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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. QUARTERLY TECHNICAL PROGRESS REPORT, DECEMBER 19, 1979-MARCH 18, 1980

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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period December 19, 1979 to March 18, 1980

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DEPARTMENT OF ENERGY

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FOREWORD

This report summarizes technical progress during the second quarter (December 19, 1979 to March 18, 1980) of a three-year study conducted for the Department of Energy (DOE) under Contract No. DE-AC01-79ET14809. The principal investigator for this work was Dr. Calvin H. Bartholomew; Mr. Henry W. Pennline was the technical representative for DOE.

The following students contributed to the technical accomplishments and to this report: Glenn W. Davis and Jeffery L. Rankin. Mr. Rankin and Dr. Bartholomew were the principal authors. Karen Barrett and Oscar Delgado provided typing and drafting services.

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ABSTRACT

During the second quarter, a 15% Fe/SiO_2 catalyst was prepared. H_2 and CO chemisorption uptakes were measured for the catalysts prepared to date. Very small uptakes were noted for the silica supported iron catalysts. Reactor activity tests in synthesis gas were conducted for 3% Fe/SiO_2, 15% Fe/SiO_2 and 10% Co-B/Al_2O_3 catalysts. These preliminary tests aided the final development of a laboratory microreactor system. Criteria for avoiding heat and mass transfer limitations on intrinsic rate measurements were examined and applied to the catalyst activity tests. The principal investigator and students presented papers at the Fifth Rocky Mountain Fuel Symposium, the Spring Meeting of the California Catalysis Society Meeting and the 179th National ACS Meeting in Houston and entertained one visitor. The PI also presented a seminar at Cornell University and visited the University of Delaware.

I. OBJECTIVES AND SCOPE

A. Background

Cobalt and iron catalysts find wide application in the oil, gas and chemical industries, particularly in ammonia synthesis, hydrotreating and hydrocarbon synthesis reactions. They are expected to find even broader application in future energy technologies, especially in production of synthetic fuels from coal.

Although cobalt and iron containing catalysts for synthesis of aliphatic and aromatic hydrocarbons from coal-derived gases (Fischer-Tropsch Synthesis) were developed 2-3 decades ago and are even used on a very limited basis commercially to produce gasoline, their activity, selectivity and stability properties leave much to be desired. Most Fischer-Tropsch (FT) catalysts, for example, evidence poor selectivity for highly desirable products such as gasoline (C_6-C_{12}) or chemical (C_2-C_5) feedstocks; that is, the hydrocarbon products range from gases to heavy waxes. Thus, there is clearly a need to find more selective catalysts. Since much of the recent work has been directed at synthesis of gaseous hydrocarbons for chemical feedstocks, there is clearly a need to focus on catalysts selective for the production of liquid aliphatics and aromatics, particularly in the C_6-C_{12} gasoline feedstock range.

With the exception of a few recent studies, previous investigations have emphasized a trial and error (screening) approach to finding the best FT catalysts. Much of the previous work was carried out using large catalyst beds under conditions such that the kinetics were influenced by diffusional resistance, temperature gradients and heat/mass transport effects. Generally, there was relatively little characterization of the physical and chemical properties of the catalysts. Yet recent evidence indicates that FT catalysts are complex, multiphase solids and that structural and chemical promoters and surface additives (including sulfur) can profoundly influence the activity, selectivity and stability of these catalysts. Moreover, poisoning by sulfur compounds at levels as low as 1 ppm can result in rapid significant losses of activity and dramatic changes in selectivity; yet there has been very little definitive work to characterize the effects of sulfur poisoning. Therefore, the need is evident for a comprehensive, systematic scientific investigation of these phenomena which includes careful characterization of bulk and surface catalytic properties and activity studies under chemical-reaction-controlled conditions.

B. Objectives

This report describes recent progress in a comprehensive, quantitative investigation of catalyst metal-additive interactions and their effects upon activity, selectivity and resistance to sulfur poisoning in Fischer-Tropsch Synthesis, the objectives of which are to:

1. Determine and explain the effects of the interaction of sulfur, nitrogen and boron additives with unsupported and supported cobalt and iron catalysts (promoted and unpromoted) on activity, selectivity and sulfur tolerance in Fischer-Tropsch synthesis.
2. Correlate the activity/selectivity and sulfur tolerance properties for hydrocarbon synthesis with the oxidation state, dispersion and adsorption properties of the catalytically active phases in iron and cobalt catalysts.
3. Seek more active, sulfur tolerant Fe and Co metal/metal oxide catalysts for selective production of premium feedstocks such as C_2-C_5 hydrocarbons or C_6-C_{12} hydrocarbons, with emphasis on gasoline liquids.

C. Technical Approach

In order to accomplish the above listed objectives, the proposed work has been divided into three areas of study (three tasks) to be completed over a period of three years:

Task 1. Preparation and characterization of promoted and unpromoted, supported and unsupported cobalt and iron synthesis catalysts.

Task 2. Measurement of hydrocarbon synthesis activity/selectivity properties of cobalt and iron catalysts under typical reaction conditions.

Task 3. Measurement of the deactivation rates of cobalt and iron catalysts during synthesis in a reaction mixture containing dilute H_2S.

The experimental approach for each of these tasks is described below.

Task 1: Catalyst Preparation and Characterization

Catalysts to be prepared as part of this study are listed in Table 1. Except for a 3 wt.% Fe/Al_2O_3, all of the catalysts will have metal loadings of approximately 15 wt.%. The alumina-supported catalysts will be prepared mainly by impregnation of an alkali-free γ-Al_2O_3, (Conoco) with aqueous solutions of cobalt and iron nitrates. Co/SiO_2 and Fe/SiO_2 will be prepared by a modification of a new developed controlled-pH precipitation technique which results in very high nickel dispersions in Ni/SiO_2 catalysts. Fe/MgO catalysts will be prepared by a new coprecipitation technique developed at Haldor Topsoe which enables very high iron dispersions to be obtained. The Al_2O_3 and SiO_2 supported catalysts will be dried directly without precalcination and all catalysts will be reduced in flowing hydrogen 12-16 hours at 725 K. Promoted catalysts will be prepared by separating each of the dried catalysts into two batches and reimpregnating one batch of each kind with a solution of KNO_3 or $Zn(NO_3)_2$ in such proportions as to obtain 0.5% K_2O and 15% ZnO in the final product.

Table 1

Catalyst Preparation Plans[a] (Task 1)

Metal-Support Combination	Unpromoted	Promoted		Additive Pretreatments			No. Catalysts
		K_2O	ZnO	S	N	B	
Fe (unsupported)	x	x		x(2)[b]	x	x	6
Co (unsupported)	x			x		x	3
Co/SiO_2	x	x				x	3
Fe/SiO_2	x	x	x	x(3)[b]	x	x	8
Fe/MgO	x						1
Fe/Al_2O_3	x(2)[c]						2
						Total	23

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[a] 15 wt.% metal unless otherwise noted; 0.5 wt.% K_2O, 15% ZnO.

[b] Promoted and unpromoted catalysts will be sulfided.

[c] 3 and 15 wt.% metal loadings.

Catalysts will be sulfided by passing a gaseous mixture of 3% H_2S/H_2 over reduced samples at 575 K for a period of 12-16 hours. They will be nitrided by exposing the reduced catalyst to ammonia at 625 K for 12-16 hours folowed by treatment in H_2 at 575 K for 12-16 hours to remove all traces of ammonia; thus preventing formation of urea during synthesis. Silica supported iron boride will be prepared according to special techniques recently developed in this laboratory for preparation of supported cobalt and nickel borides. This approach involves a nonaqueous, low temperature reduction of the impregnated or deposited metal nitrate/support with sodium borohydride followed by washing, drying and high temperature reduction in hydrogen.

