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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES. QUARTERLY TECHNICAL PROGRESS REPORT, SEPTEMBER 20--DECEMBER 20, 1977

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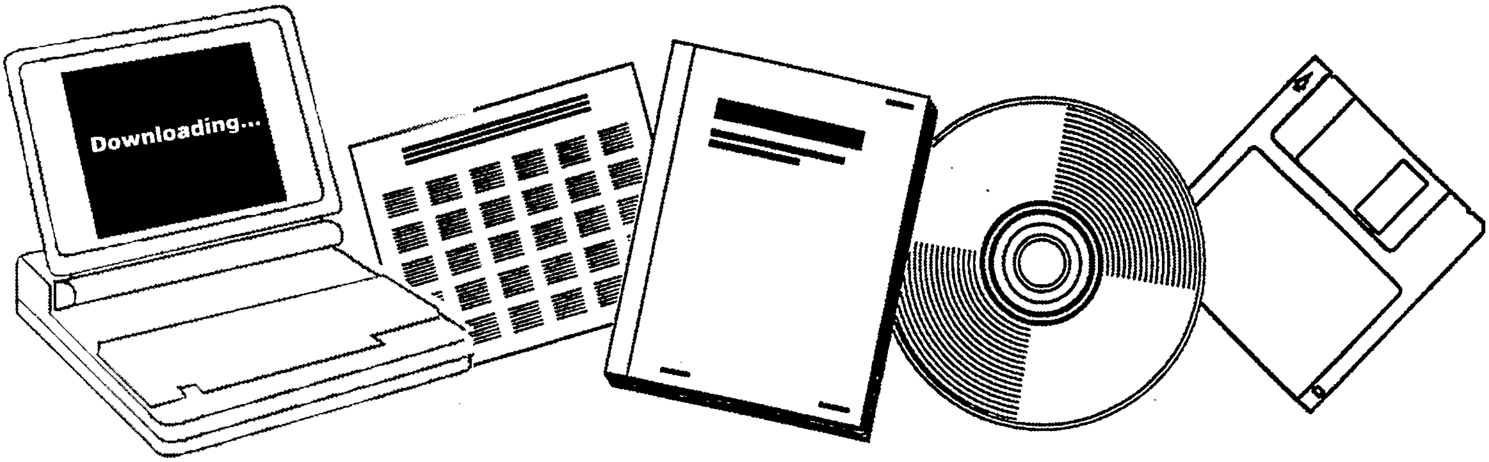

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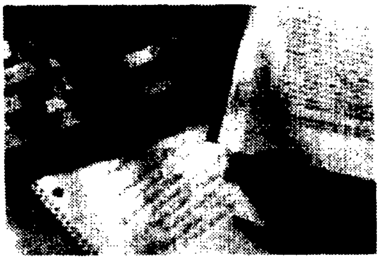

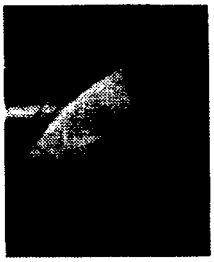

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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period September 20, 1977 to December 20, 1977

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DEPARTMENT OF ENERGY

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FOREWORD

This report summarizes technical progress during the first quarter (September 20 to December 20, 1977) of a study conducted for the Department of Energy (DOE) under Contract No. EF-77-S-01-2729. The principal investigator for this work was Dr. Calvin H. Bartholomew; Dr. Paul Scott was the technical representative for DOE.

The following students contributed to the technical accomplishments and to this report: Graduates - Erek Erekson, George Jarvi, Ed Sughrue, and Gordon Weatherbee, and Undergraduates - Kevin Mayo, Don Mustard, and John Watkins. Elaine Alger and Scott Folster provided typing and drafting services.

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ABSTRACT

The effects of carbon deposition and in situ exposure to 10 ppm H_2S during reaction on the methanation activity of pelleted and monolithic alumina-supported Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Rh, and Ni-Ru were investigated during the past quarter. For monolithic supported catalysts the order of decreasing resistance to carbon deposition is Ni-Pt > Ni-Co > Ni-Ru > Ni > Ni-MoO_3. These results are in qualitative agreement with results of carbon deposition tests for pelleted catalysts. Activity tests made at 250 °C and 1 atm with 10 ppm H_2S in the reactant mixture show that for pelleted catalysts the order of decreasing sulfur tolerance is Ni > Ni-Co > Ni-Pt (14-20 wt.% catalysts) and Ni-MoO_3 > Ni = Ni-Rh > Ni-Ru (3-5 wt.% catalysts). For the monolithic catalysts the order of activity following exposure to H_2S is Ni-MoO_3 > Ni > Ni-Co > Ni-Ru > Ni-Pt. Activity tests of nickel supported on pure alumina monoliths show these samples to be less selective and less active on a volume basis than wash-coated monolithic samples of Ni/Al_2O_3/cordierite. These and other significant results obtained during this past quarter are presented and discussed. An account of technical communications with other workers and visits to other laboratories is also included.

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, economic 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 each 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 appear to be important economical advantages in the development of more efficient, stable catalysts.

From the literature (1,2), three major catalyst problems are apparent which relate to stability: (i) sulfur poisoning, (ii) carbon deposition with associated plugging, and (iii) sintering. Our understanding of these problems is at best sorely inadequate, and the need to develop new and better catalyst technology is obvious. Nevertheless, there has been very little research dealing with new catalyst concepts such as bimetallic (alloy) or monolithic-supported catalysts for methanation. 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 the kinetics of methanation for a few selected catalysts tested during the first two years, (ii) to investigate these catalysts for resistance to deactivation due to sulfur poisoning and thermal degradation. The work is divided into five tasks.

Task 1. Characterize the surface bulk, and phase compositions, surface areas, and metal crystallite sizes for alumina-supported Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Ru and Ru catalysts.

Task 2. Continue activity testing and support geometry studies of Ni-and Ni bimetallic catalysts initiated during the first two years. The tests include (i) conversion vs. temperature runs at low and high pressures, (ii) steady-state carbon deposition tests, (iii) in situ H_2S tolerance tests, and (iv) support geometry comparisons.

Task 3. Perform kinetic studies to find intrinsic rate data for alumina-supported Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Ru, and Ru catalysts over a range of pressures and feed compositions. Detailed rate expressions for each catalyst will be determined at low and high pressure. Effectiveness factors for monolithic and pellet-supported nickel on alumina will be obtained by comparing specific rates to those of finely powdered nickel on alumina.

Task 4. Determine H_2S poisoning rates, thermal deactivation rates, and operating temperature limits for Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Ru, and Ru catalysts.

Task 5. Continue laboratory visits and technical communications. Interact closely with industrial and governmental representatives to promote large scale testing and development of the two or three best monolithic or pelleted alloy catalysts from this study.

C. Technical Approach

The technical approach which will be used to accomplish the tasks outlined above is presented in the statement of work dated May 20, 1977. 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 Characterization

A comprehensive examination of alumina-supported Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Ru, and Ru catalysts will be carried out to determine surface, bulk, and phase compositions, surface areas, and metal crystallite sizes using the following techniques: chemisorption, x-ray diffraction, chemical analysis, ESCA and SIMS spectrocopy, Auger spectroscopy and transmission electron microscopy.

Hydrogen chemisorption uptakes will be measured using a conventional volumetric apparatus before each reactor test and before and after deactivation tests. 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, chemical analysis, and perhaps ESCA) to determine carbon content and possible changes in phase composition or particle size. Also, transmission electron micrographs will be made to determine particle size distributions for catalyst samples. A few samples will be analyzed by EDAX to determine composition.

Task 2: Activity Testing and Support Geometry Design

Methanation activity and sulfur tolerance measurements initiated during the previous two years of study (3) will be completed. Pellet and monolithic alumina-supported Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Ru, and Ru catalysts, (both high and low metal loadings) will be activity tested over a range of temperatures, pressures, and H_2S concentations. A comparison of steady state conversions for nickel on different pellet and monolith supports of varying geometry will be made. Low pressure activity and sulfur tolerance tests will also be made for pelleted Co/Al_2O_3 and unsupported Ni-Co and Ni-Mo alloys. A summary of the five test procedures and corresponding experimental conditions is listed in Table 1.

Task 3: Kinetic Studies

In order to make more extensive kinetic studies of the six catalyst metal combinations a new mixed flow reactor system will be constructed. This system will be capable of operation to 1000 psi and 500°C and over a range of reactant compositions. The reactor for this system will be a "Berty" type constant volume mixed flow Autoclave reactor.

Intrinsic rate data will be obtained for alumina-suported Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Ru, and Ru catalysts over a range of pressures and feed compositions in order to obtain detailed rate expressions at low and high pressures. To insure gradientless operation in the reaction-limited regime the rates will be measured at low conversions (0-5%) and low temperatures (250-325°C) for samples which have been crushed to obtain small particles.

Isothermal effectiveness factors for monolithic and pellet-supported nickel on alumina will be obtained by comparing their specific rates to those of finely powdered nickel on alumina using the same mixed flow reactor.

Task 4: Degradation Studies

H_2S poisoning rates and thermal deactivation rates at low pressure will be studied using a new quartz reactor system. Quartz was selected as the material for the reactor because it must operate at high temperatures (500-750°C) and in a corrosive (H_2S) environment. This reactor is also a constant volume mixed flow type reactor according to the design of Katzer (4). The quartz reactor system will be constructed during the early part of the contract period. Thermal deactivation at high pressures will be studied using a tubular stainless steel reactor previously discussed (3).

Operating temperature limits (and specific reaction rates within this range), thermal deactivation rates near the upper use temperature (in the presence and absence of steam), and H_2S poisoning rates (at 250°C in the presence of 1 and 10 ppm H_2S in H_2) will be determined for Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Ru, and Ru catalysts. The extent of carbon-carbide deposited in the thermal deactivation runs will be determined by chemical analysis and x-ray diffraction.

TABLE 1

Description of Reactor Tests for Task 2

Test Procedures	Experimental Conditions
1. Temperature-Conversion Test: Measure CO conversion and methane production as a function of temperature, with and without 1% (by vol.) of steam present in the reactant mixture.	200-400°C 8 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2 (dry basis)
2. Temperature-Conversion Test (high pressure): Measure CO conversion and methane production as a function of temperature at 350 psig.	200-400°C 350 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2
3. Steady State (24 Hr.) Carbon Deposition Test: Measure CO conversion and methane production at 225 and 250°C (250,000 hr^{-1}) before and after an exposure of 24 hours at 400°C.	400°C (24 hrs.) 8 psig 200,000-250,000 hr^{-1} 25% CO, 50% H_2, 25% N_2 $H_2/CO = 2$
4. In situ H_2S Tolerance Test: Measure intermittently the production of methane and hydrocarbons (by FID) during 24 hours exposure to feed containing 1 or 10 ppm H_2S using a glass reactor.	250°C 8 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2 1 or 10 ppm H_2S
5. Support Geometry Tests: Measure CO conversion and methane production as a function of temperature for the same Ni/Al_2O_3 catalyst supported on monoliths and pellets of varying geometries.	300-400°C 8 psig 30,000 hr^{-1} 1% CO, 4% H_2, 95% N_2

Task 5: Technical Interaction and Technology Transfer

The principal investigator will continue to communicate closely with other workers in methanation catalysis, continue distribution of quarterly reports to selected laboratories to stimulate interest and feedback, attend important coal and catalysis meetings, and visit other methanation laboratories.

He will also interact closely with Mr. A.L. Lee at the Institute of Gas Technology, with personnel at the Pittsburgh Energy Research Center and with other coal gasification representatives to promote large scale testing and development of the two or three best catalysts from this study.

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.

Accomplishments and results from the last quarter are best summarized according to task:

Task 1. Ten monolithic alumina supported catalysts were prepared using pure alumina monoliths. Hydrogen chemisorption measurements were carried out for eleven different catalysts, some before and after exposure to H_2S in a reaction mixture. Electron microscopy measurements were made for fresh and sintered Ni/Al_2O_3 catalysts. The results show that sintering causes a broadening of the metal crystallite size distribution.

