# DEACTIVATION BY CARBON OF IRON CATALYSTS FOR INDIRECT LIQUEFACTION. FINAL TECHNICAL PROGRESS REPORT FOR THE PERIOD SEPTEMBER 16, 1986-SEPTEMBER 15, 1990

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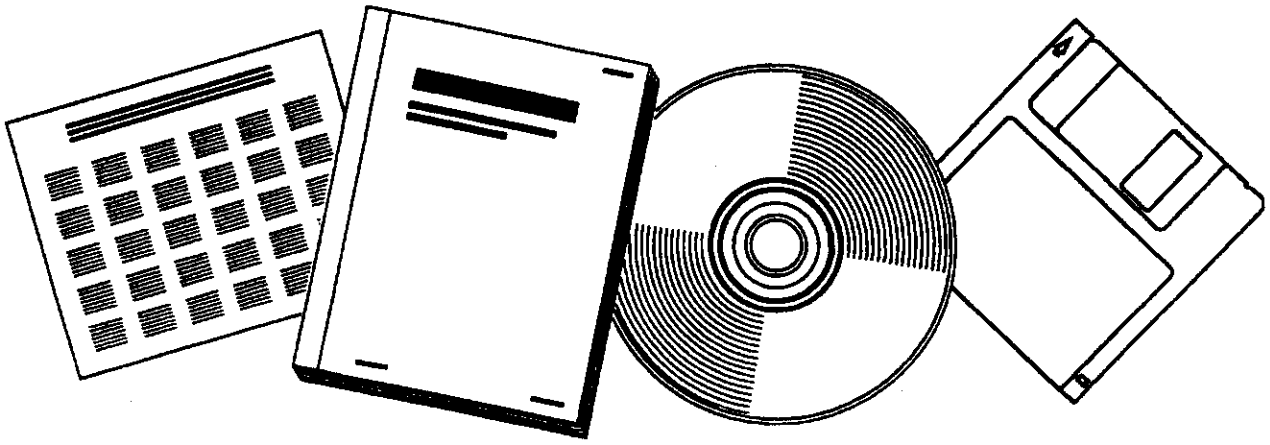

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# DEACTIVATION BY CARBON OF IRON CATALYSTS FOR INDIRECT LIQUEFACTION

## 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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DOE/PC/90533-16
(DE91011276)
Distribution Category UC-108

# DEACTIVATION BY CARBON OF IRON CATALYSTS FOR INDIRECT LIQUEFACTION

Final Technical Progress Report
For the Period Sept. 16, 1986 to Sept. 15, 1990

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

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 $3.6 \times 10^{-3}$ 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

