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Development of Precipitated Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
for the Period 1 April 1995 – 30 June 1995

Texas Engineering Experiment Station Project 32525-44580

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I. EXECUTIVE SUMMARY

The following accomplishments were made on Task 4. Reproducibility of Catalyst Preparation: (1) We synthesized another batch of catalyst B with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2, in the amount of 405 g (S-5624-5); (2) Fixed bed reactor tests of catalyst C (100 Fe/3 Cu/4 K/16 SiO2) from batch 4 (S-3416-4) and catalyst B from batch 3 (S-5624-3) were completed (runs FA-1605 and FB-1715); and (3) Stirred tank slurry reactor tests of these two catalysts were completed (run SB-1295 with catalyst B from batch 3, and run SA-1665 with catalyst C from batch 4). Performance of catalysts from new batches (activity, selectivity and deactivation rates) was similar to that of catalysts from the original batch (synthesized during DOE Contract DE-AC22-89PC89868). Thus, another major objective of the present contract, demonstration of reproducibility of catalyst preparation procedure and performance, has been accomplished. We plan to conduct another slurry reactor test of catalyst C during the next quarter, to verify reproducibility of catalyst performance of batch 4 catalyst.

Six catalysts (four containing CaO as a promoter, and two using potassium silicate solution as the source of potassium promoter) were synthesized for future testing under Task 5. The Effect of Source of Potassium and Basic Oxide Promoter. Four of the synthesized catalysts containing CaO promoter were tested in a fixed bed reactor to determine their activity and selectivity during Fischer-Tropsch synthesis. It was found that addition of small amounts of CaO promoter results in similar performance as that of baseline catalysts, whereas addition of a larger amount of CaO promoter results in lower activity. The latter is probably due to partial pore blocking by CaO resulting in decrease of total surface area and pore volume of the catalyst.

Also, we completed characterization of all synthesized catalysts by atomic absorption, and BET surface area and pore size distribution measurements (Task 8. Catalyst Characterization).

II. OBJECTIVES AND SCOPE OF WORK

The overall contract objectives are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron Fischer-Tropsch catalysts synthesized at Texas A&M University (TAMU) during the DOE Contract DE-AC22-89PC89868; (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst synthesis; (3) investigate performance of catalysts in a small scale bubble column slurry reactor, and (4) investigate feasibility of producing catalysts on a large scale in collaboration with a catalyst manufacturer. In order to achieve these objectives the work is divided into a number of tasks, which are described below together with the time schedule for their execution.

Task 1. Project Work Plan (April 1-April 30, 1994)

The objectives of this task are: (1) Prepare in detail all activities which shall be performed for the successful completion of the work for the entire duration of the contract; and (2) Provide a project work chart showing the key personnel/groups planned for each task, and the percentage of their time to be devoted to individual tasks.

Task 2. Engineering, Modification and Training of New Personnel (April 1-September 30, 1994)

The objective of this task is to perform the engineering design, procurement of new equipment, installation of the instruments and auxiliary gas supply lines and to provide training for new personnel prior to catalyst testing in laboratory reactors.

Task 3. Testing of Previously Synthesized Catalysts (October 1, 1994 - March 31, 1995)

The purpose of this task is to verify reproducibility of results obtained previously at TAMU with catalysts designated B (100 Fe/5 Cu/6 K/24 SiO_2) and C (100 Fe/3 Cu/4 K/16 SiO_2). The catalysts from the same preparation batch shall be used, and the same pretreatment and process conditions shall be employed as in the previous slurry reactor tests of these two catalysts.

Task 4. Reproducibility of Catalyst Preparation (October 1, 1994 - September 30, 1995)

The objective of this task is to demonstrate reproducibility of catalyst preparation procedure on a laboratory scale. Catalysts B and C will be synthesized following procedures developed at TAMU. Catalysts with satisfactory physico-chemical properties will be initially tested in a fixed bed reactor for screening purposes (5 day tests). Following this the two catalysts will be tested in a stirred tank slurry reactor (STSR) using standard pretreatment and process conditions. The activity, selectivity, deactivation behavior of these new catalyst batches will be compared to that of the catalysts from the original (existing) batches.

Task 5. The Effect of Source of Potassium and Basic Oxide Promoter (October 1, 1994 - December 31, 1995)

The objective of this task is to determine effects of two different sources of potassium and addition of another promoter on the catalyst performance. Catalysts B and C will be synthesized using potassium silicate solution as the source of potassium promoter, and performance of these catalysts will be compared with that of catalysts synthesized using our standard procedure (i.e. using potassium bicarbonate as the source of potassium promoter).

The effect of CaO promotion on performance of catalysts B and C (two levels of promotion per catalyst) shall be investigated. Synthesized catalysts will be tested first in a fixed bed reactor, and if the satisfactory results are obtained the most promising catalyst formulations will be tested in the STSR.

Task 6. Pretreatment Effect Research (October 1, 1995 - November 30, 1996)

The effect of four different pretreatment procedures, in addition to the baseline procedure, on the performance of catalyst B (or C) will be studied in a STSR. In addition to STSR tests, the pretreatment effects will be studied by thermogravimetric analysis (TGA) , differential thermal analysis (DTA) and temperature programmed reduction (TPR). Iron phases in the catalyst will be determined by X-ray powder diffraction (XRPD).

Task 7. Calcination Effect Research (October 1, 1995 - July 31, 1996)

The effect of calcination temperature (300-500°C) on the catalyst physical properties and performance during FT synthesis shall be studied in a fixed bed reactor and a STSR. In addition to the baseline calcination temperature of 300°C, the calcination temperatures of 400 and 500°C will be employed in a fixed bed reactor with flowing air. Also, the effect of rapid heating (flash calcination) on performance of catalysts B and C shall be investigated.

Task 8. Catalyst Characterization (December 1, 1994 - March 28, 1997)

The objectives of this task are: (1) Provide basic characterization (by AA, BET, XRPD) of synthesized catalysts, and used catalysts (by XRPD, Mössbauer spectroscopy) in support of other tasks of the project; (2) Attempt to identify and quantify "surface" species on the catalyst after exposure to CO and/or synthesis gas by temperature programmed techniques (TPR/ TPD/ TPO/ TPRX) coupled with on-line gas analysis by mass spectrometry and gas chromatography.

Task 9. Catalyst Testing in a Bubble Column Slurry Reactor (October 1, 1996 - March 28, 1997)

A laboratory bubble column slurry reactor (BCSR) shall be designed, constructed and used for testing of catalysts B and C to quantify differences in the reactor space-time-yield and hydrocarbon selectivities between the STSR and the BCSR. This unit will be approximately 2.5 cm (~1 in) in diameter and 1.5 m (~5 ft) tall, with the effective (unexpanded or static) slurry volume of about 500 cm^3.

Task 10. Scale-Up of a Catalyst Synthesis Procedure (April 1, 1996 - March 28, 1997)

By the end of the first eighteen months of this project, the repeatability of the catalyst performance and catalyst preparation procedure shall be demonstrated. Subsequently, if the performance of the catalysts is found satisfactory by DOE the Contractor shall work with a catalyst manufacturer on synthesis of a large batches (~100 lb) of catalysts B and C. The cost estimate for the catalyst preparation will be provided upon reviewing details of the preparation procedure, and submitted to DOE for approval. Upon the DOE approval the Contractor will test catalysts synthesized by a catalyst manufacturer in a STSR.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

III. 1 Task 1. Project Work Plan

The work on this task was completed. No additional activity to report.

III. 2 Task 2. Engineering Modifications and Training of New Personnel

The work on this task was completed. No additional activity to report.

III. 3 Task 3. Testing of Previously Synthesized Catalysts

The work on this task was completed. No additional activity to report.

III. 4 Task 4. Reproducibility of Catalyst Preparation

Two fixed bed and two stirred tank slurry reactor (STSR) tests were conducted during the past quarter. Catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2 from batch #3 (S-5624-3) was tested in a fixed bed reactor run FB-1715, and STSR run SB-1295, whereas catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2 from batch #4 (S-3416-4) was evaluated in a fixed bed reactor run FA-1605, and STSR run SA-1665. The objective of fixed bed reactor tests was to obtain preliminary information on catalyst activity and selectivity (screening tests), before extensive tests in slurry reactors. The objective of STSR tests was to obtain data on catalyst activity/selectivity, and stability with time, and compare them with previously obtained data with these two catalysts from the original preparation batch.

Fixed Bed Reactor Tests

Prior to Fischer-Tropsch synthesis the catalysts were reduced in-situ with hydrogen at atmospheric pressure, and 240°C for 2 h (100 Fe/3 Cu/4 K/16 SiO_2 catalyst), or 250°C for 4 h (100 Fe/5 Cu/6 K/24 SiO_2 catalyst). After the conditioning period of about 24 h, during which the reaction temperature was gradually increased from 210 to 250°C, both catalysts were tested at : 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h using syngas with H_2 to CO molar feed ratio of about 0.67. Test duration was about 120 h including the conditioning period.

III. 4. 1 Run FA-1605 with 100 Fe/3 Cu/4 K/16 SiO_2 (batch 4) Catalyst

Variations in syngas conversion and methane selectivity (%C basis) with time-on-stream (TOS) are shown in Fig. 1. After 6 h of FT synthesis at 250°C (TOS >30 h) the conversion was fairly stable, and decreased slowly from 74 to 71% during 90 h of testing (Fig. 1a). Methane selectivity was about 5.5% (5.1-5.8%) throughout the test. Methane selectivity was significantly higher than that obtained in STSR tests of the same catalyst (from batch 1) during testing at 260°C (2-3.2%) - runs SB-0261, SB-0045 and SA-0705, as well as in the STSR test SA-1665 of the catalyst from batch 4 (1.8-2.8%). This is probably due to a better temperature control in the STSR in comparison to the fixed bed reactor.

III. 4. 2 Run FB-1715 with 100 Fe/5 Cu/6 K/24 SiO_2 (batch 3) Catalyst

Variations in syngas conversion and methane selectivity (%C basis) with TOS are shown in Fig. 2. Initial (H_2 + CO) conversion was about 74% (TOS = 25 h), but it decreased to 64% at about 56 h on stream, and then remained constant during the next 60 h of testing. Methane selectivity increased with time, from 4.6% initially to 5.5% at the end of the run. Deactivation behavior of the catalyst in this test was similar to that observed in recent STSR tests of this catalyst (from batch 1)- runs SB-3354 and SB-0665, as well as in run SB-1295 (batch 3) conducted during this reporting period. Methane and gaseous hydrocarbon selectivities were higher in the fixed bed reactor than in the STSR tests.

Stirred Tank Slurry Reactor Tests

After the successful fixed bed reactor tests, the two catalysts were evaluated in STSR to determine their long term activity/selectivity and deactivation behavior. Prior to Fischer-Tropsch synthesis the catalysts were reduced in-situ with hydrogen at 0.8 MPa (100 psig), and 240°C for 2 h (100 Fe/3 Cu/4 K/16 SiO_2 catalyst - run SA-1665), or 250°C for 4 h (100 Fe/5 Cu/6 K/24 SiO_2 catalyst - run SB-1295). Ethylflo (Durasyn) 164 oil was used as the start-up fluid in both tests. The process conditions after the reduction were different in these two tests, as described below.

III. 4. 3 Run SB-1295 with 100 Fe/5 Cu/6 K/24 SiO_2 (batch 3) Catalyst

Ten grams of the catalyst (< 270 mesh in size) from batch 3 (S-5624-3) was loaded for the test, in 300 g of Ethylflo 164 oil, prior to the reduction. Major events during the run are shown in Table 1 and detailed results from four mass balances are summarized in Table 2. Following the reduction with H_2 at 250°C for 4 h, the catalyst was initially tested at 260°C, 1.48 MPa (200 psig), synthesis gas molar feed ratio of 0.67 ($H_2/CO = 0.67$) and space velocity of 2.2 Nl/g-cat/h for 47 h, then at 1.8 Nl/g-cat/h for 89 h and finally at 1.6 Nl/g-cat/h for 217 h. Changes in catalyst activity (in terms of H_2+CO conversion) and selectivity (CH_4 and $C_1 + C_2$ hydrocarbons) are shown in Figure 3, as a function of gas space velocity and time-on-stream. Initially the catalyst exhibited high activity, but it deactivated with time. The (H_2+CO) conversion after 8 h at the initial conditions was about 78 %, and it decreased to 71 % at 46 h (Figure 3a). Catalyst deactivation continued when the space velocity was decreased to 1.8 Nl/g-cat/h (47-135 h) and further to 1.6 Nl/g-cat/h (136-350 h), but at a lower rate. At 350 h on stream the (H_2+CO) conversion was 66 %. The (H_2/CO) usage ratio was fairly stable, and varied between 0.55 and 0.58, throughout the test.

Low molecular weight hydrocarbon selectivities increased during the first 150 h of testing, and then remained relatively stable as the catalyst activity stabilized. As shown in Figure 3b, during the first 150 h of testing methane selectivity increased from 2.7 to 4 mol%, and then varied between 3.6 and 4 % during the next 200 h of testing. Similar trends were also observed for other gaseous hydrocarbons. For example, the $C_1 + C_2$ selectivity was initially about 6 mol% (Figure 3c), and it increased to 8 % between 19 and 150 h on stream. However, in the latter portion of the test the selectivity became more stable (about 8 %) and varied between 7.4 and 8.2 %.

Comparison of Data from Runs SB-1931, SB-3354, SB-0665 and SB-1295

Comparisons of the (H_2+CO) conversions and usage ratios obtained in four tests with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst is given in Figure 4. The first three tests (runs SB-1931, SB-

3354 and SB-0665) were conducted using the catalyst from the original preparation batch (S-5624-1), and their comparison was made in the previous quarterly report (Quarterly Technical Progress Report for the period January-March, 1995). Here we focus on comparison of results from run SB-1295 (catalyst from batch 3, S-5624-3) with those obtained using the catalyst from batch 1. In the original test SB-1931 (with n-octacosane as the initial slurry medium), the syngas conversion was stable with time. However, in tests SB-3354, SB-0665 and SB-1295 (with Ethylflo 164 oil as the initial slurry medium) the catalyst deactivated during the first 150 h of testing (Figure 4a). Comparison of catalyst activity is observed better in Figure 5, where the apparent first order rate constant, k, is plotted as a function of time. The apparent rate constant depends on temperature only, which was kept constant in all three tests, and thus provides a direct comparison of the catalyst activity. Initial activities in all three tests were about the same, k = 340-380 mmol/g-Fe/h/MPa. In run SB-1931, the apparent rate constant gradually decreased from 350 to 300 mmol/g-Fe/h/MPa over a period of 400 h. However, in runs SB-3354, SB-0665 and SB-1295 the apparent rate constant was only 200-220 mmol/g-Fe/h/MPa at 400 h on stream. The activity of catalyst from batch 3 (run SB-1295) was very similar to those observed in runs SB-3354 and SB-0665 with batch 1 catalyst (Fig. 5).

