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): Undergraduate Students (Hampton University) N. Reeves and J. Carpenter

Ph.D. Student (University of Pittsburgh) Rabin Zhao

GRANT NO: DE-FG22-96PC96217

DOE PROJECT OFFICER: Dr. Richard E. Tischer

PERIOD OF PERFORMANCE: September 1, 1996-August 31, 1999

ABSTRACT

OBJECTIVE

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 $100\text{Fe/5Cu/4.2K/25SiO}_2$ was obtained and tested for FT activity in a 1 cm i.d. high pressure fixed bed micro-reactor system. This catalyst will serve as a baseline catalyst for this work from which improvements in attrition resistance and activity will be sought.

The addition of binder silica to precipitated 100/Fe/5 Cu/4.2K FT catalyst followed by spray drying increases the attrition resistance significantly. Within the range of the non-proprietary catalysts tested here, the optimum binder silica content is 10 to 12 wt%. The FT activity and selectivity of this catalyst are better than a Ruhrchemie catalyst at 250 °C and 1.48 MPa. The addition of precipitated silica to catalysts containing 10 to 12 wt% binder silica decreases attrition resistance and increases methane selectivity. Based on the experience gained, a proprietary HPR-43 catalyst has been successfully spray dried in 500-g quantity. This catalyst showed 95% CO conversion over 125 h of testing at 250 °C, 1.48 MPa, and 2 NL/g-cat/h (1,800 h⁻¹) and had less than 4% methane selectivity. Its attrition resistance was one of the highest among the catalysts tested. Negotiations are under way with an industrial party for testing this catalyst in an SBCR.

ARTICLES AND PRESENTATIONS

Conference 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.
- R. Zhao, J.G. Goodwin, Jr., and R. Oukaci, "Characteristics of Cobalt Fischer-Tropsch Catalysts," Spring Symposium of Tri State Catalyst Club, Charleston, WV., April 20-21, 1998.
- R. Zhao, J.G. Goodwin, Jr., and R. Oukaci, "Comparison of Catalyst Attrition Assessment Methods," 36th Annual Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Pittsburgh, PA., May 14-15, 1998.
- R. Zhao, J.G. Goodwin, Jr., and R. Oukaci, "Attrition Assessment Methods for Slurry Bubble Column Reactor Catalysts," AIChE Annual Meeting, Miami, FL., Nov. 15-20, 1998.
- K. Jothimurugesan, "Attrition Resistant Iron-Based Fischer-Tropsch Catalysts", 7th Annual HBCUand OMI Conference, Miami, FL, March 16-18, 1999.
- K. Jothimurugesan, J.J. Spivey, S.K. Gangwal and J.G. Goodwin, Jr., "Development of Fe Fischer-Tropsch Catalysts with High Attrition Resistance, Activity and Selectivity", Spring AIChE National Meeting, Houston, TX, March 14-18, 1999.
- K. Jothimurugesan, J.J. Spivey, S.K. Gangwal and J.G. Goodwin, Jr., "Development of Fe Fischer-Tropsch Catalysts for Slurry Bubble Column Reactors", 217 th Amercian Chemical Society National Meeting, Anaheim, CA, March 21-25, 1999.
- R. Zhao, J.G. Goodwin, Jr., and K. Jothimurugesan, "Attrition Resistance Study of Spray-Dried Iron-Based Fischer-Tropsch Catalysts," 37th Annual Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Pittsburgh, PA., May 3-4, 1999.
- K.Jothimurugesan, J.J. Spivey, S.K. Gangwal and J.G. Goodwin, Jr., "Attrition Resistant Iron-Based Fischer-Tropsch Catalysts" 16th North American Catalysis Society Meeting, Boston, MA., May 31-June 4, 1999.
- R. Zhao, D.G. Wei, J.G. Goodwin, Jr. and R. Oukaci, "Attrition Assessment for Slurry Bubble Column Reactor Catalysts," 16th North American Catalysis Society Meeting, Boston, MA., May 31-June 4, 1999.
- R. Zhao, J.G. Goodwin, Jr., and K. Jothimurugesan, "Attrition Resistance Study of Iron-Based Fischer-Tropsch Catalysts," 16th Annual International Pittsburgh Coal Conference, Pittsburgh, PA., Oct. 11-15, 1999.

Journal Articles

- K. Jothimurugesan, J.J. Spivey, S.K. Gangwal and J.G. Goodwin, Jr., "Effect of Silica on Iron-Based Fischer-Tropsch Catalysts," Studies in Surface Science and Catalysis: Natural Gas Conversion V, Elsevier Science, 215-220 (1998).
- K. Jothimurugesan, J.J. Spivey, S.K. Gangwal and J.G. Goodwin, Jr., "Development of Fe Fischer-Tropsch Catalysts for Slurry Bubble Column Reactors", ACS Preprints, Volume 44, No.1, 111-114, 1999.
- R. Zhao, J.G. Goodwin, Jr., and R. Oukaci, "Attrition Assessment Methods for Slurry Bubble Column Reactor Catalysts," submitted to Applied Catalysis A.
- K.Jothimurugesan, J.J. Spivey, S.K. Gangwal and J.G. Goodwin, Jr., "Attrition Resistant Iron-Based Fischer-Tropsch Catalysts". in preparation for submission to J. Catal.