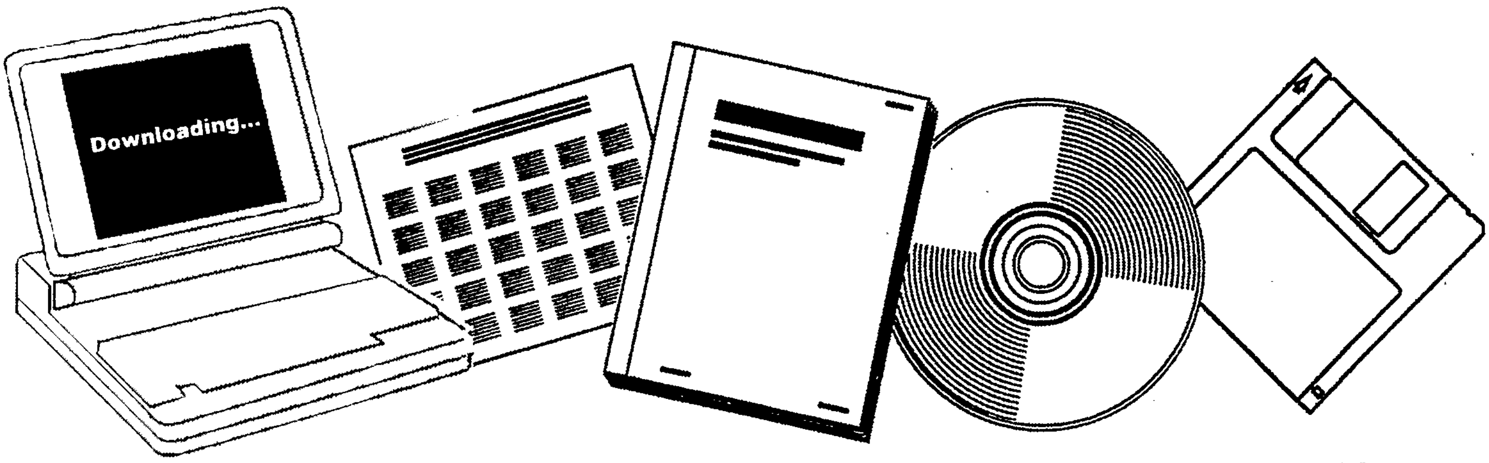
DE83000310

# INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. QUARTERLY TECHNICAL PROGRESS REPORT, MARCH 19-JUNE 18, 1982

BRIGHAM YOUNG UNIV.
PROVO, UT

01 JUL 1982



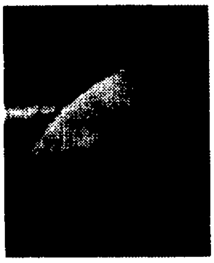
U.S. Department of Commerce
**National Technical Information Service**

**One Source. One Search. One Solution.**

**NTIS**

**Providing Permanent, Easy Access to U.S. Government Information**

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.



**Search the NTIS Database from 1990 forward**

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **www.ntis.gov.** You now have access to information on more than 600,000 government research information products from this web site.

**Link to Full Text Documents at Government Web Sites**

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

**Download Publications (1997 - Present)**

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

**www.ntis.gov**

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

DE83000310

DOE/ET/14809--11

DE83 000310

DOE-ET-14809-11

DOE-ET-14809-11
Dist. Category UC-90

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

MASTER

Quarterly Technical Progress Report
For Period March 19, 1982 to June 18, 1982

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

Date Published - July 1, 1982

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-AC~~01~~22-7~~0~~9ET14809

# DISCLAIMER

# FORWARD

This report summarizes technical progress during the eleventh quarter (March 20, 1982 to June 20, 1982) 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: Richard M. Bowman, Duane M. Davis and Jeffery L. Rankin. Mr. Bowman and Dr. Bartholomew were the principal authors. Laurie A. Witt provided typing services.

# TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

# ABSTRACT

During the eleventh quarter, more active supported boride-promoted catalysts were prepared by heating less rapidly during reduction. Unsupported iron and 15% iron on silicalite catalysts were also prepared. Thermogravimetric analysis of prepared samples was also begun.

Two silica supported catalysts derived from $Fe(CO)_5$ were tested. Both catalysts lost over half their initial activity within five hours, but both steady state activity and product selectivities are comparable with other iron catalysts. A silica supported, boron-promoted cobalt catalyst was tested and exhibited a selectivity of 72% to $C_5$ - $C_{15}$ hydrocarbons at temperatures above 485 K.

Data analysis was completed on in situ poisoning tests. Exposure to 2 ppm $H_2S$ resulted in much more rapid deactivation than exposure to 4-8 ppm $H_2S$. Deactivation at 525 K caused an increase in the $C_2$ olefin/paraffin ratio.

# 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 syntnetic 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 desireable 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 caried 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 (1-3). 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 phenomen 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 rreaction 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 $\gamma$-$Al_2O_3$, (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. 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 $KNO_3$ in such proportions as to obtain a K/Fe ratio of 0.2 in the final product.

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 follwed by treatment in $H_2$ at 575 K for 12-15 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 (1,2). 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

Table 1

Catalyst Preparation Plans[a] (Task 1)

| Metal-Suppport Combination | Unpromoted | Promoted | Additive Pretreatment | | | No. Catalysts |
|---|---|---|---|---|---|---|
| | | $K_2O$ | S | N | B | |
| Fe (unsupported) | x | x | x(2)[b] | x | x | 6 |
| Co (unsupported) | x | | x | | x | 3 |
| Co/$SiO_2$ | x(2)[c] | x | | | x | 4 |
| Fe/$SiO_2$ | x(2)[c] | x | x(2)[b] | x | x | 7 |
| Fe/$Al_2O_3$ | x | | | | | 1 |
| Fe/ZSM-5 | x | | | | | 1 |
| Fe/Silicalite | x | x | x[d] | | | 3 |
| Fe/C | x | | | | | 1 |
| | | | | | Total | 26 |

[a] 15 wt.% metal unless otherwise noted; 0.5 to 3 wt.% $K_2O$.

[b] Promoted and unpromoted catalysts will be sulfided.

