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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES. QUARTERLY TECHNICAL PROGRESS REPORT, DECEMBER 21, 1978-MARCH 20, 1979

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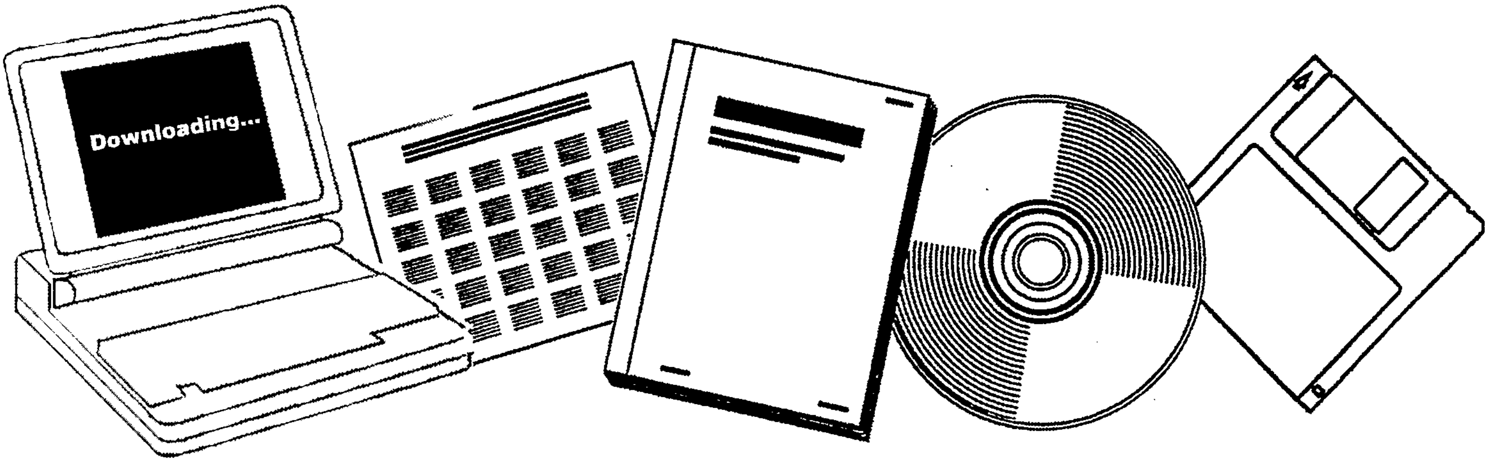

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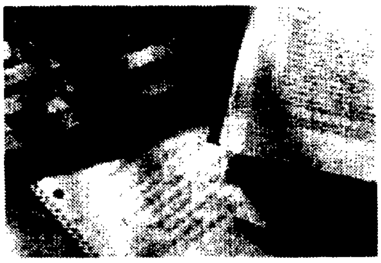

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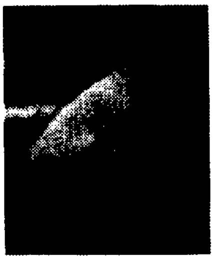

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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period December 21, 1978 to March 20, 1979

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FOREWORD

This report summarizes technical progress during the sixth quarter (December 21, 1978 to March 20, 1979) of a two-year 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: Erek Erekson, Ed Sughrue, Gordon Weatherbee, Don Mustard, and John Watkins. Mr. Erekson and Dr. Bartholomew were the principal authors. April Washburn and Steve Kvalve provided typing and drafting services. In this report data are reported in SI units.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

During the sixth quarter, carbon monoxide chemisorption measurements on Ni/Al_2O_3 catalysts showed large differences in CO uptake versus temperature of titration. No detectable $Ni(CO)_4$ was formed at CO titration temperatures of 273°K or below. Mixing tests and preliminary activity tests in the quartz CSTR (continuous-flow stirred tank reactor) showed the reactor system performance to be very near to that of an ideal mixed flow reactor and activity data obtained is quite comparable to previously reported work. Long term degradation tests with reactant steam showed no loss of activity over 24 h. Conversion versus temperature tests at two levels of reactant steam concentrations gave similar data. Carbon analysis of catalysts samples from long term degradation tests without steam showed that massive carbon lay-down occurred in decreasing quantities through the catalyst bed in the direction of flow. These and other pertinent data are reported and compared.

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 spectroscopy, 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 concentrations. 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 7500 kPa and 775 K 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-supported 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 (525-600 K) 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 (750-1000 K) 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 525 K 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.	475-675 K 140 kPa 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 2500 kPa.	475-675 K 2500 kPa 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 500 and 525 K (250,000 hr^{-1}) before and after an exposure of 24 hours at 675 K.	675 K (24 hrs.) 140 kPa 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.	525 K 140 kPa 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.	575-675 K 140 kPa 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 most task accomplishments are on schedule.

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

Task 1. Hydrogen chemisorptive uptakes were measured for three catalyst samples used in long term, high temperature tests. The carbon content of these samples was also determined. Carbon monoxide chemisorption measurements were performed at various temperatures on Ni/Al_2O_3 catalysts. The CO chemisorptive uptake was found to vary significantly with titration temperature. No $Ni(CO)_4$ formation was observed upon titration below 273 K.

Task 2. Several sponge monoliths of different geometries were ordered and received. These will be tested in the near future for methanation activity along with conventional ceramic monoliths of varying geometry.

Task 3. Mixing tests were performed on the quartz CSTR reactor. Good mixing is obtained at flows of 150 ml/min and less. Activity tests of nickel powders, pellets, and monoliths gave results in good agreement with previous work.

