

Development of Precipitated Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
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I. EXECUTIVE SUMMARY

The work on Task 3. Testing of Previously Synthesized Catalysts was initiated in early October as scheduled. Two initial tests were not successful (runs SB-2764 and SB-3064). It took us a great deal of time and effort to overcome these problems, which included conducting a blank test (run SB-3184) and a test of commercial Ruhrchemie catalyst (run SB-3254). Finally, a successful test of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO₂ (run SB-3354) was completed using a different slurry medium (Ethylflo 164 oil). Low activities in unsuccessful tests SB-2764 and SB-3064 may be due to catalyst poisoning by impurities in the initial slurry medium (purified n-octacosane from Humphrey Chemical Co.).

Following the reduction with H₂ at 250°C, 0.8 MPa (100 psig), 4,000 cc/min for 4 h, the catalyst in run SB- 3354 was first tested at 260°C, 1.48 MPa (200 psig), 1.8 NI/g-cat/h and synthesis gas with molar feed ratio of 0.67 (H₂/CO = 2/3). During the test, which lasted about 400 h, the catalyst was also tested at gas space velocities of 1.6 NI/g-cat/h (120-303 h on stream) and 1.2 NI/g-cat/h (308 - 408 h on stream). The syngas conversion varied between 68 and 77%, and was about 5-10% (relative difference) lower than that observed in run SB-1931 with the same catalyst. The latter was the most successful run during our previous DOE Contract DE-AC22-89PC89868. Methane selectivity in the current test was about 10-20% higher than in the run SB-1931, which is within experimental errors. The ethane and ethylene selectivities, as well as total C₁+C₂ mol% selectivity, were similar to those in the run SB-1931. Overall this was a successful reproducibility test both in terms of activity and selectivity behavior.

Also, we have initiated work on Task 4 (Reproducibility of Catalyst Preparation), Task 5 (The Effect of Source of Potassium and Basic Oxide Promoters) and Task 8 (Catalyst Characterization). During the reporting period we have completed synthesis of 90 g of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO₂, and initiated synthesis of about 100 g of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO₂.

II. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

II. 1 Task 3. Testing of Previously Synthesized Catalysts

The work on Task 3. Testing of Previously Synthesized Catalysts was initiated in early October as scheduled. Two initial tests were not successful (runs SB-2764 and SB-3064). It took us a great deal of time and effort to overcome these problems, which included conducting a blank test (run SB-3184) and a test of commercial Ruhrchemie catalyst (run SB-3254). Finally, a successful test (run SB-3354) was completed using a new slurry medium. The details of each tests are reported in the following sections, along with descriptions of problems encountered and attempts to alleviate them.

II. 1. 1 Run SB-2764 with 100 Fe/5 Cu/6 K/24 SiO₂ Catalyst

The first stirred tank slurry reactor test, designated run SB-2764, with 100 Fe/5 Cu/6 K/24 SiO₂ catalyst was initiated in early October. The objective of this run was to check reproducibility of results obtained during the previous DOE Contract DE-AC22-89PC89868 in a slurry reactor test SB-1931, with the same catalyst.

About 11 g of catalyst (< 270 mesh in size) and 310 g of octacosane (as slurry medium) were loaded for the test. The catalyst was reduced with H₂ at 250°C, 0.8 MPa (100 psig), 7,500 cc/min for 4 h, 1,200 rpm stirrer speed. At the end of the reduction, a slurry sample of 23 g was withdrawn from the reactor through a dip tube. The catalyst was then tested at 260°C, 200 psig, 1.8 NI/g-cat/h and synthesis gas molar feed ratio of 0.67 (H₂/CO = 0.67). After reaching the process condition, about 25 g of wax was withdrawn through a porous metal filter. During the first 12 h on stream, the (H₂+CO) conversion decreased from 49 to 43 %, whereas the methane selectivity was about 20 mol% (Figure 1). These results were significantly different from those obtained in Run SB-1931 (75 % (H₂+CO) conversion, 3 mol% methane selectivity). At 13 h on stream, the Autoclave reactor head temperature was lowered from 240 to 215°C (consequently, the carbonyl trap and the inlet gas feed line temperatures also decreased because they were

heated by the same heating coil used for the Autoclave reactor head), in an attempt to suppress high methane formation. As a result of this, the syngas conversion decreased to about 17 %, whereas the methane selectivity was about 5 %. Similar behavior was encountered before in our Laboratory, due to a loss of slurry liquid inside the Autoclave reactor and deposition of catalyst onto the Autoclave reactor wall. Therefore, at 18 h on stream, about 155 g (200 cc) of Ethylflo oil (C₃₀) was added to the reactor in order to raise the slurry level in the reactor and wash out catalyst on the reactor wall. However, this did not result in the improvement of catalyst activity. Between 20 and 22 h on stream, the reactor was purged with He, its temperature lowered to 235°C, then another 170 g of Ethylflo oil was added to the Autoclave reactor. The excess 290 g of liquid was then withdrawn from the reactor through a filter, and the FT synthesis resumed at 27 h on stream. The conversion remained at about 17 %, with methane selectivity at about 9 mol %. At 64 h on stream, the temperature of the Autoclave reactor head was increased back to 240°C (as well as the carbonyl trap and inlet line temperatures). The syngas conversion then increased to 40 % and methane selectivity to 21 mol%. This demonstrated that temperatures of the reactor head, the inlet feed line and the carbonyl trap had significant effect on the conversion during the test, indicating that a portion of the catalyst was outside the reactor. The test was terminated at 86 h on stream.