Task 2. Conversion-temperature tests were performed at 1 atm and 30,000 hr^{-1} on three nickel/alumina monolith catalysts. The results show that nickel supported on the pure alumina monolithic are less selective and less active on a volume basis than wash-coated monolithic nickel.

Steady state carbon deposition tests were performed at 400 °C and 1 atm for 5 monolithic nickel and nickel bimetallic catalysts. Accordingly the order of decreasing resistance to carbon deposition was observed to be Ni-Pt > Ni-Co > Ni-Ru > Ni > Ni-MoO_3. These results are in qualitative agreement with results for carbon deposition tests on the corresponding pelleted catalysts.

Activity tests in the presence of 10 ppm H_2S at 250°C and 1 atm were performed for 7 pelleted and 5 monolithic alumina-supported nickel and nickel bimetallic catalysts. The order of decreasing sulfur tolerance for the pellet samples was found to be Ni > Ni-Co > Ni-Pt (14-20 wt.% catalysts) and Ni-MoO_3 > Ni = Ni-Rh ≥ Ni-Ru (3-6% catalysts). For monolithic catalysts the order was found to be Ni-MoO_3 > Ni > Ni-Co > Ni-Ru > Ni-Pt.

Task 3. Construction of a high pressure mixed flow reactor system was initiated. A Berty Autoclave reactor was ordered and received. All other reactor components including mass flow meters, a compressor, valves and regulators were ordered. A Perkin-Elmer Sigma I chromatograph was also ordered.

Task 4. Construction of a quartz mixed flow reactor was also initiated. The quartz mixed flow reactor was ordered, fabricated, and received. All other materials and components have been ordered.

Task 5. The principal investigator visited the University of Kentucky and the Institute of Mining and Minerals Research in Lexington where he presented a seminar. He also attended and presented a paper at the Fall California Catalysis Meeting. Dr. Henry Dou of CNRS visited our laboratory.

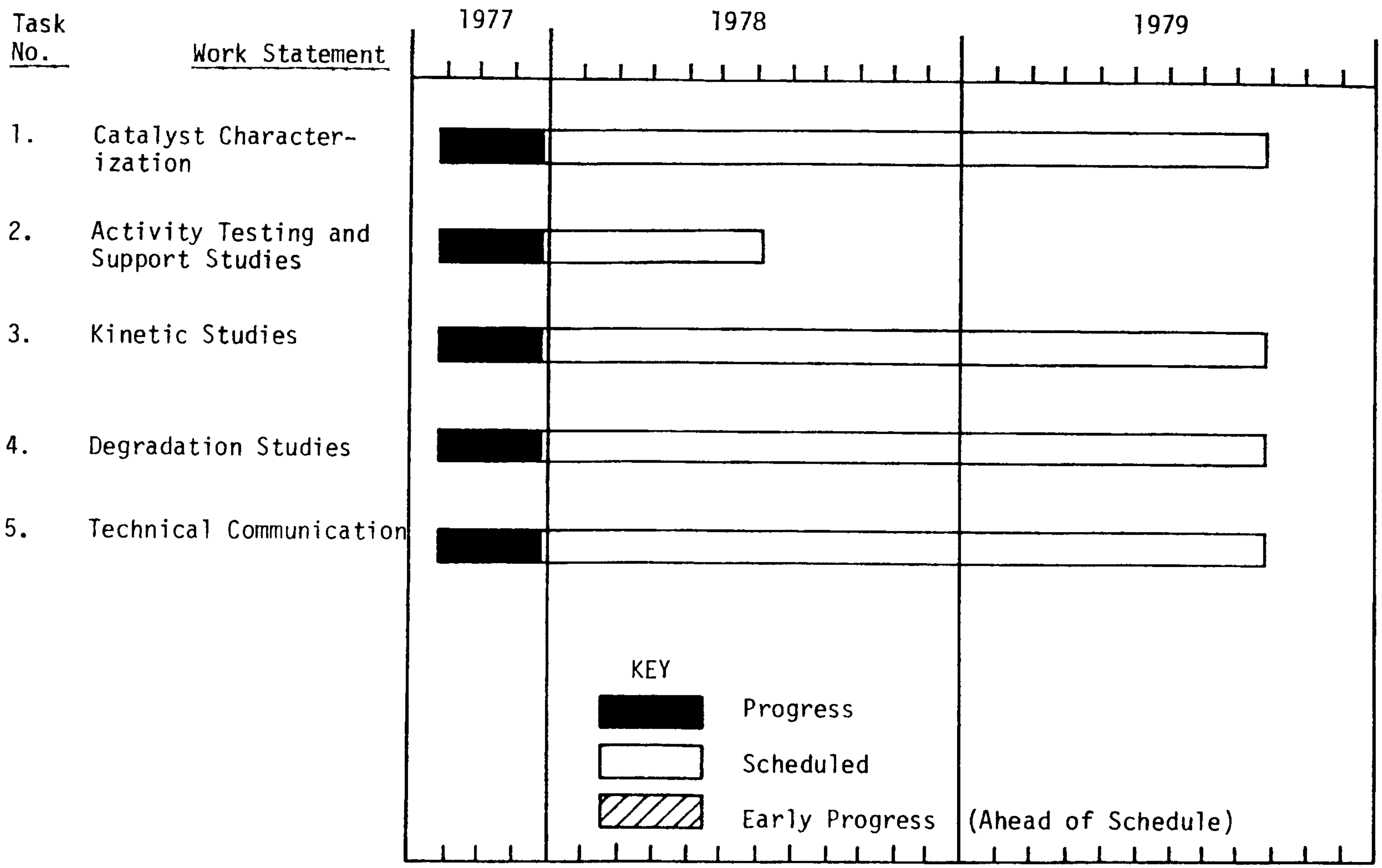

Figure 1. Project Progress Summary.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1: Catalyst Characterization

1. Catalyst Preparation

During this quarter ten monolithic supported nickel catalysts were prepared by impregnation of pure alumina monoliths obtained from Corning Glass Works. The monoliths used were of two different geometries: 200 square channels per square inch and 236 triangular channels per square inch. These catalysts differ from the monolithic supported catalysts previously prepared in this laboratory in that the support is entirely alumina and the catalyst metal is impregnated throughout the monolithic support. The previously prepared monoliths consisted of a cordierite monolithic support (obtained from Corning Glass Works) coated with a layer of alumina into which the metal was impregnated. The alumina monolithic supports were used in order to see what difference there might be between catalysts where metal was impregnated directly into the monolithic support and catalysts where metal was impregnated into an alumina layer on the monolithic support.

The alumina monolithic catalysts were prepared by a procedure similar to that used previously in this laboratory (3). In order to reduce the amount gas needed to test the catalysts at a space velocity of 30,000 hr^{-1} the 1 inch O.D. by 3 inch long monoliths received from Corning were cut into 1/2 inch lengths. These monoliths were then cleaned and rinsed in nitric acid to remove any interfering ions. These alumina monoliths were then impregnated with nickel nitrate by immersion in a saturated solution of nickel nitrate for several minutes followed by drying at approximately 150°C for 1.5 hours. This impregnation procedure was repeated until the desired nickel nitrate loading was obtained. When a sufficient amount of nickel nitrate had been impregnated on the monoliths they were reduced at 450°C in flowing hydrogen (GHSV = 2000 hr^{-1}) for 10 hours. (5).

Table 2 is a summary of the alumina monolithic catalysts prepared during this quarter. Note the code for these catalysts is (Metal) -AM-(3 digit number). The code for cordierite monoliths is (Metal) -M- (3 digit number).

2. Chemisorption

Hydrogen chemisorption uptakes, reported in Table 3, were measured for 11 different catalysts. Seven catalysts were monolithic supported catalysts and four catalysts were pellet supported.

The hydrogen chemisorptions were carried out using the same procedure previously reported by this laboratory (3). The catalysts were reduced at 450°C in flowing hydrogen (GHSV = 2000 hr^{-1}) for 2 hours, evacuated to 5×10^{-5} Torr at 400°C, and chemisorption was carried out at 25°C and 40 cm Hg.

Table 2

Composition of Nickel on Alumina Monolith Catalysts

Catalyst	Code	Nickel Loading (wt.%)
Nickel on 200□/in^2 Alumina Monoliths	Ni-AM-101	29.7
	Ni-AM-102	27.8
	Ni-AM-103	27.4
	Ni-AM-104	27.9
	Ni-AM-105	29.9
Nickel on 236△/in^2 Alumina Monoliths	Ni-AM-201	25.5
	Ni-AM-202	25.8
	Ni-AM-203	25.5
	Ni-AM-204	27.5
	Ni-AM-205	26.9

Table 3

Summary of Metal Surface Area Measurements Using H_2 Chemisorption at 25°C

Catalyst	Nominal Composition (wt.%)	Uptake (µmoles/gram)
Pellet Catalysts:		
Ni-Co-A-100	10% Ni 10% CO	107[a]
Ni-Co-A-100	10% Ni 10% CO	0[b]
Ni-Rh-A-100	2.5% Ni 0.5% Rh	19.0[a]
Ni-Rh-A-100	2.5% Ni 0.5% Rh	0[b]
G-87		167.3[a]
Ni-A-116	14% Ni	0[b]
Monolithic Catalysts:		
Ni-Ru-M-110		8.6[c]
Ni-Ru-M-111		11.5[d]
Ni-Pt-M-108		69.3[e]
Ni-Co-M-108		43.2[e]
Ni-AM-101	29.7% Ni	221.7[a]
Ni-AM-102	27.8% Ni	196.0[a]
Ni-AM-201	25.5% Ni	201.1[a]
Ni-M-250	22.2% Ni	154.8[a,f]

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[a] Bulk reduced

[b] Long term H_2S in situ poisoning tested

[c] Conversion vs. temperatures tested

[d] High pressure reactor tested

[e] Steam in reactant stream, conversion vs. temperature tested

[f] Previously reported, see Reference 3

From examination of data for the pelleted catalysts in Table 3 it can be seen that long term in situ H_2S poisoning reduces the hydrogen chemisorption to zero.

From the data for the monolithic supported catalysts in Table 3 it is interesting to observe the difference in H_2 uptake between Ni-AM-201 and Ni-M-250. Ni-AM-201 is nickel impregnated on an alumina monolith having 236 triangular channels per square inch, whereas Ni-M-250 is nickel impregnated on an alumina layer (20 wt.%) on a cordierite monolith (from Corning Glass Works) having 236 triangular channels per square inch (see Reference 3 for preparation). By normalizing the H_2 uptakes to a per gram nickel basis it can be seen that the H_2 uptake per gram nickel for Ni-AM-201 is 13 percent greater than that for Ni-M-250. It can be seen that the alumina monolith has better nickel dispersion than does the alumina layer. This would be expected since the alumina monolith would provide a larger volume for nickel dispersion than would the alumina layer.

3. Electron Microscopy

Transmission Electron Micrographs were made of both fresh and sintered 15 % Ni/Al_2O_3 (Ni-A-119) catalyst samples. The fresh sample was crushed in a mortar and pestle, placed in n-butanol and ground to a fine powder in a 7 mm tissue grinder. The resulting mixture was ultrasonicated for 5 minutes to evenly distribute the fine particles. A drop of this mixture was placed on a formvar coated grid, the n-butanol allowed to evaporate and the grid coated with a fine layer of carbon to permit sample stability in the electron beam. The sintered sample was originally in powder form, therefore, the crushing stage was omitted.

The prepared grids were then examined using a Hitachi HU-11E transmission electron microscope. Several photographs of each sample were used in obtaining a particle size distribution. The micrographs in Figures 2 and 3 are of two separate samples from the same catalyst batch. In Figure 2 the catalyst had been reduced at 450° C and passivated at room temperature before being micrographed.

In Table 4 the number per cent of particles is given for each size range. For the fresh sample 76% of the particles are less than 37 Å, but only 18% are less than 37Å for the sintered sample. It appears that in the sintered sample the larger particles grew at the expense of particles in the lower size ranges. The particle distribution in the fresh sample is very steep with most particles less than 37 Å and none more than 67Å. However, the sintered sample has a very broad particle distribution with particles less than 30 Å and greater than 100 Å. This suggests that the mechanism for sintering may be atomic migration (6) since redispersion occurs in the particle size range of <30 Å and because growth occurs above 50 Å where continued growth by metal crystallite growth might not be possible.