Usage ratios in all four tests (Figure 4b) were between 0.56 and 0.62 (small variation), and were somewhat higher (lower water-gas-shift activity) in run SB-1931 (0.6-0.62).

Methane and C_1+C_2 selectivities in run SB-1295 (catalyst from batch 3) were slightly higher than those obtained in three tests with the catalyst from batch 1 (runs SB-1931, SB-3354 and SB-0665), as shown in Figure 6. For example, methane and C_2-C_4 selectivities in run SB-1295 were 3-4 % and 14-16 %, respectively, whereas the respective values in tests with batch 1 catalyst were: 2.5-3.6 % (methane) and 12-15 % (C_2-C_4 hydrocarbons). This may be due to the fact that potassium content of batch 3 catalyst is lower than that of the batch 1 catalyst (5.2 K per 100 Fe (batch 3) vs. 6.4 K per 100 Fe (batch 1)).

III. 4. 4 Run SA-1665 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

About 10.1 g of catalyst (< 270 mesh in size), from batch 4 (S-3416-4), was loaded into the SA reactor system together with 3o3 g of Durasyn (Ethylflo) 164 oil (a hydrogenated 1-decene homopolymer liquid - C_{30}, obtained from Albemarle Co.). After the reduction with H_2 at 240°C for 2 h, the catalyst was tested at 260°C, 1.48 MPa (200 psig), 1.4 Nl/g-cat/h and syngas molar feed ratio of 0.67 ($H_2/CO = 0.67$).

During the first 257 h on stream, the syngas conversion decreased slowly from 81 to 79 % (Figure 7a). During the same time period the usage ratio, a measure of the water-gas-shift (WGS) activity, varied between 0.55 and 0.57. Methane selectivity was low, 1.6 - 2.9 mol% (Figure 7b); the lumped selectivity of $C_1 + C_2$ hydrocarbons was 4 - 6.3 % (Figure 7c), and total C_2 - C_4 hydrocarbon selectivity was between 10 and 13 % (not shown in Figure 7). At 259 h on stream, the reaction pressure and space velocity were increased proportionally to 2.17 MPa (300 psig) and 2.05 Nl/g-cat/h, respectively. The catalyst activity decreased moderately during the next 150 h of testing at higher pressure (up to 410 h on stream), and more rapidly between 410 and 500 h. The syngas conversion decreased from 77 % at 290 h, to 68 % at 500 h on stream, whereas the usage ratio increased slightly to about 0.58. The methane selectivity was between 2.5 and 2.9 mol%. The total $C_1 + C_2$ selectivity was between 6 and 6.6 mol%, and that of C_2 - C_4 hydrocarbons was between 13 and 14 mol%. The test was terminated after 500 h on stream. Table 3 lists major events during the test, whereas Table 4 summarizes results from four complete mass balances.

Comparison of Data from Runs SB-0261, SB-0045, SA-0705 and SA-1665

Comparison of conversions and the usage ratio among four STSR tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst is made in Figure 8, of the apparent rate constant in Figure 9 and of gaseous hydrocarbon selectivities in Figure 10. The first three tests (runs SB-0261, SB-0045 and SA-0705) were conducted using the catalyst from the original preparation batch (S-3416-1), and their comparison was made in the previous quarterly report (Quarterly Technical Progress Report for the period January-March, 1995). Here we focus on comparison of results from run SA-1665 (catalyst from batch 4, S-3416-4) with those obtained using the catalyst from batch 1.

The catalyst from the new batch (run SA-1665) had slightly lower activity (lower syngas conversion - Figure 8a, and lower apparent rate constant - Figure 9) during the first 400 h of testing, than the catalyst from batch 1 in tests SB-0045 and SA-0705. Its deactivation behavior up to 400 h was also similar to that observed in tests SB-0045 and SA-0705. However, after 400 h on stream the catalyst in run SA-1665, deactivated faster than the catalyst in run SA-0705, under the same process conditions. Its stability at higher reaction pressure (2.17 MPa) was not as good as that of catalyst from batch 1 (run SA-0705). The usage ratios (Figure 8b) in the current test (SA-1665) were similar to those obtained in three tests with the catalyst from batch 1.

Methane and $C_1 + C_2$ selectivities in run SA-1665, were between the values obtained three tests with the catalyst from batch 1 (Figures 10a and 10b). The methane selectivity varied between 2 and 2.9 mol% in run SA-1665, and it varied between 2 and 3.2 mol% in runs SB-0261, SB-0045 and SA-0705. Similarly, selectivities of C_2 - C_4 hydrocarbons were between 10 and 14 mol% in run SA-1665, whereas in runs SB-0261, SB-0045 and SA-0705 selectivities of C_2 - C_4 hydrocarbons varied between 8 and 14 % (not shown in Fig. 10).

Concluding Remarks on Multiple Tests with 100 Fe/3 Cu/4 K/16 SiO_2 and 100 Fe/5 Cu/4 K/24 SiO_2 Catalysts from Two Batches

Four tests were conducted with each of the two catalysts. Three tests were made with each of the two catalysts, using catalysts from the same preparation batch (batch 1 catalysts), whereas one test with each of the two catalysts was made with catalysts from new batches. In the original tests conducted in 1991 (SB-0261 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst, and SB-1931 with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst) n-octacosane was used as the initial medium. In the six tests conducted since December 1994, Durasyn (Ethylflo) 164 oil was used as the starting fluid. Comparison of results from multiple tests with the same catalyst (from batch 1) was made in the previous quarterly report (Quarterly Technical Progress Report for the period January-March, 1995). It was concluded that the reproducibility of results from multiple tests with the same catalyst may be regarded as satisfactory.

On the basis of new results obtained during the current quarter, with catalysts from different batches (run SB-1295 with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst from batch 3, and run SA-1665 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst from batch 4) we conclude that reproducibility of catalyst preparation procedure may be also regarded as satisfactory. Performance of catalysts from new batches (activity, selectivity and deactivation rates) was similar to that of catalysts from the original batch.

III. 5 Task 5. The Effect Of Source of Potassium and Basic Oxide Promoter

The objective of this task is to investigate effects of two different sources of potassium or addition of another promoter (CaO) on the catalyst performance. During the reporting period we synthesized six catalysts (four containing CaO as a promoter, and two using potassium silicate solution as the source of potassium promoter). The synthesized catalysts were characterized by atomic absorption spectroscopy (AAS), and BET surface area (SA) and pore size distribution (PSD) measurements (Table 6). Results are described in a section describing progress on Task 8. Catalyst Characterization.

Four of the synthesized catalysts containing CaO promoter were tested in a fixed bed reactor to determine their activity and selectivity during Fischer-Tropsch synthesis. Prior to Fischer-Tropsch synthesis the catalysts were reduced in-situ with hydrogen at atmospheric pressure, and 240°C for 2 h (catalysts containing 16 parts of SiO_2 per 100 parts of Fe on a mass basis), or 250°C for 4 h (catalysts containing 24 parts of SiO_2 per 100 parts of Fe on a mass basis). After the conditioning period of about 24 h, during which the reaction temperature was gradually increased from 210 to 250°C, all catalysts were tested at : 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h using syngas with H_2 to CO molar feed ratio of about 0.67. Test duration was 120 - 140 h including the conditioning period.

Fixed Bed Reactor Tests of Catalysts Containing 16 g of SiO_2 per 100 g of Fe

III. 5. 1 Run FA-1525 with 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 Catalyst

Variations in syngas conversion and methane selectivity (mol % C basis) with time-on-stream are shown in Figure 11. After 6 h of FT synthesis at 250°C (TOS >30 h) the conversion was fairly stable, and decreased slowly from 72 to 69% during 90 h of testing (Fig. 11a). Methane selectivity increased slightly with time on stream, and throughout the entire test it varied between 5.7 and 6.6 %.

III. 5. 2 Run FB-1515 with 100 Fe/3 Cu/4 K/6 Ca/16 SiO_2 Catalyst

Variations in syngas conversion and methane selectivity (mol % C basis) with TOS are shown in Figure 12. Initial (H_2 + CO) conversion was about 46 % (TOS = 29 h), but it increased gradually with time to 52-54 % (Fig. 12a). Methane selectivity varied between 6.2 and 6.6 % between 30 and 85 h on stream (Fig. 12b), and then decreased to about 5.3 % at the end of the test (140 h).

Comparison of Results from Fixed Bed Reactor Tests of Catalysts Containing 16 g of SiO_2 per 100 g of Fe

Performance of catalysts containing CaO promoter is compared with that of the catalyst without CaO (100 Fe/3 Cu/4 K/16 SiO_2 catalyst from batch 4; note that the actual potassium content of this catalyst is 6.6 K) in Figures 13 and 14. The syngas conversions decreased with increase in CaO promotion. The activity of the catalyst with lower amount of CaO promoter (run FA-1525 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst) was similar to that of the baseline catalyst (run FA-1605 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst from batch 4), whereas the activity (syngas conversion) of the catalyst containing 6 parts of Ca per 100 parts of Fe (run FB-1515) was markedly lower (Fig. 13a). This may be due to significantly lower surface area of the latter catalyst in comparison to the other two catalysts (see Table 6). Usage ratios in all three tests were similar (about 0.6), indicating similar water-gas-shift activities (Fig. 13b). Methane

(Fig. 14a) and gaseous (C_2 - C_4) hydrocarbon selectivities (Fig. 14b) were slightly higher on the CaO promoted catalysts, than on the baseline catalyst.

Fixed Bed Reactor Tests of Catalysts Containing 24 g of SiO_2 per 100 g of Fe

III. 5. 3 Run FB-1425 with 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 Catalyst

The activity (measured by syngas conversion) and methane selectivity of this catalyst were stable during 120 h of testing (Figure 15). After 40 h on stream, the (H_2 + CO) conversion was about 68 %, whereas the methane selectivity was about 6 mol %. These values are similar to the ones obtained in run FA-1525 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst.

III. 5. 4 Run FA-1705 with 100 Fe/5 Cu/5 K/6 Ca/24 SiO_2 Catalyst

Results illustrating variations in catalyst activity (syngas conversion) and methane selectivity with time on stream are shown in Figure 16. The syngas conversion increased slowly with time, from 31 % at 28 h to 36 % at 118 h on stream (Fig. 16a). This is in a qualitative agreement with results obtained in run FB-1515 with the 100 Fe/3 Cu/4 K/6 Ca/16 SiO_2 catalyst, but syngas conversions in the present test were significantly lower than those in run FB-1515. Methane selectivity was about 6.4 % (5.8-6.8 %).

Comparison of Results from Fixed Bed Reactor Tests of Catalysts Containing 24 g of SiO_2 per 100 g of Fe

Performance of two catalysts containing CaO promoter is compared with that of the catalyst without CaO (100 Fe/5 Cu/6 K/24 SiO_2 catalyst from batch 3) in Figures 17 and 18. Again, the syngas conversions decreased with increase in CaO promotion. The activity of the catalyst with lower amount of CaO promoter (run FB-1425 with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst) was similar to that of the baseline catalyst (run FB-1715 with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst from batch 3), whereas the activity (syngas conversion) of the 100 Fe/5 Cu/5 K/6 Ca/24 SiO_2 catalyst (run FA-1705) was markedly lower (Fig. 17a). This may be due to significantly lower surface area of the latter catalyst in comparison to the other two catalysts (see Table 6). Usage ratios in run FA-1705 were higher than in the other two tests, indicating lower water-gas-shift activity (Fig. 17b). Methane (Fig. 18a) and gaseous (C_2 - C_4) hydrocarbon selectivities (Fig. 18b) were slightly higher on the CaO promoted catalysts, than on the baseline catalyst.

Concluding Remarks on the Effect of CaO Promotion

Two levels of CaO promotion were used with catalysts containing 16 or 24 g of SiO_2 per 100 g of Fe, i.e. 100 Fe/3 Cu/4 K/x Ca/16 SiO_2; and 100 Fe/5 Cu/5 K/x Ca/24 SiO_2 where x = 2 or 6. The addition of small amounts of CaO promoter results in performance similar to that of the baseline catalysts (x = 0), whereas addition of a larger amount of CaO promoter results in lower activity. The latter is probably due to partial pore blocking by CaO resulting in decrease of total surface area and pore volume of the catalysts (see Table 6 for catalysts with x = 0, 2 and 6). Anticipated beneficial effects of CaO promotion, i.e. increase in catalyst activity and/or increase in selectivity of high molecular weight products, have not been realized. Catalysts containing smaller amounts of CaO promoter (x = 2), will be evaluated in slurry reactors, to determine the impact of CaO promotion on the long term catalyst stability (deactivation).

III. 6 Task 6. Pretreatment Effect Research

The work on this task is not scheduled to begin yet. No activity to report.

III. 7 Task 7. Calcination Effect Research

The work on this task is not scheduled to begin yet. No activity to report.

III. 8 Task 8. Catalyst Characterization

Catalysts synthesized during the current reporting period were characterized by atomic absorption spectroscopy (elemental analysis) and BET surface area and pore size distribution. Results of physico-chemical characterization of all catalysts synthesized during the current contract are summarized in Table 5 (catalysts without CaO promoter) and Table 6 (catalysts with CaO promoter and those prepared using potassium silicate solution as the source of potassium promoter).

Major findings from results of elemental analysis are summarized below:

(1) For catalysts with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2, both the copper and the silica contents agree well among different batches, however, the original potassium contents of batch 2 (3.6 parts K/100 parts of Fe) and batch 3 (3.5 parts K/100 parts Fe) catalysts were significantly lower than that in batch 1 (5.8-6.7 parts of K per 100 parts of Fe). The actual potassium content in the catalysts synthesized during the current contract (batches 2 and 3) were closer to the nominal one, than that in batch 1 (synthesized during the previous contract). However, in order to obtain the desired catalytic performance, additional amounts of potassium were added, by incipient wetness impregnation, to the catalysts from batches 2 and 3, to obtain about 6.7 parts of K per 100 parts of Fe. Also, results obtained from different laboratories with the same catalyst batch (S-3416-1) agree well with each other (Table 5).

