DEACTIVATION BY CARBON OF IRON CATALYSTS FOR INDIRECT LIQUEFACTION

Quarterly Technical Progress Report
For Period September 16, 1989 to December 15, 1989

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

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FORWARD

This report summarizes technical progress during the thirteenth quarter (September 16, 1989 to December 15, 1989) of a three-year study 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.

Scott Eliason, Ph.D. candidate, contributed to the technical accomplishments and to this report. Dr. Bartholomew was the principal author.
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ABSTRACT

During the thirteenth quarter design of software for a computer-automated reactor system to be used in the kinetic and deactivation studies was continued. Further progress was made towards the completion of the control language, control routines, and software for operating this system. Progress was also made on the testing of the system hardware and software. H2 chemisorption capacities and activity selectivity data were also measured for three iron catalysts promoted with 1% alumina. The PI, one associate and several students attended Advances in Catalytic Chemistry IV held October 1-6 at Snowbird, Utah where the PI presented a paper.
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 H₂: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:H₂ 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 H₂/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 H2: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 the CSTR Berty reactor. 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**

   During the thirteenth quarter design of software for a computer-automated reactor system to be used in the kinetic and deactivation studies was continued. Further progress was made towards the completion of the control language, control routines, and software for operating this system. Progress was also made on the operating manual and testing of the system hardware and software.

   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 H2/CO = 2, normalized activity decreases 75%.

B. **Task 2: Study of Carbon Reactivities and Types**

   No experiments are scheduled for this Task until Fall 1990, although literature study is being conducted.

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

   This task is scheduled to begin in Winter 1991.

D. **Task 4: Technical Communication and Miscellaneous Accomplishments**

   The PI, 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."
III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Kinetic/Deactivation Studies


During the thirteenth quarter design of software for a computer-automated reactor system to be used in the kinetic and deactivation studies was continued. Further progress was made towards the completion of the control language, control routines, and software for operating this system. Progress was also made on testing of the system hardware and software. Pressure and flow tests of the hardware were conducted, and defective flow meters, solenoids, and wiring were repaired. Some bugs in the control software were found and corrected.

2. Kinetic Studies.

Hydrogen adsorption and CO hydrogenation kinetic studies were conducted on three different samples of iron catalyst promoted with 1% alumina from the same batch. The results are reported by catalyst below.

Results for Fe-A-203. Hydrogen chemisorption uptakes were measured on the fresh 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 H2 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 previous data obtained on catalyst Fe-A-201 which averaged 37.0 μmoles/g. Because of the problems associated with these later chemisorptions the previous value of 37.0 is used in activity calculations. 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.

Reactions were run on catalyst Fe-A-203 following the chemisorption measurements at temperatures ranging from 200 to 230°C and at H2/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 1 shows the reaction sequence and conditions for the runs performed on this catalyst. Shown are the intended H2/CO ratios, the actual flows of H2, 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 H2 or CO while varying the H2/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 H2/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 1). Figure 1 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 89.0 kJ/mol was calculated for the lower three temperatures. This compares with 102 kJ/mol for catalyst Fe-A-201 reported previously (also at 3/1 H2/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.

Figure 2 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 are values of olefin content (of C3-C7 hydrocarbons) and CO2 production (as fraction of CO converted to CO2). The olefin content increases with time indicating an increase of carbon and/or decrease of hydrogen on the surface. CO2 production decreases with time from 0.53 at the first measurement to 0.41 at the last.
<table>
<thead>
<tr>
<th>Rxn Set</th>
<th>Reaction conditions</th>
<th>H₂/CO/He flow (cc/min)</th>
<th>Sample times</th>
</tr>
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<tbody>
<tr>
<td>3/1 (A):</td>
<td>Reduced fresh catalyst at 400°C for 1 hr</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>H₂/CO = 3 at 200 for 16 hrs</td>
<td>(30/10/0)</td>
<td>Samples taken at 27 and 28 hrs</td>
</tr>
<tr>
<td></td>
<td>H₂/CO = 3 at 212 for 33 hrs</td>
<td>(30/10/0)</td>
<td>Samples taken at 20 and 21 hrs</td>
</tr>
<tr>
<td></td>
<td>H₂/CO = 3 at 227 for 22 hrs</td>
<td>(30/10/0)</td>
<td></td>
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<tr>
<td><strong>Re-reduced at 400°C for 2 hrs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/1 (B):</td>
<td>H₂/CO = 3 at 207 for 38.5 hrs</td>
<td>(30/10/0)</td>
<td>Samples taken at 24 and 25 hrs</td>
</tr>
<tr>
<td></td>
<td>H₂/CO = 3 at 200 for 22 hrs</td>
<td>(30/10/0)</td>
<td>Samples taken at 9 and 10 hrs</td>
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<tr>
<td></td>
<td>H₂/CO = 3 at 220 for 11 hrs</td>
<td>(30/10/0)</td>
<td>Samples taken at 9 and 10 hrs</td>
</tr>
<tr>
<td></td>
<td>H₂/CO = 3 at 230 for 17 hrs</td>
<td>(30/10/0)</td>
<td>Samples taken at 9 and 10 hrs</td>
</tr>
<tr>
<td><strong>Re-reduced at 400°C for 2 hrs</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2/1:</td>
<td>H₂/CO = 2 at 200 for 75 hrs</td>
<td>(23/10/6)</td>
<td>Samples taken at 21 and 22 hrs</td>
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<tr>
<td></td>
<td>H₂/CO = 2 at 209 for 12 hrs</td>
<td>(22/8/13)</td>
<td>Samples taken at 8 and 9 hrs</td>
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<tr>
<td></td>
<td>H₂/CO = 2 at 220 for 12 hrs</td>
<td>(20/10/10)</td>
<td>Samples taken at 8 and 9 hrs</td>
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<tr>
<td></td>
<td>H₂/CO = 2 at 229 for 18 hrs</td>
<td>(20/10/10)</td>
<td>Samples taken at 9 and 10 hrs</td>
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<tr>
<td><strong>Re-reduced at 388°C for 16 hrs</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1/1:</td>
<td>H₂/CO = 1 at 200 for 27 hrs</td>
<td>(10/11/0)</td>
<td>Samples taken at 8 and 9 hrs</td>
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<td></td>
<td>H₂/CO = 1 at 210 for 21 hrs</td>
<td>(10/10/0)</td>
<td>Samples taken at 6 and 7 hrs</td>
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<td></td>
<td>H₂/CO = 1 at 220 for 22 hrs</td>
<td>(10/10/0)</td>
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<tr>
<td></td>
<td>H₂/CO = 1 at 230 for 35 hrs</td>
<td>(10/10/0)</td>
<td>Samples taken at 9 and 10 hrs</td>
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<tr>
<td><strong>Re-reduced at 404°C for 12 hrs</strong></td>
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</tr>
<tr>
<td>1.5/1:</td>
<td>H₂/CO = 1.5 at 230 for 67 hrs</td>
<td>(20/13/0)</td>
<td>Samples taken at 6, 10, 14, 17, 21, 25, 29, 32, 36, 40, 43, 47, 51, 55, 58, 62 hrs</td>
</tr>
</tbody>
</table>
Figure 1. Activation energy plot at 3/1 H₂/CO ratio.