Task 2: Activity Testing and Support Geometry Design

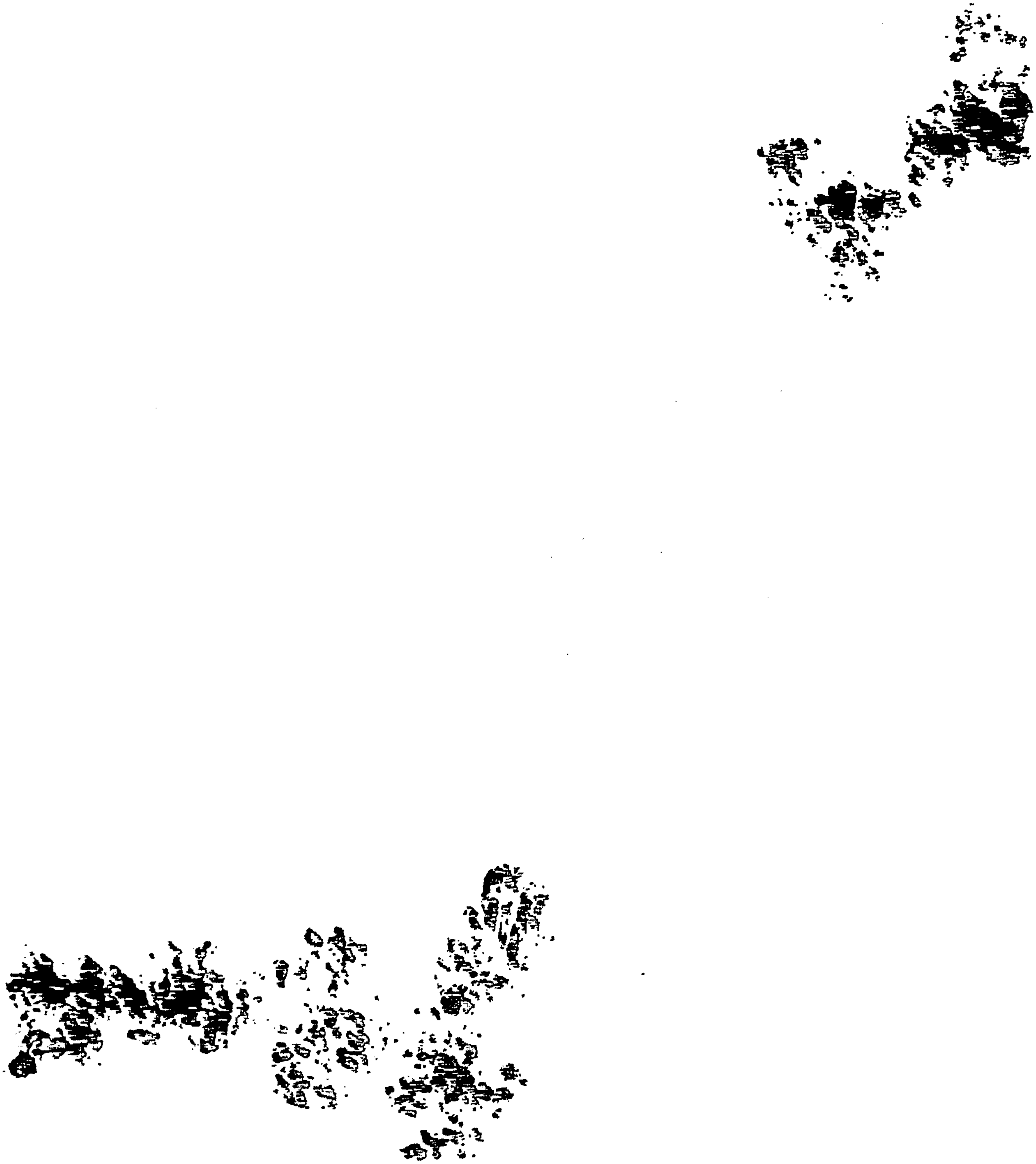

Figure 2. Electron Micrograph of Fresh Ni-A-119 (15% Ni) 295,000 x.

Figure 3. Electron Micrograph of Sintered Ni-A-119 (15% Ni) 295,000 x.

Table 4

Particle Size Distributions for Ni-A-119 Before and After Sintering Measured by Electron Microscopy

Sample	Treatment	Percent Particles in each Size Range[1]								Mean[2]
		<30	30-33	34-37	38-53	54-67	68-83	84-100	>100	Diameter
Ni-A-119	Reduced and passivated	23	29	24	19	5	---	---	---	37
Ni-A-119	Sintered at 750°C	11	6	1	18	29	9	14	12	93

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[1] Size Ranges are in Å (10^{-10} m).

[2] Mean diameter is surface-averaged mean, expressed in Å.

1. Support Geometry Tests:

Conversion vs. temperature tests were conducted on three nickel on alumina monolithic catalysts: Ni-AM-101, Ni-AM-102, and Ni-AM-201. These tests are summarized in Table 5 along with the results of some previously reported tests (3). Figure 4 is a representative example of the results of these tests. The test conditions included a space velocity of 30,000 hr^{-1}, a reaction mixture of 95% N_2, 4% H_2, and 1% CO, and a pressure of 20.5 psia.

From Table 5 it can be seen that the three alumina monoliths tested compare fairly well with one another, with the triangular channeled monolith being slightly more selective to methane and having a slightly lower rate per gram catalyst for methane production.

Table 5 also shows how the nickel on alumina monolith catalysts compare with other monolithic catalysts previously tested in this laboratory. It appears as though the nickel on alumina catalysts are less selective towards methane than are the alumina-coated monoliths. The difference in selectivity may be due to diffusional effects.

Also from Table 5 it can be seen that the rates per gram catalyst for the nickel on alumina monoliths are much larger than the rates of the other catalysts at 325°C. This can be explained by the smaller catalyst density of the alumina monolith relative to the cordierite monolithic support. Therefore, since all of the catalysts tested had the same volume and approximately the same nickel loading, the rate of reaction based on catalyst volume is actually less for the alumina monolith catalysts. This is to be expected since there is actually less nickel per volume contained in the nickel on alumina monolith catalysts (see Table 6), moreover, a smaller precentage of the nickel is available for reaction in the alumina monolith catalysts since the reaction encounters mass transfer limitations at 325°C.

2. Steady State Carbon Deposition Tests:

The reaction conditions for the monoliths were necessarily different from those employed for powdered catalysts. There was no apparent carbon depositions at H_2:CO of 2 or 3 when the carbon monoxide concentration was 1%. Accordingly it was necessary to increase CO concentration and space velocity, the latter to avoid high conversions and high pressures of water at the surface. In order to increase the space velocity and prevent iron carbonyl formation, the reaction was carried out in a glass sample cell with a preheater section, rather than in the stainless steel reactor. Also, the effective volume of the catalyst sample was reduced by sealing off most of the channels with cement in order to provide a high space velocity. The difficulties encountered previously in testing powdered samples were avoided by using a fresh molecular sieve trap to prevent iron carbonyl from the CO cylinder from entering the reaction cell.

Accordingly, each of the monolithic catalysts samples listed in Table 7 was exposed to 5% CO and 10% H_2 for an extended period of time at 400°C and tested for methanation activity. Activity, the

Table 5

Temperature Conversion Tests for Monolithic Catalysts

GHSV = 30,000 hr^{-1}; Reactant Composition: 95% N_2, 4% H_2, 1% CO; 20.5 psia

Catalyst[b]	Temperature for CO Conversion of		At 95% CO Conversion % CO converted to		At 325°C	
	50%	95%	CH_4	CO_2	% CO converted to CH_4	Rate of CH_4 Formation (moles/gram-sec x 10^7)
a. Monoliths having 200 square channels per square inch						
Ni -AM-101	265	310	73	14	78	80
Ni -AM-102	270	320	77	10	78	74
Ni-M-151[a]	245	295	93	6	93	36
Ni-M-154[a]	260	310	83	5	93	37
b. Monoliths having 236 triangular channels per square inch						
Ni -AM-201	265	205	80	11	86	71
Ni-M-250[a]	250	320	87	7	86	44
Ni-M-252[a]	250	300	86	10	92	47
Ni-M-254[a]	255	300	83	10	91	46

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[a] Previously reported catalysts (3), nickel impregnated on alumina layer on cordierite monolith catalyst support.

[b] For compositions see Table 6.

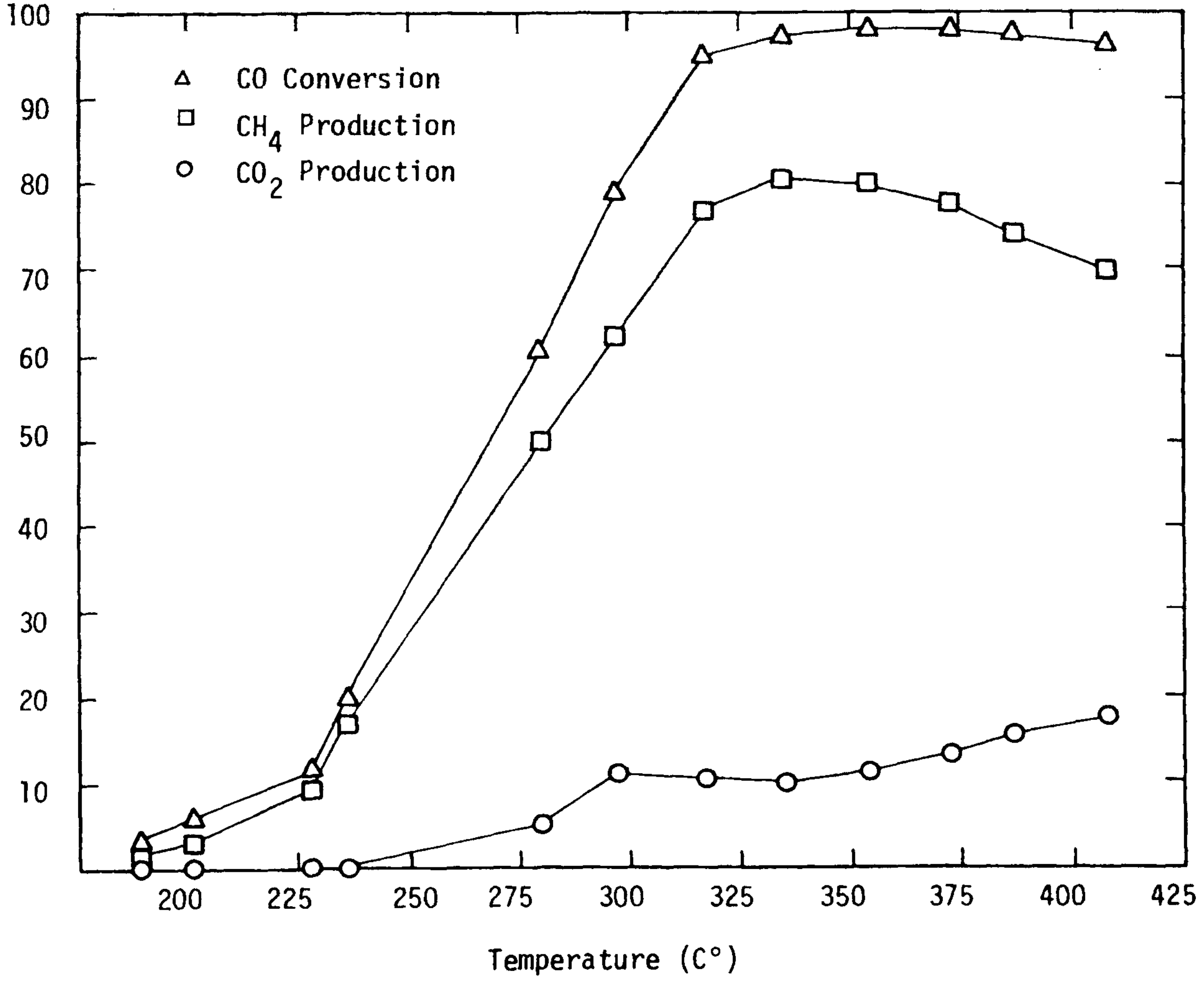

Figure 4. Conversion vs. temperature for Ni-AM-201 (20.5 psia, GHSV = 30,000 hr^{-1}).

