

IMPROVED IRON CATALYSTS FOR SLURRY PHASE FISCHER-TROPSCH SYNTHESIS

First Annual Technical Progress Report

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Submitted by

Dr. Dragomir B. Bukur (Professor, PI)

Contributors:

Dr. Lech Nowicki (Postdoctoral fellow)
Victor Carreto-Vazquez (Graduate Student)
Dr. Wen-Ping Ma (Postdoctoral fellow)
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3122

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Texas A&M University
318 Administrative Building
College Station, TX 77843-3121

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Abstract

This report describes research conducted to support the DOE program in development of improved (attrition resistant) catalysts for converting coal-derived synthesis gas to liquid fuels via slurry phase Fischer-Tropsch (F-T) synthesis. The primary objective of this research program is to develop highly active and selective attrition resistant iron F-T catalysts by spray drying. Texas A&M University (TAMU) and Hampton University (HU) will work together to synthesize spray dried catalysts. The synthesis of catalyst precursors, measurement of attrition properties and testing of spray dried catalysts will be performed at TAMU. Hampton University will prepare final catalysts in a bench scale spray drier unit, and provide expertise in selection of binders and their properties required to produce catalysts of high attrition strength. During the reporting period we have completed one slurry reactor test of a spray-dried catalyst synthesized at HU.

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Executive Summary

This report covers the first year of this three-year research grant under the University Coal Research program. This research program involves a collaboration between Texas A&M University (TAMU) and Hampton University (HU) in the area of synthesis of spray dried catalysts. The Hampton University has a bench scale spray drier (Niro), which will be utilized for synthesis of promoted iron catalysts by spray drying method. Catalysts synthesized at HU will be tested in fixed bed and/or stirred tank slurry reactors at TAMU.

During the first year of this grant we have assembled a research team at TAMU, consisting of Mr. Victor Carreto-Vazquez (MS student since May 2001) and Dr. Wen-Ping Ma (postdoctoral fellow from PR China since August 2001). Also, Dr. Lech Nowicki (a former postdoctoral fellow from Poland) spent about a month (July 13-August 11) working on this project. He trained Mr. Carreto-Vazquez in the use of gas chromatographs for analysis of liquid products, and software for product identification and mass balance calculation. Dr. Nowicki completed a slurry reactor test (384 h on stream) of a spray dried iron F-T catalyst with nominal composition 100 Fe/5 Cu/4.2 K/11 SiO₂ (in parts per weight) synthesized at Hampton University. This test was conducted as a part of our scheduled collaborative activities with the Hampton University. Selectivity of the catalyst was excellent (methane selectivity of 2-2.2%, and C₅+ selectivity of 85-87%, both on carbon atom basis) but the catalyst started to deactivate after about 80 h on stream.

Dr. Wen-Ping Ma has learned to operate all three types of gas chromatographs, perform calibrations and analyze F-T products. Also, he became familiar with the use of our software for product analysis and mass balance calculations. He is becoming familiar with the operation of a slurry reactor and the auxiliary instruments.

Technical Project Objectives

The objective of this research project is to develop highly active and selective attrition resistant iron F-T catalysts for converting coal derived synthesis gas ($H_2/CO \approx 0.7$) into liquid hydrocarbons and high molecular weight hydrocarbon wax. The overall program is divided into the following tasks:

Task 1. Literature Review and Equipment Testing (9/1/00-5/31/01)

Task 2. Catalyst Synthesis and Spray Drying (6/1/01-3/31/03)

Task 3. Attrition Resistance Tests (9/1/01-6/30/03)

Task 4. Catalyst Testing and Data Analysis (9/1/01-8/31/03)

In task 1, research personnel will become familiar with the existing equipment for catalyst synthesis, operation of fixed-bed and slurry reactors, and gas chromatographs for product analysis. Shakedown runs with reactors will be conducted, and standard mixtures representative of F-T products (aqueous phase, organic phase and wax) will also be analyzed.

In task 2, synthesis of precipitated Fe catalysts will be performed collaboratively at TAMU and HU. Preparation of catalyst precursors will be done at TAMU whereas final steps including spray drying will be performed at HU.

In task 3, attrition tests will be performed in a stirred tank slurry reactor (STSR) and/or a slurry bubble column reactor (SBCR). Particle size distributions will be measured by a Coulter counter particle size analyzer or by Malvern analyzer after soxhlet extraction of the wax from the powder. Scanning electron microscope (SEM) will be used to investigate the mechanism of attrition (erosion vs. fracture).

In task 4, the prepared catalysts with a high mechanical strength will be tested in a fixed-bed reactor (runs up to 5 days on stream) and/or STSR (tests up to 21 days on stream). Slurry samples from the STSR runs will be periodically withdrawn from the reactor in an inert atmosphere for particle size distribution measurements.

