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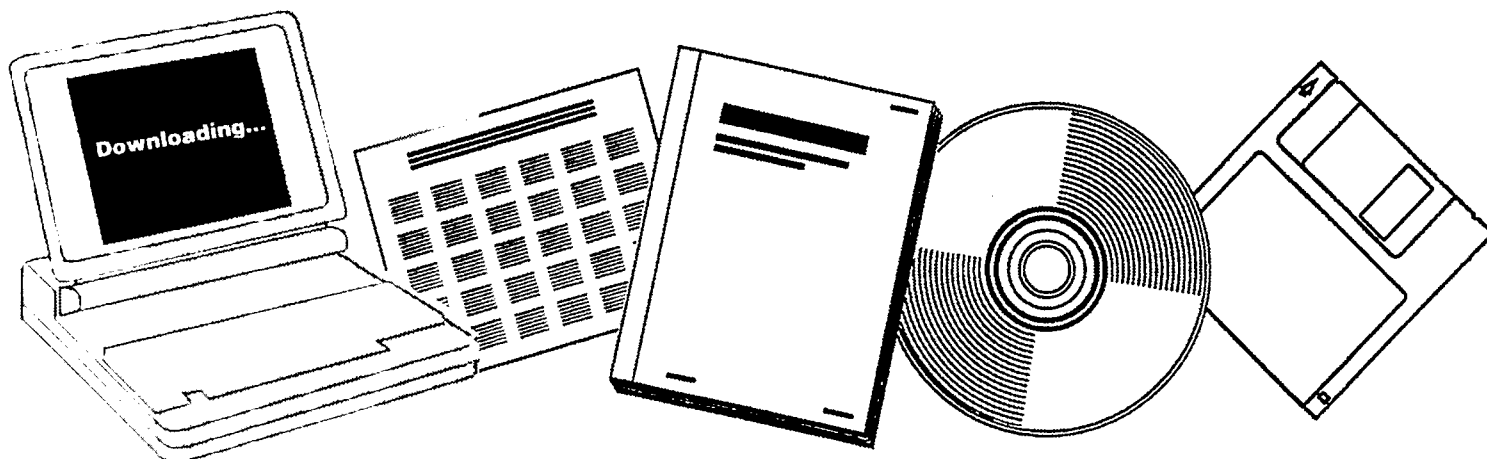
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**INVESTIGATION OF SULFUR-TOLERANT CATALYSTS
FOR SELECTIVE SYNTHESIS OF HYDROCARBON
LIQUIDS FROM COAL-DERIVED GASES. QUARTERLY
TECHNICAL PROGRESS REPORT, DECEMBER 19,
1980-MARCH 18, 1981**

BRIGHAM YOUNG UNIV.
PROVO, UT

20 APR 1981



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

MASTER

Quarterly Technical Progress Report
For Period December 19, 1980 to March 18, 1981

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Provo, Utah 84602

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FOREWORD

This report summarizes technical progress during the sixth quarter (December 19, 1980 to March 18, 1981) 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: Duane M. Davis, Jeffery L. Rankin, and Glen Witt. Mr. Rankin and Dr. Bartholomew were the principal authors. Laurie A. Witt provided typing services.

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ABSTRACT

During the sixth quarter, a 15 weight % boride-promoted, silica-supported iron catalyst was prepared. Preparations of unsupported cobalt and iron borides were in progress. Characterization of supported iron catalysts by O_2 titration and H_2 and CO chemisorption showed dispersions to range from 1.6% to 9.3% and percent reductions to range from 12 to 80%. Reduction was essentially optimum after 36 hours in flowing H_2 at 725 K. CO_2 chemisorption on potassium-promoted and unpromoted iron catalysts showed surface concentration of the potassium to be markedly greater than bulk concentration.

Activity/selectivity measurements were performed on four iron/silica catalysts and one iron boride/silica catalyst. The iron boride/ SiO_2 catalyst was found to be relatively inactive in comparison to the iron/silica catalysts. Increasing H_2/CO ratio shifted selectivity of iron/silica to lower molecular weight products; the addition of potassium greatly enhanced production of higher molecular weight hydrocarbons at the expense of CH_4 production. Alcohols and CO_2 were also detected as products of the reaction.

