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DEACTIVATION BY CARBON OF IRON CATALYSTS FOR INDIRECT LIQUEFACTION

Final Technical Progress Report for the Period September 16, 1986–September 15, 1990

By
Calvin H. Bartholomew

Work Performed Under Contract No. FG22-86PC90533

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Brigham Young University
Provo, Utah

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Date Published - February 14, 1991

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-FG22-86PC90533

FORWARD

This report summarizes technical progress during a four-year study (Sept. 16, 1986 to Sept. 15, 1990) (originally 3 years) conducted for the Department of Energy (DOE) under Contract No. DE-FG22-86PC90533. The principal investigator for this work was Dr. Calvin H. Bartholomew; Dr. Sayeed Akhtar was the technical representative for DOE during the first three years. A no-cost one year extension was granted during the third year to extend the grant to 4 years; during the fourth year, Mr. Robert C. Dolence was the project manager.

The following students contributed to the technical accomplishments and to this report: Mike Bayles and Scott Eliason. Dr. Bartholomew was the principal author. Sherri Wardinsky provided typing services.

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ABSTRACT

Progress is reported for a four-year fundamental investigation of carbon formation and its effects on the activity and selectivity of promoted iron catalysts for FT synthesis, the objectives of which were to (1) determine rates and mechanisms of carbon deactivation of unsupported Fe and Fe/K catalysts during CO hydrogenation and (2) model the global rates of deactivation at the surface of the catalyst for the same catalysts. A computer-automated reactor system to be used in the kinetic and deactivation studies was designed, constructed and tested. Kinetic data for CO hydrogenation on unsupported, unpromoted iron, 99% Fe/1% Al_2O_3, and K-promoted 99% Fe/1% Al_2O_3 catalysts were obtained as functions of temperature, reactant partial pressures and time. The activity/selectivity and kinetic data are consistent with those previously reported for supported, unpromoted and promoted iron. Two kinds of deactivation were observed during FT synthesis on these samples: (1) loss of surface area after rereduction of unsupported, unpromoted iron at 400°C and (2) loss of activity with time due to carbon deposition, especially in the case of K-promoted 99%Fe/1% Al_2O_3. Deactivation rate data were obtained for CO hydrogenation on K-promoted Fe as a function of time, temperature, and H_2/CO ratio. The PI and students published 3 papers and 16 reports, presented 4 papers at technical meetings, and interacted with several visitors in connection with the contract work.

I. OBJECTIVES AND SCOPE

A. Background

Although promoted cobalt and iron catalysts for Fischer-Tropsch (FT) synthesis [1] of gasoline feedstock were first developed more than three decades ago, a major technical problem still limiting the commercial use of these catalysts today is carbon deactivation. Carbon deactivation is especially severe in processes that directly use synthesis gas with an H_2:CO ratio of approximately 1:2 or less. Because these conditions are thermodynamically and kinetically favorable for carbon formation, rapid deactivation and physical disintegration of the catalyst are possible. Indeed, carbon formation is the major cause for loss of catalyst activity in the only presently commercial FT process in South Africa [1]. Thus, there is considerable motivation for understanding the fundamental mechanisms of carbon deactivation in order to find means of mitigating these problems. Models and/or data for predicting rate of carbon formation and its effects are needed so that the deleterious effects on catalysts and processes can be minimized. Data are especially needed for Fe/K catalysts because of their clear cost advantage and commercial significance.

B. Objectives

This report describes recent progress in a fundamental, three-year investigation of carbon formation and its effects on the activity and selectivity of promoted iron catalysts for FT synthesis, the objectives of which are:

1. Determine rates and mechanisms of carbon deactivation of unsupported Fe and Fe/K catalysts during CO hydrogenation over a range of CO concentrations, CO:H_2 ratios, and temperatures.
2. Model the rates of deactivation of the same catalysts in fixed-bed reactors.

C. Technical Approach

To accomplish the above objectives, the project will be divided into the following tasks:

1. Determine the kinetics of reaction and of carbon deactivation during CO hydrogenation on Fe and Fe/K catalysts coated on monolith bodies.
2. Determine the reactivities and types of carbon deposited during reaction on the same catalysts from temperature-programmed-surface-reaction spectroscopy (TPSR) and transmission electron microscopy (TEM). Determine the types of iron carbides formed at various temperatures and H_2/CO ratios using x-ray diffraction and Moessbauer spectroscopy.

3. Using a reaction model for FT synthesis developed in this laboratory, the kinetics of reaction and deactivation measured in Task 1, and models of fixed-bed reactors from other workers, develop mathematical deactivation models which include heat and mass transport contributions for FT synthesis in packed-bed reactors.

The approach for each of these areas of study is described below:

Task 1: Kinetic/Deactivation Studies. While some kinetic data are available for CO hydrogenation on Fe/K [2-4], it is proposed that additional data be obtained with catalysts prepared in this study to confirm the previous work and to extend the range of experimental conditions, e.g. temperature and CO:H_2 ratio. Wash-coated monolithic catalysts will be used to minimize the effects of pore diffusion on the rate of reaction [5,6]. Iron catalysts used in the kinetic studies will be prepared by wash-coating Celcor (Corning Glass Works) monoliths (2.5 cm diam. by 1 cm long) with aqueous slurries containing previously reduced and passivated Fe or Fe/K catalysts. Washcoating procedures have been developed in this laboratory [5-8] which enable thin layers of either supported or unsupported catalysts to be deposited on the walls of monolith channels. These washcoated monolithic catalysts are ideal for kinetic studies because of their low pressure drops and high effectiveness factors [5,6].

Fe and Fe/K catalysts will be prepared according to procedures recently developed in our lab (9,10): (1) decomposition of iron nitrate (or iron and potassium nitrates) at 200°C in inert gas followed by reduction and/or (2) impregnation of the dehydroxylated alumina support with Fe pentacarbonyl/pentane followed by drying and reduction. The latter technique results in Fe/alumina catalysts of high dispersion and extent of reduction. Thus, this latter technique could be used to some advantage in the preparation of Fe/alumina/monolith catalysts for the kinetic/deactivation studies. After drying, the catalysts will be reduced in flowing hydrogen at 400-450°C, using an established heating schedule that maximizes surface area [10,11]. Hydrogen uptakes of the reduced catalysts will then be measured so that reaction rates can be compared on the basis of catalytic surface area. These measurements will also be based on techniques recently developed in this laboratory [9,11]. Data obtained in this laboratory [9,10,12] indicate that the activities and selectivities of Fe and Fe/K catalysts prepared by our techniques have catalytic properties typical of iron FT catalysts.

Reaction kinetic and deactivation studies will be carried out using a Berty internal recycle reactor system previously described [5, 13]. The Berty CSTR reactor has the advantages of (i) gradientless operation with respect to temperature and reactant concentrations, and (ii) the capability of adjusting the stirring speed to eliminate effects of external mass transport. The combination of the Berty reactor and wash-coated monolithic catalysts will ensure the collection of intrinsic surface reaction rates in the absence of pore-diffusional and external film diffusional disguises [5,13]. The use of the Berty reactor also enables deactivation kinetics to be measured directly and unambiguously for each given set of conditions [7,14]. As part of this task the Berty Reactor System will be computer automated and the analysis will be augmented by the addition of a new H.P. 5890 chromatograph slaved to a micro computer.

Reaction kinetics will be obtained by measuring CO conversion over a range of temperatures and reactant concentrations, e.g. 180-250°C, P_{CO} = 10-50 kPa, P_{H2} = 10-50 kPa, and H_2:CO = 1.1-3.1. To ensure the collection of intrinsic kinetic data in the absence of deactivation phenomena, the reactant gasses and argon diluent will be carefully purified of oxygen, sulfur compounds, and iron pentacarbonyl. Deactivation effects due to carbon will be avoided during kinetic measurements by careful choice of operating conditions and by periodically treating the catalyst in pure hydrogen just prior to changing gas composition and temperature. Kinetic data will be obtained over a period of 24 hours at each condition so that both initial and steady-state rates and product distributions are obtained. Product distributions will be measured on-line using heated lines to carry the products to a chromatograph equipped with glass capillary and Chromosorb 102 columns connected to flame ionization and thermal conductivity detectors, respectively, as described previously [15]. The study of Fe and Fe/K catalysts will enable the effects of potassium on the reaction kinetics to be determined.

Deactivation kinetics due to carbon formation will be obtained by measuring CO conversion and product distribution as a function of time for 24-48 hours at a given set of reaction conditions. Temperatures and reactant concentrations will be varied from run to run, e.g. 250-350°C; P_{CO} = 10-50 kPa; and H_2:CO = 0.5-2.0. Again the study of both Fe and Fe/K catalysts will permit effects of potassium on the kinetics of deactivation to be determined.

Task 2: Study of Carbon Reactivities and Types. The reactivities of carbon species deposited during CO hydrogenation on Fe and Fe/K catalysts will be determined using temperature-programmed-surface-reaction spectroscopy (TPSR) with hydrogen [7,16]. The data will be obtained using a TPD system featuring a UTI-100C quadrupole mass spectrometer and programmable peak selector [17]. The peak selector enables up to 9 different peaks to be selected simultaneously and will facilitate analysis of methane and C_{2+} hydrocarbons during TPSR of the carbon-deactivated catalysts with hydrogen.

Catalysts will be pretreated in synthesis gas (H_2:CO = 0.5 to 2.0) at various reaction temperatures (e.g. 250 to 350°C) over a period of 16-24 hours, cooled in He carrier gas to 25°C, and then reacted with H_2 (10% H_2 in He or Ar) while increasing the temperature of the sample at a linear rate of 30°C/min. The use of small, powdered samples (50-100 mg; 80-100 mesh) and low carrier gas flow rates (20-40 cm3/min) will ensure the absence of intra- and interparticle concentration gradients [17-21] These conditions have been shown in previous TPD studies conducted in this laboratory [17-19] to be optimum for minimizing pore diffusion effects, sample measurement lag times, and concentration gradients [20,21]. Previous studies of carbon-deactivated catalysts with TPSR [7,16,22] have enabled identification of different carbon species having a range of reactivities. Again, it is important to investigate both Fe and Fe/K catalysts since Dwyer [23] found evidence of different forms of carbon on clean iron and potassium-covered iron surfaces.

Different forms of carbon deposited during CO hydrogenation on iron catalysts will be identified by submitting samples from the deactivation rate studies for examination by transmission electron microscopy (TEM). TEM has been used in several previous investigations in this laboratory to identify different forms of carbon--particularly vermicular (filamentous) carbons [24-26]. By submitting samples tested at various temperatures, it will be possible to determine at which temperature vermicular carbon formation occurs.

The role of iron carbides in deactivation during CO hydrogenation will be determined by analyzing spent catalysts from the deactivation runs by x-ray diffraction and Moessbauer spectroscopy. Moessbauer spectroscopy has already proven itself as a useful tool for identifying various iron carbides formed during CO hydrogenation [27-29]. It will be interesting to determine if certain carbides are associated with the more severe conditions of carbon deactivation, i.e. high temperature and low H_2:CO ratio and how potassium affects carbide formation.

Task 3: Mathematical Modeling of Catalyst Deactivation by Carbon. The development of a chemical mathematical model for deactivation of iron catalysts during Fischer-Tropsch synthesis will follow an approach similar to that used previously in this laboratory to model methanation in fixed beds [5,30,31]. The one-dimensional, quasi-steady-state model will feature simultaneous solution of (i) the rate equations for the main reaction and for deactivation [14,32,33]. The kinetics for the main reaction will be calculated according to the model recently developed by Rankin and Bartholomew [34] and will be based on the dissociation of adsorbed carbon monoxide, subsequent hydrogenation of the surface carbide [7,16, 35-37], and provision for the Anderson-Schulz-Flory polymerization mechanism [38-41]. This reaction model enables the calculation of intrinsic rate constants for initiation, termination, and propagation, as well as values for the polymerization probability. This reaction model also has a provision which accounts for the formation of olefins and oxygenates in the case of the iron catalysts. In addition, the kinetics of the water-gas-shift reaction [42] will be added. The effects of pore diffusion resistance will not be considered at this point. The coupled differential equations will be solved by finite difference [43]. Model predictions will be closely compared with experimental results obtained at high conversions in a computer-automated CSTR Berty reactor [44-47]. The model will be used initially to predict catalytic activity, selectivity, reactant concentration, and temperature as functions of time and position in the fixed-bed reactor.

II. SUMMARY OF PROGRESS

Progress can be most efficiently summarized by task:

A. Task 1: Kinetic/Deactivation Studies

A computer-automated reactor system to be used in the kinetic and deactivation studies was designed and fabricated. Computer software was written and reactor hardware was assembled and tested enabling completely automated programming and operation of pressure, temperature, flows and chromatographic analysis. A new HP 5890 chromatograph was received, installed and tested to complete this system. Modifications were made to our fixed bed reactor to enable H_2 and CO flows to be varied systematically for kinetic studies of CO hydrogenation on iron.

During the first year kinetic data were obtained for FT synthesis on two samples of an unsupported, unpromoted Fe catalyst (reduced at 300 and 400°C, respectively) as a function of time at different temperatures. Each sample was run for a total of 50-70 hours during which chromatographic analyses were made about every other hour. Products ranged from methane to C_{11} hydrocarbons with propagation probabilities of 0.45-0.55 at 493 K. Activation energies of 99.5 and 88.0 kJ/mole and a turnover frequency of 3.6×10^{-3} at 493 K were observed in good agreement with previously reported values for unpromoted iron.

During the fifth and sixth quarters CO hydrogenation activity/selectivity tests were conducted on unsupported iron catalysts reduced at 300 or 400°C in hydrogen. A separate sample reduced at 400°C and transferred to the reactor system following chemisorption experiments was also found to be inactive. In both cases the sample was sintered as a result of the previous treatments.

During the seventh and eighth quarters additional CO hydrogenation activity/selectivity tests were conducted on unsupported iron catalysts reduced at 300 or 400°C in hydrogen. Samples rereduced at 400°C were found to be less active than the freshly reduced catalyst. The sample was sintered as a result of these treatments. The observed sintering is thought to result from decomposition of iron carbides during rereduction.

During the ninth quarter several CO hydrogenation activity/selectivity tests were conducted on a new alumina-promoted iron catalyst Fe-A-201 at a H_2/CO ratio of 3 in the temperature range of 200-230°C over a period of 150 hours. The specific activity (CO turnover frequency) of this catalyst was the same within experimental error as previously tested unsupported, unpromoted iron catalysts [48]. However, this new alumina-promoted catalyst was found to have greater thermal stability against sintering upon rereduction in hydrogen relative to the unpromoted iron catalysts [48]. Effects of long term reaction on activity and hydrocarbon selectivities were also measured over the 150 hour period. The results are consistent with loss of specific activity and an increase in methane selectivity due to carbon deposition after reaction at 230°C

During Quarters 10-13 hydrogen adsorption capacities and activity/selectivity properties were measured over a range of temperatures and reactant concentrations for three alumina-promoted iron catalysts (Fe-A-203, -204, and 205). Activities and selectivities were also measured as a function of time. From these data it is evident that activity and selectivity properties reach steady-state conditions after about 20 hours. Deactivation is observable at higher reaction temperatures, especially at 230°C; during 72 hours of reaction at 230°C, 1 atm, and $H_2/CO = 2$, normalized activity decreases 75%.

During the 14-16th quarters two new $Fe/K/Al_2O_3$ catalysts were prepared and H_2 adsorption data were obtained for these and unpromoted catalysts by two different methods. Kinetic and deactivation data were obtained for CO hydrogenation on K-promoted Fe as a function of time, temperature, and H_2/CO ratio.

B. Task 2: Study of Carbon Reactivities and Types

No experiments are scheduled for this Task until Spring 1991.

C. Task 3: Mathematical Modeling of Catalyst Deactivation by Carbon

This task is scheduled to begin in Spring 1991.

D. Technical Communication and Miscellaneous Accomplishments

Two graduate students, Mr. Mike Bayles (MS Candidate) and Mr. Scott Eliason (Ph.D. Candidate) were hired in 1986 to construct the automated reactor system and conduct kinetic/deactivation experiments. The PI attended the Anaheim ACS meeting held Sept. 7-12, 1987, in Anaheim at which he chaired a symposium on CO hydrogenation which included a paper from the BYU Catalysis Laboratory. Professor Jim Goodwin visited BYU and presented a seminar dealing with promoters in CO hydrogenation.

The PI and several students attended the 2nd Annual Symposium of the Western States Catalysis Club. Visitors to the Catalysis Lab included Professors Robert Merrill and John Sears of Cornell and Montana State University, respectively. Mike Bayles and the PI published an article on the new computer-automated reactor system.

The BYU Catalysis Laboratory hosted Professor James Schwarz and Dr. Bob Huang of the University of Syracuse on May 13-15, 1987. The PI and several graduate students including Mr. Scott Eliason attended the Tenth North American Meeting of the Catalysis Society held May 17-22 in San Diego; Dr. Bartholomew and Mr. Won Ho Lee presented papers while Dr. Bartholomew also served as Program Chairman. The PI also attended the ASEE/ERC Conference in Reno on June 24th and 25th where he presented a paper. Dr. Fred Steffgen, our DOE/PETC Project Manager, visited and reviewed our program on June 26, 1987.