Table 6

Catalyst Weights, Densities and Total Nickel

Catalyst	Weight (grams)	Volume (ml's)	Wt.% Nickel	Density (g/ml)	Total Nickel (grams)
Ni-AM-101	2.380	6.3	29.7	0.378	0.707
Ni-AM-102	2.622	6.3	27.8	0.416	0.729
Ni-M-151	5.651	6.3	19.1	0.897	1.08
Ni-M-154	5.538	6.3	18.6	0.879	1.03
Ni-AM-201	2.580	6.3	25.5	0.409	0.658
Ni-M-250	4.556	6.3	22.2	0.723	1.011
Ni-M-252	4.469	6.3	21.8	0.709	0.974
Ni-M-254	4.555	6.3	21.7	0.723	0.988

Table 7

Results of Carbon Deposition Tests of Monolithic-Supported Nickel and Nickel Bimetallic Catalysts
(Deposition occured at 400°C, 75,000 hr^{-1} GHSV, 85% N_2, 10% H_2, 5% CO.
Activity was measured at 250°C, 80,000 hr^{-1} GHSV, 95% N_2. 4% H_2, & 1% CO)

Catalyst	Composition	Fresh Methane* Turnover Number	Time (hr.)	Fouled Turnover Number	Fouled Activity
Ni-M-121	6% Ni, 20% alumina 74% ceramic	36.6	4.5 16.5	13.7 14.7	.37 .40
Ni-Co-M-106	4.8% Nickel 4.8% Cobalt 19.6% alumina 70.8% ceramic	17.8	4.25 23.0	13.3 14.6	.75 .82
Ni-MoO_3-M-101	4% Nickel 4% Molybate 20% alumina 72% ceramic	43.5	12.0 22.8	4.6 1.75	.11 .04
Ni-Pt-M-109	10.3% Nickel .55% Platinum 19.7% alumina 69.5% ceramic	11.1	11.0 17.0	12.2 11.0	1.10 .99
Ni-Ru-M-112	10% Nickel 1% Ruthenium 18.5% alumina 70.5% ceramic	2.37	21.5 24.0	1.36 1.75	.57 .74

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*Turnover numbers are expressed as molecules of methane formed per active site per second.

ratio of fouled rate to fresh rate, is plotted in Figure 5 as a function of time. Activity was measured before and after exposure and at one intermediate time by lowering the temperature to 250°C adjusting the flow to the normal reaction mixture.

The data in Figure 5 and Table 7 show that except for Ni-Pt all of the catalysts lost more than 25% of their initial activity within the first 12 hours. Based on these data the order of decreasing resistance to carbon deposition is Ni-Pt > Ni-Co > Ni-Ru > Ni > Ni-MoO_3. These results are in qualitative agreement with results of carbon deposition tests reported earlier for pellet-supported catalysts having about the same nominal compositions (3). Apparently Ru, Co, and Pt act in combination with nickel as promoters to slow the rate of carbon deposition. Pt is the most effective, especially in view of its very low concentration in the Ni-Pt catalyst of only 0.6 wt.% (3).

An attempt to regenerate the deactivated nickel-molybdate monolith was made using hydrogen at 300°C for six hours. The turnover number for methanation following this treatment was 4.9×10^{-3} molecules/site/second. This value is a factor of 3 larger than the value of 1.75 reported after 24 hours but unfortunately still a factor of 10 lower than the initial metal activity. While oxygen treatments are generally used to burn off carbon deposits, it is interesting that hydrogen alone can restore activity to 10% of the initial activity.

3. In situ H_2S Tolerance Tests:

a. Pelleted Samples. H_2S in situ poisoning tests were conducted on 7 Ni and Ni bimetallic catalysts. All tests were conducted at 250° C with a GHSV of 30,000 hr^{-1} and a reactant gas mixture of 95% N_2, 4% H_2, 1% CO and 10 ppm H_2S, using 0.1 cm^3 powdered catalyst samples.

The activity (poisoned rate/fresh rate) versus time is plotted in Figures 6 and 7 for 3% Ni/Al_2O_3 and 20% Ni-Co respectively and smoothed curves are plotted in Figure 8 for each of the catalysts. A brief summary of the data is listed in Table 8. It can be seen that the high loading catalysts are poisoned much more slowly than the low loading catalysts. For the high loading catalysts the order of decreasing sulfur tolerance is apparently Ni > Ni-Co > Ni-Pt. For the 3-5 wt.% catalysts: Ni-MoO_3 > Ni = Ni-Rh > Ni-Ru.

All of the catalysts tested remained active longer than we had anticipated. For the Ni-Rh-A-100 catalyst (2.5% Ni, 0.5% Rh) the original H_2 uptake was 19.0 micromoles/gram. Assuming 0.75 sulfur atoms per surface Ni atom (7) and a GHSV of 30,000 hr^{-1} with 10 ppm H_2S it should take 1.0 hours to saturate the catalyst if there were no sulfur breakthrough. The sulfur content in the exit stream was analyzed by wet chemical techniques during this run. After 1.25 hours only a small fraction of the sulfur was breaking through, as can be seen in Figure 9. However, the activity had not dropped significantly at this point. Since there was still activity remaining, some of the sulfur must have been absorbed somewhere other than the active metal surface sites. Perhaps sulfur is absorbed into the bulk metal,

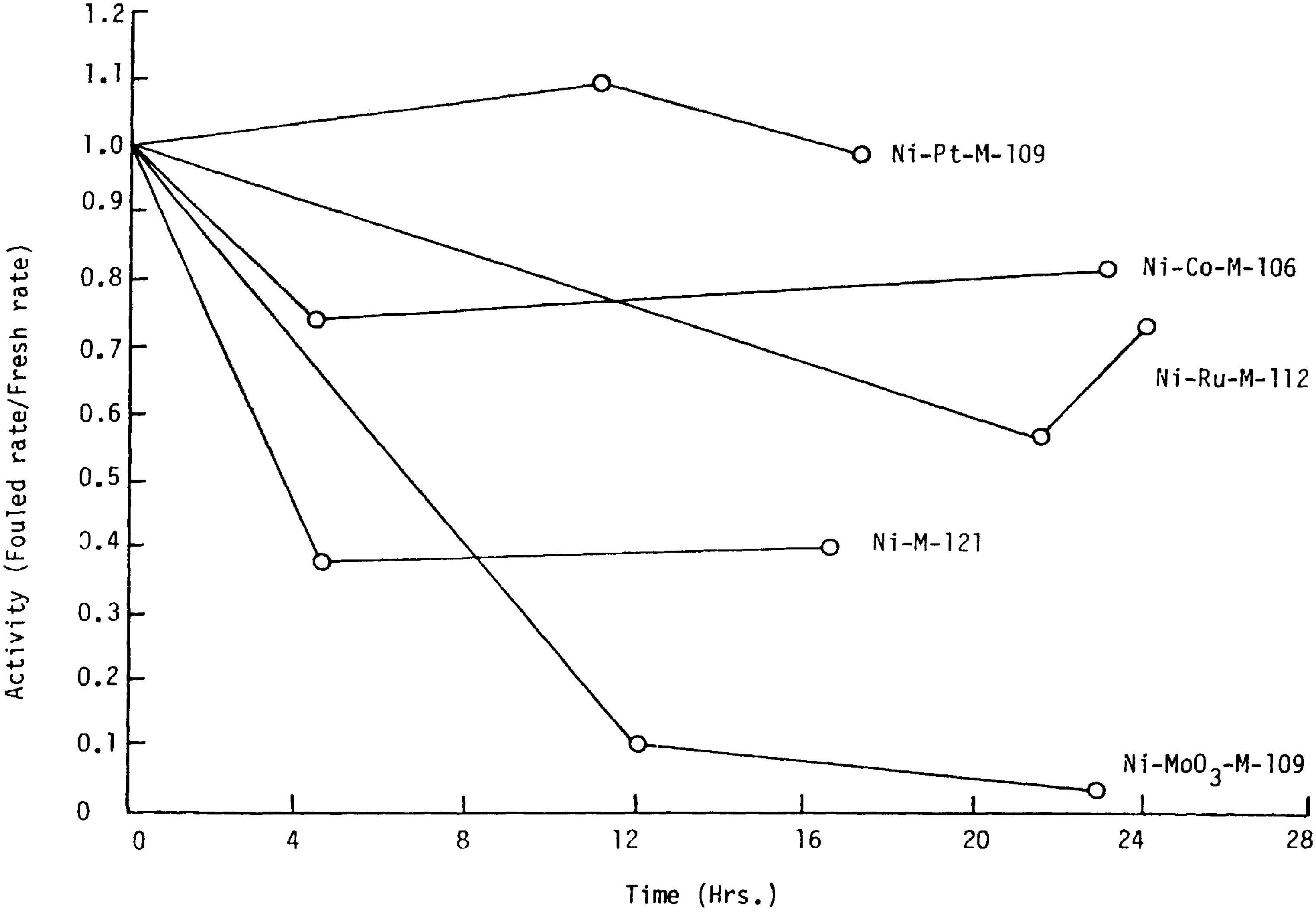

Figure 5. Activity versus Time during Carbon Deposition Tests for Various Monolithic Catalysts (Test Conditions: 400°C, 75,000 hr^{-1} GHSV, 1 atm, 85% N_2, 10% H_2, 5% CO. Activity measured at: 250°C, 80,000 hr^{-1} GHSV, 1 atm, 95% N_2, 4% H_2, 1% CO, 1 atm).

