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Development of Precipitated Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
for the Period 1 July 1995 – 30 September 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) Five slurry reactor tests were completed. Three tests were conducted using catalyst C (100 Fe/3 Cu/4 K/16 SiO2) from three different batches (runs SB-2695, SB-2145 and SA-2715), and two tests were conducted with catalyst B (100 Fe/5 Cu/6 K/24 SiO2) from two different preparation batches (runs SA-2615 and SB-2585). Performance of catalysts from different 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. With these tests the work on Task 4, has been successfully completed.

Two fixed bed reactor tests of catalysts B and C synthesized using potassium silicate solution as the source of potassium promoter were completed during this period (Task 5. The Effect of Source of Potassium and Basic Oxide Promoter). Activity of catalysts prepared using potassium silicate as the source of potassium promotion was somewhat higher, and their methane selectivities were higher than those of the corresponding catalysts prepared by incipient wetness impregnation using $KHCO_3$ as the source of potassium promoter. However, these differences were not large, and may have been caused by experimental artifacts (e.g. existence of local hot spots in a reactor). A slurry reactor test (SA-2405) of catalyst with nominal composition 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 was completed (Task 5). In general, the catalyst activity, space-time-yield, and hydrocarbon selectivities in this run during testing at : 260°C, 2.17 MPa (300 psig), 2 - 2.6 Nl/g-cat/h and $H_2/CO = 0.67$ were quite good, and comparable to the best results obtained in our Laboratory.

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

Five stirred tank slurry reactor (STSR) tests were conducted during the past quarter. Catalyst C with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2 from batch #4 (S-3416-4) was evaluated in a STSR run SB-2145, to check reproducibility of reactor performance by comparing results from this test with those obtained in run SA-1665 with the same catalyst (Quarterly Report April - June, 1995). Two additional tests were conducted with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from batch #2 (SB-2695) and batch #3 (SA-2715) to determine reproducibility of catalyst preparation procedures, by comparing performance of catalysts from different preparation batches. Also, two STSR tests were conducted with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) from batch #4 (run SA-2615) and batch #5 (run SB-2585) to determine performance of catalyst B from different batches.

III. 4. 1 Run SB-2145 with 100 Fe/3 Cu/4 K/16 SiO_2 (batch 4) Catalyst

About thirty grams of the catalyst (< 270 mesh in size) from batch 4 (S-3416-4) was loaded for the test, together with 349 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 ($H_2/CO = 0.67$). Major events during the run are shown in Table 1 and detailed results from six mass balances are summarized in Table 2.

During 400 h of testing, the syngas conversion decreased from 82 to 59 % (Figure 1 a). 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 increased from 1.5 mol% (Figure 1b) to 3.5% during the first 200 h of testing, and then stabilized at about 3.3-3.5 %. Similarly, the lumped selectivity of $C_1 + C_2$ hydrocarbons increased from 3.4 to 7 %, and then remained fairly stable at about 7 mol% (Figure 1c), whereas C_2 - C_4 hydrocarbon selectivity was between 10 and 14 % (not shown in Figure 1).

Results from a previous test of this catalyst (SA-1665) are also shown in Figure 1 for comparison. As can be seen, the syngas conversion (catalyst activity), and gaseous hydrocarbon selectivities (methane, and $C_1 + C_2$ hydrocarbons) were similar to each other, during the first 100 h of testing. After 100 h on stream the catalyst in run SB-2145 deactivated more rapidly, and had higher methane and $C_1 + C_2$ hydrocarbons selectivities, in comparison to the catalyst performance in run SA-1665. Activities in the two tests, in terms of the apparent first order reaction rate constant, are compared in Figure 2. Deactivation rate in run SA-1665 was about 0.9 % per day, and 2.6 % per day in run SB-2145. Reasons for higher deactivation rate in SB-2145 and shift towards lower molecular weight products are not known at the present time. They may be caused by subtle changes in the operating procedures (three slurry sample withdrawals during the test, see Table 1) or by catalyst poisoning by sulfur impurities in the feed. In run SB-2145 we used about 30 g of catalyst, whereas about 10 g was used in run SA-1665. Thus, higher gas flow rates were employed in run SB-2145, and this may have resulted in the catalyst poisoning. At about 215 h on stream, we installed a sulfur removal trap in the gas feed line, but this did not result in decrease of the catalyst deactivation rate (see Figure 2), however, the catalyst selectivity stabilized at this point (no further increase in methane and $C_1 + C_2$ hydrocarbons selectivities with time on stream).

III-4.2 Runs SA-2715 and SB-2695 and Comparison of data from STSR tests of Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2)

During this quarter two additional tests were conducted with catalyst C from batch 2 (run SB-2695) and batch 3 (run SA-2715), and selected results from these two tests are shown in Figures 3 and 4, together with results from all other tests of the catalyst C. Results from three tests of catalyst C (runs SB-0261, SB-0045 and SA-0705) from the original preparation batch (S-3416-1) were described previously (Quarterly Technical Progress Report for the period January-March, 1995), as well as results from run SA-1665 - batch 4 catalyst (Quarterly Technical Progress Report for the period April-June, 1995). However, selected results from these four tests, are also shown here together with results from runs SB-2145 (batch 4), SB-2695 (batch 2) and SA-2715 (batch 3) to allow us to assess the effects of both catalyst preparation (tests of catalysts from different batches) and testing procedure (multiple tests of the catalyst from the same batch) on the catalyst performance. Tests SB-2695 and SA-2715 lasted about 120 h, whereas the other tests were of longer durations, but here we show results obtained during the first 120 h on stream, only.

Catalyst activity was similar in all seven tests. For example, syngas conversions (Figure 3a) were between 78 and 84 % (i.e., 81 ± 3%), whereas the apparent rate constant values (Figure 4) were between 225 and 290 mmol/g-Fe/h/MPa (mean value of about 250 mmol/g-Fe/h/MPa).

Methane (Figure 3b) and $C_1 + C_2$ selectivities (Figure 3c) were also similar in all seven tests. At about 100 h on stream, a mean value of methane selectivity from all seven tests is 2.6 %, whereas the minimum value is 2.1 % (SA-2715) and maximum 3.1 % (runs SB-2145 and SA-0705). Also, a mean value of $C_1 + C_2$ selectivity at about 100 h on stream is 5.7 %, whereas the minimum and the maximum are: 4.8 % (SA-2715) and 6.5 % (SA-0705), respectively.

In summary, reproducibility of catalyst synthesis and testing procedures may be considered as satisfactory for this catalyst. Lower methane and gaseous hydrocarbon selectivities obtained in tests with catalysts from batches 1-3, in comparison to the catalyst from batch 4, are consistent with higher potassium loadings of these catalysts (Table 3).

III-4.3 Runs SA-2615 and SB-2585 and Comparison of data from STSR tests of Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2)

During this quarter two additional tests were conducted with catalyst B from batch 4 (run SA-2615) and batch 5 (run SB-2585). The catalysts were tested at 260°C, 1.48 MPa, H_2/CO = 0.67 and gas space velocities of 2.15 Nl/g-cat/h (during the first 40 h on stream) and 1.8 Nl/g-cat/h during the next 80 - 100 h on stream. Selected results are shown in Figures 5 and 6, together with results from all other tests of the catalyst B. Results from three tests of catalyst B (runs SB-1931, SB-3354, and SB-0665) from the original preparation batch 1 (S-5624-1) were described previously (Quarterly Technical Progress Report for the period January-March, 1995), as well as results from run SB-1295 with batch 3 catalyst (Quarterly Technical Progress Report for the period April-June, 1995). However, selected results from these four tests, are also shown here to allow us to assess the effects of both catalyst preparation (tests of catalysts from different batches) and testing procedure (multiple tests of the catalyst from the same batch) on the catalyst performance. Elemental analysis and textural properties of catalysts tested are summarized in Table 4.

Comparison of catalyst activity in terms of (H_2+CO) conversion and the apparent first order rate constant, k, obtained in six STSR tests with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst is given in Figures 5 and 6, respectively. Syngas conversions in all six tests are within 10% of the mean value of conversion, i.e. 71 ± 6 %. Catalyst from batch 5 (run SB-2585) was the least active (66-71 % conversion), whereas the catalyst from batch 4 (SA-2615) was the most active (74-77 % conversion). Comparison of catalyst activity is observed better in Figure 6, where the apparent first order rate constant, k, is plotted as a function of time. The catalysts deactivated in all six tests. The rate of deactivation was the lowest in run SB-1931 with batch 1 catalyst, however, this was not observed in the other two tests of the catalyst from batch 1 (runs SB-3354 and SB-0665). At about 100 h on stream numerical values of the apparent rate constant were between 248 mmol/g-Fe/h/MPa (SB-2585) and 301 mmol/g-Fe/h/MPa (run SA-2615).