After the test we attempted to determine possible causes for low catalyst activity and high methane selectivity. The amount of catalyst remaining in the slurry was determined to be about 9.6 g, by burning two slurry samples in crucibles. Another 0.8 g of catalyst was estimated to be in the slurry sample withdrawn from the reactor after the reduction. Therefore, the catalyst recovery was about 95%, which excluded the loss of catalyst as the reason for low activity.

Several days after the Run SB-2764 was completed, the same catalyst and the same hydrogen gas cylinder were employed in a successful fixed bed reactor test. Therefore, the catalyst and the H₂ gas used during the reduction in Run SB-2764 were not the reason for low catalyst activity.

Small amounts of catalyst were found on the surface of the bearing and other parts of the reactor head, and each part was cleaned with Varsol (a mineral oil) before the head was reassembled. The inlet feed line and the carbonyl trap were also examined. The inlet line was replaced with new fittings and tubing and the carbonyl trap was cleaned and repacked with fresh activated alumina. Also, a separate heating tape was added for the carbonyl trap, so that the temperature of the carbonyl trap and the Autoclave reactor head could be regulated independently in the future tests.

II. 1. 2 Run SB-3064 with 100 Fe/5 Cu/6 K/24 SiO₂ Catalyst

After cleaning and modifying the reactor set up, the second slurry reactor test, designated run SB-3064, was conducted. About 10 g of 100 Fe/5 Cu/6 K/24 SiO₂ catalyst (< 270 mesh in size) and 310 g of normal octacosane (as slurry medium) were loaded for the test. The catalyst was reduced with H₂ at 250°C, 0.8 MPa (100 psig), 7,500 cc/min for 4 h, 1,200 rpm stirrer speed, and then tested at 260°C, 1.48 MPa (200 psig), 1.8 NI/g-cat/h and synthesis gas molar feed ratio of 0.67 (H₂/CO = 0.67). During the first 48 hours of testing the syngas conversion was very low, ~ 8 %, and methane selectivity was between 8 and 11.4 % (Figure 2). Upon increasing the reaction temperature to 280°C, the conversion increased to about 14 %, and methane selectivity was about 9 %. The test was terminated after 54 h on stream, due to unusually low catalyst activity.

After the test, the syngas from the cylinder used in runs SB-2764 and SB-3064, was directed through the gas feed section (via gas purification traps and the carbonyl trap) to a fixed bed reactor, in which the Ruhrchemie catalyst was tested. The (H₂ + CO) conversion in the fixed bed reactor was about 52%, before the introduction of the feed gas from the slurry B reactor system. After a brief interruption of the fixed bed test to switch to the feed gas from the slurry B reactor, the FT synthesis was resumed and the (H₂ + CO) conversion remained at about 50% during 48 h of testing. This experiment eliminated a possibility that the syngas and the

slurry B reactor feed section were responsible for low activities in runs SB-2764 and SB-3064 (due to poisoning of the catalyst).

During the run SB-3064 we verified that the syngas feed was not bypassing the reactor, due to a blockage in the gas feed lines. After the test the inlet gas feed line inside the reactor was checked for leaks. A leak in the gas feed line inside the reactor and above the slurry level would lead to bypassing of the catalyst and thus low conversions, but no leaks were found. The inlet gas feed lines were again thoroughly cleaned, as well as the Autoclave reactor internals including the interior of a hollow stirrer shaft. Also, the inlet gas feed line inside the reactor was replaced with a new one.

II. 1. 3 Run SB-3184 - Blank Reactor Test

A blank test (reactor filled with liquid, but without any catalyst) was conducted (SB-3184) at 200 psig, 260 - 310°C, $H_2/CO = 0.67$ at 150 cm^3/min , while maintaining the exit line temperature at 260 - 270°C, the carbonyl trap temperature at 310°C, and the reactor head temperature at 210 - 260°C. The system did not exhibit any Fischer-Tropsch synthesis activity at a reaction temperature of 260°C. However, the ($H_2 + CO$) conversion was about 2 % at 285°C, and 8.5 % at 310°C. It was concluded from this test that under the standard reaction conditions the reactor system does not exhibit any FT activity.

II. 1. 4 Run SB-3254 with Ruhrchemie LP 33/81 Catalyst (100 Fe/5 Cu/4.2 K/24 SiO₂)

This test was conducted with the objective to test the reactor system operability after the two unsuccessful runs with the 100 Fe/5 Cu/6 K/24 SiO₂ catalyst. For this purpose we used the Ruhrchemie catalyst LP 33/81, which has been extensively tested in our Laboratory, and Ethylflo 164 oil (a hydrogenated 1-decene homopolymer liquid - C₃₀, obtained from Ethyl Co.) as the initial slurry medium. The catalyst (5.0 g, < 270 mesh in size) was reduced with H₂ at 250°C, 0.8 MPa (100 psig), 4.000 cc/min for 4 h. It was then tested at 260°C, 1.48 MPa (200 psig), 1.8 NI/g-cat/h and feed ratio $H_2/CO = 0.67$, i.e. at the same process conditions used in runs SB-2764

and SB-3064. As shown in Figure 3, during 48 hours of testing the syngas conversion was stable 65 - 66 %, whereas methane selectivity varied between 3.2 and 3.6 mol %. These results are consistent with prior results with this catalyst, and it was concluded that the slurry reactor system B is in a good condition for further testing of catalysts synthesized in our laboratory.