The catalysts prepared in this study will be characterized by a number of different techniques including H_2 and CO chemisorption, chemical analysis, x-ray diffraction, thermal gravimetric analysis, Moessbauer Spectroscopy and ESCA. Metal dispersions will be measured using hydrogen adsorption at 298 K and will be checked in selected cases using CO chemisorption at 298 K and x-ray line broadening. X-ray diffraction scans will also be used to establish the various catalytic phases. The extent of reduction to the metallic state and bulk oxidation states will be determined by thermal gravimetric analysis and Moessbauer spectroscopy. Selected samples will be sent to Austin Science Associates, Austin, Texas for Moessbauer Analysis. ESCA and X-ray diffraction scans will also be performed at the University of Utah. Chemical analysis will be taken by Rocky Mt. Geochemical Corp.

Characterization experiments to be performed in the Principal Investigator's laboratory are summarized in Table 2. Experiments to determine the effects of promoters and sulfur poisoning on the adsorption of CO and H_2 have also been included. These experiments are affected by surface additives. Gravimetric Analysis will also be used to determine the kinetics of carbiding under reaction conditions. A TGS-2 Thermogravimetric analyzer is already available in the Catalysis laboratory.

Task 2: Activity/Selectivity Measurements

The experimental plan in Table 2 summarizes the catalysts to be tested and the purpose of their study. The conditions proposed for the activity/selectivity measurements are 525 K (and 500 K in selected cases), 1 atm, (25 atm in the case of the 4-5 most promising catalysts), $H_2/CO = 2$ and space velocities in the range of 2,000 to 30,000 h^{-1}. The space velocity will be adjusted in each test so that the CO conversion at 525 K is in the range of 5-10% in order that intrinsic activities in the absence of diffusional influences may be obtained. Catalyst samples will be crushed to fine particles in order to otherwise minimize diffusional influences; small samples on the order of 0.5 to 2 g and the use of high space velocities will minimize thermal gradients in the catalyst bed. Samples will be reduced *in situ* for 2 hours and then conditioned under the reaction conditions for a period of 6-18 hours during which time chromatograph samples will be carried out intermittently. From previous investigations it is clear that in the case of small samples 6-18 hours reaction in

Table 2

Experimental Plan

Task	Purpose of Study	Catalysts
1-Characterization:		
a. H_2 and CO Chemisorption Measurements	Determine Active Metal Surface Areas	H_2 Adsorption on All Catalysts; CO adsorption on Fe, Fe/SiO_2; Fe/Al_2O_3, Fe/MgO, Co and Co/SiO_2
b. H_2 and CO Adsorption Measurements on K_2O Promoted and Presulfided Catalysts	Determine effects of promoters and sulfur poisoning on reactant adsorption	Fe, Fe/SiO_2, Co, Co/SiO_2
c. Thermal Gravimetric Analysis and Moessbauer Spectroscopy	Determine effects of support on state of metal reduction; investigate carbide, nitride formation under reaction conditions.	Co/SiO_2, Fe, Fe/SiO_2, Fe/Al_2O_3 (2 loadings) Fe/ZSM-5[a] and Fe/Silicalite[a]
2-Activity/Selectivity Measurements	Effects of support	Fe, Fe/SiO_2, Fe/MgO Fe/Al_2O_3, Fe/ZSM-5, Fe/Silicalite, Co, Co/SiO_2
	Effects of metal	Co, Fe
	Effects of metal loading	3 and 15% Fe/Al_2O_3
	Effects of Promoter	K_2O promoted Fe, Fe/SiO_2, Co/SiO_2; ZnO promoted Fe/SiO_2
	Effects of Sulfiding	Fe, Fe/SiO_2 9unpromoted and K_2O promoted); Fe/SiO_2 ZnO promoted) and Co
	Effects of Nitriding, Boriding	Fe and Fe/SiO_2 (nitrided and borided), Co and Co/SiO_2 (borided)
	Effects of Pressure (Runs at 25 atm)	5 "best" catalysts based on runs at 1 atm

3-In situ H_2S Deactivation	Effects of support	Fe/SiO_2, Fe/MgO, Fe/Al_2O_3
	Effects of metal	Co, Fe, Co/SiO_2 and Fe/SiO_2
	Effects of metal loading	3 and 15% Fe/Al_2O_3
	Effects of Promoter	K_2O promoted Fe and Fe/SiO_2;ZnO promoted Fe/SiO_2 (sulfided and unsulfided)
	Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O promoted)
	Effects of Nitriding, Boriding	Nitrided and Borided Fe, Fe/SiO_2; Borided Co and Co/SiO_2
	Effects of Pressure (Runs at 25 atm)	5 "best" catalysts based on runs at 1 atm
	Kinetics of Deactivation	Fe/SiO_2 and Co/SiO_2

---

[a] Fe/ZSM-5 and Fe/Silicalite samples have been obtained from the Pittsburgh Energy Technology Center.

the synthesis gas mixture is adequate to reach a steady state catalyst condition, although we will be able to check this experimentally.

Since much of the recent scientific work has been carried out at 1 atm but the FT process is normally run at 20-30 atm in industry, the proposed testing of the most important catalysts at both 1 and 25 atm will combine the advantages of both worlds. That is, specific activity/selectivity properties of iron and cobalt catalysts can be compared with those from other scientific laboratories and the performance of these same catalysts can be compared with commercial catalysts tested under industrial relevant conditions. At least one representative catalyst will be tested over a range of pressure from 1-25 atm so that effects of pressure can be determined and the results at 1 atm can be extrapolated to higher pressure. It is also possible that some of the catalysts will have more desireable selectivity properties at lower pressures and this approach will reveal such a phenomenon.

Most of the activity/selectivity tests will be carried out in a tubular, differential reactor system capable of 300-1300 K, 1-30 atm operation and equipped with mass flow meters, a CO NDIR analyzer and an HP-5834 chromatograph with TCD and FID detection. Glass reactors suitable for pretreating and activity testing samples at 1 atm are already available. A tubular reactor suitable for testing of powdered samples at 25 atm will be fabricated. The reactor system will be modified by adding a trap for hydrocarbon liquids in addition to the presently available water trap. Gaseous, liquid and aqueous phase hydrocarbons will be collected and analyzed using 10 foot Porapak Q, 5% Carbowax/Chromosorb W and Chromosorb 102 columns. Selected runs will be carried out over the temperature range 500-575 K in a Berty Autoclave mixed flow reactor in order to determine conversion-temperature, selectivity-temperature behavior and the effects of pressure.

Task 3: In Situ H_2S Poisoning Measurements

The catalysts to be studied for sulfur tolerance are listed in Table 2 along with the purpose for investigation. Activity measurements will be made as a function of time during reaction at 525 K, 1 atm (again the 4-5 most promising catalysts also at 25 atm), $H_2/CO = 2$ and space velocities of 5,000 to 30,000 hr^{-1} with 10 ppm H_2S in the reactant mixture. The analysis of gaseous hydrocarbons will be made intermittantly using chromatography over a period of 24 hours. Liquid hydrocarbons will be analyzed at the beginning (following 6-8 hours of conditioning) and the end of the 24 hour deactivation runs. During the majority of tests, each catalyst will be housed in a Pyrex differential tubular reactor cell. Selected runs with Fe/SiO_2 and Co/SiO_2 will be made using (i) a quartz mixed flow reactor at 1 atm and 525-575 K to determine the kinetics of deactivation and (ii) an aluminized stainless steel tubular reactor at 25 atm, 525 K to determine effects of pressure.

To ensure reproducibility in both activity and poisoning experiments, chromatographic samples will be analyzed repeatedly until consistent results are obtained. Duplicate samples of the same catalyst will be tested in selected instances.

