Development of Improved Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
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TABLE OF CONTENTS

I.	Abstract.....	1
II.	Objective and Scope of Work.....	2
III.	Detailed Description of Technical Progress	4
III-1.	Task 1. Project Management.....	4
III-2.	Task 2. Catalyst Pretreatment Research.....	4
III-3.	Task 3. Improved Iron/Silica Catalysts.....	5
IV.	References.....	7

I. Abstract

The Project Work Plan and other required reports (Cost Plan, Notice of R&D Project Form, Management Plan, Milestone Schedule/Plan and WBS Dictionary) have been prepared and submitted on schedule to the Department of Energy.

All new instruments (equipment) for this contract have been ordered, and Varian 3400 gas chromatograph has been received, installed and tested. Several modifications have been made in the feed section of the fixed bed reactor experimental apparatus. A new gas manifold system was designed and installed, and two cylinder cabinets for storage of flammable and health hazard gases have been connected to ventilated hoods in our laboratories. A fixed bed reactor test of the Ruhrchemie catalyst LP 33/81 (Run FA-99-3509) has been initiated and is still in progress. The catalyst did not show any sign of deactivation during the first 330 h at 250°C, 1.5 MPa, $H_2/CO = 0.67$ and 2 nL/g-cat/h.

II. Objective and Scope of Work

The objective of proposed research is development of catalysts with enhanced slurry phase activity and better selectivity to fuel range products, through a more detailed understanding and systematic studies of the effects of pretreatment procedures and promoters/binders (silica) on catalyst performance. In order to accomplish this objective, the work shall be divided into several tasks which are described in the following subsections.

Task 1 – Project Management

Within 60 days of project initiation, the contractor shall prepare and submit to the DOE Project Manager a detailed project work plan covering the entire period of performance of the project. The plan shall present, in detail, all activities that will be performed to successfully complete proposed research and it shall consist of the following: (1) detailed description of the methods and technical approach that shall be used to achieve the objectives of this project; (2) a detailed project schedule for each task or other logical segment of work to be performed; (3) graphs reflecting cumulative estimated costs and person-hours expended by month for each task or other logical segment of work, and for the total project effort; (4) a project work chart showing the key personnel/groups planned to work on each task and the percentage of their time devoted to the tasks; and (5) a Work Breakdown Structure (WBS) dictionary to establish the framework for contract execution and to report cost schedule and technical performance.

All project status, milestone schedule, and cost management reports, as well as topical reports, if any, shall be submitted in accordance with the DOE reporting requirements.

Task 2 – Catalyst Pretreatment Research

This task is aimed at developing optimal pretreatment conditions for precipitated unsupported (1 catalyst) and supported (or silica containing; 1-2) iron catalysts, and at providing a better understanding of the role of pretreatment on subsequent catalyst activity, selectivity and longevity during Fischer-Tropsch (F-T) synthesis. This shall be accomplished by examining the effect of various activation conditions on physical and chemical properties of the catalyst as well as on catalytic behavior in fixed and slurry bed reactors. Parameters such as type of reductant (H_2 vs. CO vs. syngas), reductant flow rate, temperature and duration shall be studied. Selected catalysts shall be extensively characterized using a variety of physical, chemical and instrumental techniques with the objective to establish correlations between the physical/chemical properties of the catalysts and their observed catalytic behavior during F-T synthesis.

Task 3 – Improved Iron/Silica Catalysts

The objective of this task is to determine optimal concentrations of silica and K_2O in a catalyst with composition $100\text{ Fe}/5\text{ Cu}/x\text{ K}_2\text{O}/y\text{ SiO}_2$ (in parts per weight). The effect of SiO_2 and K_2O on catalytic activity, selectivity and stability shall be determined to arrive at promoter/binder concentrations for an improved catalyst performance. The screening tests shall be conducted in fixed bed reactors to obtain preliminary indication of F-T activity and selectivity at different process conditions. Catalysts which show enhanced activity and/or selectivity towards transportation fuels shall be tested in slurry reactors up to 30 days on stream. Selected catalysts shall be extensively characterized, to determine relations between the physico-chemical properties of catalyst and their catalytic behavior during F-T synthesis.

III. Detailed Description of Technical Progress

III-1. Task 1 – Project Management

The Project Work Plan and several other required reports (Cost Plan, Management Plan, Milestone Schedule/Plan and WBS Dictionary) have been submitted to the DOE in November 1989.

III-2. Task 2 – Catalyst Pretreatment Research

A. Equipment Purchase and Modifications

All capital equipment items have been ordered: (1) Varian 3400 gas chromatograph (GC); (2) Hewlett Packard GC integrator; (3) Ametek mass spectrometer; and (4) two Brooks mass flow meters. The Varian 3400 GC was received in December, and it has been installed and tested. It will be used for analysis of aqueous and organic phase product samples. Delivery of the other instruments is expected in January.

Two major modifications in the feed section of the two fixed bed reactor systems have been made. The gas supply manifold has been redesigned so that each reactor has a separate feed system which is capable of supplying three types of gases: reductant, synthesis feed gas (premixed $H_2 + CO$) and the purge gas (helium or nitrogen). Also, two cylinder cabinets, with exhaust, for storage of up to four cylinders each, have been installed in compliance with safety regulations. These two cabinets are used to store flammable (H_2) and health hazard gases (CO or synthesis gas mixture) needed for operation of two fixed bed and two stirred tank slurry reactors.

B. Run FA-99-3509 with the Ruhrchemie catalyst LP 33/81

Following routine pressure testing, feed gas trap regeneration and instrument calibrations, a fixed bed reactor test of commercial Ruhrchemie catalyst LP 33/81 (100 Fe/4.3 Cu/4.1 K/25 SiO_2 in parts per weight) was initiated. The catalyst was reduced

according to manufacturer's recommended procedure (H_2 at 220°C, 0.101 MPa and linear gas velocity of 1.5 m/s for 1 h). Following reduction the initial process conditions were: 250°C, 1.5 MPa, $(H_2/CO) = 0.67$ and 2 nL/g-cat/h (nL = normal liter at 0°C and 0.101 MPa). These conditions are the same as those employed in the earlier tests with this catalyst conducted in our laboratory (Runs FB-99-1588 and SA-99-0888 with the CO reduced catalyst, Bukur et al., 1988). By the end of this reporting period, the catalyst has been on stream over 350 h, and its activity increased gradually with time-on-stream (TOS). Four mass balances were made during this time period, but the product selectivities will not be discussed due to problems with analysis of gas phase products (H_2 , CO, CO_2 , $C_1 - C_5$ hydrocarbons) on Carle 400 gas chromatograph. The effort is underway to repair this instrument, and after this is accomplished we plan to reexamine our results and discuss selectivities in the next quarterly report.

Activity comparison, in terms of volumetric contraction and $(H_2 + CO)$ conversion, between the current test (H_2 reduced catalyst) and the Run FB-99-1588 (CO reduced catalyst) is shown in Figure 1. As can be seen from this figure, H_2 reduction gives higher activity and better stability (activity increases with TOS). The values of conversion from the current run should be treated with caution due to afore mentioned problems with the gas phase analysis.

III-3. Task 3 – Improved Iron/Silica Catalysts

The work on this task is scheduled to begin on March 1, 1990.

Figure 1. Effect of time on stream and reductant on catalyst activity

IV. References

Bukur, D. B., Lang, X., Patel, S. A., Zimmerman, W. H., Rosynek, M. P. and Withers, H. P., Indirect Liquefaction Contractors' Review Meeting Proc., pp. 453-482, Pittsburgh, PA, November 15-17, 1988.

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