Description of Technical Progress

Task 1. Literature Review and Equipment Testing

We have had a late start due to difficulties in recruiting research personnel for the project. After we were not able to recruit a Ph. D. graduate student for this project during fall 2000 semester, we have attempted to recruit a postdoctoral fellow. Between January 2001 and April 2001 we made two offers, both of which were initially accepted, but ultimately declined. Finally, in early June, an offer was made to Dr. Wen-Ping Ma (PR China), who has had prior research experience in the area of Fischer-Tropsch synthesis. Dr. Ma joined the project on August 9, and has learned how to operate gas chromatographs for product analysis, and has become familiar with the use of software for mass balance calculations.

During May 2001, Mr. Victor Carreto-Vazques (a graduate student seeking MS degree) has joined the project. He has been trained in the use of gas chromatographs and software for product analysis and mass balance calculations. He'll be primarily involved with catalyst synthesis and attrition testing of synthesized catalysts including particle size distribution measurements.

The only item remaining to be completed under this task is a shakedown of fixed bed and slurry reactors. We plan to conduct a shakedown run in a STSR during the next quarter (September-December, 2001).

Task 2. Catalyst Synthesis and Spray Drying

We have established contact with Professor Adeyiga at Hampton University, who is presently directing a project on development of attrition resistant iron-based Fischer-Tropsch catalyst. He has confirmed prior commitment made by Dr. Jothimurugesan (previous PI on Hampton's University Fischer-Tropsch project) to prepare TAMU developed catalysts by spray drying in a Niro bench scale spray drier unit (3 ft in diameter x 6 ft high).

Task 3. Attrition Resistance Tests

The work on this task has not been scheduled to begin during the reporting period.

Task 4. Catalyst Testing and Data Analysis

Even though the work on this task was scheduled to begin only after September 1, 2001, we have completed a slurry reactor test of a spray dried precipitated iron catalyst 100 Fe/5 Cu/4.2 K/11 SiO₂ (in parts per weight) supplied by Professor Adeyiga at Hampton University. The Fe/Cu/SiO₂ precursor was prepared by a single step co-precipitation. The desired amount of potassium was added to the precursor, and slurry was fed to a spray drier. This catalyst was prepared for the on-going project at HU supported by the DOE. The catalyst was tested in our Laboratory at TAMU to provide information on activity, stability and selectivity in a slurry reactor over a long period of time, since HU does not have slurry reactors.

Experimental

This test (run SB-2061) was conducted in a 1 dm³ stirred tank slurry reactor (Autoclave Engineers). The feed gas flow rate was adjusted with a mass flow controller and passed through a series of oxygen removal, alumina and activated charcoal traps to remove trace impurities. After leaving the reactor, the exit gas passed through a series of high and low (ambient) pressure traps to condense liquid products. High molecular weight hydrocarbons (wax), withdrawn from a slurry reactor through a porous cylindrical sintered metal filter, and liquid products, collected in the high and low pressure traps, were analyzed by capillary gas chromatography. The reactants and noncondensable products leaving the ice traps were analyzed on an on-line GC (Carle AGC 400) with multiple columns using both flame ionization and thermal conductivity detectors. Further details on the experimental set up, operating procedures and product quantification can be found elsewhere (1-3).

As received catalyst (14.8 g) and 320 g of Durasyn 164 oil (a hydrogenated 1-decene homopolymer, ~ C₃₀ obtained from Albemarle Co.) were loaded into the reactor. The catalyst was pretreated in CO at 280°C, 0.8 MPa (100 psig), 3 NI/g-cat/h for 12 hours. After the pretreatment the catalyst was tested initially at 260°C, 2.1 MPa, 2 NI/g-cat/h (where, NI/h, denotes volumetric gas flow rate at 0°C and 1 bar) using CO rich synthesis gas (H₂/CO molar feed ratio of 0.67). After 224 hours of testing at these conditions the gas space velocity was increased to 3 NI/g-cat/h for the next 110 hours (TOS =225-334 h) while keeping other conditions constant. At 335 on stream the gas space velocity was changed back to 2 NI/g-cat/h and the catalyst was tested at the baseline conditions for 48 hours, in order to assess the extent of deactivation. Slurry samples (containing ~1 g of catalyst) were withdrawn from the reactor after the pretreatment and at the end of the run for particle size distribution measurements.

Results

Syngas and CO changes with time and/or process conditions are shown in Figure 1. During the first 80 hours of testing at baseline conditions (260°C, 2.1 MPa, 2 NI/g-cat/h) both the syngas and CO conversion increased with time reaching 85% and 90%, respectively. After that the catalyst started to deactivate, and at 224 hours on stream the syngas and CO conversions were 72% and 75%, respectively. After increasing gas space velocity to 3 NI/g-cat/h the conversion decreased as expected, and the catalyst continued to deactivate between 225 and 280 hours on stream. Between 280 and 334 hours the conversion was fairly stable (43-44% for both syngas and CO). After returning to the baseline conditions at 335 h, the conversions were about 60%, but the catalyst activity decreased with time and at the end of the run (384 h) the conversions were about 48%. The average loss in syngas conversion (catalyst deactivation rate) between 80 and 224 hours was 0.09%/hour, whereas the average conversion loss for the time period between 80 and 384 hours was 0.145%/hour. This shows that catalyst deactivation was faster during the latter portion of the test.