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 1 and 2 accomplishments are on schedule.

Results from the past quarter are best summarized according to task:

Task 1. A 15% Fe/SiO_2 catalyst was prepared. All catalysts prepared to date were characterized by H_2 and CO adsorption.

Task 2. Plans were finalized for construction of a high pressure laboratory microreactor system. Several components are on order while others are presently being fabricated. Activity measurements on 3% Fe/SiO_2, 15% Fe/SiO_2 and 10% Co-B/Al_2O_3 were carried out in a Pyrex reactor cell at 1 atm pressure.

Task 3. Sulfur poisoning studies are scheduled to begin in March 1981.

Misc. Dr. Bartholomew and several students including Mr. Rankin attended the Fifth Rocky Mountain Fuel Symposium. Mr. Edward L. Sughrue presented a paper on methanation kinetics. The PI also attended and presented papers at the Spring Meeting of the California Catalysis Society and the 179th National Meeting of the American Chemical Society. He also visited Professor Robert Merrill at Cornell University where he presented a seminar and Professor James Katzer of Delaware. Mr. Richard Pannell of Gulf Research visited our laboratory and presented an informal seminar.

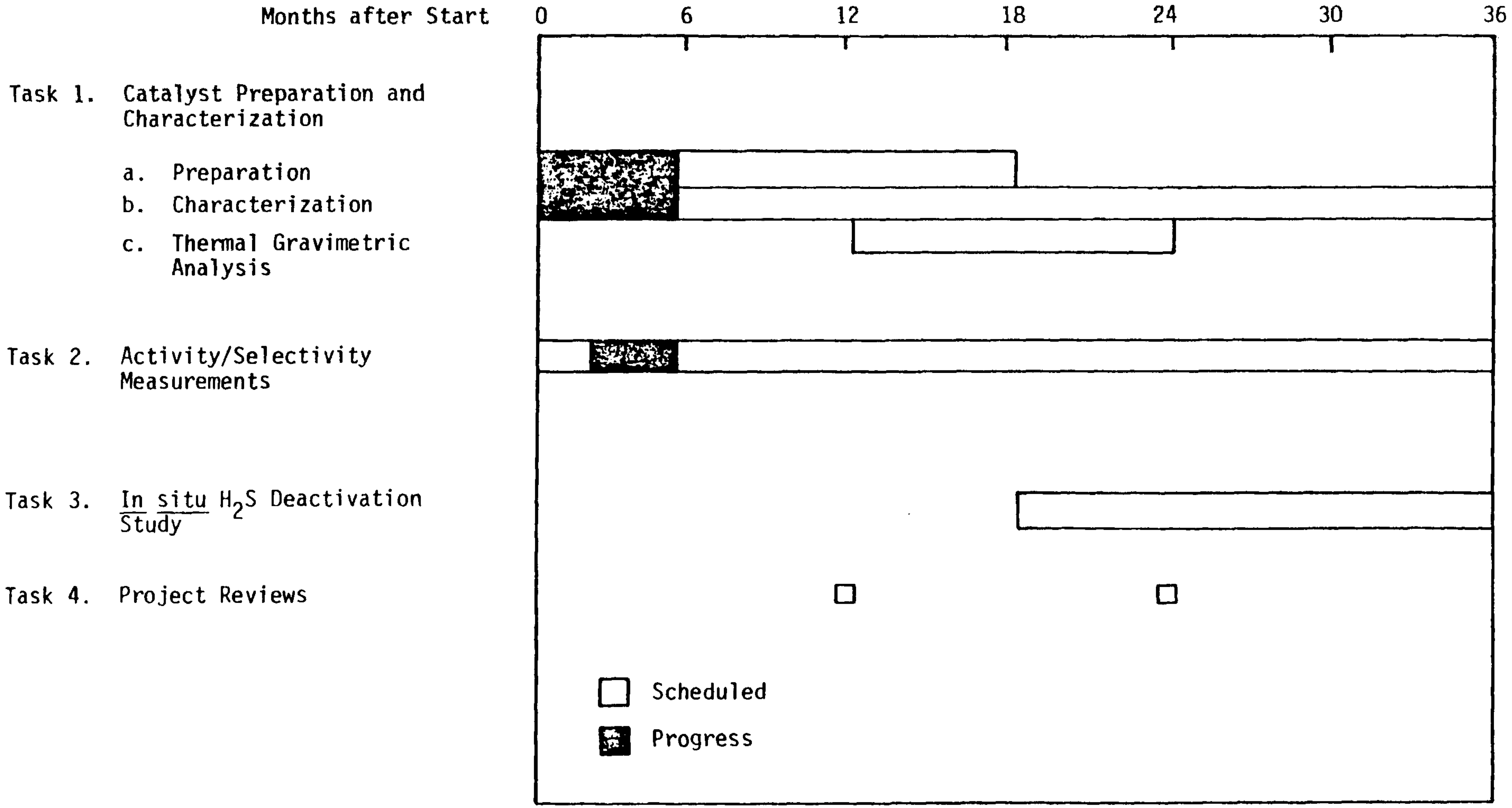

Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

In the past quarter, a 15% Fe/SiO_2 catalyst coded Fe-S-101, was prepared. Analytically pure $Fe(NO_3)_3 \cdot 9H_2O$ was used in aqueous solution to impregnate a commercial Cab-O-Sil silica support material. Several impregnations to incipient wetness were necessary to achieve the loading desired. These impregnations were followed by drying in an oven at 355-375 K for several hours. After being crushed to a fine powder, the catalyst was bulk reduced in flowing hydrogen at a space velocity of 2000 hr^{-1} at 725 K for 12 hours. Reduction was followed by passivation with 1% air in nitrogen.

2. Catalyst Characterization

Further chemisorption measurements were made this quarter using both H_2 and CO gases as adsorbates. These chemisorptions were performed at 298 K in a conventional high vacuum apparatus. Following reduction in hydrogen at 725 K, samples were evacuated to 10^{-6} torr at 675 K. Gas adsorption uptakes were measured as a function of pressure and the isotherm was extrapolated to obtain the adsorption at zero pressure.

In the case of CO chemisorption, a second titration of the gas followed to make correction for physisorption of CO on the metal. The difference between the two extrapolated uptakes was taken as the chemisorption uptake. Similar experiments on samples of pure silica support showed that both chemisorption and physisorption on the support are negligible. These silica samples underwent the same preparation treatment as the impregnated catalysts to insure comparability.

Results of the chemisorption measurements are listed in Table 3. The cobalt boride catalyst uptake was measured both before and after a long term reaction test in synthesis gas. Last quarter, the uptakes for Co-B-A-101 were reported using an estimated weight for the sample. Those reported this quarter are the correct values after weighing. The very small uptakes obtained for the iron catalysts are probably due to a strong iron-silica metal support interaction, causing the iron to be extremely difficult to reduce to the zero valent state.

3. Future Plans

Preparation of alumina supported Fe and K_2O and ZnO promoted iron on silica catalysts is planned for the next quarter. Further chemisorption measurements will be taken, including oxygen titration to measure the degree of reduction of the metal. This will allow definitive dispersion calculations.

Table 3

Hydrogen and Carbon Monoxide Chemisorption Measurements (298 K) for Supported Cobalt and Iron Catalysts

Catalyst Code	H_2 Uptake (μmoles/g)	CO Uptake (μmoles/g)	CO/H[c]
Fe-S-100	2.1	2.7	0.64
Fe-S-101	3.5	4.7	0.67
Co-S-101	17.1	--	
Co-B-A-101[a]	58.6	73.7	0.63
Co-B-A-101[b]	66.9	66.2	0.50

---

[a] Before long term reactor test.

[b] After long term reactor test.

[c] Ratio of CO molecules to H atoms adsorbed.

