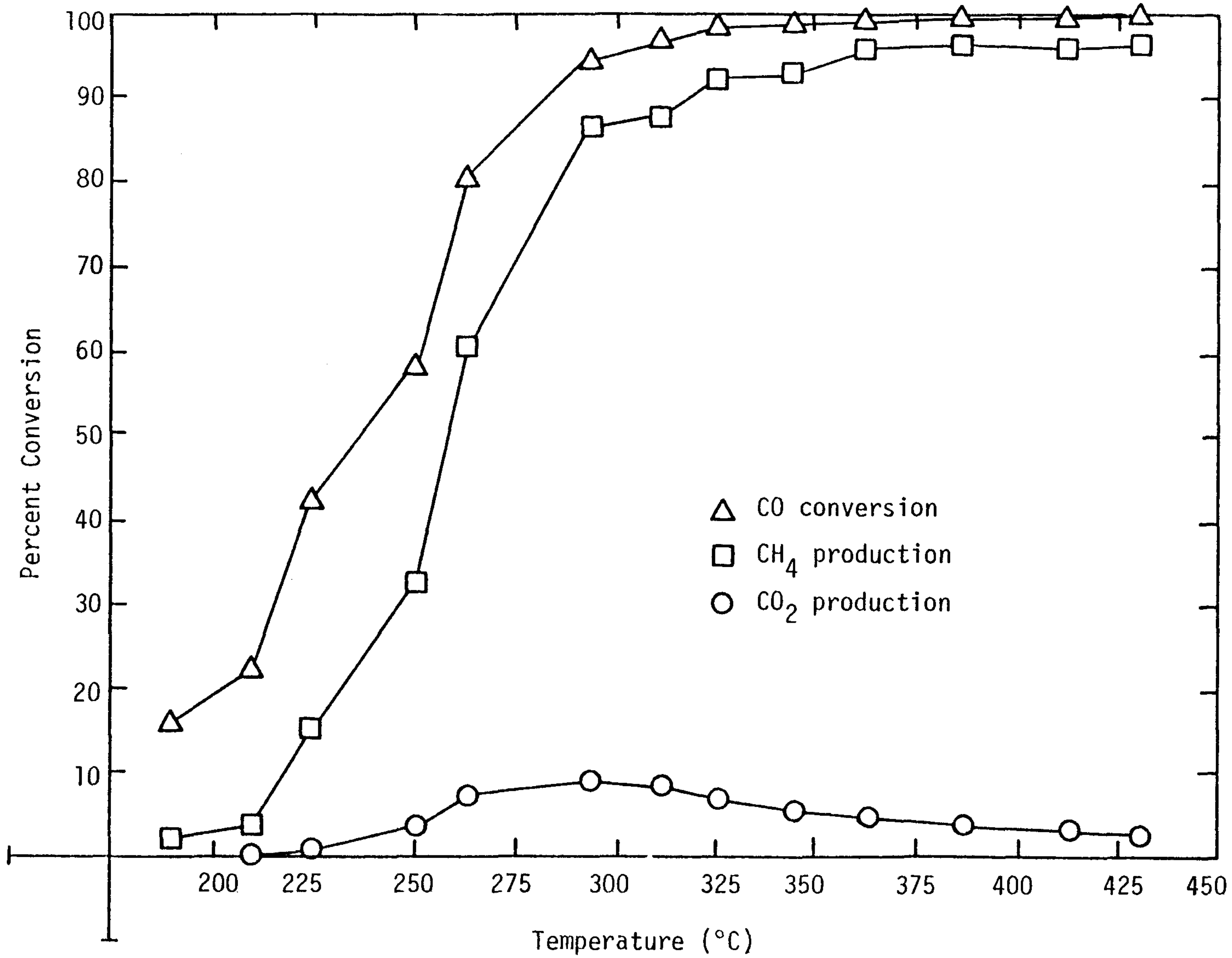

Figure 5. Conversion versus temperature for Co-A-100 (20% Co/Al_2O_3) (365 psia; GHSV = 30,000 hr^{-1}).

TABLE 3

Summary High Pressure Tests
(365 psia, GHSV = 30,000 hr^{-1})

a. At 50% CO Conversion

Catalyst	Temp.	$\%CH_4$ Prod.	%Sel. CH_4	N_{CH_4}	N_{CO}
Ni-A-116	225	38	69	6.1	8.0
Ni-Co-A-100	215	26	47	7.6	14.7
Ni-Pt-A-100	220	24	46	5.5	11.6
Ni-Ru-A-106	280	37	75	4.2	5.6
Ni-Rh-A-101	245	35	68	7.5	10.7
Co-A-100	240	23	45	14.8	31.5

b. At 95% CO Conversion

Catalyst	Temp.	$\%CH_4$ Prod.	%Sel. CH_4	N_{CH_4}	N_{CO}
Ni-A-116	275	92	97	15.0	15.5
Ni-Co-A-100	280	90	94	26.0	27.5
Ni-Pt-A-100	295	91	96	20.5	21.4
Ni-Ru-A-106	365	93	98	10.1	10.3
Ni-Rh-A-101	310	94	99	20.0	20.1
Co-A-100	292	85	90	53.6	60.0