Participants in this project attended the Rocky Mountain Fuel Symposium and entertained 3 visitors.

I. OBJECTIVES AND SCOPE

A. Background

Cobalt and iron catalysts find wide application in the oil, gas and chemical industries, particularly in ammonia synthesis, hydro-treating 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 (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 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 C₂-C₅ hydrocarbons or C₆-C₁₂ 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 H₂S.

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/Al₂O₃, 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-Al₂O₃, (Conoco) with aqueous solutions of cobalt and iron nitrates. Co/SiO₂ and Fe/SiO₂ will be prepared by a modification of a new developed controlled-pH precipitation technique which results in very high nickel dispersions in Ni/SiO₂ catalysts. The Al₂O₃ and SiO₂ 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 KNO₃ or Zn(NO₃)₂ in such proportions as to obtain 3.0% K₂O and 15% ZnO in the final product.

Table 1
Catalyst Preparation Plans^a (Task 1)

<u>Metal-Support Combination</u>	<u>Unpromoted</u>	<u>Promoted</u>		<u>Additive Pretreatments</u>			<u>No. Catalysts</u>
		<u>K₂O</u>	<u>ZnO</u>	<u>S</u>	<u>N</u>	<u>B</u>	
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	x(3) ^b	x	x	9
Fe/Al ₂ O ₃	x						1
Fe/ZSM-5	x	x		x ^d			3
<u>Fe/Silicalite</u>	<u>x</u>	<u>x</u>					<u>2</u>
						Total	28

^a15 wt.% metal unless otherwise noted;
3 wt.% K₂O, 15% ZnO.

^bPromoted and unpromoted catalysts will be sulfided.

^c3 and 15 wt.% metal loadings.

^dPromoted catalyst will be sulfided.

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 nitrified by exposing the reduced catalyst to ammonia at 625 K for 12-16 hours followed 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 (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 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 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 Thermo-gravimetric 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 (4-22, Appendix A). 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

Table 2
Experimental Plan

<u>Task</u>	<u>Purpose of Study</u>	<u>Catalysts</u>
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 ₂ O ₃ , Fe/MgO, Co and Co/SiO ₂
b. H ₂ and CO Adsorption Measurements on K ₂ O 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 ₂ O 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 ₂ O ₃ , Fe/ZSM-5, Fe/Silicalite, Co, Co/SiO ₂
	Effects of metal	Co, Fe
	Effects of metal loading	3 and 15% Fe/Al ₂ O ₃
	Effects of Promoter	K ₂ O promoted Fe, Fe/SiO ₂ , Co/SiO ₂ ; ZnO promoted Fe/SiO ₂
	Effects of Sulfiding	Fe, Fe/SiO ₂ (unpromoted and K ₂ O 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 ₂ S Deactivation	Effects of support	Fe/SiO ₂ , Fe/MgO, Fe/Al ₂ O ₃
	Effects of metal	Co, Fe, Co/SiO ₂ and Fe/SiO ₂
	Effects of metal loading	3 and 15% Fe/Al ₂ O ₃
	Effects of Promoter	K ₂ O promoted Fe and Fe/SiO ₂ ; ZnO promoted Fe/SiO ₂ (sulfided and unsulfided)
	Effects of Sulfiding	Fe, Fe/SiO ₂ (unpromoted and K ₂ O 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

^aFe/ZSM-5 and Fe/Silicalite samples have been obtained from the Pittsburgh Energy Technology Center.

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 higher pressure. It is also possible that some of the catalyst will have more desirable 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 H₂S 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), H₂/CO = 2 and space velocities of 5,000 to 30,000 hr⁻¹ with 10 ppm H₂S 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/SiO₂ and Co/SiO₂ 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 all Tasks to be proceeding either on schedule or within 3 months of the projected schedule.

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

Task 1:

A 15% FeB/SiO₂ catalyst was prepared during the past quarter. Characterization of silica-supported iron catalysts by H₂, CO, and CO₂ chemisorption was completed. O₂ titration of iron catalysts reduced 36 hours in flowing H₂ at 725 K. provided information to calculate metal dispersions.