Task 4. A long term, high temperature test of Ni-A-122 (20% Ni/Al_2O_3) was performed with 29% steam added to the reactant gas. No decrease in CO conversion was observed over a 24 h period. In an additional conversion versus temperature test performed using 4% reactant steam results were very similar to those obtained in previous conversion-temperature tests.

Task 5. The PI and 8 students attended the Rocky Mountain Fuel Symposium where Ed Sughrue presented a paper. The principal investigator and Erek Erekson also attended the Chicago meeting of the Catalysis Society and presented a paper. Dr. Frank Williams of the University of New Mexico, Dr. William Thomson of the University of Idaho, Dr. Frank Hanson of the University of Utah, and Drs. Wayne Pretzer and Richard Pannell of Gulf Research and Development Company all visited the BYU Catalysis Laboratory.

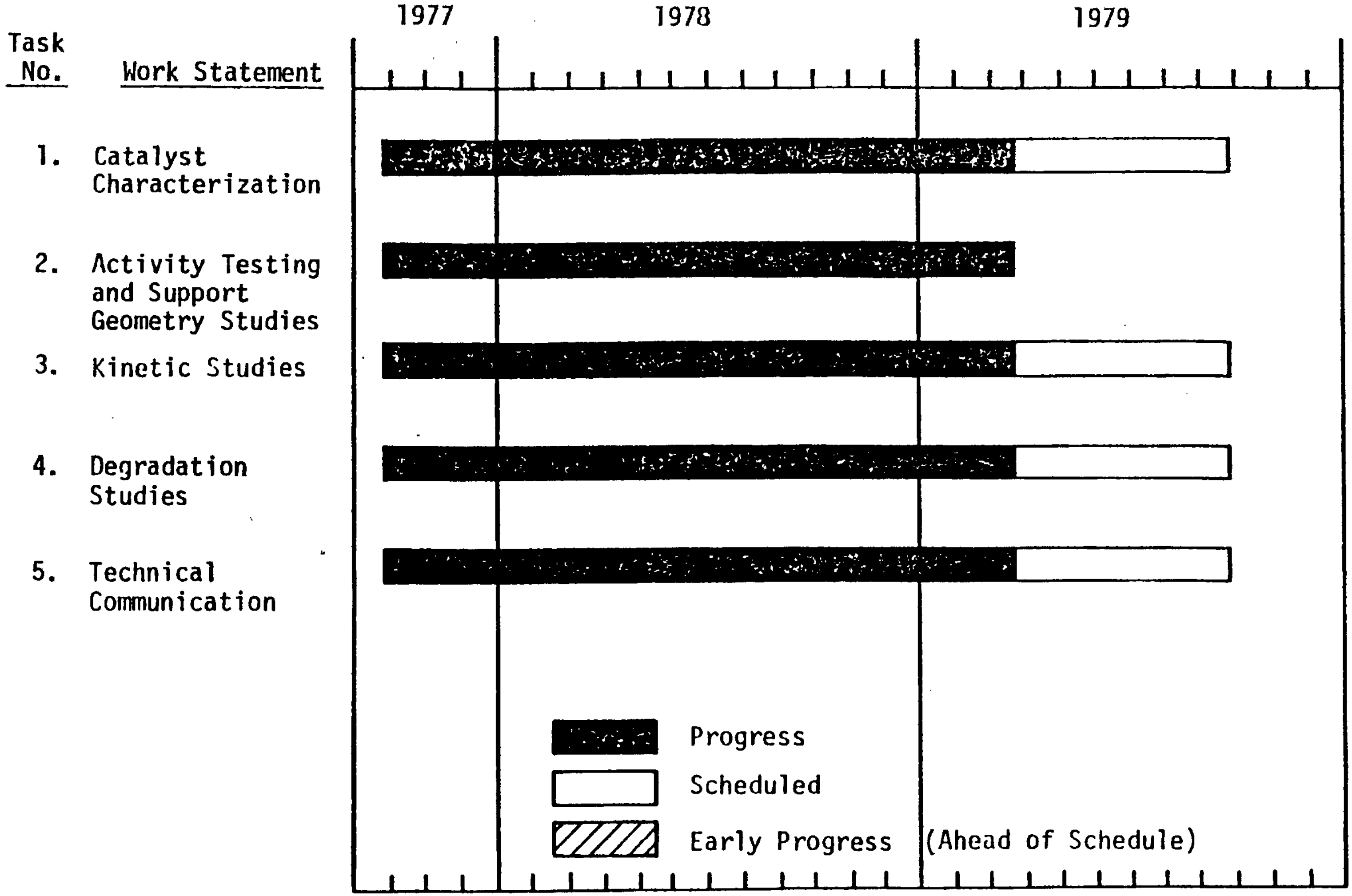

Figure 1. Project Progress Summary

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1: Catalyst Characterization

1. Hydrogen Chemisorption Measurements

Hydrogen chemisorptive uptakes of several catalysts are listed in Table 2. For Ni-A-122 (20% Ni) the results show that long term, high temperature testing of this powdered catalyst resulted in substantial loss of metal surface area. The sample from the higher temperature (773 K) run did not lose as much surface area as the lower temperature (723 K) one. This may be because the high temperature run was aborted after 16 hrs. because of carbon plugging (5). Also, it is apparent from carbon monoxide decomposition work in this laboratory (5) and Rostrup-Nielson (6) that nickel crystallites grow carbon filaments under carbon forming conditions. These carbon filaments grow out of the support material, thus extracting nickel from the support. This process may yield higher H_2 uptakes because the carbon filament "support" is lighter than alumina or because the filament growing procedure breaks up some nickel crystallites into smaller ones. Carbon analysis of these catalysts showed that in the higher temperature run substantially more carbon was deposited (See Figure 2). Also, in Figure 2 it can be seen that carbon lay-down decreases through the catalyst bed in the direction of flow. Other data reported in Table 2 have been previously reported and are added for comparison.