Methane and C_1+C_2 selectivities are also shown in Figure 5. Similar values of selectivities were obtained in all three tests of the catalyst from batch 1 (runs SB-1931, SB-3354, and SB-0665), and in run SB-2585 with batch 5 catalyst, whereas higher values were obtained in tests with batch 3 (SB-1295) and batch 4 (SA-2615) catalysts. A possible reason for higher methane and C_1+C_2 selectivities obtained in run SB-1295 is that potassium content of batch 3 catalyst is lower than that of the other batches (5.2 K per 100 Fe (batch 3) vs. 6.2 - 7.8 K per 100 Fe in other batches). However, the catalyst from batch 4 (SA-2615) had higher potassium loading (6.5 K per 100 Fe) than the catalyst from batch 3, and yet its methane and C_1+C_2 selectivities were higher. The reasons for this are not understood at the present time, and perhaps future catalyst characterization studies by XRD and Mössbauer spectroscopy may provide rationale for the observed results.

On the basis of results obtained during the current quarter, with catalysts from different batches we conclude that reproducibility of catalyst preparation procedure may be regarded as satisfactory. In general, catalysts from different preparation batches had similar performance (activity, selectivity and deactivation rates). The work on this task has been successfully completed.

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

During the reporting period we completed two fixed bed reactor tests of catalysts B (100 Fe/5 Cu/6 K/24 SiO_2) and C (100 Fe/3 Cu/4 K/16 SiO_2), which were synthesized previously (Quarterly Technical Progress Report for the period April-June, 1995), using potassium silicate solution as a source of potassium promoter. Prior to Fischer-Tropsch synthesis the catalysts were reduced in-situ with hydrogen at atmospheric pressure, and 240°C for 2 h (catalyst C - run FB-1985), or at 250°C for 4 h (catalyst B - run FA-1795). After the conditioning period of about 24 h, during which the reaction temperature was gradually increased from 210 to 250°C, the 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.

Also, we completed a stirred tank slurry reactor test of catalyst with nominal composition 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 (run SA-2405). This catalyst was tested previously in a fixed bed reactor run FB-1425 (Quarterly Technical Progress Report for the period April-June, 1995).

Fixed Bed Reactor Tests of Catalysts B and C

III. 5. 1 Run FB-1985 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

Results illustrating variations in catalyst activity and gaseous hydrocarbon selectivities with time are shown in Figures 7 and 8. Results from the previous test FB-1605 of catalyst C prepared using potassium bicarbonate ($KHCO_3$) as the source of potassium promoter are also shown for comparison. The syngas conversion and the usage ratio in test FB-1985 were stable with time, and their numerical values were about 80 % and 0.61, respectively (Figure 7). Methane selectivity (Fig. 8a) was between 6 and 7 mol %, and gaseous (C_2 - C_4) hydrocarbon selectivity (Fig. 8b) was between 20 and 22 mol %.

By comparison, the catalyst synthesized using $KHCO_3$ as the source of potassium (FA-1605) was less active (syngas conversion of about 72 %), and had lower methane selectivity (5.1 - 5.9 mol %). Its usage ratio (0.59) and (C_2 - C_4) hydrocarbon selectivity (21-24 %) were similar to the corresponding values obtain in run FB-1985 (Figures 7b and 8b).

III. 5. 2 Run FA-1725 with 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst

Catalyst FTS activity, measured by syngas conversion, and the water-gas-shift (WGS) activity, measured by usage ratio (lower usage ratio implies higher WGS activity) increased slightly during 120 h of testing (Figure 9). After the catalyst had reached the steady state (at about 50 h on stream) methane selectivity varied between 6.6 and 7.3 mol %, whereas C_2 - C_4 selectivity was between 21 and 23 % (Figure 10).

Results from run FB-1715, of the catalyst B synthesized using $KHCO_3$ as the source of potassium promoter, are also included for comparison. The activity of this catalyst decreased during the first 60 h of testing, and then stabilized at about 64 %, which is lower than that obtained in run FA-1795 (68-70 %). The usage ratio in run FB-1715 was about 0.59 (Figure 9b)

implying a slightly higher WGS activity in comparison to run FA-1795. Methane selectivity in run FB-1715 was lower (5 - 5.5 mol %) than that in run FA-1795 (Figure 10a), whereas gaseous C_2 - C_4 hydrocarbon selectivities were similar in both tests (Figure 10b).

Concluding Remarks on the Effect of Source of Potassium Promotion

Two catalysts (B and C) were prepared by using different methods of potassium promotion. Baseline catalysts were prepared by incipient wetness impregnation of Fe-Cu-SiO_2 precursor with an aqueous solution of $KHCO_3$. In a modified procedure, aqueous solution of potassium silicate is added to the Fe-Cu precursor as a source of silicon oxide, and then the excess amount of potassium is removed by washing to get a desired level of potassium promotion. Elemental analysis and textural properties of catalysts prepared by different methods are shown in Table 5. In general, differences in textural properties (surface area and pore volume) of catalysts prepared by these two procedures, as well as in the elemental analysis are within 20 %.

Some differences in catalyst performance were noticed in fixed bed tests of catalysts B and C prepared by different methods. In both cases, the activity of catalysts prepared using potassium silicate as the source of potassium promotion was somewhat higher, and their methane selectivities were higher than those of the corresponding catalysts prepared by incipient wetness impregnation using $KHCO_3$ as the source of potassium promoter. However, these differences are not that large, and may have been caused by experimental artifacts (e.g. existence of local hot spots in a reactor). Before making any definite conclusions about the importance of method of addition of potassium promoter, we plan to evaluate one of these two catalysts in a slurry reactor. This test will provide information on catalyst long term performance under conditions of better temperature control.

III. 5. 3 Run SA-2405 with 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 Catalyst

This catalyst was tested previously in a fixed bed reactor (run FB-1425), and its performance was found to be similar to that of the baseline B catalyst (100 Fe/5 Cu/6K/24 SiO_2), as described in the last quarterly report (Quarterly Technical Progress Report for the period April-June, 1995).

For this test about 9.5 g of the catalyst was loaded into a slurry reactor with 312 g of Durasyn 164 oil. After the reduction with hydrogen at 250°C for 4 h, the catalyst was tested initially at: 260°C, 1.48 MPa, 2.2 Nl/g-cat/h and $H_2/CO = 0.67$. Major events during the run are shown in Table 6, and results from complete mass balances are given in Table 7.

Syngas conversion decreased rapidly from 75 % to 69 % during 40 h of testing at the above process conditions (Figure 11a). Between 41 and 239 h on stream, the catalyst was tested at a lower gas space velocity of 1.8 Nl/g-cat/g (the other conditions being the same). Upon decreasing the gas space velocity the syngas conversion increased to 73 %, but then started to decline reaching 69 % at about 90 h on stream. Between 90 and 237 h, the syngas conversion was very stable. During testing at SV = 2.2 and 1.8 Nl/g-cat/h, methane (Fig. 11b), and gaseous hydrocarbon selectivities (Fig. 12) first increased with time, and then began to level off at about 150 h on stream.

Between 240 and 477 h the catalyst was tested at 260°C, 2.17 MPa, 2.6 Nl/g-cat/h and $H_2/CO = 0.67$. Syngas conversion decreased with time slightly, reaching 61 % at 470 h on stream. During this time period methane and gaseous hydrocarbon selectivities decreased dramatically (Figs. 11b and 12). For example, methane selectivity decreased from 5.3 % at 237 h, to 3.2 % at 470 h, and similar trends were observed with $C_1 + C_2$ and C_2-C4 selectivities (Figure 12).

Between 477 and 555 h on stream the catalyst was tested at 260°C, 2.17 MPa, 2.0 Nl/g-cat/h and $H_2/CO = 0.67$. During this period the syngas conversion was between 68 and 71 %, whereas hydrocarbon selectivities remained stable (Figures 11 and 12).

At this time it was decided to perform in situ catalyst activation with pure CO at 280 °C for 12 h (556-568) in attempt to increase the catalyst activity. After the activation the catalyst was tested at: 260°C, 1.48 MPa, 1.8 Nl/g-cat/h and $H_2/CO = 0.67$ (the same process conditions used between 41 and 239 h on stream) for the next 28 h. At 597 h the syngas conversion reached 69 %, which is the same as the value at 237 h on stream, indicating that the activation procedure was effective in improving the catalyst activity. Hydrocarbon selectivities at 597 h were similar to the corresponding values at 237 h on stream.

At 598 h the process conditions were changed to: 260°C, 2.17 MPa, 2.0 Nl/g-cat/h and $H_2/CO = 0.67$. These conditions were employed immediately before the CO activation (477-555 h on stream). The syngas conversion at 606 h was about 75 %, which is significantly higher than 65 % at 555 h on stream, but it declined during the next 80 h of testing reaching 70 % at 690 h. Methane, and gaseous hydrocarbon selectivities were initially significantly higher than their corresponding values at 555 h on stream, but continued to decline and at 690 h were approaching their respective values before the CO activation. These data indicate that the increase in activity following the CO activation was of a temporary nature, and was accompanied by increase in gaseous hydrocarbon selectivities. The latter may be due to reaction between syngas and excess surface carbon, which was deposited during the CO activation. The test was terminated voluntarily at 693 h, immediately after a slurry sample withdrawal for catalyst characterization.