Comments on the Possible Causes of Unsuccessful Tests

After two consecutive bad runs (SB-2764 and SB-3064), we have tested many possibilities of why things went wrong. Based on the results reported here, we could eliminate the following factors: the catalyst itself (successfully tested in a separate fixed bed run), feed gases (hydrogen for reduction and syngas), the reactor apparatus and the testing procedures. This led us to examine the possibility of catalyst poisoning by n-octacosane (the initial slurry medium). We have employed n-octacosane as initial slurry medium in many successful slurry reactor tests since 1989. Before loading to the reactor, the n-octacosane (99 % purity, The Humphrey Chemical Company, North Haven, CT) was extracted with tetrahydrofuran (THF) to remove the impurity bromotetradecane, since bromine is known to be the catalyst poison. A sample of slurry from run SB-3064 was sent Galbraith Laboratories, Inc. (Knoxville, TN) for bromine and sulfur trace analysis. Their results indicate the presence of both bromine (16 ppm) and sulfur (14 ppm) in this sample. Whereas the presence of the former was anticipated, the presence of the latter was not. As far as we know, sulfur compounds are not used in preparation of n-octacosane. These findings will be investigated further, and these results suggest that low activity in run SB-3064 may be due to catalyst poisoning by impurities in the initial slurry medium.

II. 1.5 Run SB-3354 with 100 Fe/5 Cu/6 K/24 SiO₂ Catalyst

After the completion of successful run SB-3254 with the Ruhrchemie catalyst, we resumed our testing of the 100 Fe/5 Cu/6 K/24 SiO₂ catalyst (run SB-3354). About 7.0 g of catalyst (< 270 mesh in size) was loaded for the test. As in the run SB-3254, Ethylflo 164 oil was used as the initial slurry medium, replacing n-octacosane used in runs SB-2764 and SB-

3064. Following the reduction with H₂ at 250°C, 0.8 MPa (100 psig), 4,000 cc/min for 4 h, the catalyst was first tested at 260°C, 1.48 MPa (200 psig), 1.8 NI/g-cat/h and synthesis gas with molar feed ratio of 0.67 (H₂/CO = 2/3). Changes in the catalyst activity (in terms of CO, H₂+CO conversions and usage ratio) and selectivity (CH₄, C₂H₄, C₂H₆, and C₁ + C₂ hydrocarbons) are shown in Figures 4 to 6, as a function of space velocity and time on stream (open symbols). Corresponding results from the earlier test SB-1931 (closed symbols) are also shown in these figures for the purpose of comparison. During the first 116 hours of testing at the initial process conditions, the CO conversion (Figure 4a) decreased from 83% (22 h) to 74% (116 h), whereas the syngas conversion (Figure 4b) decreased from 78% (22 h) to 70% (116 h). After that, the gas space velocity was decreased to 1.6 NI/g-cat/h, and the catalyst activity was fairly stable during the next 200 h of testing. The CO conversion varied between 74 and 79%, and the syngas conversion between 70 and 75% during this period of time. Variations in activity during this period were partly caused by variations in the reaction pressure (200 - 210 psig). The (H₂/CO) usage ratio, a measure of the water-gas shift activity, was fairly stable at about 0.57. During the last 100 h of testing at the gas space velocity of 1.2 NI/g-cat/h, the CO conversion varied between 79 and 82%, whereas the syngas conversion was between 74 and 77%.

Low molecular weight hydrocarbon selectivities increased markedly with time during the first 100 h of testing, and then at a much lower rate. For example methane selectivity increased from 2 mol% to 3% during the first 100 h of testing, and then from 3 to 3.3% during the next 300 h of testing (Figure 5b). Similar trends were observed with ethylene selectivity: an increase from 1 to 1.8% during the first 100 h followed by a period of fairly stable selectivity (Figure 6a). Ethane selectivity increased from 1% to 1.3% during the first 100 h, and then again to about 1.4% between 300 and 400 h on stream (Figure 6b).

Comparison of Data from Runs SB-1931 and SB-3354

The observed conversions were 5-10% (relative difference) lower than the corresponding ones in Run SB-1931 (Figure 4b). The catalyst deactivation was more rapid in the present test

than in run SB-1931, and the difference in FT activity was the most pronounced during testing at $SV = 1.2 \text{ NI/g-cat/h}$.

Methane selectivity in the current test was about 10-20% higher than in the run SB-1931. The ethane and ethylene selectivities were similar to those in the run SB-1931 (Figures 6a and 6b). The total C_1+C_2 mol% selectivity (Figure 6c) was similar in both tests (4-7%, during the first 400 h on stream).

At the present time, it is not clear whether the observed differences in activity were influenced by the use of different initial slurry liquids and/or differences in the initial process conditions ($SV = 1.8 \text{ NI/g-cat/h}$ in SB-3354 vs. $SV = 2.2 \text{ NI/g-cat/h}$ in SB-1931). We plan to conduct another test with this catalyst, in which some of these questions may be resolved.