On November 24, 1987 the BYU Catalysis Laboratory hosted Professor Eric Suuberg from Brown University who presented a seminar and discussed research on coal char characterization and oxidation which is being studied on a separate contract. The PI attended the International Conference on Catalyst Deactivation help September 29-October 1 in Antwerp, Belguim where he presented a Plenary Lecture; he also visited the Universities of Eindhoven and Utrecht, presented a lecture, and visited with catalysis researchers. On October 14-16 he attended a Catalysis/Surface Science Meeting sponsored by DOE/BES in Washington D.C. He also attended the Annual Meeting of the AIChE held November 15-20 in New York, chaired a session on catalyst deactivation, and presented a paper on Modeling of Combustion processes. The Principal Investigator and several students attended and participated in a symposium on Catalysis sponsored by the Western States Catalysis Club and held in conjunction with the Rocky Mountain ACS Meeting on March 28th in Las Vegas. Mr. Scott Eliason and Dr. Bartholomew also attended the Ninth International Catalysis Congress held June 26-July 1 in Calgary, Canada where the PI presented a paper. The PI also participated in the Annual DOE Coal Contractors Meeting held July 26-28 in Pittsburgh.

The Principal Investigator (Calvin H. Bartholomew) attended and presented a paper at the 196th ACS National Meeting held September 25-30, 1988 in Los Angeles. He was also a coauthor of a paper presented at the 1988 Annual Meeting of the American Institute of Chemical Engineers held November 27-December 2, 1988 in Washington D. C. The BYU Catalysis Laboratory hosted Professor George Gavalas of the California Institute of Technology on November 23, 1988. The PI and students attended the Western States Catalysis Club held in conjunction with the Rocky Mountain ACS Meeting on February 24th in Denver where Mr. Scott Eliason made a presentation on FT kinetics on Fe catalysts based on work from this grant. Dr. Heinz Heinemann of UC Berkeley visited the BYU Catalysis Laboratory on March 15th and presented a seminar. The PI, Calvin H. Bartholomew, his associate William C. Hecker, and 2 students attended the Eleventh North American Meeting of the Catalysis Society held May 7-11, 1989 in Dearborn, Michigan and presented 3 papers. The PI presented a short course on Catalyst Deactivation at BYU on May 24-26 and at Amoco on May 31-June 2. Professors Bartholomew and Hecker and 2 students also attended a conference held June 14th at Snowbird on Spectroscopy of Coal. The PI also attended the 4th Japan-China-USA Symposium on Catalysis held July 3-7, 1989 in Sapporo, Japan and presented a paper dealing with activation of methane on nickel.

The PI, Calvin H. Bartholomew, his associate William C. Hecker, and several students attended Advances in Catalytic Chemistry held Oct. 1-6, 1989 at Snowbird, Utah. The PI presented an invited paper dealing with "Effects of Structure on CO Hydrogenation on Alumina-supported Cobalt and Iron."

The PI attended the International Chemical Congress of the Pacific Basin Societies in Honolulu, Dec. 17-22 where he presented three papers. The PI, one associate and several students attended the Rocky Mountain Fuel Society and Western States Catalysis Club joint meeting on March 1 and 2 in Salt Lake City where they presented several papers.

The PI and Scott Eliason attended the 1990 Spring National Meeting of the AIChE in Orlando, Florida, March 17-21 where the PI presented two invited papers at the Symposium on Fischer-Tropsch Synthesis. He also attended the 7th BES Catalysis and Surface Chemistry Research Conference held March 25-28 in Gaithersburg, Maryland where he presented a poster paper. He hosted the annual ASME Corrosion Meeting April 5-6 at BYU which focused on coal mineral transformations at which he presented a paper on CaO catalysis of char oxidation. On April 30 Professor Bartholomew presented a short course on Catalyst Deactivation at Catalytica Associates; he also presented a 3-day course on the same subject at Shell R&D in Houston on May 21-23 and visited with Shell personnel on May 24th. On May 7th the Catalysis Laboratory hosted Dr. Lynn Slaugh, distinguished scientist at Shell.

During August 6-10 Professors Bartholomew and Hecker presented a short course on Heterogeneous Catalysis and Catalyst Deactivation to 30 professionals at Corning Inc. in Corning, New York. Dr. Jeffery Ullman of Morton Chemical visited the Catalysis Laboratory on August 31st. During Fall 1990 Mr. Scott Eliason presented a paper related to the contract on "Deactivation by Carbon of Iron Fischer-Tropsch Catalysts" at the 1990 National AIChE Meeting in Chicago (Nov. 11-16) and two papers related to the contract were accepted for publication. The latter of these will be presented at the 5th International Symposium on Catalyst Deactivation to be held June 24-26, 1991 at Northwestern.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Kinetic/Deactivation Studies

1. Construction and Testing of the Automated Berty Reaction System.

A computer-automated CSTR (Berty) reactor system to be used in the kinetic and deactivation studies was designed, constructed and tested. The system includes a Berty (Autoclave) CSTR reactor that can operate at 1-75 atm and up to 750°C with a catalyst charge of 1-50 g in either pellet or monolithic form. A schematic of this reactor was shown in a previous report [45]. The reactor system hardware includes solenoid valves, mass flow meters, thermocouples and transducers which enable flow rates, temperatures, and pressures to be automated. A control panel display provides information on the status of gas routing, temperature and pressure control, and computer control. Software for controlling and automating the system is written in a topdown, modular format in a fast Basic language for a Macintosh Plus computer; it includes (1) low level software routines for controlling the operating parameters, (2) high-level routines, (3) graphics displays, (4) a control language parser routine and (5) interactive graphics routines for displaying and controlling the status of the Berty system. (When a user clicks on a piece of equipment on the computer generated schematic, he can observe the values and make changes in the setpoints). A new HP 5890 chromatograph was purchased and integrated into the reactor system for purposes of online reactant/product analysis; the analysis of fixed gases such as CO and hydrogen and of C_1-C_{20} hydrocarbons is likewise automated and controlled by computer. Due to its complexity the complete construction and testing of the system hardware and software required over 3 years of effort. The reactor system was described in a previous publication [46].

2. Catalyst Preparation

Several unsupported iron catalysts were used in this work, including iron, iron with 1% alumina and iron with 1% alumina promoted with potassium. The unsupported iron catalyst (Fe-100) was prepared by decomposing iron nitrate at 100°C for 2 hours and 200°C for 12 hrs in air followed by reduction in flowing hydrogen at 300 or 400°C for 24 hours. A batch of catalysts containing alumina (Fe-A-200) was prepared by decomposing aluminum nitrate with iron nitrate to give a 1% by wt Al/Fe.

A potassium-promoted catalyst (Fe/K-A-300) was prepared by dissolving KNO_3 in water and mixing a portion of the Fe-A-200 catalyst that was previously reduced and passivated. KNO_3 was added to achieve a total K/Fe molar ratio of 0.06. Arakawa and Bell [48] have shown that CO consumption and olefin production pass through a maximum at this ratio. The first (Fe/K-A-301) of two samples of this new catalyst was used to probe the conditions required for obtaining activity similar to the unpromoted catalysts. The second sample (Fe/K-A-302) was used to measure hydrogen chemisorption uptakes.

A batch of (Fe/K-A-400) was prepared by dissolving 0.1118 g KNO_3 in 10 ml water and adding to 5.0009 g reduced and passivated Fe-A-200 catalyst to achieve a total K/Fe ratio of 0.013. The catalyst was then dried at 110°C.

3. Adsorption Measurements

a. Hydrogen Adsorption Measurements. Two methods were used to measure active surface areas of the catalysts. Method 1 involves evacuating the sample at 400°C for one hour, admitting hydrogen to contact the catalyst, cooling in hydrogen to room temperature and then measuring the isotherm. It has been shown, however, that there may be significant spillover of hydrogen on iron catalysts at temperatures where these chemisorptions have been performed and that admitting hydrogen into the cell at 100°C and then measuring the uptake at that temperature gives results consistent with surface areas measured by CO chemisorption [48]. Indeed, this second method gave an uptake 40 to 68% less than the first method, depending on the catalyst.

Uptakes of 42.6 and 47.1 μmoles H_2 uptake/gram catalyst were obtained in the two measurements made on Fe-102 (Fig. 1). The average of the two runs, 45 μmoles/g, was used in obtaining turnover numbers and activation energies for this catalyst.

Hydrogen uptake data are summarized in Table 1 for the catalysts studied. Chemisorption uptake data were obtained for the two methods for both K-promoted and unpromoted catalysts before and after reaction. There is a general trend of decreasing uptake from method 1 to method 2. For (Fe/K-A-302), cooling in hydrogen from 400°C to room temperature resulted in an uptake of 30.2 ± 6.7 μmoles/g while the adsorption at 100°C gave 9.66 ± 3.2, a decrease of 68%. The substantially larger uptakes obtained by the first method suggest that spillover is important at high adsorption temperatures in both catalysts systems but more pronounced on the promoted catalyst. Except for the Fe-100 series catalysts, results

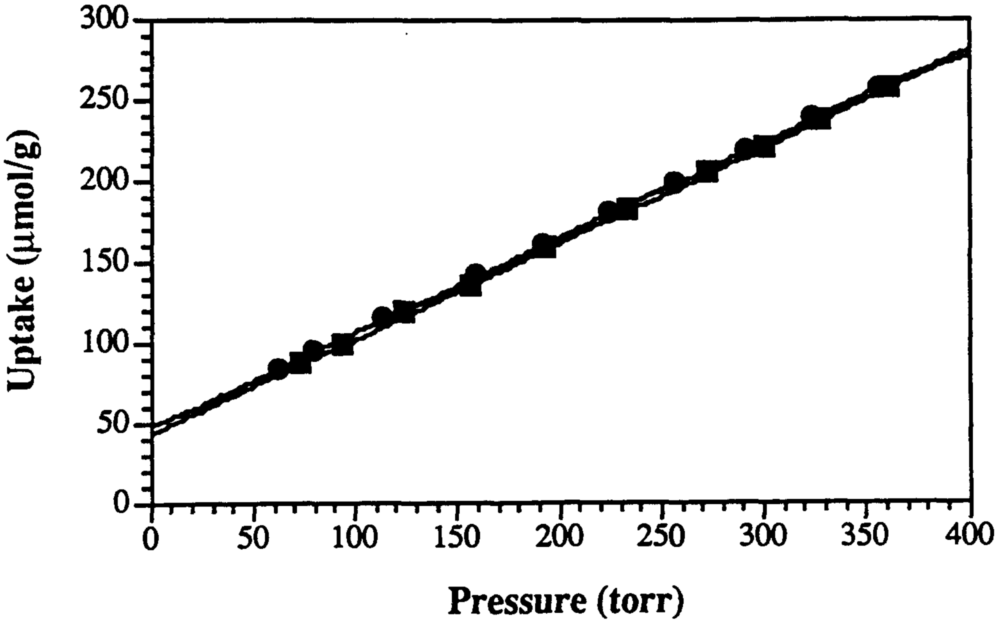

Figure 1. Hydrogen chemisorption uptakes measured by cooling in hydrogen from 400°C to room temperature gave 45 μmoles/g (catalyst Fe-102).

TABLE 1

Hydrogen chemisorption uptakes (μmoles/g) for various unpromoted and potassium-promoted catalysts. Numbers in parentheses are the 95% confidence intervals.

Catalyst	Hydrogen uptake, μmoles/g		
	Fresh/Reduced	Spent/Unreduced	Spent/Reduced
Fe-102[a]			44.8 (29)
Fe-A-205[a]			55.3 (2.8)
Fe-A-206[a]	54.3 (4.7)		
Fe-A-206[b]	32.9 (2.7)		
Fe/K-A-302[a,c]	30.2 (6.7)		
Fe/K-A-302[b,c]	9.66 (3.2)		
Fe/K-A-401[b,d]		4.77 (1.6)	11.0 (12.)
Fe/K-A-402[b,d]	19.3 (3.5)	8.75 (1.1)	12.6 (2.7)
Fe/K-A-403[b,d]		4.37 (3.6)	6.61 (3.5)

[a] Method 1: Cool from 400°C to RT in hydrogen; isotherm measured at RT.
[b] Method 2: Isotherm measured at 100°C.
[c] K/Fe molar ratio = 0.061.
[d] K/Fe molar ratio = 0.013.

from the second chemisorption method were used in calculating turnover numbers, etc.

Hydrogen chemisorption uptakes were measured on fresh Fe-A-203 catalyst using two different precision pressure gages. Chemisorptions 1 through 5 were performed with one gage and 6 through 11 were performed with the other. The reason for the change was a leak in the system causing unstable pressures when performing the chemisorptions. It was thought that there was a leak in the Bourdon tube from the pressure side to the reference side. The results from the first set of chemisorptions gave 30.0 ± 4.2 μmoles H_2 uptake per gram of catalyst (with 95% confidence) and ranging from 26 to 35 μmoles/g. The second set, which still appeared to have the same leak problem, gave 54.6 ± 12.3 μmoles/g with a range from 36 to 70 μmoles/g. These numbers compare with data obtained on catalyst Fe-A-201 which averaged 37.0 μmoles/g. It was later found out that part of the problem was that it takes a significant amount of time to evacuate the reference side of the Bourdon tube because of the relatively large volume (80 cc) and small diameter channel to the vacuum apparatus. Some additional leakage may have occurred from some Swagelock connectors at the gage.

Hydrogen chemisorption measurements were performed on the spent, reduced Fe-A-205 catalyst after evacuation at 400°C for 1 hr and cooling in hydrogen to room temperature. The average of seven measurements with the corresponding 95% confidence interval was 55.3 ± 2.8 μmoles/g catalyst. Chemisorption measurements were also obtained on Fe-A-206, a catalyst from the same batch as Fe-A-

205, resulting in an uptake of 54.3 ± 4.7 µmoles/g. Based on these results, the quantity of zero-valent surface iron can be considered the same on both the fresh and spent Fe/Al catalysts.

The surface area of K-promoted iron (Fe/K-A-402) decreases 40% from the unpromoted catalyst, showing that even a very small amount of potassium has a large effect on the adsorption characteristics of the iron. Increasing the potassium content by 5 times (Fe/K-A-302) reduces the uptake again by a factor of two. Measurement of the active surface area (zero-valent iron) by hydrogen chemisorption after synthesis indicates that deactivation of K-promoted iron occurs readily at mild reaction conditions. For example, after a series of reaction experiments, the uptake of Fe/K-A-402 decreases from 19.3 to 8.75 µmoles/g. Upon regenerating the catalyst in hydrogen at 400°C for 24 hours, some of the active surface area is regained, but significant permanent deactivation has occurred as indicated by a final uptake of 12.6 µmoles/g. On the other hand, the active surface area of the unpromoted catalyst is the same within experimental error before and after reaction, i.e. uptakes of two different unpromoted samples, one fresh and the other spent, were nearly identical.

Hydrogen chemisorptions made on the 400 series catalysts at various points along their schedules are shown in Figure 2. There is an obvious trend of active surface area decrease due to reaction but which may be partially recovered by re-reducing in hydrogen.

b. BET Surface Areas. Surface areas were measured for Fe-A-206 following ASTM standard test method D3663-84. Three separate tests on this catalyst resulted in a surface area of 11.6 ± 0.2 m^2/g

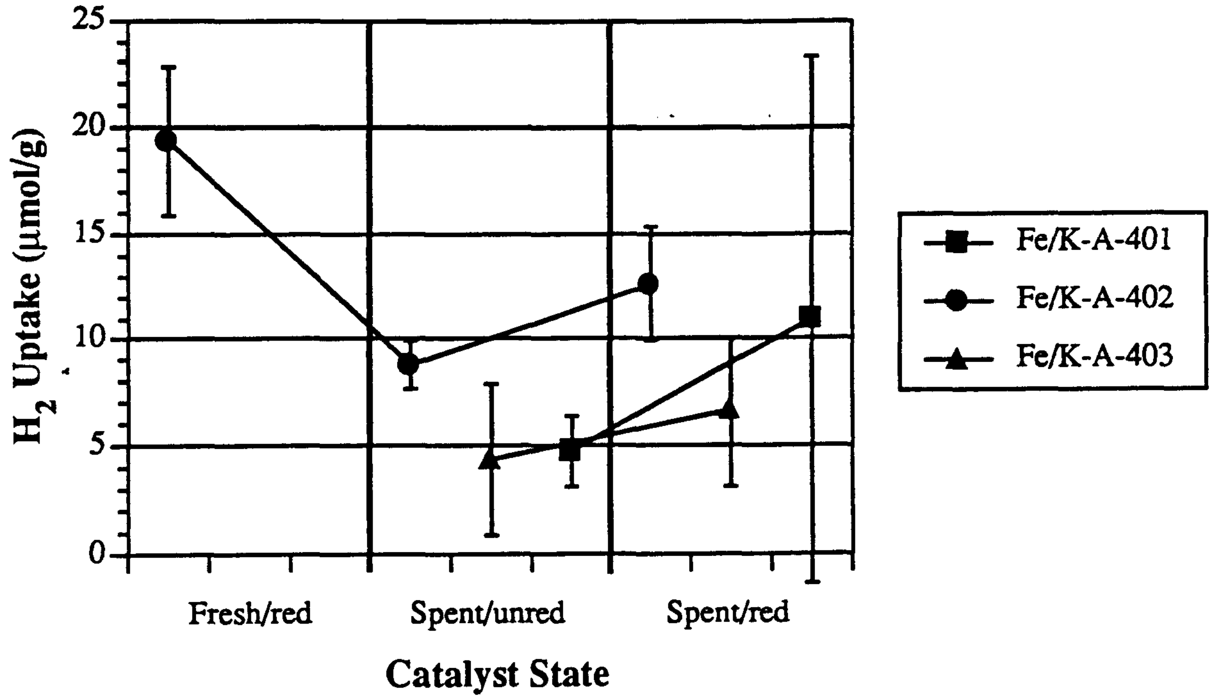

Figure 2. Hydrogen adsorption data for fresh, spent and regenerated Fe/K catalysts.

catalyst. Several BET measurements were also made on the 400 series catalysts at various reaction times. The values for the spent/reduced Fe/K-A-402 and -403 were 9.75 and 7.66 m^2/g, respectively. A value of 8.36 was obtained for the fresh/reduced Fe/K-A-404.