Comparison of Results from Runs SA-2405 and SB-1295

Results obtained in run SA-2405 with the catalyst containing CaO promoter are compared with those obtained in run SB-1295 with catalyst B (100 Fe/5 Cu/6K/24 SiO_2) from batch 3, in Figures 13-15. The same Fe-Cu-SiO_2 precursor was used in preparation of these two catalysts.

Activity comparisons are made in Figure 13a (in terms of syngas conversions) and Figure 14 (in terms of the apparent reaction rate constant). During the first 120 h on stream, the catalyst B was slightly more active than CaO containing catalyst (higher apparent rate constant), whereas after that the latter catalyst was more active. This is primarily due to the fact that the CaO

containing catalyst (SA-2405) maintained its activity better than the catalyst B (SB-1295). The catalyst B had a faster deactivation rate than the CaO catalyst.

During testing at 1.48 MPa (200 psig) catalyst B had either similar (first 30-40 h on stream) or lower methane (Figure 13b), C_1+C_2 (Figure 15a) and C_2-C_4 (Figure 15b) hydrocarbon selectivities than the CaO containing catalyst. However, when the pressure was increased to 2.17 MPa (at 237 h on stream) in run SA-2405, methane and gaseous hydrocarbon selectivities started to decrease and at 300 h were similar to those obtained in test SB-1295 (here the system pressure is still 1.48 MPa). The data show that hydrocarbon selectivities of the CaO containing catalyst are dependent upon the reaction pressure, whereas this was not observed in tests with catalyst C (without CaO promoter) - e.g. see Figure 1. We plan to investigate this further in future tests. In general, the catalyst activity, space-time-yield, and hydrocarbon selectivities in run SA-2405 at 2.17 MPa(300 psig) were quite good, and comparable to the best results obtained in our Laboratory.

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

During the reporting period we received results from Mössbauer spectroscopy measurements, conducted at CFFLS (University of Kentucky), on five used catalyst samples from slurry reactor tests conducted under Task 3 of our contract. The iron phases present in catalyst samples withdrawn from the reactor at the end of test are summarized in Table 8. Numerical values of syngas conversions and methane selectivities obtained during the last 100 h of testing are also shown in this Table. The following observations are made from these results.

(1) Syngas conversion was low (14 %) in the presence of magnetite and superparamagnetic phase (probably iron oxide) - run SB-3064. Previously (Quarterly Technical

Progress Report October - December 1994), we suggested that a possible reason for low activity in this test is the presence of impurities in the initial slurry medium. These impurities may have prevented formation of active iron phases during the reduction and synthesis. In all other tests in which the catalyst was active the iron carbides were present (Table 8).

(2) Catalyst B, which contains 24 parts of SiO_2 per 100 parts of Fe, tends to form ε'-carbide during FTS (runs SB-0665 and SB-1295), whereas in catalyst C (16 parts of SiO_2 per 100 parts of Fe) χ-carbide was formed (runs SB-0045 and SA-0705). It is not clear whether this is due to differences in silicon oxide loadings, or due to differences in process conditions employed in different tests. Namely, in runs SB-0045 and SA-0705 with catalyst C, the catalyst was tested at both 1.48 MPa and 2.17 MPa, whereas in runs SB-0665 and SB-1295, the catalyst B was tested at 1.48 MPa, only.

(3) Methane selectivities were lower in tests were χ-carbide was present (Catalyst C), in comparison to those were ε'-carbide was present. Further data are needed to confirm generality (if any) of this observation.

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) complete testing of catalysts containing CaO as promoter and/or catalysts with different source of potassium in slurry reactors (Task 5); (b) initiate work on Tasks 6 and 7 of the contract, and (c) continue with catalyst characterization of catalysts at various stages of usage (Task 8).

Table 1. Major Events in Run SB-2145 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst (batch 4)

TOS (h)	Event
	Slurry loading: 349 g of Durasyn 164 oil, 30 g of catalyst (particle size< 270 mesh)
	Catalyst pretreatment: H_2, 240°C, 0.78 MPa
	Slurry withdrawal through dip tube: 13 g slurry, 1.06 g catalyst
	Wax withdrawal through filter: 50.9 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
67	Slurry sample withdrawal: 10.5 g slurry, 0.97 g catalyst
145	Slurry sample withdrawal: 10.1 g slurry, 0.9 g catalyst
213	Slurry sample withdrawal: 8.4 g slurry, 0.74 g catalyst
215	Seal reactor under helium, add a CARUSORB 200 sulfur-removal trap in the feed line
216	Resume synthesis
401	Slurry sample withdrawal: 11.7 g slurry, 1.1 g catalyst
402	End of run: 205 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 1204 g wax, 4.8 g catalyst

Table 2. Summary of results for slurry run SB-2145 .

Catalyst: 28.96 g[a], 100Fe/3Cu/4K/16SiO_2 (batch 4) Slurry liquid: 349.0 g, Durasyn-164

Reactor volume: 430. cc[b]

Period	1	2	3	4	5	6
Time on Stream (h)	40.0	150.0	196.0	270.0	310.0	365.0
Balance Duration (h)	16.0	12.5	12.0	12.0	12.0	13.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.667	.667	.667	.667	.667	.667
Space Velocity (Nl/g-cat·h)[a]	1.39	1.40	1.40	1.40	1.40	1.40
Space Velocity (Nl/g-Fe·h)	2.42	2.44	2.44	2.44	2.44	2.44
GHSV (h^{-1})[b]	93.5	83.4	83.4	81.1	81.1	81.1
CO Conversion (%)	82.2	78.9	77.3	71.6	69.1	65.4
H_2+CO Conversion (%)	77.2	74.1	72.3	66.7	64.4	60.8
H_2/CO Usage	.564	.564	.558	.554	.554	.549
STY ($mols$ H_2+CO/g-cat·h)[a]	.048	.046	.045	.042	.040	.038
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	36.8	37.3	43.2	40.8	41.0	43.4
Weight % of Outlet						
H_2	1.41	1.55	1.64	1.88	1.96	2.14
H_2O	.768	.671	.563	.493	.469	.407
CO	17.2	20.5	22.0	27.5	29.7	33.4
CO_2	60.5	58.2	57.2	51.7	51.0	48.5
Hydrocarbons	9.23	10.0	11.3	10.5	9.46	9.15
Oxygenates	.384	.598	.673	.861	.886	.805
Wax[c]	10.5	8.44	6.52	7.04	6.51	5.55
Yield (g/Nm^3 H_2 + CO $Converted$)						
CH_4	6.19	7.57	8.08	7.82	8.02	7.84
C_2–C_4 Hydrocarbons	23.6	27.7	27.6	27.4	29.0	28.8
C_5–C_{11} Hydrocarbons	35.2	39.1	44.4	47.6	40.4	44.6
C_{12}+ Hydrocarbons	134.	118.	111.	121.	116.	107.
Wax[c]	106.	87.9	69.7	81.8	78.9	70.9
Oxygenates	3.86	6.23	7.20	10.0	10.7	10.3
Total	202.	199.	198.	214.	204.	198.
1+2 Olefins/n-Paraffin Ratio						
C_2	1.44	1.50	1.63	2.06	2.24	2.57
C_3	5.52	5.34	5.28	5.11	5.09	5.00
C_4	4.43	4.29	4.09	3.94	3.87	3.81
C_8	3.03	3.13	3.21	3.01	2.86	3.03
C_{10}	2.21	2.21	2.70	2.70	2.77	2.80

[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-2145 .

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	3.12	3.94	4.23	3.84	4.14	4.17
Ethane	1.33	1.64	1.56	1.26	1.32	1.22
Ethylene	1.79	2.29	2.37	2.41	2.75	2.93
Propane	.777	.976	.965	.923	1.03	1.06
Propylene	4.09	4.97	4.86	4.50	4.99	5.08
n–Butane	.672	.815	.873	.825	.947	.983
1+2 Butenes	2.87	3.37	3.45	3.14	3.54	3.61
C_4 Isomers	.358	.350	.398	.369	.409	.417
n–Pentane	.974	1.24	1.36	1.11	1.36	1.45
1+2 Pentenes	2.86	3.37	3.49	3.01	4.18	3.52
C_5 Isomers	.133	.175	.167	.159	.0412	.211
n–Hexane	.581	.685	.992	.759	.707	.832
1+2 Hexenes	1.94	2.28	2.40	2.29	2.11	2.49
C_6 Isomers	.327	.738	.812	.845	.582	.933
n–Heptane	.528	.708	.649	.694	.548	.661
1+2 Heptenes	1.66	1.96	2.05	2.13	1.62	1.98
C_7 Isomers	.454	.258	.725	.583	.117	.581
n–Octane	.493	.467	.544	.640	.475	.540
1+2 Octenes	1.47	1.44	1.72	1.89	1.34	1.60
C_8 Isomers	.456	.516	.597	.895	.350	.902
n–Nonane	.498	.652	.566	.609	.749	.556
1+2 Nonenes	1.29	1.04	1.58	1.70	1.14	1.53
C_9 Isomers	.187	.273	.340	.329	.299	.296
n–Decane	.545	.584	.620	.615	.539	.607
1+2 Decenes	1.19	1.28	1.65	1.64	1.47	1.67
C_{10} Isomers	.180	.284	.334	.369	.379	.376
n–Undecane	.527	.658	.656	.744	.623	.754
1+2 Undecenes	1.13	1.31	1.51	1.73	1.65	1.64
C_{11} Isomers	.295	.400	.467	.578	.597	.592
C_2–C_4	11.9	14.4	14.5	13.4	15.0	15.3
C_5–C_{11}	17.7	20.3	23.2	23.3	20.9	23.7
C_{12}+	67.3	61.3	58.1	59.4	60.0	56.8
Wax[c]	53.2	45.7	36.5	40.1	40.8	37.7