II. 1. 6 Run SA-3404 - Blank Reactor Test

In preparation for the catalyst testing in our slurry reactor system A (SA) a blank test, designate run SA-3404, was conducted at 1.48 MPa (200 psig), 250 - 260°C, $H_2/CO = 0.67$ at $175 \text{ cm}^3/\text{min}$. The exit line temperatures were maintained at 260 - 270°C, and the carbonyl trap temperature at 230-300°C. Significant amount of FT activity was observed when the carbonyl trap was at 300°C (11% syngas conversion), but no activity was observed when this temperature was lowered to 230°C. After cleaning and repacking of alumina beads in the trap we did not observe any FT activity at the carbonyl trap temperature of 280°C. Therefore, at typical operating conditions the reactor does not exhibit any FT activity.

II. 2 Task 4. Reproducibility of Catalyst Preparation

The objective of this task is to demonstrate reproducibility of catalyst preparation procedure on a laboratory scale. During the reporting period we have completed synthesis of 90 g of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO₂, and initiated synthesis of about 100 g of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO₂. The synthesis of larger quantities (250 -350 g) of these two catalysts is planned for the next quarter.

II. 2 Task 5. The Effect Of Source of Potassium and Basic Oxide Promoters

The objective of this task is to investigate effects of two different sources of potassium and addition of another promoter (CaO) on the catalyst performance. We are in the process of reviewing literature on different synthesis procedure and catalyst compositions employed in previous studies. Upon completion of the literature review we'll synthesize six new catalysts, and then test them in our fixed bed reactors.

II. 2 Task 8. Catalyst Characterization

The work on this task was initiated, as scheduled, in December. The BET surface area of the new catalyst (100 Fe/5 Cu/6 K/24 SiO₂) is 228 m²/g, which compares favorably with the BET surface area (222 m²/g) of the catalyst synthesized during the previous DOE Contract (DE-AC22-89PC89868). The X-ray diffraction patterns of as-prepared and calcined samples of this catalyst show low crystallinity (nearly amorphous structure), which was also observed in the previous contract.

Plans for the Next Quarter

During the next quarter we plan to: (a) continue with testing of catalysts 100 Fe/5 Cu/6 K/24 SiO₂ and 100 Fe/3 Cu/4 K/16 SiO₂ in slurry reactors (Task 3); (b) synthesize these two catalysts in amounts needed for all future tests, and the catalysts containing CaO as promoter (Tasks 4 and 5); (c) characterize the newly synthesized catalysts (Task 8).