Figure 2 shows changes of carbon dioxide selectivity (defined as percent of CO converted to CO₂) with time. Carbon dioxide selectivity is a measure of the extent of water-gas-shift (WGS) reaction, and 50% selectivity represents the maximum possible value corresponding to complete conversion of water produced during hydrocarbon formation reaction. Carbon dioxide selectivity

increases quickly with time and reaches a stable value of about 49% at 20 h on stream. During testing at the baseline conditions the CO₂ selectivity remained stable even though the F-T activity decreased with time (decrease in syngas conversion). This was also observed at the end of the run when the syngas conversion was only about 48%, as well as during testing at higher gas space velocity (225-334 h on stream) at syngas conversion of about 43%. The extent of WGS activity remained high throughout the test, whereas F-T activity declined with time.

Various aspects of catalyst selectivity are shown in Figures 3 to 6. Methane selectivity, calculated as $100 \times (\text{moles of CO converted to CH}_4) / (\text{total moles of CO converted} - \text{moles of CO converted to CO}_2)$, decreased from about 4.5% to 2.2% during first 130 hours of testing (Figure 3). After that methane selectivity remained stable ($2.1 \pm 0.1\%$), regardless of changes in conversion level and/or process conditions.

Selectivity of C₅+ hydrocarbons (liquids and wax) was high throughout the entire test. C₅+ selectivity increased from about 77% to 86% during the first 130 hours of testing (Figure 4), and then remained stable ($85 \pm 1\%$) up to 384 h. Liquid and wax selectivity (fraction of C₅+ hydrocarbons among total hydrocarbons on carbon atom basis) was independent of conversion level (43-75% syngas conversion) and process conditions.

Olefin selectivities, expressed as: total olefin (alkene) content ($100 \times \text{linear alkenes} / (\text{linear alkenes} + \text{n-alkanes})$) and 2-alkene content ($100 \times \text{2-alkene} / (\text{1-alkene} + \text{2-alkene})$), as a function of carbon number are shown in Figures 5 and 6. Data shown in these figures were obtained by collecting all products (gaseous, liquid and wax) at different times on stream and analyzing them by gas chromatography. As can be seen in these two figures olefin selectivities (except for ethylene) are not markedly affected by changes in conversion level (due to catalyst deactivation or changes in gas space velocity). Products are primarily olefinic (high total olefin content) and the extent of olefin isomerization is low (low 2-olefin content). Ethylene selectivity is high and ranges from 62% (at 84 hours) to 85% at 328 hours, which may be the result of differences in conversion level. Ethylene is very reactive for secondary reactions, and its selectivity is favored by lower conversions. Total olefin content decreases slightly with increase in carbon number (from ~ 87% for C₃-C₄ hydrocarbons to ~68% at C₁₅) whereas the 2-olefin content increases from ~3% at C₄ to ~11% at C₁₅.

Conclusions

A spray dried precipitated iron F-T catalyst (100 Fe/5 Cu/4.2 K/11 SiO₂) synthesized at Hampton University was tested in a stirred tank slurry reactor for 384 hours. Catalyst selectivity was excellent (low methane and high C₅+ hydrocarbon selectivity). Initially, up to 80 h, the catalyst activity increased with time, but then started to decline. The average loss in syngas conversion was 3.48%/day (for the time period between 80 and 384 hours). Further modifications in the catalyst formulation and/or preparation procedure are needed to improve the catalyst stability, while maintaining high activity and selectivity to liquid and wax hydrocarbons.

Future Work

In collaboration with Hampton University we plan to synthesize spray dried catalysts by different methods, and evaluate their attrition properties and catalytic performance (activity, selectivity and stability) in slurry reactor tests at TAMU. Also, we'll continue to test selected iron based F-T catalysts prepared at Hampton University as a part of their on going research program supported by DOE. This will allow us to make a direct comparison of attrition properties and catalytic performance of catalysts synthesized at Hampton University and at TAMU under the same (similar) conditions.

The final goal is to develop catalysts with suitable attrition characteristics for use in slurry reactors for production of diesel and gasoline from coal-derived syngas. As a result of this study DOE may select the best catalyst(s) for further development (scale-up to a commercial scale).