2. Carbon Monoxide Chemisorption Measurements

During the past quarter investigation of the formation of nickel carbonyl during CO chemisorption continued with the main thrust of the work aimed at refining the experimental techniques to give greater reproducibility.

The experiments are performed using a standard powder catalyst reactor cell developed earlier (3). The catalyst is loaded into this cell and reduced for two hours in flowing hydrogen at 723 K and subsequently evacuated to a pressure of 7×10^{-6} kPa. The catalyst is then titrated with carbon monoxide as described in earlier reports (3,5), except that after each isotherm, the titration gas is evacuated through a coil of pyrex glass immersed in liquid nitrogen. In this way any $Ni(CO)_4$ or COS formed is frozen out on the inside of the coil. After the completion of the evacuation procedures, the coil is warmed to about 323 K volatilizing the carbonyls. These gases are carried by a stream of high purity helium first through a small section of heated tube and are then allowed to bubble through a solution of cadmium acetate. The amount of nickel carbonyl formed is determined by the increase in weight in the small tube. The solution of cadmium acetate is titrated with an amine as described in earlier sulfur work (7) to determine the amount of COS formed (8).

Table 3 lists the results of tests conducted during the last quarter in the chronological order in which the experiments were performed. The alphabetic suffix indicates tests performed on a given catalyst

Table 2

H_2 Chemisorption Data

Catalyst	Nominal Composition (wt. %)	H_2 Uptake (μmoles/gram)
Pellets		
Ni-A-121	6%	73.9[a]
Powders		
Ni-A-122	20%	113.9[a]
	20%	53.8[b]
	20%	61.7[c]
Monoliths		
Ni-M-156	3%	46.0[a]

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[a] After bulk reduction.

[b] After long term deactivation run at 723 K.

[c] After long term deactivation run 773 K.

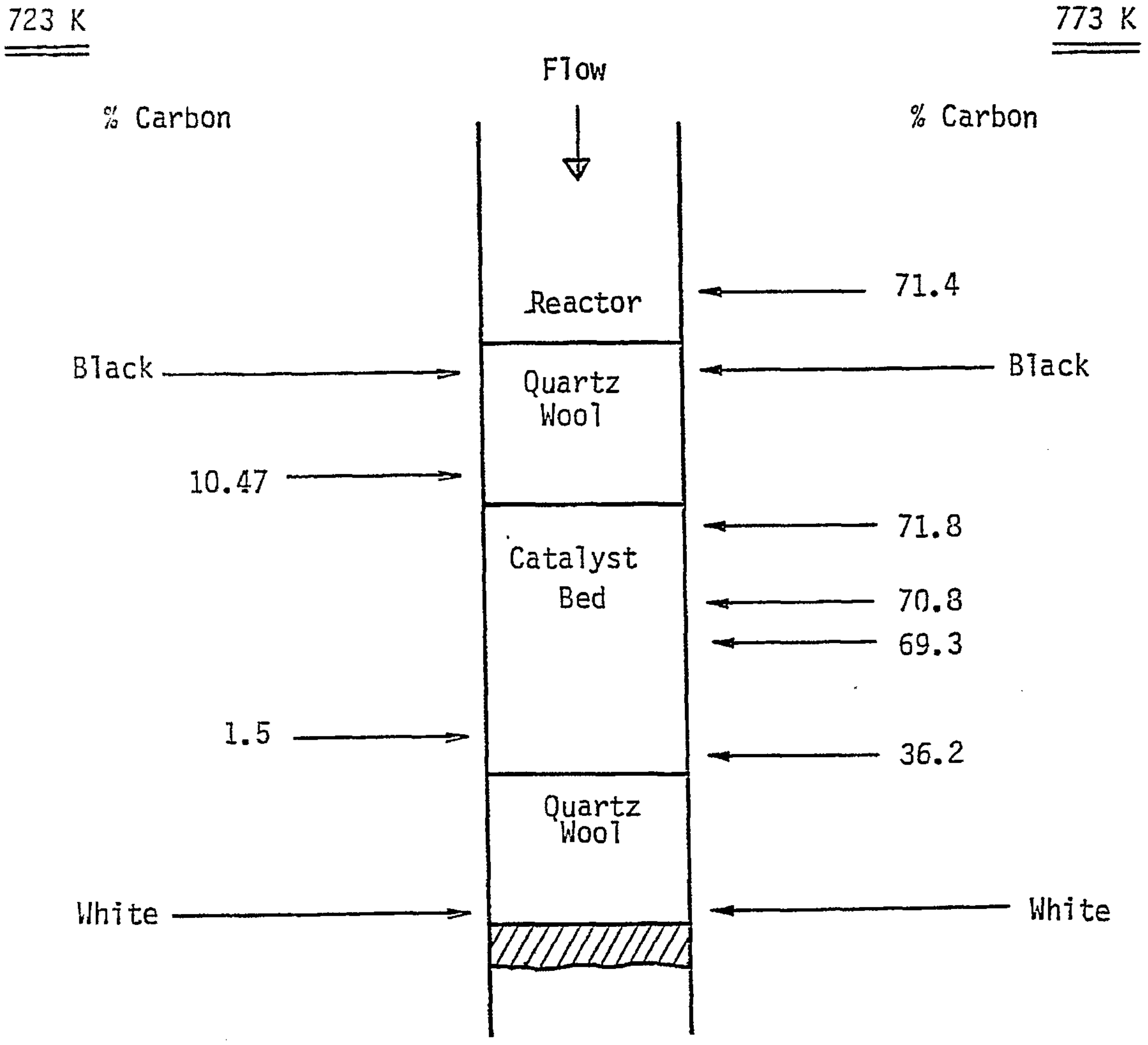

Figure 2. Carbon Analysis versus catalyst bed depth for long term deactivation runs at 723 and 773 K. Flow of gases is downward.