Task 2:

Reactor tests of Fe-S-102, Fe-S-103, FeK-S-100, and FeB-S-101 were completed. Product distributions activation energies, and turnover numbers for CO conversion were measured at low conversions to avoid any heat or mass transport limitations.

Task 3:

Sulfur poisoning studies were in the planning/set up stage and experimentation was scheduled to begin in May.

Misc.

Several students and the PI attended the 5th Annual Meeting of the Rocky Mountain Fuel Society and entertained visitors from University of Colorado and Gulf Research.

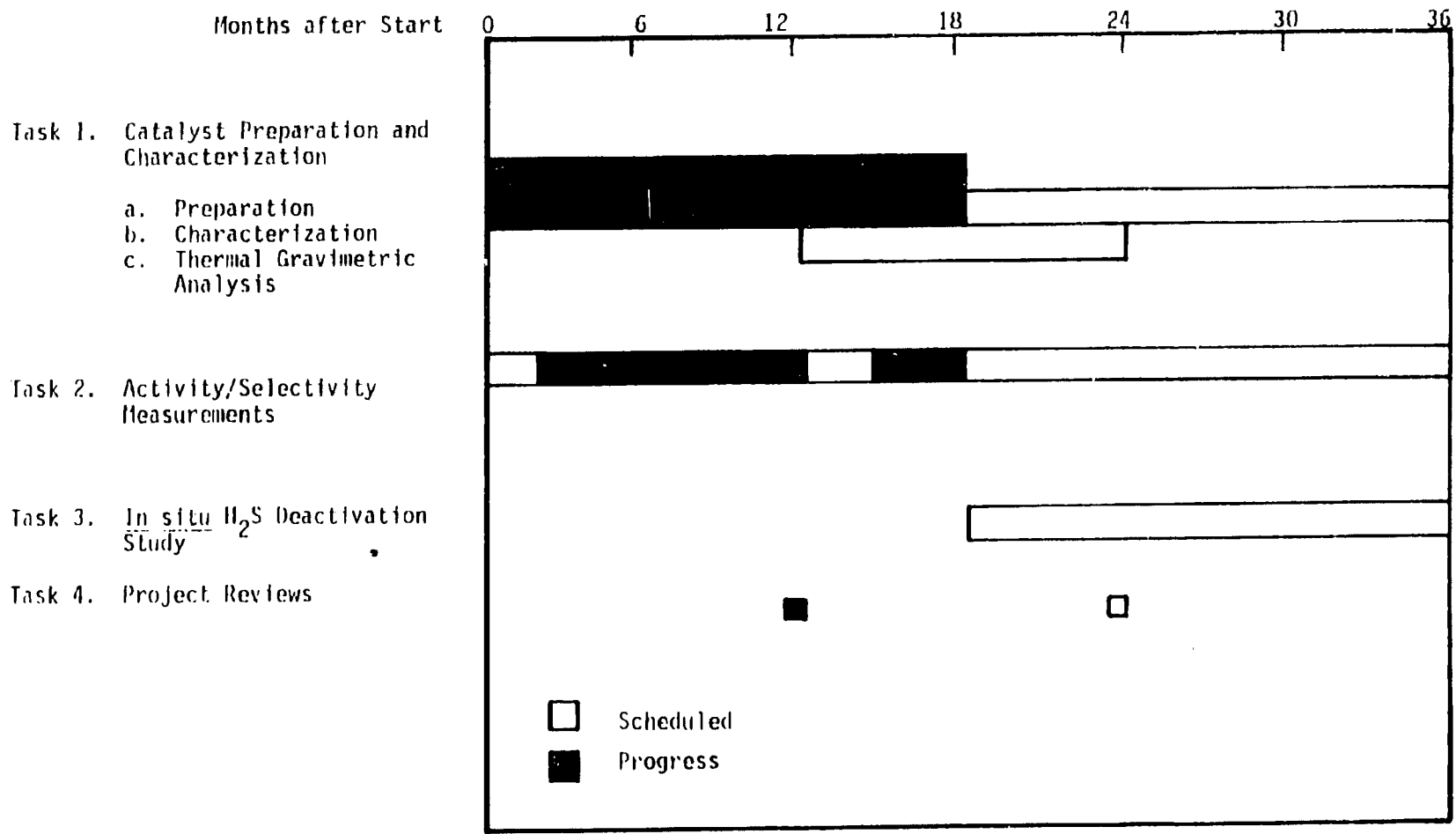


Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

During the past quarter, Fe-B-S-101, an iron boride catalyst was prepared. Sufficient $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in methanol to yield a 15% (by wt.) loading when added to a calcined silica support. A single impregnation was used and the methanol was evaporated under vacuum.

A four fold excess (stoichiometrically) of NaBH_4 was dissolved in about 1000 ml ethanol (95%) and the solution was deaerated by bubbling N_2 through the solution. Using a magnetic stirrer to keep the solution well mixed, the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ on silica was slowly added to the solution with flowing N_2 used to keep an O_2 free environment. A green-black suspension was the result of the reduction. Great amounts of H_2 were also evolved as a result of the reaction. When the reacting was completed (No more H_2) the solution was allowed to sit so the catalyst could settle out.

Impurities were washed away by decanting the liquid off from the catalyst and washing with deaerated methanol 6 times. Finally the catalyst was filtered and dried whereupon the color changed from black to brown. This catalyst was then placed in a cell and reduced in flowing H_2 at 450°C for 24 hours. Following the reduction the catalyst was cleaned by evacuating the cell at 400°C to 5×10^{-5} torr for 1 hour; then a hydrogen chemisorption was performed.

Unsupported cobalt and iron borides were also prepared by dissolving the respective nitrates in ethanol and then adding a four fold excess of NaBH_4 while under a nitrogen blanket. These catalysts are presently being washed of impurities prior to reactor runs.