[c] Unanalyzed wax withdrawn from reactor

Table 3. Elemental Analysis and Textural Properties of 100 Fe/3 Cu/4 K/16 SiO_2 Catalysts

Batch #	Code	Composition 100 Fe x Cu/y K/z SiO_2	BET Surface Area m^2/g	Pore Volume cm^3/g
1	S-3416-1	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)		
2	S-3416-2	3.5 / 6.5 / 18.1	315	0.43
3	S-3416-3	3.2 / 6.9 / 19.8	291	0.43
4	S-3416-4	3.1 / 3.6 / 19.0	306	0.45

(a): Final DOE Report for contract DE-AC22-89PC89868, (1994).
(b): measurements conducted at UOP.

Table 4. Elemental Analysis and Textural Properties of 100 Fe/5 Cu/6 K/24 SiO_2 Catalysts

Batch #	Code	Composition 100 Fe x Cu/y K/z SiO_2	BET Surface Area m^2/g	Pore Volume cm^3/g
1	S-5624-1	5.4 / 6.2 / 24.0	235	0.71
		5.1 / 8.1 / 26.0 (a)	222 (a)	0.68 (a)
		5.5 / 6.6 / 24.0 (b)		
3	S-5624-3	4.8 / 5.2 / 24.2	284	0.51
4	S-5624-4	5.2 / 6.5 / 23.2	299	0.48
5	S-5624-5	5.2 / 7.8 / 29.1	287	0.54

(a): Final DOE Report for contract DE-AC22-89PC89868, (1994).
(b): measurements conducted at PETC, DOE.

Table 5. Elemental Analysis and Textural Properties of Selected Catalysts

Catalyst Code	Composition 100 Fe/w Ca x Cu/y K/z SiO_2	BET Surface Area m^2/g	Pore Volume cm^3/g
S-3416-4	/ 3.1 / 3.6 / 19.0	306	0.45
S-3416-4-K	/ 3.2 / 5.6 / 20.6	277	0.41
S-5624-3	/ 4.8 / 5.2 / 24.2	284	0.51
S-5624-3-2Ca	2.2 / 5.5 / 5.0 / 21.7	221	0.46
S-5624-5-K	/ 5.2 / 6.6 / 30.2	270	0.59

Table 6. Major Events in Run SA-2405 with 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 Catalyst (batch 3 of Fe-Cu-SiO_2 precursor)

TOS (h)	Event
	Slurry loading: 312 g of Durasyn 164 oil, 9.45 g of catalyst (particle size< 270 mesh)
	Catalyst pretreatment: H_2, 250°C, 0.78 MPa for 4 h
	Wax withdrawal through filter: 51.2 g of wax
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P = 1.48 MPa, SV = 2.2 Nl/g-cat/h, (H_2/CO) = 0.67
41	Change space velocity to: SV = 1.8 Nl/g-cat/h
239	Change process conditions: P = 2.17 MPa, SV = 2.6 Nl/g-cat/h
377	Power failure for 30 minutes
477	Change process conditions: P = 2.17 MPa, SV = 2.0 Nl/g-cat/h
550	Slurry sample withdrawal: 26 g slurry, 0.95 g catalyst
556	Catalyst interim treatment: CO, 280°C, 1.48 MPa for 12 h
568	Resume synthesis, achieve process conditions: T = 260°C, P = 1.48 MPa, SV = 1.8 Nl/g-cat/h, (H_2/CO) = 0.67
598	Change process conditions: P = 2.17 MPa, SV = 2.0 Nl/g-cat/h
693	Slurry sample withdrawal: 26 g slurry, 0.85 g catalyst
693	End of run: 250 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 727 g wax, 1.8 g catalyst

Table 7. Summary of results for slurry run SA-2405 .

Catalyst: 9.45 g^a, 100Fe/5Cu/5K/2Ca/24SiO_2 Slurry liquid: 260.0 g, Durasyn-164

Reactor volume: 400. cc^b

Period	1	2	3	4	5	6	7	8
Time on Stream (h)	24.0	100.0	144.0	192.0	312.0	360.0	455.0	522.0
Balance Duration (h)	16.0	16.5	17.0	16.5	17.0	16.0	16.5	19.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	2.17	2.17	2.17	2.17
H_2/CO Feed Ratio	.667	.667	.667	.667	.667	.667	.663	.663
Space Velocity (Nl/g-cat·h)[a]	2.15	1.80	1.80	1.80	2.63	2.63	2.63	2.00
Space Velocity (Nl/g-Fe·h)	3.92	3.27	3.27	3.27	4.80	4.80	4.80	3.64
GHSV (h^{-1})[b]	50.8	42.5	42.5	42.5	62.2	62.2	62.2	47.2
CO Conversion (%)	74.4	72.5	72.9	72.8	68.2	67.3	66.3	70.5
H_2+CO Conversion (%)	70.2	68.6	69.0	69.1	66.0	64.9	64.1	67.8
H_2/CO Usage	.571	.578	.578	.582	.612	.606	.610	.599
STY ($mols$ H_2+CO/g-cat·h)[a]	.067	.055	.055	.055	.078	.076	.075	.060
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	29.5	27.0	30.1	27.4	14.2	12.7	10.4	12.8
Weight % of Outlet								
H_2	1.66	1.71	1.69	1.68	1.72	1.78	1.78	1.66
H_2O	.713	.722	.657	.719	1.11	1.24	1.46	1.34
CO	24.4	26.3	26.0	26.1	30.4	31.2	32.2	28.3
CO_2	54.4	52.8	53.4	53.8	49.4	48.5	48.0	51.4
Hydrocarbons	9.30	11.3	11.7	11.6	9.58	8.92	8.04	8.02
Oxygenates	.367	.422	.440	.446	.472	.460	.419	.371
Wax[c]	9.20	6.77	6.05	5.66	7.28	7.89	8.04	8.88
Yield (g/Nm^3 H_2 + CO $Converted$)								
CH_4	8.31	11.5	12.3	12.7	9.00	8.85	7.32	7.59
C_2–C_4 Hydrocarbons	31.2	38.8	40.5	41.6	35.7	35.6	31.2	31.0
C_5–C_{11} Hydrocarbons	45.0	55.5	57.6	55.9	47.7	45.1	41.3	37.2
C_{12}+ Hydrocarbons	123.	99.9	90.5	85.2	107.	114.	118.	120.
Wax[c]	103.	77.2	68.5	64.0	86.2	95.6	98.7	103.
Oxygenates	4.11	4.82	4.98	5.05	5.60	5.57	5.14	4.29
Total	211.	210.	206.	200.	205.	209.	202.	200.
1+2 Olefins/n-Paraffin Ratio								
C_2	.980	.803	.751	.729	1.20	1.33	1.73	1.46
C_3	5.45	5.55	5.35	4.86	5.35	5.03	5.52	5.04
C_4	4.16	3.95	3.90	3.87	4.12	4.23	4.36	4.58
C_8	2.22	2.13	2.16	2.11	2.21	2.59	2.08	2.87
C_{10}	1.54	1.62	1.59	1.63	1.83	2.00	2.26	2.13

[a] Based on unreduced catalyst [b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table 7 (cont'd). Summary of results for slurry run SA-2405 .