Table 3

Comparison of Carbon Monoxide Chemisorption Measurements versus Temperature of Adsorption[a]

Run #[b]	Temp K	Adsorbate Gas	Uptake μmoles/g	CO/H	Ni from $Ni(CO)_4$ decomposition (g)
9D	297	H_2	30		
10D	196	CO	52.7	0.88	ND[c]
11D	273	CO	59.3	0.99	ND
12D	295	CO	207.4	3.46	0.0025
13E	299	H_2	26.7		
14E	187	CO	163.5	3.06	ND
15E	272	CO	73.1	1.37	ND
16F	299	H_2	30.8		
17F	195	CO	145.7	2.37	ND
18F	272	CO	110.1	1.78	ND
19F	294	CO	88.5	1.34	0.0023
20F	295	H_2	26.5		
21F	299	H_2	25.3		

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[a] All runs were performed on a powdered 3% Ni/Al_2O_3 catalyst.

[b] Runs with the same alphabetic suffix represent measurements on the same catalyst sample.

[c] ND means not detectable.

sample. The runs with the alphabetic suffix F were performed using the new all glass apparatus described in the last report (5). The validity of these results is believed to be significantly greater than those obtained from previous samples, due to the improved accuracy of the procedure used in these later tests. The large variation in catalyst uptake seen in this table is probably due to experimental inaccuracies inherent in the previous experimental system.

From the data it can be seen that no detectable nickel carbonyl was formed upon titration with carbon monoxide at temperatures less than 273 K. This result substantiates earlier work by Milliams et al. (9).

Comparison of the CO adsorption data for Sample F (Run 17-19F) reveals that CO adsorption decreases with increasing temperature.

One additional point of interest is the difference in hydrogen uptake exhibited by the same sample between run 16F and runs 20F and 21F. The formation of nickel carbonyl at room temperature may cause this decrease in hydrogen uptake by removal of active nickel atoms from the surface of the catalyst. Runs 20F and 21F were performed to check the accuracy of the chemisorption method. The results agree to about 1 μmole even after passivation and re-reduction of the sample. Accordingly the difference between hydrogen uptakes measured before and after CO adsorption is significant.

Work in the next quarter in this area will include further testing of both sulfur poisoned and unpoisoned catalysts samples to further elucidate the role of sulfur in nickel carbonyl formation. In the future the amount of nickel deposited in the heated tube will be analyzed by atomic absorption to increase the accuracy of the results.

Task 2: Activity and Support Geometry Tests

No activity or geometry tests were made during the last quarter. However, several sponge monoliths of different geometries were ordered and received. During the next two quarters these will be tested for methanation activity along with conventional ceramic monoliths of varying geometry.

Task 3: Kinetic Studies

Mixing tests were performed on the quartz CSTR (continuous-flow stirred tank reactor) to find what total flow rates would result in good mixing. A gas mixture of 1% CO in N_2 was fed to the reactor until a steady state concentration obtained, as measured by gas chromatograph. Then, the feed was switched from CO in N_2 to pure nitrogen at the same total flow rate. The dynamic response of CO concentration was monitored by GC analysis. The measured time constant [slope of $\ln C/C_0]^{-1}$ was compared to the ideal time constant $\tau = V/q$ where $V = 1260$ ml (10) and q is the flow rate in ml/min. Table 4 shows the results of these tests for the reactor without catalyst present. At

Table 4

Effectiveness of Mixing for Quartz CSTR

Gas Flow Rate ml/min	τ measured	τ ideal	Percent of Ideal Mixing (τ_i/τ_m)
136	9.12	9.26	101
152	8.42	8.29	98.5
240	5.72	5.25	91.7

low flow rates (less than 150 ml/min) ideal mixing is achieved. However, at higher flows the response deviates from ideality. Tests with an alumina catalyst blank in the reactor showed no difference in mixing efficiency from tests without catalyst present.

Preliminary kinetic tests for three nickel catalysts were performed in the quartz CSTR (continuous-flow stirred tank reactor). The tests were performed at 103 kPa in a reactant gas mixture containing 95% N_2, 4% H_2, 1% CO. The temperatures and space velocities varied from sample to sample. In Table 5 test data, rates and turnover frequencies for powdered Ni-A-121 (6% Ni/Al_2O_3) are given. Also, data from other references are included for comparison. Each of these samples was reduced at 575 K for 2 hours in flowing hydrogen. The reason for this lower temperature reduction was difficulty with the quartz impeller at higher temperatures. The impeller stopped spinning above 625 K. This difficulty was later resolved by adjusting the tension of the graphite bearings on the impeller.

Comparison of the recently obtained mixed flow data with previously reported data obtained using a single pass differential reactor show that the rates and turnover frequencies were slightly lower for some of the mixed flow tests. Apparently, the 2 h reduction at 575 K was not sufficient to completely reduce the catalyst.