(2) For catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2, the potassium content in batches 2-4 varies from 5.1 to 6.5 parts of K per 100 parts of Fe, and the copper content varies between 4.8 and 5.4 parts of Cu per 100 parts of Fe, both of which are close to the desired nominal catalyst composition, as well as to the actual composition of batch 1 catalyst. The potassium content of batch 5 is too high (7.8 K/100 Fe) due to incomplete removal of potassium from the Fe/Cu/SiO_2 precursor (Potassium is present here due to the use of potassium silicate solution as the source of SiO_2, and its content in the precursor itself is 1.2 K/100 Fe. Upon impregnation with potassium, from $KHCO_3$, the total potassium content was higher than intended.) Silica contents are reasonably close to the nominal amount in all five batches, varying between 21.9 and 29.1 parts of SiO_2 per 100 parts of Fe. Results from different laboratories analyzing the same catalyst (S-5624-1) are similar for copper and silica, but show larger discrepancies for the potassium content (Table 5).

(3) Relatively high sodium content in the catalyst S-3416-3 is due to the use of washing water which was not purified properly (Table 5). Its impact on catalytic results is expected to be small, since sodium can also serve as an alkali promoter.

(4) Actual amounts of promoters (Cu, K, Ca and SiO_2) of catalysts synthesized for Task 5 of the contract are close to the intended ones (Table 6).

Surface areas and pore volumes were measured by physical adsorption of nitrogen at 77 K using a Micromeritics Digisorb 2600 instrument, and values obtained are listed in Tables 5 and 6. Surface areas obtained from the single-point BET method on a Micromeritics Pulse Chemisorb 2705 instrument are also included for comparison purposes. From the surface area and pore volume results, it can be seen that:

(1) Surface areas obtained from the single-point method are close to those obtained from the BET plot method (with relative error less than 10%, except for S-5624-3-6Ca catalyst). Such an agreement proves that the former method is applicable to the catalyst system studied.

(2) Surface areas of the 100 Fe /5 Cu/6 K/24 SiO_2 catalysts are between 222 and 299 $m^2 g^{-1}$, whereas those of the 100 Fe/3 Cu/4 K/16 SiO_2 catalysts are between 245 and 315 $m^2 g^{-1}$, i.e. the maximum variation among different batches is about 20% (Table 5). Also, multiple measurements with the same catalyst (batch 1) are in a good agreement. In general, surface areas of catalysts synthesized during the current contract are higher than those of the two catalysts synthesized during the previous contract (S-3416-1 and S-5624-1).

(3) Pore volumes for all new batches (S-3416-2 to S-3416-4, and S-5624-2 to S-5624-5) are lower - 0.43-0.54 cm^3/g (excluding S-5624-2 which has the pore volume of 0.23 cm^3/g only) than those of catalysts synthesized during the previous project (batch 1 in each series) - 0.65-0.71 cm^3/g.

(4) Surface areas and pore volumes of catalysts containing CaO promoter decrease with increasing amount of CaO (Table 6). Catalysts containing 6 Ca/100 Fe (S-3416-3-6Ca and S-5624-3-6Ca) have surface areas of 73-105 m^2/g, whereas the surface area of the catalysts without CaO is about 290 m^2/g. Also, the pore volume of these two catalysts is 0.26-0.30 cm^3/g, whereas that of the catalysts without CaO promoter is 0.43-0.54 cm^3/g.

III. 9 Catalyst Testing in a Bubble Column Slurry Reactor

The work on this task is not scheduled to begin yet. No activity to report.

III. 10 Scale-up of Catalyst Synthesis Procedure

The work on this task is not scheduled to begin yet. No activity to report.

Plans for the Next Quarter

During the next quarter we plan to: (a) conduct another test of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2 (S-3416-4) in a slurry reactor (Task 4); (b) complete screening fixed bed reactor tests of catalysts synthesized using potassium silicate as the source of potassium promotion; (c) initiate testing of catalysts containing CaO as promoter and/or catalysts with different source of potassium in slurry reactors (Task 5); and (c) characterize used catalyst samples by X-ray diffraction and Mössbauer spectroscopy (Task 8).

Table 1. **Major events in Run SB-1295 with 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst (batch 3)**

TOS (h)	Event
	Slurry loading: 300 g of Durasyn 164 oil, 10.0 g of catalyst (batch S5624-3, particle size< 270 mesh)
	Catalyst pretreatment: H_2, 250°C, 0.78 MPa for 4 h
	Wax withdrawal through filter: 34.2 g of wax
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P = 1.48 MPa, SV = 2.15 Nl/g-cat/h, (H_2/CO) = 0.67
47	Change process conditions: SV = 1.8 Nl/g-cat/h
136	Change process conditions: SV = 1.6 Nl/g-cat/h
212	Power failure for 2 hours, slurry temperature dropped to 130°C
219	Achieve process conditions
353	End of run: 198 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 419 g wax; 0 g catalyst
	Wax recovery: 90 %

Table 2. Summary of results for slurry run SB-1295 .

Catalyst: 10.00 g^a, 100Fe/5Cu/6K/24SiO_2 (batch 3) Slurry liquid: 265.0 g, Durasyn-164

Reactor volume: 430. cc^b

Period	1	2	3	4
Time on Stream (h)	38.0	122.0	243.0	338.0
Balance Duration (h)	7.8	12.0	12.0	12.5
Average Temperature (°C)	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.667	.667	.667	.667
Space Velocity (Nl/g–cat·h)[a]	2.15	1.83	1.60	1.60
Space Velocity (Nl/g–Fe·h)	4.04	3.43	2.89	2.89
GHSV (h^{-1})[b]	50.1	42.6	37.2	37.2
CO Conversion (%)	76.2	74.3	75.1	70.3
H_2+CO Conversion (%)	71.8	69.6	70.4	66.2
H_2/CO Usage	.570	.562	.561	.568
STY ($mols$ H_2+CO/g–cat·h)[a]	.069	.057	.050	.047
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	32.7	38.8	39.0	31.5
Weight % of Outlet				
H_2	1.60	1.71	1.69	1.84
H_2O	.683	.557	.575	.608
CO	22.7	24.5	23.7	28.4
CO_2	55.9	54.4	55.5	51.9
Hydrocarbons	9.93	10.0	10.6	9.22
Oxygenates	.733	.612	.738	.544
Wax[c]	8.39	8.13	7.23	7.52
Yield (g/Nm^3 H_2 + CO *Converted*)				
CH_4	7.79	9.04	8.99	8.95
C_2–C_4 Hydrocarbons	31.2	32.0	32.4	31.9
C_5–C_{11} Hydrocarbons	50.4	44.3	45.5	37.2
C_{12}+ Hydrocarbons	111.	120.	112.	120.
Wax[c]	91.8	91.7	80.7	89.2
Oxygenates	8.01	6.90	8.24	6.45
Total	208.	212.	207.	205.
1+2 Olefins/n–Paraffin Ratio				
C_2	1.26	1.31	1.43	1.69
C_3	5.09	5.97	6.09	6.02
C_4	4.14	4.29	4.21	4.06
C_8	2.36	2.72	2.86	2.92
C_{10}	1.82	2.14	2.28	2.42

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table 2 (cont'd). Summary of results for slurry run SB-1295 .

Period	1	2	3	4
Weight % of Hydrocarbons				
CH4	3.89	4.41	4.52	4.51
Ethane	1.78	1.84	1.89	1.69
Ethylene	2.10	2.24	2.52	2.67
Propane	1.07	.925	.948	.944
Propylene	5.21	5.27	5.51	5.42
n–Butane	.996	.954	.989	.997
1+2 Butenes	3.98	3.95	4.02	3.91
C_4 Isomers	.432	.425	.447	.457
n–Pentane	1.42	.953	.972	.992
1+2 Pentenes	3.77	3.99	4.01	3.81
C_5 Isomers	.170	.263	.328	.159
n–Hexane	.860	.806	.887	.866
1+2 Hexenes	2.57	2.51	2.63	2.55
C_6 Isomers	.483	.335	.490	.332
n–Heptane	.747	.601	.645	.579
1+2 Heptenes	2.00	1.79	1.90	1.81
C_7 Isomers	.569	.413	.407	.364
n–Octane	.721	.473	.477	.396
1+2 Octenes	1.67	1.27	1.34	1.14
C_8 Isomers	.488	.372	.363	.300
n–Nonane	.858	.542	.558	.390
1+2 Nonenes	1.66	1.25	1.32	.840
C_9 Isomers	.487	.355	.418	.265
n–Decane	1.06	.716	.738	.467
1+2 Decenes	1.90	1.51	1.65	1.12
C_{10} Isomers	.548	.355	.386	.254
n–Undecane	1.00	.914	.923	.592
1+2 Undecenes	1.63	1.66	1.83	1.23
C_{11} Isomers	.541	.552	.633	.321
C_2–C_4	15.6	15.6	16.3	16.1
C_5–C_{11}	25.2	21.6	22.9	18.8
C_{12}+	55.4	58.3	56.2	60.7
Wax[c]	45.8	44.7	40.6	44.9

[c] Unanalyzed wax withdrawn from reactor

Table 3. **Major events in Run SA-1665 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst (batch 4)**

TOS (h)	Event
	Slurry loading: 303 g of Durasyn 164 oil, 10.1 g of catalyst (batch S3416-4, particle size< 270 mesh)
	Catalyst pretreatment: H_2, 240°C, 0.78 MPa for 2 h
	Wax withdrawal through filter: 25.1 g of wax
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P = 1.48 MPa, SV = 1.4 Nl/g-cat/h, (H_2/CO) = 0.67
259	Change process conditions: P = 2.17 MPa, SV = 2.05 Nl/g-cat/h
500	End of run: 307 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 786 g wax, 0 g catalyst
	Wax recovery: 83 %

Table 4. Summary of results for slurry run SA-1665 .

Catalyst: 10.10 g^a, 100Fe/3Cu/4K/16SiO_2 (batch 4) Slurry liquid: 278.0 g, Durasyn-164

Reactor volume: 400. cc^b

Period	1	2	3	4
Time on Stream (h)	112.0	220.0	361.0	485.0
Balance Duration (h)	11.0	18.5	16.0	12.0
Average Temperature (°C)	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	2.17	2.17
H_2/CO Feed Ratio	.667	.667	.667	.667
Space Velocity (Nl/g–cat·h)[a]	1.40	1.40	2.05	2.04
Space Velocity (Nl/g–Fe·h)	2.34	2.34	3.43	3.41
GHSV (h^{-1})[b]	35.3	35.3	51.8	51.5
CO Conversion (%)	84.1	83.6	80.1	70.9
H_2+CO Conversion (%)	79.0	78.5	75.8	67.4
H_2/CO Usage	.566	.565	.577	.584
STY ($mols$ H_2+CO/g–cat·h)[a]	.049	.049	.069	.061
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	33.0	34.7	24.4	22.7
Weight % of Outlet				
H_2	1.32	1.34	1.41	1.75
H_2O	.918	.856	1.01	.811
CO	15.2	15.7	19.1	27.9
CO_2	61.8	61.2	58.3	51.7
Hydrocarbons	5.82	6.09	6.06	6.30
Oxygenates	.243	.277	.302	.367
Wax[c]	14.7	14.5	13.8	11.1
Yield (g/Nm^3 H_2 + CO *Converted*)				
CH_4	6.45	6.52	6.25	6.42
C_2–C_4 Hydrocarbons	25.0	24.9	28.2	30.5
C_5–C_{11} Hydrocarbons	24.4	26.2	26.1	31.6
C_{12}+ Hydrocarbons	148.	147.	145.	133.
Wax[c]	146.	144.	143.	129.
Oxygenates	2.41	2.75	3.11	4.25
Total	206.	208.	208.	206.
1+2 Olefins/n–Paraffin Ratio				
C_2	1.48	1.46	2.11	2.86
C_3	7.04	6.43	6.10	5.75
C_4	5.87	5.89	5.22	4.59
C_8	3.77	3.66	3.82	3.74
C_{10}	2.95	3.17	3.13	3.09

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table 4 (cont'd). Summary of results for slurry run SA-1665 .

Period	1a	2a	3a	4a
Weight % of Hydrocarbons				
CH4	3.17	3.18	3.04	3.19
Ethane	1.43	1.44	1.25	1.10
Ethylene	1.98	1.97	2.46	2.94
Propane	.633	.682	.809	.925
Propylene	4.25	4.19	4.71	5.08
n–Butane	.538	.528	.674	.855
1+2 Butenes	3.05	3.00	3.40	3.79
C_4 Isomers	.388	.360	.437	.466
n–Pentane	.518	.504	.669	.843
1+2 Pentenes	2.90	2.82	3.29	3.63
C_5 Isomers	.274	.265	.346	.276
n–Hexane	.414	.415	.535	.665
1+2 Hexenes	1.76	1.74	1.95	2.29
C_6 Isomers	.240	.273	.197	.428
n–Heptane	.280	.293	.315	.416
1+2 Heptenes	1.19	1.22	1.27	1.56
C_7 Isomers	.382	.366	.354	.399
n–Octane	.208	.234	.195	.233
1+2 Octenes	.768	.841	.731	.854
C_8 Isomers	.276	.311	.224	.330
n–Nonane	.212	.249	.183	.244
1+2 Nonenes	.686	.808	.606	.714
C_9 Isomers	.176	.225	.172	.259
n–Decane	.199	.235	.184	.262
1+2 Decenes	.579	.734	.567	.799
C_{10} Isomers	.177	.207	.169	.278
n–Undecane	.156	.232	.150	.238
1+2 Undecenes	.408	.575	.411	.654
C_{11} Isomers	.179	.222	.189	.297
C_2–C_4	12.3	12.2	13.7	15.1
C_5–C_{11}	12.0	12.8	12.7	15.7
C_{12}+	72.6	71.9	70.5	66.0
Wax[c]	71.6	70.4	69.5	63.8

[c] Unanalyzed wax withdrawn from reactor

Table 5. Elemental Analysis and Textural Properties of Synthesized Catalysts.

Nominal Composition Designation	Amount Prepared (g)	Composition 100 Fe x Cu/y K/z SiO_2	BET Surface Area (m^2/g) Single point	BET Surface Area (m^2/g) BET plot	Pore Volume cm^3/g
100 Fe/3 Cu/4 K/16 SiO_2					
S-3416-1	40	3.5 / 5.8 / 17.0		257	0.66
		3.0 / 6.7 / 15.5 (a)		245 (a)	0.65 (a)
		3.0 / 5.9 / 15.5 (b)			
S-3416-2	101	3.1 / 3.6 / 19.0	316	315	0.43
S-3416-2 (c)		3.5 / 6.5 / 18.1			
S-3416-3 (d)	173	2.9 / 3.5 / 16.0	262	291	0.43
S-3416-3 (c)		3.2 / 6.9 / 19.8			
S-3416-4	215	3.1 / 3.6 / 19.0	310	306	0.45
100 Fe/5 Cu/6 K/24 SiO_2					
S-5624-1	67	5.4 / 6.2 / 24.0	202	235	0.71
		5.1 / 8.1 / 26.0 (a)		222 (a)	0.68 (a)
		5.5 / 6.6 / 24.0 (e)			
S-5624-2	90	5.4 / 5.1 / 21.9	228	238	0.23
S-5624-3	240	4.8 / 5.2 / 24.2	258	284	0.51
S-5624-4	200	5.2 / 6.5 / 23.2	295	299	0.48
S-5624-5	405	5.2 / 7.8 / 29.1		287	0.54

(a): Final DOE Report for contract DE-AC22-89PC89868, (1994).
(b): measurements conducted at UOP.
(c): additional amount of K was added to obtain a better agreement with the actual K content of the original catalyst (S-3416-1).
(d): contains 0.34 wt% sodium (Na/Fe = 0.006 by mass).
(e): measurements conducted at PETC, DOE.

