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

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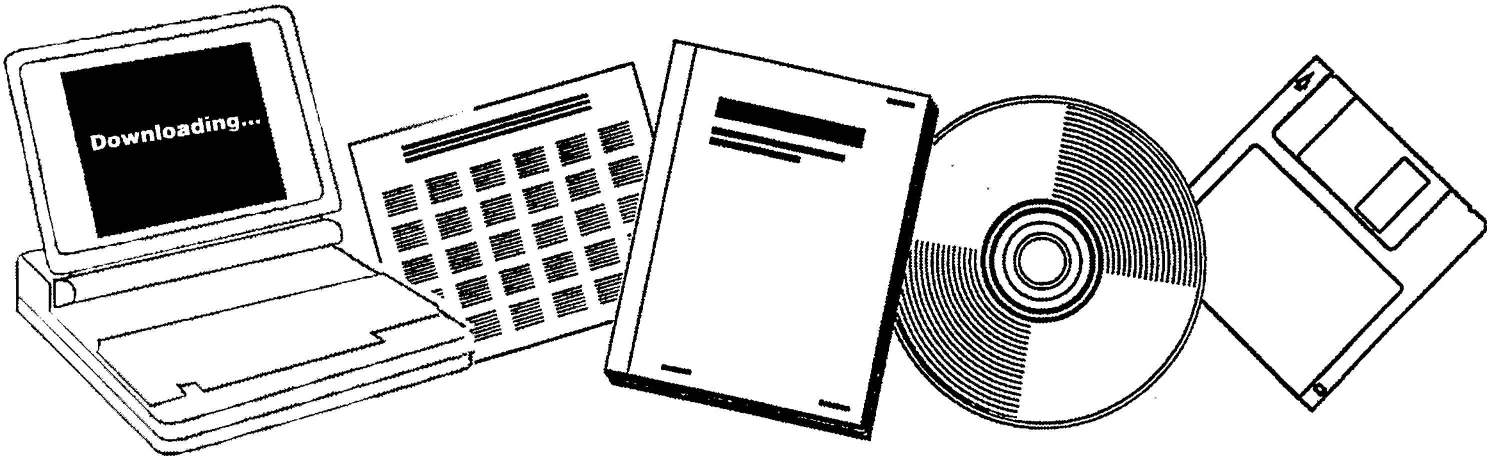

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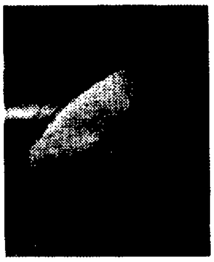

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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES

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

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DEPARTMENT OF ENERGY

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FOREWORD

This report summarizes technical progress during the fifth quarter (September 21, 1978 to December 20, 1978) 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: Graduates - Erek Erekson, Ed Sughrue, and Gordon Weatherbee, and Undergraduates - Don Mustard, and John Watkins. April Washburn and Steve Kvalve provided typing and drafting services. In this report data are reported in SI units.

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ABSTRACT

During the fifth quarter, results from previously reported support geometry studies supplemented with recent calculations were summarized in a paper submitted to the American Institute of Chemical Engineers. Calculations of Thiele moduli, effectiveness factors and mass transfer coefficients for pellets and monoliths reveal that under reactor conditions monoliths are more active than pellets because of lower pore diffusion resistance and higher rates of film mass transfer. Long-term thermal degradation tests of high loading (20% nickel on alumina indicate that the catalyst deactivates slowly at 723 and 773 K. Deactivation is mainly due to sintering and carbon fouling. A new electron microscopy technique for measuring nickel crystallite size was developed this quarter. The estimates of nickel crystallite size obtained using this technique compare favorably with those from chemisorption data.

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-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 (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 task accomplishments are either on or ahead of schedule.

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

Task 1. The chemisorptive uptake of hydrogen was measured for Ni-A-116. An all-glass apparatus for measuring CO chemisorption and nickel carbonyl formation was constructed. A new carbon deposition pretreatment was used prior to electron micrographing of Ni-A-116. This technique provides estimates of nickel crystallite size comparable to results obtained from chemisorption. Several catalyst samples were analyzed for carbon content after upper use temperature tests. The results show that addition of steam decreases carbon content.

Task 2. Calculations of Thiele moduli effectiveness factors and mass transfer coefficients for pellets and monoliths were performed this quarter for the same conditions used in the support-geometry activity experiments. Monoliths are more active than pellets under these conditions because of lower pore diffusion resistance and higher rates of film mass transfer.

Task 3. Mole sieve and zinc oxide purifying filters were added to the Berty system. This system is ready and will be used during the next quarter.

Task 4. Two long-term thermal deactivation runs were performed on powdered Ni-A-122 (20% Ni). Activity versus time plots were made. Neither sample lost very much activity during the test. However, in the test at the higher temperature (773 K) there was evidence of plugging due to carbon fouling and the test had to be shut down early.