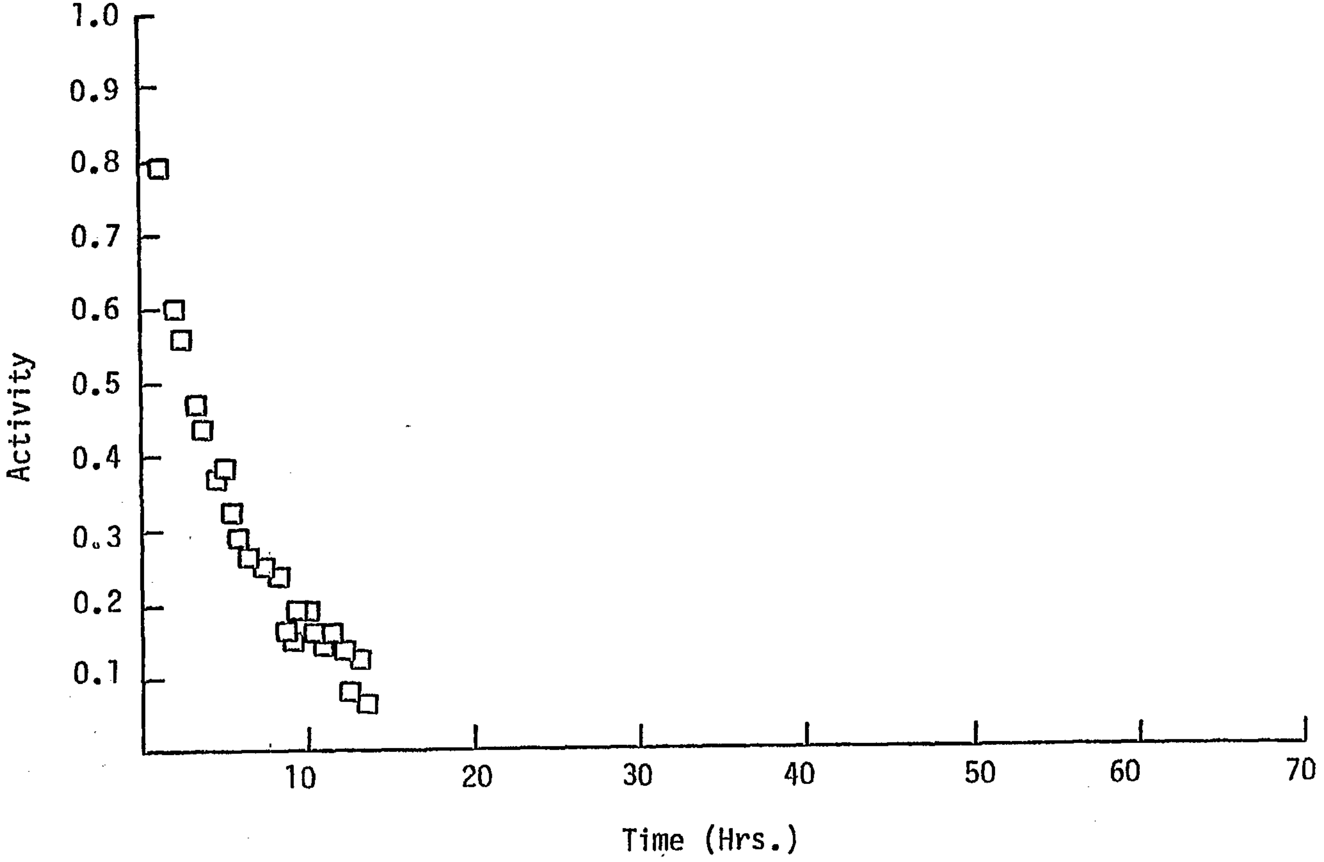

Figure 6. Methanation Activity (Poisoned rate/Fresh rate) for 3% Ni/Al_2O_3 (Ni-A-112) as a Function of Exposure Time to a Reaction Mixture Containing 10 ppm H_2S in 1% CO, 4% H_2 and 95% N_2 (GHSV = 30,000 hr^{-1}, 1 atm).

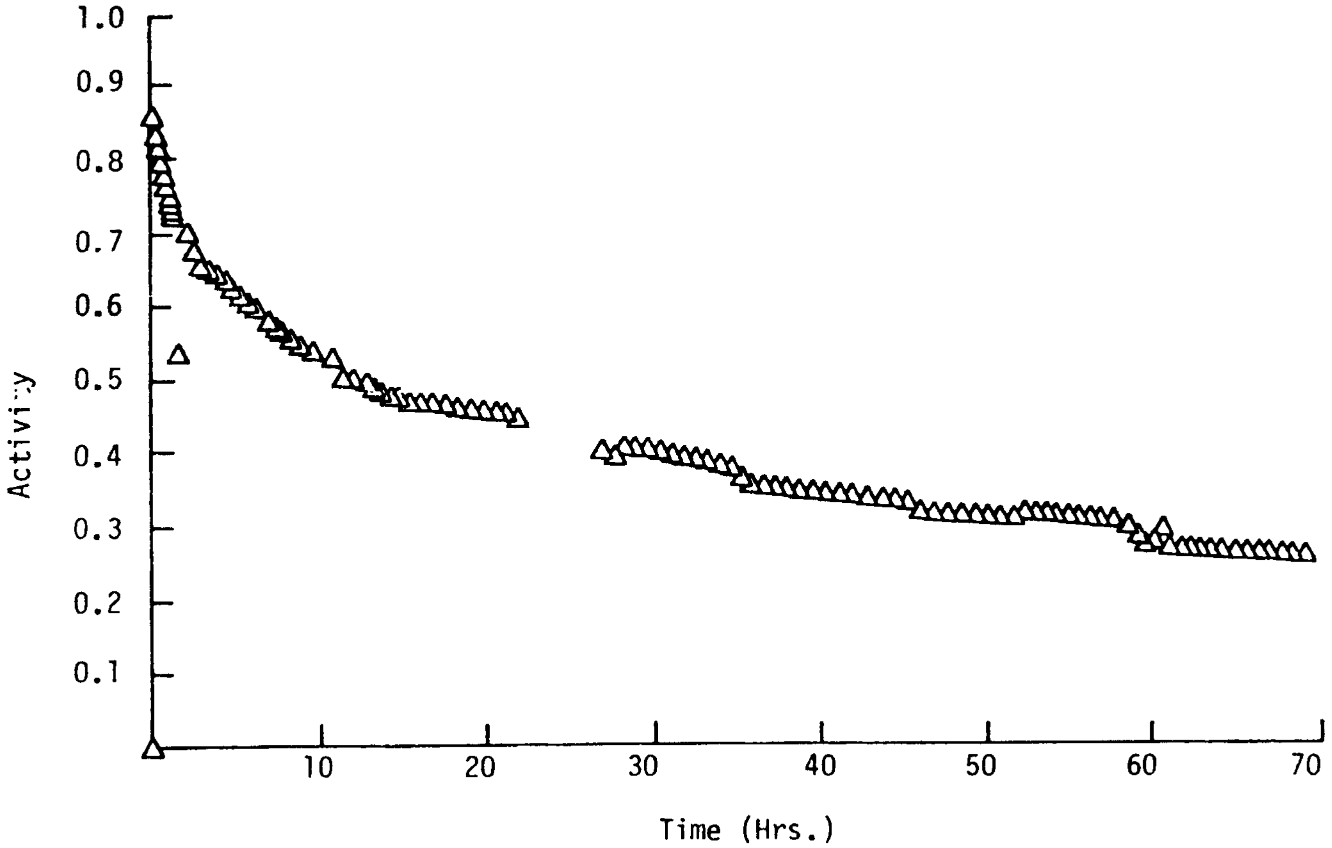

Figure 7. Methanation Activity (Poisoned rate/Fresh rate) for 20% Ni-Co/Al$_2$O$_3$ (Ni-Co-A-100) as a Function of Exposure Time to a Reaction Mixture Containing 10 ppm H$_2$S in 1% CO, 4% H$_2$, and 95% N$_2$ (GHSV = 30,000 hr^{-1}, 1 atm).

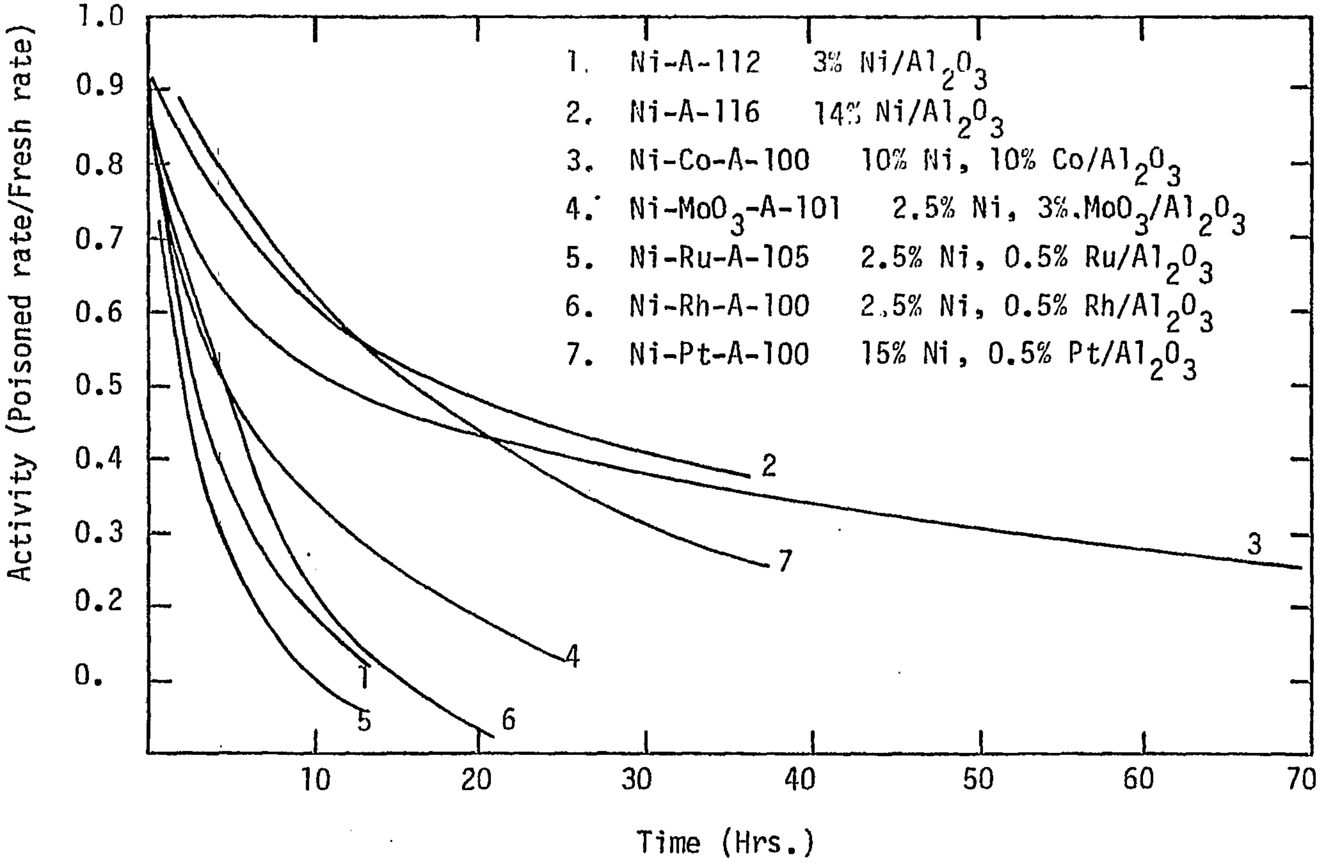

Figure 8. Smoothed Activity-Time Curves for Powdered Alumina-supported Nickel and Nickel Bimetallics during Exposure to 10 ppm H_2S in 1% CO, 4% H_2, and 95% N_2 (GHSV = 30,000 hr^{-1}, 1 atm).

Table 8

Effects of In Situ H_2S Poisoning on Activity of Powdered Alumina-Supported Nickel and Nickel Bimetallics at 250°C
(Space velocity of 30,000 hr^{-1}; Feed: 1% CO, 4% H_2, 10 ppm H_2S, 95% N_2)

Catalyst	Fresh Rate (Molecules/site sec)	Time to Reach activity=1/2[a] (hours)	Time to Reach activity=1/4[a] (hours)
Ni-A-112	10.6×10^{-3}	3	7.5
Ni-A-116	8.3	19	---
Ni-Co-A-100	10.6	12.5	70
$NiMoO_3$-A-101	12.5	5.0	15
Ni-Ru-A-105	6.7	2	5
Ni-Rh-A-100	8.0	5.5	9
Ni-Pt-A-100	7.7	16	36

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[a] activity = poisoned rate/fresh rate