Table 6. Elemental analysis and textural properties of catalysts containing CaO or potassium from a potassium silicate solution

Catalyst Code	Amount Prepared (g)	Composition 100 Fe/w Ca x Cu/y K/z SiO_2	BET Surface Area (m^2/g) Single point	BET Surface Area (m^2/g) BET plot	Pore Volume cm^3/g
S-3416-3	173	/2.9 /3.5 /17.7	262	291	0.43
S-3416-3-2Ca	12	2.2 /3.2 /4.8 /17.0	190	190	0.36
S-3416-3-6Ca	13	6.3 /3.2 /4.6 /21.7	106	105	0.30
S-3416-4-K	20	/3.2 /5.6 /20.6	312[a]		
S-5624-3	240	/4.8 /5.2 /24.2	258	284	0.51
S-5624-3-2Ca	13	2.2 /5.5 /5.0 /21.7	224	221	0.46
S-5624-3-6Ca	14	6.1 /5.1 /5.3 /30.8	100	73.2	0.26
S-5624-5-K	34	/5.2 /6.6 /30.2	300[a]		

[a] : catalyst dried at 120 °C, others were calcined at 300 °C for 5 h.

Nominal (intended) catalyst compositions:

S-3416-3-2Ca	100 Fe/2 Ca/3 Cu/4 K/16 SiO_2
S-3416-3-6Ca	100 Fe/6 Ca/3 Cu/4 K/16 SiO_2
S-5624-3-2Ca	100 Fe/2 Ca/5 Cu/5 K/24 SiO_2
S-5624-3-6Ca	100 Fe/6 Ca/5 Cu/5 K/24 SiO_2

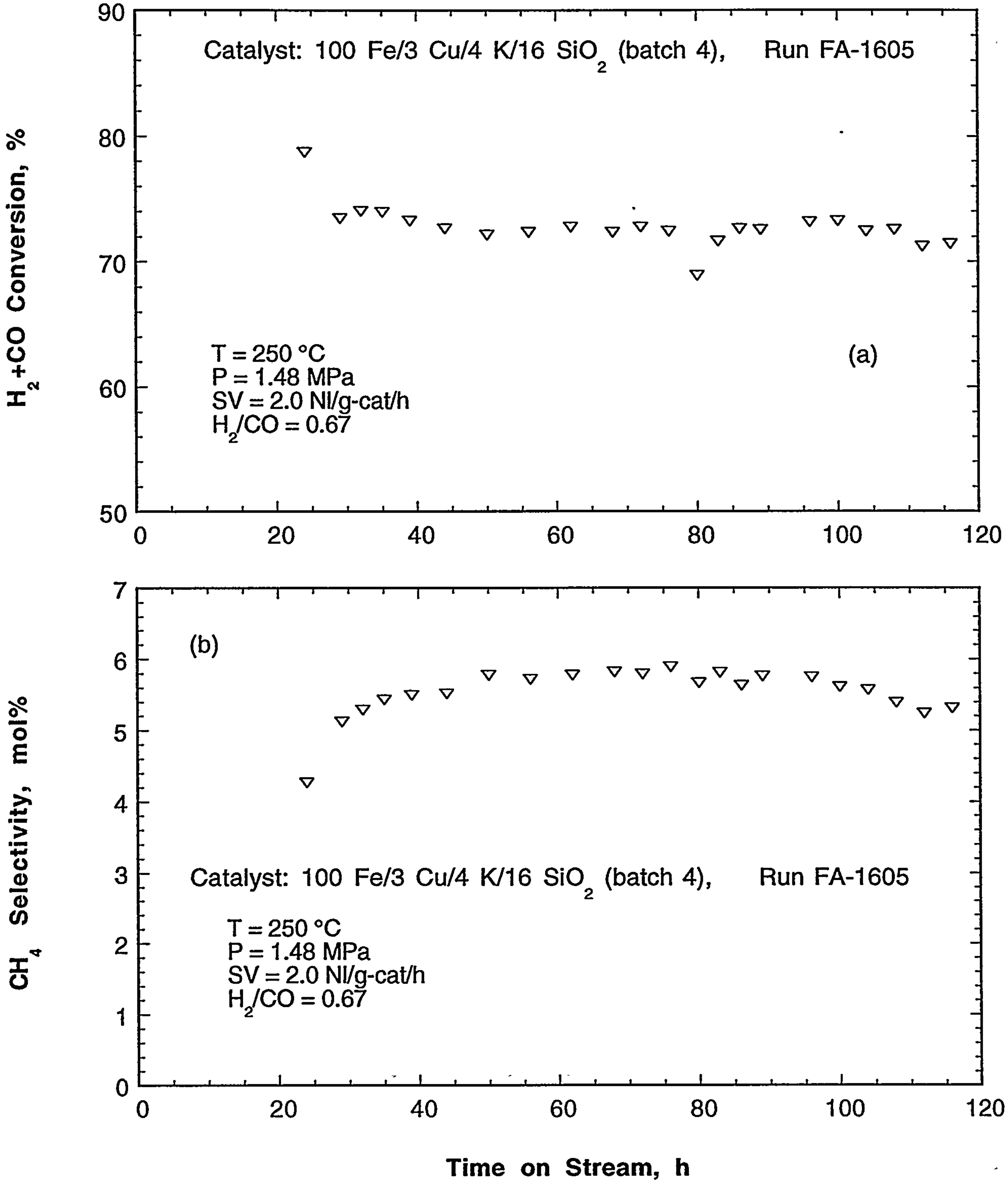

Figure 1. Variation in (a) (H_2+CO) conversion and (b) methane selectivity with time on stream in run FA-1605.

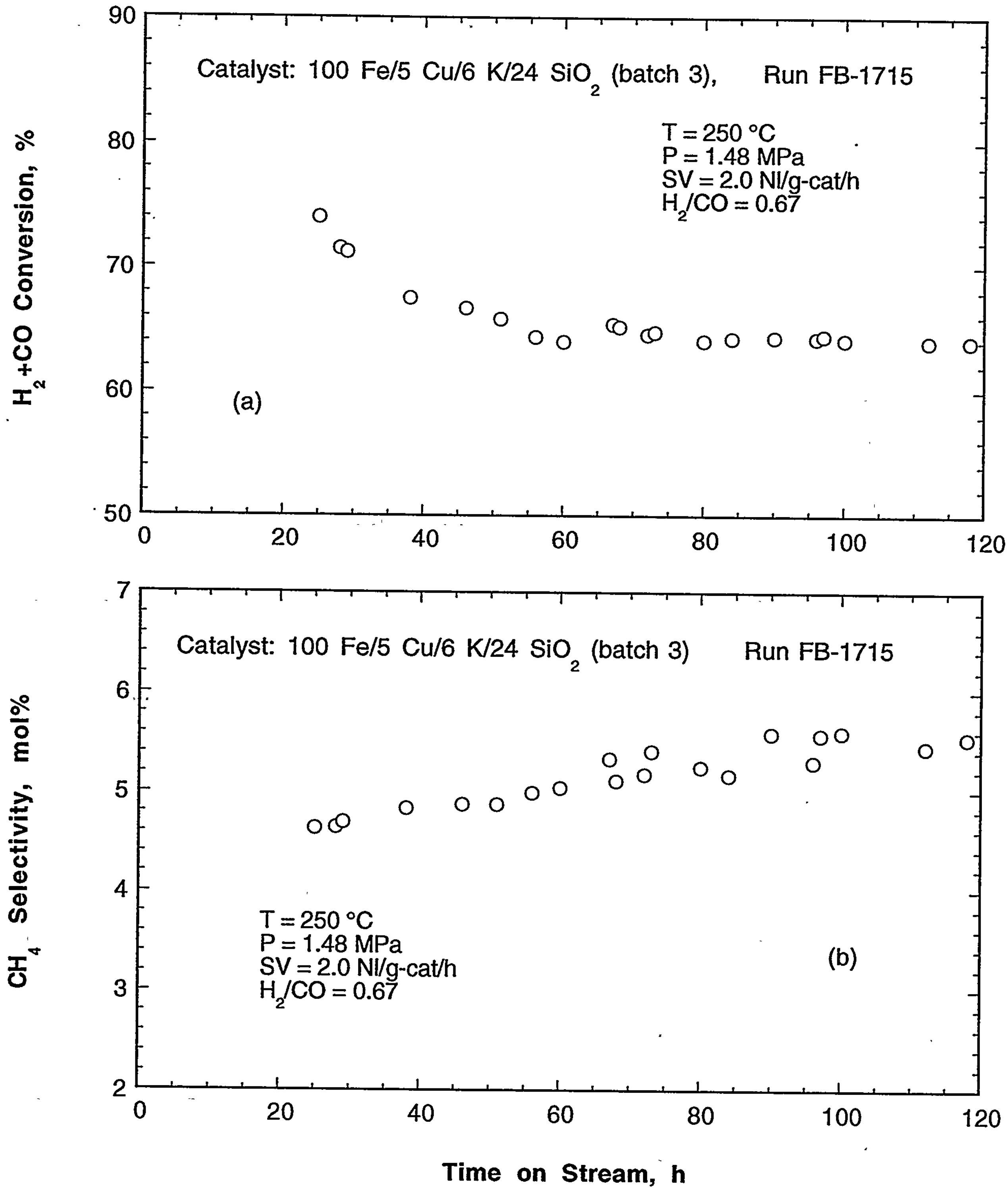

Figure 2. Variation in (a) (H_2+CO) conversion and (b) methane selectivity with time on stream in run FB-1715.

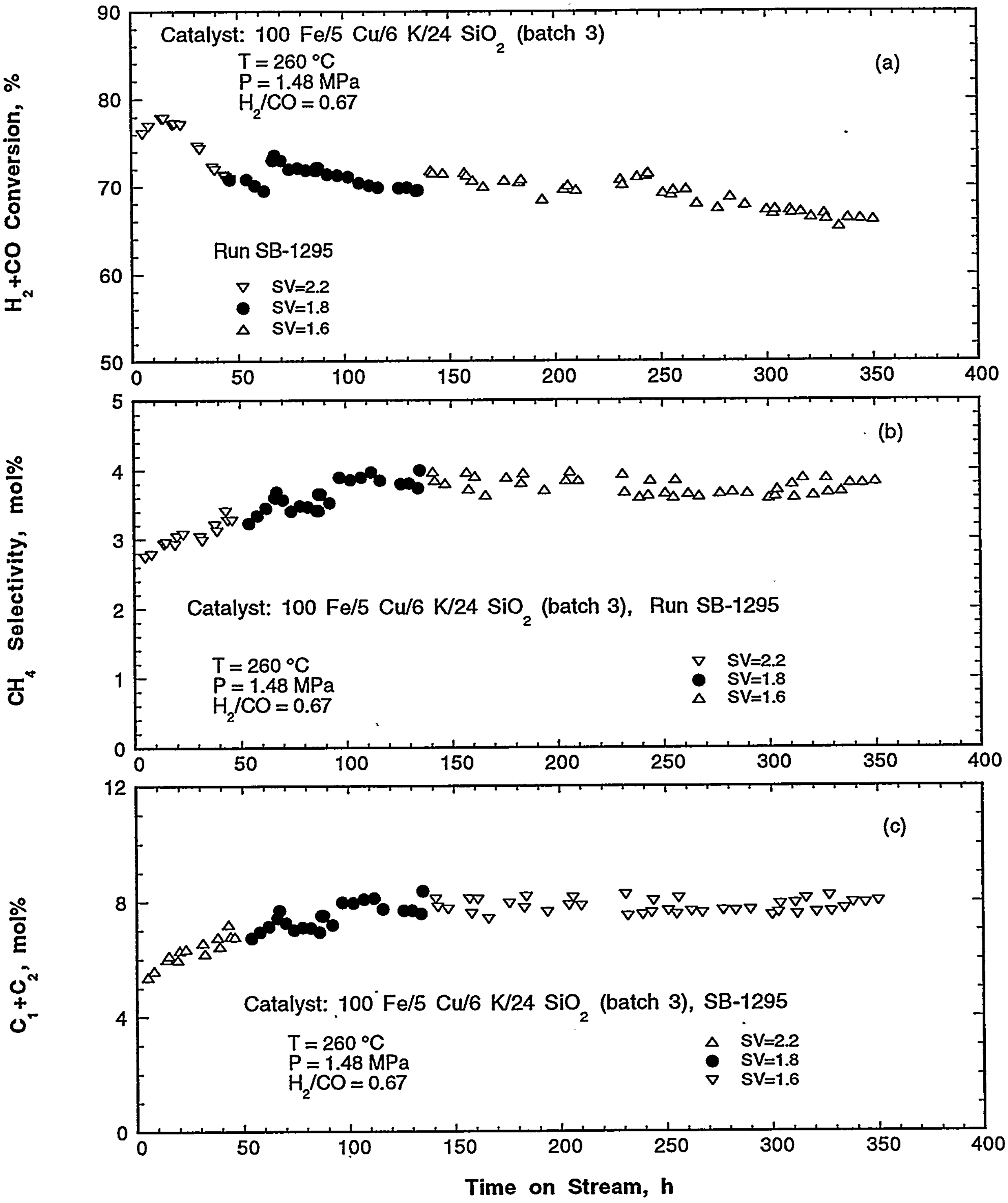

Figure 3. Variation in (a) (H_2+CO) conversion, (b) CH_4 selectivity and (c) C_1+C_2 selectivity with time on stream in run SB-1295.