Subsequent tests summarized in Table 6 were performed on nickel powder, pellets, and monolith samples reduced at 625 K in flowing H_2 for 4 hours and showed significantly higher rates of reaction. Indeed, the rate per gram for the powder was twice the previous rate at 500 K showing that longer reduction times increase catalyst activity. Pellets evidenced approximately twice the activity of monoliths on a per gram basis at 482 and 500 K; however, the turnover numbers were almost the same within experimental accuracy (estimated at 25%). These results are at variance with data previously obtained for pellets and monoliths in a single pass differential reactor which showed monoliths to be 2-4 times more active than the pellets. The earlier results in a tubular reactor may possibly be explained by the different flow patterns for monoliths and pellets. We are currently modelling the monolithic catalysts to test this hypothesis. Nevertheless, there is likely some contribution of non-ideal mixing in the mixed flow reactor because of high through-put conditions; that is, the gas velocities were two to three times greater than those used in the mixing tests. For the powder the gas flow rate was 120 ml/min, well within the ideal mixing range.

Apparent activation energies for the powder, pellets, and monolith are given in Table 7. The values for the powder are close to 24.0 kcal/mole reported by Vannice (11). For the monolith the activation energy of CO conversion is comparable to the powder but the E_{act} (activation energy) of CH_4 production is high. This may be the result of statistical error since E_{act} of CH_4 was calculated using only two points. For the pellets the E_{act} of CO and of CH_4 was low (∿17-18 kcal/mole), suggesting effects of pore diffusional resistance.

Table 5

Preliminary Kinetic Tests of
Ni-A-121 (6% Ni/Al_2O_3)[a]

Catalyst	Temperature (K)	Rate x 10^7 (gmoles/gcat-sec)		Turnover Frequency x 10^3 (molecule/site-sec)	
		CO	CH_4	CO	CH_4
Ni-A-121 Powder	500	1.3	1.1	1.8	1.5
Ni-A-112 Pellets-5% Ni (Reference 3)	498	1.8	1.3	2.3	1.6
Ni-A-121 Powder	524	2.9	2.3	3.9	3.1
Ni-A-121 Powder	551	7.4	6.4	10.0	8.7
5% Ni/Al_2O_3 (Reference 11)	551	--	--	--	9.3[b]

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[a] Test conditions 103 kPa; reactant gas 95% N_2, 4% H_2, 1% CO; Space Velocity = 19,000 to 21,000 h^{-1}. Catalysts reduced at 575K.

[b] Calculated turnover frequency using the rate expression and activation energy from Ref. 11.

Table 6

Preliminary Kinetic Tests of Nickel Catalysts[a]

Catalyst	Temperature (K)	Rate x 10^7 (gmole/gcat sec)		Turnover Frequency x 10^3 (molecule/site-sec)		Space Velocity (h^{-1})	%Conversion
		CO	CH_4	CO	CH_4		CO
Ni-A-121 Pellets	482	1.3	0.8	1.8	1.1	2,840	15.4
Ni-M-156 Monolith	482	0.6	0.3	1.4	0.7	2,880	12.4
Ni-A-121 Powder	500	3.2	2.4	4.4	3.2	21,500	6.5
Pellets	500	2.9	2.3	3.9	3.1	2,840	34.3
Ni-M-156 Monolith	500	1.3	1.0	2.9	2.2	1,920	38.1
		1.5	1.1	3.2	2.3	3,160	25.7
		1.4	1.0	3.0	2.1	3,600	21.5
Ni-A-121 Pellets	525	5.9	4.6	7.9	6.3	1,260	79.6

[a] Test conditions: 103 kPa in 1% CO, 4% H_2, 95% N_2. Catalysts were reduced at 625K.

Table 7

Apparent Activation Energies for Nickel Catalysts Tested in a Quartz CSTR Reactor[a]

Catalyst	Activation Energy (kcal/mole) CO	CH_4
Ni-A-121 Pellets	17.6	17.9[b]
Ni-A-121 Powder	20.3	22.9[c]
Ni-M-156 Monolith	22.5	31.2[b]

[a] Test conditions: 103kPa in 1% CO, 4% H_2, and 95% N_2

[b] Catalyst reduced at 625 K.

[c] Catalyst reduced at 575 K.

The quartz impeller has now been adjusted so that operation above 625 K is practical. Kinetic and deactivation tests will proceed on catalyst powders in the quartz reactor. Since space velocities were quite low ($\sim$2000 hr^{-1}) for pellets and monoliths, further atmospheric kinetic studies of these substrates will be performed in the Berty reactor where ideal mixing can be achieved at higher flow rates.

Modifications were made in the experimental design of the high pressure Berty reactor system which required an adjustment in the flow capacity of our mass flow meters. The necessary parts were ordered from Tylan Corporation and finally received after the quarter ended.

Task 4: Degradation Studies

Two tests with steam in the feed gas were performed on the Ni-A-122 catalyst. The first test was a 24-hour constant temperature test. The reactor conditions were 723 K, 2500 kPa, and a 30,000h^{-1} space velocity. The percentage steam in the gas compositions for previous steam tests was recalculated. Correcting this error revealed that all previous tests with steam had been made with 29% steam. As shown in Figure 3, there is no measureable decrease in CO conversion over the 24 hour period. This suggests that the previously observed deactivation without steam was mainly due to carbon deposits. The CH_4 production decreased early in the test with steam to a steady state value of 45 to 50%.

A conversion versus temperature test was made with 4% steam in the feed gas. The temperature range was 473 to 815 K while the pressure and space velocity were 2500 kPa and 30,000 h^{-1}, respectively. The CO conversion and CH_4 production were very high throughout the test. See Figure 4.