Acknowledgements

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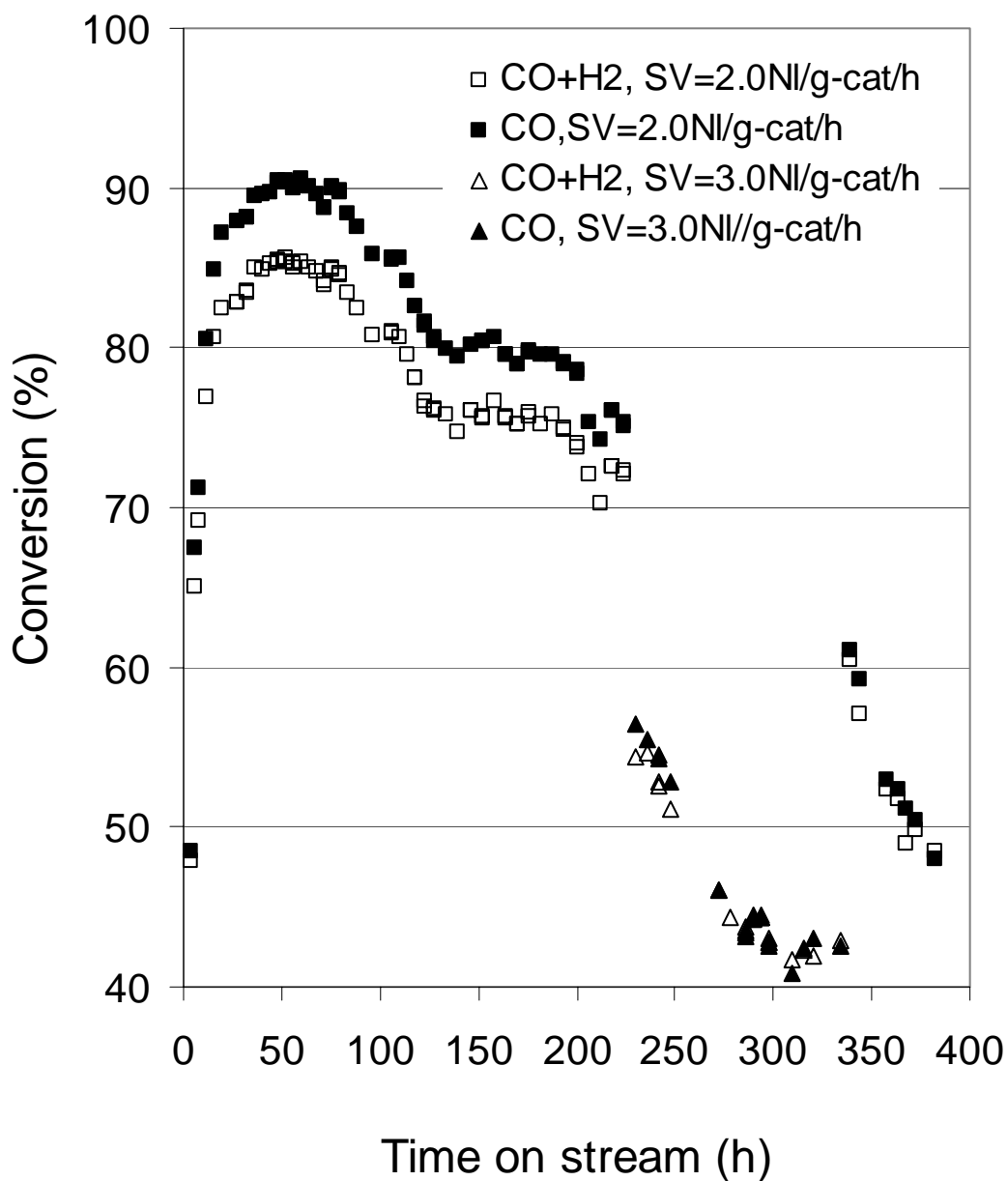


Figure 1. Effect of time-on-stream on conversion in test SB-2061
 (Reaction conditions: 260°C, 2.1 MPa, H₂/CO=0.67)