4. Activity/Selectivity/Deactivation Measurements

a. GC Response Factors. Calibration of the gas chromatograph flame ionization detector (FID) response factors (RF) resulted in significant changes from previous response factors taken from the literature (1967). Two small cylinders of gases at known concentrations were obtained from Scott Specialty Gases. One cylinder contained paraffins: methane, ethane, propane, n-butane, n-pentane and n-hexane. The other contained olefins: ethylene, propylene, 1-butene, 1-pentene, and 1-hexene. Injections of these gases were made with a 500 μ-liter syringe into the flame ionization detector port. The response factors were determined by dividing the peak area by the amount (wt.) of each component.

Figure 3 shows the plots of several injections. Because the olefin and paraffin average response factors were very close, the same response factor was assigned to the olefins and paraffins for a given carbon number. For carbon numbers greater than 6, a linear extrapolation based on C_5 and C_6 response factors was assumed. Table 2 shows the old and new response factors.

The effect of these new response factors has been to decrease the relative amounts of the heavier hydrocarbons while lighter hydrocarbons increase. The total activity based on CO converted also decreases. Table 3 compares results with the old and new response factors. These calibrations also allow us to positively identify the known gases in the chromatograms based on their retention times.

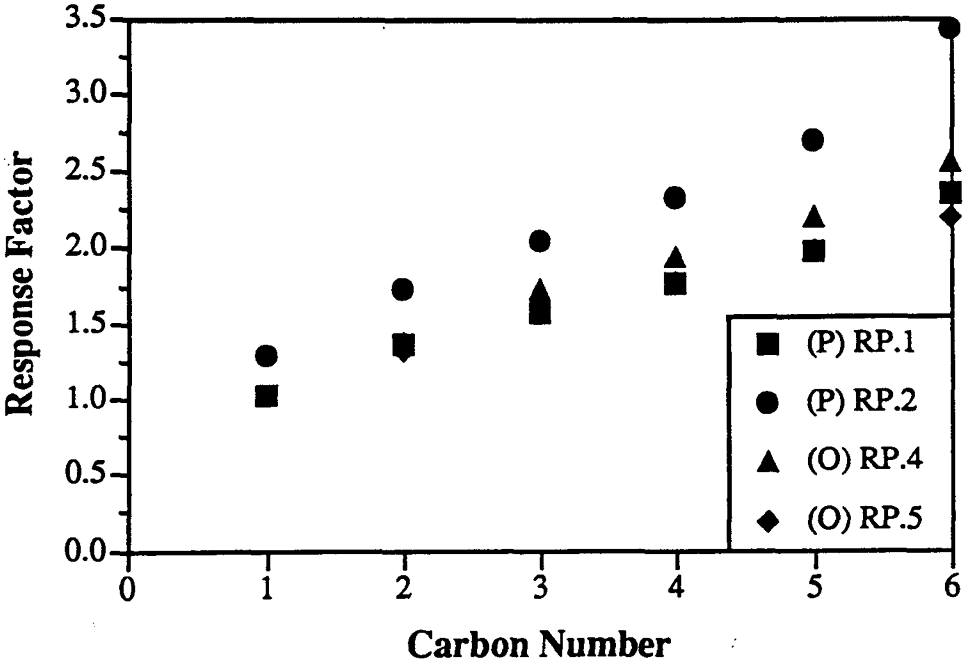

Figure 3. Paraffin and olefin response factors based on calibration gases.

Table 2. Old and new gas chromatograph (FID) response factors for olefins and paraffins.

Carbon #	Old Paraffin RF	Old Olefin RF	New Olefin/Paraffin RF
1	0.97		1.16
2	0.97	1.02	1.50
3	0.98	1.00	1.81
4	1.03	1.00	2.04
5	1.04	1.00	2.32
6	1.03	0.99	2.77
7	1.00	1.00	3.22
8	0.97	1.03	3.67
9	0.98	1.00	4.12
10	1.00	1.00	4.57
11	1.00	1.00	5.02
12	1.00	1.00	5.47
13	1.00	1.00	5.92
14	1.00	1.00	6.37
15	1.00	1.00	6.82

b. Reaction Setup. The reaction was run in a Pyrex reactor cell using about 1 gram of powdered catalyst at a series of temperatures starting at 200° C and was increased in 10° C increments to a final temperature of 230°C. Earliest runs used a reaction gas with a H_2:CO ratio of 2:1. The setup was later modified to allow flows of CO, H_2 and He (from separate tanks) to be controlled independently. A Hewlett-Packard 5890A gas chromatograph equipped with a flame-ionization detector (FID) and a thermal conductivity detector (TCD) was connected in-line downstream of the reactor. A Macintosh computer was used with a program written in this lab to control the chromatograph and take samples automatically at the programmed times. GC samples were taken about every 2 hours (or as desired) at each reaction temperature so that the approach to steady-state could be observed. Samples were run at the initial temperature for 20-24 hours and at succeeding temperatures for about 10 hours each.

c. Fe-100 Series. (Fe-101, Fe-102) Figure 4 shows Arrhenius plots for the first two unsupported catalyst samples. Fe-101 was reduced at 300°C while Fe-102 was reduced at 400°C. Reactions were carried out over these catalysts using a 2/1 mixture of H_2/CO at various temperatures. Hydrogen uptakes of 45 μmoles/g (measured on the spent Fe-102 catalyst) were used for both catalysts. From a previous study done in our laboratory over similarly prepared unsupported iron catalyst at 2/1 H_2/CO and 225°C, a turnover number of 4×10^{-3} was calculated [15,49]. This is also plotted in Figure 4. Very good agreement between this data point and the data from this study is evident.

Table 3. Sample selectivity (as weight fraction of hydrocarbons produced) and activity changes as a result of new response factors (catalyst Fe-A-203).

	C1	C2-4	C5-11	Activity (Nco)
Old	0.4053	0.4897	0.1049	2.58E-03
New	0.5269	0.4121	0.0611	2.08E-03

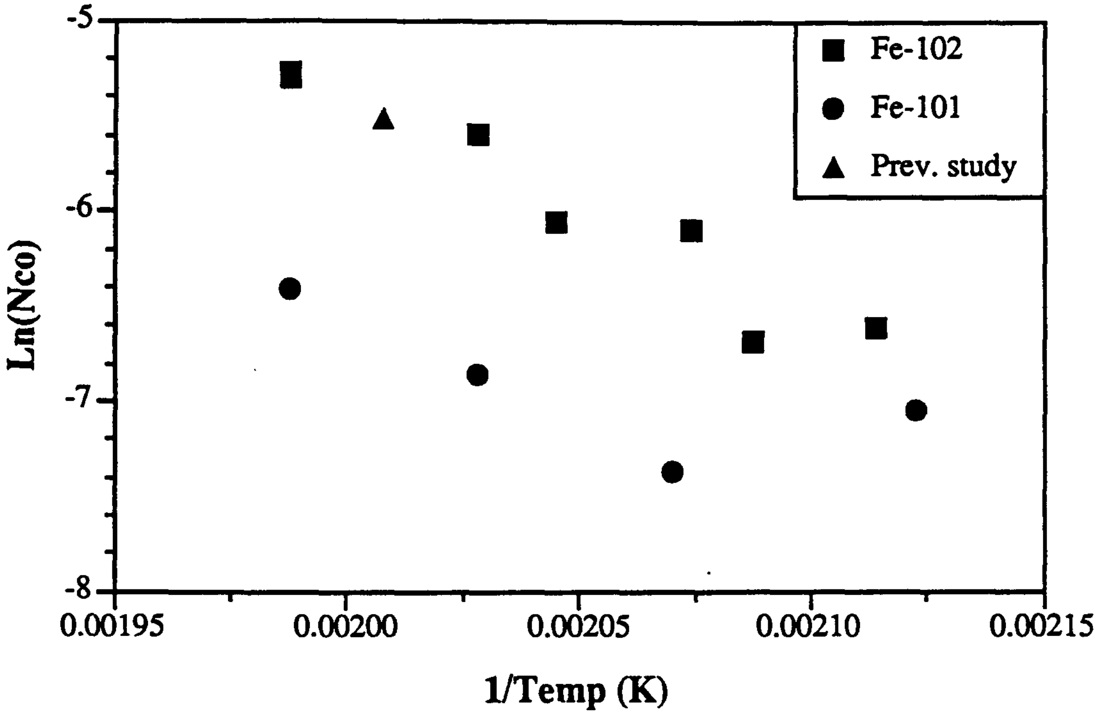

Figure 4. Activities as a function of reciprocal temperature for unsupported catalysts Fe-101 and Fe-102. Data from a previous study were obtained at 498 K, 2/1 H_2/CO.

The temperature sequence of data for Fe-102 was 200, 210, 220 and 230°C followed directly by reaction at 206 and 216°C. It is evident that some deactivation of the catalyst occurred. The turnover numbers at 206 and 216°C are lower than what would be expected for no deactivation. Ideally, they should lie along the line plotted through the other points.

Activation energies for these two catalysts were calculated to be 99 and 88 kJ/mol for Fe-101 and Fe-102, respectively. This compares to the value of 132 kJ/mol obtained in the previous study.

Catalyst selectivity is shown as a function of temperature in Figure 5. As the reaction temperature increases, methane and C_2-C_4 hydrocarbon contents increase slightly while the C_5+ hydrocarbon content decreases. Data from a previous study [15] give lower methane and C_2-C_4 fractions and a higher C_5+ fraction than in this work. The selectivity towards smaller hydrocarbons (namely, methane) with deactivation is seen in Figure 5. At 206°C and 216°C methane appears to be formed at the expense of the higher hydrocarbons (C_5+). The C_2-C_4 fraction is not noticeably affected.

Another result of deactivation can be seen in Figure 6 in which the olefin content of the C_3 to C_7 fraction of the product is plotted as a function of CO conversion. A good fit is obtained when disregarding the data points from the runs following reaction at 230°C. A possible explanation is that at 230°C the surface begins to be covered with more than the steady-state amount of carbon required for reaction. As a result, there are fewer sites for hydrogen to adsorb which increases the degree of unsaturation.

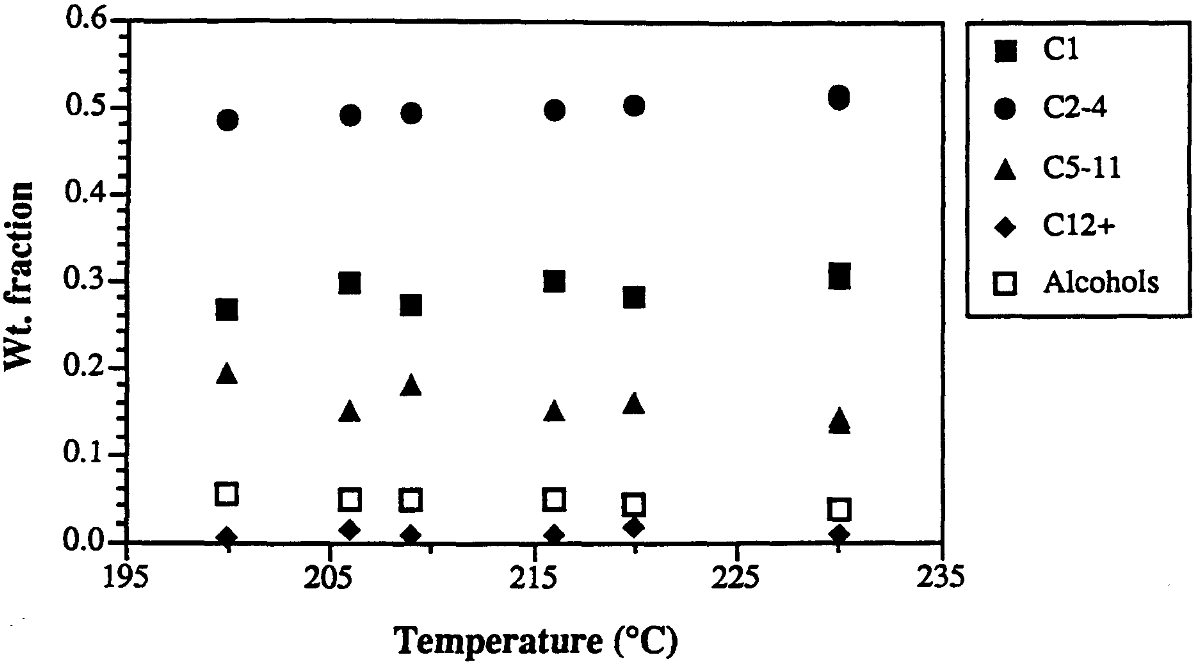

Figure 5. Product selectivity based on hydrocarbons produced (Fe-102).

It should be noted that although the gas chromatograph does not identify hydrocarbons heavier than about C_{15}, heavy waxes were observed at the outlet end of the catalyst sample and along the wall of the sample cell.

After these data were obtained the reaction apparatus was modified to allow separate H_2 and CO

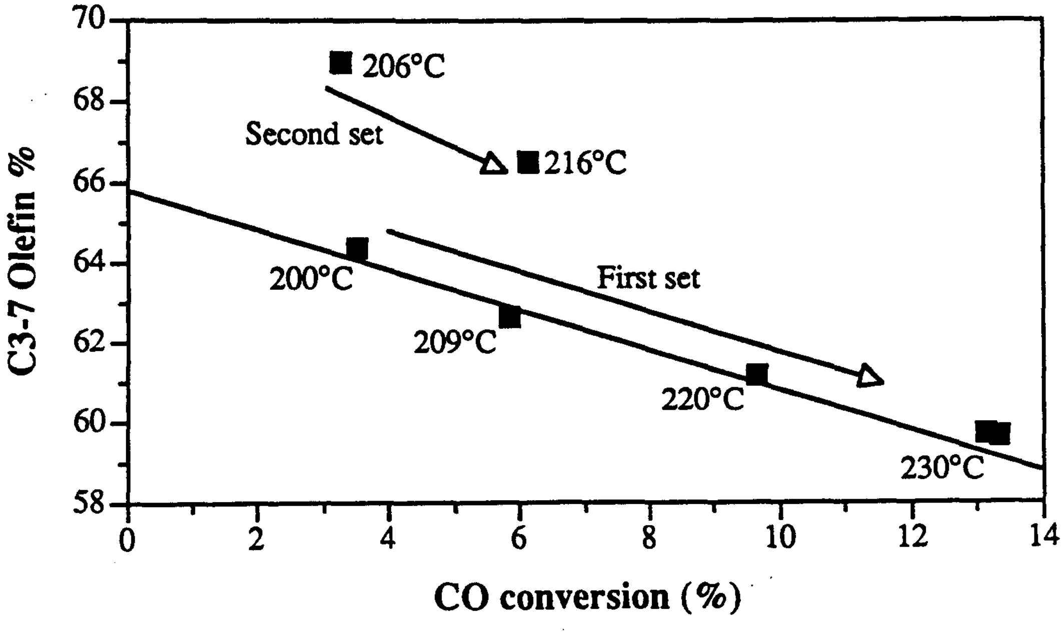

Figure 6. Correlation of conversion with olefin content (Fe-102). Arrows indicate order of runs.

tanks to be used. Originally, a single tank of 2:1 H_2:CO mixture was used and flow control was achieved with a Matheson flow controller. With the new setup, this flow controller controlled the hydrogen flow. Two manually operated, micro-metering valves were used in conjunction with a Matheson flow meter for controlling the CO flow.

(Fe-103) Once this setup was completed, several runs were made to reproduce results obtained previously. A fresh sample (Fe-103) was charged into the sample cell, the sample was reduced in flowing hydrogen at 300°C and two chemisorptions were done. Chemisorption results showed uptakes of 51 and 57 μmoles/g. Hydrogen and carbon monoxide were then reacted over this catalyst at a series of temperatures ranging from 200°C to 230°C. The catalyst was more active than the first sample of unsupported iron reduced at 300°C previously reported for similar conditions (similar flow rates and H_2/CO ratios). For this present case, reaction temperatures above 210°C gave CO conversions greater than 10% and at 230°C the conversion was 18%.

Following this reaction schedule, the catalyst was again reduced in pure hydrogen, only this time at 400°C. The catalyst was then moved from the reaction apparatus so that chemisorption measurements could be made. An uptake of about 35 μmoles/g was measured.