In Figure 5 a comparison is made between the recent test with 4% steam and previously reported tests (5,8) tests with 29% steam. Both tests show similar conversion vs. temperature plots but with the 4% steam run always significantly higher. Moreover, the percent of CO converted to methane is substantially greater at every temperature and especially at higher temperatures for the 4% steam case (compare Fig. 4 of this report with Fig. 19 of the annual report (8), remembering that the H_2O concentration in the annual report was 29%). Indeed, at 723 K methane production was 100% and 0% for 4 and 29% H_2O respectively.

Task 5: Technical Interaction and Technology Transfer

Dr. Bartholomew and Erek Erekson attended the Sixth North American Meeting of the Catalysis Society, March 18-22, in Chicago where they listened to a number of stimulating papers on recent catalytic research and discussed aspects of methanation catalysis with other workers. Of particular interest were papers dealing with catalysts prepared by partial decomposition of metal carbonyls onto support materials, and a ruthenium on MgO catalyst that was stable to 1150

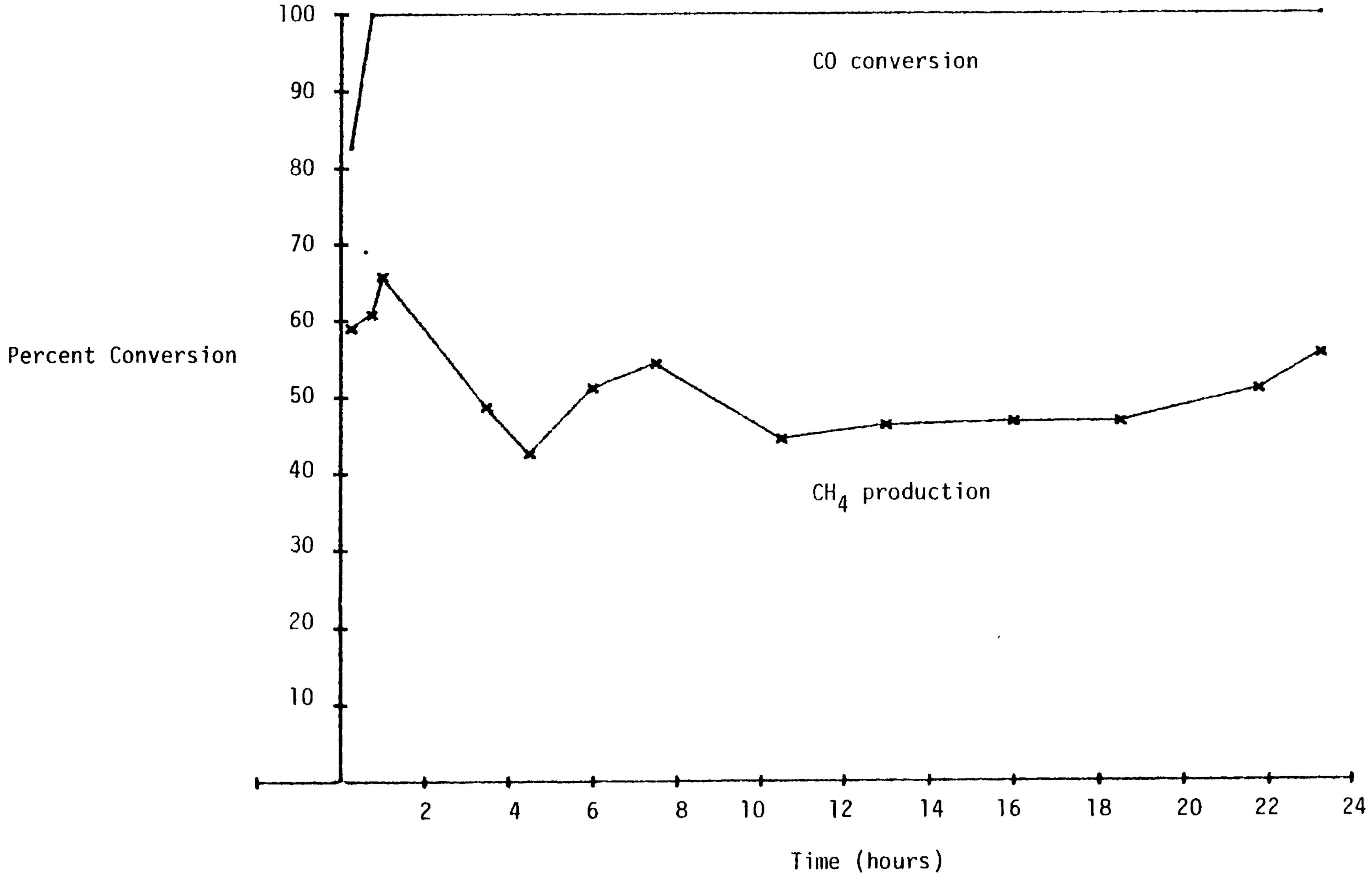

Figure 3. Conversion of CO (overall) and CO to CH_4 vs. time for Ni-A-122 (20% Ni) at 2500 kPa, 773 K GHSV = 30,000 h^{-1} and reactant gas containing 45.4% CH_4, 29% steam, 11.4% Ar, 10% H_2, 2.8% CO and 1.4% CO_2.