Task 5. The principal investigator visited Gulf Research and attended the Miami AIChE meeting where he presented a paper. Drs. Donald LaRue and Victor Kelsey of Idaho International Laboratory and Mr. Kyung Sup Chung and Professor Frank Massoth of the University of Utah visited our laboratory. The principal investigator submitted a paper to AIChE to be read in April at the Houston meeting.

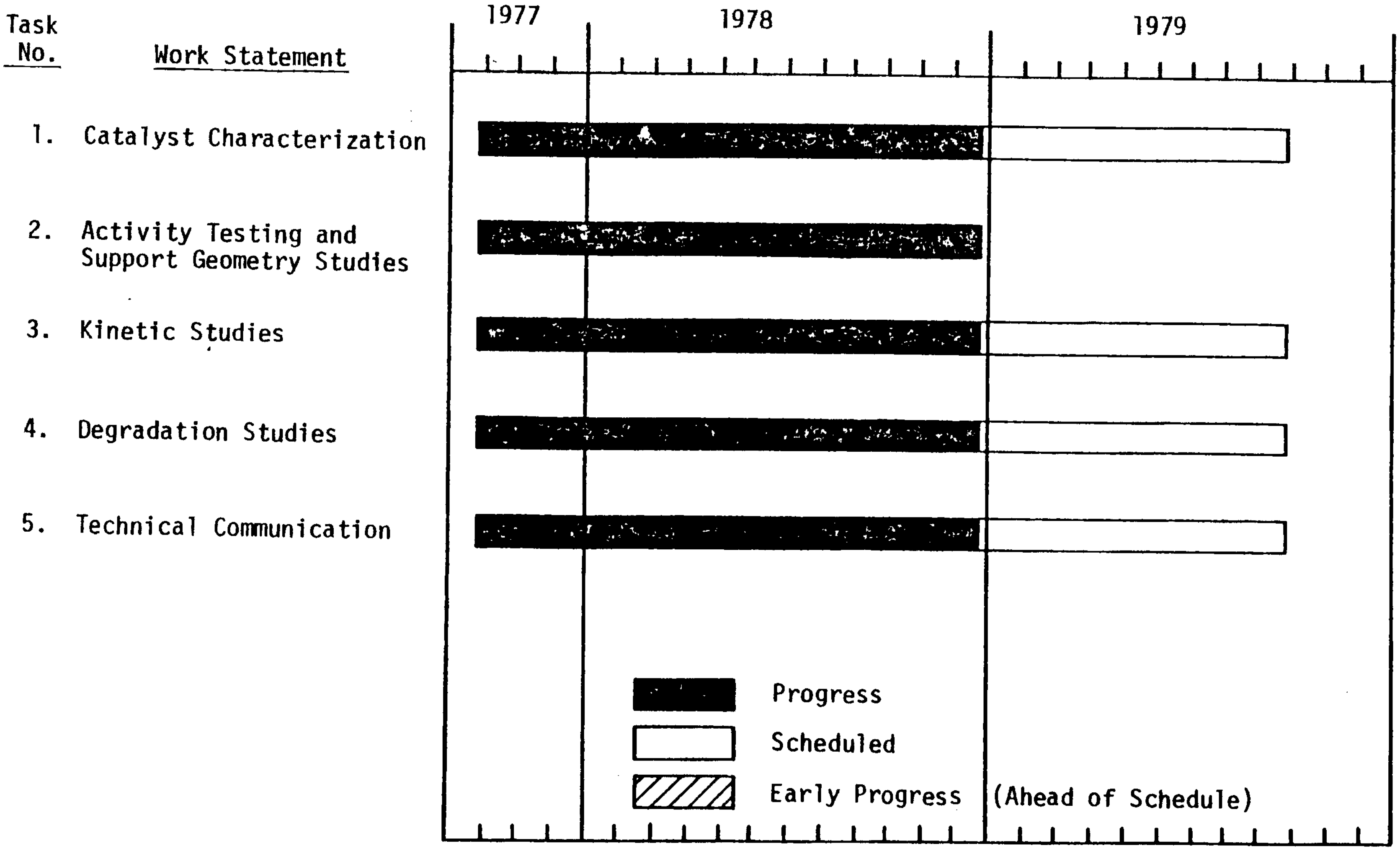

Figure 1. Project Progress Summary

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1: Catalyst Characterization

1. Chemisorption Measurements

The chemisorptive uptake of hydrogen was measured for a powdered Ni-A-116 sample (14% Ni). The hydrogen uptake and estimated nickel crystallite size are given in Table 2. The results agree well with previous adsorption measurements of Ni-A-116, indicating that the accuracy of the technique for different samples of the same catalysts is about 12%. The previously reported sample was bulk reduced at a lower space velocity which may account for some of the difference between samples.

Although some work was reported previously dealing with the formation of nickel carbonyl on nickel alumina catalysts titrated with carbon monoxide, the data taken were not very reproducible. The makeshift apparatus used in earlier experiments gave good qualitative results, but proved unsatisfactory for quantitative experimentation due to numerous joints and connecting hoses which sometimes leaked. During the last quarter, efforts were focused on perfecting the experimental apparatus and procedure in order to assure greater accuracy of the experimental results.