2. Catalyst Characterization

During the past quarter, samples of Fe-S-102, Fe-S-103, and FeK-S-100 were reduced for 36 hours at 725 K in flowing H_2 . As can be seen from the chemisorption data in Table 3, little change in H_2 uptake occurred in comparison to reduction for 24 hours. However a marked increase in CO adsorption was evident.

O_2 titration on freshly reduced samples in the volumetric apparatus was completed on the three catalysts listed above. Although dispersion of the iron was poor, reduction to metal was 50% to 80% complete for the 15% metal loading catalysts. Lower loading catalysts, such as Fe-S-103 containing 3% iron, show much poorer reducibility (e.g. 12%). It was noted that the addition of potassium promoter to the iron catalyst decreased its reducibility. These O_2 titrations were carried out at 675 K for 2 hours and appeared to be complete (i.e. resulting in Fe_2O_3 formation) as indicated by their unreduced rusty-colored state.

As a result of these experiments, the optimum reduction conditions for iron catalysts supported on silica appears to be a temperature of 725 K and 36 hour reduction time.

TABLE 3

H₂, CO, CO₂ and O₂ Uptakes on Iron 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
Fe-S-102 ^f	15	20.19	3.52	--	--	--
Fe-S-102	15	17.10	24.80	1.16	1622	80.5
Fe-S-103	3	3.10	4.82	--	50.16	12.5
FeK-S-100 ^g	15	9.11	4.94	6.56	856	42.5
FeB-S-101 ^h	10	6.37	--	--	--	--

^a At 298 K

^b At 298 K

^c At 373 K

^d At 673 K

^e Based on Fe₂O₃ stoichiometry

^f After 20 hour reduction in H₂

^g Containing 3% K₂O promoter

^h Containing Boride promoter

CO₂ chemisorption was used to measure the surface enrichment of potassium promoter, following the procedures developed by Brunnauer et al.(4). It was apparent that CO₂ adsorption was greatly enhanced by the addition of the potassium promoter. H₂ uptake decreased about 50% while CO adsorption decreased even more drastically. Assuming that the iron in the potassium-promoted catalyst accounts for the same amount of adsorption as the unpromoted catalyst, a surface concentration of K may be calculated as 87.5% for a 3% bulk potassium concentration.

