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

PI: Abhaya K. Datye

STUDENTS: Linda Mansker, Hien Pham, Yaming Jin, (all Ph. D. students). Students graduated Mehul Shroff (M. S.) and Aree Hanprasopwattana (Ph. D.)

INSTITUTION: Center for Microengineered Materials and
Department of Chemical and Nuclear Engineering
University of New Mexico, Albuquerque, NM 87131
(505) 277-0477 FAX (505) 277-1024 email: Datye@unm.edu

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I. ABSTRACT

OBJECTIVE: The objective of this project is 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 indirect liquefaction of coal.

WORK DONE OVER THE PAST YEAR: 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 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. Extraction of the catalyst from the F-T waxe by soxhlet extraction has been the most commonly used procedure. However, our analysis 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 Reitveld refinement to obtain quantitative phase compositions. A simple visual inspection of powder diffraction patterns is very deceptive. The interference by the wax remains a major problem with x-ray diffraction, particularly with high α catalysts. 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.

Over the past year, we have also brought on line a bench top spray drier. We have spray dried catalyst

formulations containing silica as binder. The attrition strength of these catalysts was tested using the ultrasonic fragmentation approach developed in our laboratory as part of this UCR program. The spray dried catalysts show improved strength compared to Fe catalysts that have been previously used in slurry bubble column reactor tests. In future work, we hope to test the activity of these catalyst formulations and to evaluate their attrition strength in a F-T synthesis reactor.

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, it 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.

II. 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
- Analysis of the phases present in iron catalysts using Reitveld refinement methods and TEM

III. 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.

Publications (submitted and in preparation)

(7) 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.

(8) Jin, Y. and Datye, A. K., "Phase transformations in Fe F-T catalysts," International Congress of Electron Microscopy, in press, 1998.

(9) Pham, H., Reardon, J. and Datye, A. K., "Measuring the Attrition Resistance of Fe F-T catalysts," in preparation for submission to Powder Technology.

(10) Mansker, L. D. and Datye, A. K., "Quantitative Reitveld Powder Diffraction Analysis of Fe phases in a Fischer-Tropsch Synthesis Catalyst," in preparation for submission to Appl. Cryst.

(11) Jin, Y. and Datye, A. K., "Temperature Programmed Reduction of Fe phases in F-T catalysts," in preparation for submission to J. Catal.

A total of **14 presentations** were made at meetings and conferences based on the research supported by this grant. Intl. Natural Gas conversion meeting (Nov. 95), AIChE meeting (Nov. 95 and Nov 98), Western States Catalysis Society [March 1996 (2), February 97(2) and February 1998(2)], Pittsburgh Coal conference (October 96), Intl. Congr. on Catalysis (Baltimore July 96), North American Catalysis Society meeting (May 97), Southwest ACS meeting, Tulsa, OK(Sept 97), DOE Contractors meeting (August 97).