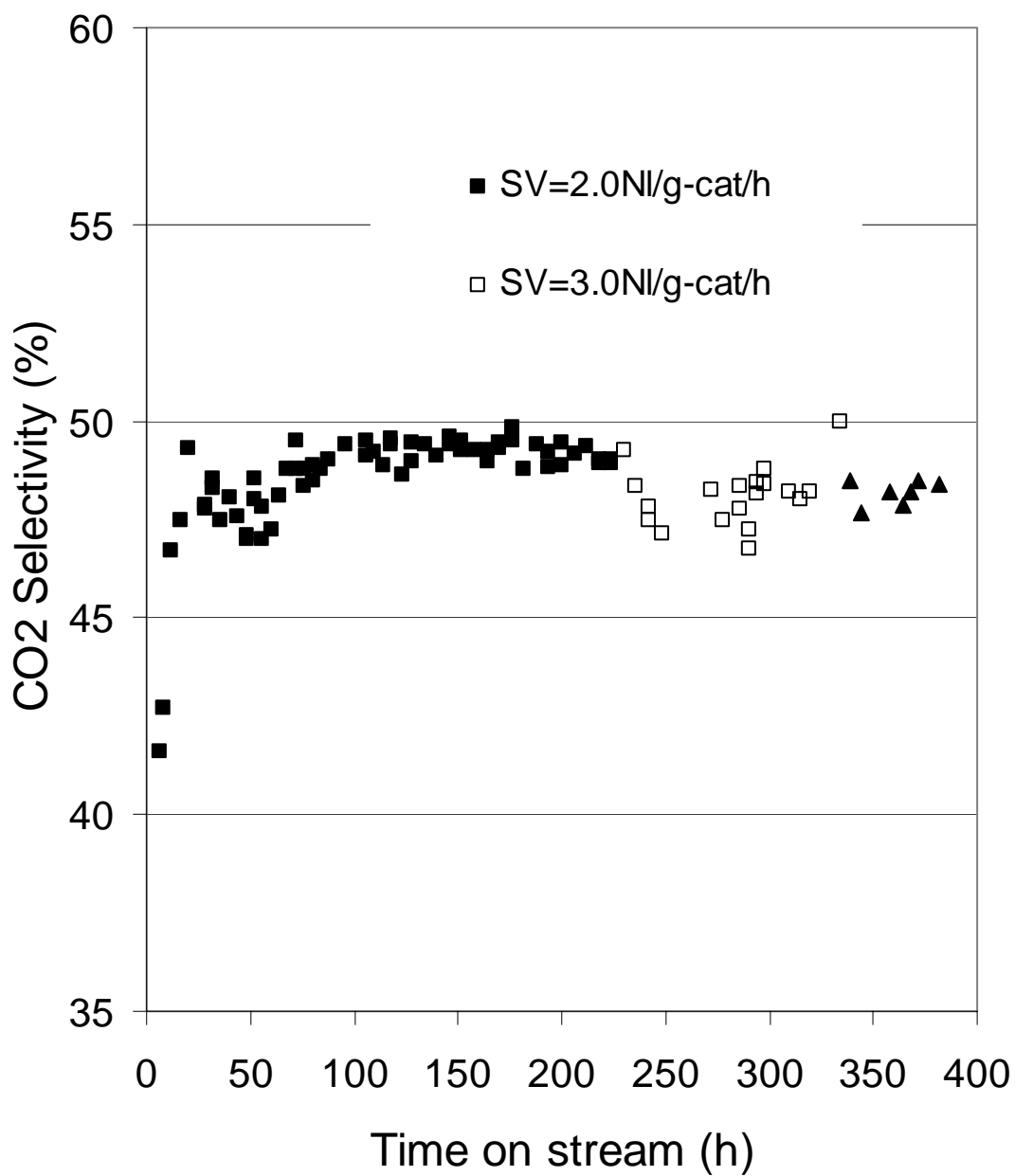


Figure 2. Effect of time-on-stream on CO₂ selectivity in test SB-2061 (Reaction conditions: 260°C, 2.1 MPa, H₂/CO=0.67)