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

[d] Promoted catalyst will be sulfided.

different techniques including $H_2$ and CO chemisorption, chemical analysis, x-ray diffraction, thermal gravimetric analysis, and Moessbauer Spectroscopy. 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 oxygen titration and Moessbauer spectroscopy using equipment in our own laboratory. 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 should also reveal how the chemical states of the metal 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 may be obtained in the absence of diffusional influences. 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 6-8 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 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 high pressure. It is also possible that some of the catalyst 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,

# 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, $Fe/SiO_2$; $Fe/Al_2O_3$, 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, $Fe/SiO_2$, $Co/SiO_2$ |
| | Effects of Sulfiding | Fe, $Fe/SiO_2$ (unpromoted and $K_2O$ promoted); and $Co/SiO_2$ |
| | 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 | $Fe/SiO_2$, $Fe/Al_2O_3$ |
| | Effects of metal | Fe, $Co/SiO_2$ and $Fe/SiO_2$ |

| | |
|---|---|
| Effects of metal loading | 3 and 15% $Fe/SiO_2$ |
| Effects of Promoter | $K_2O$ promoted Fe and $Fe/SiO_2$ |
| Effects of Sulfiding | Fe, $Fe/SiO_2$ (unpromoted and $K_2O$ promoted) |
| Effects of Nitriding, Boriding | Nitrided and Borided Fe, $Fe/SiO_2$ |
| Effects of Pressure (Runs at 25 atm) | 5 "best" catalysts based on runs at 1 atm |
| Kinetics of Deactivation | $Fe/SiO_2$ |

---

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

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 rreactor suitable for testing of powdered samples at 25 atm has been fabricated. The reactor system will be modified by adding a trap for hydrocarbon liquids. Gaseous, liquid and aqueous phase hydrocarbons will be collected and analyzed using SP2100 and Carbosieve B columns.

## 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 500 K, 1 atm (again the 4-5 most promising catalysts also at 25 atm), $H_2/CO = 2$ and space velocities of 200 to 1000 $hr^{-1}$ with 5 ppm $H_2S$ in the reactant mixture. The analysis of hydrocarbons will be made intermittantly using chromatography over a period of 24 hours. During the majority of tests, each catalyst will be housed in a Pyrex differential tubular reactor cell.

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 all tasks are on schedule except for the activity/selectivity tests.

Task 1: Three iron catalysts were prepared: Fe/Silicalite, Fe/$Al_2O_3$ and unsupported Fe. $H_2$ and CO adsorption uptakes were measured for 3 and 15% Co/$SiO_2$ and Fe/$SiO_2$ catalysts and for silica-supported iron and cobalt borides. $O_2$ titrations were performed for silica-supported Fe and Co. Cobalt catalysts are significantly better dispersed compared to iron catalysts; indeed, a 3% Co/$SiO_2$ was found to have a dispersion of 41%.

Task 2: Activity selectivity data were obtained for two Fe/$SiO_2$ catalysts prepared from decomposition of iron carbonyls and for 15% Co-B/$SiO_2$ (CoB-S-101). The carbonyl-derived Fe/$SiO_2$ catalysts are more active than conventional Fe/$SiO_2$ catalysts but rapidly lose activity during the first 5-6 hours of reaction; their steady state activities are comparable with conventional Fe/$SiO_2$. However, they show unusually high selectivities for $C_2$-$C_4$ and liquid hydrocarbons and low seletivities for methane and $CO_2$.

Task 3: Several in situ $H_2S$ deactivation tests were repeated and data analysis of most samples was completed. Fe/$SiO_2$ catalysts were found to deactivate much more rapidly at low concentrations of $H_2S$ (2 ppm) than at higher concentrations (5-8 ppm). FeB was extremely resistant to sulfur poisoning, losing only 5-6% of its initial activity after exposure to 4-6 ppm $H_2S$ for sufficient time (> 24 hrs) to have poisoned most of the available active sites.

Misc.: During the past quarter, the Principal Investigator and students attended three meetings (including the Heinemann Meeting held May 18-21 in Salt Lake City), visited Phillips Petroleum, presented 3 papers or seminars, and received 4 visitors.

## III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

### A. Task 1: Characterization and Preparation

#### 1. Catalyst Preparation

During the past quarter, three more iron catalysts were prepared and readied for testing. These were an unsupported iron (designated Fe-100) 15% iron/alumina (designated Fe-A-100) and a 15% iron/silicalite (designated Fe-L-101). The silicalite-supported catalyst was prepared by impregnation to incipient wetness of a silicalite support sample ELZ-115 received from Union Carbide. After drying in air at 100°C, the catalyst was crushed to a fine powder and stored.

Preparation of iron/alumina by impregnation was unsuccessful, yielding very large, hard lumps of material with extremely small pore volume. The preparation therefore followed the technique reported by Vannice (4,5). The appropriate amounts of support and reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ were weighed out and finely crushed in a mortar and pestal. After physically mixing the