Conceptually, this new piece of apparatus is unchanged from that which was previously used. The major modifications are in the one piece glass construction, resulting in greater compactness, and the additions of ground glass joints at all the vital connecting points, eliminating leaks. Preliminary testing has been very favorable.

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 titration, the cell 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 on 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 (6) to determine the amount of COS formed (5).

Experimental work with this new apparatus is just beginning and will go on through the next quarter with results appearing in the next report.

Table 2

Hydrogen Chemisorption Uptakes and Estimates of Metal Particle Diameters

Catalyst	Nominal Chemisorption (wt.%)	Uptake (μmole/gm)	Particle Size (nm)
Ni-A-116	14% Ni	211.1	5.48[a]
			7.43[a,b]
Ni-A-116	14% Ni	187.8	6.2[c]

---

[a] Bulk reduced at 2,000 hr^{-1} GHSV.

[b] Surface average particle size diameter from electron microscopy after carbon lay-down technique.

[c] Previously reported (see Ref. 3), bulk reduced at 1,000 hr^{-1} GHSV.

2. Chemical Analysis

Catalysts from upper use temperature tests were analyzed using a Perkin-Elmer model 240 elemental analyzer. Percentages of carbon and hydrogen by weight are reported in Table 3.

Several of the catalyst samples were previously analyzed by the Rocky Mountain Geochemical Corporation. A comparison between the two methods is provided in Table 4. No attempt was made in our analysis method to dessicate the catalyst samples. The difference in the two methods is probably due in part to water adsorption by the Al_2O_3 catalyst support and to some systematic error in analysis. Indeed, by correcting for the systematic error in our analysis of Ni-A-122, good agreement is obtained with that obtained by RMGL.

The carbon content of catalysts tested under high temperature methanation conditions is apparently a function of the reactor run conditions, sampling technique and catalyst composition. Addition of steam to the reactant gas eliminated any significant carbon formation on the catalyst. The carbon content rises with increasing maximum temperature during the run. The time at temperatures above 750 K also seems to be significant as seen by comparing Run C and D of Ni-A-122. Run D had a slightly higher maximum temperature but spent a much shorter time above 750 K and thus had a lower carbon content. Run C also employed use of a preheater coil which kept gases at higher temperatures longer. Also, there appears to be an effect of where the sample was taken from the catalyst bed. After an upper use temperature test, some of the catalyst pellets were left intact and others were pulverized to powder and in some cases this powder mixed with carbon formed on the reactor walls. There is a difference in carbon content between samples from the pellets and from the powder (see Table 3). Taking into consideration the reactor run conditions, the increasing order of carbon content appears to be Ni-MoO_3, Ni-Co, Ni-NiAl, NiPt, Ni, Ni-M-179, G87P, MC-100.

3. Transmission Electron Microscopy

Several different attempts were made to determine the accuracy of the previously reported particle size distributions (5,7-9) measured by electron microscopy. Conventional microtoming was tried. However, large amounts of time were required to produce good sections of catalyst and the resultant micrographs were inconclusive.

During the past quarter a new method for measuring particle size distribution was attempted. Powdered Ni-A-116 was purposely carbon fouled in a Thermal Gravimetric Analyzer by passing 10% CO in N_2 at 723 K over the reduced catalyst. Electron micrographs of the fouled catalyst were made. An example is shown in Figure 2. The long snake-like projections from the catalyst are apparently carbon filaments, similar to those reported by Rostrup-Nielson (10). The dark spots at the end of the filament are nickel particles. A size distribution of these particles gave a surface averaged diameter of 7.23 nm compared to the H_2 chemisorptive diameter of 5.48 nm. The agreement is within 40 percent. This may prove to be a useful technique

Table 3

Elemental Analysis of Upper Use Temperature Tested Catalysts

Catalyst	Run	Percent Carbon	Percent Hydrogen	Maximum Temperature (K)	Comments
Ni-A-122	A,a	0.38	3.9	721	
	B,a	17.6	2.3	886	Pellets only
	B,a	29.4	---	886	Powder only
	C,a	10.4	4.2	763	Pellets only
	C,a	25.1	---	763	Powder only
	D,a	2.61	---	789	
	b	0.30	5.2		
Ni-Co-A-103	a	0.29	4.9	725	
	b	0.14	3.7		
Ni-Mo-A-105	a	0.16	4.6	825	
	b	0.18	4.7		
Ni-Pt-A-101	a	6.56	3.5	820	
	b	0.20	3.9		
Ni-NiAL-100	a	1.32	2.6	803	
	b	0.20			
G-87P	a	9.80	3.7	800	
	b	0.80			
MC-100	a	15.00		820	Powder
	b	0.00	5.3		
Ni-M-179	a	5.30		818	
	b				
Blank Al_2O_3 (powder)		0.00	3.4		

NOTE: Carbon percentages not corrected for H_2O adsorbed.

a Runs were made without steam.

b Runs were made with steam.