TABLE 4

Summary Steady State Runs for Carbon Deposition

		Steady State Runs					Differential Tests Rate (moles/g sec)		
Catalyst	Run	GHSV hr^{-1}	%CO Conversion during run	Temp.	Time of run (hours)	Temp.	Before	After	% decrease
Ni-A-112	LT 1	15,000	60	420	27	225	2.12	1.55	27
Ni-A-112	LT 2	10,000	60	410	20	225	1.59	1.55	2.5
Ni-A-112	LT 3	5,000	65	425	16	225	2.57	1.80	30
Ni-A-112	LT 4	74,000	45	450	13	+++	+++	+++	+++
Ni-A-112	LT 5	250,000	10	400	21	275	21.5	9.65[d]	55
Ni-A-112	LT 6	250,000	5	400	25	275	11.7	4.85	59
Ni-A-116	LT 1	15,000			2[c]				
Ni-A-116	LT 2	75,000 150,000	25 25	400 410	6 17	250	19.0	15.9	16
Ni-A-116	LT 3	250,000[a] 180,000[b]	20 20	400 400	4 10	250	38.0	34.8	8.4

+++ data not available due to operator error

[a] H_2/CO = 2.0

[b] H_2/CO = 1.0

[c] stopped run due to temperature control problems

[d] questionable due to operator error

catalyst activity resulted. The sample was then reduced again and run at a GHSV of 10,000 hr^{-1} and a H_2 to CO ratio of 2.0. Only a 2% decrease in activity resulted from the second run. Conversion during both steady state runs was approximately 60% with neither showing any significant temperature decrease with time in the catalyst bed.

The above sample was then removed and the surface area measured by H_2 chemisorption. A 16% decrease was found. The catalysts was then treated with O_2 at 300°C for 15 minutes and another surface area measurement made. The final surface area was approximately the same as the original surface area of the catalyst (see Table 1).

Ni-A-112 LT #3

A GHSV of 5,000 hr^{-1} was used for this run with 25% N_2 diluent and a H_2 to CO ratio of 2.0. No temperature decrease with time was noted. The N_2 diluent was stopped and the temperature raised to 450°C for the last few hours of the run; no changes in temperature or conversion were observed during that period. An overall decrease in activity of 30% occurred during the run.

Ni-A-112 LT #4

In order to increase the GHSV, powdered samples were used for this and all following runs. This test was run at 450°C instead of 400°C. A 25% N_2 diluent was used with a H_2 to CO ratio of 2.0. The temperature of the catalyst bed dropped 30°C during the steady state run. However, the activity data were invalid due to various operator mistakes. When the reactor was unloaded large amounts of carbon were found on the sides of the reactor upstream from the catalyst bed. The carbon was up to 1/4 of an inch thick in some places. The same gas mixture as used in the steady state run was then diverted through a pyrex tube which was being heated by a bunsen burner. When a high enough temperature was reached carbon deposited quite rapidly on the walls of the glass tube. A thermocouple was used to measure the temperature of the tube, but the temperature measured varied over a wide range depending upon location and time; the temperature was estimated to be between 400 and 500°C. Small amounts of carbon were found on the reactor walls for some of the other steady state runs if the temperature was allowed to go above 425°C. Above this temperature the CO seems to thermally decompose, and the decomposition does not depend to any great extent on the surface involved. It is also possible that the reaction is somewhat autocatalytic since carbon deposited quite rapidly once the process was initiated on the glass tube. The copious amounts of carbon deposited on the walls of the reactor may have little connection with the carbonaceous deposit which deactivates the metal catalytic surface.

Ni-A-112 LT #5

A much higher GHSV (250,000 hr^{-1}) was used for this run with a 25% N_2 diluent and a H_2 to CO ratio of 2.0. An 8°C temperature drop over a period of 8 hours was noted with a decrease in activity of approximately 35%. However, there were instrumental problems in the differential test made after the steady state run and only one of four chromatographic runs could be analyzed. Therefore, the results are questionable since we usually base our results on the average of 5-6 chromatographic runs.

Ni-A-112 LT #6

This run was made under the same conditions as LT #5 and the results show approximately a 60% decrease in catalyst activity. A decrease in the selectivity to CH_4 production from 96% to 70% was also observed. In other runs no significant change in selectivity was noted. A large decrease in temperature over a period of hours caused the reaction to drop below its lite-off temperature for several hours before it was corrected. The conversion during the steady state run was approximately 5%, which was the lowest of any of the runs made.

Ni-A-116 LT #1

This run was made on a pellet sample at a relatively low GHSV. The run was terminated because the temperature could not be kept below 450°C due to the high activity of the catalyst.

Ni-A-116 LT #2

A powder was used for this run with a higher GHSV and with 25% N_2 diluent and a H_2 to CO ratio of 2.0. In order to lower the conversion during the steady state run the flows were increased, but this had very little effect in decreasing conversion. A 16% decrease in activity resulted from the steady state run.

Ni-A-116 LT #3

A GHSV of 250,000 hr^{-1} was used at the start of this run with 25% N_2 diluent. No temperature decrease resulted, so the H_2 to CO level was dropped to 1.0 after which there was a 15°C temperature drop over 10 hours. However, there was only a 8% decrease in activity.

Most of the problems that were encountered during the steady state runs have been solved. Therefore, steady state runs will be conducted on the remaining catalysts during the coming quarter. In order to keep the conversion as low as possible during the steady state runs a GHSV of 250,000 hr^{-1} or greater will be used. H_2 to CO ratios will be 2.0 and 3.0 as outlined previously.

2. Accomplishments - Monolithic-Supported Catalysts. The effects of monolithic channel geometry were examined by low pressure integral testing of Ni-M-303, -304, -305, -308 (20 wt.% Ni supported on 300 squares per square inch monoliths). Representative conversion versus temperature data for two of the samples are given in Figures 6-7. Due to small differences in monolith size, the space velocity used may have varied by a few per cent from 30,000 hr^{-1}. The conversion curves are similar to those previously reported for nickel on 200 squares per sq. in. monoliths. A summary of temperature and conversion data is given in Table 5.