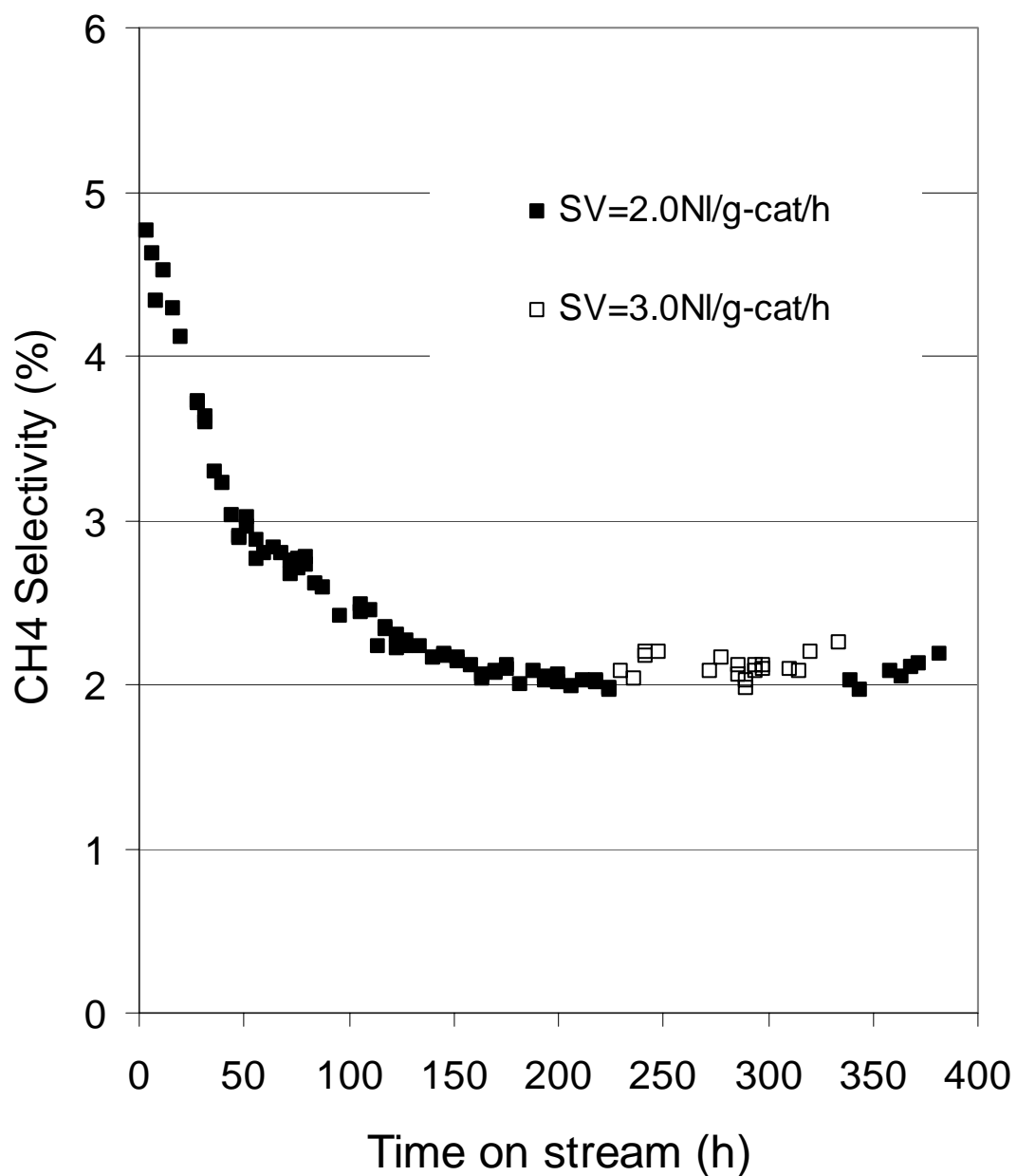


Figure 3. Effect of time-on-stream on CH₄ selectivity in test SB-2061 (Reaction conditions: 260°C, 2.1 MPa, H₂/CO=0.67)