Some effort will be concentrated on the preparation of a more easily reduced iron on silica catalyst. Calcination of the catalyst in air before reduction may be a possible way to obtain a higher degree of metal reduction.

A cobalt boride on silica catalyst will also be prepared this quarter using the previously developed techniques of reduction of the cobalt on silica with $NaBH_4$ in dry ethanol (1). An investigation of techniques for measuring the dispersion and percent of cobalt reduced on Co-B-A-101 and the silica supported cobalt boride will be undertaken. This will be difficult because of the boron's affinity for oxygen, thus affecting the oxygen titration methods used typically for measuring percent reduction. Also, a further investigation of the structure of the cobalt boride on various supports will be undertaken.

B. Task 2: Activity Selectivity Measurements

1. Equipment Construction

After several discussions with investigators with previous experience in the Fischer-Tropsch area and a search of literature containing reactor system designs, a final reaction system and analysis scheme were decided upon. This is diagrammed in Figure 2. Several component parts are being ordered presently, and should be in operation next quarter.

When liquids and waxes being synthesized would cause reactor plugging or chromatograph fouling, two traps will be used at ice temperature. These will be constructed of 1/2" stainless steel tubing and Swagelok fittings as shown in Figure 3. Construction of these traps is presently underway.

2. Experimental Measurements

Several preliminary activity test runs were conducted this quarter using approximately a 2:1 H_2:CO ratio at 1 atm pressure in a Pyrex reactor cell. Product analysis was quantitative for CO, CH_4 and CO_2, but surface carbiding and lack of analysis for hydrocarbons did not allow complete information to be obtained. Reactant concentrations used were 96.678% N_2, 2.333% H_2, and 0.985% CO. Gases were purified using a Deoxo unit and molecular sieve trap. Dilution of the reactants was used in these preliminary tests so that reaction conversion could be controlled more closely.

The 3% iron on silica catalyst, Fe-S-100, was tested at 523 K and a space velocity of 2900 hr^{-1}. It was found that conversion was so small even at these extreme conditions that analysis was very difficult. An approximate turnover number was calculated, as shown in Table 4.

Fe-S-101 with a 15% metal loading showed considerably greater activity. At a space velocity of 1900 hr^{-1}, an initial conversion of CO of 1.23% was obtained. This steadily decreased to 0.2% conversion

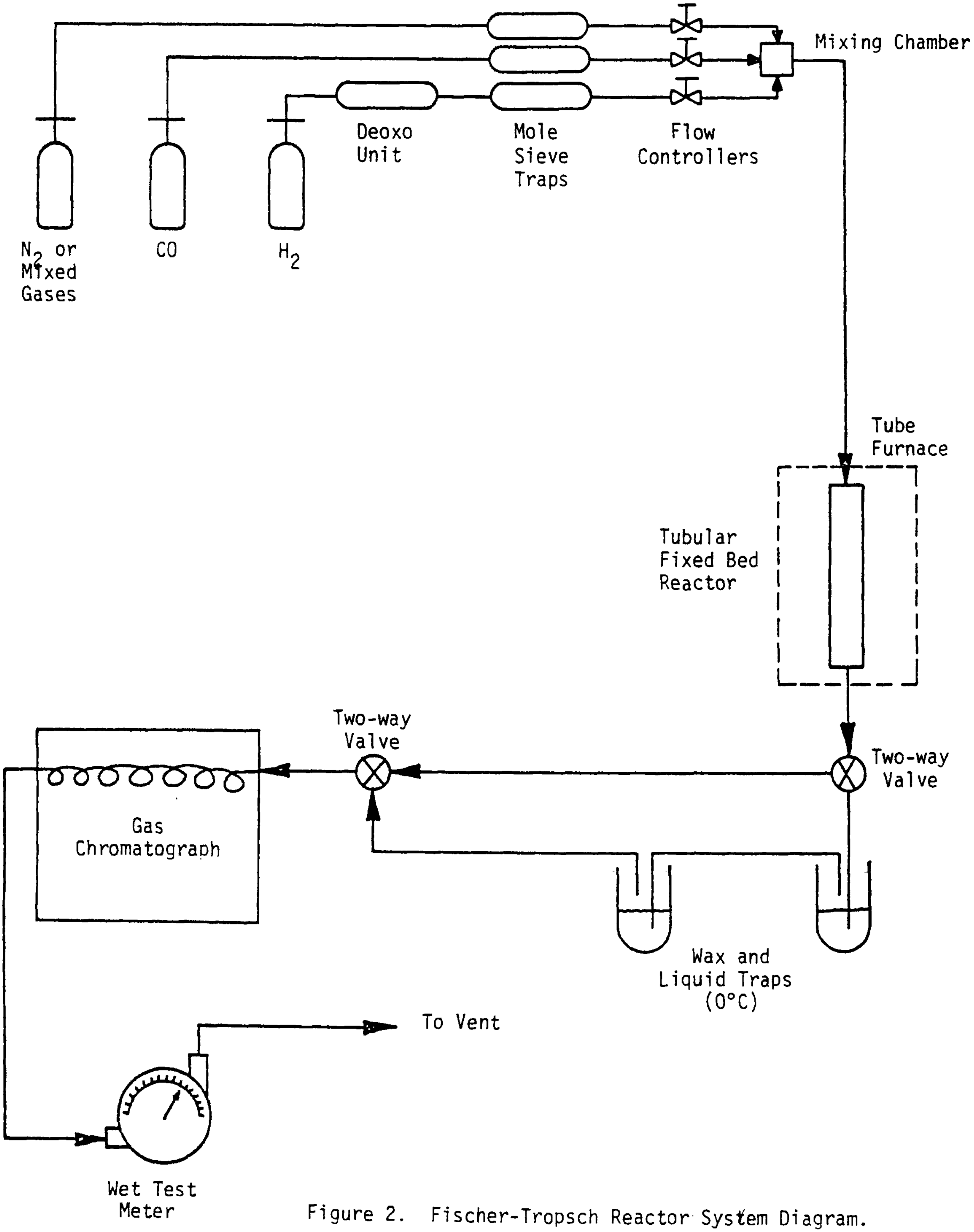

Figure 2. Fischer-Tropsch Reactor System Diagram.