Period	1	2	3	4	5	6	7	8
Weight % of Hydrocarbons								
CH4	4.01	5.58	6.12	6.51	4.50	4.35	3.71	3.89
Ethane	1.92	2.70	2.98	3.15	2.12	1.97	1.57	1.77
Ethylene	1.75	2.02	2.09	2.14	2.38	2.45	2.53	2.41
Propane	.972	1.19	1.31	1.52	1.16	1.21	1.02	1.10
Propylene	5.06	6.29	6.67	7.03	5.94	5.80	5.36	5.31
n–Butane	.984	1.27	1.37	1.45	1.15	1.09	.934	.887
1+2 Butenes	3.95	4.86	5.16	5.41	4.58	4.47	3.93	3.92
C_4 Isomers	.415	.512	.598	.594	.547	.510	.468	.453
n–Pentane	1.07	1.34	1.42	1.46	1.18	1.10	1.29	.873
1+2 Pentenes	4.00	5.10	5.33	5.44	4.42	4.40	3.65	3.68
C_5 Isomers	.284	.360	.387	.404	.431	.381	.337	.394
n–Hexane	.836	1.05	1.11	1.12	.885	.802	.852	.681
1+2 Hexenes	2.57	3.20	3.37	3.43	2.74	2.61	2.84	2.25
C_6 Isomers	.398	.463	.521	.498	.434	.440	.315	.316
n–Heptane	.712	.849	.926	.914	.747	.652	.664	.529
1+2 Heptenes	1.89	2.21	2.37	2.35	1.99	1.88	2.28	1.64
C_7 Isomers	.541	.450	.513	.495	.444	.433	.264	.417
n–Octane	.679	.835	.909	.899	.749	.539	.520	.416
1+2 Octenes	1.48	1.75	1.93	1.87	1.63	1.37	1.07	1.17
C_8 Isomers	.398	.565	.554	.587	.589	.551	.369	.453
n–Nonane	.725	.950	1.01	1.02	.707	.628	.531	.492
1+2 Nonenes	1.31	1.73	1.79	1.78	1.35	1.26	1.18	1.11
C_9 Isomers	.286	.447	.486	.516	.446	.432	.389	.374
n–Decane	.843	1.02	1.06	1.01	.776	.650	.544	.564
1+2 Decenes	1.28	1.62	1.66	1.62	1.40	1.28	1.21	1.18
C_{10} Isomers	.253	.431	.463	.484	.457	.394	.423	.400
n–Undecane	.761	.919	1.02	.951	.770	.667	.575	.570
1+2 Undecenes	1.09	1.31	1.39	1.32	1.27	1.22	1.18	1.10
C_{11} Isomers	.289	.410	.434	.440	.443	.442	.428	.395
C_2–C_4	15.1	18.8	20.2	21.3	17.9	17.5	15.8	15.9
C_5–C_{11}	21.7	27.0	28.7	28.6	23.8	22.1	20.9	19.0
C_{12}+	59.2	48.6	45.0	43.6	53.8	56.0	59.6	61.2
Wax[c]	49.7	37.5	34.1	32.8	43.2	47.0	50.0	52.5

[c] Unanalyzed wax withdrawn from reactor

Table 8. Iron Phases in Used Catalyst B and C Samples by Mössbauer Spectroscopy

Test #	Catalyst	Phase (% Fe)	TOS (h)	X(H_2+CO)* (%)	CH_4* (mol%)
SB-3064	100 Fe/5 Cu/6 K/24 SiO_2 (batch 3)	Spm (73), Fe_3O_4 (27)	54	8-14	8.2-11.4
SB-0665	ibid.	Spm (52), ε'-$Fe_{2.2}C$ (46), χ-Fe_5C_2 (2)	377	64-67	3.5-3.7
SB-1295	ibid.	Spm (30), ε'-$Fe_{2.2}C$ (68), χ-Fe_5C_2 (2)	353	66-69	3.6-3.9
SB-0045	100 Fe/3 Cu/4 K/16 SiO_2 (batch 4)	Spm (40), χ-Fe_5C_2 (60)	400	78-81	2.2-2.4
SA-0705	ibid.	Spm (38) , $FeCO_3$ (10), χ-Fe_5C_2 (52)	526	76-78	2.9-3.1

*: range of values during the last 100 h on stream prior to sample taking.

FTS process conditions for 100 Fe/5 Cu/6 K/24 SiO_2 catalyst testing are: T = 260°C, P = 1.48 MPa, H_2/CO = 0.67, SV = 2.2 - 1.6 Nl/g-cat/h; and for 100 Fe/3 Cu/4 K/16 SiO_2 catalyst testing: T = 260°C, P = 1.48 MPa, H_2/CO = 0.67, SV = 1.4 Nl/g-cat/h during the first 260 h on stream, P = 2.17 MPa, SV = 2.05 Nl/g-cat/h until the end.

Spm: superparamagnetic iron oxide(s) and/or carbide(s).

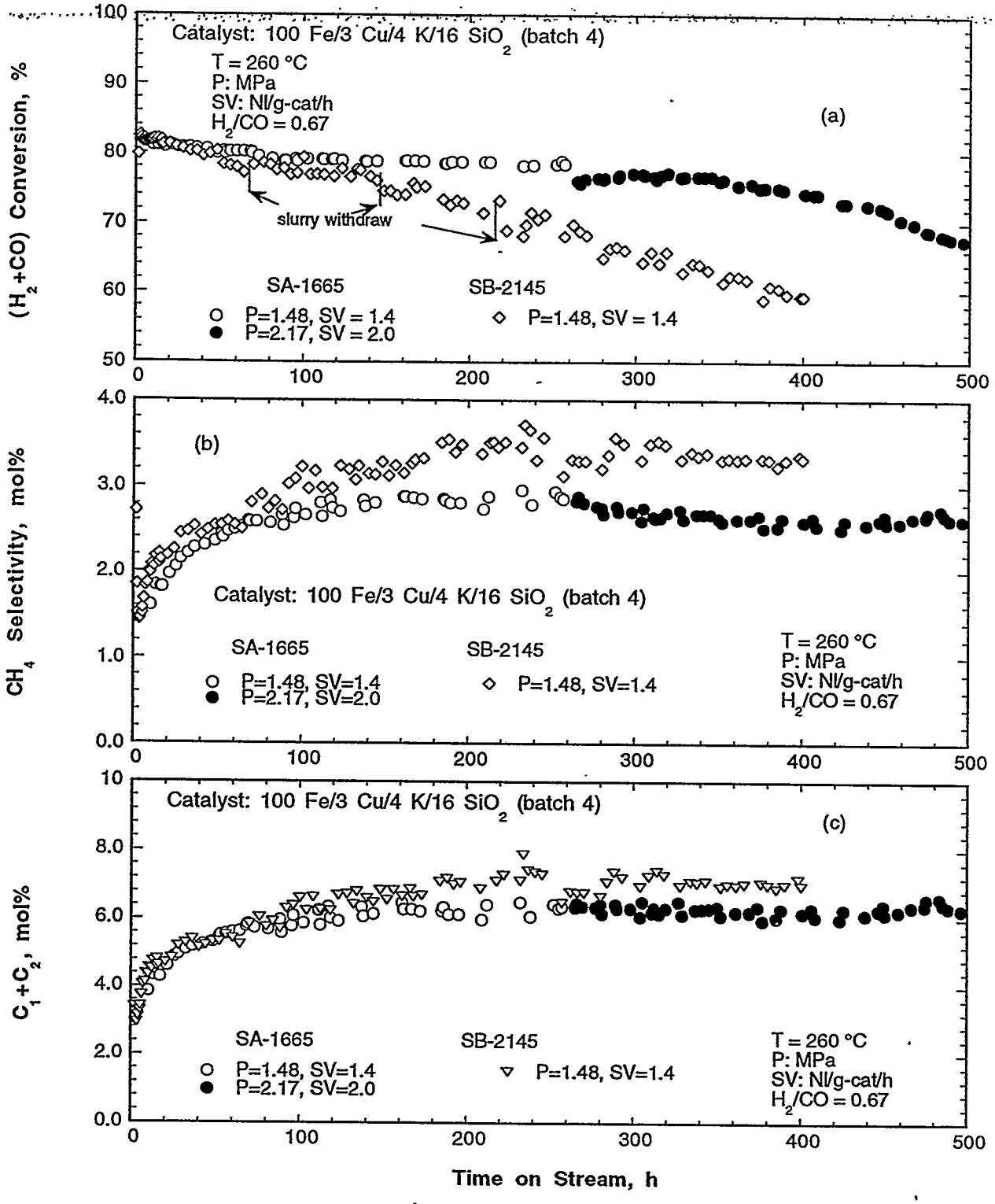

Figure 1. Change in (a) (H_2+CO) conversion, (b) methane selectivity and (c) C_1+C_2 selectivity with time on stream in run SB-2145 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst (batch 4), and their comparison with run SA-1665.