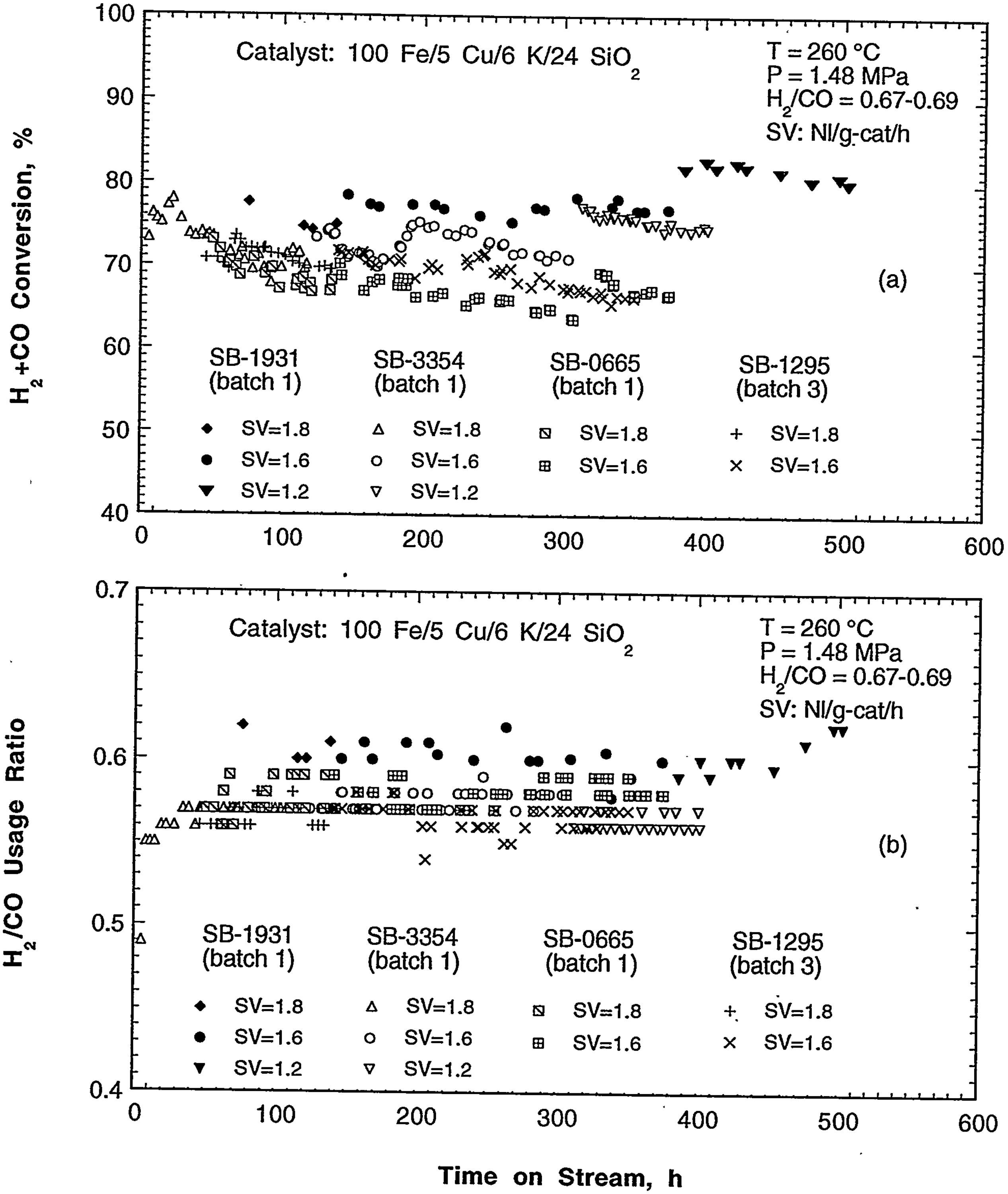

Figure 4. Comparison of STSR tests with catalyst B from two batches: (a) (H_2+CO) conversion and (b) H_2/CO usage ratio.

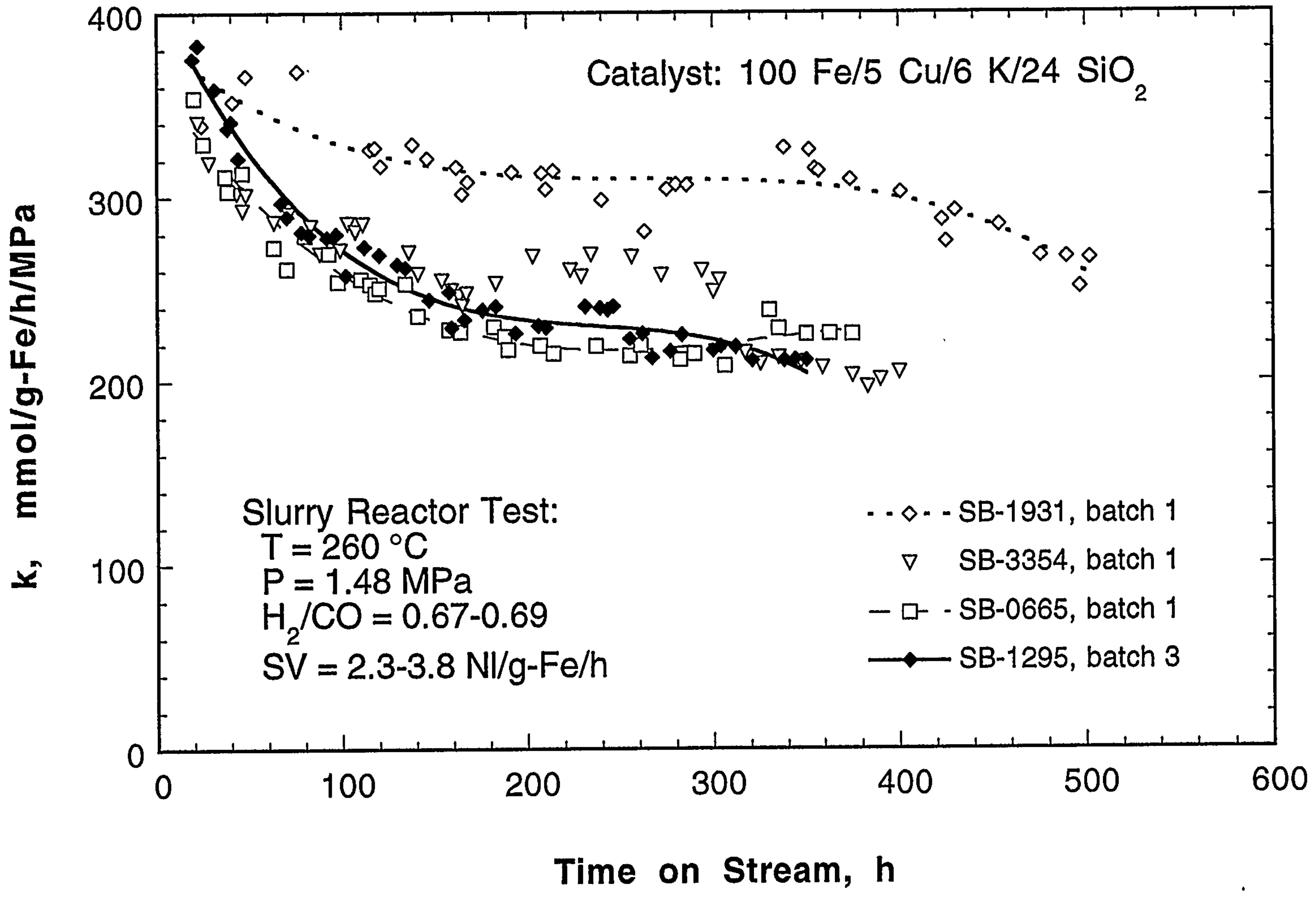

Figure 5. Comparison of reaction rate constant in STSR tests with catalyst B from two batches.

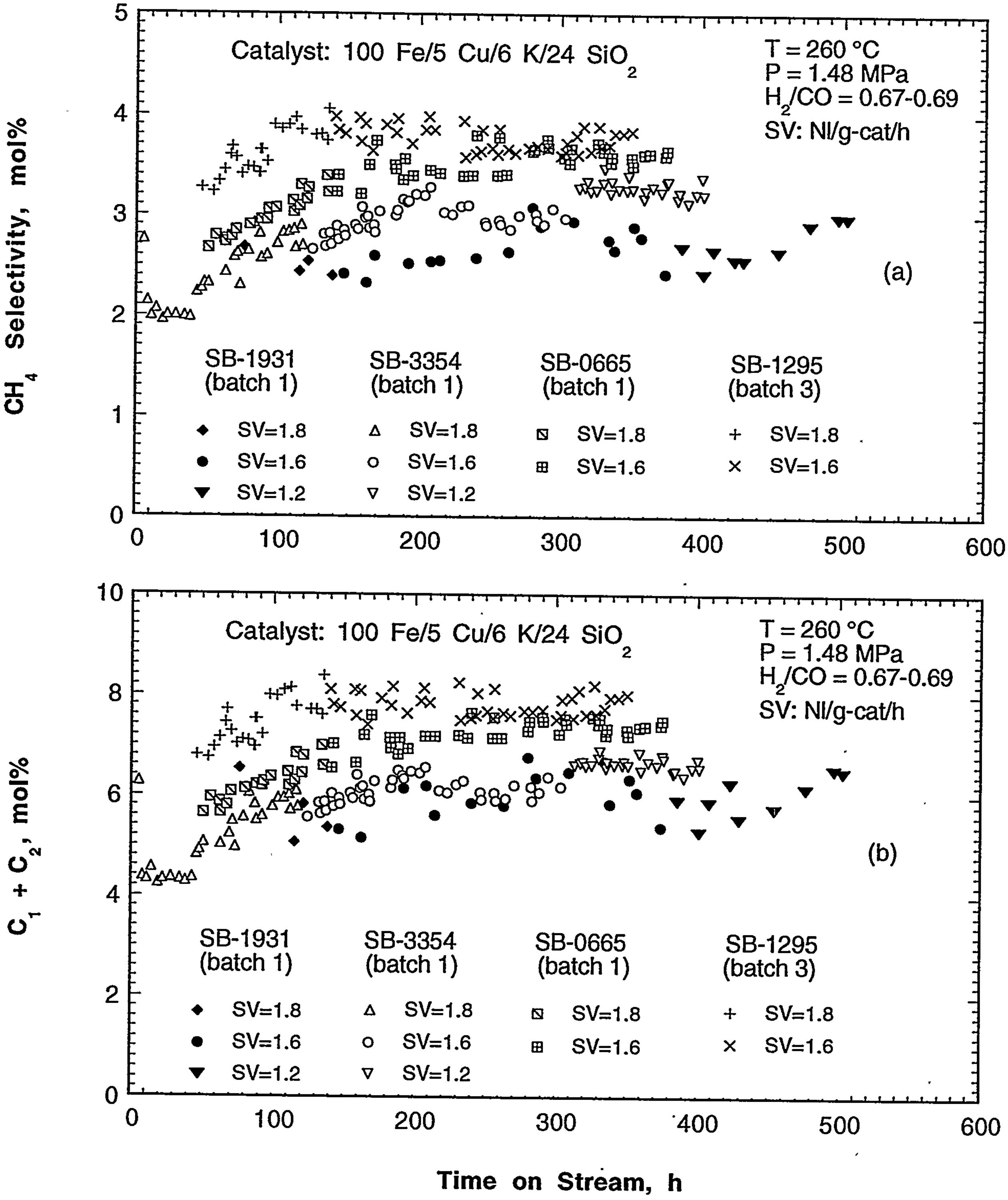

Figure 6. Comparison of STSR tests with catalyst B from two batches: (a) methane and (b) C_1+C_2 selectivities.

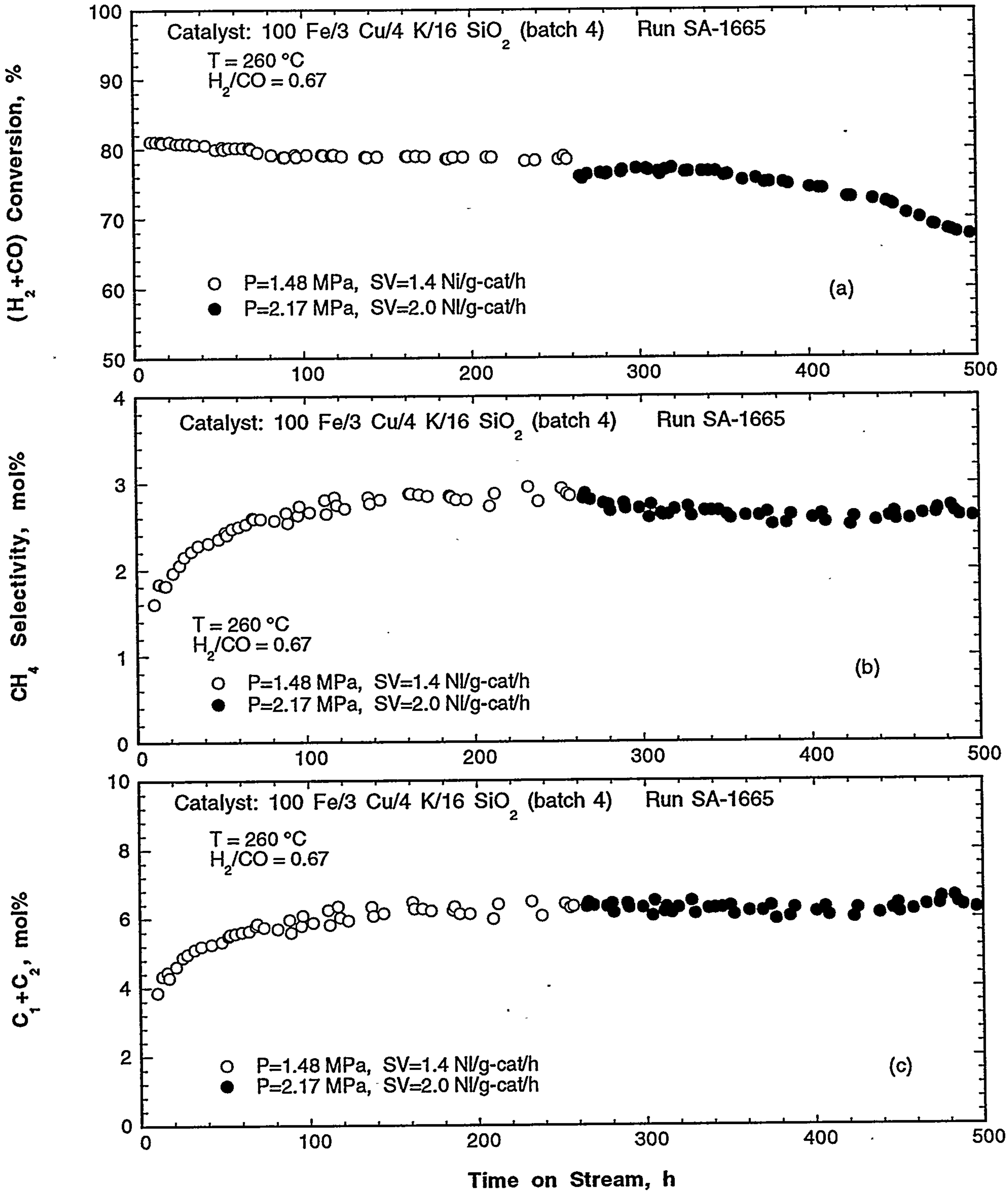

Figure 7. Variation in (a) (H_2+CO) conversion, (b) CH_4 selectivity and (c) C_1+C_2 selectivity with time on stream in run SA-1665.