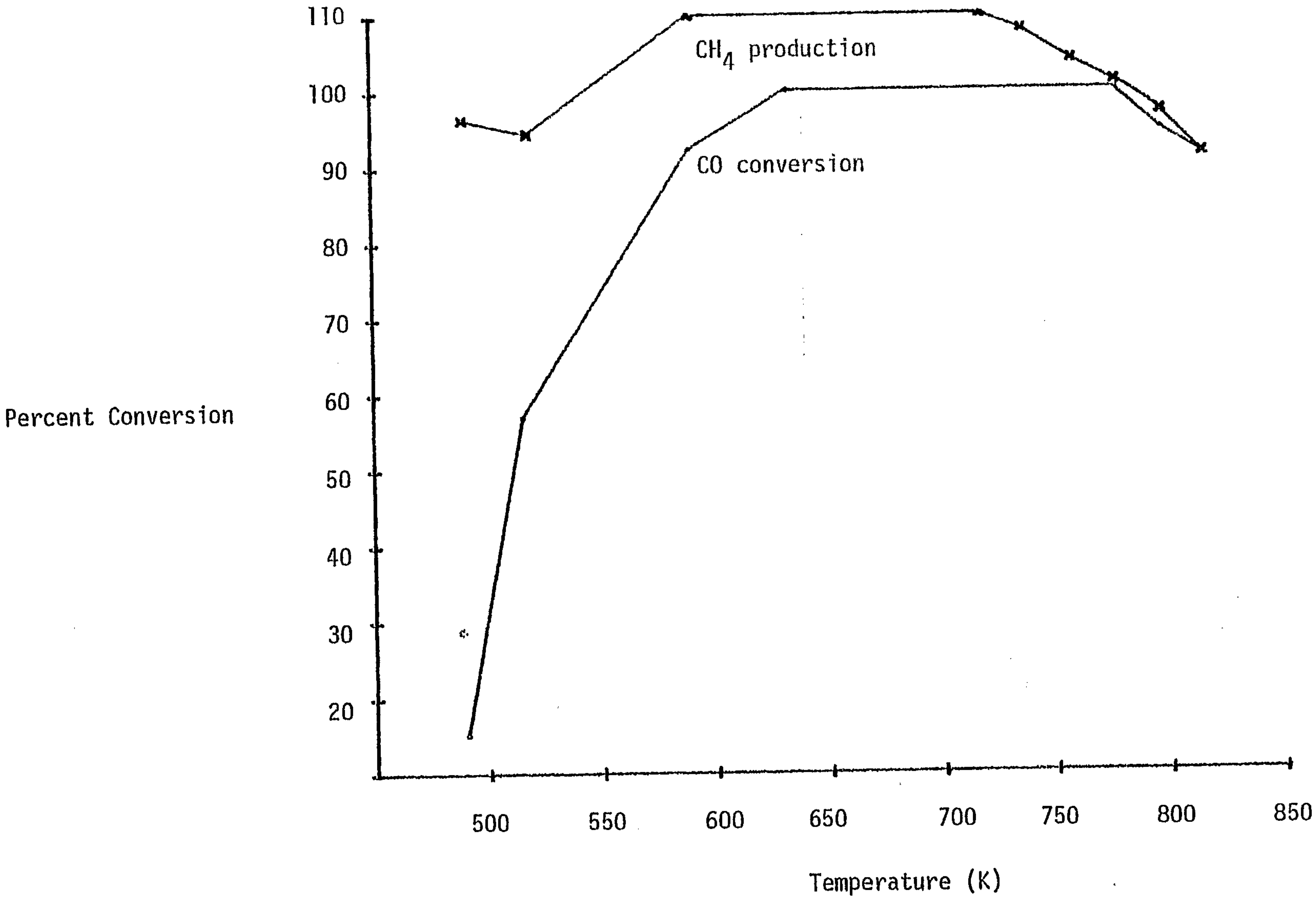

Figure 4. Conversion of CO (overall) and CO to CH_4 vs. Temperature for Ni-A-122 (20% Ni) at 2500 kPa, GHSV = 30,000 h^{-1}, and reactant gas containing 61.4% CH, 4% steam, 15.4% Ar, 13.4% H_2, 3.8% CO and 1.9% CO_2