A total flow rate of 30 cc/min (twice the previous rate) was used in the reaction experiments that followed in order to maintain conversion less than 10%. However, the catalyst showed very little activity, producing only C_1-C_3 hydrocarbons. Even when the total flow was reduced, the activity (ie. conversion) did not increase substantially.

(Fe-104) Another fresh sample (Fe-104) was charged into the cell, reduced at 400°C and the hydrogen uptake measured, giving about 20 μmoles/g. After transferring this sample to the reaction setup and running at 190°C, $H_2/CO=2$, and 15 cc (total flow)/min for 7 hours, there was very little conversion of CO to hydrocarbons. Further reaction at 200°C showed similar results.

Several important observations were made following these experiments. The spent catalyst had sintered into large particles, possibly as a result of (1) oxygen reacting with the reduced catalyst or (2) sintering upon decomposition of the iron carbide during rereduction. The oxygen could have come from several sources. After the first sample became inactive, the hydrogen and CO feed lines were checked for leaks and several substantial leaks were found and eliminated. However, the results of the last sample indicated that there was still a problem. Plastic tubing, which had been used for a major portion of the feed lines, is permeable to oxygen. This plastic tubing was changed to stainless steel before further work was done. Another source of oxygen could be in the transfer of the cell from the chemisorption apparatus to the reaction setup. A small, but possibly significant, amount of air is left in the glass connectors connecting the feed line to the sample cell. A change of procedure was instituted to correct this problem. Reduction of the catalyst was thereafter done in-situ during the test setup, immediately followed by reaction experiments. Chemisorption measurements were henceforth conducted on separate samples. In this way, all possibilities of oxygen contacting the active catalyst were eliminated.

It was observed that several chemisorptions did not give reasonable slopes and intercepts. A minor error in the computer analysis program was found but it did not explain the erroneous results. It was later found that the zeroing of the Texas Instruments precision pressure gauge had been done improperly before each chemisorption. Making a crude estimate of the error in the last set of data changed the uptake from 54 to 19 μmoles/g and the slope and intercept took on reasonable values.

(Fe-105) Additional runs were made on a new unsupported Fe catalyst sample (Fe-105). The catalyst was reduced in hydrogen at 400°C after which a 2:1 H_2/CO ratio synthesis gas (15 total cc/min) was reacted over it for about 90 hours at temperatures ranging from 200° to 230°C. The catalyst was then rereduced at 400°C and similar reactions conditions followed. This combination of reduction and reaction was performed a third time. The activity data for these runs are summarized in Figure 7.

The activity of the catalyst (measured by CO conversion) during the first reaction sequence was quite low, ranging from about 0.6% at the lowest temperature to only 2.3% at the highest temperature. An Arrhenius plot gave an activation energy of 86 kJ/mole (see Fig. 7).

After rereduction at 400°C for 16 hours, however, the activity decreased by about a factor of 2 (see Fig. 7). (The total flow had been increased from 15 to 20 cc/min but the H_2/CO ratio was still the same.) Because of the lower activity the maximum reaction temperature was increased to 240°C. Even at this higher temperature the CO conversion was only 1.2%. There was also a significant change in the activation energy to 68 kJ/mole. The third reduction at 400°C was carried out for only 7 hours. Activity

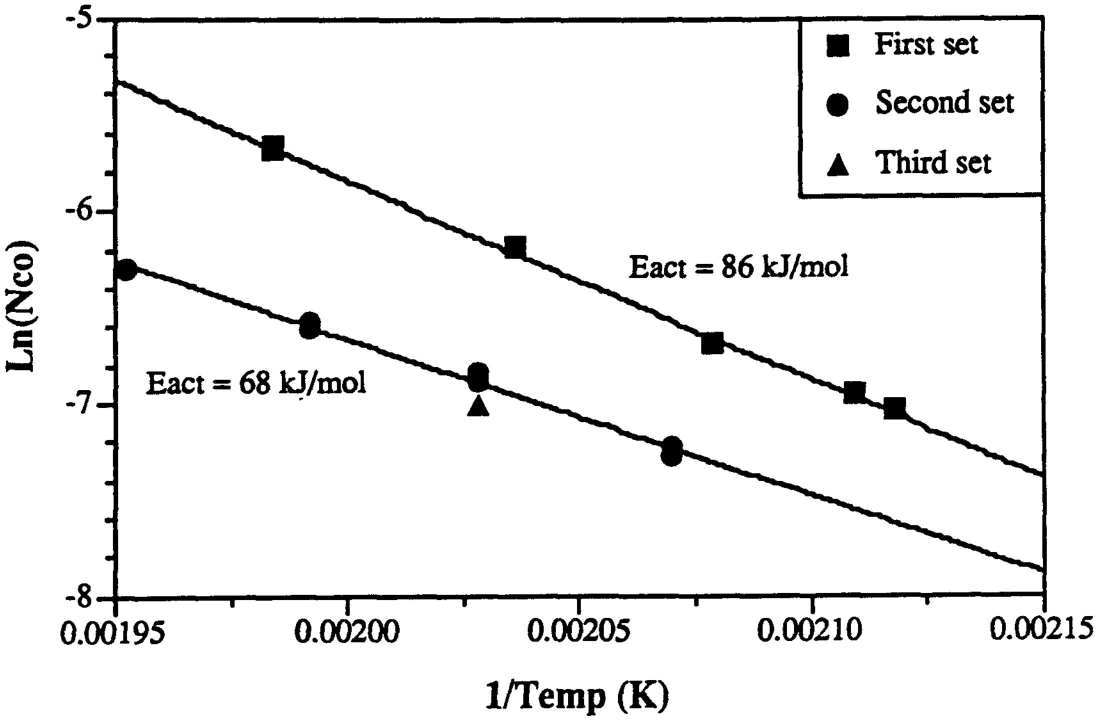

Figure 7. CO hydrogenation activity of unsupported Fe reduced at 400°C; Fe-105, H2/CO = 2, 1 atm.

was only slightly lower than the previous set.

It was obvious from examination of the catalyst that the small iron particles had fused together into much larger ones, probably due to sintering. The decrease in activity at each reaction stage was most likely a result of lower active surface area and not a result of a drop in the specific activity. Reducing the catalyst in hydrogen following reaction may have caused the iron to sinter as the iron carbide decomposed. Hence the most significant decrease in activity occurred between the first and second reaction sequences.

Because of the thermal stability problems with unsupported, unpromoted iron, work thereafter used unsupported iron with 1% alumina as a structural promoter. This catalyst was prepared by calcination (at 200°C) of the mixed iron and aluminum nitrates.

d. Fe-A-200 Series. (Fe-A-201) A new catalyst sample, Fe-A-201, was prepared by decomposing aluminum nitrate with iron nitrate to give a 1% by wt. Al/Fe. This new sample was subjected to the same treatments as the previous catalyst with much improved stability. No significant differences in initial specific activity were observed with the Al-promoted catalyst (Fe-A-201) compared to the unpromoted catalyst. However, the major difference was observed after re-reduction in hydrogen. The Al-promoted catalyst did not sinter and the initial specific activity was restored after re-reduction. This can be seen in the activation energy plot (Figure 8).

Reaction conditions for Fe-A-201 included 3:1 H_2/CO ratio, temperatures ranging from 200-230°C, and reaction times for a given temperature of 12-24 hours. Output data from GC sample #7

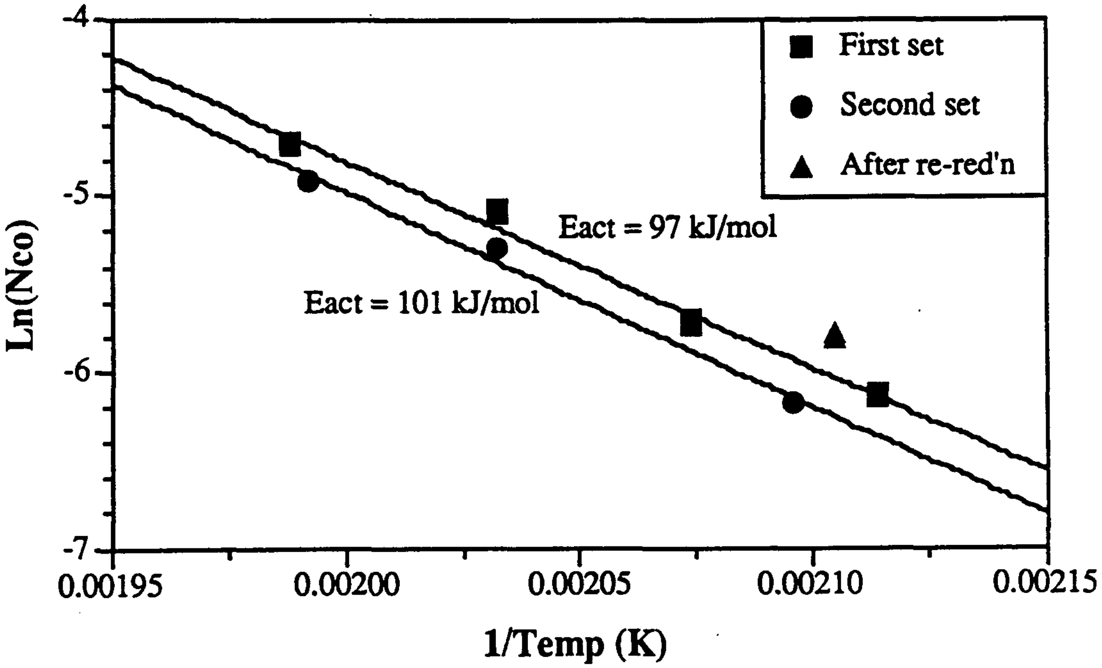

Figure 8. Arrhenius plot for Fe-A-201 (99% Fe, 1% Al) at 3/1 H_2/CO; 200-230°C.

(200°C) are given in Table 4. Figures 9 and 10 show the Anderson-Schulz-Flory (ASF) and product distribution plots that correspond to this sample.

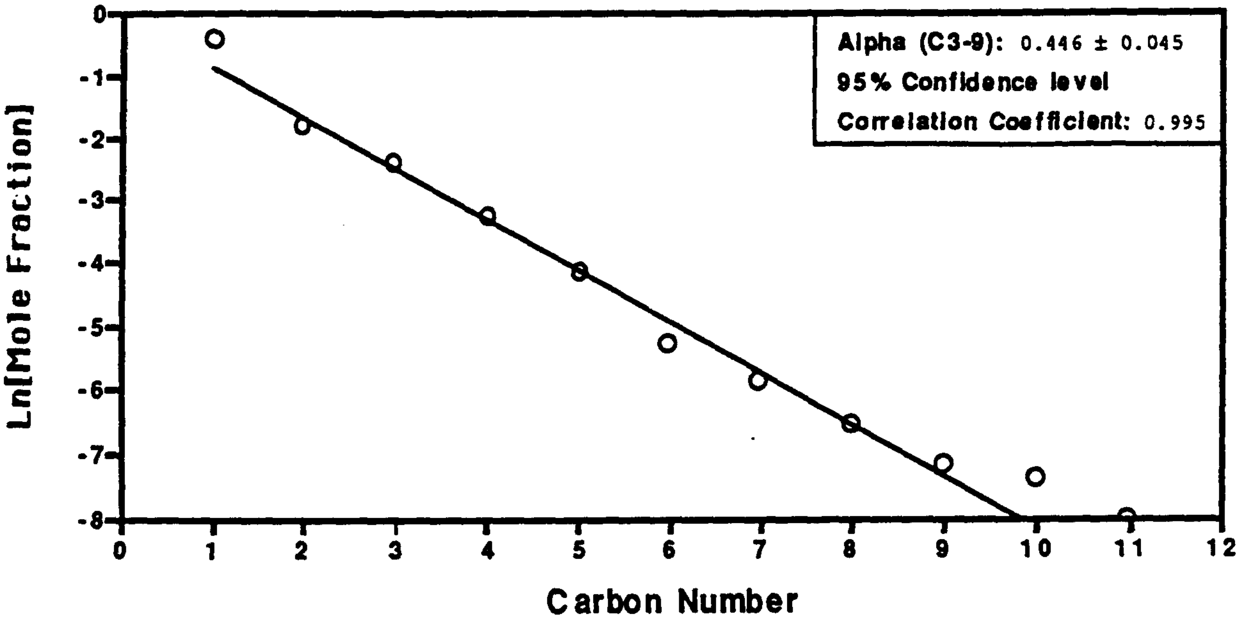

Figure 9. Anderson-Schulz-Flory (ASF) plot for reaction on Fe-A-201 at 200°C.

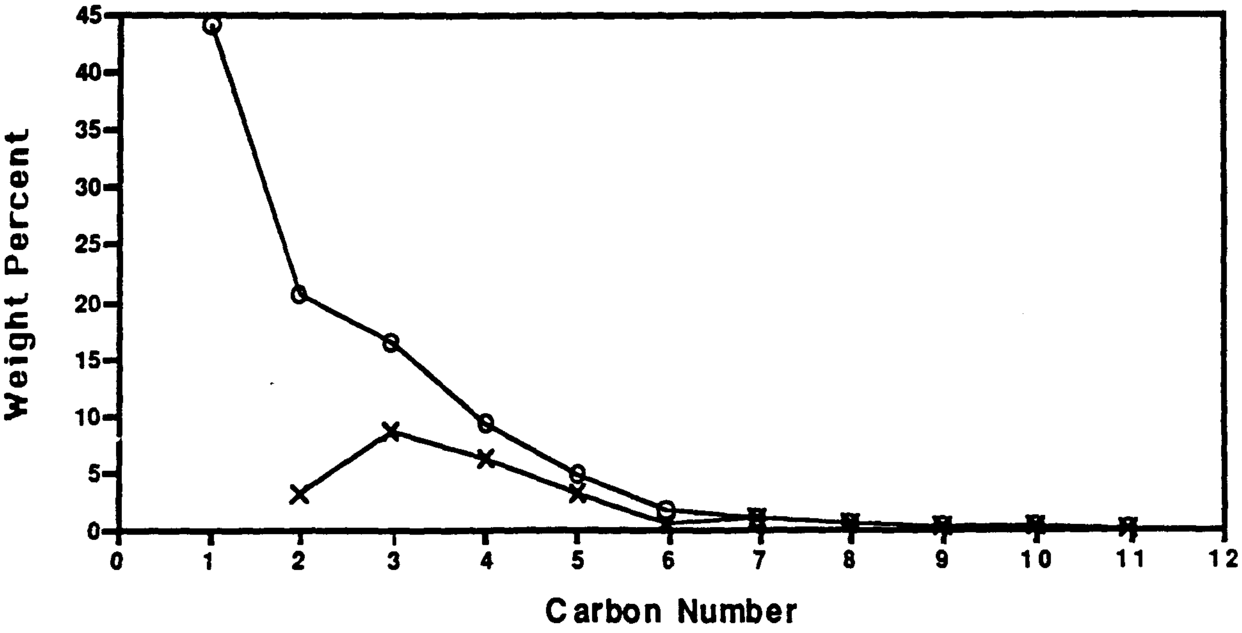

Figure 10. Distribution of total hydrocarbons (upper curve) and olefins (lower curve) on Fe-A-201 at 200°C.

A summary of the data from this catalyst is given in Table 5. Data shown for each GC sample include temperature, hydrogen and carbon monoxide flowrates and conversion, and the CO turnover frequency (Nco). The second page of Table 5 shows the selectivity to hydrocarbons and CO_2 and also the distribution of products based on the total hydrocarbons produced.

Table 4. Reaction parameters and results from GC sample #7 on Fe-A-201 at 200°C.

Run Number 7 **OCT/14/88 11:05:44**

Catalyst: Fe/1% Al
Sample Weight: 1.0281 g **H2 Chemisorption Uptake:** 33.00 µmoles/g
Sample Volume: 1.0000 ml

Reaction Parameters:
Temperature: 473 K **Flows:** **H2:** 15.00 cc/min
Pressure: 1.00 Atm **CO:** 5.00 cc/min
Reactor Run Time: 1448 Min
H2/CO Ratio: 3.00/1
Space Velocity at 298K and 1 Atm: 1200.0/Hour
Space Velocity at Reactor Conditions: 1904.7/Hour
Reactants Mass Flowrate: 6.965E-03 g/min
Average Molecular Weight of Feed: 8.514 g/gMole

Results:
CO Conversion: 4.2377%
H2 Conversion: 15.7565% **H2/CO Usage Ratio:** 11.155/1
Number of Active Sites: 4.0869E+19
CO Turnover Number: 2.1285E-03 molecules CO/site-sec
Rate Weight Basis: 8.4290E-06 mole CO/g cat-min
Average Molecular Weight of Products: 24.538 g/gMole
TCD to FID Conversion Factor (RK): 1.619
Error in H2 Balance: -12.164%

Product Selectivities:
Selectivity Based on CO Converted (Carbon Atom %)

C1	C2-4	C5-11	C12+	Alcohols	Total HC	CO2
0.2912	0.3218	0.0712	0.0000	0.0110	0.6952	0.3048

Distribution of Total Hydrocarbons (Weight %)

C1	C2-4	C5-11	C12+	Alcohols
0.4407	0.4644	0.0949	0.0000	0.0238

Hydrogen selectivity

Hydrocarbon	H2O
0.4221	0.5779

C3-7 Olefin Content (mole Basis): 0.5884
C3-7 Olefin/Paraffin ratio (mole Basis): 1.4294

	Weight Fractions				Mole Fractions						
C#	**Par**	**Ole**	**Alc**	**Total**	**Par**	**Ole**	**Alc**	**Total**	**OleCont**	**O/P**	**Ln(Tot)**
1	.4407		.0000	.4407	.6741		.0000	.6741			-0.3944
2	.1516	.0312	.0238	.2067	.1238	.0273	.0127	.1638	.1808	0.2207	-1.8094
3	.0780	.0854	.0000	.1635	.0434	.0498	.0000	.0932	.5344	1.1477	-2.3726
4	.0312	.0631	.0000	.0943	.0132	.0276	.0000	.0408	.6768	2.0936	-3.2001
5	.0165	.0318	.0000	.0483	.0056	.0111	.0000	.0168	.6652	1.9867	-4.0893
6	.0112	.0070	.0000	.0182	.0032	.0020	.0000	.0052	.3901	0.6395	-5.2514
7	.0000	.0115	.0000	.0115	.0000	.0029	.0000	.0029	.9900	99.0000	-5.8503
8	.0000	.0068	.0000	.0068	.0000	.0015	.0000	.0015	.9900	99.0000	-6.5069
9	.0000	.0041	.0000	.0041	.0000	.0008	.0000	.0008	.9900	99.0000	-7.1261
10	.0000	.0036	.0000	.0036	.0000	.0006	.0000	.0006	.9900	99.0000	-7.3595
11	.0000	.0022	.0000	.0022	.0000	.0003	.0000	.0003	.9900	99.0000	-7.9601

Table 5. Summary of reaction conditions and results on Fe-A-201.