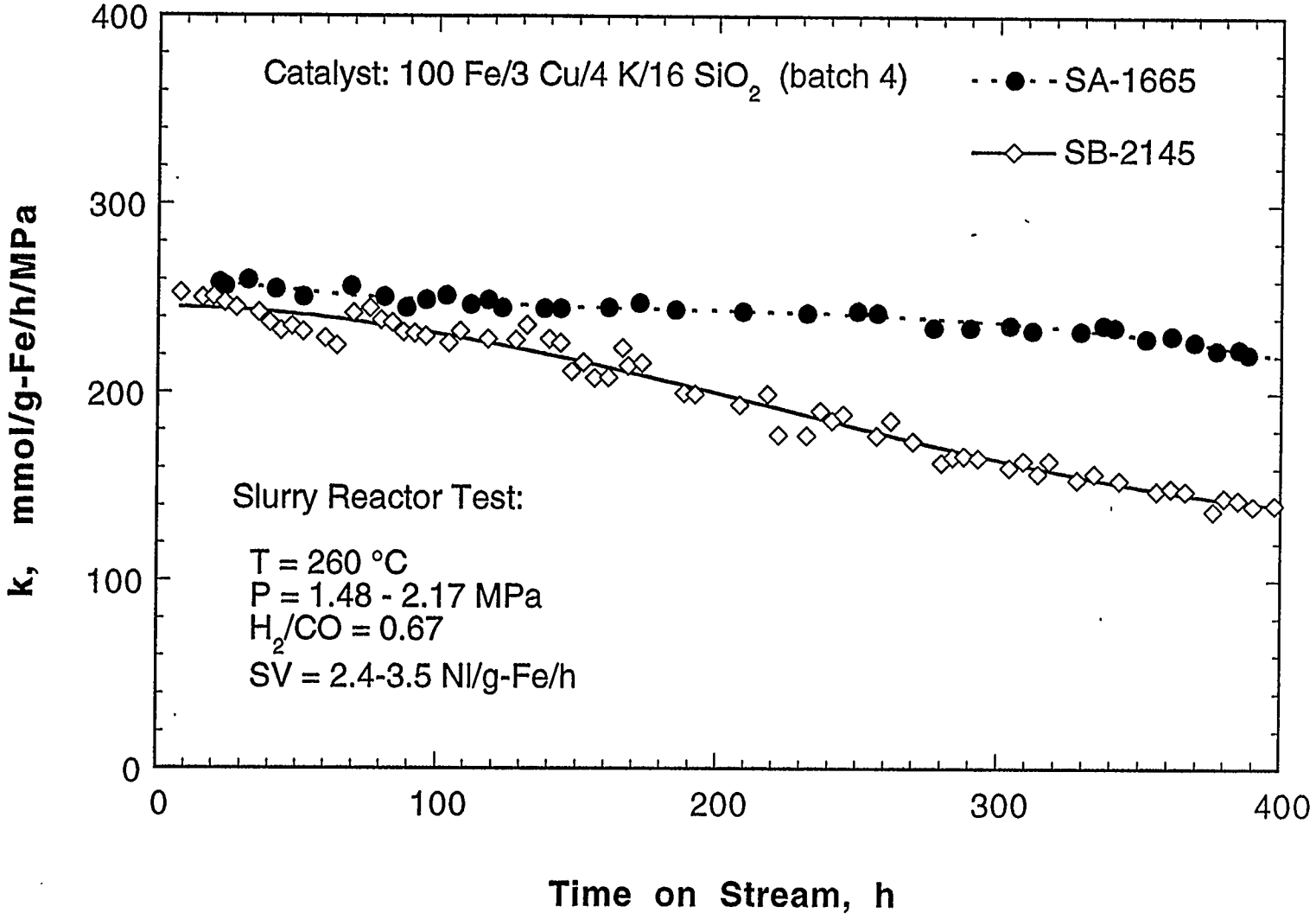

Figure 2. Comparison of an apparent first order reaction rate constant between runs SA-1665 and SB-2145 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

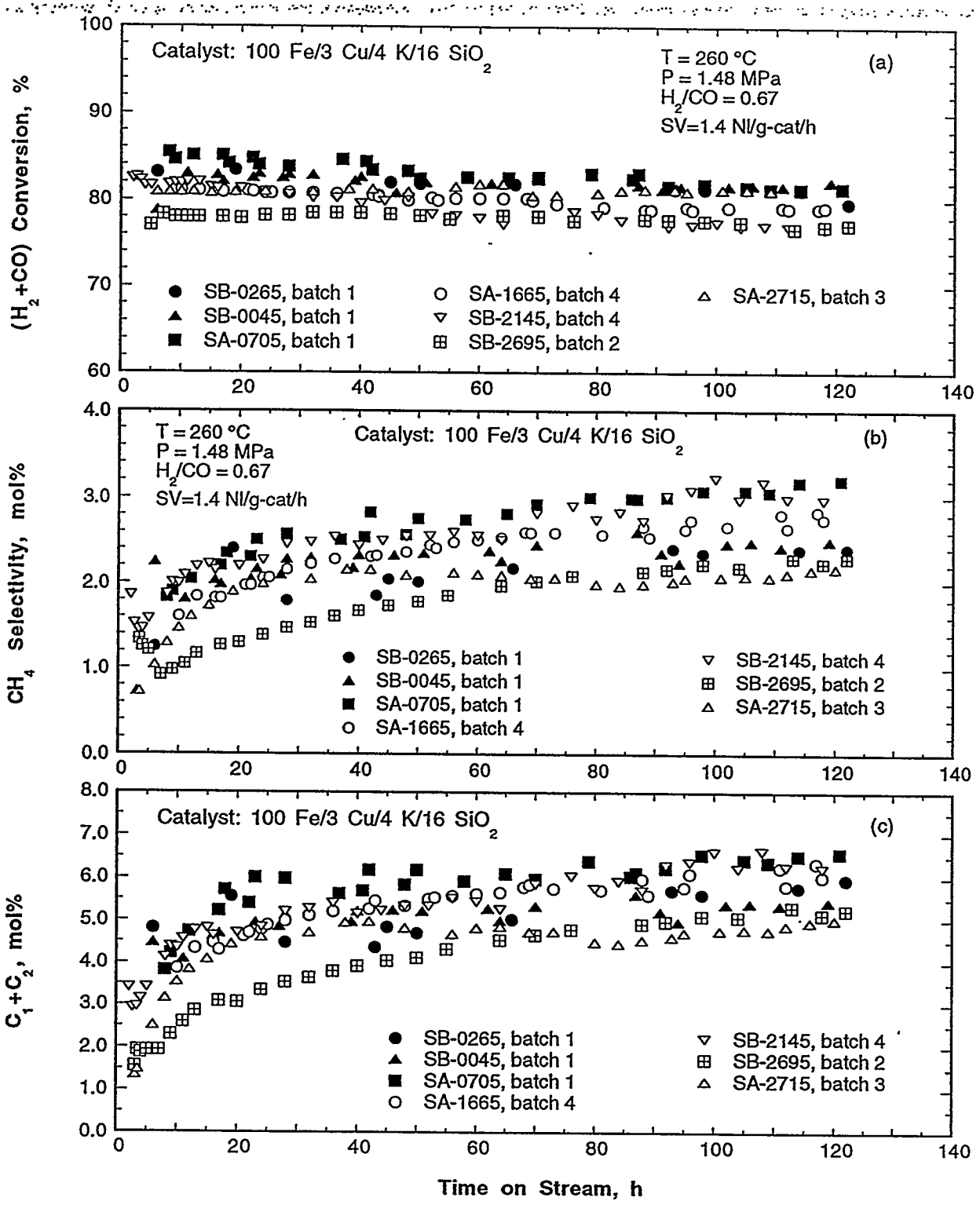

Figure 3. Comparison of data from STSR tests of Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2): (a) (H_2+CO) conversion, (b) methane selectivity and (c) C_1+C_2 selectivity with time on stream.