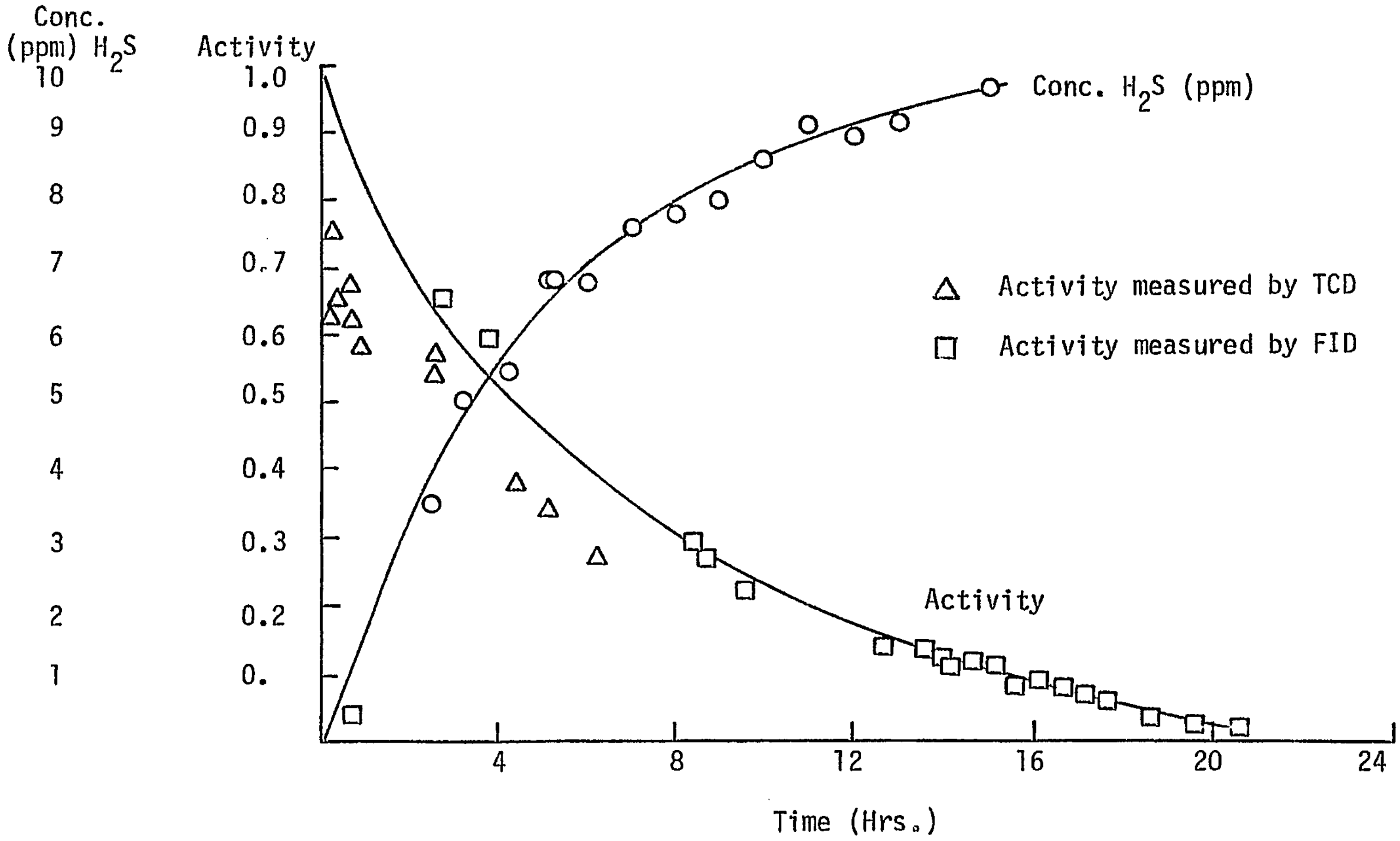

Figure 9. Activity and H_2S Concentration in the Reactor Outlet as a Function of Time for 3% Ni-Rh/Al_2O_3 (Ni-Rh-A-100) during Exposure to 10 ppm H_2S in 1% CO, 4% H_2 and 95% N_2 (GHSV = 30,000 hr^{-1}, 1 atm).

or adsorbed onto the support.

Numerous attempts were made to regenerate the poisoned catalysts by heating them in pure H_2 or H_2/CO mixtures. Hydrogen uptakes were measured before each run and after selected runs. Uptakes after poisoning were found to be zero for all samples tested. After treating the catalyst in H_2 at 450 °C for 12-24 hours it was possible to recover 5-15% of the original H_2 uptake. In no case, however, was any methanation activity recovered. In fact after treatment at 450°C the activity dropped to zero, even when samples were tested at elevated temperatures. Treatment in H_2 at 250°C also resulted in further loss of activity, although, samples were active when tested at high temperatures.

After poisoning the Ni-Ru-A-105 sample for 13 hours the activity had dropped to 0.07. The H_2S was then shut off and the temperature raised to 360 °C. Samples taken every 6-8 minutes showed that activity was falling with time. After 40 minutes the temperature was raised to 420 °C. Over the next 2 hours the activity fell by a factor of three. It is interesting that a hydrogen regeneration treatment recovered some of the H_2 uptake capacity but completely deactivated the catalyst. Based upon our NSF investigation of sulfur adsorption (5) we can speculate the sulfur causes the catalyst to undergo a surface reconstruction or phase transformation to a totally inactive nickel sulphide. This change apparently occurs to a greater extent at higher temperatures.

b. Monolithic Catalysts. Each of the monolithic catalysts listed in Table 9 was tested at 250°C for methanation activity before, during and after exposure to 10 ppm hydrogen sulfide. The usual reaction mixture of 95% N_2, 4% H_2, and 1% CO was combined in a 9:1 volume ratio with a stream of 90 ppm H_2S in nitrogen so as to provide a space velocity of 30,000 hr^{-1} and a reactor inlet concentration of 10 ppm H_2S. The nominal catalyst compositions, fresh and poisoned turnover numbers and the time exposed to H_2S are listed in Table 9. Activity, defined as the ratio of the poisoned rate to the fresh rate is plotted as a function of time in Figures 10 and 11 for Ni-M-117 and Ni-Co-M-105 respectively. Smooth curves of activity versus time are plotted in Figure 12 for all of the monolithic catalysts tested.

That data in Table 9 and Figure 12 show that during in situ exposure to 10 ppm H_2S at 250 °C all of the catalysts lose approximately 40-50% of their initial activity within 20 hours. Before exposure to H_2S the order of specific activity for methane production is Ni-MoO_3 > Ni-Co > Ni > Ni-Ru > Ni-Pt. However, after 20 hours exposure to 10 ppm H_2S at 250°C the order of activity is Ni-MoO_3 > Ni > Ni-Co > Ni-Ru > Ni-Pt. Apparently, Ni-Co deactivates at a slightly faster rate than Ni.

Comparison of the data in Table 9 for monoliths with the data in Table 8 for pellet catalysts (high metal loading samples) shows that monolithic-supported Ni-Co is slightly more sulfur tolerant than the pellet-supported Ni-Co. That is, 50% activity is lost in 12.5 hours for pelleted Ni-Co compared to less than 17 hours for the monolithic Ni-Co. Pellet-supported and monolithic-supported Ni and Ni-Pt behave about the same losing 50% activity after about 20 hours. These results

Table 9

Effects of In Situ Poisoning on the Activities of Nickel Bimetallic Monolithic Catalysts with 10 ppm H_2S at 250°C (30,000 hr^{-1} GHSV, 95% N_2, 4% H_2, 1% CO)
(Turnover number = μmole CH_4 produced per active site per sec)

Catalyst	Nominal Composition	Fresh Turnover No.	Poisoning Time	Poisoned Turnover No.	Activity after Poisoning
Ni-M-117	12% Nickel, 20% alumina, 68% ceramic	23.4	20	12.2	0.52
Ni-Co-M-105	5.5% Nickel, 5.5% Cobalt, 18.5% alumina 70% ceramic	25.5	17.1	10.7	0.42
Ni-MoO_3-M-111	6% Nickel, 6% MoO_3 20% alumina 68% ceramic	41.5	20.2 42.8	18.2 14.7	0.44 0.35
Ni-Pt-M-107	0.58% Platinum 11% Nickel 20% alumina 68% ceramic	17.7	20.2 26.7	8.8 8.2	0.50 0.46
Ni-Ru-M-108	5.8% Nickel 1.2% Ruthenium 19.3% alumina 74% ceramic	18.7	12.1 19.6	10.9 10.2	0.58 0.54

Turnover Number = molecules CH_4 formed per second per fresh H chemisorption site.

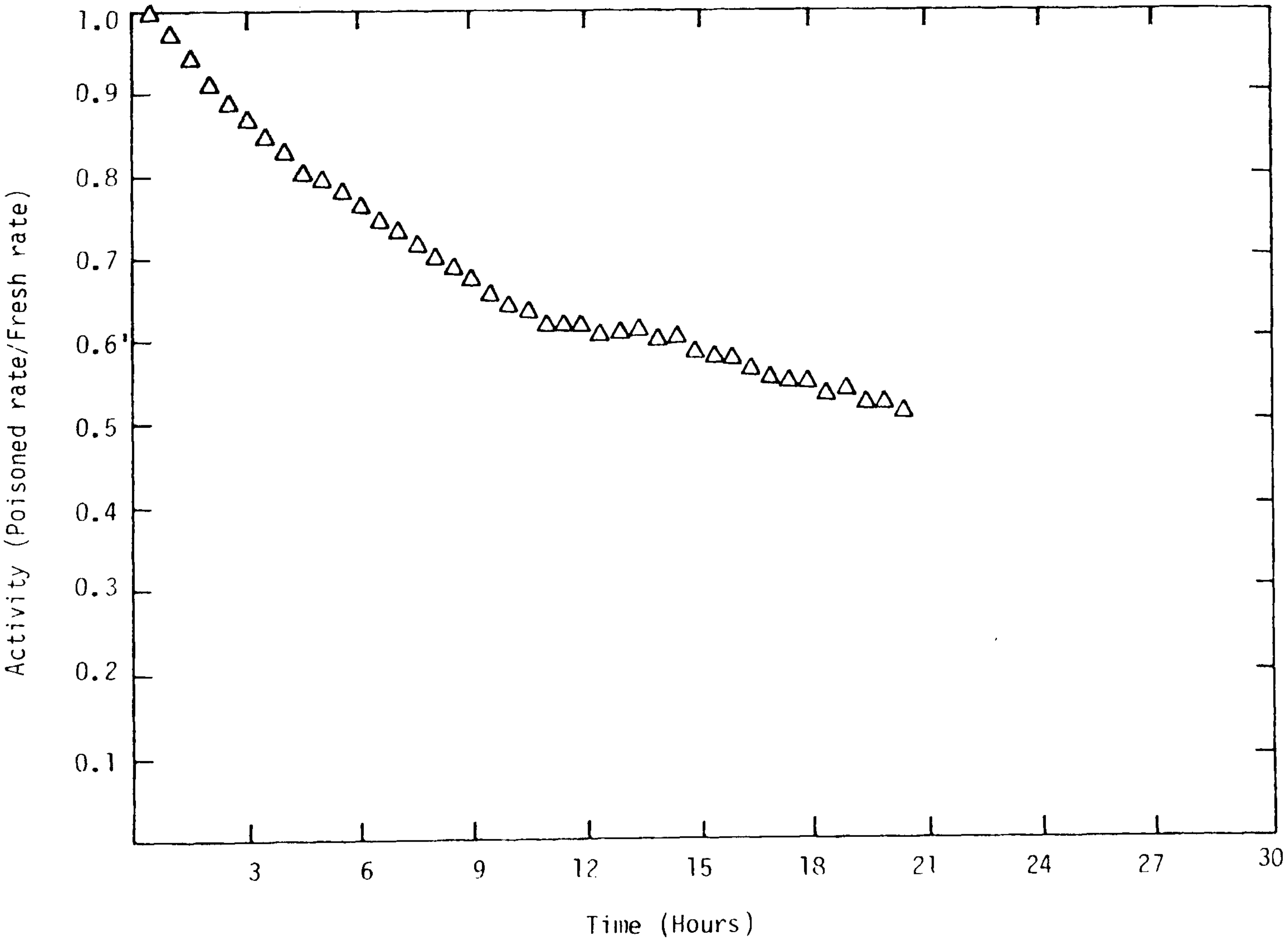

Figure 10. Methanation Activity (Poisoned rate/Fresh rate) for Ni-M-117 as a Function of Exposure Time to a Reaction Mixture Containing 10 ppm H_2S in 1 CO, 4% H_2, and 95% N_2 (GHSV = 30,000 hr^{-1}, 1 atm)

