TITLE: **Attrition Resistant Iron-Based Fischer-Tropsch Catalysts**

AUTHOR(S): K. Jothimurugesan (jothi@et.hamptonu.edu; 757-727-5817)
Department of Chemical Engineering
Hampton University, Hampton, Virginia 23668

James G. Goodwin, Jr. (Goodwin@engrng.pitt.edu; 412-624-9642)
Chemical and Petroleum Engineering Department
1249 Benedum Hall
University of Pittsburgh
Pittsburgh, PA 15260

James J. Spivey (jjs@rti.org; 919-541-8030)
Santosh K. Gangwal (skg@rti.org; 919-541-8033)
Research Triangle Institute
3040 Cornwallis Road, P.O. Box 12194
Research Triangle Park, NC 27709-2194

STUDENT(S): Ph.D. Student (University of Pittsburgh), Robin Zhao
Undergraduate Students (Hampton University), T. Jones, and J. Carpenter

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ABSTRACT

OBJECTIVE

The Fischer-Tropsch (F-T) reaction provides a way of converting coal-derived synthesis gas ($CO+H_2$) to liquid fuels. Since the reaction is highly exothermic, one of the major problems in control of the reaction is heat removal. Recent work has shown that the use of slurry bubble column reactors (SBCRs) can largely solve this problem. Iron-based (Fe) catalysts are preferred catalysts for F-T when using low CO/H_2 ratio synthesis gases derived from modern coal gasifiers. This is because in addition to reasonable F-T activity, the FT catalysts also possess high water gas shift (WGS) activity. However, a serious problem with the use of Fe catalysts in a SBCR is their tendency to undergo attrition. This can cause fouling/plugging of downstream filters and equipment, making the separation of catalyst from the oil/wax product very difficult if not impossible, and results in a steady loss of catalyst from the reactor.

The objectives of this research are to develop a better understanding of the parameters affecting attrition of Fe F-T catalysts suitable for use in SBCRs and to incorporate this understanding into the design of novel Fe catalysts having superior attrition resistance. Catalyst preparations will be based on the use of spray drying and will be scalable using commercially available equipment. The research will employ among other measurements, attrition testing and F-T synthesis, including long duration slurry reactor runs in order to ascertain the degree of success of the various preparations. The goal is to

develop an Fe catalyst which can be used in a SBCR having only an internal filter for separation of the catalyst from the liquid product, without sacrificing F-T activity and selectivity.

WORK DONE AND CONCLUSIONS

A Ruhrchemie iron catalyst of composition 100Fe/5Cu/4.2K/25SiO_2 was obtained and tested for FT activity in a 1 cm i.d. high pressure fixed bed micro-reactor system. This catalyst serves as a baseline catalyst for this work from which improvements in attrition resistance and activity will be sought.

The effect of silica addition via coprecipitation and as a binder to a doubly promoted F-T synthesis iron catalysts (100 Fe/5Cu/4.2K) was studied. The catalysts were prepared by coprecipitation, followed by binder addition and spray drying in a 1 m diameter, 2 m tall spray dryer. The binder silica content was varied from 0 to 20 wt%. A catalyst with 12 wt% binder silica was found to have the highest attrition resistance. F-T reaction studies over 100 hours in a fixed-bed reactor showed that this catalyst maintained around 95% CO conversion with a methane selectivity of less than 7 wt% and a C_5^+ selectivity of greater than 73 wt%. The effect of adding precipitated silica from 0 to 20 parts by weight to this catalyst was also studied. Addition of precipitated silica was found to be detrimental to attrition resistance and resulted in increased methane and reduced wax formation.

Several test methods have been modified to develop suitable test methods for evaluating the attrition of small batches of spray dried F-T iron catalysts. In the first stage of this research, test results of different methods are being compared for catalysts used in FTS in order to establish a better understanding of the suitability of the various methods for predicting attrition in an SBCR.

HIGHLIGHTS OF ACCOMPLISHMENTS

- A fixed-bed high-pressure micro-reactor system has been commissioned for FT testing
- A bench-mark iron FT catalyst has been procured and tested
- A large bench-scale spray drier has been purchased and installed
- Two apparatus have been constructed and tested based on ASTM attrition measurement methods except requiring only 5 g of catalyst
- Four methods have been applied to measuring attrition and the results have been compared to attrition results from actual SBCR runs
- Several F-T catalysts have been prepared and tested. Preparation procedures have been optimized with respect to attrition resistance, activity, and selectivity.

ARTICLES AND PRESENTATIONS

K. Jothimurugesan, J.J. Spivey, S.K. Gangwal and J.G. Goodwin, Jr., “Effect of Silica on Iron-Based Fischer-Tropsch Catalysts”, Fifth Natural Gas Conversion Symposium, Italy, September 20-25, 1998. Abstract Accepted.

R. Zhao, J.G. Goodwin, Jr., and R. Oukaci, “ Comparison of Catalyst Attrition Assessment Methods” AIChE National Meeting, Miami Beach, FL, November, 1998. Proposed for Presentation.