GC Sample #	Date	Temp (K)	Rxn Runtime (min)	Runtime (hr)	CO conv (%)	H2 conv (%)	Nco (33 µmoles/g)	LN (Nco) (33 µmoles/g	1/T 1/(K)	HC Selectivity
1										
2							First set			
3	10/13/88 13:37:28	473	159	2.65	3.28	22.90	1.647E-03	-6.409	0.00211	0.5327
4	10/13/88 19:18:31	473	157	2.62	2.96	14.25	1.487E-03	-6.511	0.00211	0.6921
5	10/14/88 01:37:58	473	872	14.53	3.93	14.67	1.975E-03	-6.227	0.00211	0.6970
6	10/14/88 10:20:00	473	1402	23.37	4.28	14.60	2.150E-03	-6.142	0.00211	0.6970
7	10/14/88 11:05:44	473	1448	24.13	4.24	15.76	2.129E-03	-6.152	0.00211	0.6952
8	10/14/88 15:25:51	482	182	3.03	6.66	17.76	3.348E-03	-5.699	0.00207	0.6352
9	10/14/88 22:06:21	482	647	10.78	6.56	17.04	3.295E-03	-5.715	0.00207	0.6370
10	10/14/88 22:52:14	482	693	11.55	6.43	17.45	3.230E-03	-5.735	0.00207	0.6530
11	10/15/88 11:54:06	492	742	12.37	11.94	20.12	6.000E-03	-5.116	0.00203	0.5283
12										
13	10/15/88 13:03:49	492	812	13.53	12.20	22.23	6.130E-03	-5.095	0.00203	0.5626
14	10/15/88 13:49:53	492	858	14.30	12.08	22.66	6.069E-03	-5.105	0.00203	0.5489
15	10/16/88 13:50:21	503	1332	22.20	8.97	16.68	9.006E-03	-4.710	0.00199	0.5730
16	10/16/88 14:36:11	503	1378	22.97	8.92	17.65	8.962E-03	-4.715	0.00199	0.5728
							Second set			
17	10/17/88 12:13:23	477	1262	21.03	2.06	8.71	2.071E-03	-6.180	0.00210	0.7510
18	10/17/88 13:15:51	477	1332	22.20	2.02	8.81	2.031E-03	-6.199	0.00210	0.7514
19	10/18/88 00:41:07	492	577	9.62	4.93	11.99	4.956E-03	-5.307	0.00203	0.6539
20	10/18/88 14:11:56	502	742	12.37	7.22	14.18	7.249E-03	-4.927	0.00199	0.5915
21	10/18/88 15:10:06	502	800	13.33	7.29	14.78	7.328E-03	-4.916	0.00199	0.5869
22							After re-red'n			
23	10/19/88 13:22:40	475	917	15.28	3.04	10.79	3.055E-03	-5.791	0.00211	0.7732
24	10/19/88 16:15:06	475	1042	17.37	2.96	9.66	2.975E-03	-5.817	0.00211	0.7772

Table 5 (cont). Summary of reaction conditions and results on Fe-A-201.

GC Sample #	CO2 Selectivity	H2O Selectivity	H2 flow (cc/min)	CO flow (cc/min)	Alpha (α)	± (α)	Carbon # (α)	Distribution of total hydrocarbons (wt fraction)					C3-7 Olefin content
								C1	C2-C4	C5-C11	C12+	Alcohols	
1													
2													
3	0.4673	0.7357	15	5	0.388	0.106	C3-8	0.4687	0.4581	0.0732			0.6102
4	0.3079	0.6323	15	5	0.392	0.058	C3-8	0.4338	0.4868	0.0795		0.0435	0.6387
5	0.3030	0.5806	15	5	0.436	0.500	C3-9	0.4321	0.4687	0.0992	0.0000	0.0195	0.6195
6	0.3030	0.5602	15	5	0.461	0.071	C3-10	0.4351	0.4679	0.0949	0.0021	0.0277	0.5998
7	0.3048	0.5779	15	5	0.446	0.045	C3-9	0.4407	0.4644	0.0949	0.0000	0.0238	0.6062
8	0.3648	0.5121	15	5	0.422	0.019	C3-9	0.4214	0.4746	0.1015	0.0025	0.0357	0.5998
9	0.3630	0.5061	15	5	0.433	0.026	C3-9	0.4227	0.4760	0.0988	0.0025	0.0353	0.5968
10	0.3470	0.5153	15	5	0.439	0.044	C3-9	0.4261	0.4749	0.0976	0.0014	0.0343	0.5937
11	0.4717	0.3856	15	5	0.426	0.032	C3-10	0.4500	0.4642	0.0840	0.0018	0.0261	0.5140
12													
13	0.4374	0.4212	15	5	0.538	0.078	C3-10	0.4111	0.4487	0.1340	0.0062	0.0219	0.5320
14	0.4511	0.4203	15	5	0.430	0.028	C3-10	0.4328	0.4791	0.0863	0.0018	0.0335	0.5456
15	0.4270	0.4135	30	10	0.381	0.041	C3-9	0.5011	0.4446	0.0543	0.0000	0.0173	0.5856
16	0.4272	0.4282	30	10	0.363	0.045	C3-8	0.5066	0.4411	0.0523		0.0085	0.5930
17	0.2490	0.5894	30	10	0.367	0.095	C3-7	0.5204	0.4360	0.0436	0.0000		0.6498
18	0.2486	0.5955	30	10	0.334	0.015	C3-7	0.5215	0.4419	0.0367			0.6521
19	0.3461	0.4805	30	10	0.410	0.077	C3-9	0.5035	0.4430	0.0535	0.0000	0.0200	0.6261
20	0.4085	0.4280	30	10	0.345	0.033	C3-8	0.5106	0.4412	0.0482		0.0213	0.6255
21	0.4131	0.4352	30	10	0.343	0.043	C3-8	0.5201	0.4303	0.0496			0.6224
22													
23	0.2268	0.5576	30	10	0.432	0.045	C3-9	0.4941	0.4253	0.0806			0.6023
24	0.2228	0.5402	30	10	0.403	0.102	C3-8	0.4998	0.4255	0.0746	0.0001		0.6081

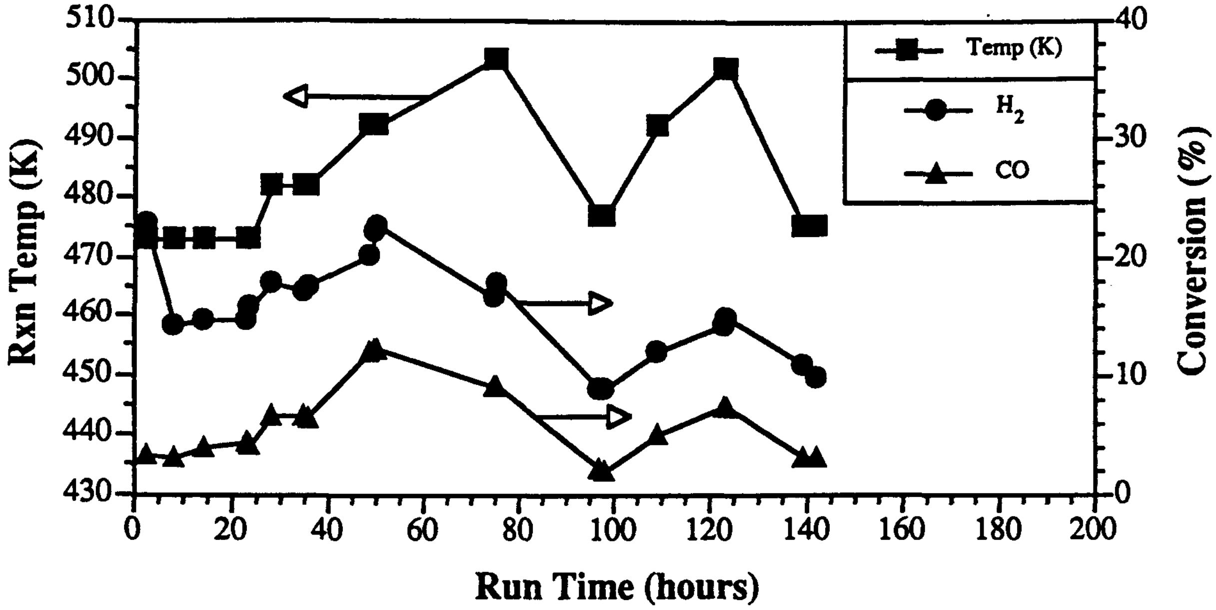

Figure 11. Temperature history and corresponding H_2 and CO conversions (%).

The temperature history is shown along with the conversions of CO and H_2 in Figure 11. The drop in conversions from 50-75 hours is due to a doubling of the space velocity in order to maintain CO conversion less than 10%. (Conversion at 220°C was 12% and doubling the space velocity reduced CO conversion at 230°C to about 9%.)

Figure 12 shows how the specific activity increases with temperature. During the second reaction

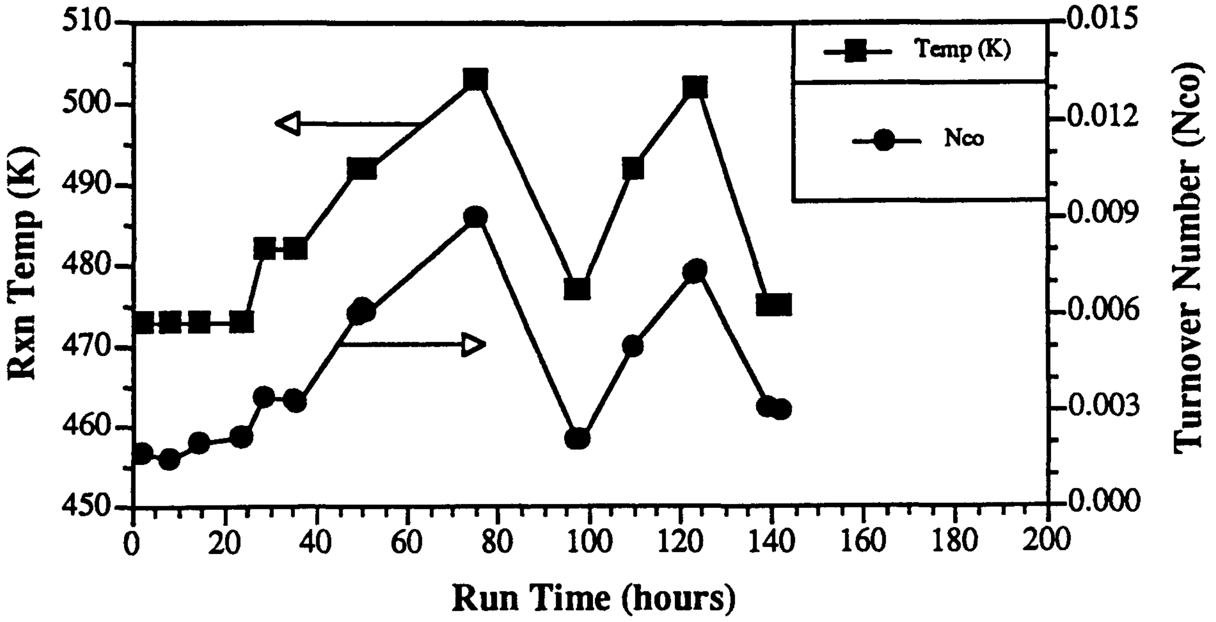

Figure 12. Specific activity (N_{CO}) change with temperature.

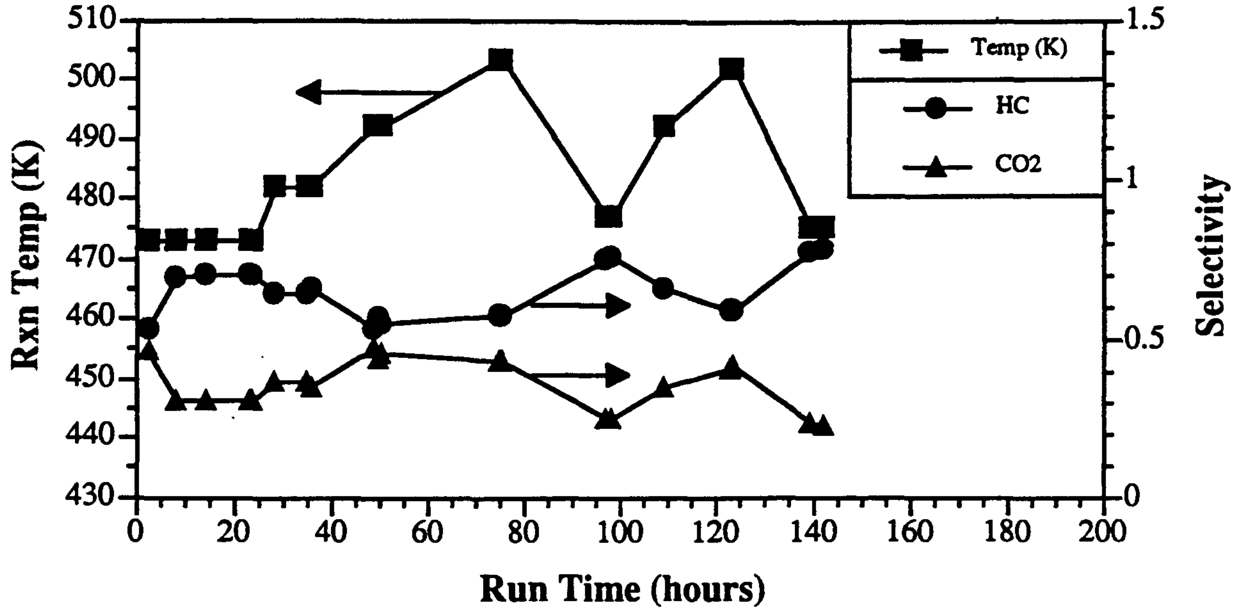

Figure 13. Selectivities to hydrocarbons (HC) and CO_2.

sequence (80-125 hours) the TOF for a given temperature is seen to be less than at the same temperature from the first sequence. This can also be seen in Fig. 8. This decrease in activity is attributed to carbon on the surface.

As the temperature increases, selectivity to hydrocarbon products decreases (Figure 13) while CO_2 selectivity increases. The selectivity to the different hydrocarbon fractions is more complex (Figure 14). The relative amounts of the three fractions shown do not change significantly over the first 50 hours of reaction (200-220°C). However, as the temperature reaches 230°C (503K) fractions of methane and C_2-C_4 hydrocarbons increase and decrease respectively. Over the second reaction sequence very little further change is observed. What is the cause of this behavior? One possibility is an increase in carbon on the surface at 230°C temperature. This carbon coverage may be maximum at this temperature and may correspond to the maximum production of methane. Another possibility is that the effect was caused by the increase in space velocity. Although the partial pressures were unchanged, there may have been some mass transport limitations due to the high conversions (CO:12% and H_2:23%).