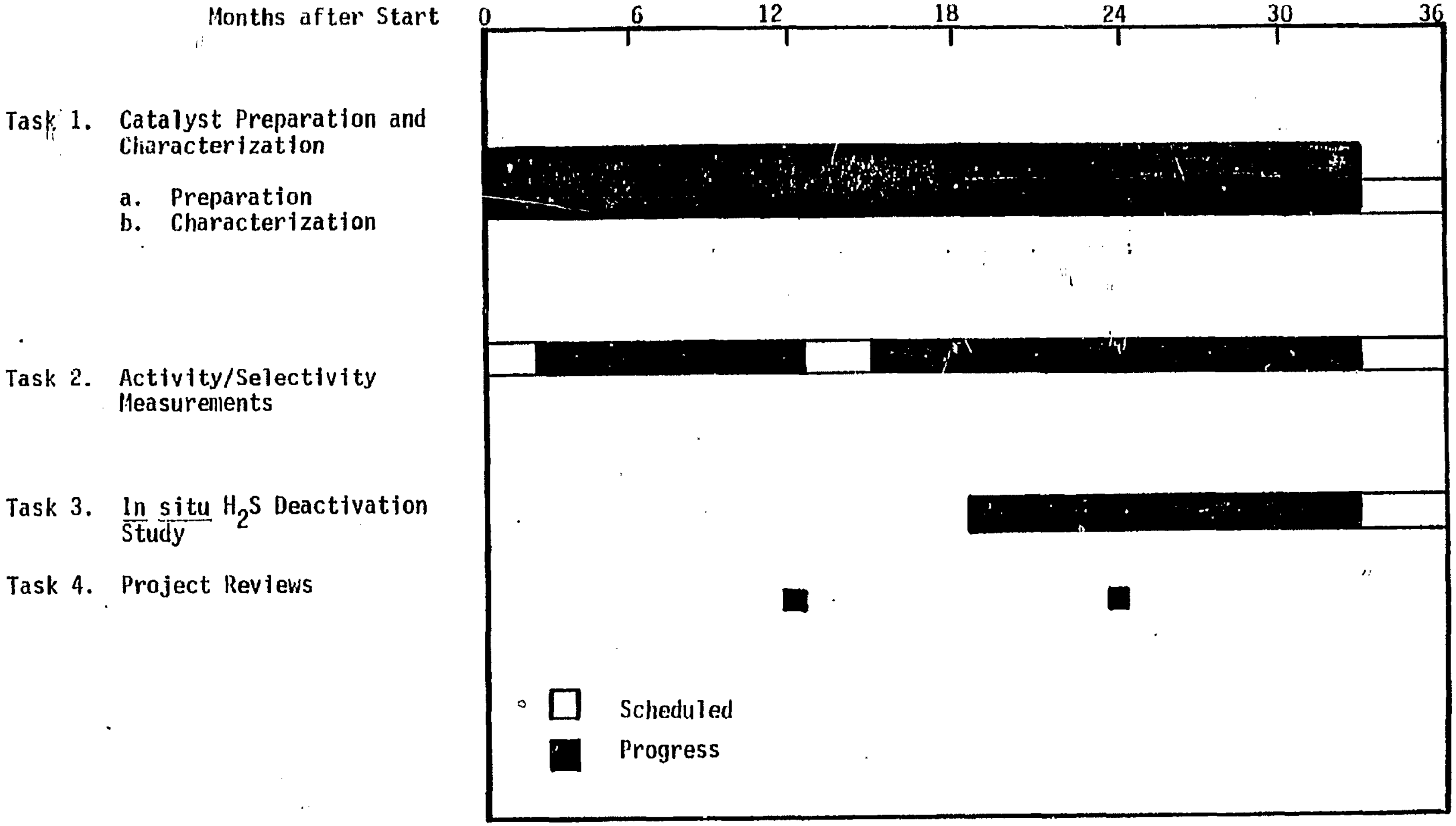


Figure 1. Schedule of Proposed Research Activities and Progress.

materials, they were placed in a muffle furnace and slowly heated to 100°C. This melted the nitrate into the alumina, 2 hours after which the temperature was raised to 200°C to drive off any remaining water. After drying, the catalyst was crushed and stored.

Unsupported iron was prepared using the same heat treatment as that in the preparation of iron/alumina. The $H_2$ adsorption has not yet been performed to determine if the surface area of this catalyst is adequate, but will be determined during the next quarter.

### 2. Catalyst Characterization

Table 3 lists chemisorption data performed to date on iron and cobalt catalysts. As can be seen, cobalt is generally more dispersed, absorbs CO more readily and also chemisorbs $CO_2$ to a much greater extent than iron. Of particular interest are the low extents of reduction determined from the $O_2$ titrations and the unexpectedly high percent dispersion of 41% for the 3% $Co/SiO_2$ (Co-S-103). To our knowledge there are no previous reports of such highly dispersed cobalt! Currently, thermogravimetric analysis is being performed on the cobalt catalysts to determine $O_2$ titration uptakes as an independent confirmation of these data.

A sample of reduced 15% Fe/silica was submitted for TEM measurement, but results have not yet been obtained.

### 3. Future Plans

During the next quarter, efforts will be made to complete the characterization on all catalysts particularly the zeolite-supported, nitrided and sulfided catalysts.

## B. Task 2: Activity/Selectivity Properties

### 1. Experimental Measurements

During the past quarter two silica-supported iron catalysts derived from $Fe(CO)_5$ (C6 and C7) were tested in $H_2/CO$ mixture of ratio 2 to 1 at 498 K. Data were also obtained for $CoB/SiO_2$ (CoB-S-101). Reaction data are summarized in Tables 4-6 for these and previously tested catalysts. Figure 2 shows the product distribution for CoB-S-101 as a function of carbon number and Figure 3 shows its activity versus time.

Catalysts C6 and C7 both produced very little methane and high yields of $C_2$-$C_4$ hydrocarbons. Unfortunately, much of the $C_5$+ products were in the $C_{18}$-$C_{22}$ wax range. Deactivation of the catalysts was significant. That is, after five hours of operation the C6 sample lost 41% of its initial activity, while C7 lost 73% of its initial activity. Nevertheless, initial activities were significantly greater and hence steady-state activities were comparable to conventional iron supported on silica. The C6 and C7 catalysts were significantly more selective for $C_2$-$C_4$ and $C_{5+}$ hydrocarbons and less selective for $CH_4$ and $CO_2$.

$CoB/SiO_2$ (CoB-S-101) is clearly very active with a turnover frequency at 500 K comparable with that of $Co/SiO_2$. Moreover, its activity increases

## TABLE 3

### $H_2$, CO, $CO_2$ and $O_2$ Uptakes on Iron and Cobalt Catalysts After 36-Hour Reductions in Hydrogen

| Catalyst Code | % Metal Loading | $H_2$ Uptake[a] (µmoles/g) | CO Uptake[b] (µmoles/g) | $CO_2$ Uptake[c] (µmoles/g) | $O_2$ Uptake[d] (µmoles/g) | %[e] Reduction | % D[j] |
|---|---|---|---|---|---|---|---|
| Fe-S-102[f] | 15 | 20.19 | 3.52 | -- | -- | -- | -- |
| Fe-S-102 | 15 | 16.02 | 12.16 | 1.09 | 1588 | 79 | 1.51 |
| Fe-S-103 | 3 | 2.36 | 1.21 | -- | 590 | 35 | 11.85 |
| FeK-S-100[g] | 15 | 9.11 | 4.94 | 6.56 | 856 | 42.5 | 1.7 |
| FeB-S-101[h] | 10 | 6.37 | -- | -- | -- | -- | -- |
| CoS-101 | 3 | 13.24 | 24.80 | -- | 242 | 71.2 | 7.2 |
| Co-S-102 | 15 | 52.39 | 89.94 | 17.87 | 590 | 35 | 11.85 |
| Co-S-103 | 3 | 18.76 | 55.50 | -- | 60.5 | 18 | 41.36 |
| CoB-102[b] | 10 | 47.5 | 32.6 | -- | -- | -- | -- |
| CoB-S-100[i] | 15 | 6.20 | 4.11 | -- | -- | -- | -- |
| FeB-102 | | 4.13 | 1.85 | -- | -- | -- | -- |
| CoB-S-101 | 15 | 21.19 | 24.37 | -- | -- | -- | -- |
| FeB-S-105 | 15 | 10.72 | 3.58 | -- | -- | -- | -- |