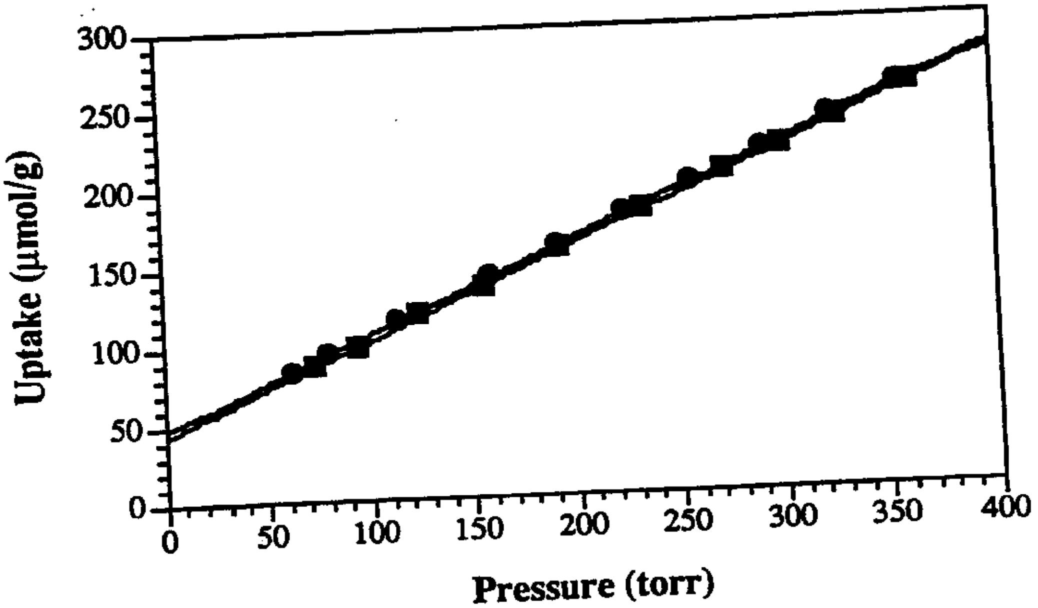

Figure 1. Hydrogen chemisorption uptakes measured by cooling in hydrogen from 400°C to room temperature gave 45 µmoles/g (catalyst Fe-102).

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 $m^2/g$

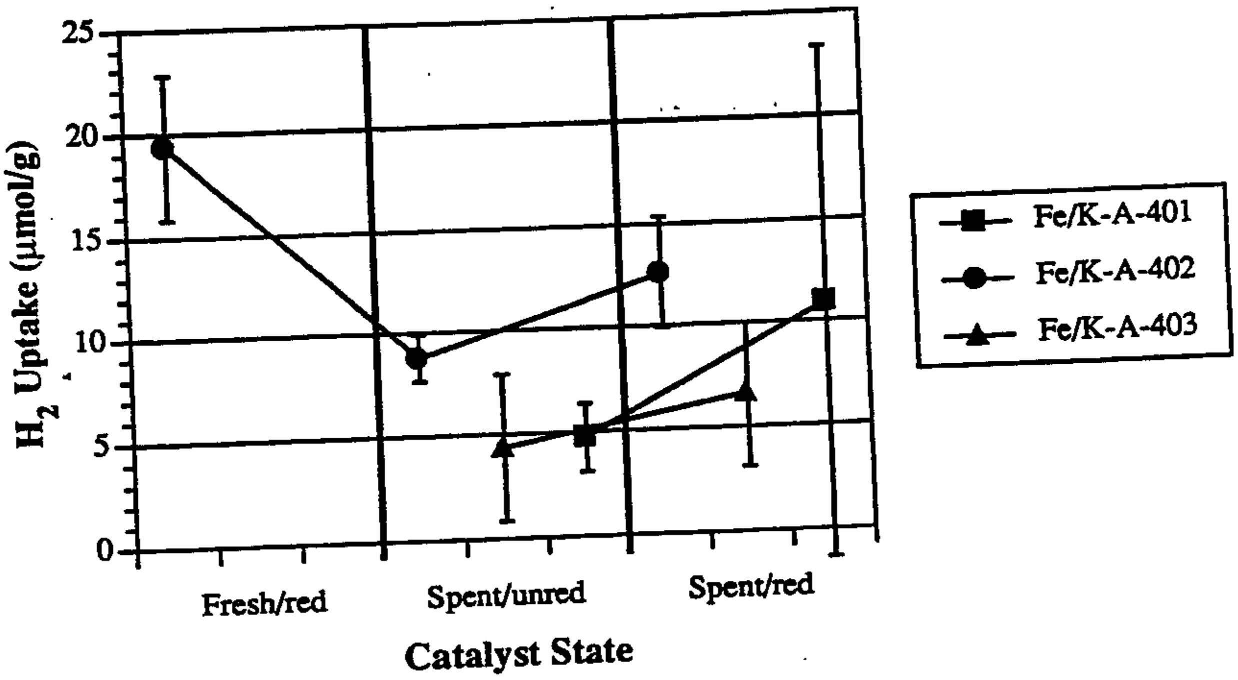

Figure 2. Hydrogen adsorption data for fresh, spent and regenerated Fe/K catalysts.