(Fe-A-203) Following chemisorption measurements reactions were run on Catalyst Fe-A-203 at temperatures ranging from 200 to 230°C and at H_2/CO ratios from 3/1 to 1/1. The schedule previously set up in which the catalyst was reacted at 200°C for 20-24 hours followed by reactions at successive 10° increments in temperature for 12 hours was not adhered to strictly. This previous schedule was chosen because the catalyst appeared to reach a steady-state condition after about 24 hours on stream. However, because of deactivation at higher temperatures the schedule was changed. Table 5 shows the reaction sequence and conditions for the runs performed on this catalyst. Shown are the intended H_2/CO

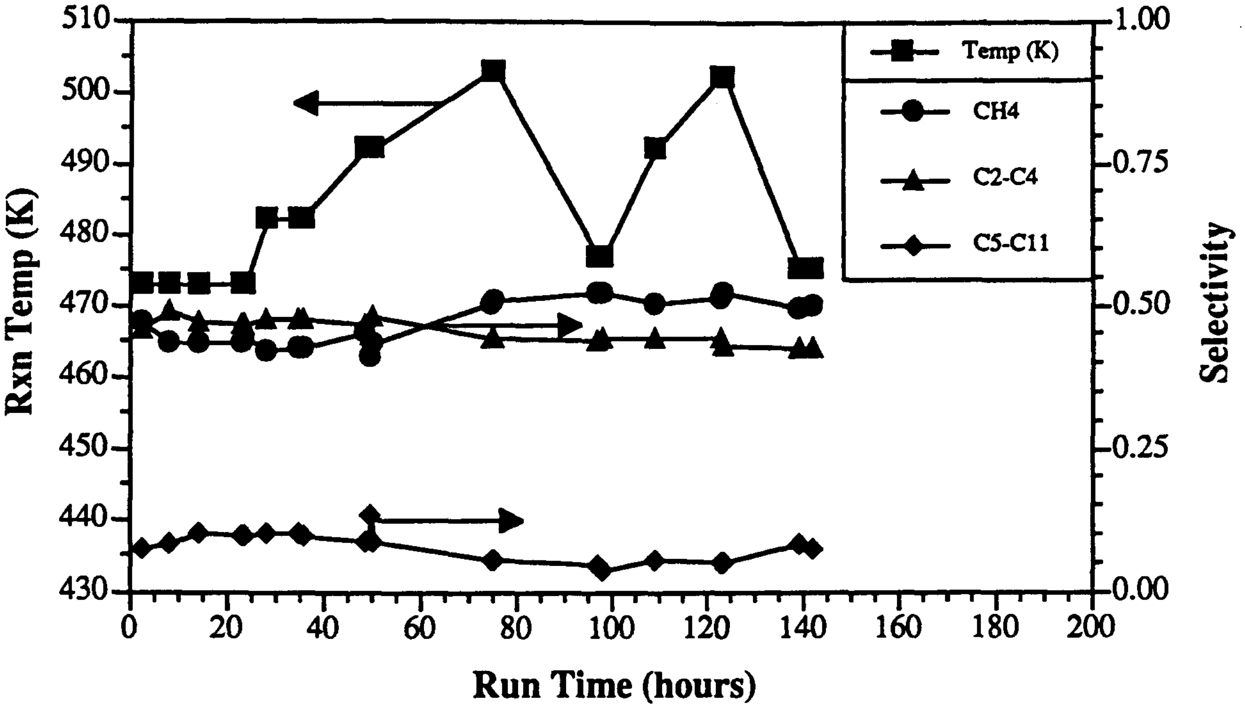

Figure 14. Selectivity to various hydrocarbon fractions.

ratios, the actual flows of H_2, CO and He (in cc/min), time of reaction at the given temperature, and sample times. Helium was used as diluent in some cases so that reaction results could be obtained at constant reactant partial pressures of H_2 or CO while varying the H_2/CO ratio. However, addition of a reactant line for He increased the instability of the reactant flows and thus some of the flow settings are not precisely at the desired conditions. The catalyst was rereduced at about 400°C between each reaction set to minimize deviations due to deactivation. Finally the catalyst was operated at 230°C and H_2/CO = 1.5 for 67 hours to observe effects of deactivation.

The most reliable results are from 3/1(B) and the deactivation run (see Table 5). Figure 15 is an activation energy plot showing the activity (total CO turnover number) on a log scale as a function of the reciprocal temperature. The catalyst activity at the highest temperature (230°C) is lower than expected based on the trend at the lower temperatures. An activation energy of 88.9 kJ/mol was calculated for the lower three temperatures. This compares with 97 kJ/mol for catalyst Fe-A-201 reported previously (also at 3/1 H_2/CO ratio). The fit is very good for these data considering the reversal of the first two temperature runs (207°C and then 200°C instead of 200 followed by 207). The extended time on stream before reacting at 230°C (71 hours compared to 48 preferred under ideal schedule) may have had an impact on the activity at that temperature. Indeed, longer reaction times deactivated the catalyst by allowing refractory carbon deposits to form which are not easily removed with hydrogen, thus lowering the intrinsic activity.

Table 5. Reaction schedule for catalyst Fe-A-203.

Rxn Set	Reaction conditions	H_2/CO/He flow(cc/min)	Sample times
3/1 (A):	**Reduced fresh catalyst at 400°C for 1 hr**		
	H2/CO = 3 at 200 for 16 hrs	(30/10/0)	
	H2/CO = 3 at 212 for 33 hrs	(30/10/0)	Samples taken at 27 and 28 hrs
	H2/CO = 3 at 227 for 22 hrs	(30/10/0)	Samples taken at 20 and 21 hrs
	Re-reduced at 400°C for 2 hrs		
3/1 (B):	H2/CO = 3 at 207 for 38.5 hrs	(30/10/0)	Samples taken at 24 and 25 hrs
	H2/CO = 3 at 200 for 22 hrs	(30/10/0)	Samples taken at 9 and 10 hrs
	H2/CO = 3 at 220 for 11 hrs	(30/10/0)	Samples taken at 9 and 10 hrs
	H2/CO = 3 at 230 for 17 hrs	(30/10/0)	Samples taken at 9 and 10 hrs
	Re-reduced at 400°C for 2 hrs		
2/1:	H2/CO = 2 at 200 for 25 hrs	(23/10/6)	Samples taken at 21 and 22 hrs
	H2/CO = 2 at 209 for 12 hrs	(22/8/13)	Samples taken at 8 and 9 hrs
	H2/CO = 2 at 220 for 12 hrs	(20/10/10)	Samples taken at 8 and 9 hrs
	H2/CO = 2 at 229 for 18 hrs	(20/10/10)	Samples taken at 9 and 10 hrs
	Re-reduced at 388°C for 16 hrs		
1/1:	H2/CO = 1 at 200 for 27 hrs	(10/11/0)	Samples taken at 8 and 9 hrs
	H2/CO = 1 at 210 for 21 hrs	(10/10/0)	Samples taken at 6 and 7 hrs
	H2/CO = 1 at 220 for 22 hrs	(10/10/0)	Samples taken at 6 and 7 hrs
	H2/CO = 1 at 230 for 35 hrs	(10/10/0)	Samples taken at 9 and 10 hrs
	Re-reduced at 404°C for 12 hrs		
1.5/1: **(Deactivation)**	H2/CO = 1.5 at 230 for 67 hrs	(20/13/0)	Samples taken at 6, 10, 14, 17, 21, 25, 29, 32, 36, 40, 43, 47, 51, 55, 58, 62 hrs

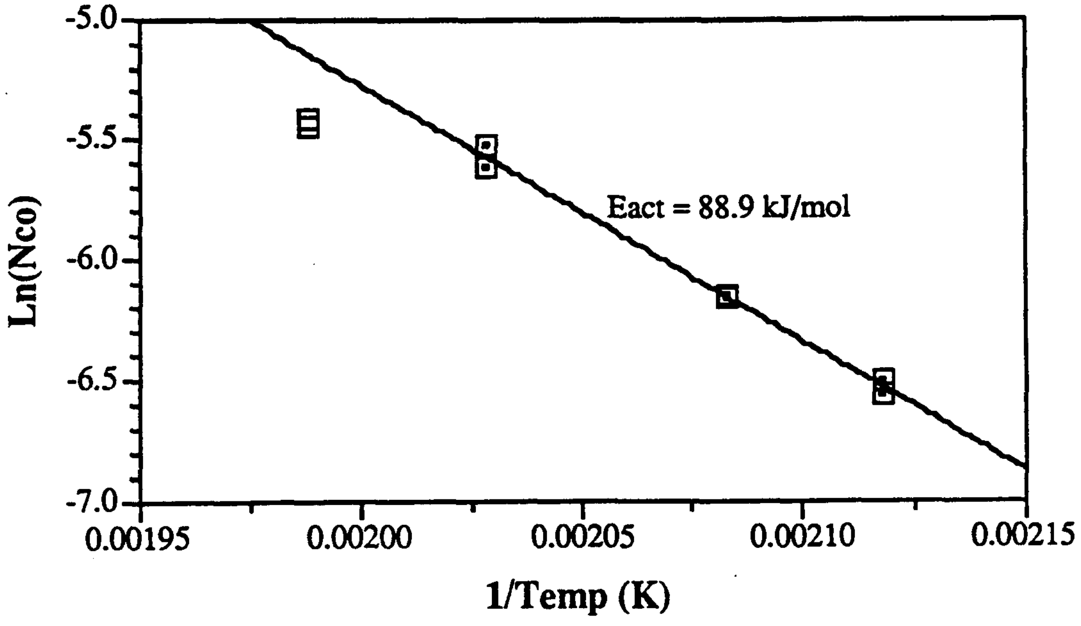

Figure 15. Activation energy plot for catalyst Fe-A-203 at 3/1 H_2/CO ratio.

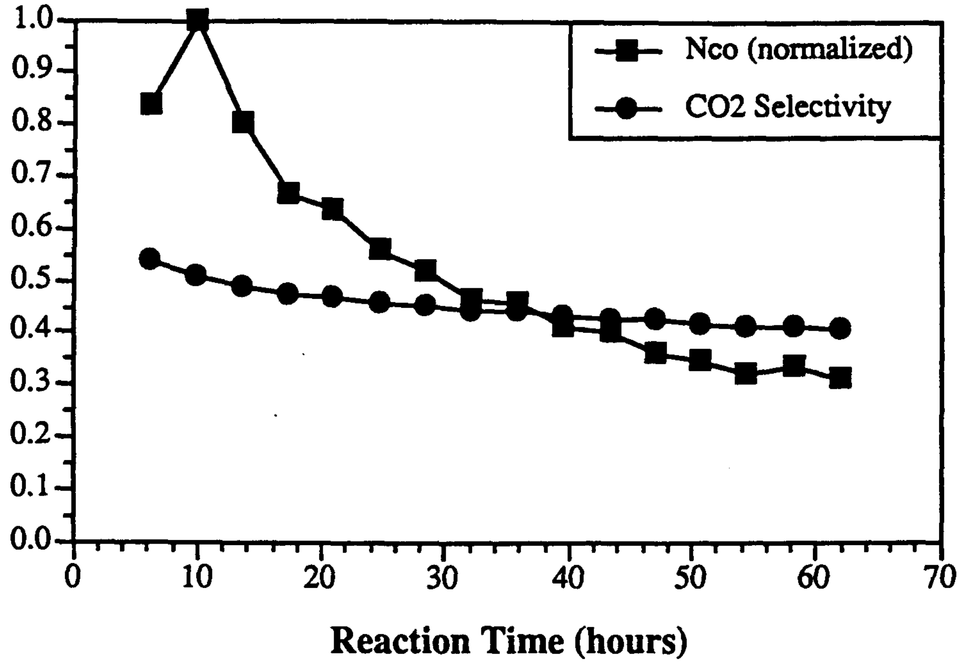

Figure 16. Fe-A-203 deactivation plot.

Figure 16 is a plot of activity (normalized to highest rate) as a function of time. The maximum activity was measured at 10 hours on stream. In the next 40 hours the activity decreased by nearly 70%. Also shown is the CO_2 production (as fraction of CO converted to CO_2). CO_2 production decreases with time from 0.54 at the first measurement to 0.41 at the last. From this plot a deactivation order of 0.9 was obtained [50].

(Fe-A-204.) This catalyst was to be used to supplement Fe-A-203 at H_2/CO ratios of 2/1 and 1/1. However, after reacting at 200-220°C for 48 hours and not being able to obtain steady CO and He flows the reaction runs were cancelled.

(Fe-A-205.) Runs were made for this catalyst sample at H_2/CO/He ratios of 3/1/0, 2/1/1, 1/1/0 and 1/1/2 with the total flow kept constant at 40 cc/min for each. At each set of flows reaction data were obtained at 200, 210, 220 and 230°C. Figure 17 shows the activity data (total CO turnover number) for each set of gas flows and temperatures. The first and third set of data appear to have the expected trend—activity increases with increasing temperature. However, the second set did not exhibit those same characteristics. Activity increased for the lower three temperatures but decreased at the highest temperature (230°C). This drop may be due to deactivation as the samples were taken at 22 and 23 hrs on stream rather than 10-12. The last set (1/1/2) was incomplete due to a crack that developed in the ten-port sampling valve in the gas chromatograph. Because of these inconsistencies the second and fourth sets (H_2/CO/He ratios of 2/1/1 and 1/1/2) were later redone. One of the temperatures at the 1/1/0 ratio was also redone to measure the reproducibility of the data.

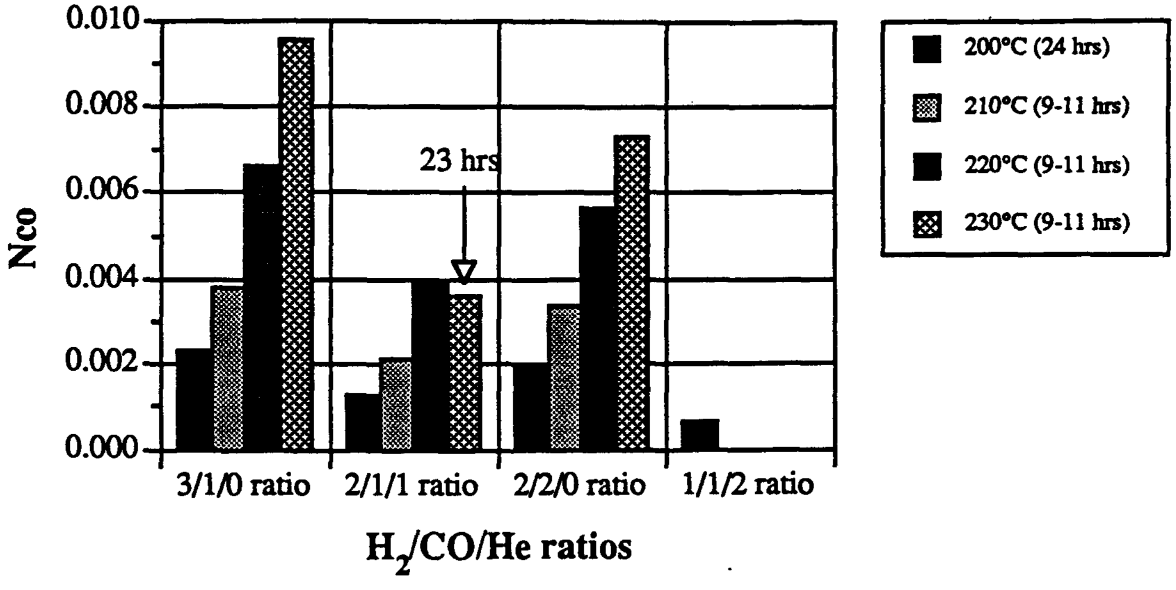

Figure 17. Fe-A-205 catalyst activity (CO TOF).