The specific external (geometric) area of the ceramic support with the smaller channels is 27 cm^2/cm^3, while the larger channelled monoliths have an area of 22 cm^2/cm^3. One could expect that the catalyst with greater external surface area would achieve higher conversions at the same temperature. The data in Table 5 show that while this is true, the differences are quite small and certainly not proportionl to the difference in external surface area of 20 to 25%. As we do not yet have conversion temperature data for pelleted nickel under comparable conditions, a direct comparison of monolith versus pellet performance is not possible. However, in the coming quarter we will test a number of pelleted catalysts of different sizes and geometries under the same condition of space velocity and temperature range.

We also plan to test several Ni/Al_2O_3/monoliths having 236 triangles per square inch. The analysis for the three different monolith geometries should provide data for a comparison with the model of Hegedus (5) and also with the correlation of Carberry and Kulkarni (6) for CO oxidation. Their correlations combined with our reaction rate data should enable us to predict whether an overtemperature may be a problem in industrial methanation monoliths. Also, concentration and temperature profile prediction may be possible.

Figure 8 presents Arrhenius plots of some of the integral runs for square channelled monoliths at low and high pressure. Each curve shows three distinct kinetic regimes as one would expect for film, pore and kinetic limitations. From the slope of each curve in the low temperature region an apparent activation energy of about 18 kcal/mole is obtained. This is somewhat less than the value of 25 kcal/mole expected, if there were no pore diffusion resistance. Apparently then, pore diffusional influences intrude even at 175-250°C under the conditions

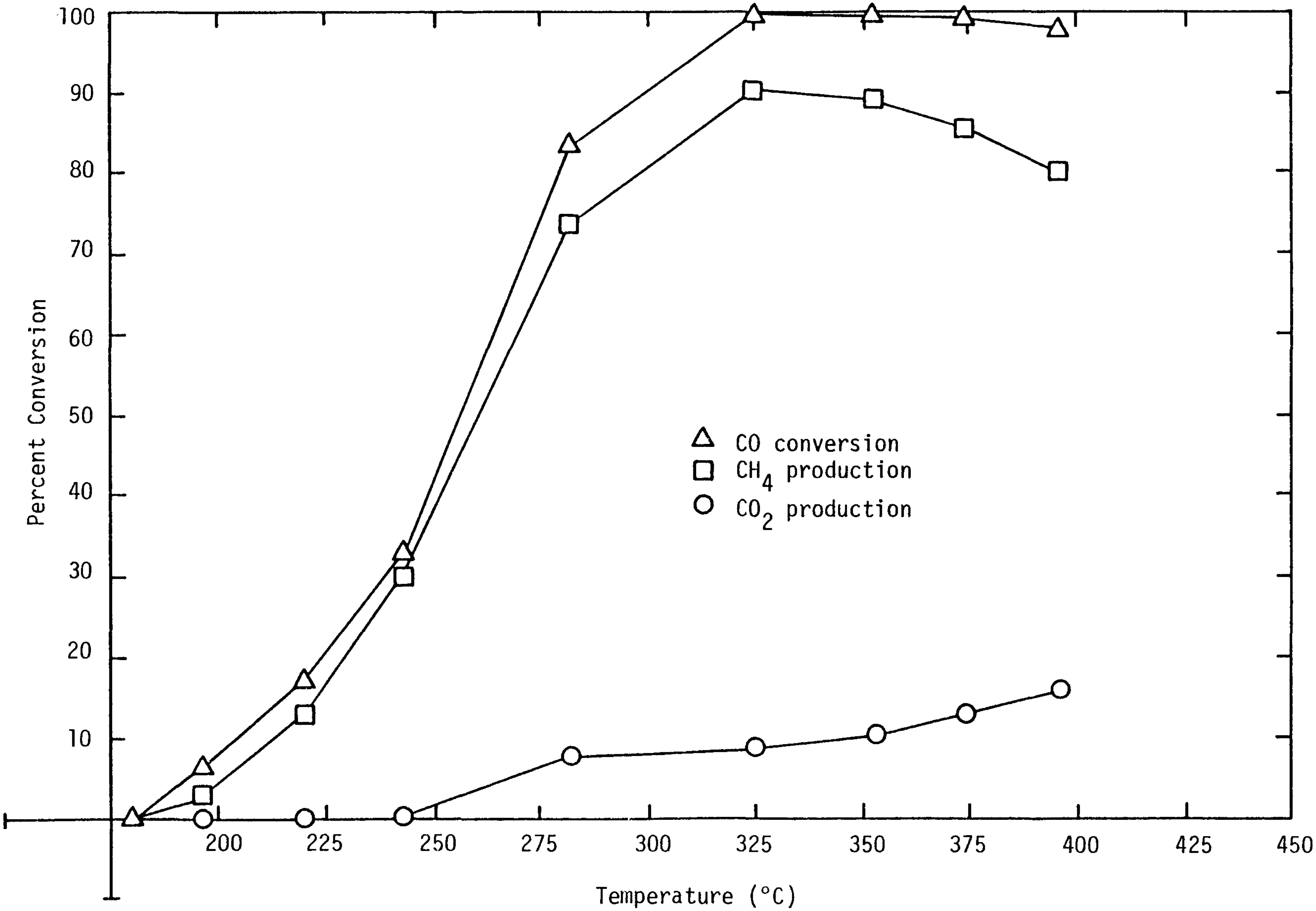

Figure 6. Conversion versus temperature for Ni-M-305 (20% Ni/Al_2O_3/Monolith) 20.5 psia, GHSV = 30,000 hr^{-1}.