---

[a] At 298 K

[b] At 298 K

[c] At 373 K

[d] At 673 K

[e] Based on $Fe_2O_3$ or $Co_3O_4$ stoichiometry

[f] After 20 hour reduction in $H_2$

[g] Containing 3% $K_2O$ promoter

[h] Containing Boride promoter

[i] After 12 hour reduction in $H_2$

[j] Percent dispersion or percent exposed

## TABLE 4

## CO Turnover Numbers for Supported Iron and Cobalt Catalysts

| Catalyst Code | $H_2/CO$ Ratio | Temperature (K) | Turnover Number ($N_{CO} \times 10^3$) | Activation Energy (kJ/g mole) |
|---|---|---|---|---|
| Fe-S-102 | 2 | 460 | 0.64 | 92.5 |
| | 2 | 483 | 2.5 | |
| | 2 | 498 | 3.9 | |
| | 1 | 449 | 0.19 | 99.3 |
| | 1 | 483 | 1.4 | |
| | 1 | 498 | 2.5 | |
| Fe-S-103 | 2 | 448 | 0.72 | 82.8 |
| | 2 | 483 | 3.2 | |
| | 2 | 498 | 7.0 | |
| | 1 | 448 | 0.79 | 80.8 |
| | 1 | 473 | 2.3 | |
| | 1 | 498 | 7.0 | |
| FeK-S-100 | 2 | 498 | 6.6 | -- |
| FeB-S-101 | 2 | 498 | 0.33 | -- |
| Co-S-101 | 2 | 463 | 5.9 | |
| CoB-102 | 2 | 453 | 0.31 | 151.6 |
| | 2 | 473 | 1.7 | -- |
| CoB-102 | 1 | 458 | 0.28 | 139.6 |
| | 1 | 470 | 0.64 | |
| | 1 | 485 | 1.55 | |
| CoB-S-100 | 1 | 504 | 16.49 | 79.1 |
| | 1 | 520 | 29.46 | |
| FeB-102 | 1 | 483 | 8.05 | 81.4 |
| | 1 | 493 | 14.58 | |
| | 1 | 503 | 22.92 | |
| | 1 | 513 | 25.42 | |
| | 1 | 523 | 42.24 | |
| CoB-S-101 | 2 | 468 | 1.48 | 153.9 |
| | 2 | 486 | 6.28 | |
| | 2 | 499 | 20.62 | |
| C6 | 2 | 498 | 18 | -- |
| C7 | 2 | 498 | 10 | -- |

TABLE 5

Product Selectivities for Iron Catalysts at 498 K
and Cobalt Catalysts at 473 K

| Catalyst Code | Selectivity | | | | | Ave. Molecular Weight Hydrocarbon Product |
|---|---|---|---|---|---|---|
| | $CH_4$ | $C_2$-$C_4$ | $C_5$+ | $CO_2$ | Alcohols | |
| Fe-S-102[a] | 0.16 | 0.27 | 0.03 | 0.47 | 0.07 | 27.77 |
| Fe-S-102[b] | 0.12 | 0.23 | 0.02 | 0.56 | 0.07 | 28.68 |
| Fe-S-103[a] | 0.25 | 0.33 | 0.04 | 0.30 | 0.08 | 26.27 |
| Fe-S-103[b] | 0.20 | 0.31 | 0.03 | 0.36 | 0.10 | 27.54 |
| FeK-S-100[a] | 0.08 | 0.19 | 0.03 | 0.65 | 0.05 | 30.26 |
| FeB-S-100[a] | 0.26 | 0.19 | 0 | 0.55 | 0 | 20.25 |
| Co-S-101[a] | 0.27 | 0.24 | 0.34 | 0.04 | 0.11 | 31.21 |
| CoB-S-102[a] | 0.15 | 0.24 | 0.50 | 0.07 | 0.04 | 40.25 |
| FeB-102[b] | 0.17 | 0.44 | 0.23 | 0.10 | 0.06 | -- |
| CoB-S-100[b] | 0.31 | 0.26 | 0.31 | 0.06 | 0.06 | -- |
| CoB-103[b] | 0.18 | 0.16 | 0.20 | 0.40 | 0.06 | -- |
| CoB-S-101[a] | 0.07 | 0.20 | 0.72 | 0.01 | 0.00 | -- |
| C6 | 0.02 | 0.17 | 0.76 | 0.06 | -- | -- |
| C7 | 0.01 | 0.47 | 0.50 | 0.03 | -- | -- |

---

[a] $H_2/CO = 2$

[b] $H_2/CO = 1$

TABLE 6

Product Distributions for $CoB/SiO_2$ (CoB-S-101)

| | 226°C | | | 213°C | | |
|---|---|---|---|---|---|---|
| | wt.% P[a] | wt.% O[b] | O/P[c] | wt.% P | wt.% O | O/P |
| $C_1$ | 8.88 | -- | -- | 6.56 | -- | -- |
| $C_2$ | 2.12 | -- | -- | 1.52 | -- | -- |
| $C_3$ | 4.82 | -- | -- | 3.73 | -- | -- |
| $C_4$ | 1.43 | 3.71 | 2.59 | 3.93 | -- | -- |
| $C_5$ | 4.13 | 1.62 | 0.39 | 2.15 | 2.29 | 1.07 |
| $C_6$ | 4.99 | 1.19 | 0.24 | 2.82 | 1.63 | 0.58 |
| $C_7$ | 7.02 | 0.91 | 0.13 | 4.54 | 1.32 | 0.29 |
| $C_8$ | 9.78 | 0.57 | 0.06 | 7.34 | 1.02 | 0.14 |
| $C_9$ | 13.17 | 0.48 | 0.04 | 10.82 | 0.93 | 0.09 |
| $C_{10}$ | 13.61 | 0.29 | 0.02 | 13.20 | 0.71 | 0.05 |
| $C_{11}$ | 9.70 | 0.40 | 0.04 | 9.33 | 0.63 | 0.07 |
| $C_{12}$ | 5.85 | 0.18 | 0.03 | 7.19 | 0.35 | 0.05 |
| $C_{13}$ | 2.97 | 0.07 | 0.02 | 4.75 | 0.22 | 0.05 |
| $C_{14}$ | 0.15 | -- | -- | | | |
| $C_{15}$ | 0.42 | -- | -- | | | |
| $C_{16}$ | 0.77 | -- | -- | | | |
| $C_{17}$ | 0.61 | -- | -- | | | |
| $C_{18}$ | 0.59 | -- | -- | | | |
| $C_{19}$ | 0.29 | -- | -- | | | |
| $C_{20}$ | 0.09 | -- | -- | | | |