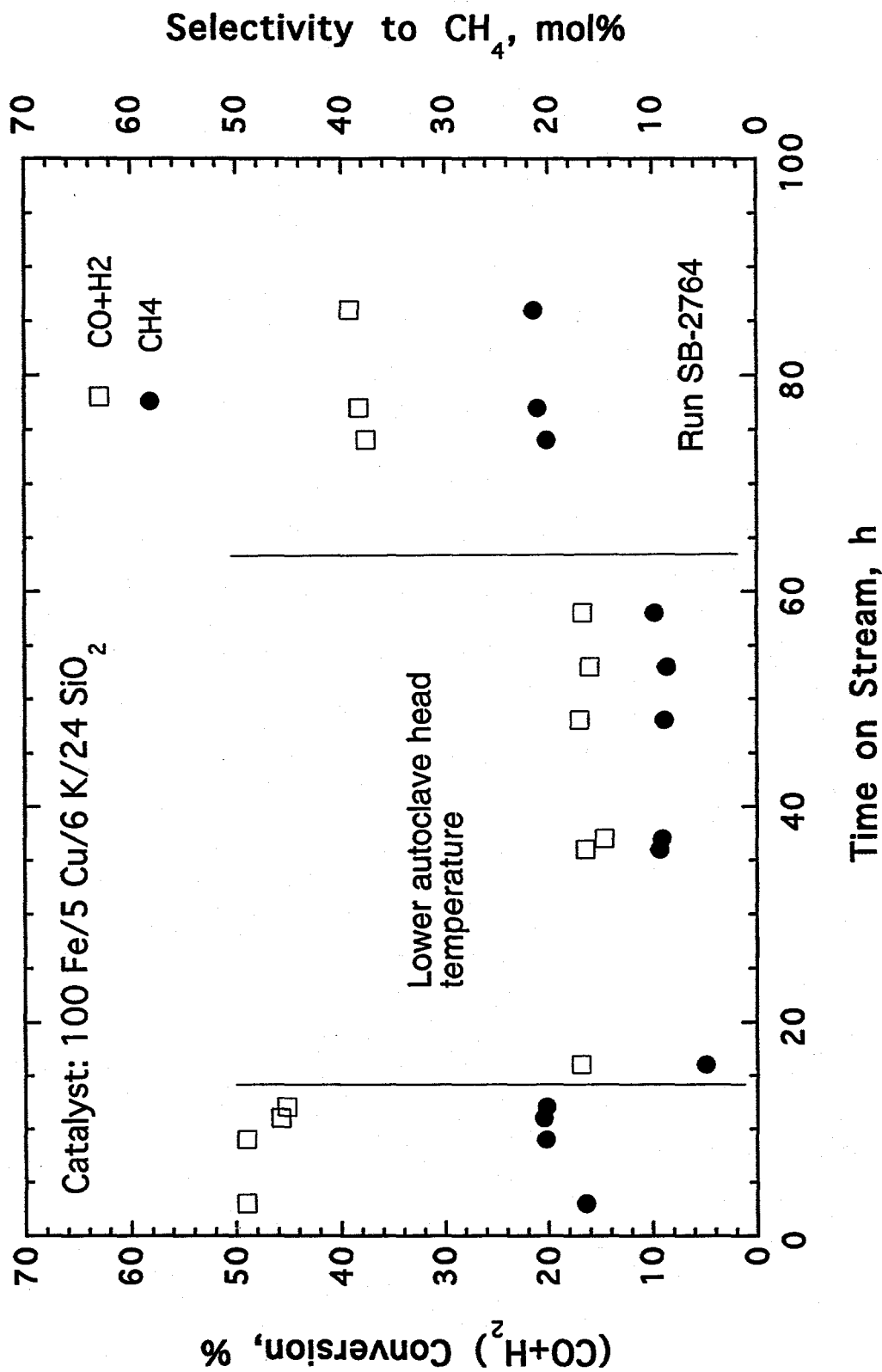


Figure 1. Change in (CO+H₂) conversion and CH₄ selectivity with time on stream in Run SB-2764 (T = 260 C, P = 1.48 MPa, SV = 1.8 Ni/g-cat/h, H₂/CO = 0.67).

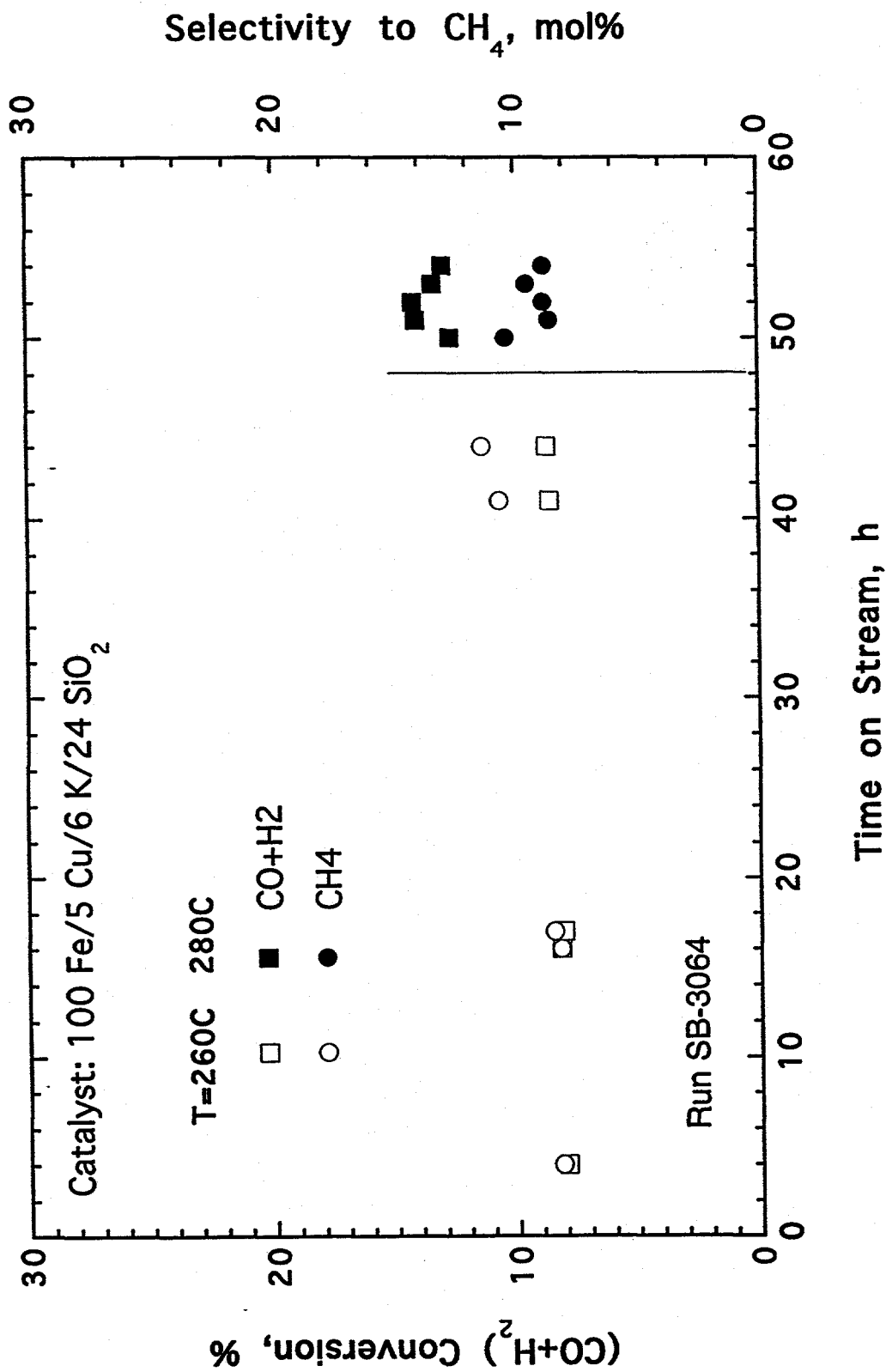


Figure 2. Change in (CO+H₂) conversion and CH₄ selectivity with time on stream in Run SB-3064 (P = 1.48 MPa, SV = 1.8 Ni/g-cat/h, H₂/CO = 0.67).

