TITLE: **Slurry Phase Iron Catalysts for Indirect Coal Liquefaction**

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GRANT NO: DE-FG22-95PC95210

PERIOD OF PERFORMANCE: July 5, 1995 - July 4, 1998

OBJECTIVE

The objective of this project was to investigate the causes of catalyst attrition in slurry phase iron Fischer-Tropsch catalysts and to synthesize catalysts with improved attrition resistance for this process. Precipitated iron catalysts are being considered by the DOE for conversion of coal-derived syngas where the H_2/CO ratio is around 0.7. The high water-gas shift activity of Fe makes it possible to work at such low H_2/CO ratios, hence Fe catalysts are desirable for the indirect liquefaction of coal.

EXECUTIVE SUMMARY

In this section, we present an overview of the research performed in this DOE-UCR grant. The specific research findings are described in the 10 publications that resulted from this work. Out of these 10 publications, 5 were published prior to 1997, but the other 5 represent the most recent work and several of them are still in the review process. Therefore, we have included these 5 manuscripts as part of this final report. The work was disseminated widely in the form of 17 presentations at both national and international conferences. This research program also provided fertile training ground for the education and training of students. A total of 5 graduate students were supported with this research grant (4 Ph. D. and 1 M. S.). The grant could not have provided complete support for all these students, therefore partial support was obtained from other sources such as NSF and national laboratories, as well as industry support. In addition, 4 undergraduate students participated in this research as part of their summer internships (supported either by DOE or NSF) and 2 of these students are co-authors on the resulting research publications. The narrative (below) is grouped into three sub-tasks:

Task 1:Synthesis of Attrition Resistant Catalysts

We have synthesized different spray-dried catalyst formulations containing silica as binder. We have evaluated several approaches to measure attrition strength of Fe F-T synthesis catalyst and have concluded that the ultrasonic fragmentation test is most sensitive to differences in strength among these catalysts. Hence, the spray-dried catalysts show improved strength compared to the Fe catalysts that have been previously used in slurry bubble column reactor tests. In future work, we hope to test the activity of these catalysts in a F-T synthesis reactor and to evaluate their attrition strength under working conditions.

Task 2:Catalyst-Binder Interactions

We have completed the temperature programmed reduction studies of model supported and unsupported UCI binderless F-T synthesis catalyst. Model supported catalysts were prepared in our laboratories using Stöber silica spheres as support. We have concluded that the silica binder does not retard the reduction of the iron phase. By TEM, we have seen no evidence of any silicate interfacial phases when the iron was deposited on the silica. However, as described in reference 4, when the iron is co-precipitated with the silica, we do form an unreducible amorphous phase. In our catalysts, the binder does retard the sintering of the carbide phases, and helps to maintain a well-dispersed catalyst with nanophase particle size.

Task 3:Characterization of working catalysts

The working catalalyst samples were supplied to UNM by two of our collaborators: Prof. Dragomir Bukur of Texas A&M University, College Station, TX, and Dr. Burtron Davis of the Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky. We have used x-ray diffraction and transmission electron microscopy to study working F-T catalysts. These catalysts had been used in a medium pressure slurry phase CSTR and were discharged during the course of F-T runs at different times on stream. Every step of the catalyst removal and sample preparation steps was examined carefully to eliminate any possible artifacts in the analytical scheme. It was found that removal of hot, catalyst-containing wax from the reactor in air could potentially cause oxidation of the most reactive components. Hence, wax removal under inert atmosphere was deemed necessary to protect the sample against oxidation. Separation of the catalyst from the F-T wax by Soxhlet extraction has been the most commonly used procedure to obtain a sample suitable for analysis. However, our study showed that this process could also introduce artifacts in sample composition. Hence, we concluded that it was necessary to keep the catalyst in the hydrocarbon wax to preserve its composition.

X-ray diffraction was used to study the types of Fe phases present in the working catalyst. It was found that the scattering efficiencies vary markedly for the different phases, making it necessary to use Rietveld structure refinement to obtain quantitative phase compositions. A simple visual inspection of powder diffraction patterns is very deceptive, because of these differences in x-ray scattering efficiencies. The interference by the wax with the catalyst remains a major problem with using x-ray diffraction, particularly with high a catalysts. We've been exploring separation methods, other than Soxhlet extraction, to provide a reasonable powder sample for analysis, as well as having success in using the Rietveld method, along with a low-density polyethylene crystal structure, to deconvolute the wax diffraction pattern, from that of the catalyst. The XRD analysis was complemented by cross-section TEM, which allows the particle size distribution and morphology of the various Fe phases to be determined. The results to date are very encouraging and, for the first time, provide clues to the nature of the phases responsible for F-T activity. These results help us to understand the activation and deactivation of Fe F-T catalysts.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM

Fischer-Tropsch synthesis represents a commercially viable technology for converting syngas to liquid fuels. While the conversion of coal into liquid fuels is currently being practiced in South Africa, the process is expected to become increasingly attractive in the U. S. as the price of crude oil increases. The DOE is therefore interested in a viable F-T technology for converting coal-derived syngas, for which Fe is the preferred catalyst. This research has provided some of the fundamental information necessary for the design of Fe F-T catalysts.