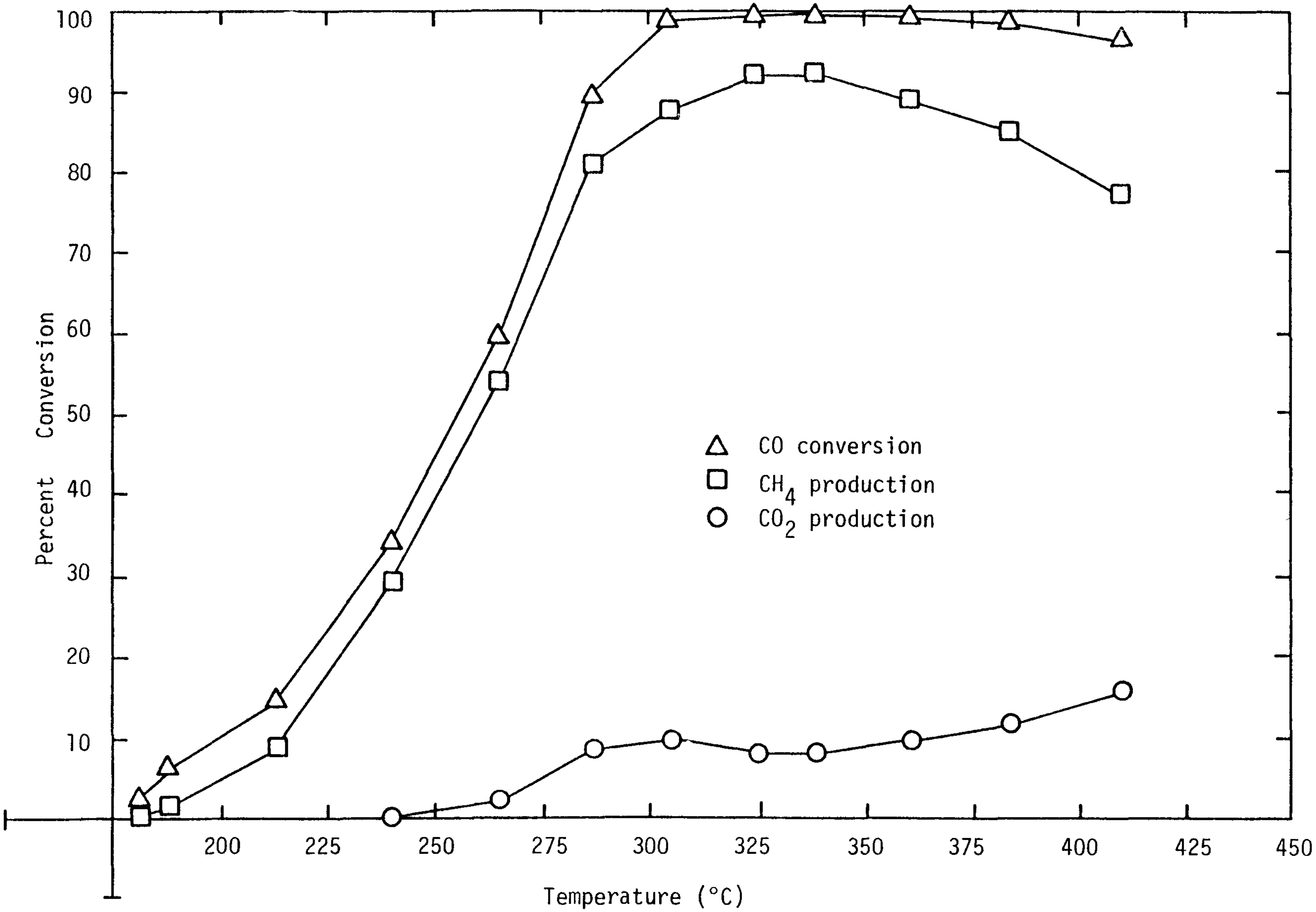

Figure 7. Conversion versus temperature for Ni-M-308 (20% Ni/Al_2O_3/Monolith) (20.5 psia, GHSV = 30,000 hr^{-1}).

TABLE 5

Summary of Integral Test Results for Monolithic Catalysts with Different Channel Geometries (GHSV = 30,000 hr^{-1})

Catalyst	Temp. of CO conversion of		At 95% CO conversion	
(200 Squares/in^2)	50%	95%	% CH_4 production	% CO_2 production
Ni-M-114 (20% Ni)	265	325	85%	13%
Ni-M-115 (20% Ni)	275	325	76%	12%
Ni-M-117 (11% Ni)	275	315	82%	11%
Ni-M-118 (12% Ni)	270	305	84%	10%
(300 squares/in^2)				
Ni-M-303 (20% Ni)	265	325	83%	10%
Ni-M-304 (20% Ni)	260	310	85%	11%
Ni-M-305 (20% Ni)	255	312	85%	7%
Ni-M-308 (20%)	255	300	84%	9%