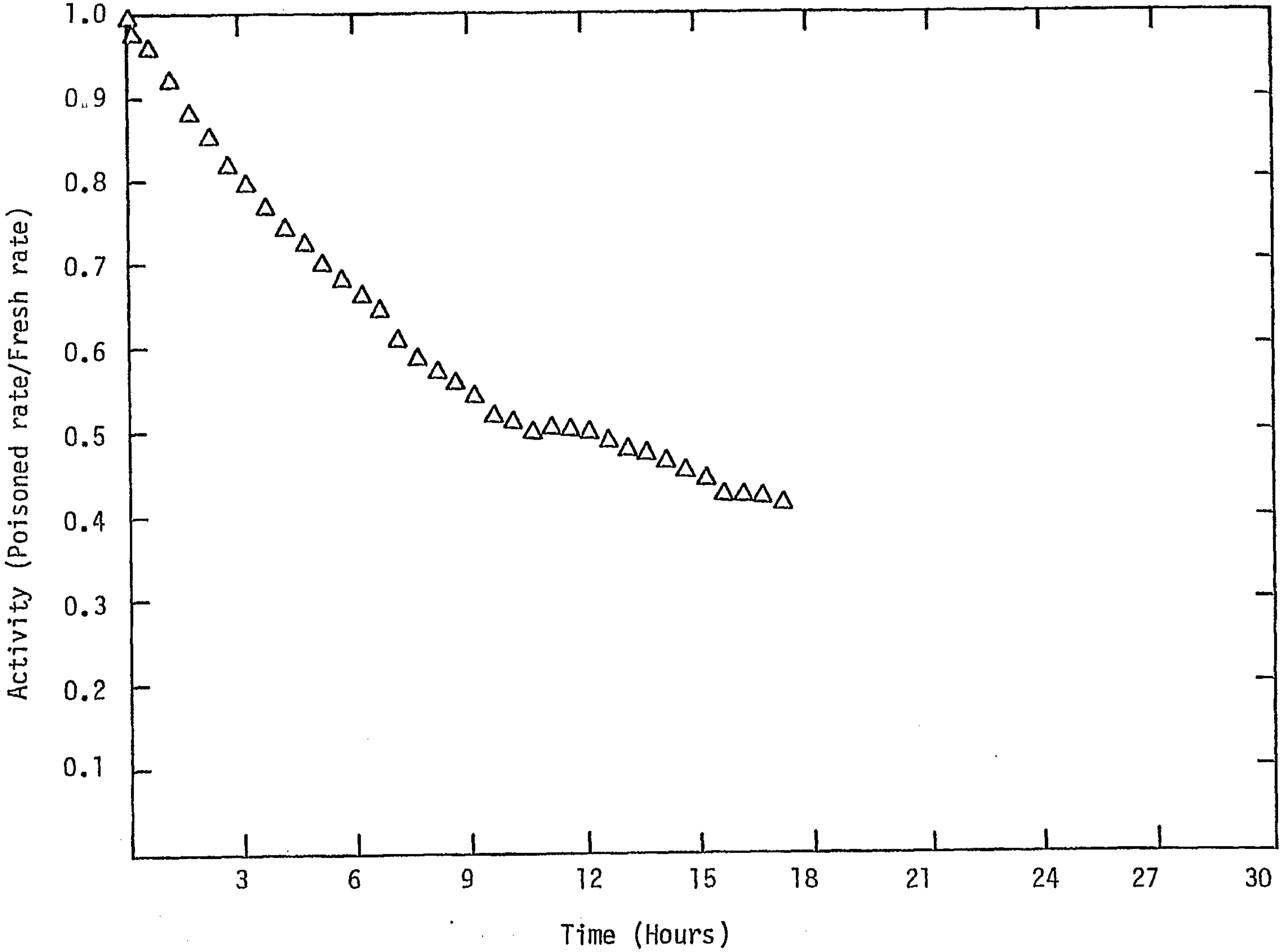

Figure 11. Methanation Activity (Poisoned rate/Fresh rate) for Ni-Co-M-105 as a Function of Exposure Time to a Reaction Mixture Containing 10 ppm H_2S in 1% CO, 4% H_2, and 95% N_2 (GHSV = 30,000 hr^{-1}, 1 atm).

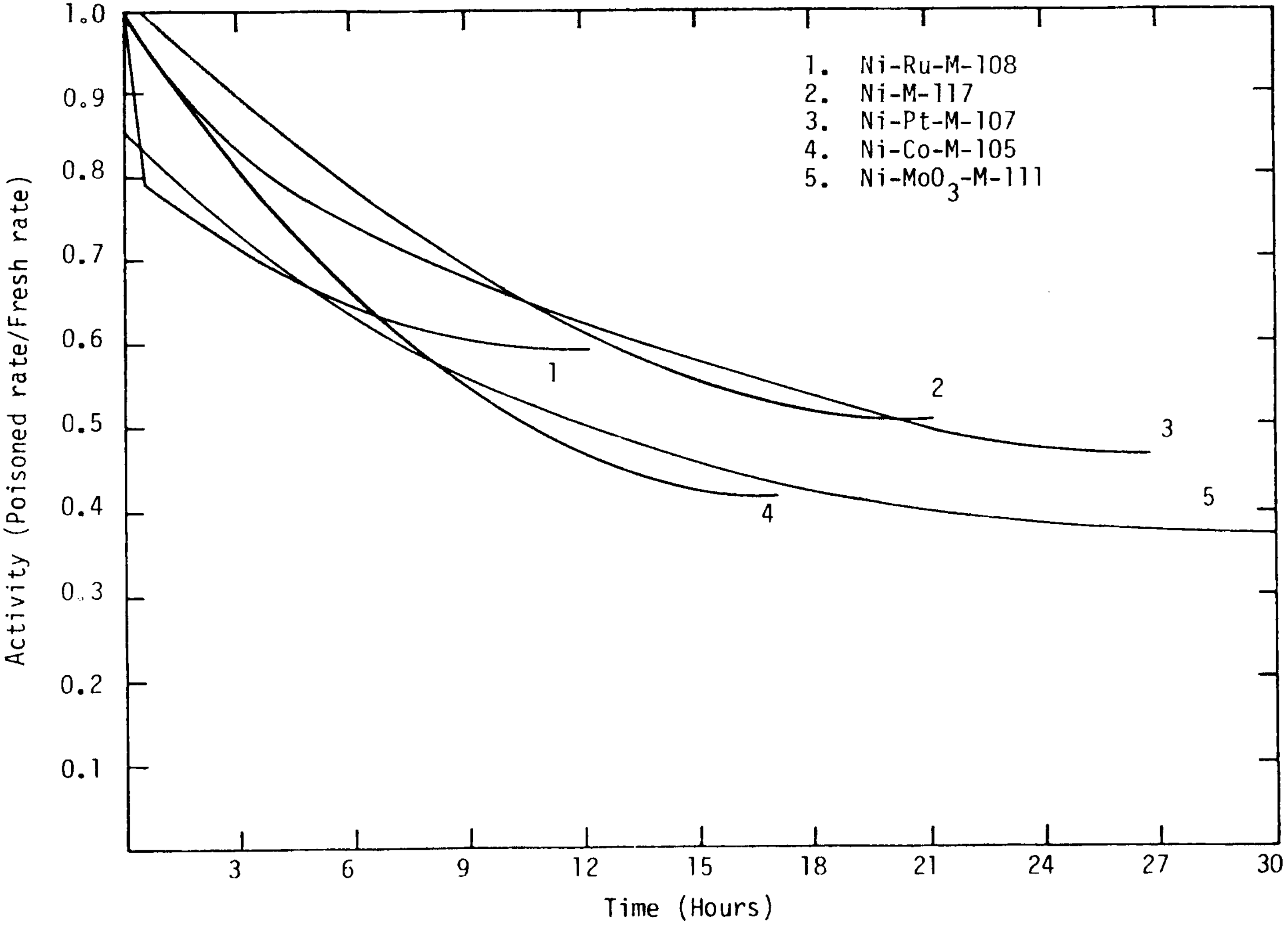

Figure 12. Smoothed Activity-Time curves for Monolithic-Supported Nickel and Nickel Bimetallics during Exposure to 10 ppm in 1% CO, 4% H_2, and 95% N_2 (GHSV = 30,000 hr^{-1}, 1 atm.)

are quite sigificant because they suggest that monolithic catalysts are at least as tolerant to sulfur poisoning as pellet catalysts and perhaps more so because these monolithic catalysts contain 30-40% less active metal by weight.

Attempts to regenerate sulfur poisoned monolithic catalysts in flowing pure hydrogen met with different results than with pelleted catalysts. The monoliths heated in the presence of the reaction mixture for up to 4 hours at various temperatures between 250 and 400°C did not lose additional activity beyond that which had occurred during the poisoning test.

4. Forecast for the Next Quarter:

During the next quarter the results of conversion-temperature, sulfur poisoning and carbon deposition tests will be written in a form suitable for journal publication. The investigation of monolithic-supported catalysts of different geometry will continue. Work will be initiated to extend the *in situ* sulfur poisoning and carbon deposition tests to catalysts spheres, since effects of catalyst geometry in tests of powder and monolith samples are evident. Effects of reactant steam on the conversion-temperature behavior of Ni/Al_2O_3 at high pressure will also be investigated.

Task 3: Kinetic Studies

Work on Task 3 has dealt primarily with ordering major equipment for the new high pressure reactor system (Figure 13). The major component of the high pressure mixed flow system is a Berty-type constant volume mixed flow reactor. This reactor has been received from Autoclave Engineering. It is constructed of 316 stainless steel and has a pressure rating of 2000 psia at 1000°F. Other major equipment which has been ordered includes: high pressure flow meters, CO and H_2S detector alarms, and a high pressure compressor. The flow meters are Tylan FM-361 mass flowmeters, pressure tested to 2500 psi in the flow range from 0 to 20 slpm. It was decided to use premixed gas tanks for the feed gases to the system. This will allow for a simpler experimental design and for fewer flow meters to monitor the flow. To premix the gases, a small high pressure gas booster compressor, Haskell Engineering AG75-C, has been purchased.

Analysis of the reactant and product gases will be done with a Perkin-Elmer Sigma I Gas Chromatograph. This chromatograph which will have capabilities for analyzing sulfur compounds, hydrocarbons, and fixed gases has been ordered and delivery is anticipated in January.

This high pressure reactor system will be built, and tests are scheduled to begin on it during the next quarter.

Task 4: Degradation Studies

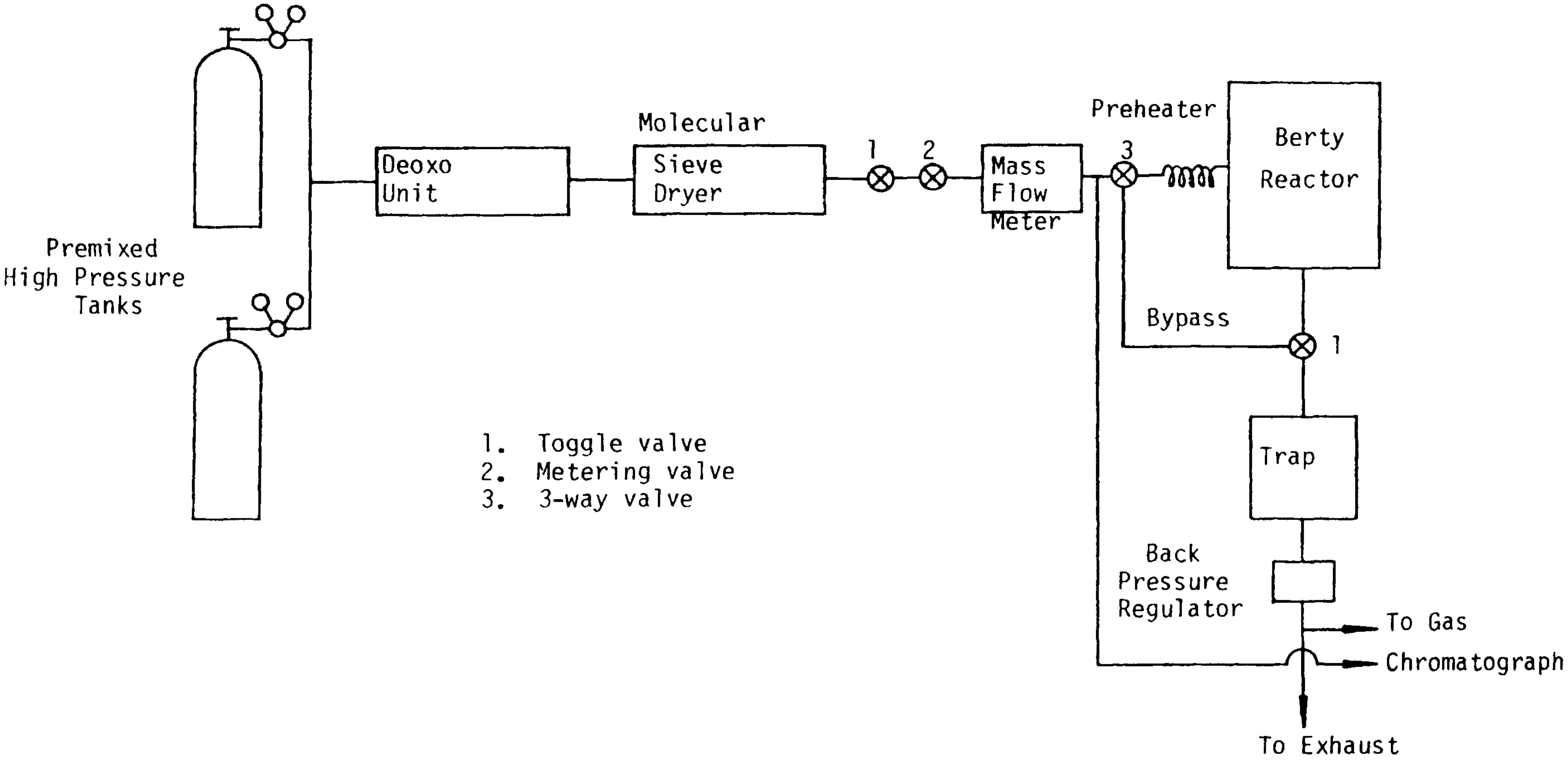

Figure 13. High Pressure Mixed Flow Reactor System, R-2 (Berty Autoclave Design).