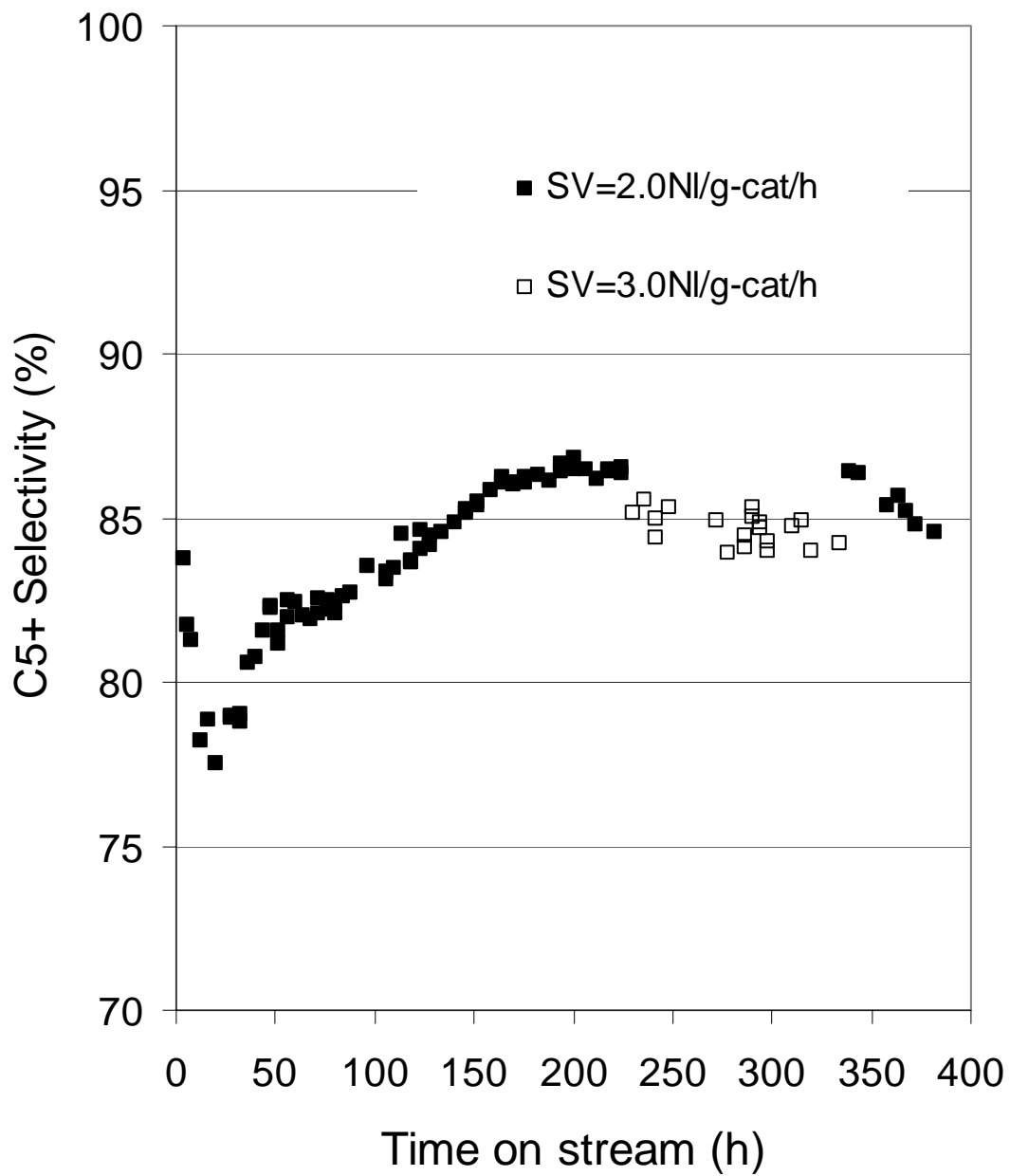


Figure 4. Effect of time-on-stream on C₅⁺ selectivity in test SB-2061 (Reaction conditions: 260°C, 2.1 MPa, H₂/CO=0.67)