| | 195°C | | |
|---|---|---|---|
| | wt.% P | wt.% O | O/P |
| $C_1$ | 6.90 | -- | -- |
| $C_2$ | 0.0 | -- | -- |
| $C_3$ | 9.13 | -- | -- |
| $C_4$ | 9.11 | -- | -- |
| $C_5$ | 5.69 | 4.14 | 0.73 |
| $C_6$ | 5.95 | 3.31 | 0.56 |
| $C_7$ | 6.08 | 1.30 | 0.21 |
| $C_8$ | 6.47 | 0.66 | 0.10 |
| $C_9$ | 6.46 | -- | |
| $C_{10}$ | 5.22 | -- | |
| $C_{11}$ | 5.15 | -- | |
| $C_{12}$ | 5.69 | -- | |
| $C_{13}$ | 6.80 | -- | |
| $C_{14}$ | 10.02 | -- | |
| $C_{15}$ | 0.61 | -- | |
| $C_{16}$ | | | |
| $C_{17}$ | | | |
| $C_{18}$ | | | |
| $C_{19}$ | | | |
| C20 | | | |

Table 6 (cont.)

---

[a] Weight percent paraffin in product.
[b] Weight percent olefin.
[c] Olefin to paraffin ratio (wasn't possible to determine for $C_2$ and $C_3$).

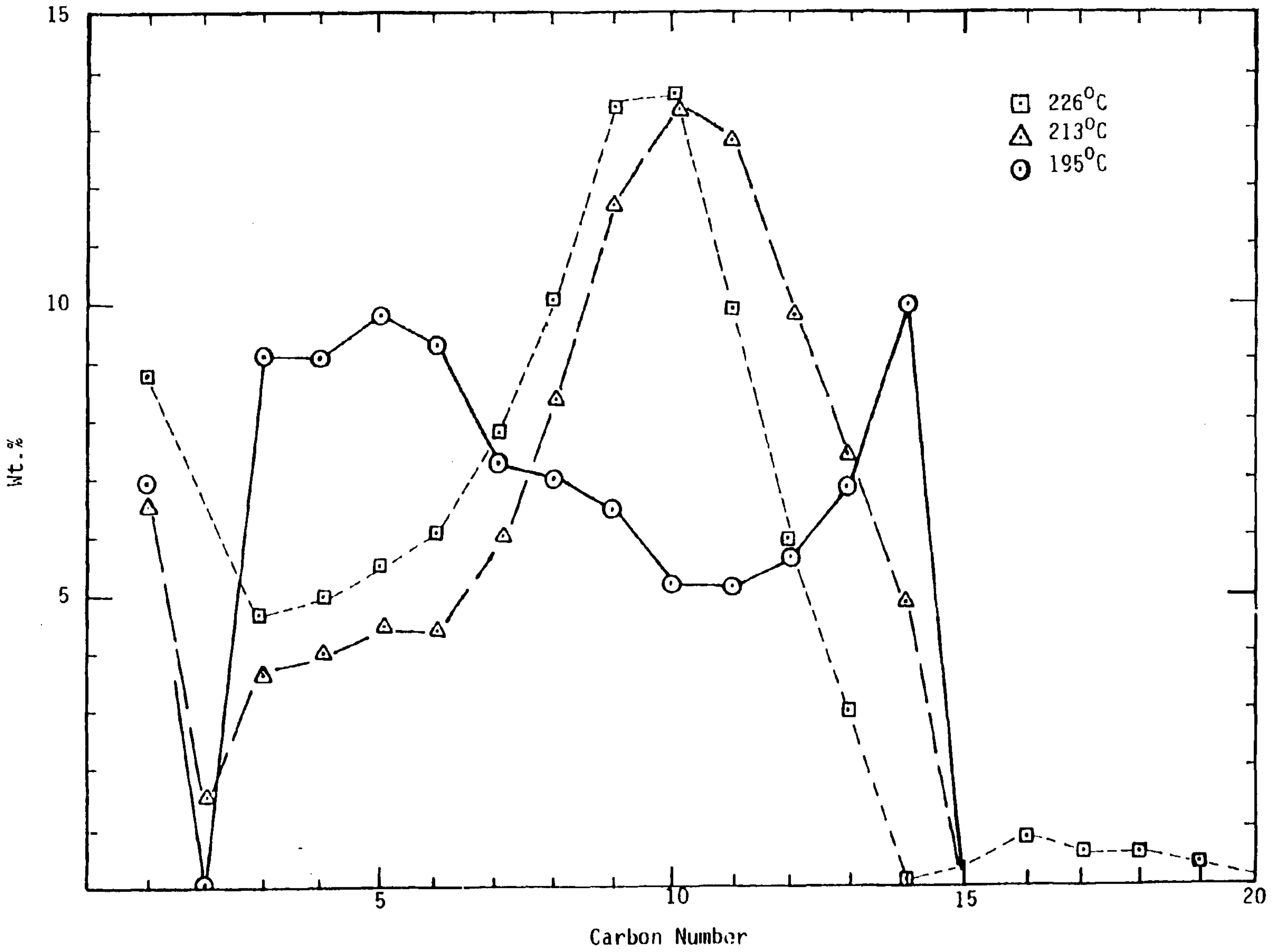


Figure 2. Product Distribution for CoB-S-101 at 1 atm, $H_2/CO = 2/1$.