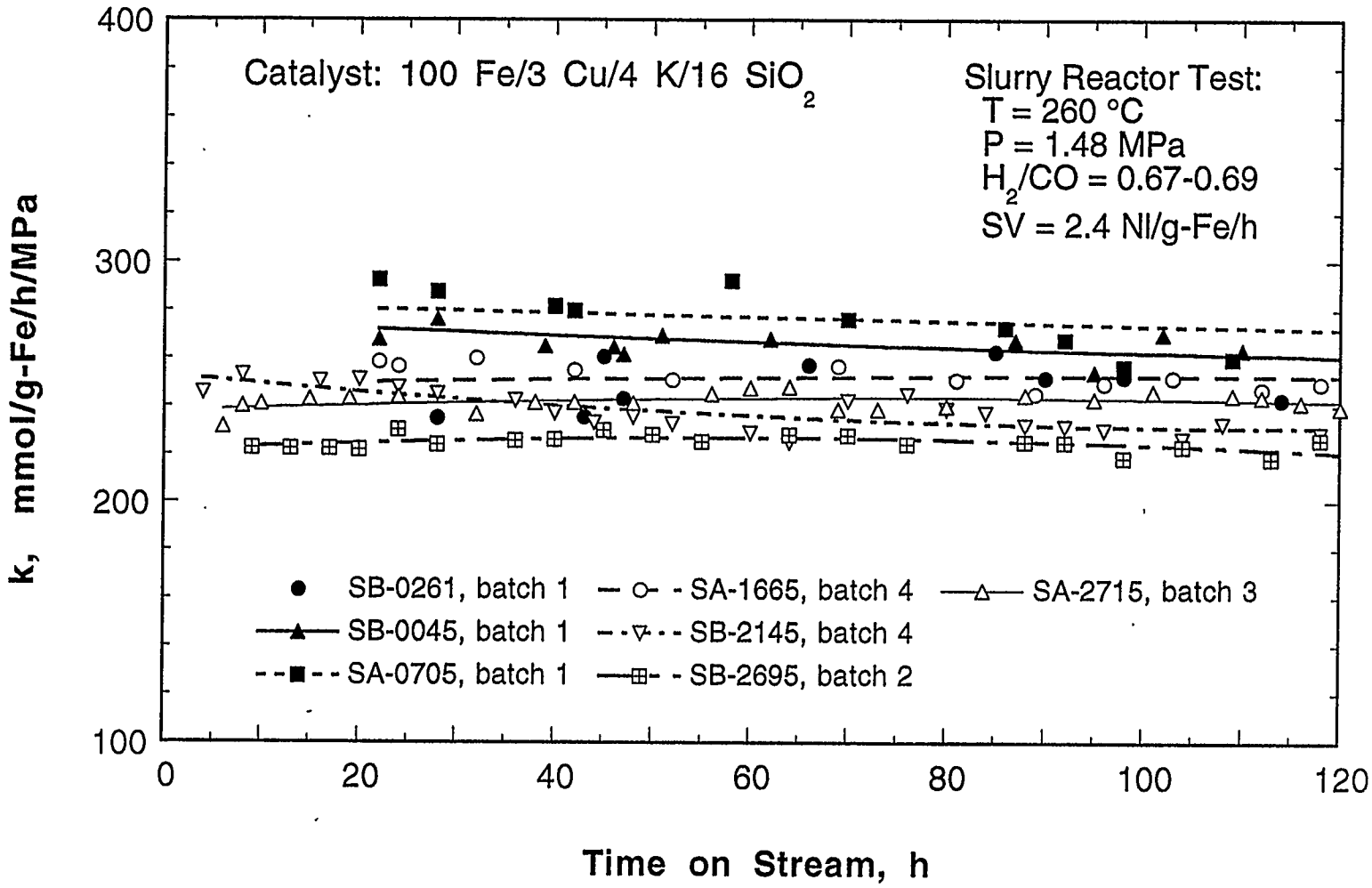

Figure 4. Comparison of an apparent first order reaction rate constant from STSR tests of Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2).

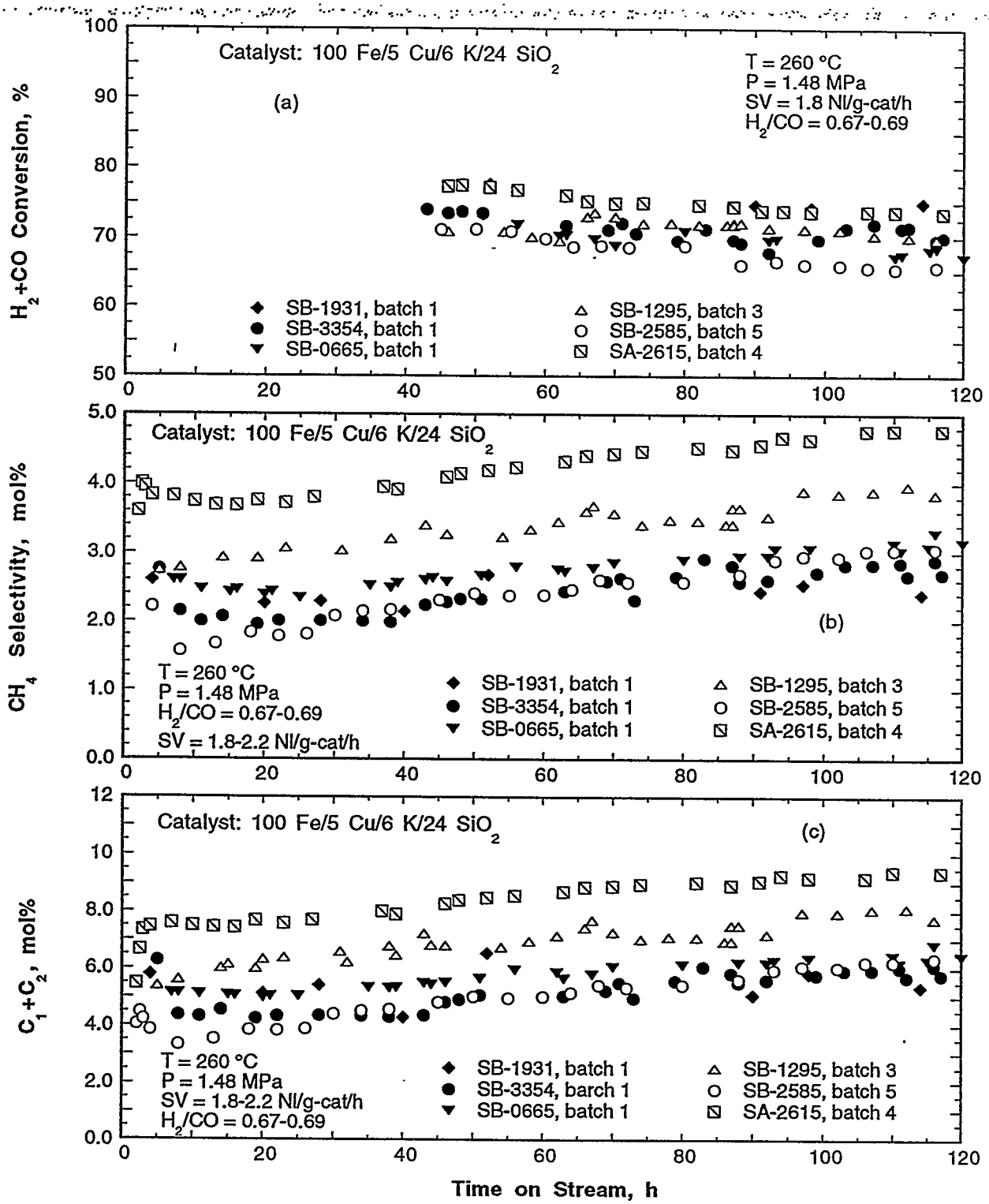

Figure 5. Comparison of data from STSR tests of Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2): (a) (H_2+CO) conversion, (b) methane selectivity and (c) C_1+C_2 selectivity with time on stream.

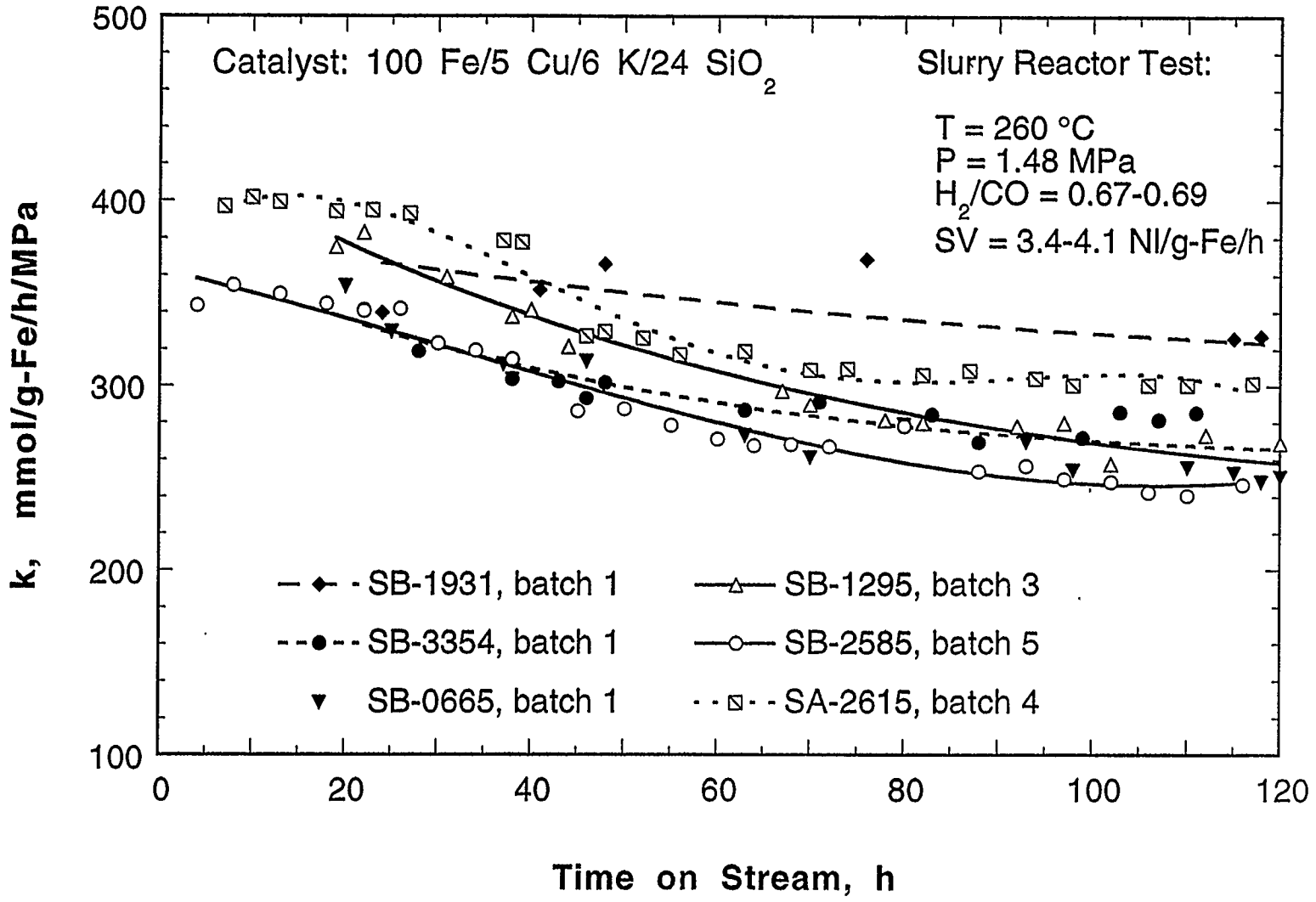

Figure 6. Comparison of an apparent first order reaction rate constant from STSR tests of Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2).