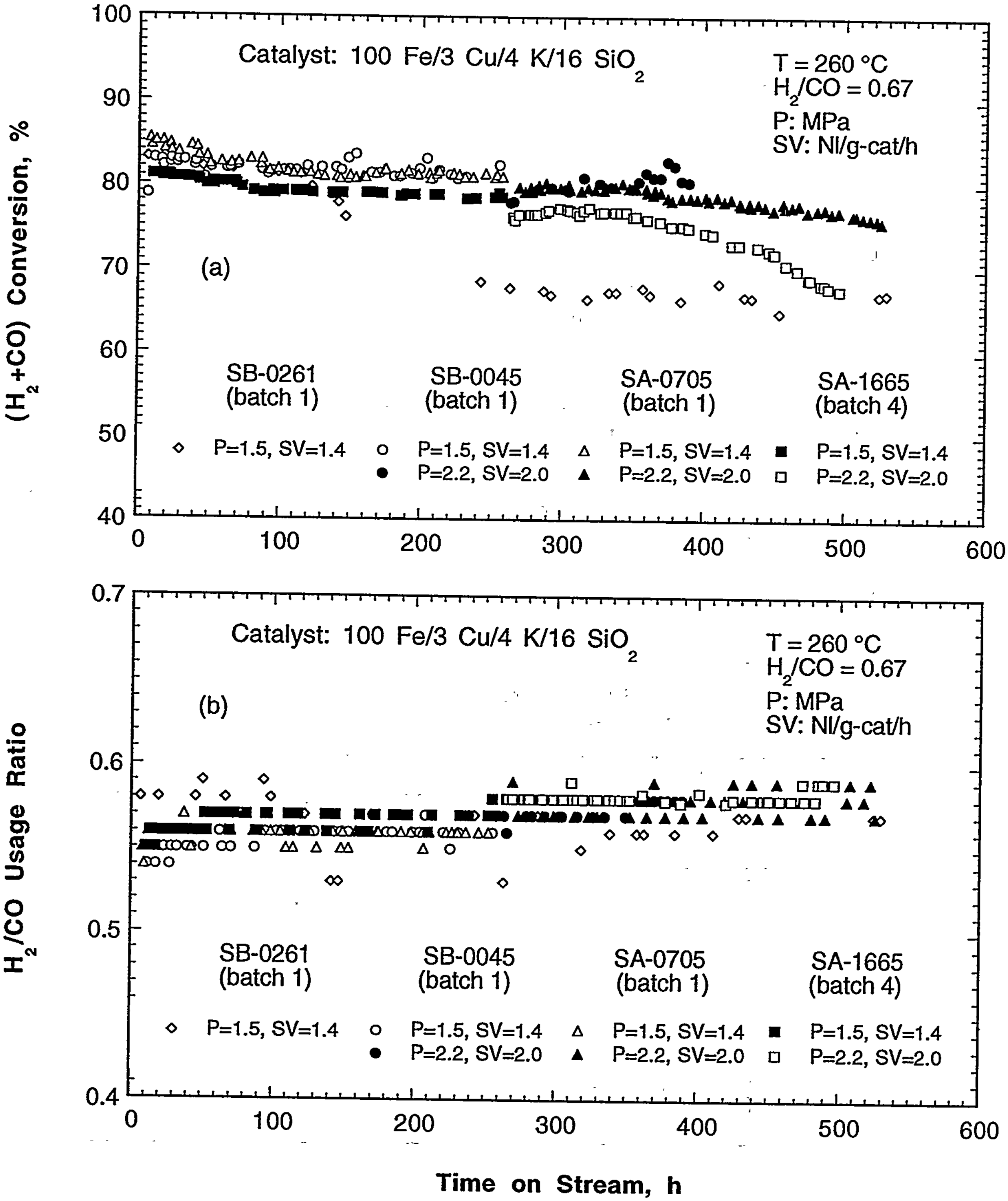

Figure 8. Comparison of STSR tests with catalyst C from two batches: (a) (H_2+CO) conversion and (b) H_2/CO usage ratio.

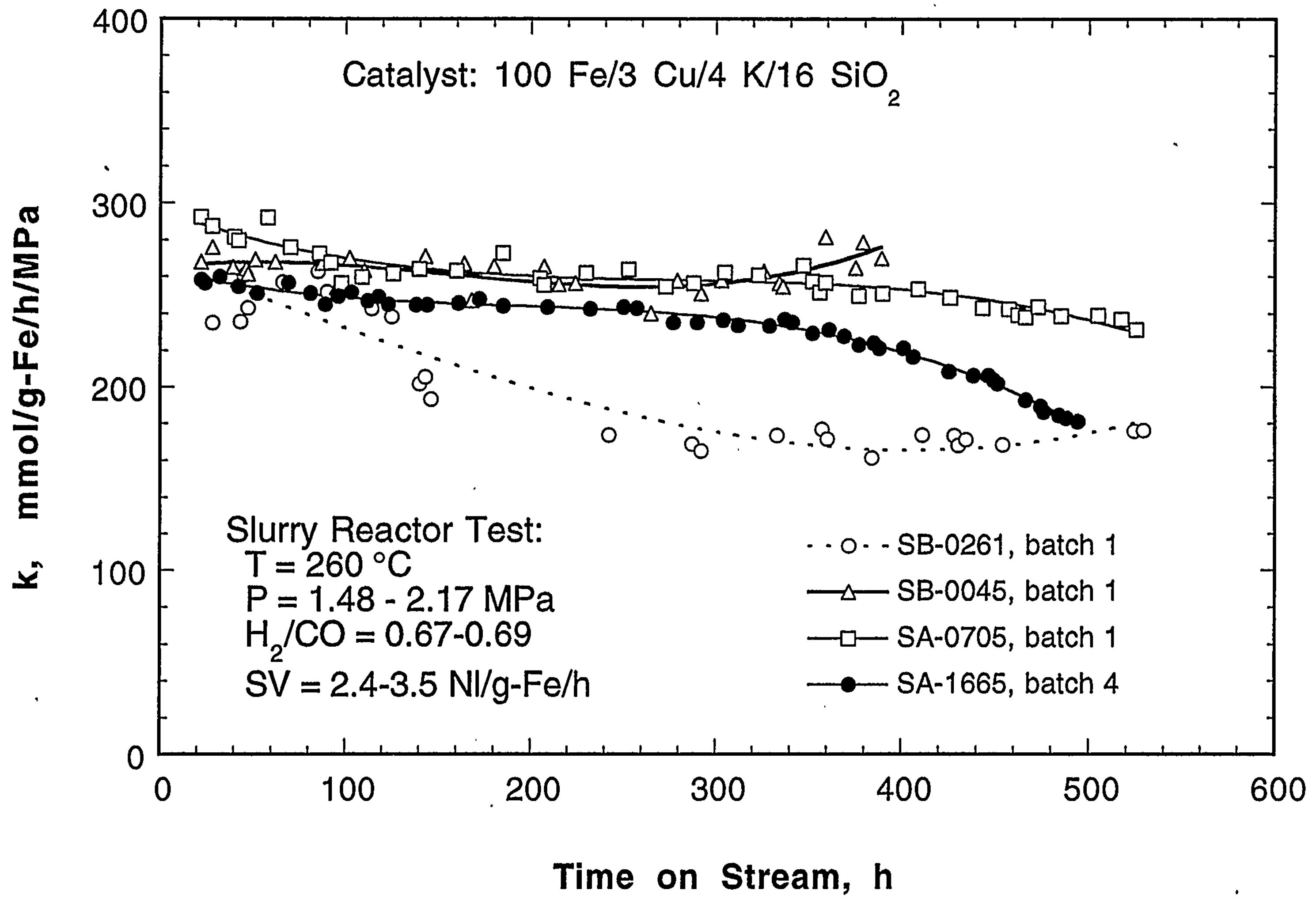

Figure 9. Comparison of reaction rate constant in STSR tests with catalyst C from two batches.

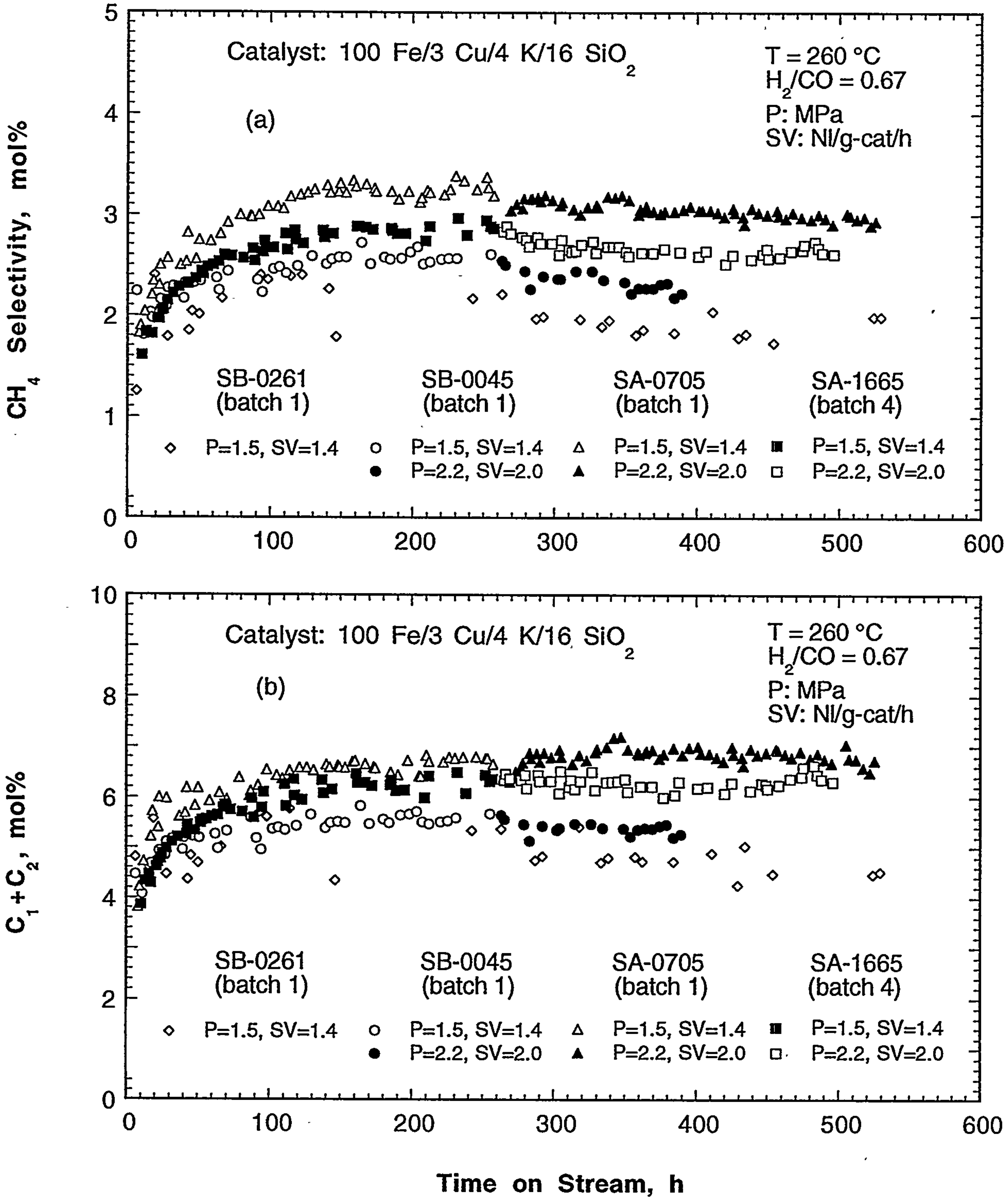

Figure 10. Comparison of STSR tests with catalyst C from two batches: (a) methane and (b) C_1+C_2 selectivities.

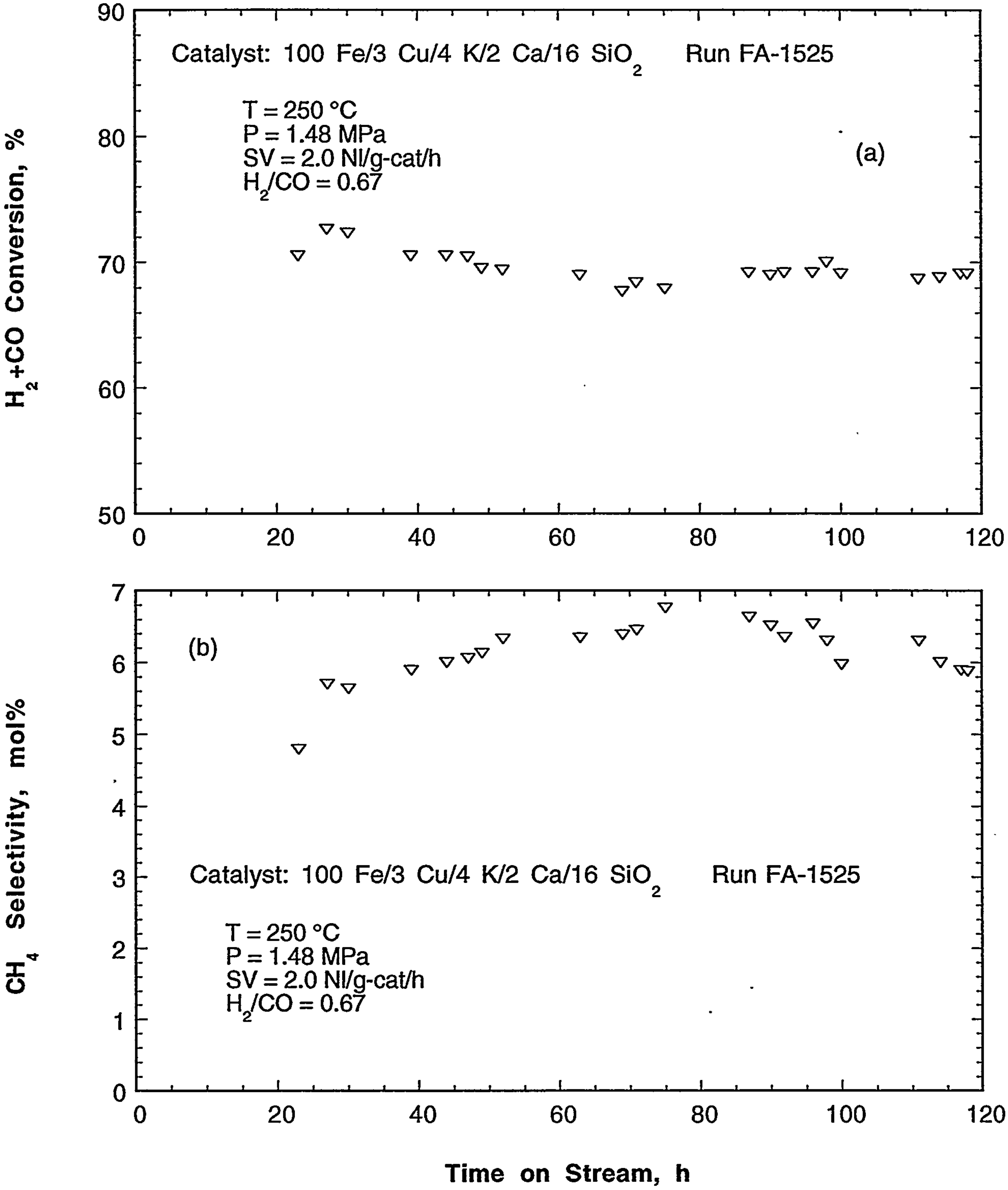

Figure 11. Variation in (a) (H_2+CO) conversion and (b) methane selectivity with time on stream in run FA-1525.