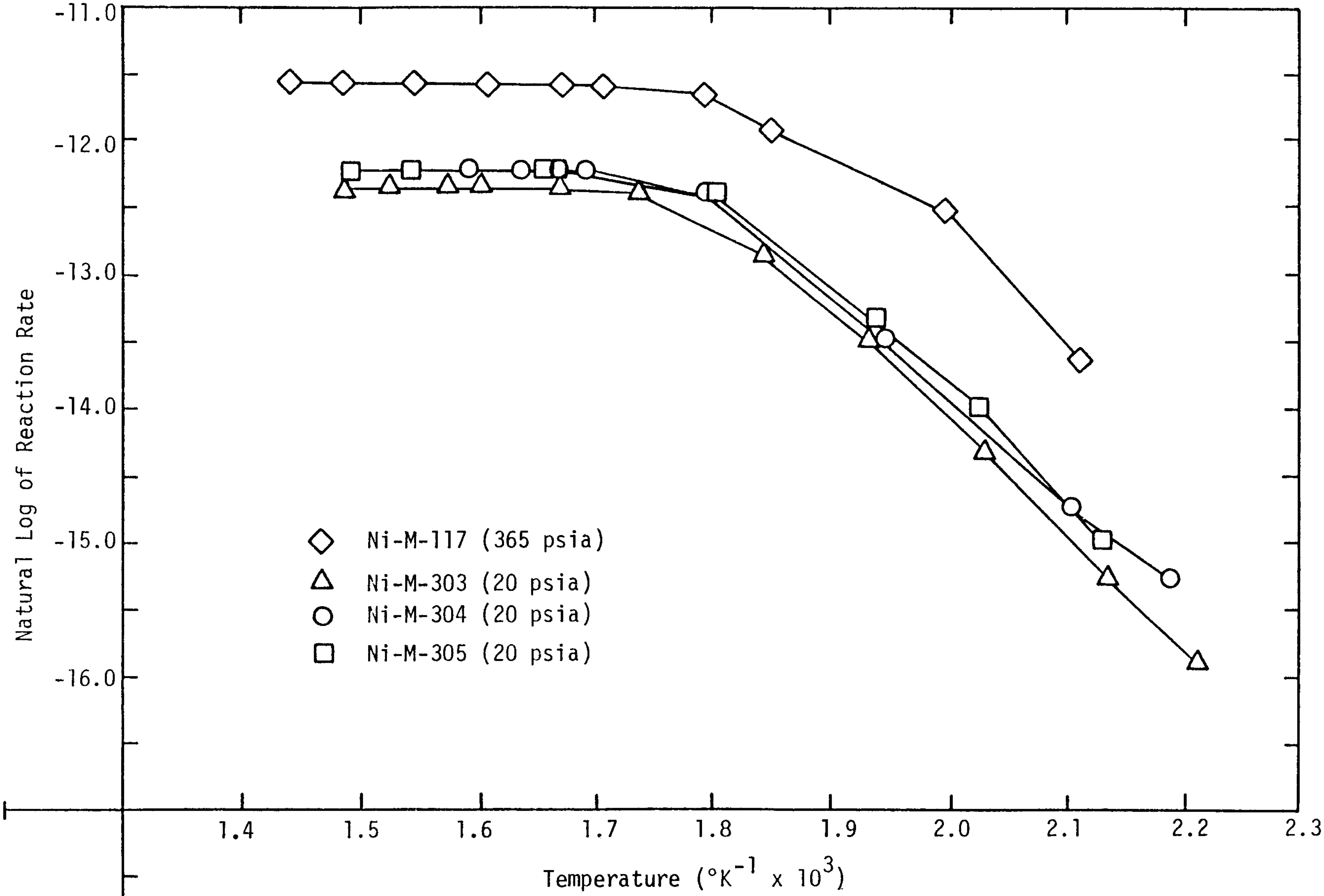

Figure 8. Arrhenius plot of logarithmic reaction rate versus reciprocal temperature. Rate is expressed as per H_2 chemisorptive site. GHSV = 30,000 hr^{-1}.

of this test. In order to obtain specific rates in the complete absence of diffusional effects it will be necessary to operate at even higher space velocities and lower conversions. This will be accomplished in monolithic catalysts by plugging off some of the outer channels of the monolith with high temperature cement.

E. Task 5: Technical Visits and Communications

Accomplishments. The principal investigator, Dr. Bartholomew, and six students attended the 2nd Rocky Mountain Fuel Symposium held February 17 and 18 at the Salt Lake Hilton. Dr. Bartholomew was symposium co-chairman and Mr. George Jarvi presented a paper entitled "Investigation of Nickel and Nickel-Alloy Monolithic Methanation Catalysts" based on research supported by this contract. Attendance at the meeting was well over one hundred and the program consisted of 36 papers most of which pertained to coal gasification and liquification, tar sands, and oil shale. A business meeting was held on February 17 to organize the Rocky Mountain Fuel Society, and Dr. Bartholomew was elected to the organizing committee with Dr. Frank Massoth and Dr. Ralph Coates.

On February 24th, Dr. Bartholomew participated in a faculty lecture series by presenting an address entitled: "What Can Be Done About the Energy Crisis,". Copies of this address were sent to Utah Senators, Congressmen, the Governor of Utah, Dr. James Schlesinger and President Jimmy Carter.

On March 16, Dr. Bartholomew visited by invitation the Department of Chemical Engineering at the University of Wisconsin at Madison where he visited with faculty members and presented a seminar on methanation kinetics and catalyst poisoning based on work supported by NSF and this contract. Discussions with Professor James Dumesic, active in catalysis research (especially characterization by Moessbauer and ESCA) related to synthesis and shift reactions, were especially fruitful. The potential for using Moessbauer to study nickel alloy catalysts was a part of this discussion.