Table 4

Comparison of Elemental Analysis with Rocky Mountain Geochemical Labs

		Percent Carbon		
Catalyst	Run	BYU	Corrected to Run C	RMGL
Ni-A-122	A	0.38	0.46	0.40
	B	29.39	35.58	35.72
	C	25.14	30.44	30.44
	D	2.61	3.16	3.19
Ni-Co-A-103		0.30	0.35	0.42

NOTE: Correction based on Run C of Ni-A-122, Correction Factor = 1.2108.

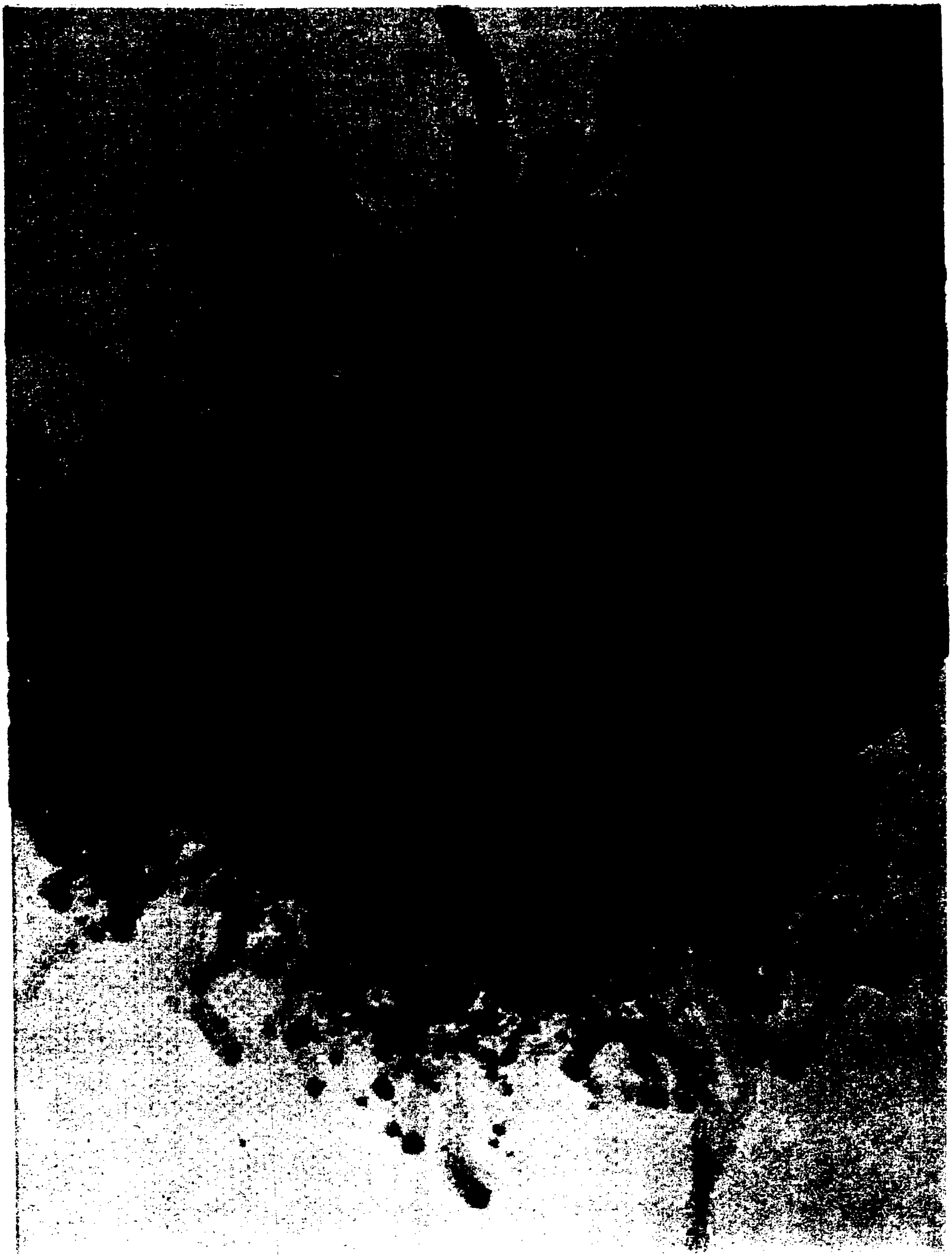

Figure 2. Electron micrograph of Ni-A-116 (14% Ni) after carbon deposition pretreatment.

for measuring nickel particle diameters on alumina catlysts. However, whether the particles extracted by the carbon filaments are representative of the nickel particles originally in the catalyst pores must yet be determined. Further investigation of this technique will be made during the next quarter. Also, a graphitized carbon standard purchased during this quarter will be used next quarter to measure distances more accurately on micrographs.