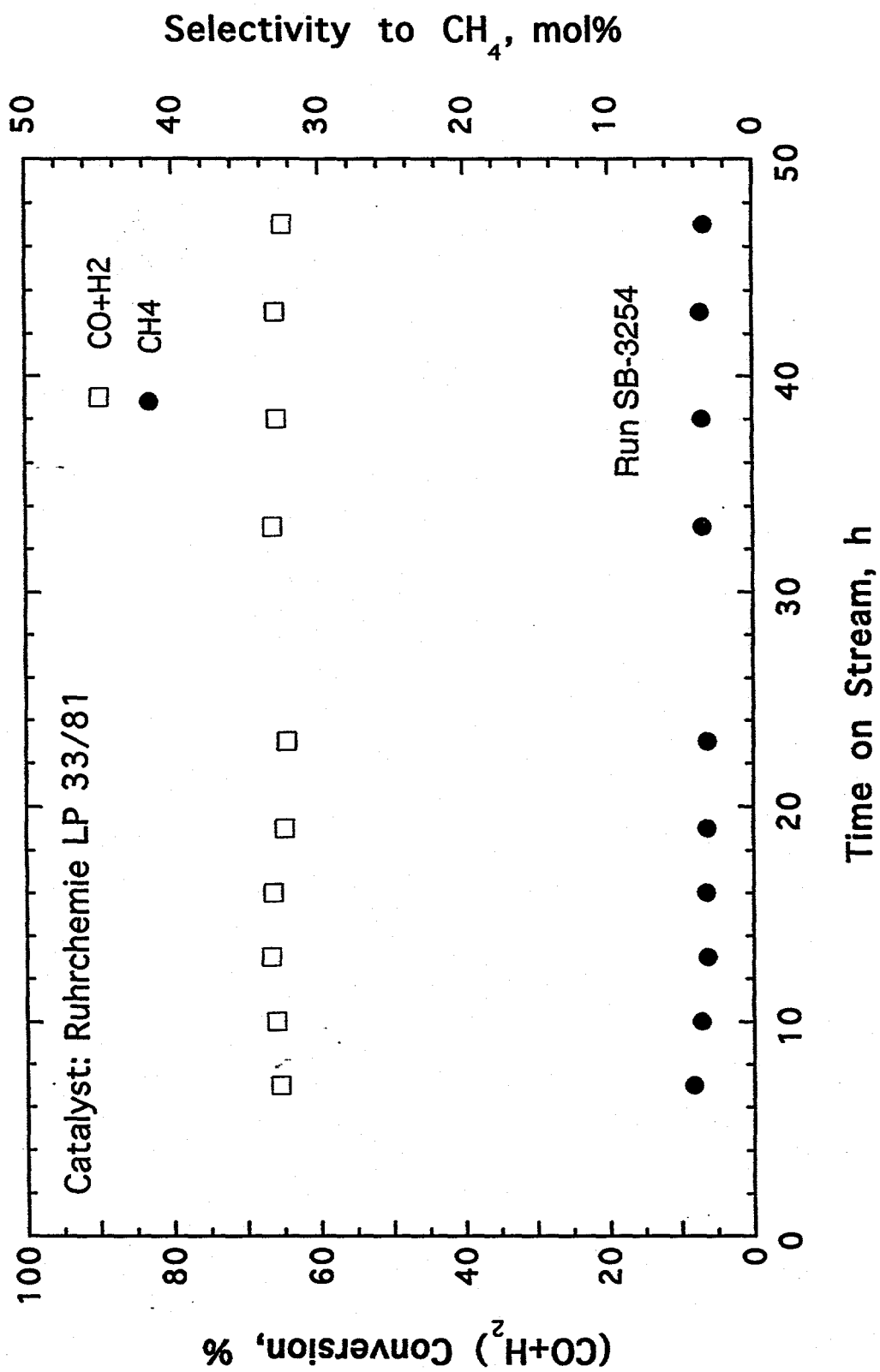


Figure 3. Change in (CO+H₂) conversion and CH₄ selectivity with time on stream in Run SB-3254 (T = 260 C, P = 1.48 MPa, SV = 1.8 NI/g-cat/h, H₂/CO = 0.67).

