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

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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 AND CONCLUSIONS: In this work, we have studied two approaches to characterize the attrition resistance of precipitated catalysts. These include uniaxial compaction and ultrasonic fragmentation. While uniaxial compaction is the conventional approach used in the ceramics literature, we feel that the compressive stresses used here do not adequately represent the forces experienced by a particle in a slurry reactor . Ultrasonic fragmentation was therefore used in an attempt to simulate the forces that lead to particle break up in a slurry reactor. Precipitated iron catalysts were found to be very weak compared to silica or alumina spray dried catalysts. The morphology of the primary iron oxide particles as well as lack of a suitable binder makes these catalysts very weak. In our work, we have studied differing morphologies of the silica binder, and effect of binder on catalyst strength.

Besides physical breakup of the catalyst, there is a second mechanism that leads to nano-scale attrition of Fe catalysts. This is due to the transformation of hematite (Fe_2O_3) into magnetite (Fe_3O_4), α-Fe as well as iron carbides. A working Fe catalyst is known to consist of a mixture of these phases, however the role of each phase and the nature of the catalytically active phase is not yet conclusively established. We feel this information is critical to the design of attrition resistant catalysts. Therefore, we have used techniques such transmission electron microscopy (TEM) and x-ray diffraction (XRD) to identify the nature and morphology of phases present in these catalysts. We conclude that transformation into the carbide phase is essential to obtain a high activity catalyst. However, there may be more than one type of carbide present in the catalyst, explaining why it has been generally difficult to obtain structure-activity correlations. The large change in specific volume in going from the iron oxide tcarbide phase is responsible for the nanoscale attrition of the catalyst. Hence, the use of a suitable binder is essential to prepare attrition resistant catalysts.

Since silica binders have been reported to cause loss of catalyst activity, a third area of investigation has been the nature of iron-silica interactions. By using high resolution TEM of model catalysts, we have studied the atomic-scale structure of the iron-silica interface to determine the presence, if any, of interfacial phases such as iron silicates. A combination of temperature programmed reduction and TEM has helped provide a better understanding of the reduction and activation of these iron catalysts. Our work to date shows that the presence of Cu helps in enhancing reducibility of these catalysts, however at calcination temperatures up to 700 °C, we have not detected any interfacial silicate phase. The particle size of the iron phase markedly influences the kinetics of iron carbide formation. Direct reduction in CO may help provide higher surface areas of carbide, especially in unsupported catalysts. We have also also explored methods to deposit controlled morphology coatings of oxides such as TiO_2 on silica to modify the iron-silica interaction.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM

Fischer-Tropsch synthesis represents a commercially viable technology for converting syngas to liquid fuels. This past year has seen announcements of new plants to convert natural gas to liquid fuels via Fischer-Tropsch technology. 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. With dwindling fossil energy reserves, the DOE is therefore interested in a viable F-T technology for converting coal-derived syngas. This research has provided some of the fundamental information necessary for the design of attrition resistant catalysts.

PLANS FOR THE COMING YEAR

- Neutron and X-ray Diffraction to identify specific carbide phases present in the working catalyst.
- Investigate causes of catalyst deactivation.
- Synthesis of attrition resistant 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

III. PRESENTATIONS AND 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, in press.

(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., Catalyst Deactivation, in press..

(6) Presentations at the Intl. Natural Gas conversion meeting (Nov. 95), AIChE meeting (Nov. 95), Western States Catalysis Society (March 1996 and February 97), Pittsburgh Coal conference (October 96), Intl. Congr. on Catalysis (Baltimore July 96).