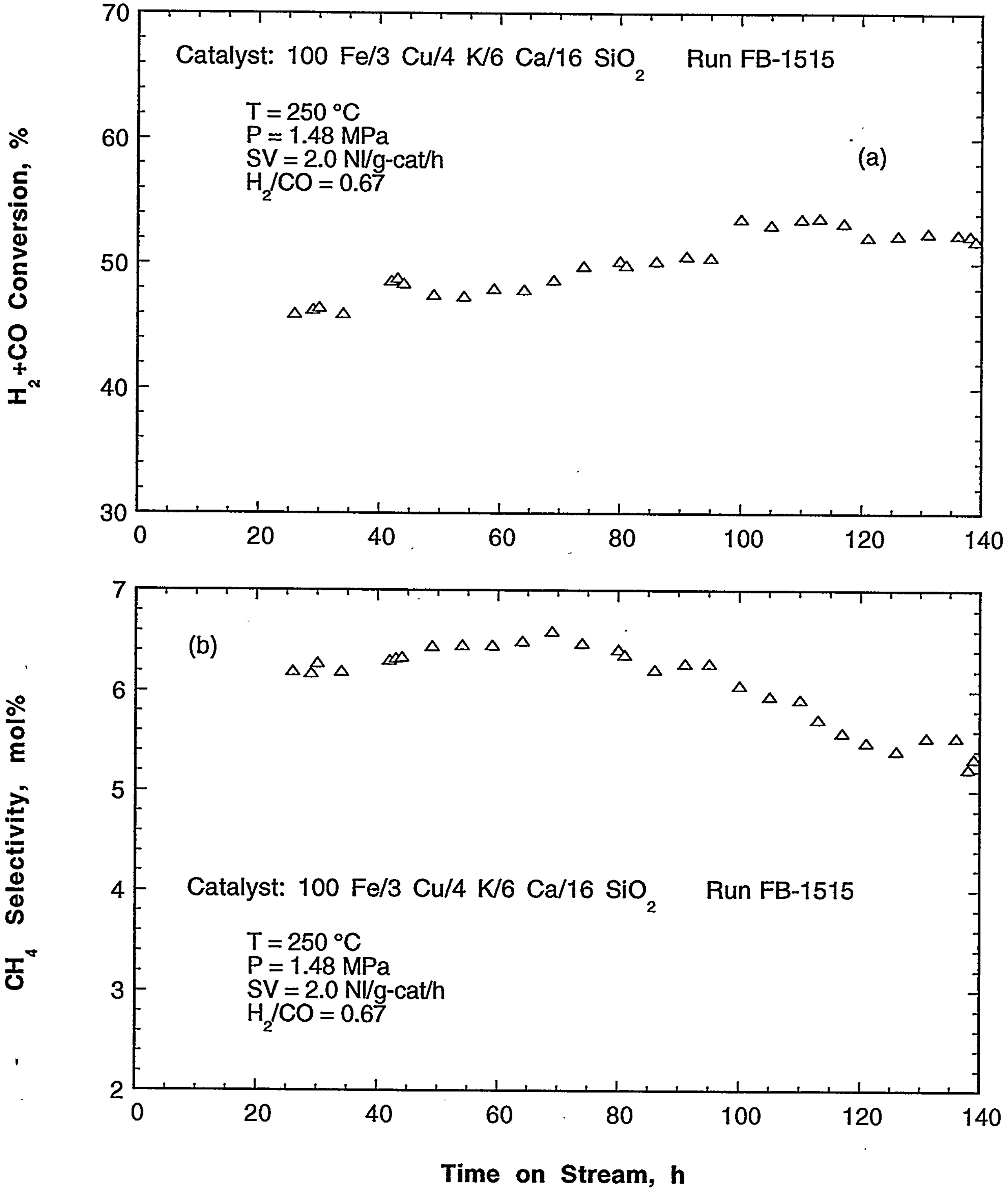

Figure 12. Variation in (a) (H_2+CO) conversion and (b) methane selectivity with time on stream in run FB-1515.

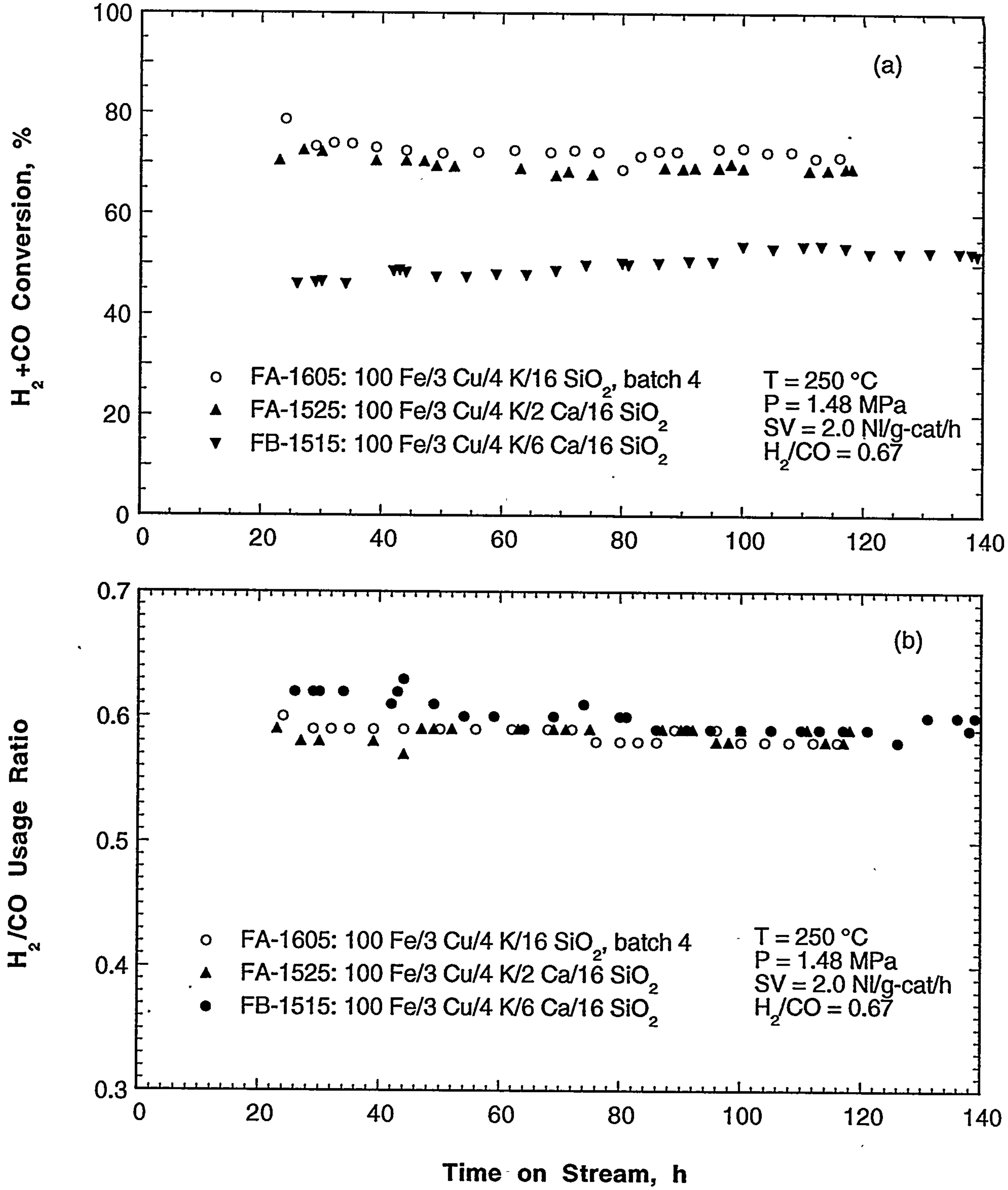

Figure 13. Effect of CaO promotion on 16 SiO_2 catalyst: (a) (H_2+CO) conversion and (b) H_2/CO usage ratio.

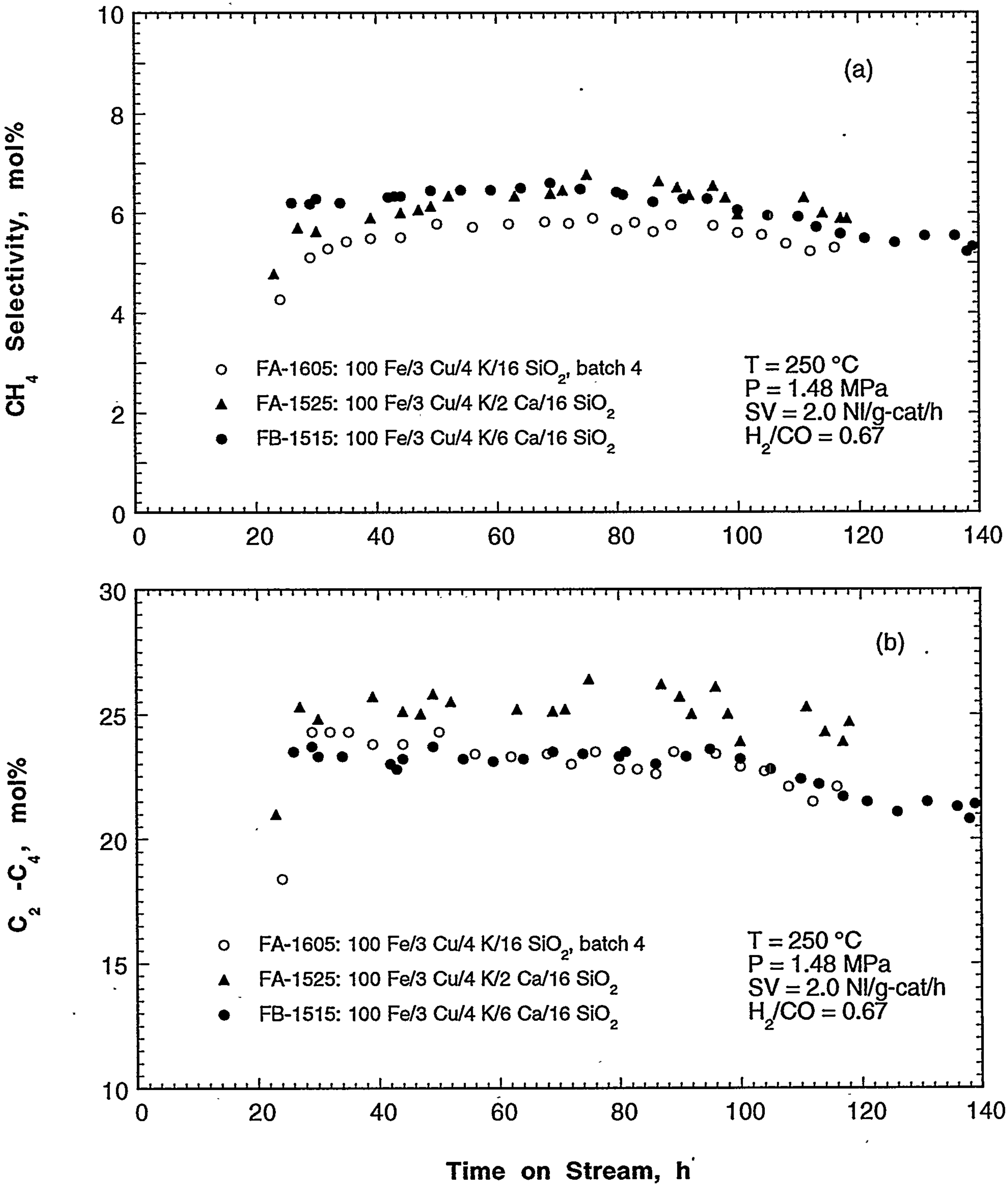

Figure 14. Effect of CaO promotion on 16 SiO_2 catalyst: (a) methane and (b) C_2-C_4 selectivities.