At the Spring meeting of the California Catalysis Society hosted by SRI (Menlo Park, Calif.) on March 31 and April 1, Dr. Bartholomew presented a paper on "Magnetic Studies of Supported Platinum-Iron Alloys" based on research performed during his graduate studies at Stanford. Dr. Ken Sancier of SRI presented magnetic data from the study of carburization of iron in Fischer-Tropsch catalysts. The principal investigator was impressed with the potential of using magnetic susceptibility to characterize nickel and nickel alloy catalysts and the surface reactions of carbon on these catalysts in methanation. Dwyer and Somorjai of Berkley presented an interesting paper on the role of carbon layers in methanation on rhodium and iron foils. Rewick and Wise (SRI) presented a study of H_2S

and CO adsorption of Ni-alumina catalysts very pertinent to our work, and Wise discussed an Auger study of a SiO_2 supported alloy to determine surface composition using a special technique to avoid charging problems. This is likely the first example of an Auger study of a supported catalysts and suggests interesting possiblities for characterizing some of our supported nickel alloys. An interesting EXAFS study of $NiMoO_3/Al_2O_3$ reported by Chevron may not apply directly to our work because of the differences in catalyst preparation, but nevertheless illustrates another developing technique for surface analysis.

Just at the end of this quarter, Mr. Richard Pannell and Dr. Bartholomew attended the North American Catalysis Society Meeting in Pittsburgh (April 26-28) where they presented papers on sulfur adsorption and methanation kinetics and poisoning studies based on NSF and ERDA-supported research. The presentations appeared to have stimulated quite a bit of interest and discussion. These were also many other interesting and pertinent papers and private discussions relating to our research too numerous to mention. Some of the most useful exchanges of information dealt with catalyst preparation and characterization; for example we learned of recently developed techniques for preparing uniformly dispersed nickel on silica and unsupported Pt, Ni, and Co blacks. A paper from the National Bureau of Standards showing tungsten to be more active than nickel for methanation makes us wonder if we might not be able to prepare a Ni-W alloy.

While in Pittsburgh, Dr. Bartholomew participated in the April 28-29 meeting of the ASTM D-32 Catalysts Committee, of which he is a task force leader for determination metal surface areas. This task force is presently developing standards for hydrogen chemisorption on nickel and platinum catalysts. The following Monday (May 2) Dr. Bartholomew visited the Ventron Corporation where he was invited to present a seminar on methanation catalysis research and tour research facilities. He discussed with Ventron research personnel the possibilities of a joint research program in the study of Ni and Co borides for methanation. He was also recently in telephone communication with personnel at Climax Molybdenum Corporation about obtaining some new Co and Mo alloys for testing.

Forecast. During the first week in August, Dr. Bartholomew will attend a special conference of Chemical Engineering Educators in Snowmass, Colorado; the major topics will include catalysis and kinetics. He will attend the ERDA Contractors Conference in Pittsburgh on August 25-26 and present a paper on Sintering of Nickel Catalysts at the August 30-September 2 meeting of the ACS in Chicago.

IV. CONCLUSIONS

1. High pressure tests result in surface area losses on the order of 10-40%. Significant surface area decreases have not been observed for low pressure tests except in the presence of water. The deactivation at high pressures may also be due to water generated in the reaction at high conversions.

2. Commercially prepared NiMoO$_4$/Al$_2$O$_3$ is a factor of four less active than our NiMoO$_3$/Al$_2$O$_3$. The difference in activity may relate to the calcination of the commercial catalyst at 500°C which is likely to cause formation of NiAl$_2$O$_4$ and MoO$_4$-Al$_2$O$_3$ spinels. Since our catalyst was reduced directly in hydrogen after drying at 100°C, the formation of oxide phases is minimized and the production of lower oxidation states of Mo and perhaps even Ni-Mo alloys is maximized.

3. The best conditions for controlled deposition of carbon on nickel catalysts at atmospheric pressure are 400°C, very high space velocities (200,000 - 250,000 hr^{-1} and low conversions of CO. It may be necessary to operate at low conversions of CO in order to maintain a high partial pressure of CO or perhaps low partial pressure of H_2O at the surface and thus maximize the rate of carbon deposition. If this is true, then carbon formation might be minimized in commercial methanators by maintaining high conversions through the reactor by use of recycle.

4. Preliminary integral tests at high conversions indicate little difference in the performance of two different square-holed monoliths having external surface areas of 22 and 27 cm^2/cm^3 respectively. Hence the effect of external specific area on conversion appears to be unexpectedly small compared to earlier experience of the principal investigator in atuo emission control. Our preliminary calculations of mass transfer coefficients at high conversions suggest the reaction is primarily mass transfer limited at 400-500°C.

5. Calculations based on theories for binary alloys suggest that Ni-Pt and Ni-Rh catalysts should form homogeneous solutions under conditions of our preparation; the data for Ni-Ru are inconclusive. The surfaces of Ni-Ru, Ni-Rh, and Ni-Pt crystallites are predicted to be very nickel rich whereas the surface composition of Ni-Co should be the same as the bulk. These predictions are reasonably consistent with our experimental adsorption and kinetic data, although the activation energies and specific activities for the Ni-Ru, Ni-Rh, and Ni-Pt catalysts are measurably different than for Ni, thus suggesting alloying effects. In the case of Ni-Co the initial activity is about the same as nickel and significantly less than Co; however, after exposure to H_2S the activity of Ni-Co is definitely greater than either Ni or Co indicating an alloying or synergistic effect.

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APPENDIX A
THE SURFACE COMPOSITION OF NICKEL ALLOYS

Introduction

During recent years alloy catalysts have found increased application in a variety of industrial processes, mainly because of enhanced activity, selectivity, and stability relative to their monometallic counterparts. Examples are the develoment of Pt-Rh alloys for ammonia oxidation and the new KX-130 reforming catalyst by Exxon. In this laboratory Ni alloys of Co, Ru, Rh, and Pt are being tested as possible methanation catalysts. The surface structure of a heterogeneous catalyst largely determines the catalytic properties. Therefore, knowing the surface as well as the phase composition of binary alloy catalyst is extremely important. Moreover, the surface and phase compositions are generally different from the bulk phase. Several theories have been developed for predicting the surface and phase compositions of binary alloys. Several of these are reviewed here as they apply to the Ni alloys being tested in this laboratory.