Task 2: Activity and Support Geometry Tests

Data comparing rates (per volume and per nickel surface rate) of methane production for Ni/Al_2O_3 catalysts in monolith and pellet form were presented in the annual report (5) and our final report for the previous contract (3). The results reveal that monolithic catalysts are significantly more active than pellet catalyst for methane production under any and all reaction conditions (i.e., 500-700 K, 140-2500 kPa and 15,000 to 50,000 hr^{-1}). This can be explained by (i) lower pore diffusion resistance and (ii) higher rates of film mass transfer in the monlithic catalysts.

These conclusions are supported by calculations of Thiele moduli, effectiveness factors and mass transfer coefficients for monoliths and pellets performed during this past quarter and listed in Tables 5 and 6. The calculation of the Thiele modulus for monoliths and pellets was based on the Generalized Thiele Modulus (11) for a flat plate and sphere respectively assuming an irreversible reaction of 1/2 order, consistent with the kinetics of Vannice (12). The effective diffusivity was calculated from the combined diffusivity for bulk diffusion of CO in N_2 and of Knudsen diffusion of CO in pores having an average radius of 7 nm. Knudsen diffusion was found to predominate at 140 and 1000 kPa. The tortuosity factor of 4.5 was based on literature data for a similar nickel catalyst (13). Nonisothermal effectiveness factors were calculated according to the methods of Weisz and Hicks (14) for pellets and Carberry and Kulkarni (15) for monoliths. At 600 K and 140 kPa, the maximum temperature gradient across either pellet or monolith coating was estimated to be 0.2 K. In other words, the catalyst solid was found to be essentially isothermal.

From the estimates of Thiele modulus and effectiveness factor in Table 5, it is clear that (i) reaction-controlled conditions obtained at 500 K in low nickel loading pellets and in all monolith catalysts, (ii) pellet catalysts operate at low effectiveness at higher temperatures (e.g. 600 K) and (iii) monolithic catalysts operate at near unity effectiveness even at high temperatures and conversions.

Theoretical mass transfer coefficients for monoliths were calculated according to methods described previously (5,9). Theoretical values of k_c for pellets were based upon the correlations of Petrovic and Thodos (13,16).

The experimental values of k_s (first order rate constant) and theoretical values of k_c are compared in Table 6. From these data, it is apparent that the experiments at 1 atm (140 kPa) were

Table 5. Values of the Thiele Modulus and Effectiveness Factor for Monolithic and Pellet Catalysts

Catalyst	Thiele Modulus[a]		Isothermal Effectiveness Factor		Nonisothermal Effectiveness Factor[b] at 600 K
	500 K	525 K	500 K	525 K	
a. Data at 140 kPa:					
3% Ni/10% Al_2O_3/ Monolith (46.5 □/cm^2)	0.016	0.024	1.00	1.00	---
20% Ni/20% Al_2O_3/ Monolith (31 □/cm^2)	0.033	0.055	1.00	1.00	0.98
3% Ni/Al_2O_3 0.32 cm spheres	0.30	0.48	0.95	0.89	---
14% Ni/Al_2O_3 0.32 cm spheres	0.74	1.28	0.77	0.58	0.09
b. Data at 1000 kPa:					
3% Ni/10% Al_2O_3/ Monolith (46.5 □/cm^2)	0.009	0.016	1.00	1.00	---
6% Ni/Al_2O_3 0.32 cm spheres	0.19	0.38	0.99	0.92	---

---

[a] Generalized Thiele Modulus (Ref. 11) based on 1/2 order kinetics of Vannice (Ref. 12).

[b] ΔT particle = 0.2 K; in other words, the particle is essentially isothermal.

Table 6. Experimental First Order Rate Constants and Theoretical Mass Transfer Coefficients

		1 atm and 700 K		10 atm and 650 K	
Catalyst	GSA (cm^2/cm^3)	Experimental[a] k_s (cm/sec)	Theoretical[b] k_c (cm/sec)	Experimental[a] k_s (cm/sec)	Theoretical[b] k_c (cm/sec)
3% Ni/10% Al_2O_3/ Monolith, 46.5□/cm^2	17.8	5.1	20	1.8-2.0[c]	2.0
3% Ni/Al_2O_3 0.32 cm spheres	8.7	2.7	14	--	--
6% Ni/Al_2O_3 0.32 cm spheres	8.7	5.0	14	0.79	1.2

[a] Calculated assuming first order and log mean concentration.

[b] Calculated from mass transfer correlations for packed beds and monoliths; k_c defined by $J_x = k_c(C_b - C_s)$ where J_x is the molar flux, C_b the bulk concentration and C_s the concentration at the particle surface.

[c] Very approximate estimate since CO conversion was nearly 100%.

carried out in the mass transfer influenced regime, but that mass transfer was not the rate limiting step, since the experimental rate constants are significantly smaller than the theoretical mass transfer coefficients. Since diffusivity and, hence, the mass transfer coefficient are inversely dependent upon pressure, the calculated mass transfer coefficient should be about a factor of 10 less at 10 atm, suggesting that truly mass-transfer-limiting conditions will obtain under these conditions. Indeed, the data at 10 atm (1000 kPa) appear to be completely mass-transfer-limited since the experimental and theoretical values are approximately the same.

