DOE-PC-90533-14

NOV 05 1990

DOE/PC/90533--14

DE91 002417

**DEACTIVATION BY CARBON OF
IRON CATALYSTS FOR INDIRECT LIQUEFACTION**

Quarterly Technical Progress Report
For Period December 16, 1989 to March 15, 1990

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

Date Published - October 29, 1990

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-FG22-86PC90533

"US/DOE Patent Clearance is not required prior to
the publication of this document"

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

FORWARD

This report summarizes technical progress during the fourteenth quarter (December 16, 1989 to March 15, 1990) 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, a Ph.D. candidate contributed to the technical accomplishments and to this report. Dr. Bartholomew was the principal author.

TABLE OF CONTENTS

DISCLAIMER.....	ii
FOREWORD.....	iii
ABSTRACT.....	v
I. OBJECTIVES AND SCOPE	1
A. Background	1
B. Objectives.....	1
C. Technical Approach.....	1
II. SUMMARY OF PROGRESS	5
III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS.....	6
A. Task 1: Kinetic/Deactivation Studies.....	6
B. Task 2: Study of Carbon Reactivities and Types	6
C. Task 3: Mathematical Modeling of Catalyst Deactivation by Carbon.....	6
D. Technical Communication and Miscellaneous Accomplishments.....	6
IV. REFERENCES.....	7
APPENDIX.....	10

ABSTRACT

During the fourteenth 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 towards testing of the system hardware and software. 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.

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:H₂ 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, $P_{\text{CO}} = 10\text{-}50$ kPa, $P_{\text{H}_2} = 10\text{-}50$ kPa, and $\text{H}_2\text{:CO} = 1.1\text{-}3.1$. 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; $P_{\text{CO}} = 10\text{-}50$ kPa; and $\text{H}_2\text{:CO} = 0.5\text{-}2.0$. 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 ($\text{H}_2\text{:CO} = 0.5$ 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 cm^3/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 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 fourteenth 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.

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 attended the International Chemical Congress of the Pacific Basin Societies in Honolulu, Dec. 17-22 where he presented three papers dealing with . 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.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Kinetic/Deactivation Studies

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

During the fourteenth 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. 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.

No progress was made during this period due to equipment problems.

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 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.

REFERENCES

1. a. Dry, M.E., "The Fischer-Tropsch Synthesis," in Catalysis Science and Technology, J.R. Anderson and M. Boudart, editors, Springer-Verlag, New York 1981, pp. 159-256.
 b. Dry, M.E., Private Communication, Synfuels Workshop, Aug., 1985.
2. Atwood, H.J.E., and Bennett, C.O., Ind. Eng. Chem. Process Des. Dev., 18, 163 (1979).
3. Huff, G.A., Jr., and Satterfield, C.N., "Kinetics of the Fischer-Tropsch Synthesis on Reduced, Fused Magnetite," Presented at the Annual AIChE Meeting, Los Angeles, 1982.
4. Dictor, R.A. and Bell, A.T., "Fischer-Tropsch Synthesis over Reduced and Unreduced Iron Oxide Catalysts," J. Catal. 97, 121 (1986).
5. Sughrue, E.L., "Kinetic and Carbon Deactivation Studies of Nickel Catalysts," Ph.D. dissertation, Brigham Young University, 1980.
6. Jarvi, G.A., Mayo, K.B., and Bartholomew, C.H., "Monolithic-Supported Catalysts; I. Methanation Activity Relative to Pellet Catalysts," Chem. Eng. Commun., 4, 325 (1980).
7. Bowman, R.M., and Bartholomew, C.H., "Deactivation by Carbon of Ru/Al₂O₃ During CO Hydrogenation," Appl. Catal. 7, 179 (1983).
8. Bartholomew, C.H., Weatherbee, G.D., and Jarvi, G.A., Chem. Eng. Commun., 5, 125 (1980).
9. Rameswaren, M. and Bartholomew, C.H., "Physical and Chemical Properties of Fe(co)5/Alumina CO Hydrogenation Catalysts," presented at the 192nd Meeting of the American Chemical Society, Anaheim, Sept. 7-12, 1986
10. Rameswaren, M., "A Study of CO Hydrogenation on Carbonyl-Derived and Conventionally-Prepared Fe/Alumina Catalysts," Ph.D. Dissertation, Brigham Young University, Provo, Utah, Dec. 1986.
11. Reuel, R.C., and Bartholomew, C.H., "The Stoichiometries of H₂ and CO adsorptions on Cobalt: Effects of Support and Preparation," J. Catal, 85, 63 (1986).
12. Rankin, J.L., and Bartholomew, C.H., "Effects of Support on the Adsorption and CO Hydrogenation Activity/Selectivity Properties of Iron," paper in preparation, 1987.
13. Sughrue, E.L., and Bartholomew, C.H., "Kinetics of CO Methanation of Nickel Monolithic Catalysts," Appl. Catal., 2, 239 (1983).
14. Levenspiel, O., "Chemical Reaction Engineering," John Wiley, New York, 1972.
15. Bartholomew, C.H., "Investigation of Sulfur-Tolerant Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," Annual Report to DOE, DOE-ET-14809-4, October 10, 1980.
16. Duncan, T.M., Winslow, P., and Bell, J. Catal., 93, 1 (1985).
17. Zowtiak, J.M., "Metal-Support Interactions in Cobalt Catalysts: Their Effects on Adsorption/Desorption Kinetics of Hydrogen and Carbon Monoxide," M.S. Thesis, Brigham Young University, 1983.
18. Zowtiak, J.M., and Bartholomew, C.H., "The Kinetics of H₂ Adsorption and Desorption from Cobalt and the Effects of Support Thereon," J. Catal., 83, 107 (1983).