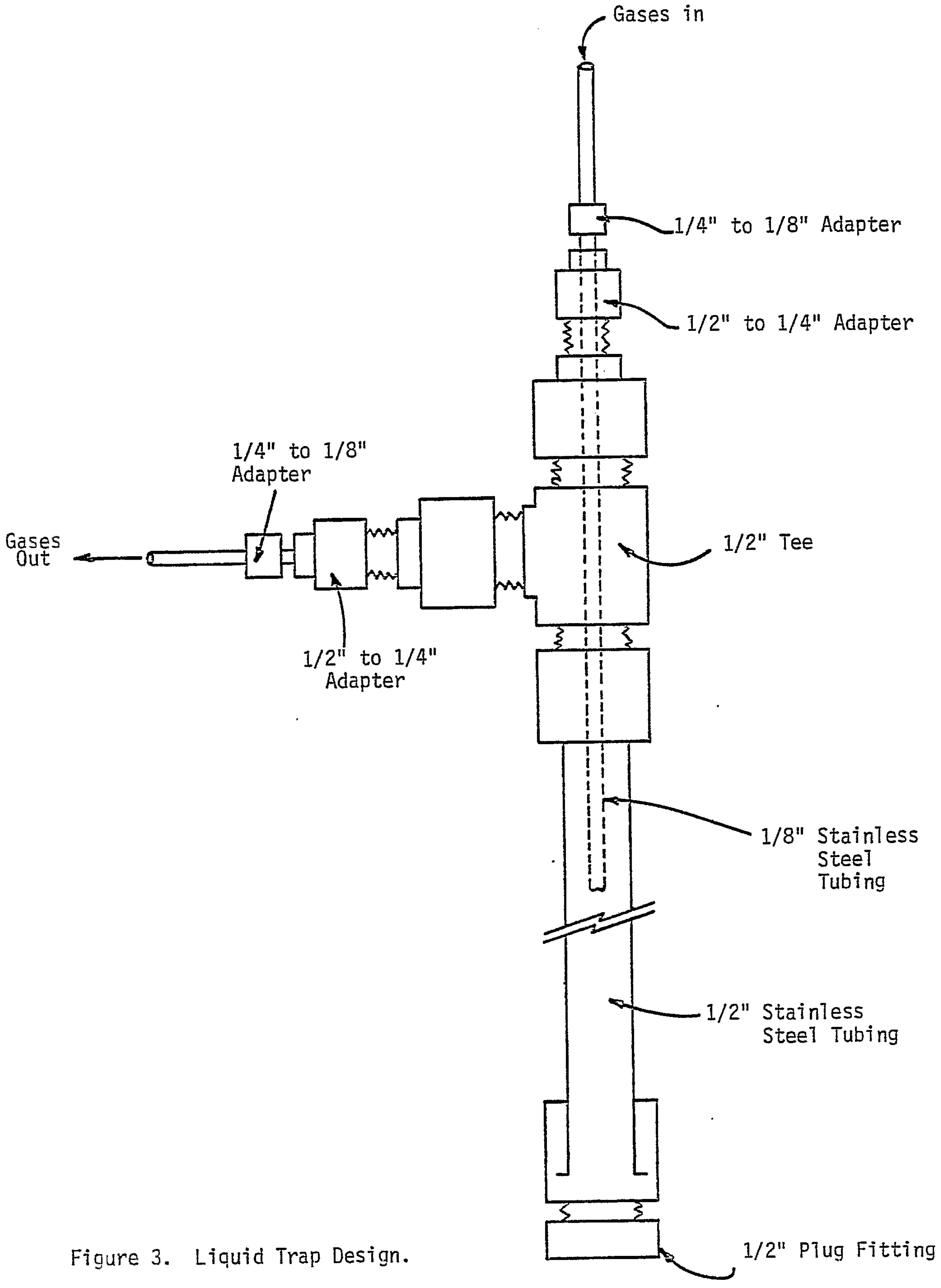

Figure 3. Liquid Trap Design.

Table 4

Turnover Numbers Obtained for Catalysts Tested at 1 atm Pressure and $H_2/CO = 2.33$

Catalyst Code	Temperature (K)	% CO Conv.	N_{CO} (molecule/site-s)	% Yield CH_4	% Yield CO_2	% Yield C_{2+}
Fe-S-100	523	0.2	0.57×10^{-3}	--	--	--
Fe-S-101	473	1.23	0.81×10^{-3}	--	--	--
Co-B-A-101	460	4.05	0.44×10^{-3}	34	0	66
Co-B-A-101	500	7.71	1.4×10^{-3}	31	5.6	63
Co-B-A-101	525	10.8	3.4×10^{-3}	72	31	0
Co-B-A-101	550	21.1	7.8×10^{-3}	57	31	12

after 36 hours of running, as shown in Figure 4. It is planned in the future to use nondiluted reactants to improve rate of reaction and analysis of products since it is apparent that rates are low on silica supported iron.

The Co-B-A-101 was pretreated for 27 hours at 525 K and 20,600 hr^{-1} space velocity. Figure 5 is a plot showing conversion of CO and production of CH_4 and CO_2 versus time for the pretreatment run. Steady state conversion was not obtained in 27 hours at the above conditions as shown in Figure 5. However, the same catalyst was then run at 460 K and 7100 hr^{-1} space velocity and CO conversion remained constant at 4.11% for 30 hours. Further tests for pretreatment time needed for undiluted reactant H_2 and CO in a 2 to 1 ratio will be done as the analysis scheme is developed.

Conversion over Co-B-A-101 was measured at 4 temperatures in the range of 460 to 550 K and an activation energy plot was made by plotting logarithm of the CO turnover numbers versus inverse temperature as shown in Figure 6. An activation energy of 68 to 79 kJ/mol was obtained by linear regression. These values are in good agreement with the value of 63 kJ/mol reported previously for unsupported borided cobalt (1,2).

Table 4 lists the turnover numbers and product distributions obtained for the various catalysts tested. The turnover number for Co-B-101 is about a factor of 10 lower than that reported earlier for unsupported cobalt boride and about the same as for Ni (1,2). The product distribution at 525 K is about the same as for unsupported cobalt boride.

3. Transport Limitation Calculations

During the past quarter, criteria for avoiding mass and heat transfer limitations in reactors of the fixed bed type were examined, including the following areas:

1. Intraparticle mass transfer (pore diffusion)
2. Intraparticle heat transfer
3. Interparticle mass transfer (film diffusion)
4. Interparticle heat transfer
5. Wall effects
6. Radial mass transfer
7. Radial heat transfer
8. Axial mass transfer