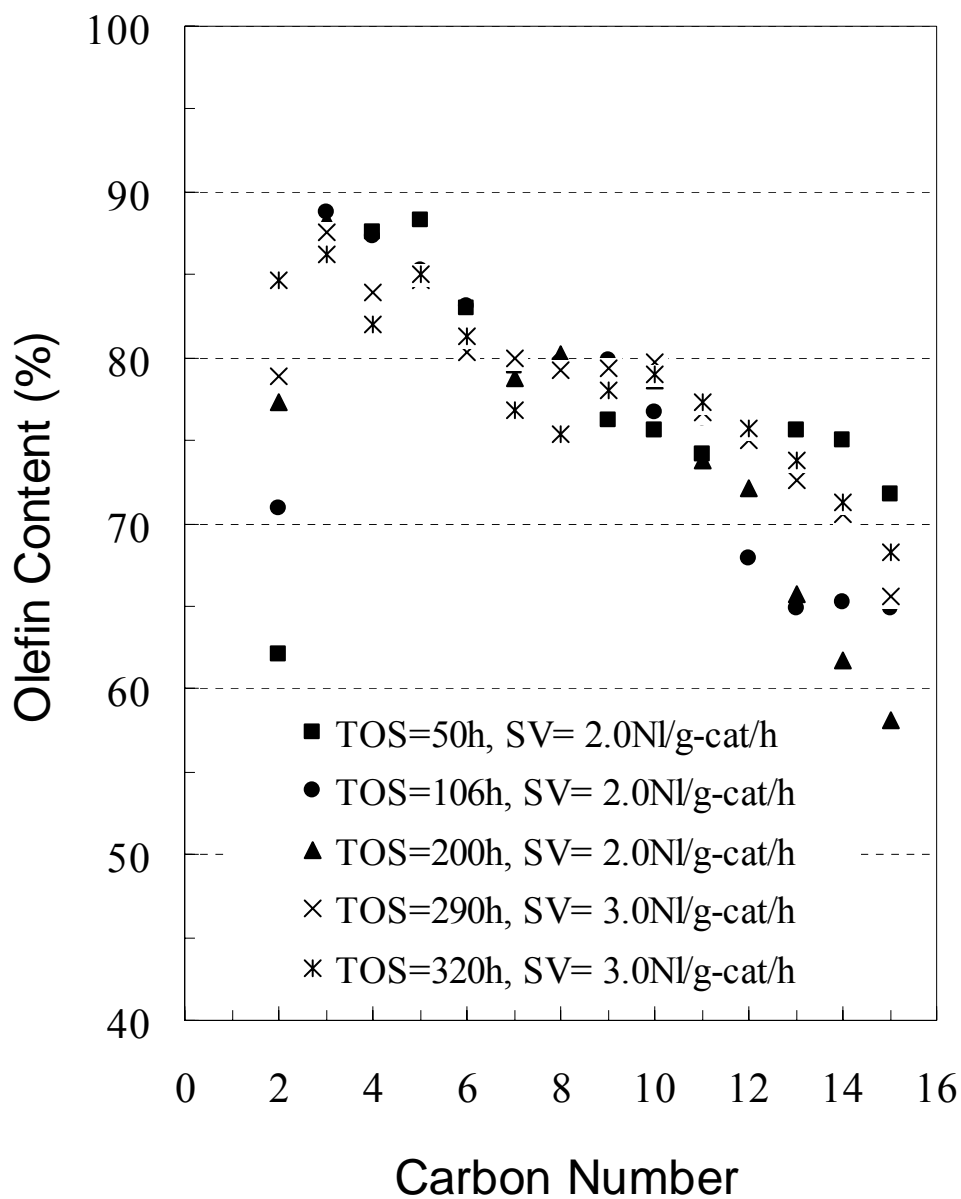


Figure 5. Olefin selectivity as a function of time and reaction conditions (Reaction conditions: 260°C, 2.1 MPa, H₂/CO=0.67)

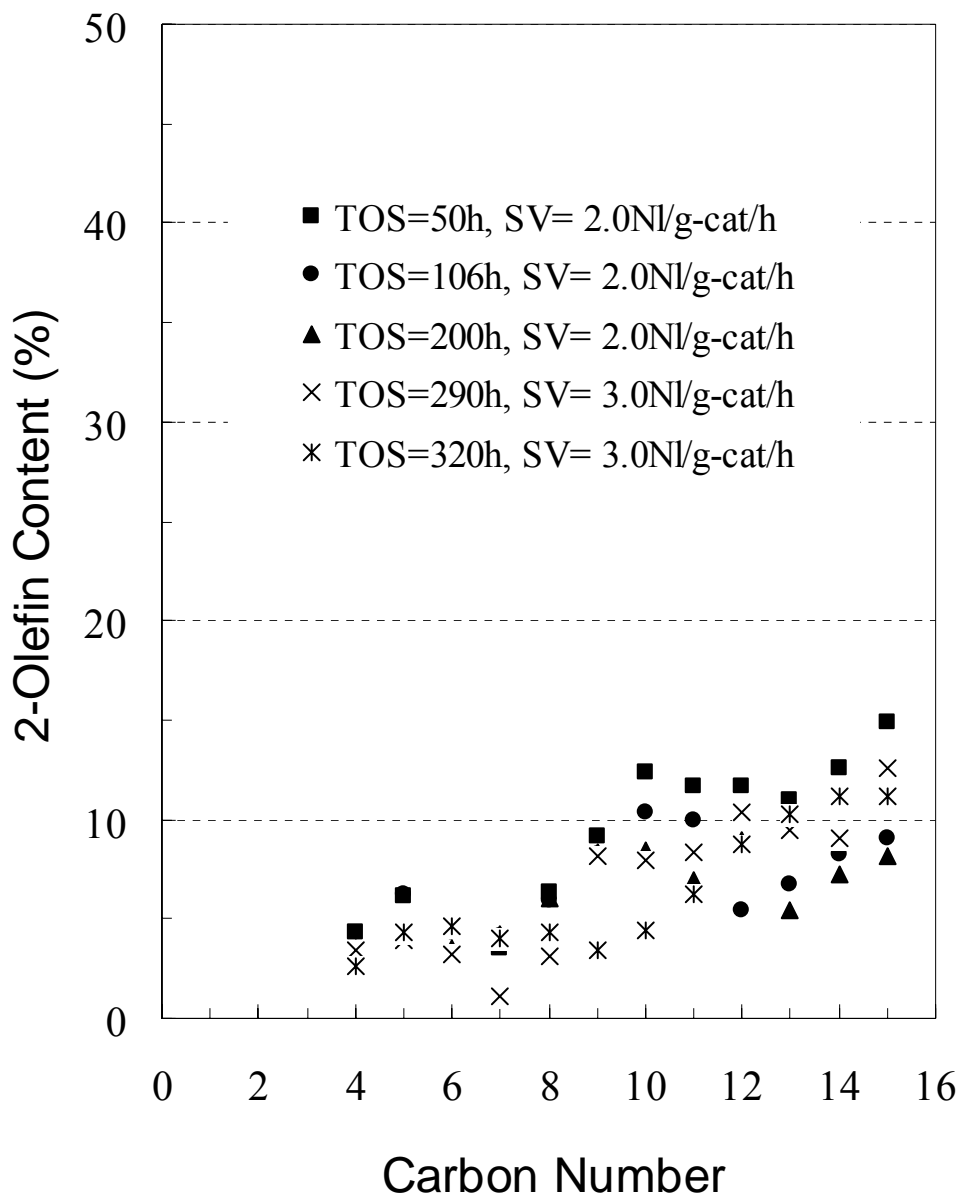


Figure 6. 2-Olefin selectivity as a function of time and reaction conditions
 (Reaction conditions: 260°C, 2.1 MPa, H₂/CO=0.67)