Figure 2. Fe-A-203 deactivation plot.

Results for Fe-A-204. This catalyst was to be used to supplement Fe-A-203 at H₂/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. The catalyst was then re-reduced and one chemisorption was then performed on it which resulted in a H₂ uptake of 29.1 μmoles/g.

Results for Fe-A-205. Runs were made for this catalyst sample at H₂/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 3 shows the activity data (total CC 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 (H₂/CO/He ratios of 2/1/1 and 1/1/2) will be redone. One of the temperatures at the 1/1/0 ratio will also be redone to measure the reproducibility of the data.

**Figure 3. 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 4 and 5 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 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 CO2 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 CO2 production. Indeed, the CO2 production (shown as fraction of CO converted to CO2) 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 CO2 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. 

![Figure 4](image)

**Figure 4.** Catalyst activity as a function of total CO consumption and HC production. (200°C, 3/1/0 H2/CO/He ratio)
Figure 5. Catalyst activity as a function of total CO consumption and HC production. (200°C, 2/1/1 H₂/CO/He ratio)

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 6 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 102 kJ/mol for Fe-A-201 (at 3/1/0 H₂/CO/He).

From this new set of data it is possible to calculate reaction orders (x and y) in the reaction rate expression \(-r_{\text{CO}} = k(P_{\text{CO}})^x (P_{\text{H₂}})^y\). To calculate x, for example, requires that data be obtained at a constant partial pressure of H₂ 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 \(C = x \ln(P_{\text{CO}})\) where C is a constant. A plot of C versus \(\ln(P_{\text{CO}})\) yields a regression slope equal to x. Figures 7 and 8 show the plots from which the coefficients were calculated. The rate expression becomes \(-r_{\text{CO}} = k(P_{\text{CO}})^{0.60} (P_{\text{H₂}})^{1.36}\) 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 6. Arrhenius plots for Fe-A-205.

Figure 7. Reaction orders for constant P_{CO} (25 kPa) at 200-220°C.
Figure 8. Reaction orders for constant $P_{H_2}$ (50 kPa) at 200-220°C.

B. Task 2: Study of Carbon Reactivities and Types
No experiments are scheduled for this task until Fall 1990. 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 Winter 1991.

D. Task 4: Technical Communication and Miscellaneous Accomplishments
The Principal Investigator, Calvin L. 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."
REFERENCES


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Chemical Engineering Faculty (Circulate)
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Mr. Scott Eliason

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DEACTIVATION BY CARBON OF IRON CATALYSTS FOR INDIRECT LIQUEFACTION

Calvin H. Bartholomew

Brigham Young University Catalysis Laboratory
350 CB
Provo, UT 84602

Brigham Young University
Provo, UT 84602

During the thirteenth quarter design of software for a computer-automated reactor system to be used in the kinetic and deactivation studies was continued. Further progress was made towards the completion of the control language, control routines, and software for operating this system. Progress was also made on the testing of the system hardware and software. H₂ chemisorption capacities and activity selectivity data were also measured for three iron catalysts promoted with 1% alumina. The PI, one associate and several students attended Advances in Catalytic Chemistry IV held October 1-6 at Snowbird, Utah were the PI presented a paper.

CO Hydrogenation, Fe Deactivation, FT Catalysts FT Synthesis, Fe