Task 3: Kinetic Studies

Mole sieve and zinc oxide purifying filters were purchased and prepared for the Berty reactor system. This system is ready and will be used during the next quarter.

Task 4: Degradation Studies

During the past quarter long term thermal deactivation runs were carried out on powdered samples of Ni-A-122 (20% Ni). The reaction conditions were similar to the upper use temperature tests with a gas composition of 63% CH_4, 16 Ar, 15% H_2, 2% CO_2, space velocity of 30,000 hr^{-1}, and a pressure of 2500 kPa. However, the temperature was held constant at 723 K or 773 K. The plots of activity vs. time are shown in Figures 3 and 4.

At 723 K the Ni-A-122 deactivated slowly, losing only 5.2% conversion of CO over 24 hours. 723 K is about 50° K above the maximum conversion temperature as shown in the upper operating temperature tests (5).

The powdered Ni-A-122 also deactivated slowly at 773 K. Over a period of 16 hours the CO conversion dropped from 78.7% to 73.4%. After 17 hours the reactor apparently plugged and conversion dropped drastically to about 21%. During the last hour of the test, the pressure drop was very high across the catalyst bed, i.e. essentially 2500 kPa. When the reactor was opened, it was plugged with carbon. Even the quartz wool before the bed the catalyst was full of carbon. However, the quartz wool after the catalyst bed was clean. It appeared that the plugging was due in part to carbon lay-down on the reactor walls. Samples of the catalyst bed, carbon from the reactor walls, and quartz wool were preserved, and elemental analysis, electron micrographs and chemisorptions will be made next quarter.

From these two runs it appears that Ni-A-122 loses activity slowly at high temperature (723 K), probably due to carbon fouling and sintering. The principle difficulty, however, occurs when the reactor becomes plugged with carbon, forcing the system to be shut down.