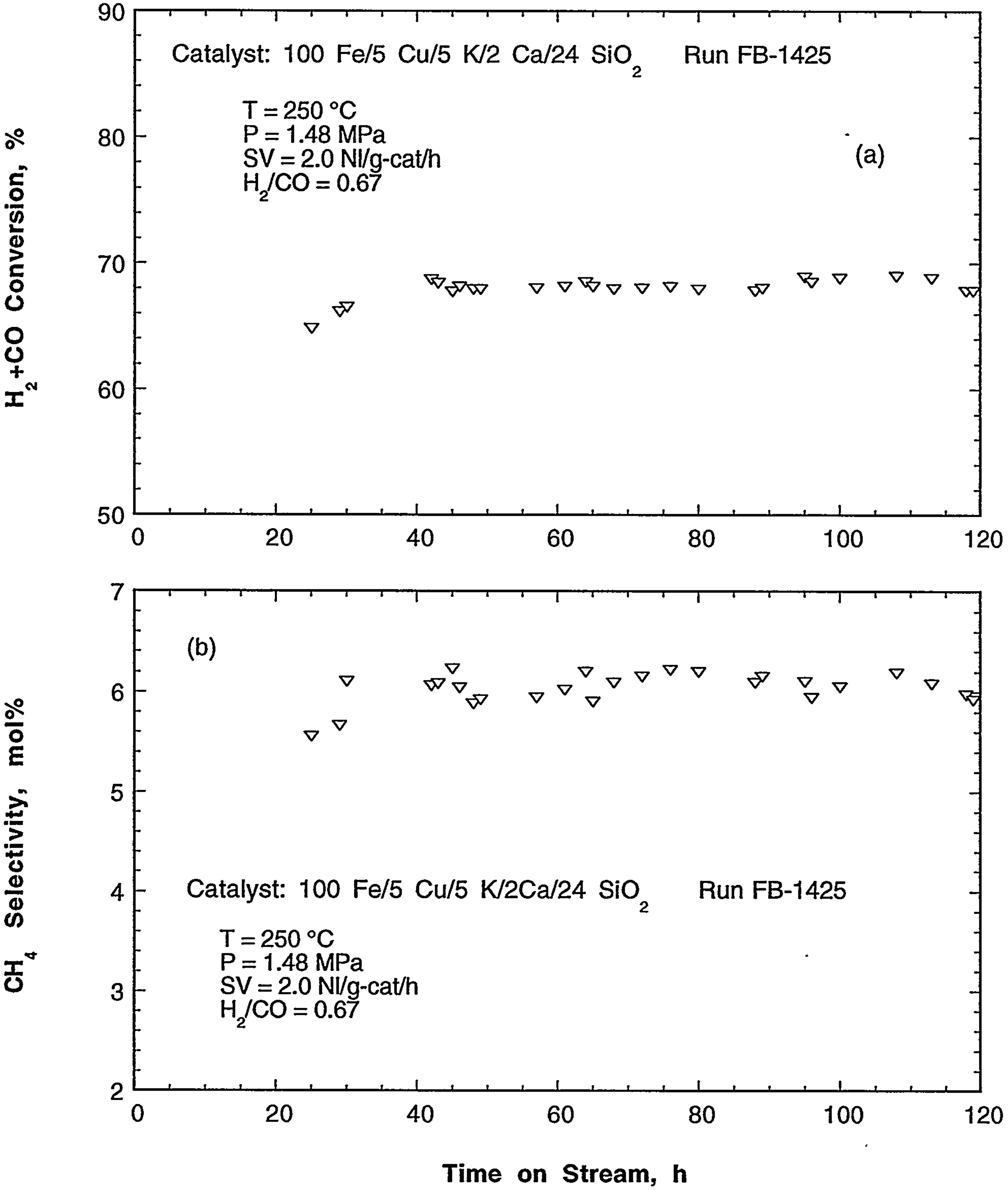

Figure 15. Variation in (a) (H_2+CO) conversion and (b) methane selectivity with time on stream in run FB-1425.

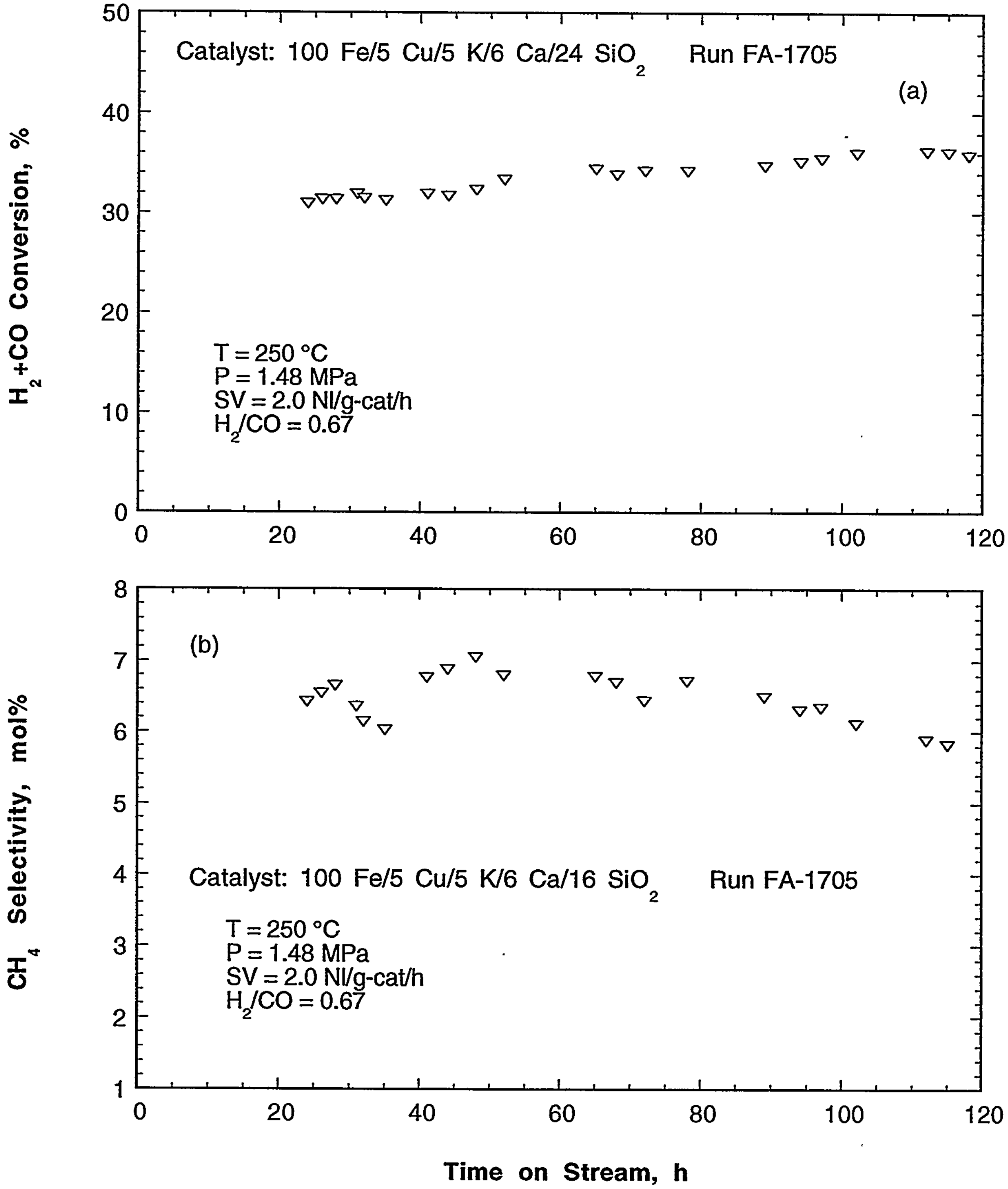

Figure 16. Variation in (a) (H_2+CO) conversion and (b) methane selectivity with time on stream in run FA-1705.

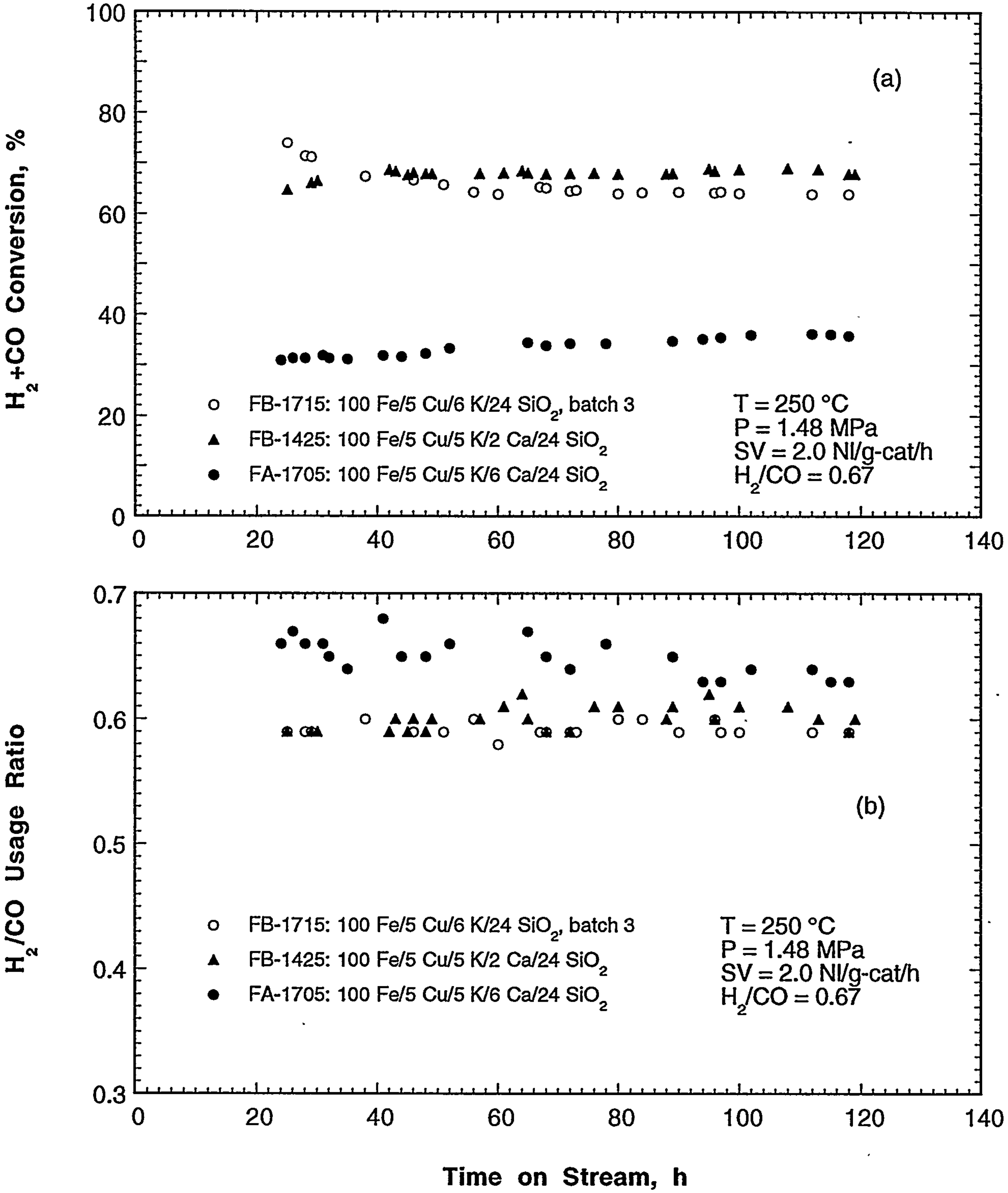

Figure 17. Effect of CaO promotion on 24 SiO_2 catalyst: (a) (H_2+CO) conversion and (b) H_2/CO usage ratio.

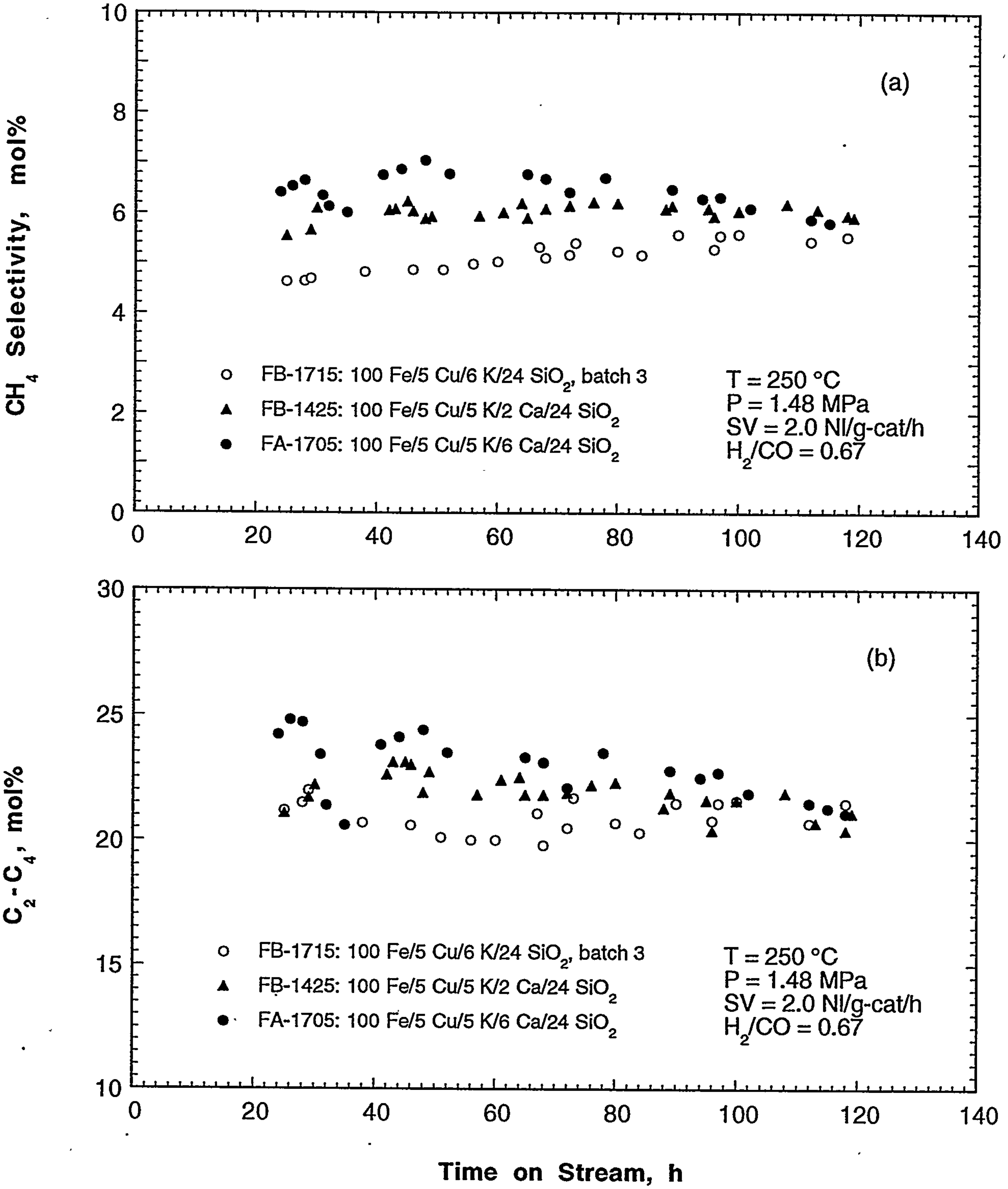

Figure 18. Effect of CaO promotion on 24 SiO$_2$ catalyst: (a) methane and (b) C$_2$-C$_4$ selectivities.