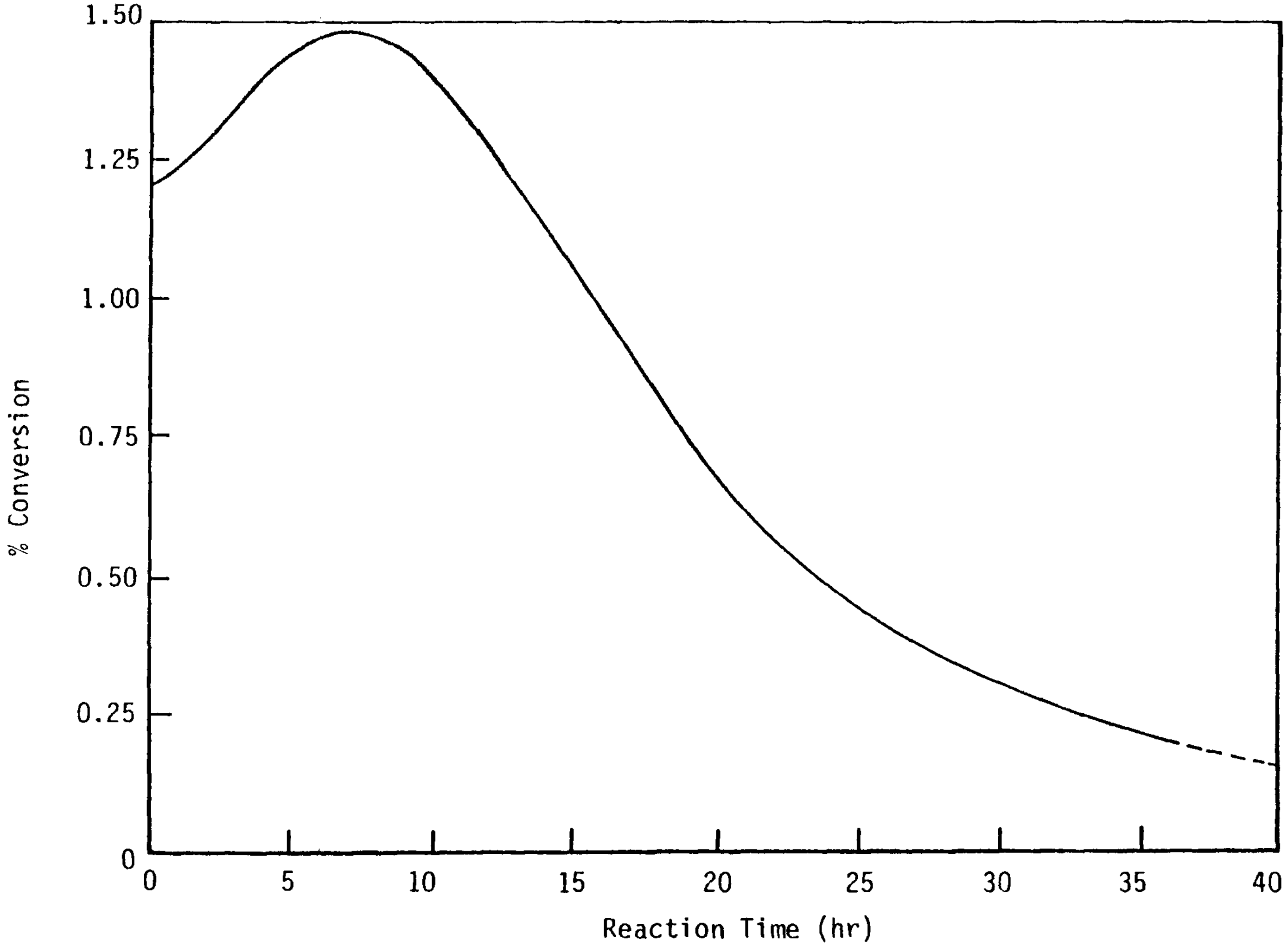

Figure 4. Percent CO Conversion vs. Reaction Time For Fe-S-101 (473 K).

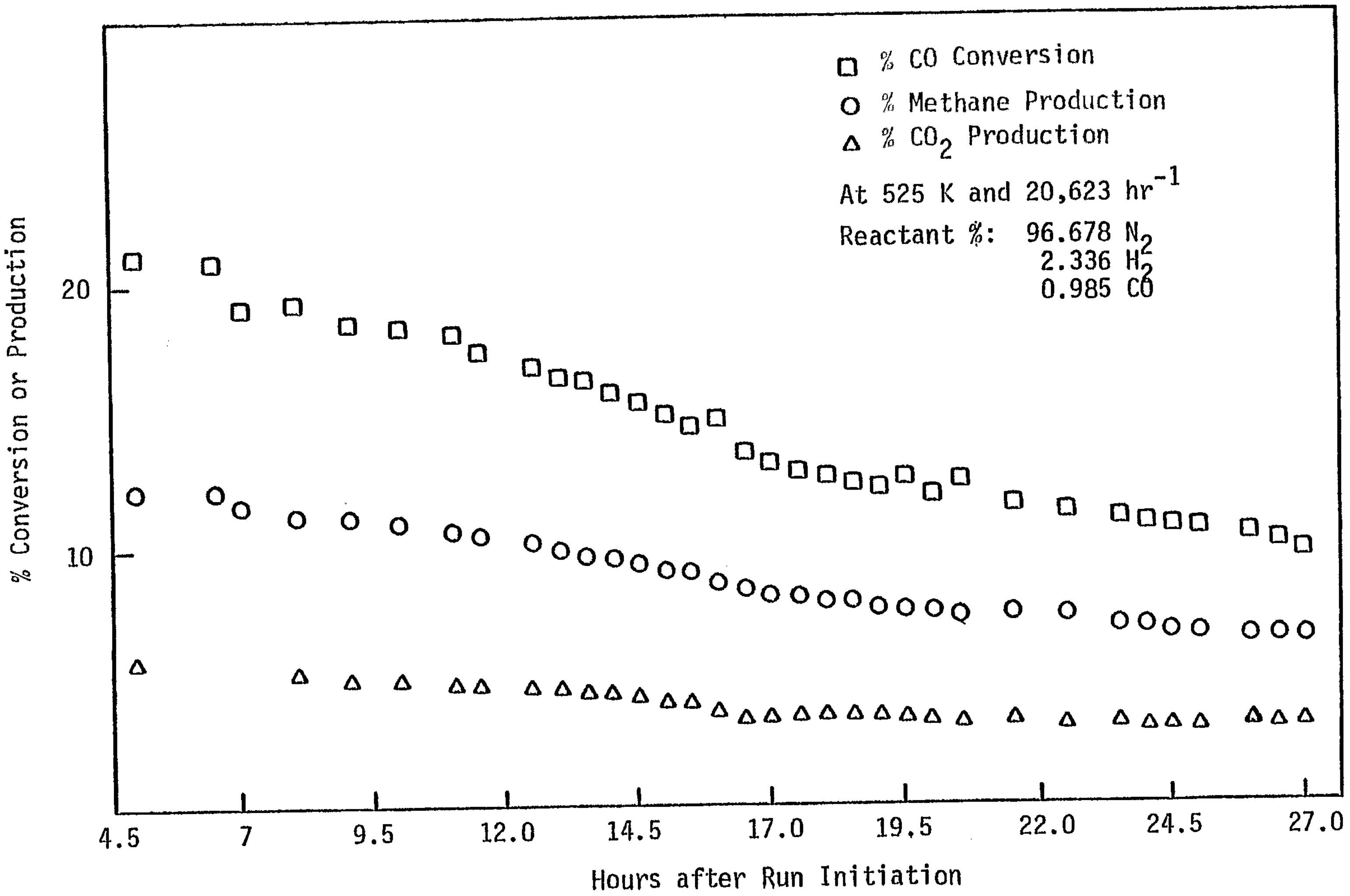

Figure 5. Percent CO Conversion, Percent CH_4 and CO_2 Production vs. Reaction Time for Co-B-A-101.