Percent dispersions of the three catalysts were based on an H/Fe ratio of 1 and accounted for the unreduced portion of the metal via the O₂ titration results. They are as follows:

Fe-S-102	(15 wt. % Fe)	1.59%
Fe-S-103	(3 wt. % Fe)	9.32%
FeK-S-100	(15 wt. % Fe)	1.60%

3. Future Plans

During the next quarter, chemisorption of H₂, CO, and CO₂ will be completed on cobalt-silica catalysts of similar compositions. O₂ titration on freshly reduced samples will be completed to determine percent reduction to metal and dispersions.

Iron catalysts supported on other materials such as alumina and zeolite as outlined in the experimental plan will also be characterized by chemisorption and O₂ titration. These experiments will yield considerable data relating to metal-support effects and effects of metal loading.

Electron microscopy and chemical analysis of catalysts tested this quarter are currently underway and will be continued for catalysts to be tested in the next quarter.

B. Task 2: Activity/Selectivity Measurements

1. Chromatographic Analysis

During the past quarter as testing of iron catalysts proceeded, it was discovered that the column packing in use failed to separate alcohols adequately due to their interaction with the support material. Consultation with various manufacturers of chromatographic materials showed the separation of hydrocarbons and alcohols on one column to be extremely difficult. It was found that addition of a short section of 1/8" packed column containing 20% SP-2100 and 0.1% carbowax 1500 on Supelcoport support material greatly enhanced alcohol analysis and reproducibility of concentration measurements. This analysis is presently in use. However, the carbowax additive reduces the maximum temperature limit of the column from 625 K to 450 K minimizing the opportunity of analyzing for higher hydrocarbons.

Orders have been placed with Hewlett-Packard, Inc. to supply a capillary column apparatus to be used with our present chromatograph. This equipment will remove the limitations now present with the packed column analytical technique.

2. Experimental Measurements

Activity/selectivity tests were performed with the four iron catalysts previously characterized. The resultant turnover numbers for CO conversion and product analyses are summarized in Tables 4 and 5 respectively. Samples of Fe-S-102 and Fe-S-103 were analyzed at three temperatures and H_2/CO ratios of 2 and 1 to allow the measurement of activation energies and effects of H_2/CO ratio on product distributions. Conversions were maintained at $< 10\%$ to minimize transport effects.

As H_2/CO ratio decreased, methane production decreased. More CO_2 was generated, and the average molecular weight of the hydrocarbon product increased as expected. It is interesting to note the high levels of C_2 hydrocarbon production over these iron catalysts as shown in Figure 2 for Fe-S-102. In comparison, cobalt catalysts tested previously appear to have much lower selectivities to C_2 hydrocarbons.

The effects of metal loading are also seen in comparing the selectivity of Fe-S-103, 3% metal catalyst, to that of Fe-S-102, a 15% metal catalyst. Fe-S-103 produced much greater amounts of methane (nearly double) and less CO_2 . The product molecular weight decreased accordingly.

The potassium-promoted catalyst, though slightly less active, produced a much higher molecular weight product. Its product distribution is also shown graphically on Figure 2 to contrast it to that of the unpromoted catalyst of the same loading. A shift from methane to C_2-C_4 and higher hydrocarbons is evident.

The boride-promoted catalyst was relatively inactive, and produced large quantities of methane and no higher molecular weight hydrocarbons beyond C_4 . Further experimentation with unsupported boride catalysts is being undertaken to attempt preparation of a more active catalyst.

3. Future Plans

During the next quarter activity/selectivity measurements will continue with emphasis on cobalt supported catalysts and iron catalysts prepared from supports other than SiO_2 to determine effects of metal and metal-support interactions on product selectivities. The installation of the new capillary system on the gas chromatograph is also planned.

C. Task 3: In Situ H_2S Deactivation Study

Plans were made to involve Mr. Richard Bowman an undergraduate with 1 1/2 years experience in catalyst research in this investigation as an M.S. project. Mr. Bowman has ordered valves, thermocouples, a glass cell and other materials for these experiments. Experimental work on this task is not scheduled to begin until the next quarter, possibly in May.