Accomplishments in Task 3 were primarily the designing and ordering of a new quartz reactor system (Figure 14). The major component of this system is a constant volume mixed flow quartz reactor according to the design of Katzer (4). This reactor and its heating mantle have already been received. The regulators, rotameter, and flow controller have also been received. This system will also use the Perkin-Elmer Sigma I Gas Chromatograph.

This system should be built, and tests will begin during the next quarter.

Task 5: Technical Interaction and Technology Transfer

On October 10, Dr. Bartholomew visited the University of Kentucky and the Institute for Mining and Minerals Research where he presented a seminar on methanation catalysis research at Brigham Young University. Arrangements were made with Phil Reucroft, Professor of Materials Science, and John Hahn, Associate Director of the Institute to exchange samples and provide each other with data on nickel catalysts. The Institute will perform ESCA and X-ray diffraction measurements on well-characterized nickel catalysts prepared at BYU and the BYU Catalysis Laboratory will measure methanation activities of the commercial catalysts under study at the Institute.

Dr. Bartholomew also attended the Fall Meeting of the California Catalysis Society held in Pasadena in Oct. 20-21 and presented a paper on sintering of Ni/Al_2O_3 catalysts. The meeting also provided opportunities to communicate with methanation researchers on recent developments, especially in the areas of sulfur poisoning and carbon deposition. Arrangements were made with Bob Lewis at Chevron to perform ESCA work on our $Ni-MoO_3$ catalyst. Dr. Lewis has the capability of reducing the catalysts in situ before running the spectra - a feature which is not yet available at the University of Utah where most of our work has been done.

On November the 8th, Professor Henry Dou of Le Centre National de la Recherche Scientifique (the French equivalent of NSF) visited our laboratory as part of a nationwide tour of research labs and universities. He presented a seminar on phase transfer catalysis dealing with reactions of an ammonium catalyst.

Dr. Bartholomew also made 2 visits this quarter to IITRI in Chicago to consult on a difficult nickel catalyst problem not unrelated to methanation.

Altogether these and other meetings, visits, discussions, and communications were helpful in keeping up-to-date while letting others benefit from our research.

During the coming quarter Dr. Bartholomew and a number of students will attend and participate in the 3rd Rocky Mountain Fuel Symposium to be held Feb. 10-11 in Albuquerque.

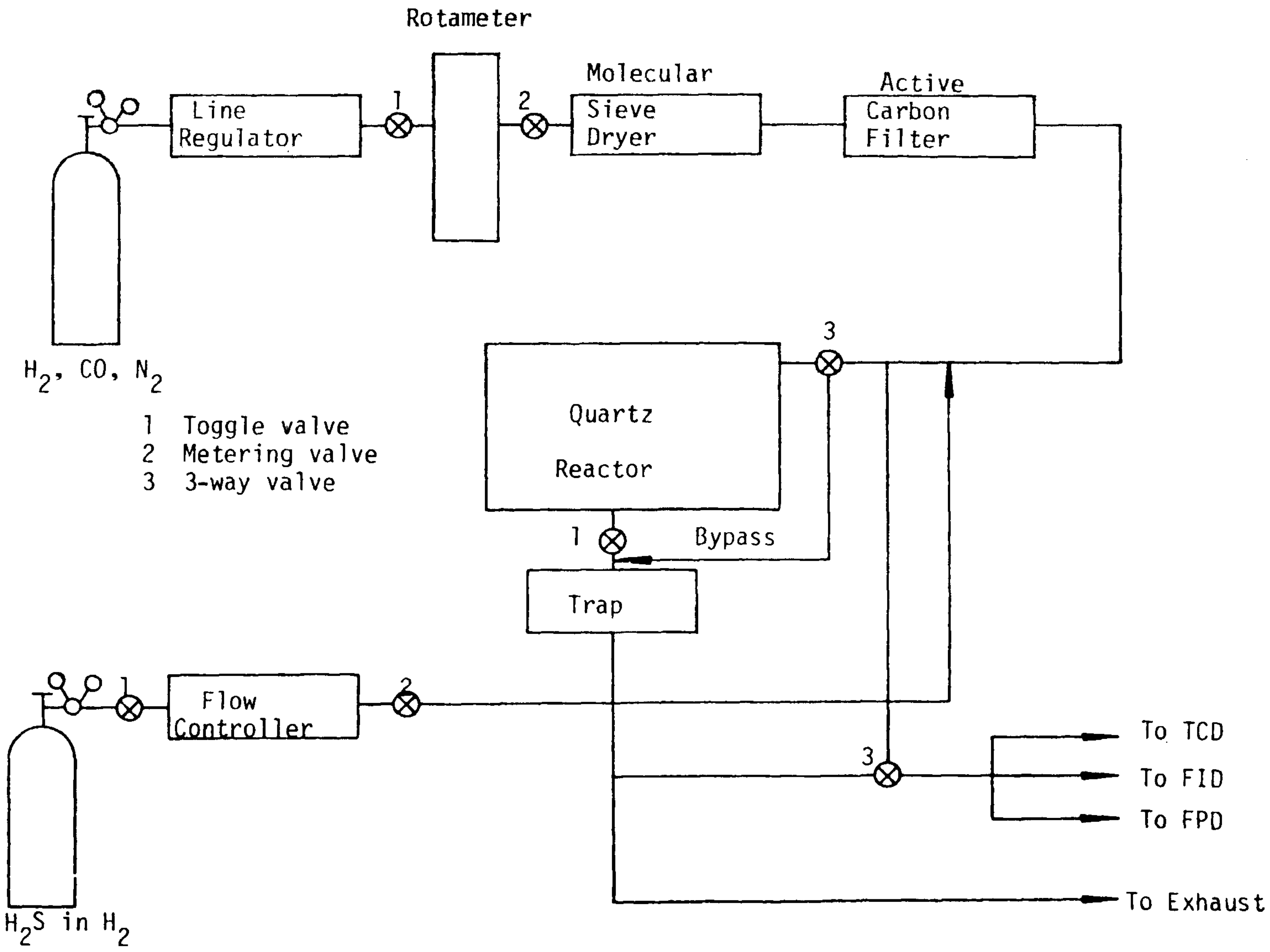

Figure 14. Quartz Mixed Flow Reactor System (R-3) for H_2S Poisoning and Low Pressure Kinetic Tests.

IV. CONCLUSIONS

1. In situ H_2S poisoning (10 ppm) of pelleted catalysts showed the order of poisoning resistance to be Ni > Ni-Co > Ni-Pt for high loading samples and Ni-MoO_3 > Ni = Ni-Rh > Ni-Ru for low loading samples. Attempts to regenerate the in situ poisoned catalysts with H_2 and H_2-CO mixtures failed. During treatment with H_2 or H_2-CO, there is probably a surface reconstruction or a phase transformation to a totally inactive metal sulfide.

2. In situ H_2S poisoning (10 ppm) of monolithic catalysts show the order of activity after poisoning to be Ni-MoO_3 > Ni > Ni-Co > Ni-Ru > Ni-Pt. Monoliths are at least as tolerant to H_2S poisoning as pelleted catalysts. Attempts to regenerate poisoned monoliths in H_2 and H_2-CO mixtures were likewise unsuccessful.

3. Carbon deposition tests for monolithic catalysts showed the order of resistance to carbon deactivation is Ni-Pt > Ni-Co > Ni-Ru > Ni > Ni-MoO_3 in qualitative agreement with previously reported tests for pelleted catalysts. Flowing H_2 can regenerate some activity after carbon deactivation.

4. H_2 chemisorption uptakes on alumina monolithic supported Ni showed better metal dispersions than alumina-coated cordierite supported Ni. Activity tests showed that the alumina monolithic catalysts had higher rates/gram but lower rates/catalyst volume and lower selectivities to methane.

5. Electron micrographs of a nickel catalyst before and after sintering showed that the fresh sample had a very steep size distribution, while the sintered sample had a very broad size distribution. The average particle diameter was 37 Å and 93 Å for the fresh and sintered samples, respectively.

V. REFERENCES

1. M. Greyson, "Methanation" in "Catalysts" Vol. IV., ed. P.H. Emmett, Rheinhold Pub. Corp., New York, 1956.

2. G.A. Mills and F.W. Steffgen, "Catalytic Methanation," Catalysis Reviews 8, 159 (1973).

3. C.H. Bartholomew, "Alloy Catalysts with Monolith Supports for Methanation of Coal-Derived Gases," Final Technical Progress Report Fe-1790-9 (ERDA), Sept. 6, 1977.

4. J.R. Katzer, private communication.

5. C.H. Bartholomew, "Alloy Catalysts with Monolith Supports for Methanation of Coal-Derived Gases," Quarterly Technical Progress Report FE-1790-7 (ERDA), FEb. 6, 1977.

6. S.E. Wanke and P.C. Flynn, "The Sintering of Supported Metal Catalysts," Catal. Rev.- Sci. Eng. 12, 93 (1975).

7. C.H. Bartholomew, Oliphant, J.L., Fowler, R.W., and Pannell, R.B., Journal of Catalysis, in press.

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16. Abstracts

The effects of carbon deposition and in situ exposure to 10 ppm H_2S during reaction on the methanation activity of pelleted and monolithic alumina-supported Ni, Ni-Co, Ni-MoO_3, Ni-Pt, Ni-Rh, and Ni-Ru were investigated during the past quarter. For monolithic supported catalysts the order of decreasing resistance to carbon deposition is Ni-Pt > Ni-Co > Ni-Ru > Ni > Ni-MoO_3. These results are in qualitative agreement with results of carbon deposition tests for pelleted catalysts. Activity tests made at 250°C and 1 atm with 10 ppm H_2S in the reactant mixture show that for pelleted catalysts the order of decreasing sulfur tolerance is Ni > Ni-Co > Ni-Pt (14-20 wt.% catalysts) and Ni-MoO_3 > Ni = Ni-Rh > Ni-Ru (3-5 wt.% catalysts). For the monolithic catalysts the order of activity following exposure to H_2S is Ni-MoO_3 > Ni > Ni-Co > Ni-Ru > Ni-Pt. Activity tests of nickel supported on pure alumina monoliths show these samples to be less selective and less active on a volume basis than wash-coated monolithic samples of Ni/Al_2O_3/cordierite. These and other significant results obtained during this past quarter are presented and discussed. An account of technical communications with other workers and visits to other laboratories is also included.

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