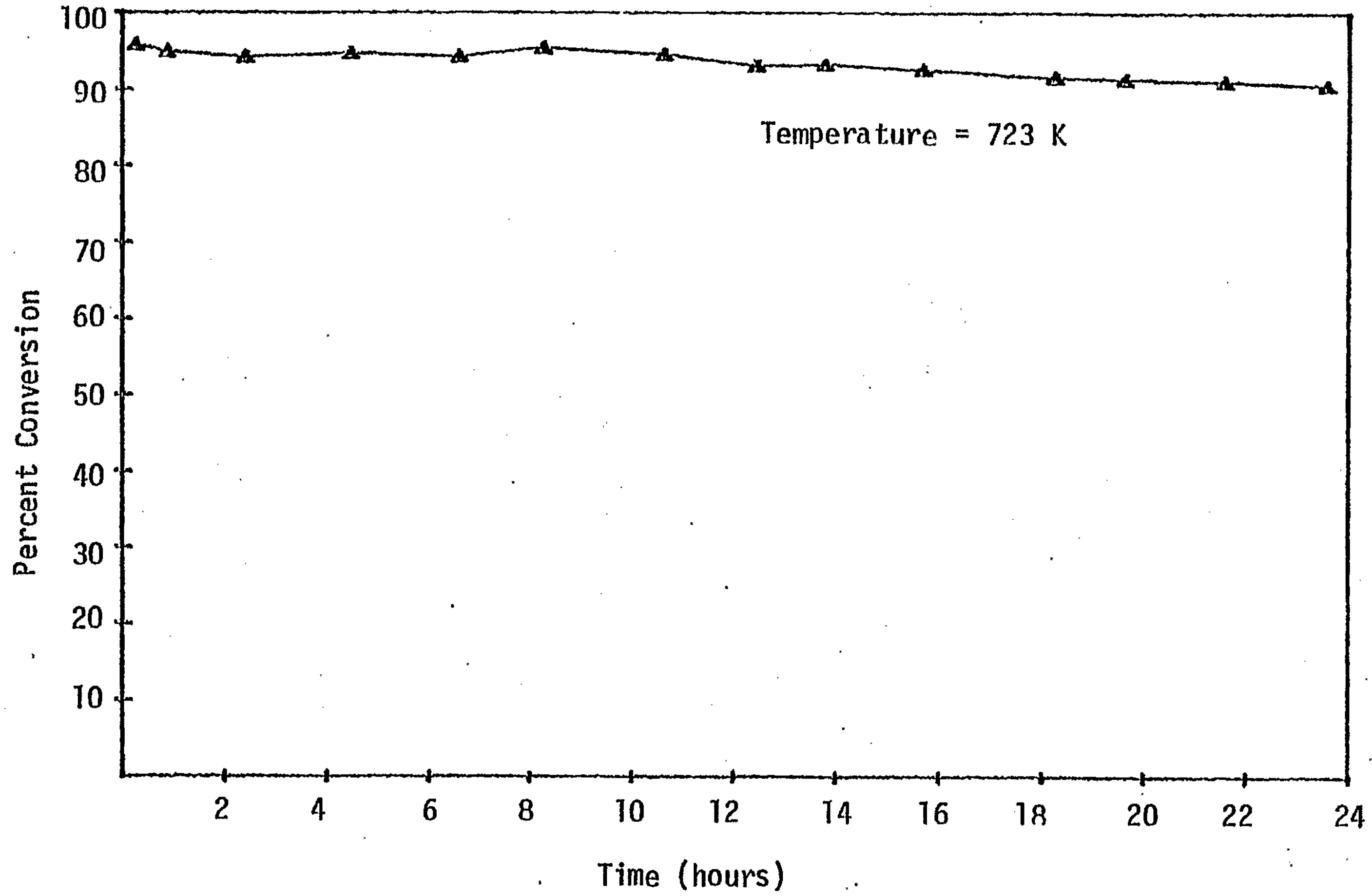

Figure 3. Conversion of CO (overall) vs. time for Ni-A-122 (20% Ni) at 2500 kPa, 723 K, GHSV = 30,000 hr^{-1}, and reaction mixture containing 63% CH_4, 16% Ar, 15% H_2, 4% CO and 2% CO_2.

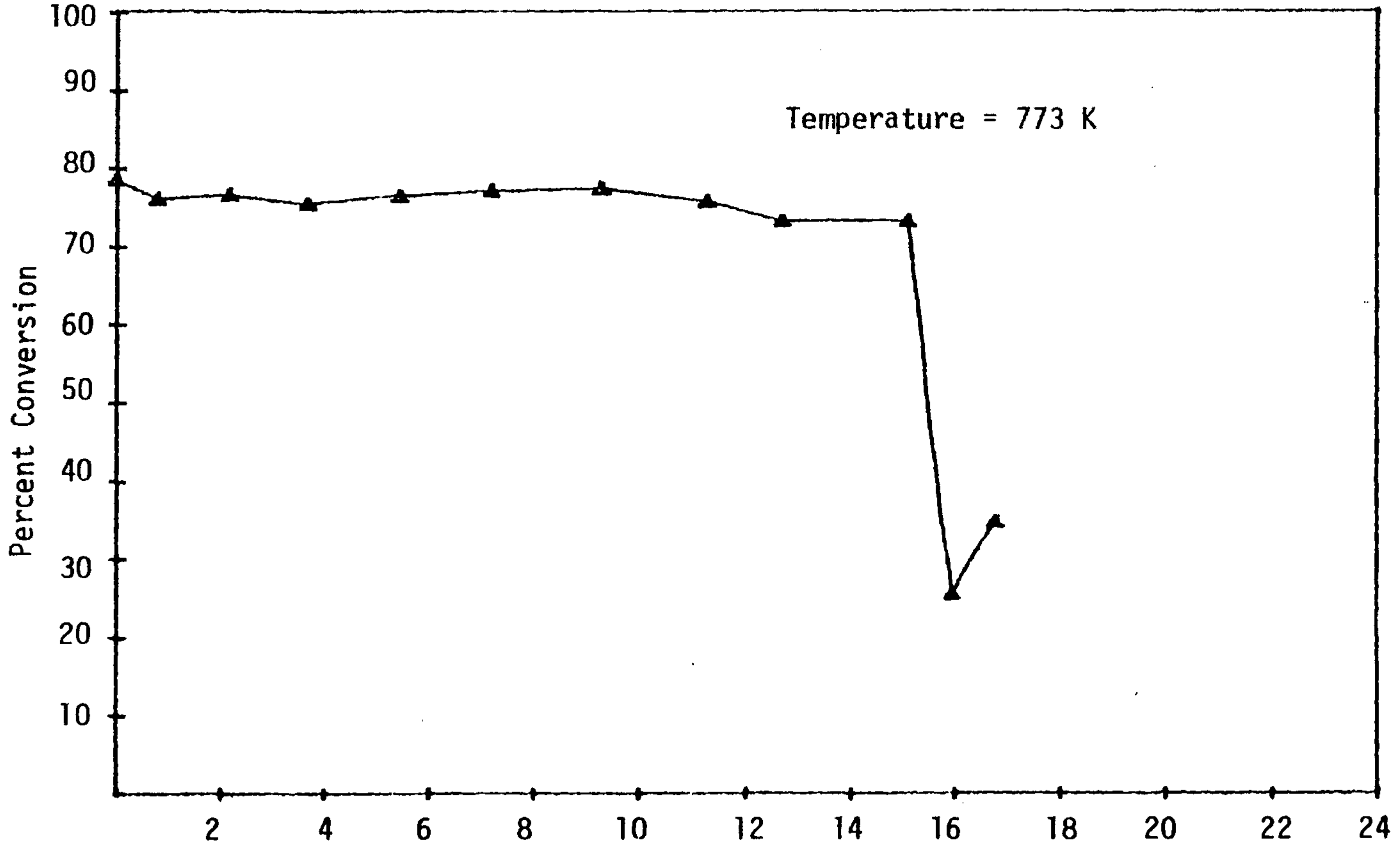

Figure 4. Conversion of CO (overall) vs. time for Ni-A-122 (20% Ni) at 2500 kPa, 773 K, GHSV = 30,000 hr^{-1} and reactor mixing containing 63% CH_4, 16% Ar, 15% H_2, 4% CO and 2% CO_2.