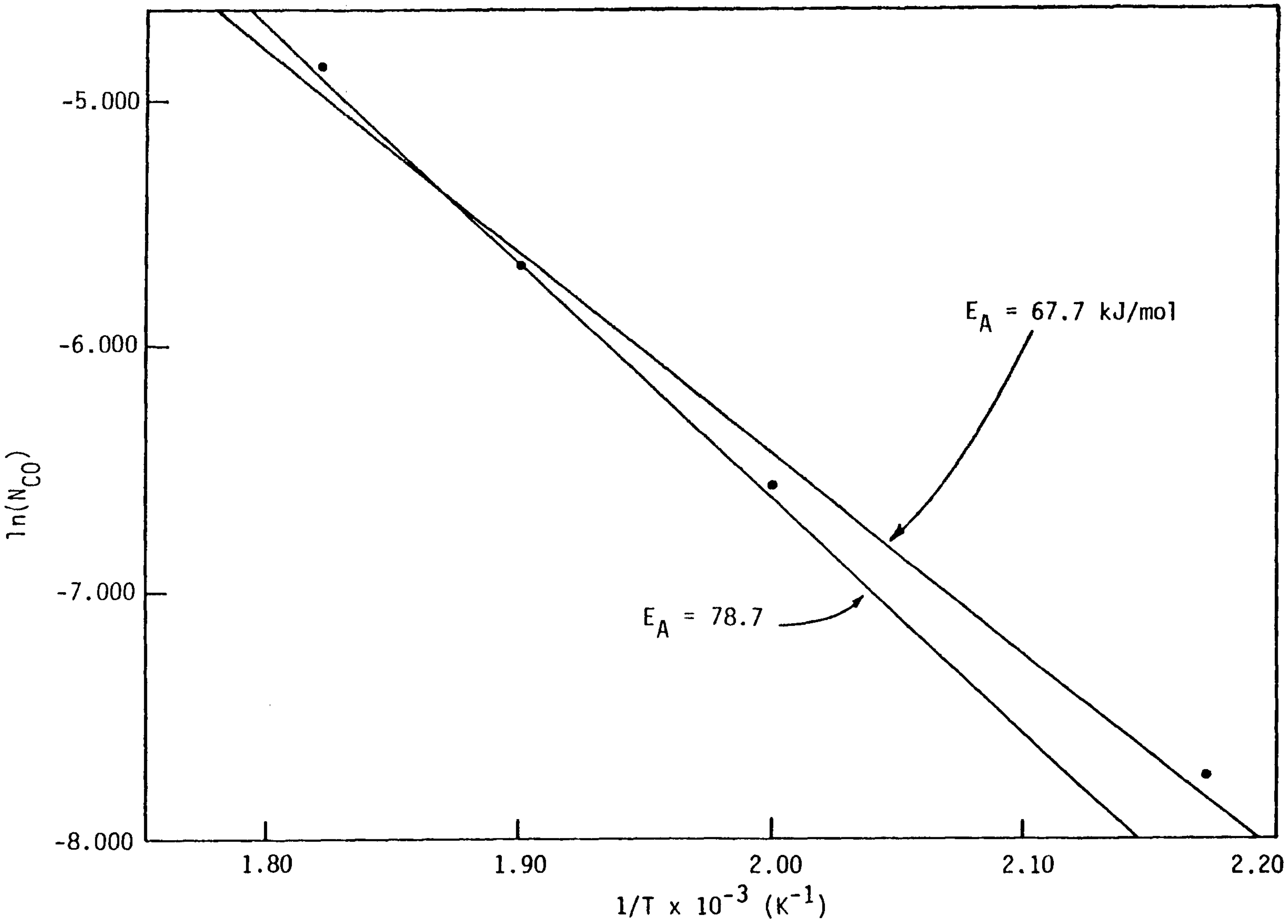

Figure 6. Activation Energy Plot for Co-B-A-101.

9. Axial heat transfer

These criteria were applied to a powder with particles of diameter 0.1 mm and less, a reactor made from 1/4" tubing, a H_2/CO ratio of 2, a pressure of 1 atm, and a reaction temperature of 473 K. It was felt these conditions would represent the proposed experiments on the average reasonably well and disclose any transport limitations that must be dealt with. These calculations, summarized in Appendix A, show that the measurement of intrinsic rate is not influenced by any of these phenomena with the possible exception of axial temperature gradients in the reactor bed ("hot spots"). From the literature examined, it appears this effect, if it does exist, will be minor. It is interesting that the use of powders eliminates many transport limitations which undoubtedly have masked true intrinsic rates in much of the previous Fischer-Tropsch work.

4. Future Plans

During the coming quarter, a series of iron catalysts on alumina and silica supports will be tested for activity. Also, novel iron zeolite catalysts obtained last quarter will be examined under reaction conditions. Activity and selectivity measurements will be made on both Co-B-A-101 and the cobalt boride on silica support catalyst to be prepared, varying reactant concentrations and temperature.

Plans are essentially complete for analysis of hydrocarbon products during the progress of reaction. This will aid the interpretation of reactor test data obtained. Nondiluted reactant gases will be used in these upcoming experiments.

C. Task 3: In Situ H_2S Deactivation Study

Experimental work on this task is not scheduled to begin until March 1981.

D. Miscellaneous Accomplishments and Technical Communication

During the past quarter, the principal investigator, Dr. Bartholomew, and several students attended and participated in several technical meetings, communicated with other workers regarding research problems related to CO/H_2 synthesis, and visited other laboratories. On February 14th, Dr. Bartholomew visited with Professor Robert Merrill at Cornell University and presented a Surface Science Seminar dealing with "Adsorbed Species in CO Hydrogenation on Nickel." He also visited with Professor James Katzer at the University of Delaware the following two days (February 15 and 16th) to work with him on a literature review of sulfur poisoning. On February 21-22 the principal investigator and several students including Mr. Rankin attended the Fifth Rocky Mountain Fuel symposium. The meeting featured a presentation by Dr. Heinz Heineman of the Lawrence Berkeley Laboratory on Liquid Fuels from Coal (including indirect liquefaction). Mr. Edward L. Sughrue of our group presented a paper on "Kinetic Studies of Nickel Methanation Catalysts."

Dr. Richard Pannell of Gulf Research visited us on February 26 and presented an informal seminar on CO hydrogenation on cobalt and iron. On March 13-14 Dr. Bartholomew attended the Spring meeting of the California Society and presented a paper on "Determination Metal Crystallite Size in Supported Nickel Catalysts." He also attended the 179th meeting of the American Chemical Society in Houston on March 25-27 and presented two papers: "Nickel-Support Interactions: Their Effects on Particle Morphology, Adsorption and Activity Selectivity Properties," and "Sulfur Poisoning of CO and H_2 Adsorption on Supported Nickel." Mr. A Douglas Moeller, a recent M.S. graduate from our group presented a paper dealing with "Deactivation by Carbon and Regeneration of Nickel and Nickel Molybdenum Methanation Catalysts."

IV. CONCLUSIONS

1. The CO/H adsorption ratios of 0.5-0.7 observed for 3% Fe/SiO_2, 15% Fe/SiO_2, and ∿10% $Co\text{-}B/Al_2O_3$. Catalysts suggests the bridged CO species are predominant during CO adsorption on these catalysts.

2. A 3% Fe/SiO_2 shows poor activity under typical low pressure synthesis conditions presumably as a result of its low metal surface area and low extent of reduction to the metal.

3. The specific activities (turnover numbers) of 15% Fe/SiO_2 and ∿10% $Co\text{-}B/Al_2O_3$ at 473 K, 1 atm are the same within a factor of 2.

4. The apparent activation energy of 68-79 kJ/mol observed for CO hydrogenation on $Co\text{-}B/Al_2O_3$ is about the same as the value of 63 kJ/mol for unsupported cobalt boride; however, its activity is significantly lower than that observed for unsupported borided cobalt.

5. Transport limitations on intrinsic rate measurement may be avoided during Fischer-Tropsch synthesis if finely crushed powders are used.

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APPENDIX A

TRANSPORT LIMITATION CALCULATIONS

I. Internal Effects

A. Intraparticle Mass Transfer (Pore Diffusion)

1. Weisz - Prater Criterion (4)

$$\frac{r^2 R_V}{D_e C_s} < 1$$

where r = particle radius
R_V = reaction rate per unit volume
D_e = effective mass diffusivity
C_s = surface reactant concentration

2. Calculation of D_e using Wilkie-Chang Equation (5)

a. $$D = (7.4 \times 10^{-8}) \frac{T M_s^{1/2}}{\mu_M V_{CO}^{0.6}}$$

where D = bulk mass diffusivity in cm^2/s
T = absolute temperature in K
M_3 = molecular weight of solvent
μ_M = viscosity of mixture in cp
V_{CO} = molar volume of solute (CO) at normal boiling point in cm^3/gmole

b. Data used:

T = 473.15 K
M_s = 422.826 g/gmole for n-C_{30} as solvent in pores
μ_M = 0.12 cp for liquid hydrocarbon (6)
V_{CO} = 30.7 cm^3/gmole (7)

3. Data used:

$C_s = 1.43 \times 10^{-5}$ gmole/cm^3 for CO at 1 atm (8)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3 from preliminary runs

4. Conclusion - since the powders being used have $r < 0.005$ cm, the criterion is obeyed.

B. Intraparticle Heat Transfer

1. Anderson Criterion (9)

$$\frac{q R_V r^2}{T k_p} < \frac{3}{4} \frac{T R}{E}$$

where q = heat of reaction
R_V = reaction rate per unit volume

r = particle radius
T = absolute temperature at particle surface
k_p = thermal conductivity of the catalyst particle
R = gas constant
E = activation energy of the reaction

2. Data used:

q = 209,000 J/gmole (10)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3
T = 473.15 K
$k_p = 4.184 \times 10^{-4}$ J/s-cm-K (11)
R = 8.31 J/gmole-K
E = 100,416 J/gmole (12)