TABLE 4

CO Turnover Numbers for Supported Iron Catalysts

<u>Catalyst Code</u>	<u>H₂/CO Ratio</u>	<u>Temperature (K)</u>	<u>Turnover Number (N_{CO} × 10³)</u>	<u>Activation Energy (kJ/g mole)</u>
Fe-S-102	2	460	0.64	97.1
	2	483	2.5	
	2	498	3.9	
	1	449	0.19	60.9
	1	483	1.4	
	1	498	2.5	
Fe-S-103	2	448	0.72	49.4
	2	483	3.2	
	2	498	7.0	
	1	448	0.79	54.0
	1	473	2.3	
	1	498	7.0	
FeK-S-100	2	498	6.6	--
FeB-S-101	2	498	0.33	--

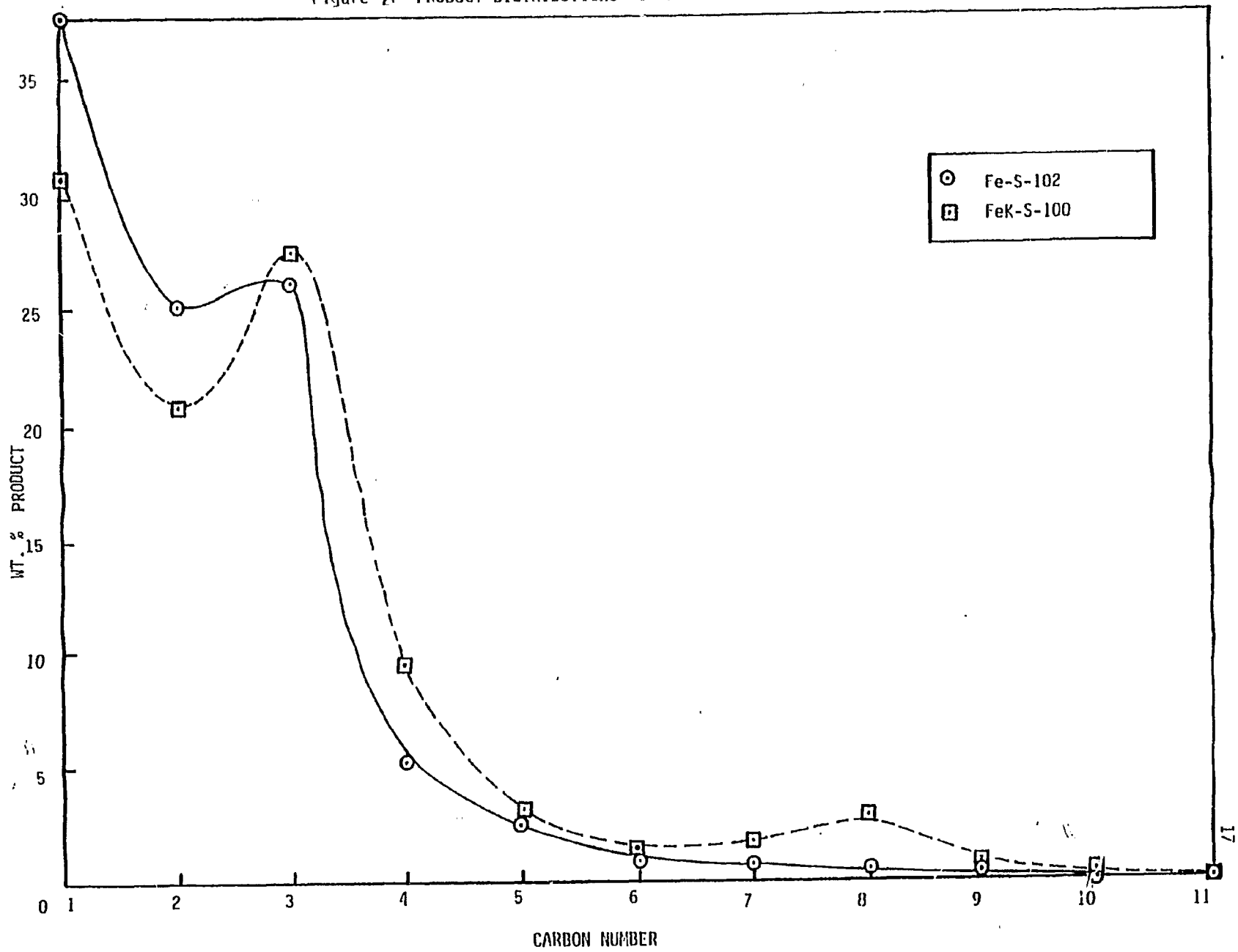
TABLE 5

Product Selectivities for Supported Iron Catalysts at 498 K

Catalyst Code	Selectivity					Ave. Molecular Weight Hydrocarbon Product
	<u>CH₄</u>	<u>C₂-C₄</u>	<u>C₅⁺</u>	<u>CO₂</u>	<u>Alcohols</u>	
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

^a H₂/CO = 2^b H₂/CO = 1

Figure 2. PRODUCT DISTRIBUTIONS FOR Fe-S-102 AND FeK-S-100



D. Miscellaneous Accomplishments and Technical Communication

The Principal Investigator and several students including Mr. Rankin attended the 5th Meeting of the Rocky Mountain Fuel Society. Mr. Gordon Weatherbee of our group presented a paper on CO₂ methanation, based on a study supported by NSF. Other papers at the meeting dealt with various aspects of coal, oil shale and tar sand utilization, including hydrotreating of coal liquids.

During the past quarter we enjoyed visits from Professor John Falconer, University of Colorado, who presented a seminar on his temperature programmed methanation reaction studies on nickel catalysts; Dr. Tony Perotta, Gulf Research, who discussed his interesting work on coking of hydrotreating catalysts; and Dr. Richard Panneil, Gulf Research, who discussed his recent work on supported cobalt catalysts in Fischer-Tropsch synthesis.

Mr. Richard Bowman, an undergraduate in Chem Eng., joined this project this past quarter. He will pursue an M.S. research into the effects of sulfur poisoning on activity/selectivity properties of cobalt and iron catalysts.

Mr. Duane Davis, a senior in Chemical engineering is starting a Ph.D. program and will continue work on the boride catalysts as part of his dissertation work.