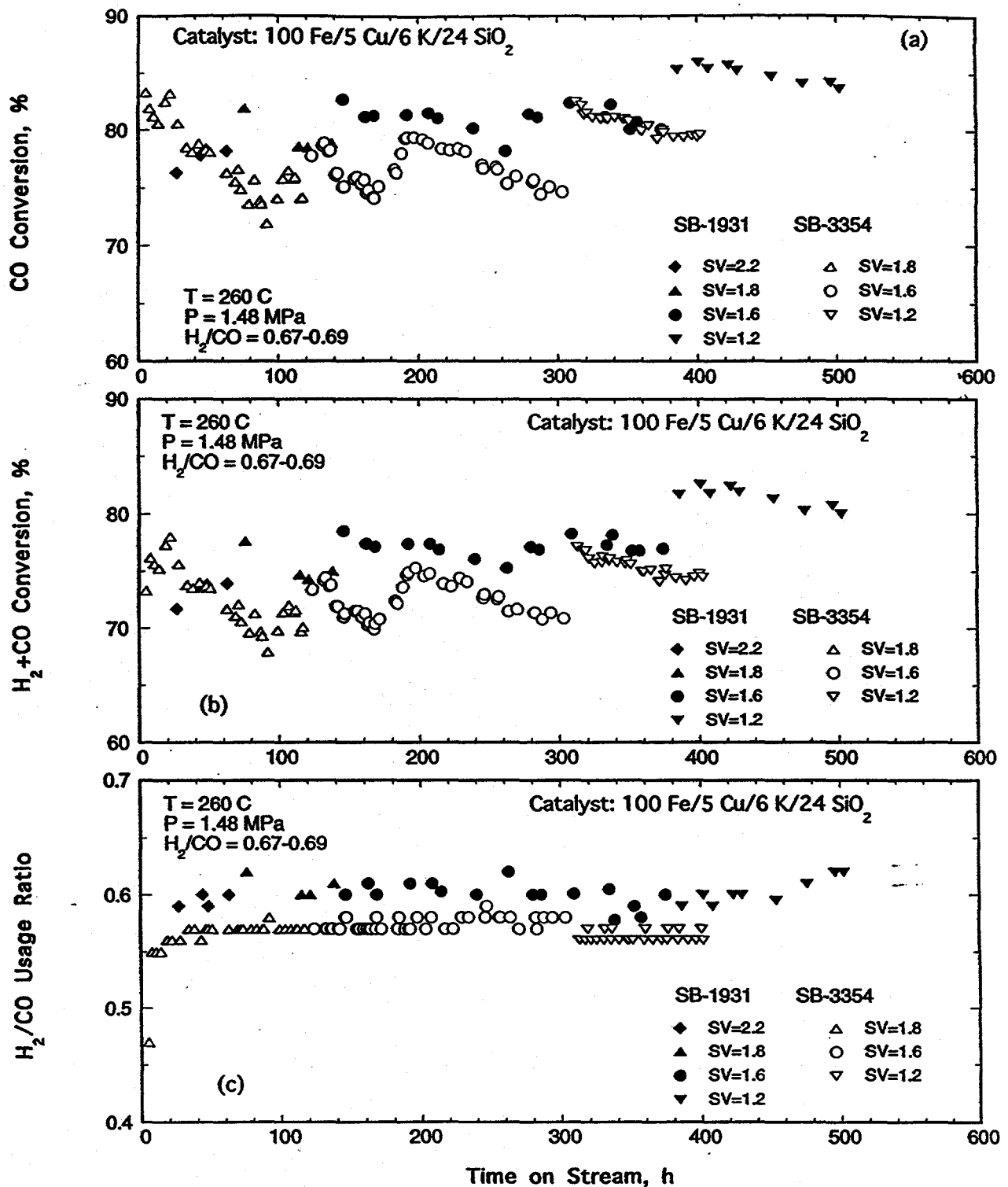


Figure 4. Variation in (a) CO conversion, (b) (H₂+CO) conversion and (c) usage ratio with time on stream in run SB-3354.