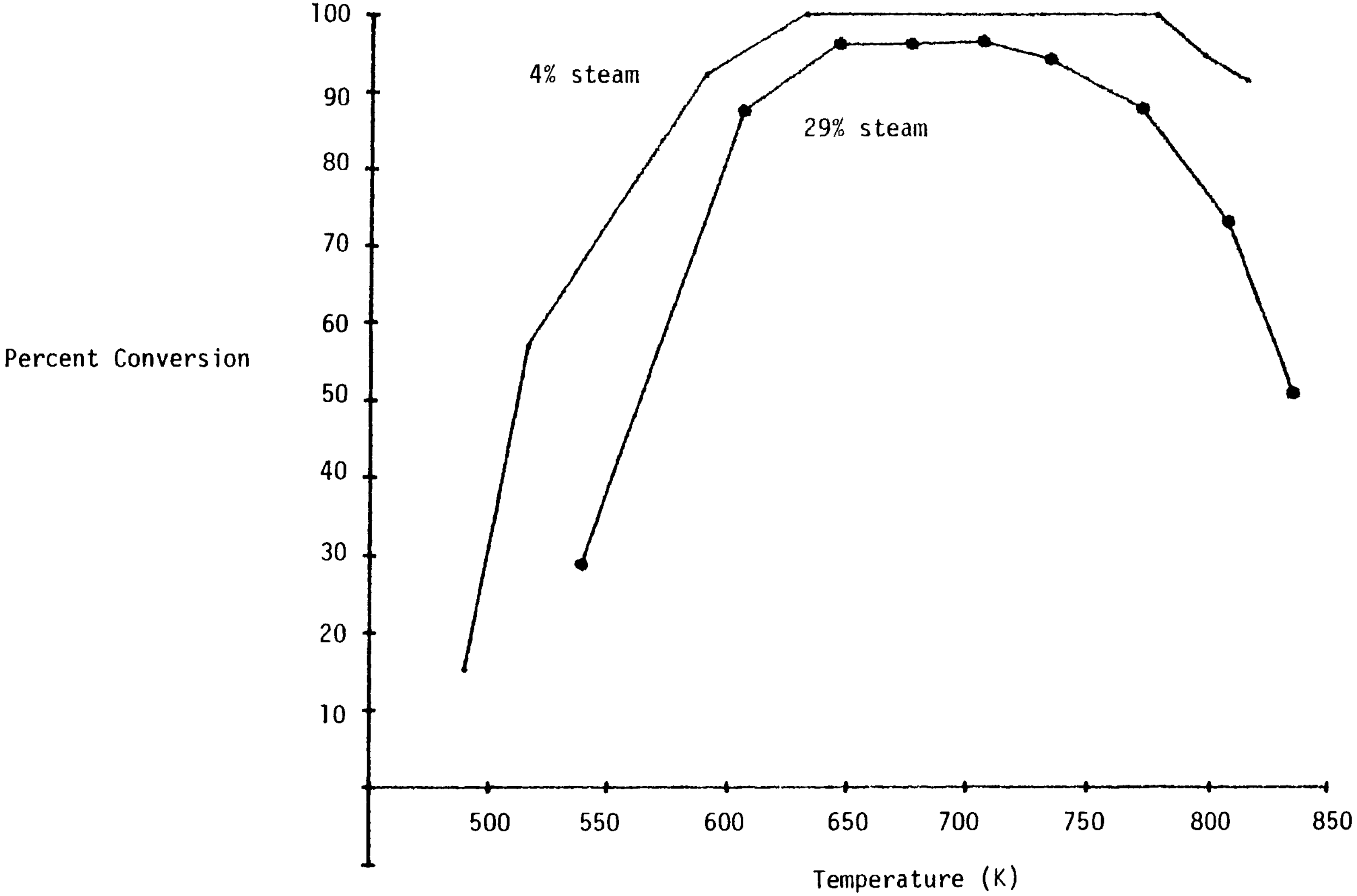

Figure 5. Conversion of CO (overall) vs temperature for Ni-A-122(20%Ni) at 2500 kPa, GHSV = 30,000 h^{-1} and different concentrations of steam.

K in an oxygen containing atmosphere. Dr. Bartholomew gave a paper on deactivation of methanation catalysts by carbon deposits which was well received.

The principal investigator and eight students attended the Fourth Rocky Mountain Fuel Symposium February 9 and 10 in Salt Lake City. Mr. Edward Sughrue presented a paper on high temperature degradation of methanation catalysts. Many other pertinent papers were presented on catalysis, coal gasification, coal liquifaction, and other fuel topics.

During the past quarter our laboratory received visits from a number of catalyst researchers. On February 8 Dr. Frank Williams of the University of New Mexico visited BYU and presented a seminar on "Alloy Catalyst Surface Studies." Dr. William Thomson of the University of Idaho presented a seminar on methanation catalysis on February 13. Dr. Frank Hanson, University of Utah, gave a seminar on hydrogen and oxygen reactions over platinum catalysts on March 29. We received two separate visits of researchers from Gulf Research and Development Company. Dr. Wayne Pretzer discussed his research on metal cluster complexes in a seminar. Also, Dr. Richard Pannell gave a stimulating seminar on Fischer-Tropsch synthesis, and gave us suggestions on experimental equipment during his visit.

IV. Conclusions

1. Carbon monoxide chemisorption measurements at various titration temperatures showed that the temperature of titration significantly affects chemisorptive uptake. No detectable $Ni(CO)_4$ was formed at titration temperatures of 273 K or below. Hydrogen uptake is slightly lowered after $Ni(CO)_4$ has been formed over a catalyst.

2. Mixing tests with our quartz CSTR (continuous-flow stirred tank reactor) showed that near perfect mixing is obtained at flows below 150 ml/min.

3. Activity tests of powders, pellets, and monolith in the quartz CSTR resulted in data comparable to previously reported work. The turnover frequencies of the monolith and pellets were the same within experimental error. Apparent activation energies for the powders and monolith agree well with reported values, while the E_{act} of the pellets showed diffusional effects.

4. Long term degradation tests on Ni-A-122 (20% Ni) with reactant steam showed no loss of CO conversion activity over 24 h. This suggests that previously observed deactivation without reactant steam was mainly due to carbon deposits.

5. Conversion versus temperature plots of Ni-A-122 show that significantly higher CO conversions and substantially greater values of methane production occur with 4% reactant steam compared to 29% reactant steam.

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15. Supplementary Notes

16. Abstracts

During the sixth quarter, carbon monoxide chemisorption measurements on Ni/Al$_2$O$_3$ catalysts showed large diferences in CO uptake versus temperature of titration. No detectable Ni(CO)$_4$ was formed at CO titration temperatures of 273 K or below. Mixing tests and preliminary activity tests in the quartz CSTR (continuous-flow stirred tank reactor) showed the reactor system performance to be very near to that of an ideal mixed flow reactor and activity data obtained is quite comparable to previously reported work. Long term degradation tests with reactant steam showed no loss of activity over 24 h. Conversion versus temperature tests at two levels of reactant steam concentrations gave similar data. Carbon analysis of catalysts samples from long term degradation tests without steam showed that massive carbon lay-down occurred in decreasing quantities through the catalyst bed in the direction of flow. These and other pertinent data are reported and compared.

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