Effect of Particle Size on Phase Composition

Hansen (1) and Shunk (2) give bulk phase diagrams for Ni-Co, Ni-Ru, and Ni-Pt. Of these Ni-Ru and Ni-Pt show large immiscibility gaps. The data for Ni-Rh is somewhat incomplete and contradictory. If an immiscibility gap does occur it is expected to have a critical temperature of approximately 500°C.

Bimetallic systems which are immiscible in the bulk phase may be miscible for small particles. Assuming regular solution theory for an ideal solution Ollis (3) derives an expression for the free energy change as a binary alloy goes from a single to a two phase system. An iterative procedure is used to find the temperature and phase compositions where the free energy change is zero. The locus of these points defines the boundaries of the immiscible region of the phase diagram. As can be seen in Figure 1A, the particle diameter has a significant effect on the phase diagram. Since the procedure is quite complex a rough estimate of the critical temperature for a 100 Å particle of Ni-Ru and Ni-Pt is made using the scaling technique given by Ollis. Upper and lower bounds were taken for values of parameters not readily available for the systems. The critical temperature for Ni-Pt is expected to be below 450°C and that for Ni-Ru between 700 and 1000°C. Ni-Pt is therefore expected to form a homogeneous solution at 400°C. Ni-Ru could possibly form a homogeneous solution since it has a diameter of 52 Å and a bulk phase composition of 17% Ru. However, a more rigorous calculation would have to be made to be certain.

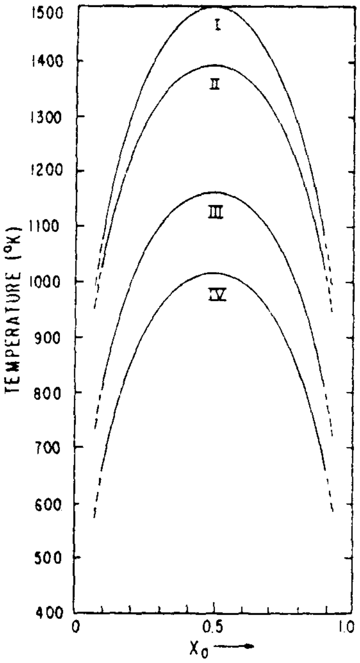

FIG. 5. Effect of crystallite diameter on phase diagram of regular solution ($T_c = 1500°K$, $\Delta G^s =$ 600 ergs/cm^2). d(Å) = ∞(I), 2000 Å(II), 200 Å(III), 100 Å(IV).

Figure 1A (From Ref. 3)

Surface Composition of Bimetallic Crystallites

For miscible as well as immiscible systems there is generally a difference between the surface and the bulk phase composition. Using regular solution theory Williams (4) and later Burton (5) developed the following equation for finding the surface composition.

$$X_1 = a/(a+1) \tag{1}$$

$a = (X_b/(1 - X_b))\ \exp((- H_{sub}Z_{1_v})/Z_1kT)$
$\Delta H_{sub} = (\Delta H_A)_v - (\Delta H_B)_v$
X_1 = atom fraction in first layer (surface layer)
X_b = bulk atom fraction
ΔH_{sub} = difference in heat of vaporization of the two metals
k = Boltzman constant
T = Temperature in °K
z_{1_v}/z_1 = fraction of neighbors missing

It can be seen from Equation 1 that the component with the higher heat of vaporization desorbs from the surface and the other component is correspondingly increased. It can also be seen that the surface composition depends on the temperature, fraction of neighbors missing, and on the bulk atom concentration. More accurate results are obtained if second nearest neighbors are considered. The effect of the second nearest neighbors changes the fraction of missing neighbors in Equation 1. The effect is not too pronounced but does tend to increase the desorption slightly. Figure 2A shows the degree of desorption for various conditions. Most crystal structures have a higher degree of missing neighbors at the surface than the fcc (111) used in Figure 2A. Burton also points out that edges and corners have higher fractions of missing neighbors. Therefore, the actual desorption for the whole surface would be greater than that shown in Figure 2A.

For the Ni alloys under investigation in this laboratory, Equation 1 was used to predict the surface composition. The values obtained are presented in Table 1A. It can be seen that the surface and bulk compositions are quite different for the Ni-Ru, Ni-Rh, and Ni-Pt systems, with nickel atoms predominating at the surface.

William (4) and Sachtler (6) point out that chemisorption of a foreign species tends to increase the surface composition of the component which forms the stronger bond with the adsorbate. For the Ni alloys being tested, H_2 chemisorption would tend to increase the Ni content at the surface while CO chemisorption would tend to decrease it.