The activity of the initial fresh catalysts was followed from about 1 to 30 hrs on stream for the 3/1/0 and 2/1/1 ratios at 200°C. Figures 18 and 19 show the catalyst activity in terms of total CO converted and of hydrocarbons (HC) produced. Both figures exhibit similar characteristics but the deactivation effects are more pronounced in the 3/1/0 run, that is, the total CO consumption decreases

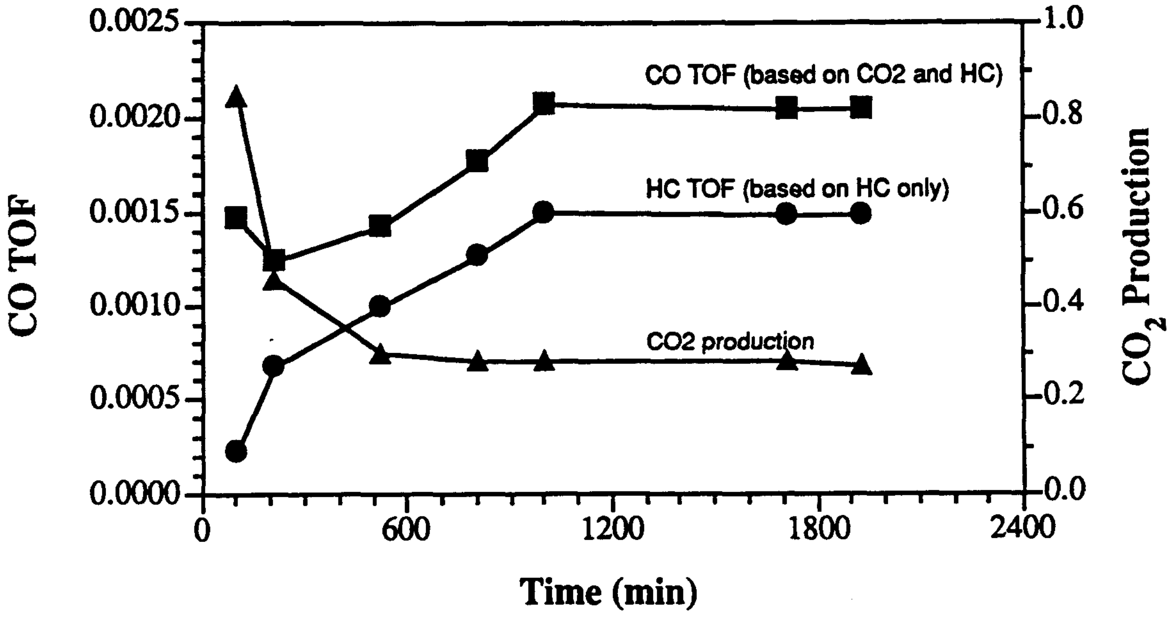

Figure 18. Catalyst activity as a function of total CO consumption and HC production. (Fe-A-205, 200°C, 3/1/0 H_2/CO/He ratio)

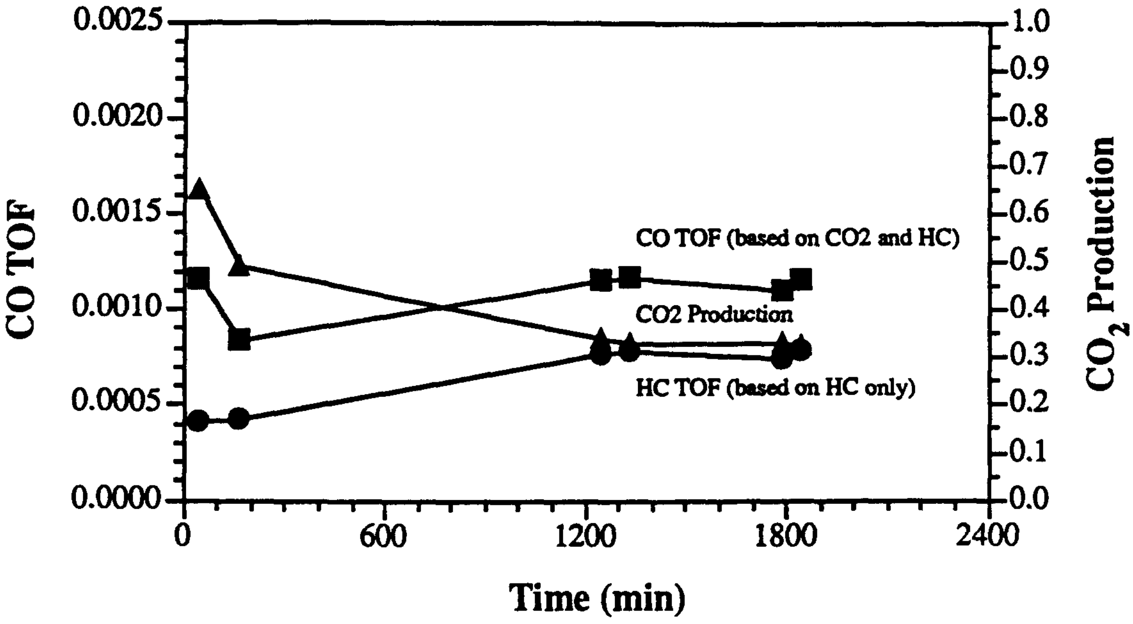

Figure 19. Catalyst activity as a function of total CO consumption and HC production. (Fe-A-205, 200°C, 2/1/1 H_2/CO/He ratio)

initially somewhat and then increases to a constant value after about 20 hours. The reason for this behavior is evident when the total CO consumption is broken down into the CO_2 and HC components. Hydrocarbon production is seen to rise until it reaches a constant value after 20 hours. The drop in total CO consumption then must be due to changes in CO_2 production. Indeed, the CO_2 production (shown as fraction of CO converted to CO_2) decreases from initial values of 85% (3/1/0) and 65% (2/1/1) to about 30% in both cases. Initially, the reaction to produce CO_2 accounts for most of the CO consumed but as the catalyst becomes more covered with carbon the reaction of CO to hydrocarbons becomes the dominating reaction.

Activation energies were calculated from the activity data by plotting the natural logarithm of the CO turnover number against the reciprocal temperature (Arrhenius plot). Figure 20 shows the data and the regression parameters. The lowest three temperatures were used to calculate the activation energies since the effect of deactivation appears to be significant at 230°C as seen by activities that fall below the regression lines. The values of 102 and 107 kJ/mol are consistent with previous values of 97 kJ/mol for Fe-A-201 (at 3/1/0 H_2/CO/He).

From this new set of data it is possible to calculate reaction orders (x and y) in the reaction rate expression $-r_{CO} = k(P_{CO})^x (P_{H2})^y$. To calculate x, for example, requires that data be obtained at a constant partial pressure of H_2 at two or more pressures of CO. Taking the logarithm of both sides of the rate expression and lumping all constants together gives an expression of the form $C = x\ LN(P_{CO})$ where C is a constant. A plot of C versus $LN(P_{CO})$ yields a regression slope equal to x. Figures 21 and 22

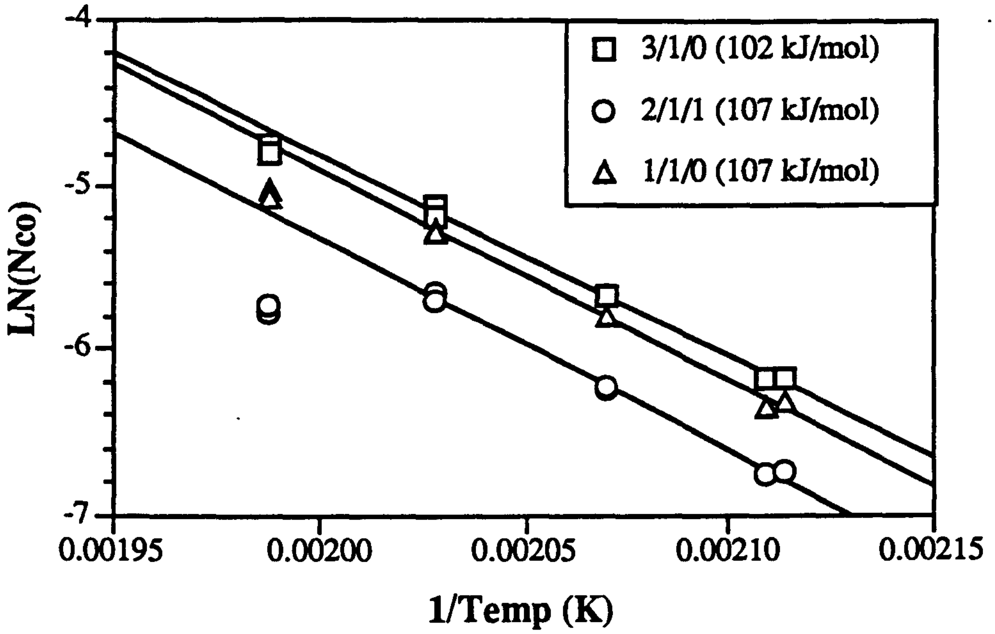

Figure 20. Arrhenius plots for Fe-A-205.

show the plots from which the coefficients were calculated. The rate expression becomes $-r_{CO} = k(P_{CO})^{0.60} \cdot (P_{H_2})^{1.36}$ with the values obtained from these plots. For the conditions of these experiments this indicates that the rate is more dependent upon the hydrogen partial pressure than the CO partial pressure but that increases in either one will increase the rate. Extrapolating to conditions outside the bounds of these experiments may result in incorrect conclusions.

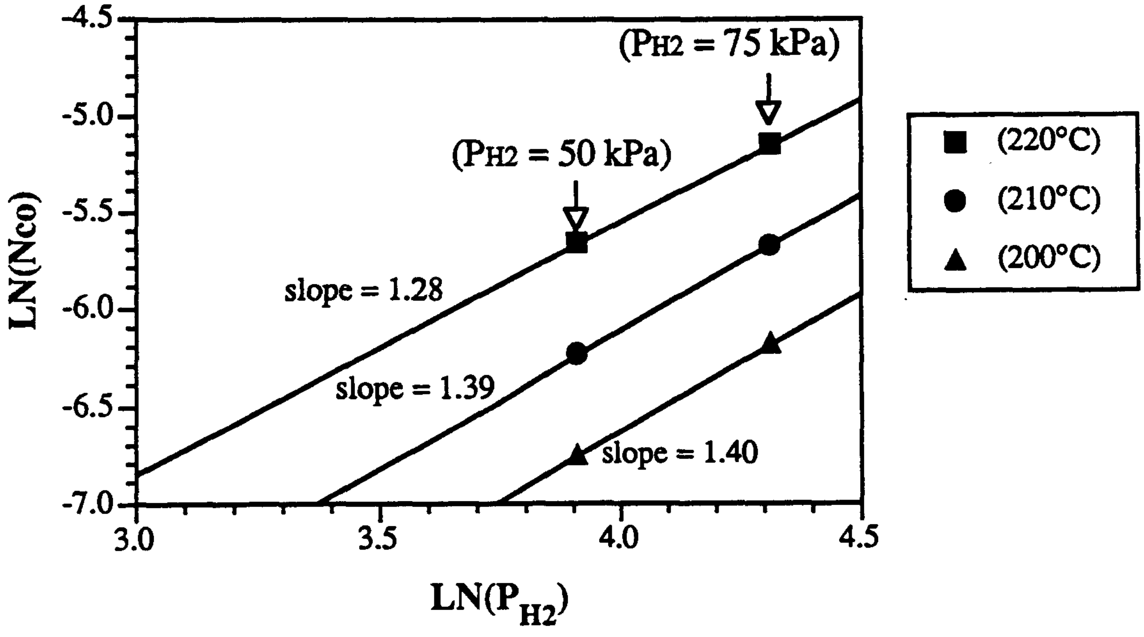

Figure 21. Reaction orders for constant P_{CO} (25 kPa) at 200-220°C.

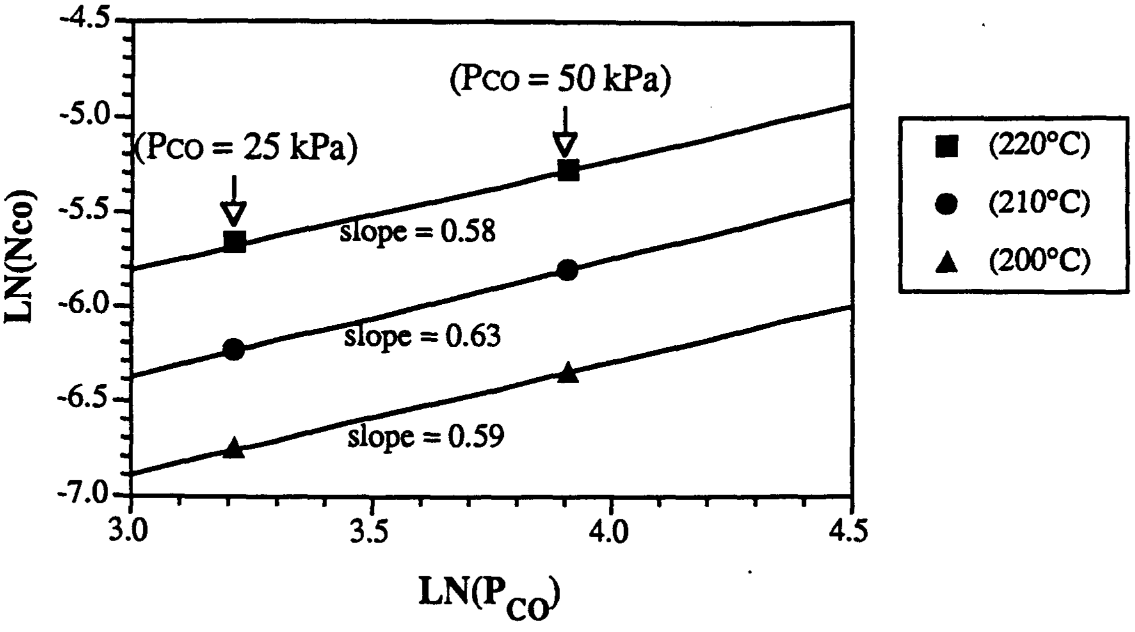

Figure 22. Reaction orders for constant P_{H_2} (50 kPa) at 200-220°C.

e. Fe/K-A-300 Series. (Fe/K-A-301) Reaction conditions were initially 200°C and $H_2/CO = 3$. Temperatures were increased in 10 degree increments after reacting at each temperature for 10 to 24 hours. The catalyst was not active enough for the thermal conductivity detector to register a methane peak until the reaction temperature reached 250°C. The CO conversion did not exceed 3% until a reaction temperature of 350°C. Based on the low activity of the potassium promoted catalyst it is concluded that the potassium content on the surface of the catalyst was significantly higher than the calculated total molar ratio. A rough estimate of the surface ratio based on hydrogen uptakes of the unpromoted and promoted catalysts gives a maximum K/Fe surface ratio of 20, nearly three orders of magnitude greater than the desired amount. When compared to activity data of catalysts with varying potassium contents [48], the activity of Fe/K-A-301 more closely resembles a catalyst having a K/Fe ratio of 0.2 to 0.3. Because of the low activity of Fe/K-A-301 it was decided that the amount of potassium added to make a new K-promoted catalyst would be decreased to one-fifth of the previous amount. No further reactions were performed with this catalyst.

f. Fe/K-A-400 Series. (Fe/K-A-401) From the results for Fe/K-A-301, it is clear that potassium promoted catalysts require higher temperatures to achieve comparable CO conversions to those of the unpromoted catalysts. For this reason, the initial reaction conditions chosen for catalyst Fe/K-A-401 were 230°C at a H_2/CO ratio of 3/1. The activity was a maximum after one hour on stream and decreased by 75% over the next 19 hours.

The purpose of the kinetic study is to obtain kinetic data at conditions where the effect of deactivation is minimal or non-existent. The apparent deactivation at 230°C indicates that lower

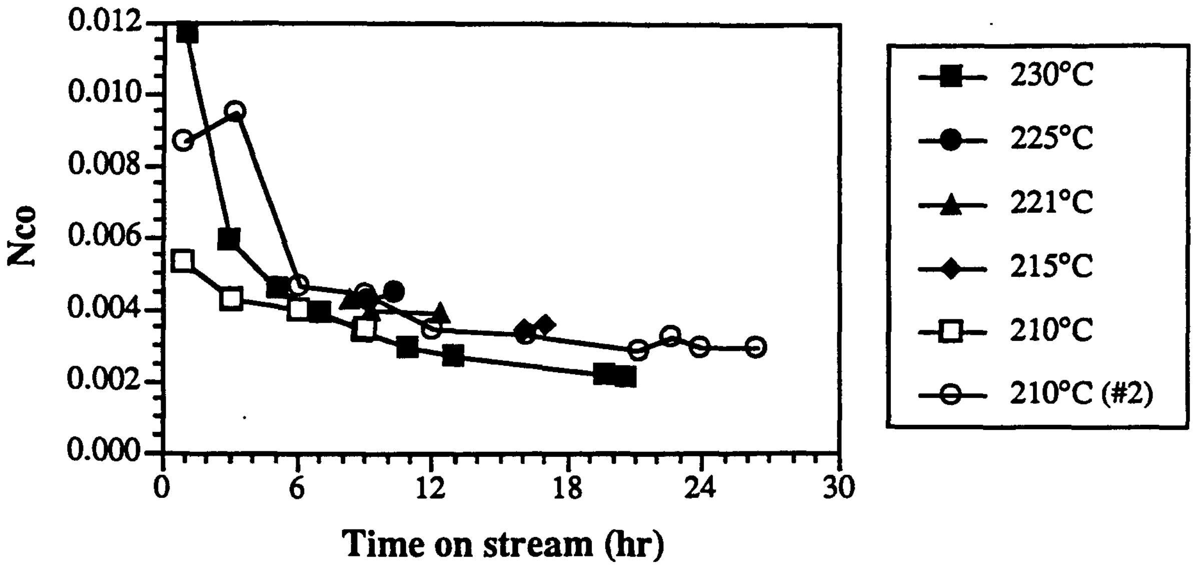

Figure 23. Activity versus time for Fe/K-A-401 at 210-230°C.

temperature tests are necessary if deactivation was to be minimized.

The sample was re-reduced in hydrogen at 400°C for about 24 hours prior to reacting further. This extended reduction time was necessary to obtain a state of catalyst in which no more (or very little) methane was being produced. Subsequent re-reductions on the potassium-promoted catalysts were done for a standard length of 20 hours. This compares to reduction times for the unpromoted catalysts of only two hours to obtain similar states.

Reaction temperatures for continued runs on Fe/K-A-401 ranged from 200 to 230°C. However, at 200°C the activity was too low to measure. Figure 23 shows the activity versus time curves at various temperatures. The two sets of data with the highest initial activities were obtained (following reduction in hydrogen) at 210 and 230°C. The time zero point is the time at which the reactor reached the given temperature. Although sample data for each temperature do not cover the full range, they do indicate that after several (about 9) hours on stream the activity at each temperature reaches a value that is within about 20% of the other temperatures. For reaction sets at 210 and 230°C where data were obtained on the freshly reduced catalyst, the higher initial activity of the higher temperature leads to a lower "steady-state" value (about 20 hours). Thus, the effect of deactivation becomes more pronounced at higher temperatures.

(Fe/K-A-402, Fe/K-A-403) Figure 24 shows the data from three different samples all reacted at 230°C at H_2/CO ratio of 3/1. The catalyst histories for the other two samples (Fe/K-A-402 and Fe/K-A-403) are given here. Hydrogen chemisorptions had been performed on the fresh Fe/K-A-402 catalyst. Reaction runs were then commenced at 210°C for 36 hours followed directly by reaction at 230°C. Fe/K-A-403 had been reacted at 210°C for 12 hours, reduced for 12 hours at 400°C and then reacted at 230°C.