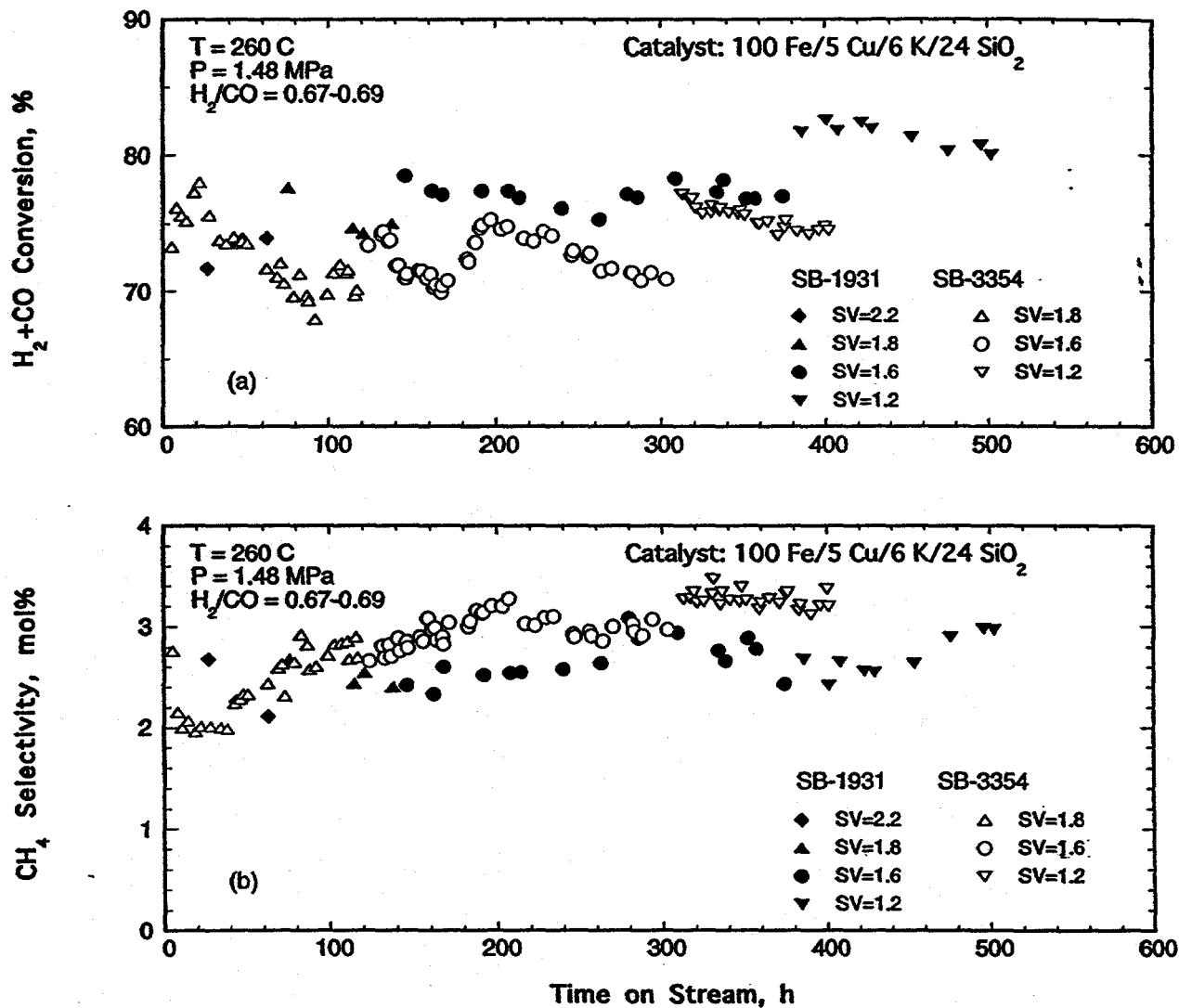


Figure 5. Variation in (a) (H₂+CO) conversion and (b) methane selectivity with time on stream in run SB-3354.

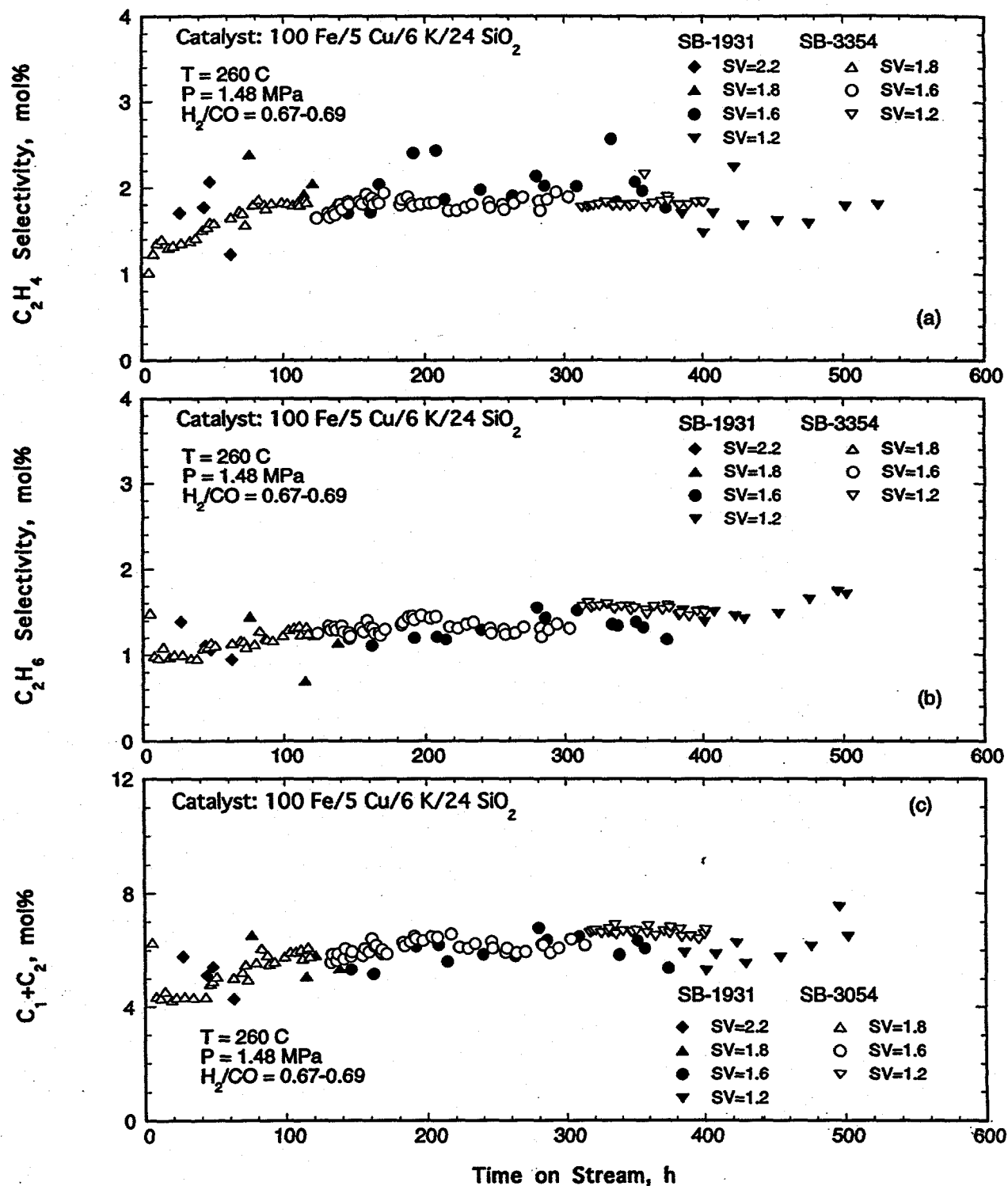


Figure 6. Variation in (a) ethene, (b) ethane, and (c) (C₁+C₂) selectivity with time on stream in run SB-3354.