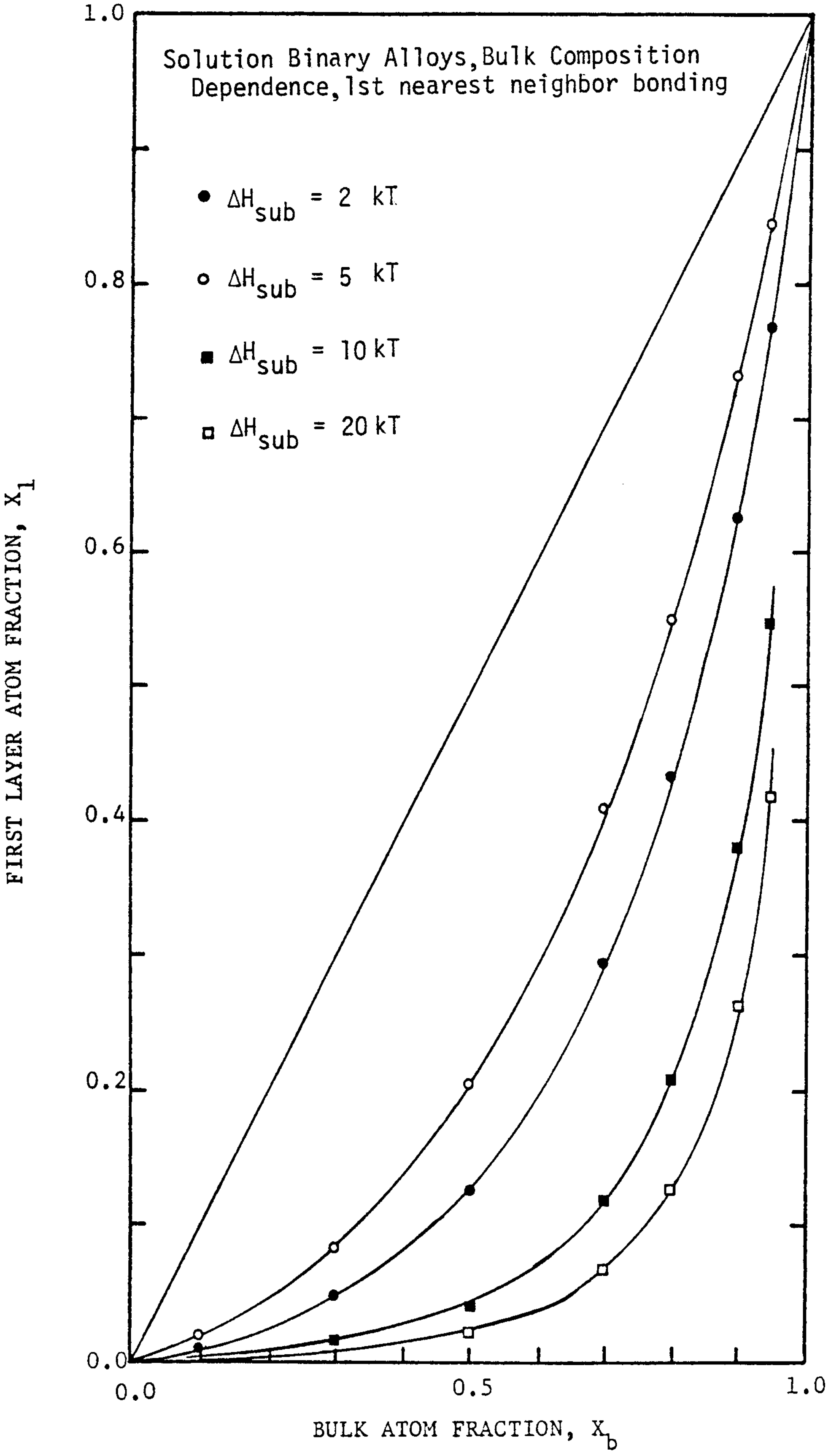

Figure 2A
(From Ref. 4)

TABLE 1A

Surface Compositions of Ni Alloy Systems
T = 400°C, based on fcc(111), plane, $Z_{1_v}/Z_1 = .3$

Catalyst	$\Delta H_{sub}/kT$	Bulk Phase Composition	Surface Composition
Ni-Co	- 0.30	0.50	.52
Ni-Rh	22.0	0.102	1.5×10^{-4}
Ni-Ru	39.6	0.104	8.0×10^{-7}
Ni-Pt	24.1	0.0095	6.9×10^{-6}

Composition given is atom fraction of metal alloyed with Ni

Crystallite size can have a significant effect on the surface composition of a binary alloy. For a large crystallite the desorption of one component from the surface does not significantly change the bulk composition but for a small particle it does. A limiting value for the surface composition can be obtained from an atom balance. For the alloys being tested in this laboratory the dispersion is not high enough to have any significant effect on the surface composition.

For bimetallic systems which tend to be immiscible in the bulk phase a system of 4 simultaneous equations needs to be solved to accurately predict the surface composition. For those systems the degree of desorption would be greater than that predicted by Equation 1. The Ru and Pt content at the surface would therefore be expected to be less than that listed in Table 1, if the metals are immiscible.

Time Dependence of Surface Compositions

The time required for a bimetallic system to come to equilibrium seems to be somewhat in doubt. Bouwman and Sachtler (6) define the Tamman temperature to be 0.3 of the melting point of the metal. They report that equilibrium was reached after a few hours at a temperature between the Tamman temperature of the two metals for Pt-Au, Cu-Ni, and Pt-Ru systems. At 400°C the Ni alloys being tested are expected to come to equilibrium in a few hours since the Tamman temperature is less than 400°C for all of the metals except Ru.

Conclusions

Of the Ni alloys under study the Ni-Ru, Ni-Pt and possibly Ni-Rh have large immiscibilities in the bulk phase. Of these, Ni-Pt, and Ni-Rh are expected to form homogeneous solutions. Ni-Ru could possibly form a homogeneous solution but a more rigorous calculation will need to be made to be certain. The surface composition of Ni-Ru, Ni-Rh and Ni-Pt are all predicted to be significantly different than the bulk phase, while the Ni-Co system should be approximately the same.

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