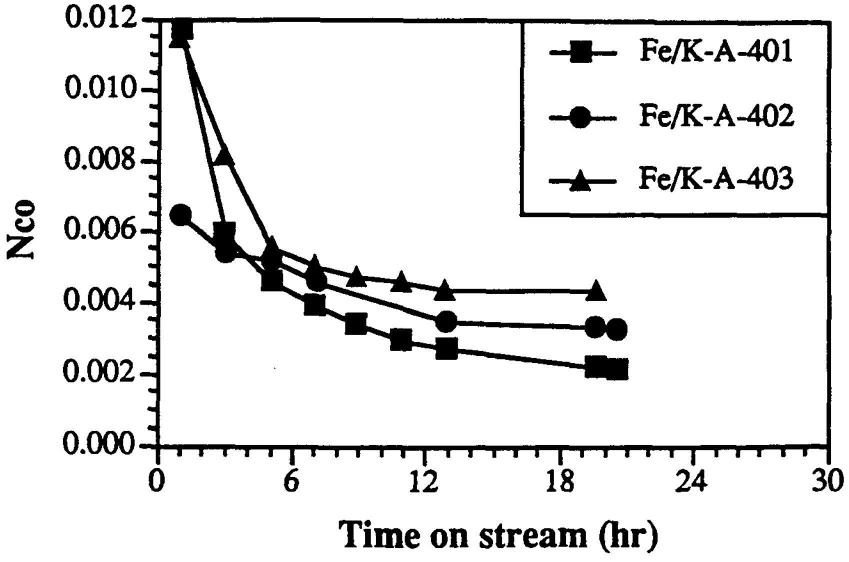

Figure 24. Specific activity versus time for Fe/K-A-401, 402, and 403 at 230°C and 3/1 H_2/CO.

As seen in Fig. 24, the two freshly reduced samples (401 and 403) have similar initial activities but 401 drops to a significantly lower value than 403. After 20 hours at 230°C, 401 activity is about half of the measured activity for 403. The fact that catalyst 403 had previously been reacted at 210°C may be the reason for the difference, even though the catalyst was reduced between the two runs. The conditions which the catalyst is subjected to initially appear to have a large impact on the "long-term" (i.e., 20 hour) state of the catalyst.

After reaction for 36 hours at 210°C, the temperature for catalyst Fe/K-A-402 was increased to 230°C. While the initial activity was only about half that for the other two catalysts, the activity after 3 hours was similar to catalyst 401 and for the rest of the time shown was intermediate between the other two catalysts.

(Fe/K-A-404) Another potassium-promoted sample (Fe/K-A-404) was used to measure activities as a function of H_2/CO ratio so that an estimate of the reaction orders for hydrogen and CO could be obtained, similar to what was done previously for the unpromoted catalysts. The catalyst was first reacted at 3/1 H_2/CO at temperatures ranging from 220-240°C so that the data for determining reaction orders would not affected by errors introduced by using different samples. Subsequent treatment at 2/1 H_2/CO (with 1 part He diluent) showed a stronger effect of deactivation on the activity of the catalyst. No further reaction experiments were performed with the potassium-promoted catalyst since kinetic data could not be obtained without significant effects of deactivation.

B. Task 2: Study of Carbon Reactivities and Types

No experiments are scheduled for this task until Spring 1991. The research assistants working on this project are presently familiarizing themselves with the literature dealing with deactivation by carbon.

C. Task 3: Mathematical Modeling of Catalyst Deactivation by Carbon

This task is scheduled to begin in the Spring 1991.

D. Technical Communication and Miscellaneous Accomplishments

During the first period, the PI hired two graduate assistants to work on this project: Mr. Mike Bayles, an MS candidate who is assigned the task of designing and constructing the computer-automated reactor system, including the writing/testing of software and Mr. Scott Eliason, a Ph.D. candidate who is assigned to carry out much of the kinetic/deactivation experiments, the study of carbon reactivities and types and a portion of the mathematical modeling. The PI also attended the 192nd Meeting of the ACS in Anaheim held September 7-12 at which he chaired a symposium dealing with CO hydrogenation; Mr. Rameswaren of the BYU catalysis lab presented a paper dealing with CO hydrogenation on carbonyl-derived Fe/alumina catalysts. Professor Jim Goodwin of the University of Pittsburgh also visited our laboratory on September 11th and presented a seminar dealing with the effects of promoters in CO hydrogenation.

During the second quarter the PI and several students attended the 2nd Annual Symposium of the Western States Catalysis Club held March 26-27 in Salt Lake City. The meeting included several papers pertinent to this study; the PI also had the opportunity to visit with Michel Boudart about progress in catalysis and combustion research at BYU and Stanford. Professor Robert Merrill of Cornell visited BYU Thursday February 5th, presented a college lecture, and conversed with the PI regarding mutual interests in catalysis and surface science research. On March 9th Professor John Sears, Chairman of Chemical Engineering at Montana State University, visited BYU to discuss with the PI research in the new Combustion Center and the BYU Catalysis Laboratory. Mike Bayles, an M.S. graduate student in Chemical Engineering, and Dr. Bartholomew published an article dealing with the computer-automated reactor system in the Macintosh Journal [46].

The BYU Catalysis Laboratory hosted Professor James Schwarz and Dr. Bob Huang of the University of Syracuse May 13-15. Professor Schwarz presented a seminar dealing with the effects of nickel catalyst preparation on chemical makeup and catalytic activity; discussions focused on catalyst preparation/characterization, TPD/TPSR measurements, and CO hydrogenation catalysis.

The PI and several graduate students, including Mr. Scott Eliason, attended the Tenth North American Meeting of the Catalysis Society held May 17-22 in San Diego; Dr. Bartholomew presented a paper dealing with CO hydrogenation on clean polycrystalline cobalt; Mr. Won Ho Lee discussed the results of a TPSR study of hydrogen with adsorbed CO on cobalt/alumina catalysts. Dr. Bartholomew also served as Program Chairman for the meeting. The technical program, which included 204 oral papers and 80 poster papers, was very stimulating. There were several papers presented in the Symposium on Catalyst Deactivation that were pertinent to this study.

The PI also attended the Am. Soc. Eng. Educ./Eng. Res. Centers Meeting June 24-25 in Reno at which he presented a paper on characterization of coals in the Advanced Combustion Engineering Research Center at BYU and the University of Utah. The following day (June 26th) Dr. Fred Steffgen, our DOE/PETC Project Manager, visited our laboratory and reviewed this DOE/PETC research program.

The Principal Investigator, Calvin H. Bartholomew, attended the International Conference on Catalyst Deactivation held September 29-October 1 in Antwerp, Belgium where he presented an invited plenary lecture on "Mechanisms of Nickel Catalyst Poisoning". He also visited the Eindhoven University of Technology on October 2 where he presented a seminar on "The Effects of Crystallite Size on the Physical, Chemical and Catalytic Properites of Iron/Carbon Catalysts," and visited with Hans Niemantsverdriet (Host), V.H.F. de Beer, A.M. van der Kraan and other scientists working in Catalysis. On October 3 he visited John Geus at the University of Utrecht and discussed mutual interests in catalysis and surface science research. On October 14-16 Professor Bartholomew attended the Sixth DOE Catalysis and Surface Chemistry Research Conference held in Gaithersburg, MD, presented a poster paper dealing with BYU's work on effects of crystallite size and support on the adsorption and catalytic properites of cobalt/alumina, and interacted with many other well-known scientists in the fields of catalysis and surface science. He also attended the 1987 Annual Meeting of the AIChE held November 15-20 in New York, chaired a session on catalyst deactivation, presented a paper on "Advanced Combustion Modeling at ACERC", and coauthored a paper on "Effects of Loading and Reduction Temperature/Time on the CO Desorption and CO Hydrogenation Kinetics on Cobalt/Titania" presented by Mr. W.H. Lee at the Symposium on Fundamentals of Catalysis. The BYU Catalysis Laboratory hosted Professor Eric Suuberg from Brown University on November 24th and discussed work on coal char characterization and oxidation, which is the subject of a research supported by a contract through the new NSF-supported Combustion Center at BYU; Professor Suuberg presented a seminar on "Active Sites and their Role in Oxidation."

A new graduate student, Pierre Smith, was hired during the fifth quarter for purposes of characterizing the iron catalysts in study by Moessbauer spectroscopy. During the past year Mr. Smith became familiar with the literature and techniques related to this spectroscopy and has begun experimentation.

During the seventh quarter the Principal Investigator and several students attended and participated in a symposium on "Catalysis in Fuel Conversion" co-sponsored by the Western States Catalysis Club and the American Chemical Society and held March 28th in Las Vegas. Mr. Byron Johnson presented a paper on the "Structural and Chemisorptive Behavior of Ultrathin Cobalt Overlayers on W(100) and W(110);" Mr. Troy Elkington presented a paper on "Ammonia Oxidation over Monolithic-Supported Platinum and Platinum-Rhodium Catalysts."

During the eighth quarter Dr. Bartholomew and Mr. Scott Eliason attended the Ninth International Catalysis Congress held June 26-July 1, 1988 in Calgary, Canada at which the PI presented a paper dealing with CO hydrogenation on Cobalt Borides and co-chaired a session on CO hydrogenation. The Pi also attended the University Coal Research Contractors Meeting held July 25-28, 1988 in Pittsburgh at which he presented a talk on recent results obtained under the present contract.

The Principal Investigator (Calvin H. Bartholomew) attended and presented a paper dealing with the "Surface and Pore Properties of ANL and PETC Coals" at the 196th ACS National Meeting held September 25-30, 1988 in Los Angeles. He attended several symposia at this meeting dealing with catalysis. He was also a coauthor of a paper on "Effects of Preparation Method and Extent of Reduction on the Apparent Structure Sensitivity of Fe CO Hydrogenation Catalysts," presented at the 1988 Annual Meeting of the American Institute of Chemicai Engineers held November 27-December 2, 1988 in Washington D. C. The BYU Catalysis Laboratory hosted Professor George Gavalas of the California Institute of Technoiogy on November 23, 1988; during his visit Professor Gavalas discussed with members of the laboratory interests in catalysis and coal combustion and gave a seminar dealing with coal char combustion. The PI and students attended the Western States Catalysis Club held in conjunction with the Rocky Mountain ACS Meeting on February 24th in Denver where Mr. Scott A. Eiiason made a presentation on "Fischer-Tropsch Kinetics of Unpromoted and Alumina-Promoted, Unsupported Iron Catalysts" based on work from this grant. Mr. Byron G. Johnson of the BYU Catalysis Laboratory also made a presentation on "The Structure Sensitivity of Cobalt Fischer-Tropsch Catalysts" while Paul G. Clemmer (also BYU) discussed "The Effects of Ceria Addition to Rh/Alumina Catalysts on NO reduction by CO. On March 15th, Dr. Heinz Heinemann of Lawrence, Livermore Labs, the University of California at Berkeley, visited the BYU Cataiysis Laboratory and Advanced Combustion Engineering Research Center, presented a seminar dealing with catalytic gasification of coal, and discussed energy and environmental-related catalysis with members of the laboratory.The PI, Calvin H. Bartholomew, his associate Wiliam C. Hecker, and 2 students attended the Eleventh North American Meeting of the Cataiysis Society held May 7-11 in Dearbom, Michigan and presented 3 papers. Mr. Byron G. Johnson presented a paper on "The Structural and Chemisorptive Properties of Ultrathin Cobalt Overlayers on W(110) and W(110), Professor William C. Hecker discussed "The Effects of Molybdena and Ceria Addition to Supported Rh Catalysts for the Reaction of Nitric Oxide with Carbon Monoxide, and Professor Calvin H. Bartholomew presented a poster paper on "Adsorption, Catalytic and Electronic Properties of Dilute Cobalt Alumina Catalysts. The PI presented a short course on Catalyst Deactivation to several students and faculty at BYU on May 24-26 and to 50 professionals at Amoco on May 31-June 2. Professors Bartholomew and Hecker and 2 students also attended an ACERC-sponsored conference held June 14th at Snowbird on Spectroscopy of Coal. Professor Bartholomew also attended the 4th Japan-China-USA Symposium on Catalysis held July 3-7, 1989 in Sapporo, Japan and presented a paper on "Temperature-Programmed Reaction of Hydrogen and Water with Preadsorbed Methane and Ethane on Nickel.

The Principal Investigator, Calvin H. Bartholomew, his associate William C. Hecker, and several students attended Advances in Catalytic Chemistry held October 1-6 at Snowbird, Utah. The PI presented an invited paper dealing with "Effects of Structure on CO Hydrogenation on Alumina-supported Cobalt and Iron."

The Principal Investigator, Calvin H. Bartholomew, attended the International Chemical Congress of the Pacific Basin Societies in Honolulu, Dec. 17-22 where he presented three papers. The PI, one associate and several students attended the Rocky Mountain Fuel Society and Western States Catalysis Club joint meeting on March 1 and 2 in Salt Lake City where they presented several papers, one of which was a paper by Mr. Scott Eliason on the "Kinetics of FT Synthesis on Unsupported Iron Catalysts," based on this contract work.

The PI and Scott Eliason attended the 1990 Spring National Meeting of the AIChE in Orlando, Florida, March 17-21 where the PI presented two invited papers at the Symposium on Applications of Fischer-Tropsch Synthesis dealing with "Hydrogen Adsorption on Supported Cobalt, Iron and Nickel" and "Recent Technological Developments in Fischer-Tropsch Catalysis". The PI also attended the 7th BES Catalysis and Surface Chemistry Research Conference held March 25-28 in Gaithersburg, Maryland where he presented a poster paper on "Effects of Dispersion and Support on Adsorption, Catalytic and Electronic Properties of Cobalt/Alumina CO Hydrogenation Catalysts." He also hosted the annual ASME Corrosion Meeting April 5-6 at BYU which focused on coal mineral transformations at which he presented a paper on CaO catalysis of char oxidation. On April 30 Professor Bartholomew presented a short course on Catalyst Deactivation at Catalytica Associates; he also presented a 3-day course on the same subject at Shell R&D in Houston on May 21-23 and visited with Shell personnel on May 24th. On May 7th the Catalysis Laboratory hosted Dr. Lynn Slaugh, distinguished scientist at Shell.

During August 6-10 Professors Bartholomew and Hecker presented a short course on Heterogeneous Catalysis and Catalyst Deactivation to 30 professionals at Corning Inc. in Corning, New York. Dr. Jeffery Ullman of Morton Chemical visited the Catalysis Laboratory on August 31st. During Fall 1990 Mr. Scott Eliason presented a paper related to the contract on "Deactivation by Carbon of Iron Fischer-Tropsch Catalysts" at the 1990 National AIChE Meeting in Chicago (Nov. 11-16) and two papers [49, 50] related to the contract were accepted for publication. The latter of these will be presented at the 5th International Symposium on Catalyst Deactivation to be held June 24-26, 1991 at Northwestern.

IV. CONCLUSIONS

1. Hydrogen adsorption at 100°C on Fe, Fe/alumina and Fe/K/alumina catalysts apparently provides the best measure of the iron metal surface area.
2. Unsupported, unpromoted iron catalysts prepared from decomposition of iron nitrate are apparently thermally stable when reduced at 300°C and run at reaction temperatures of up to 250°C in FT synthesis; however, they suffer considerable loss of surface area and heated to 400°C for extended periods and lose essentially all of their surface area when exposed to FT synthesis conditions and are then rereduced at either 300 or 400°C, probably as a result of extensive sintering during the decomposition in hydrogen of the iron carbide formed previously during synthesis.
3. Carbon forms play important roles as intermediates, catalyst additives and deactivating species in Fischer-Tropsch synthesis on iron catalysts. Deactivation may be due to poisoning or fouling of the surface by atomic carbidic carbon, graphitic carbon, inactive carbides or vermicular forms of carbon, all of which derive from carbidic carbon atoms formed during CO dissociation. While the study did not focus thus far on the chemistry of the carbon species responsible for deactivation, some important observations can be made to this end.

   a. During re-reduction of both unpromoted and K-promoted spent catalysts, methane was produced indicating that hydrogen was reacting with carbon deposited during reaction on the catalyst surface. One difference between the two catalyst types of this study (unpromoted and potassium-promoted) was the length of time required to remove the carbon. After only six hours of rereduction at 400°C the unpromoted catalyst did not produce any observable methane while the promoted catalyst produced a significant amount of methane even after 24 hours of reaction with hydrogen. Thus, it can be concluded that the surface of the potassium-containing catalyst contained more carbon after reaction, a result in agreement with previously reported work [50].

   b. Based on surface area measurements (hydrogen chemisorptions) the catalyst with 1% alumina did not sinter as a result of reaction. This was in distinct contrast to the alumina-free catalyst initially used that sintered so completely upon re-reduction in hydrogen as to lose nearly 100% of its surface area. As for the potassium-promoted catalyst, SA measurements indicate a decrease in active metal sites of around 35% but it is not known whether this is due to sintering or unreduced carbon/carbide. It is more likely due to the presence of refractory carbons that are not easily removed during rereduction.

   c. The deactivation of unpromoted 99%Fe/1% alumina catalysts during the first 30-50 hours of FT synthesis is apparently first order in catalyst activity.

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