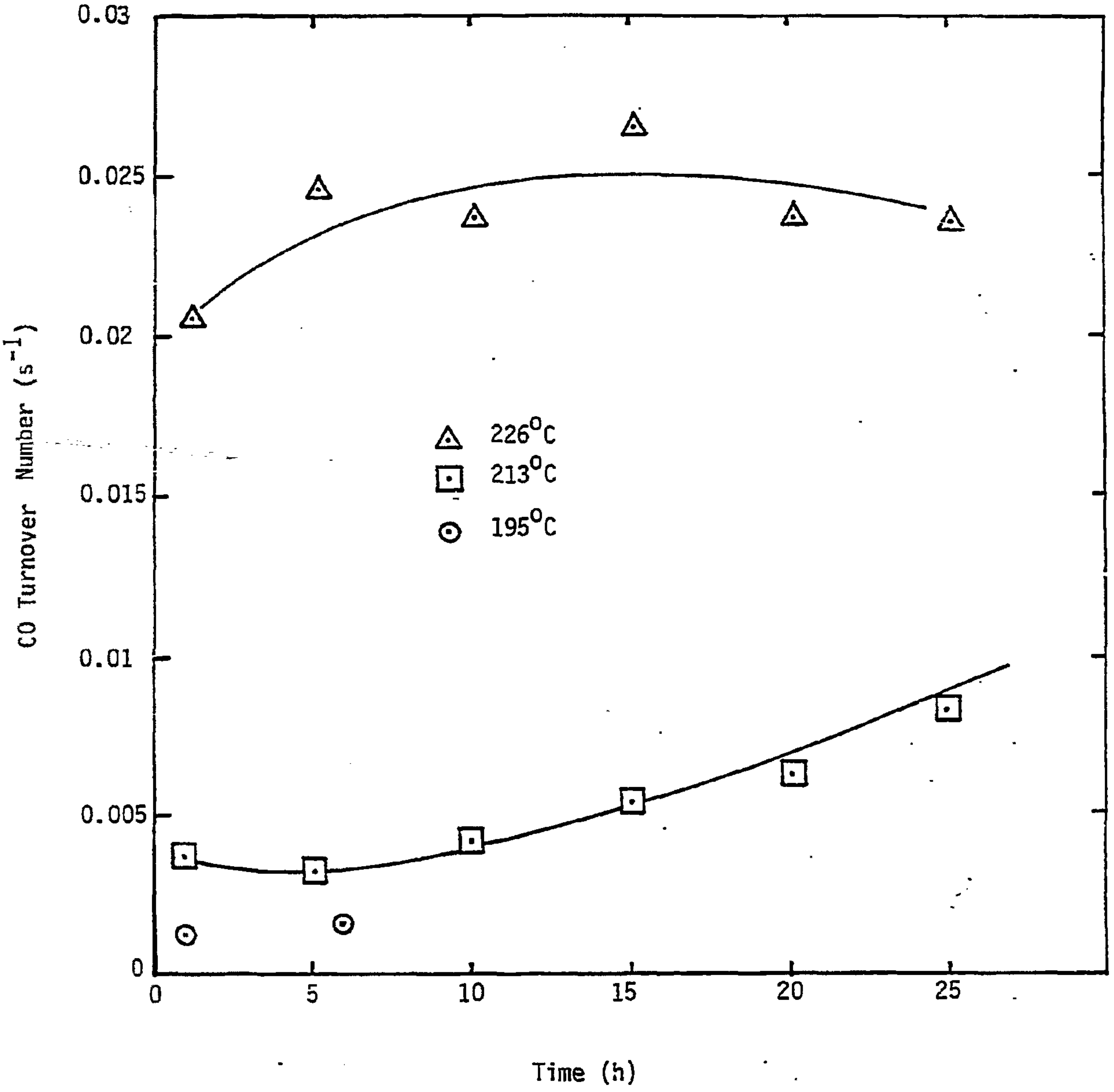


Figure 3. Turnover Number vs. Time for CoB-S-101 (15% CoB/$SiO_2$).

rather than decreases with time. More importantly, its selectivity for $C_{5+}$ gasoline range products is on the order of 70%, a value significantly better than predicted by Schultz-Flory and better than any previously tested catalysts. For example, under comparable conditions, Co/$SiO_2$ produces 30% $C_{5+}$ gasoline range products. Moreover, the selectivity of CoB/$SiO_2$ for $C_4$ olefins is very high ($C_2$ and $C_3$ olefins could not be resolved).

### 2. Future Plans

In the next 3 months, low pressure (1 atm) activity tests will be completed for the remaining catalysts. These tests will be made in $H_2$/CO = 2 and 1 to determine the effects of $H_2$/CO ratio on selectivity.

## C. Task 3: In Situ $H_2S$ Deactivation Study

Several earlier tests were repeated this quarter and data analysis was completed on other tests. 15% iron on silica catalyst samples were tested at 250°C in the presence of 2 ppm and 8 ppm $H_2S$. Another 15% Fe/$SiO_2$ sample was tested at 225°C with 2 ppm $H_2S$ in the feed.

Figure 4 shows normalized activity plotted as a function of sulfur to surface metal ratio (based on metal surface area measured by $H_2$ adsorption) for the catalysts tested to date in 4-6 ppm $H_2S$. As previously reported the unsupported iron boride catalyst is by far the least affected by sulfur. In fact, it loses only 5-6% activity after exposure to sufficient sulfur to completely deactivate most of its available sites. The potassium promoted iron catalyst is significantly more resistant than its unpromoted counterpart under similar conditions. Fe/$SiO_2$ is apparently more sulfur resistant than Co/$SiO_2$.

Figure 5 shows deactivation versus sulfur coverage data for Fe/$SiO_2$ tested at different $H_2S$ concentrations. The Fe/$SiO_2$ catalyst is most rapidly deactivated by lower $H_2S$ concentrations, i.e., the two Fe/$SiO_2$ samples exposed to 2 ppm $H_2S$ deactivated much more rapidly than samples exposed to 4-8 ppm $H_2S$ (see Fig. 5). The two samples exposed to 2 ppm $H_2S$ also exhibited a slight shift to lighter molecular weight products as deactivation occurred. In both cases the selectivity of the catalyst to $C_{6+}$ hydrocarbons decreased as poisoning occurred. This was not observed with those samples exposed to higher concentrations of $H_2S$. The samples tested at 250°C also evidenced significant change in product distribution with increasing severity of poisoning. For example, the ratio of $C_2H_4$ to $C_2H_6$ formed increased greatly as the catalysts deactivated. This was mainly due to the more rapid decrease in $C_2H_6$ production.