SPECIFIC ACCOMPLISHMENTS

- Development of a method to determine the attrition strength of precipitated catalysts
- Investigation of the role of particle and binder morphology on attrition strength
- Discovery of the importance of proper catalyst passivation for study of iron catalysts and the development of procedures for catalyst removal from F-T reactors
- Development of new x-ray and TEM analytical protocols for the characterization of the working F-T synthesis catalyst
    - Analysis of the phases present in iron catalysts using x-ray and neutron diffraction data with Rietveld structure methods
    - Analysis of catalyst embedded in the wax, using cross-section TEM

PUBLICATIONS

(1) Shroff, M. D. and Datye, A. K., "The importance of passivation in Fe catalysts," Catal. Lett. 37, 101 (1996).

(2) Hanprasopwattana, A., Rieker, T., Sault, A. and Datye, A. K., "Morphology of TiO_2 coatings on silica," Catal. Lett., 45, 165 (1997).

(3) Datye, A. K., Shroff, M. D., Harrington, M. S., Sault, A. G. and Jackson, N. B., "The Role of Catalyst Activation on the Activity and Attrition of Iron Fischer-Tropsch Catalysts," Stud. Surf. Sci. and Catal., Natural Gas Conversion IV, vol. 107, pg 169, 1997.

(4) Datye, A. K., Shroff, M. D., Jin, Y., Brooks, R. P., "Nanoscale Attrition of Fe F-T catalysts: Implications for Catalyst Design," Stud. Surf. Sci. Catal., vo. 101, 11th Intl. Congr. Catal., pg 1421, 1996.

(5) Jackson, N. B., Datye, A. K., Mansker, L., O'Brien, R. J. and Davis, B. H., "Deactivation and Attrition of Fe F-T catalysts," Stud. Surf. Sci. Catal., vol. 111, Catalyst Deactivation 1997, p 501.

(6) Mansker, L.D., Jin, Y.; and Datye, A. K.; Proceedings of the 1997 Coal Liquefaction & Solid Fuels Contractors Review Conference, Federal Energies and Technologies Center, Pittsburgh, Pennsylvania; 1997; WEB URL: http://www.fetc.doe.gov/events/97conferences/coal_liq/97cl_pdf/datye.pdf/.

(7) Hien N. Pham, Alexander Viergutz, Robert J. Gormley, and Abhaya K. Datye, "Improving the Attrition Resistance of Slurry Phase Heterogeneous Catalysts," submitted to Powder Technology.

(8) Pham, H., Reardon, J. and Datye, A. K., "Measuring the Attrition Resistance of Fe F-T catalysts," Powder Technology, in press.

(9) Jin, Y. and Datye, A. K., "Phase transformations in Fe F-T catalysts," International Congress of Electron Microscopy, Cancun 1998, vol II, page 391, Institute of Physics Publishing, 1998.

(10) Jin, Y. and Datye, A. K., "Characterization of Bubble Column Slurry Phase Iron Fischer-Tropsch Catalysts, Natural Gas Conversion V, Stud. Surf. Sci. Catal., vol 119, page 209, 1998.

(11) Mansker, L. D., Jin, Y., Bukur, D. B. and Datye, A. K., "Characterization of Fe Fischer-Tropsch Catalysts," submitted to the special issue of Applied Catalysis being edited by Prof. Hans Schulz.

PRESENTATIONS AT MEETINGS AND CONFERENCES

A total of **17 presentations** were made at meetings and conferences based on the research supported by this grant.

Natural Gas conversion meeting, South Africa (November 95), AIChE meeting (November 95 and November 98), Western States Catalysis Society [March 1996 (2), February 97 (2) and March 1998 (2)], Pittsburgh Coal conference (October 96), Intl. Congr. on Catalysis, Baltimore, MD (July 96), North American Catalysis Society meeting Chicago, IL (May 97), American Crystallographic

Association meeting, St. Louis, MS, (July 97), Southwestern regional ACS meeting, Tulsa, OK (October 97), DOE Contractors meeting (August 97), Catalyst Deactivation symposium in Cancun (November 97) and Natural Gas Conversion meeting in Sicily, Italy (September 98).