3. Conclusion - For powders being used with $r < 0.005$ cm, the criterion is obeyed.

II. External Effects

A. Interparticle Mass Transfer (Film Diffusion)

1. Hudgins Criterion (13)

$$\frac{2R_V r}{k_m} \cdot \frac{R_V'(C)}{R_V(C)} < 0.3$$

where $R_V(C)$ = reaction rate per unit volume as a function of concentration
r = particle radius
k_m = interphase mass transfer coefficient

2. Calculation of k_m using Chilton-Colburn analysis (14)

a. $$\left(\frac{k_m}{v}\right)\left(\frac{\mu}{\rho D}\right)^{2/3} = 0.91\ Re^{-0.51}\ \psi$$

where k_m = interphase mass transfer coefficient
v = gas velocity
μ = gas mixture viscosity
ρ = gas misture density
D = gas mixture binary diffusion coefficient
Re = Reynolds number
ψ = shape factor

b. Calculation of D by Gilliland correlation (15)

1. $$D = \frac{(0.0043)T^{3/2}\ (1/M_A + 1/M_B)^{1/2}}{(V_A^{1/3}+V_B^{1/3})^2\ P}$$

where T = absolute temperature in K

M_A, M_B = molecular weights
V_A, V_B = molar volumes at normal boiling points in cm^3/gmole
P = pressure in atm

2. Data used:

T = 473.15 K
M_{CO} = 28.01 g/gmole
M_{H_2} = 2.016 g/gmole
V_{CO} = 30.7 cm^3/gmole (7)
V_{H_2} = 14.3 cm^3/gmole (7)
P = 1 atm

c. Data used:

v = 0.66 cm/s for space velocity of 250 hr^{-1}
$\rho = 2.75 \times 10^{-4}$ g/cm^3
μ = 0.01633 cp for $H_2/CO = 2$ (6)
ψ = 1.0 for spherical particles

3. Data used:

$R_V(C) = 3 \times 10^{-6}$ gmole/s-cm^3

$\frac{R_V(C)}{R'_V(C)} = C_{CO}$ for first order in CO

$C_{CO} = 8.5907903 \times 10^{-6}$ gmole/cm^3

4. Conclusion - For powders with $r < 0.005$ cm the criterion is obeyed.

B. Interparticle Heat Transfer

1. Mears Criterion (16)

$$\frac{q\,R_V r}{h\,T_b} < \frac{0.15\,RT_b}{E}$$

where q = heat of reaction
R_V = reaction rate per unit volume
r = particle radius
h = heat transfer coefficient
T_b = bulk gas temperature
R = gas constant
E = activation energy of reaction

2. Calculation of h using Chilton-Colburn analysis (14)

a. $$\left(\frac{h}{\rho C_p v}\right)\left(\frac{C_p\mu}{k}\right)^{2/3} = 0.91\ Re^{-0.51}\ \psi$$

where h = interphase heat transfer coefficient
ρ = gas mixture density
C_p = gas mixture heat capacity
V = gas velocity
μ = gas mixture viscosity
k = gas mixture thermal conductivity
Re = Reynolds number
ψ = shape factor

b. Data used:

$\rho = 2.75 \times 10^{-4}$ g/cm^3
C_p = 29.41 J/gmole-K (17)
V = 0.66 cm/s for space velocity of 250 hr^{-1}
μ = 0.01633 cp for $H_2/CO = 2$ (6)
k = 0.00183 J/cm-s-K for $H_2/CO = 2$ (7)
ψ = 1.0 for spherical particles

3. Data used:

q = 209,000 J/gmole (10)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3
T_b = 473.15 K
k = 8.31 J/gmole-K
E = 100,416 J/gmole (12)

4. Conclusion - For powders with $r < 0.005$ cm the criterion is obeyed.

III. Fixed Bed Effects

A. Wall Effects

1. Mears Criterion (18)

$$\frac{d_r}{d_p} > 10$$

where d_r = reactor diameter
d_p = particle diameter

2. Conclusion - For 1/4" reactor and powders with $r < 0.005$ cm, the criterion is obeyed.

B. Radial Heat Transfer

This limitation is always negligible (19,20)

C. Radial Heat Transfer

1. Mears Criterion (16)

$$\frac{q\, R_V(1-\ )r_o^{\,2}}{k_e T_w(1-b)} \qquad \frac{0.4\, RT_w/E}{\left[1 + \frac{4k_e}{h_w r_o}\right]}$$

where q = heat of reaction
R_V = reaction rate per unit volume
ε = bed void fraction
r_o = reactor radius
k_e = effective radial thermal conductivity
T_w = reactor wall absolute temperature
b = reactor wall absolute temperature
R = gas constant
E = reaction activation energy
h_w = wall heat transfer coefficient

2. Calculation of k_e

   a. $k_e/k = 8.6$ (21)

   b. $k = 0.00183$ J/cm-s-K for $H_2/CO = 2$ (7)

3. Calculation of h_w (21)

   a. $$\left(\frac{2h_w r}{k}\right) = \left(\frac{2h_w^o r}{k}\right) + 0.054\ PrRe \qquad (21)$$

   where h_w = wall heat transfer coefficient
   r = particle radius
   k = gas thermal conductivity
   h_w^o = wall heat transfer coefficient at zero flow
   Pr = Prandtl number
   Re = Reynolds number

   b. Data used:

   $k = 0.00183$ J/cm-s-K for $H_2/CO = 2$ (7)
   $\left(\frac{2h_w^o r}{k}\right) = 1.2$ (21)
   $Pr = 0.1506$
   $Re = 0.0111$

4. Data used:

   q = 209,000 J/gmole (10)
   $R_V = 3 \times 10^{-6}$ gmole/s-cm^3
   $\varepsilon = 0.5$
   $r_o = 0.3175$ cm
   $T_w = 473.15$ K
   $b = 0$ (nondiluted bed)
   $R = 8.31$ J/gmole-K
   E = 100,416 J/gmole (12)

5. Conclusion - For powders with $r < 0.005$ cm, the criterion is obeyed.

D. Axial Mass Transfer

1. Mears Criterion (16)

$$\frac{L}{2r} > \frac{20n}{Pe_a} \ln \frac{C_o}{C_f}$$

where L = bed length
r = particle radius
n = power exponent in rate law
C_o = initial reactant concentration
C_f = final reactant concentration
Pe_a = axial Peclet number = $\frac{2rv}{D_a}$
v = gas velocity
D_a = axial mass diffusivity

2. Data used:

$n = 1$ for CO first order reaction
$C_f = (0.8)\ C_o$ for 20% conversion
$v = 0.66$ cm/s
$D_a = D = 1.044\ cm^2/s$

3. Conclusion - For powders with $r < 0.005$ cm, the criterion is met if at least 0.50 g of catalyst are used.

E. Axial Heat Transfer

1. Young and Finlayson Criterion (22)

$$\frac{2qR_V r}{(T_i - T_w) v\rho\ C_p Pe_a} < 1$$

where q = heat of reaction
R_V = reaction rate per unit volume
r = particle radius
T_i = initial reactant temperature
T_w = reactor wall absolute temperature
v = gas velocity
ρ = gas mixture density
C_p = gas mixture heat capacity
Pe_a = axial Peclet number = $\frac{2vC_p r\rho}{ke_z}$
k_{ez} = effective axial thermal conductivity

2. Data used:

q = 209,000 J/gmole (10)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3
T_i = 300 K
T_w = 473.15 K
$\rho = 2.75 \times 10^{-4}\ g/cm^3$
C_p = 29.41 J/gmole-K (17)

k_{ez} = 0.0157 J/cm-s-K

3. Conclusion - For particles with r = 0.005 cm, gas velocity must exceed 0.76b cm/s to meet the criterion. This is slightly higher than the 0.66 cm/s in the average conditions used. Thus, some hot spots may develop. However, a survey of the literature shows these hot spots seldom exceed 10 K over isothermal bed operation.

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