## D. Miscellaneous Accomplishments and Technical Communication

During the past quarter the principal investigator and several students attended a Micro ACS Meeting held March 27 on the BYU Campus and sponsored by the Central Utah Section. Mr. Gordon Weatherbee presented a paper on TPD of $H_2$ from Supported Nickel Catalysts. Dr. Bartholomew attended the 183rd National ACS meeting held March 28-April 2 in Las Vegas where he presented a paper, "CO Hydrogenation on Supported Molybdenum Catalysts," and chaired a session dealing with general topics in Catalysis. There were several good presentations at Las Vegas dealing with Fischer-Tropsch synthesis.

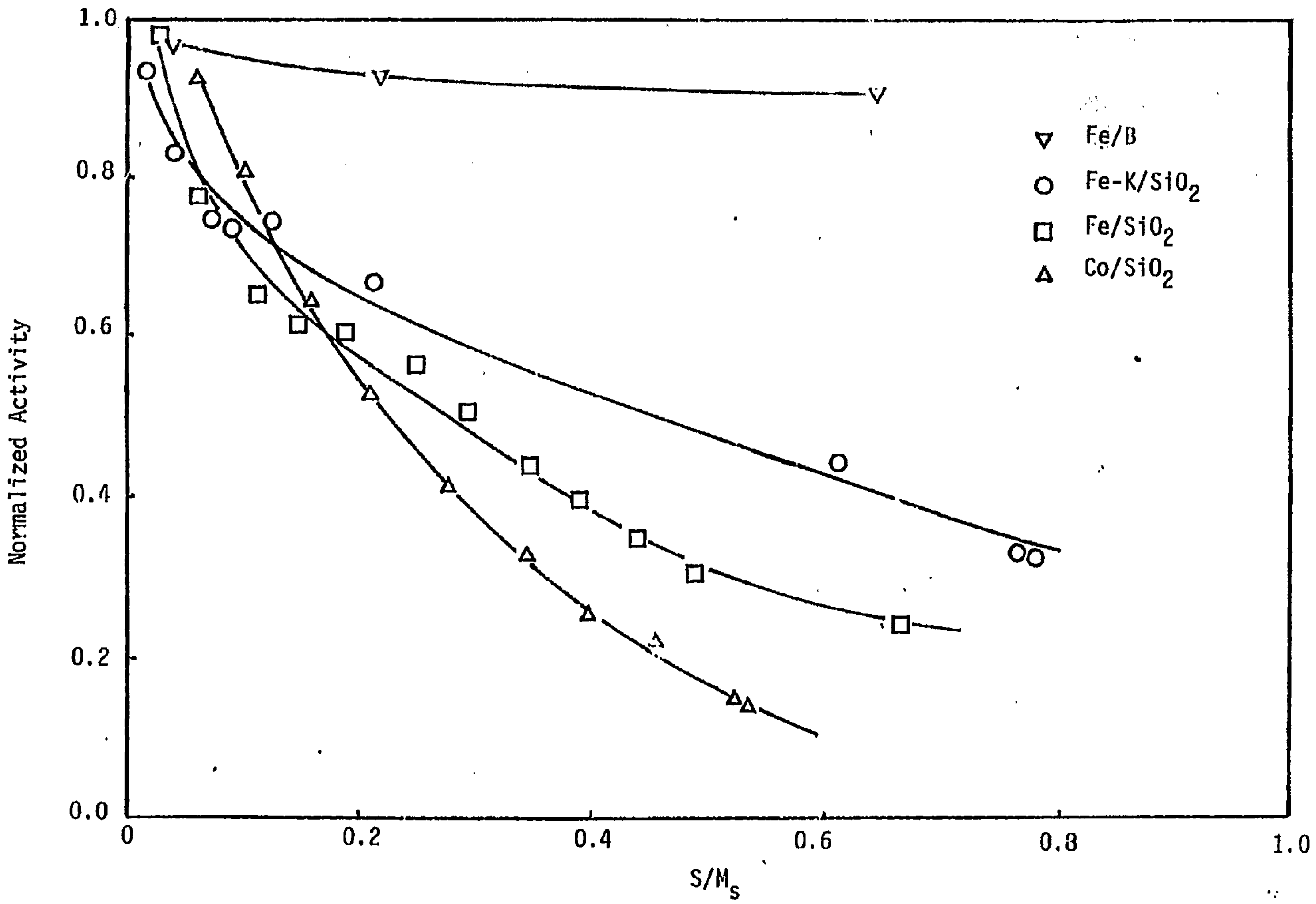


Figure 4. Normalized Activity Versus Sulfur Coverage (atoms of S adsorbed/metal surface atom) during *in situ* poisoning by 4-6 ppm $H_2S$ (500 K, 1 atm, $H_2/CO = 2$).