IV. CONCLUSIONS

1. Dispersion of Fe on Silica decreases as metal loading is increased. Dispersions of 1.6 to 9% are the highest achieved thus far.
2. O₂ titration shows that 36 hour reduction of iron/silica catalysts in flowing H₂ at 725 K is adequate. Percent reductions range from 12-80% in 3 and 15% catalysts.
3. K₂O is concentrated on the surface of the promoted iron catalyst to as much as 30 times its bulk concentration in agreement with previous work.
4. Addition of 0.1% carbowax 1500 to a packed column containing S_P-2100 liquid phase allows greater reproducibility for alcohol separation in gas analysis.
5. Decreasing H₂/CO ratio from 2 to 1 caused methane production to decrease and average molecular weight of the hydrocarbon product to increase accordingly.
6. Iron catalysts produce large amounts of C₂ relative to cobalt catalysts.
7. As metal loading is increased from 3% to 15% for iron supported on silica, less methane production is observed and an increase in molecular weight of the hydrocarbon product occurs.
8. Potassium promotion of the 15% iron/silica catalyst shifted carbon numbers at the expense of methane and ethane production.
9. Iron boride supported on silica as prepared in our laboratory is relatively less active, less selective for higher molecular weight hydrocarbons, but more selective for lower molecular weight hydrocarbons compared to Fe/SiO₂. This behavior may be due to our method of preparation.
10. Activation energies for Fischer-Tropsch synthesis were measured at H₂/CO ratios of 2 and 1 and ranged from 49.4 to 97.1 kJ/mole. The lower E_{act} for the 3% Fe/SiO₂ may be due to a strong interaction of metal and support.

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.
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4. Emmett, P.H., and Brunauer, S., "Accumulation of Alkali Promoters on Surfaces of Iron Synthetic Ammonia Catalysts," Journal of the American Chemical Society, 59, 310.

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