19. Weatherbee, G.D., and Bartholomew, C.H., "Effects of Support on Hydrogen Adsorption/Desorption Kinetics of Nickel," *J. Catal.*, 87, 55-65 (1984).
20. Gorte, R.J., *J. Catal.*, 85, 143 (1984).
21. Rieck, J.S., and Bell, A.T., *J. Catal.*, 85, 143 (1984).
22. McCarty, J.G., and Wise, H., *J. Catal.*, 57, 406 (1979).
23. Dyer, D.J., "Iron Fischer-Tropsch Catalysts: Surface Synthesis at High Pressure," Symposium of the New Surface Science in Catalysis, American Chemical Society, Philadelphia Meeting, August 26-31, 1984.
24. Bartholomew, C.H., "Carbon Deposition in Steam Reforming and Methanation," *Catal. Rev. -Sci. Eng.*, 23, 7 (1982).
25. Erekson, R.J., Sughrue, E.L., and Bartholomew, C.H., *Fuel Proc. Technol.*, 5, 91 (1981).
26. Gardner, D.C., and Bartholomew, C.H., *Ind. Eng. Chem. Prod. Res. Dev.* 20, 80 (1981).
27. Amelse, J.A., Butt, J.B., and Schwartz, L.H., *J. Phys. Chem.*, 82, 558 (1978).
28. Raupp, G.B., and Delgass, W.M., *J. Catal.*, 58, 348 (1979).
29. Lo, C., Rao, K.R.P.M., Mulay, L.N., Rao, V.U.S., Obermeyer, R.T., and Cormley, R.J., *Advances in Chem. Series*, 194, 573-588 (1981).
30. Brewster, B.S., and Bartholomew, C.H., "Performance Prediction Methods for Methanation: Monolith and Fluidized Bed Reactors," Submitted to the General Electric Company, ARSD, September 30, 1981.
31. Brewster, B.S. Sughrue, E.L., and Bartholomew, C.H., in preparation, 1986.
32. Bartholomew, C.H., "Catalyst Deactivation. Causes, Mechanisms, and Treatment," *Chemical Engineering*, 91, (23), 96 (1984).
33. Smith, J.M., *Chemical Engineering Kinetics*, 3rd Ed., McGraw-Hill, 1981.
34. Rankin, J.L., and Bartholomew, C.H., "A Mathematical Model of Activity/Selectivity of Fischer-Tropsch Catalysts," paper in preparation, 1986.
35. Rabo, J.A., Risch, A.P., and Putsma, M.D., *J. Catal.*, 53, 295 (1978).
36. Sachtler, J.W.A., Kool, J.M., and Ponec, V., *J. Catal.*, 56, 284 (1979).
37. Goodman, D.W., Kelley R.D., Madey, T.E., and White J.M., *Surf. Sci. Lett.* 90, 201 (1979).
38. Ponec, V., "Some Aspects of the Mechanism of the Methanation and Fischer-Tropsch Synthesis," *Catal. Rev. Sci. Eng.*, 18, 151 (1978).
39. Kibby, C.L., and Kobylinski, T.P., "Models of Product Distribution in Fischer-Tropsch Synthesis," Symposium in Advances in Synthetic Fuels, Presented before the ACS Division of Petroleum Chemistry, Miami Beach, September, 10-15, 1978.
40. Bell, A.T., *Catal. Rev.-Sci. Eng.*, 23, 203 (1981).
41. Bileon, P., and Sachtler, W.M.J., *Adv. Catal.*, 30, 165 (1981).

42. Grenoblé, D.C., Estadt, M.M., and Ollis, D.F., "The Chemistry and Catalysis of the Water Gas Shift Reaction," J. Catal., 67, 90-102 (1981).
43. a. Bennion, D.N., private communication, 1983.
b. Newman, J., Electrochemical Systems, Prentice-Hall, Englewood Cliffs, N.J., 1973.
44. Berty, J.M., "Testing Commercial Catalysts in Recycle Reactors," Catal. Rev. - Sci. Eng. 21, 75 (1979).
45. Bartholomew, C.H., "Deactivation by Carbon of Iron Catalysts for Indirect Liquefaction," DOE-PC-5033-1, Jan. 7, 1987.
46. Bartholomew, C.H. and Bayles, F.M., "Macintosh Process Control," Macintosh Journal, 1 (5), 10 (1987).
47. Bartholomew, C.H., "Deactivation by Carbon of Iron Catalysts for Indirect Liquefaction," Annual Report to DOE, DOE-PC-50533-4, Nov. 15, 1987.

END

DATE FILMED

11 / 27 / 90