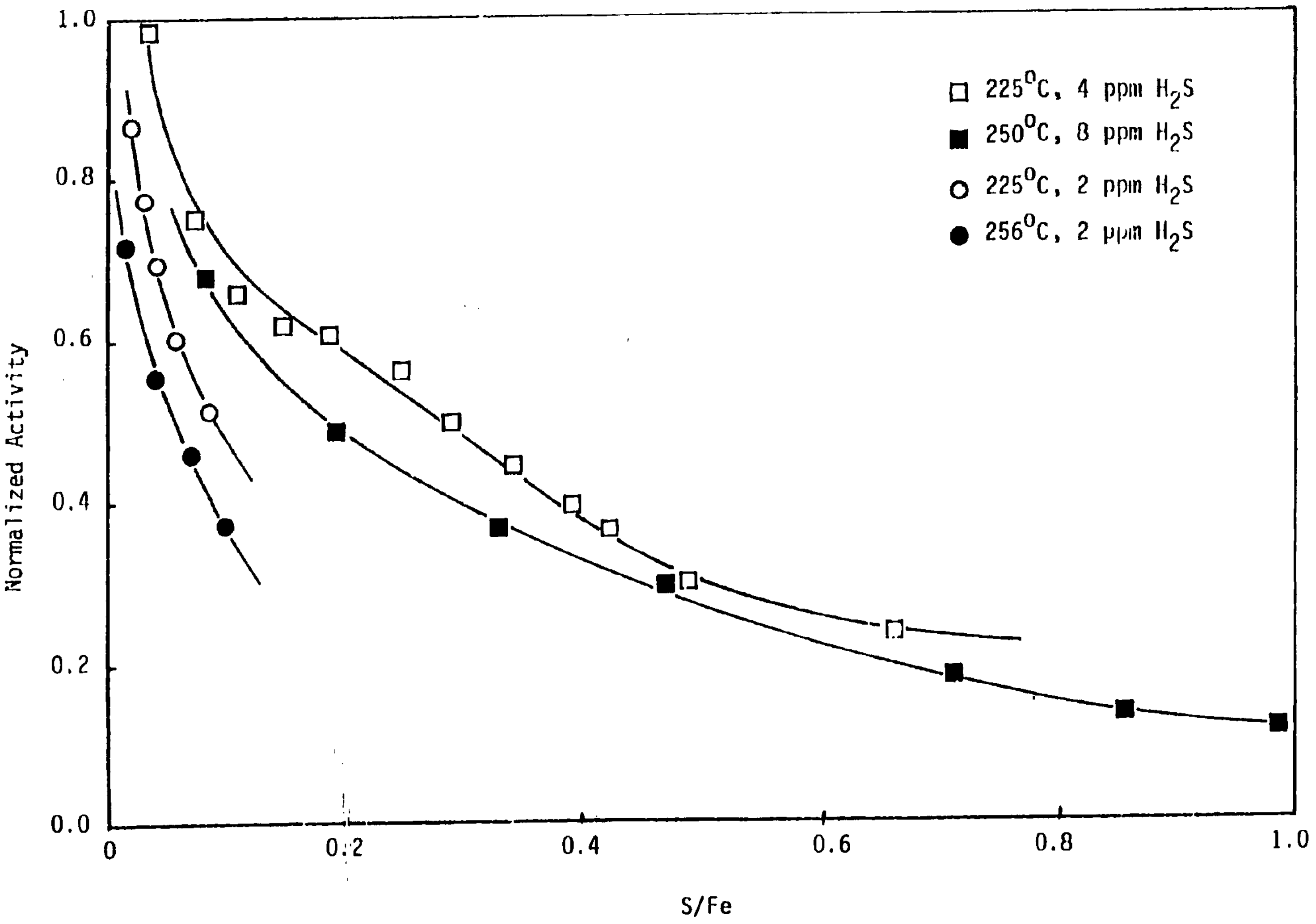


Figure 5. Normalized Activity versus Sulfur Coverage (atoms of adsorbed S/Fe surface atom) for 15% Fe/$SiO_2$ (at 1 atm, $H_2$/CO = 2).

On May 3 and 4, Dr. Bartholomew and Mr. Duane Davis visited Phillips Petroleum Research & Development in Bartlesville, Oklahoma where Mr. Davis presented a seminar on "Cobalt and Iron Boride Catalysts" based on work supported by this contract. This invitation to visit was a result of Mr. Davis receiving a Phillips graduate fellowship during the past year. The visit included a tour of the impressive research and catalyst testing facilities at Phillips.

The P.I. and 5 students, including Mr. Richard Bowman, attended Advances in Catalytic Chemistry II, a symposium held May 18-21 in honor of Heinz Heinemann. Dr. Bartholomew chaired a session dealing with "Heterogeneous CO Hydrogenation" which included several interesting papers, e.g., those by Alex Bell, John Butt and Richard Pannell, directly relating to Fischer-Tropsch synthesis.

During the past quarter the BYU Catalysis Laboratory hosted a number of visitors. On March 25th Dr. Bill Weigand of NSF visited to discuss opportunities in the Chemical and Biochemical Processes Program. Dr. Richard Pannell of Gulf Research visited our laboratory on May 17th and reviewed our work in Fischer-Tropsch synthesis. Drs. Roger Baetzold and John Monnier of Eastman Kodak visited on May 18th and toured our laboratories. On May 19th Dr. Azza Elattar of Texaco also visited and toured our facilities.

The deadline for completing our contract was originally September 18, 1982. However, due to delays in performing the proposed work--mainly due to the complex analysis of hydrocarbons and because our research assistants were required to perform teaching duties during the past 2 years, we applied for and received a no cost extension to June 18, 1983. We were also pleased to receive notice that we will be awarded a new contract to continue our investigation of the cobalt and iron borides.

## IV. CONCLUSIONS

1. $Co/SiO_2$ catalysts are significantly better dispersed than $Fe/SiO_2$ catalysts. It may be possible to achieve dispersions of cobalt as high as 40% at a loading of 3 wt.%, although the extent of reduction to the metal after 36 hours exposure to $H_2$ at 400°C is low, e.g., 18%.

2. Carbonyl-derived $Fe/SiO_2$ catalysts are very active and selective for $C_2$-$C_4$ and $C_{5+}$ hydrocarbons. Their selectivies for $CH_4$ and $CO_2$ products are low. Although they lose 50-75% of their initial activities within 5 hours, their steady state activities are comparable with conventional $Fe/SiO_2$ catlaysts.

3. $CoB/SiO_2$ is a very active, stable FT catalyst with unusually high (~ 70%) selectivity for $C_{5+}$ gasoline hydrocarbons. Its butene make is also very high.

4. FeB is extremely resistant to poisoning by $H_2S$. After exposure to 4-6 ppm $H_2S$ for sufficient time to deactivate most of the available active sites, it loses only 5-6% of its initial activity. Its activity maintenance in the absence of sulfur is also unusually high compared to conventional Fe catalysts.

# V. REFERENCES

1. Uken, A.H., "Methanation Catalysts: Activity and Sulfur Tolerance Studies of Borohydride-Reduced Catalysts," M.S. Thesis, Brigham Young University, December 1979.

2. Uken, A.H. and Bartholomew, C.H., "Metal [illegible]ide Catalysis, I. Initial Activity and Conversion-Temperature Behavior of Unsupported Catalysts," J. Catal., 65, 402 (1980).

3. Bartholomew, C.H., Pannell, R.B. and Butler, J.L., "Support and Crystallite Size Effects in CO Hydrogenation on Nickel," J. Catal., 65, 335 (1980).

4. Vannice, M.A., "Specific Activities and Product Distributions of Supported (Group VIII) Metals (For CO Hydrogenation)," J. Catal. 37, 449 (1975).

5. Carter, J.L. and Savini, C.G., U.S. Pat. 3,472,794 (1969).

# Reproduced by NTIS

National Technical Information Service
Springfield, VA 22161

***This report was printed specifically for your order from nearly 3 million titles available in our collection.***

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

## About NTIS

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at http://www.ntis.gov.

NTIS

**Ensuring Permanent, Easy Access to U.S. Government Information Assets**

**SATISFACTION GUARANTEED**

**NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.**

**▶E-mail: info@ntis.gov**
**▶Phone: 1-888-584-8332 or (703)605-6050**

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000