Deactivation rates were calculated for both runs. The rates were -0.26% CO conversion/hr at 723 K and -0.37% CO conversion/hr at 773 K. These rates are linear regression estimates taken of the initial point and points after 8 hrs. excluding the points after plugging occurred. If one extrapolated the deactivation of Ni-A-122 at 723 K from 24 hours to one week, the CO conversion would be 59.4%. At 773 K over a one week period the activity would drop from 78.7% to 26.3% CO conversion, assuming no carbon plugging of the reactor.

Task 5: Technical Interaction and Technology Transfer

On September 25, Dr. Bartholomew visited Gulf Research in Pittsburgh and presented a seminar "Sulfur Poisoning of Nickel Methanation Catalysts," based upon work supported by this contract. During the day he visited with other scientists and researchers in catalysis. Discussions focused on sulfur poisoning, monolithic catalysts, methanation and Fischer-Tropsch catalysis.

Drs. Donald LaRue and Victor Kelsey of Idaho International Laboratory visited with the principal investigator on October 12 and toured the BYU Catalysis Laboratory. The main purpose of the visit was to discuss possibilities for developing a cooperative research program in catalysis. Drs. LaRue and Kelsey offered to characterize some of our methanation catalysts with TEM.

George Hill visited the College of Engineering on October 26. Dr. Bartholomew visited with him about the past, present and future of energy research and about our catalysis research program.

The principal investigator was invited by the BYU Chemistry Department to present a seminar on October 31. The talk entitled "Future of Catalysis" included a brief description of our DOE supported research. A similar seminar was presented to the Chemical Engineering Department on November 2.

Dr. Bartholomew attended the Miami AIChE meeting November 13-15 and presented a paper on "Sulfur Poisoning of Nickel Catalysts" as part of the symposium on Catalysis by Supported Metals. He also met with Richard Schehl of the Pittsburgh Energy Research Center (PERC) and attended a number of sessions related to catalysis research and reactor design. There were a number of interesting, pertinent papers including those by Richard Schehl on modeling of the PERC methanation reactors, John Butt on structure sensitivity of supported Pt, K.H. Johnson on electronic structure of clusters, Lani Schmidt on sintering of Pt and Pd catalysts, Albert Vannice on metal-support effects in methanation, Ross Madon on Fischer-Tropsch and Bill Thomson on Ru metallic monolithic catalysts.

On December 6, the BYU catalysis group entertained Mr. Kyung Sup Chung and Professor Frank Massoth of the University of Utah, Department of Fuels Engineering. A seminar by Mr. Chung on the chemistry and characterization of Co-Mo HDS catalysts was followed by a lively discussion of our work at BYU.

The principal investigator prepared and submitted to th AIChE a manuscript entitled "Monolithic Supported Catalysts, I. Methanation Activity Relative to Pellet Catalysts." This paper, based on work performed in this and the previous contract discusses the advantages of monolithic nickel catalysts compared to pellet forms and contains the calculations discussed earlier in this report. It will be presented by Mr. George Jarvi at the April AIChE meeting in Houston.

During December, Mr. Gordon Weatherbee successfully completed the requirements for his M.S. His thesis entitled "Methanation Activity and Deactivation of Alumina Supported Nickel and Nickel Bimetallic Catalysts" is based on work performed in this and the previous contract. Mr. Weatherbee intends to continue work towards a Ph.D. in Chemical Engineering.

IV. CONCLUSIONS

1. Calculations of Thiele modulus, effectiveness factors and mass transfer coefficients for pellet and monoliths show that under all reactor conditions (i.e. 500-700 K, 140-2500 kPa, and 15,000 to 50,000 hr^{-1}) monoliths are more active than pellets because of lower pore diffusion resistance and higher rates of film mass transfer. Pellets operate at low effectiveness above 600 K while monoliths have effectiveness factors near unity at high temperatures and conversions.

2. Our H_2 chemisorption technique is accurate to within 12% even for samples bulk reduced at different space velocities.

3. A new technique for Ni crystallite size determination by Transmission Electron Microscopy was developed. Purposely carbon fouling the catalyst causes long filaments of carbon to grow away from the alumina. At the end of each filament is a nickel crystallite. The average size of these crystallites was comparable to that estimated by H_2 chemisorption.

4. Long term thermal degradation tests of Ni-A-122 (20% Ni) showed that the catalyst deactivates slowly due to carbon fouling and sintering. A test at 773 K had to be terminated after 17 hrs. because the reactor plugged with carbon. This plugging may be due to carbon lay-down on the reactor walls and not from carbon caused by the catalyst. Extrapolating the activity data from the test at 723 K showed that Ni-A-122 would retain 59.4% CO conversion after one week under reaction conditions.

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