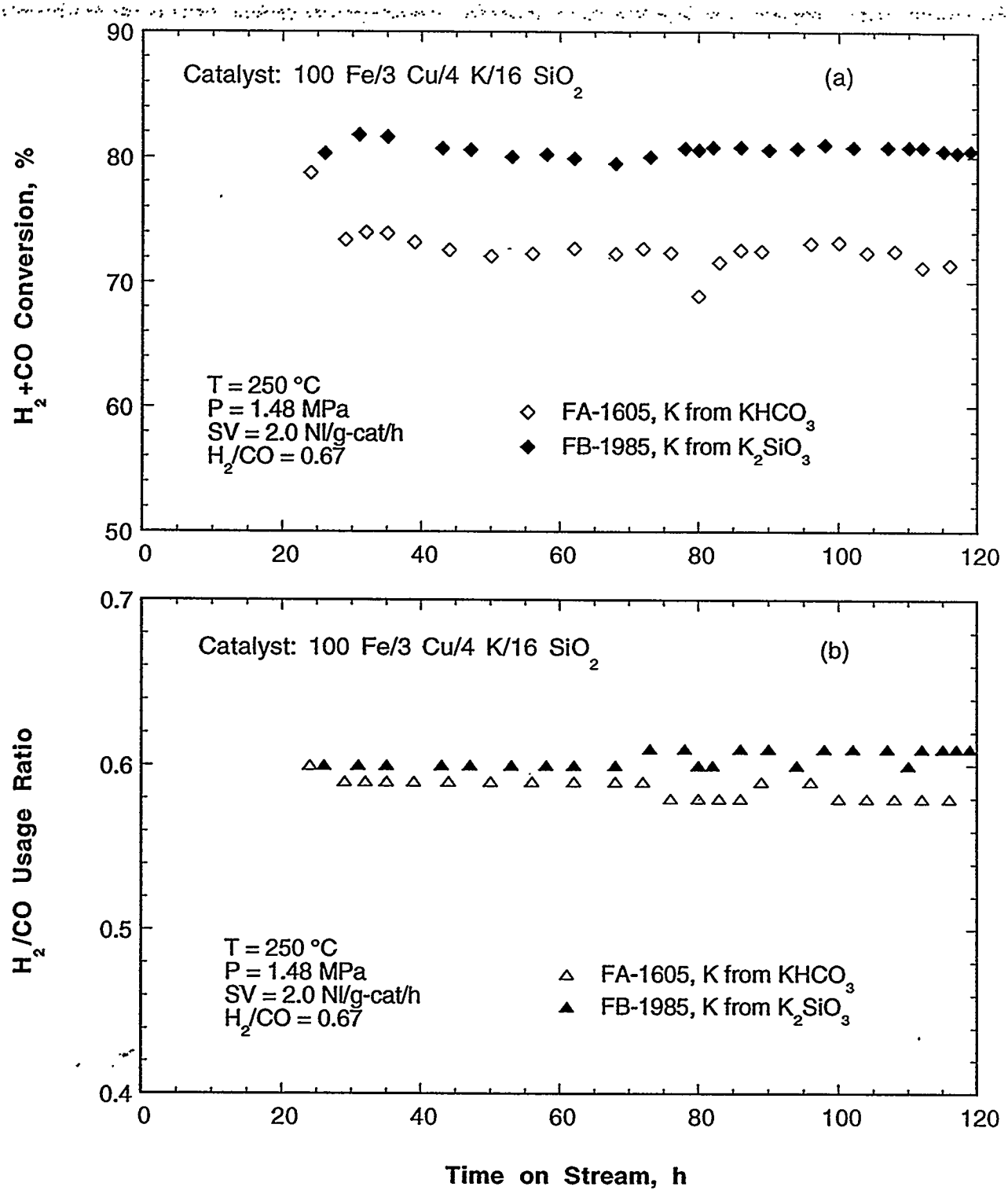

Figure 7. Variations in (a) (H_2+CO) conversion and (b) H_2/CO usage ratio with time on stream in run FB-1985 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst and comparison with run FA-1605.

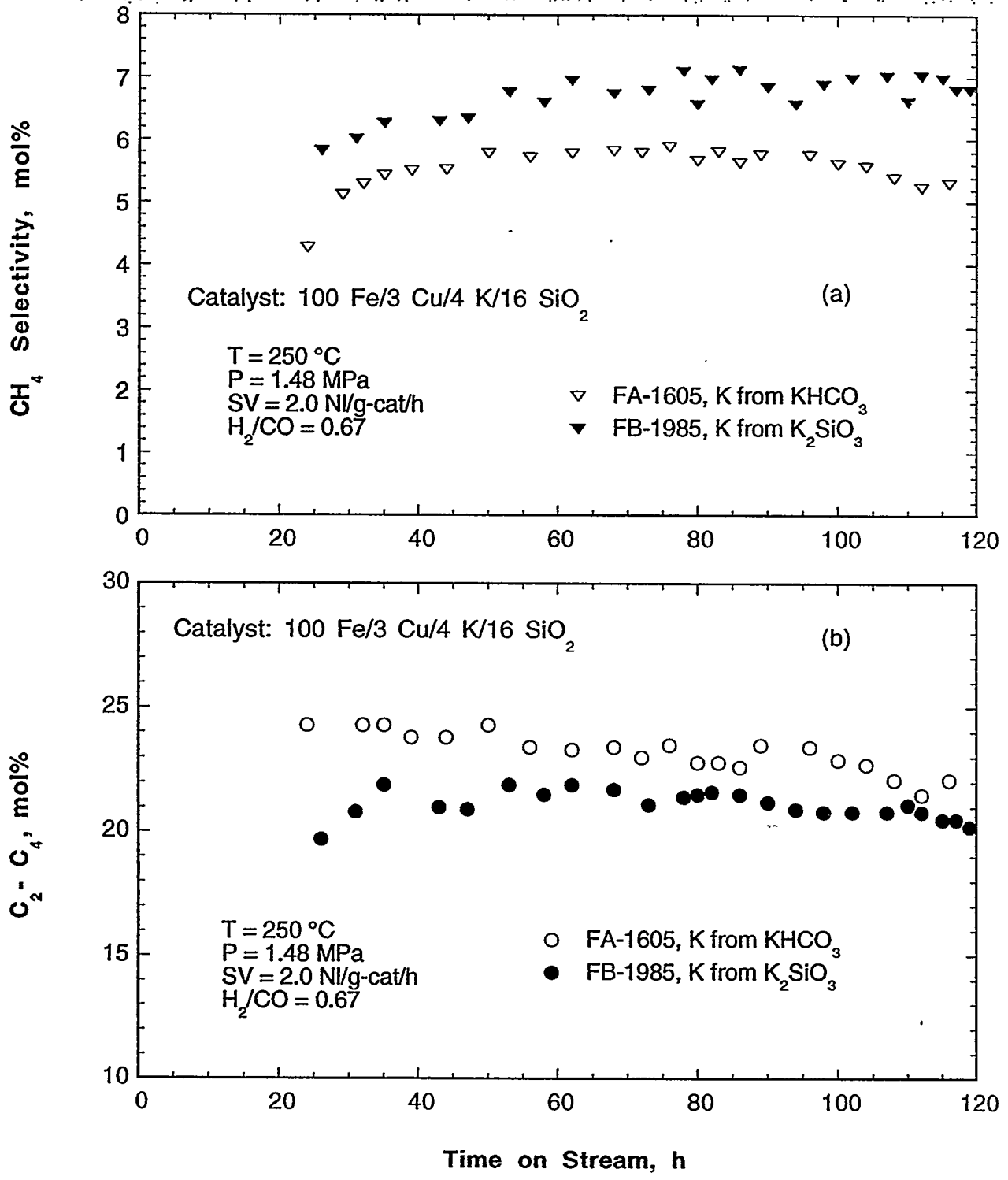

Figure 8. Variations in (a) methane and (b) (C_2-C_4) selectivity with time on stream in run FB-1985 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst and comparison with run FA-1605.

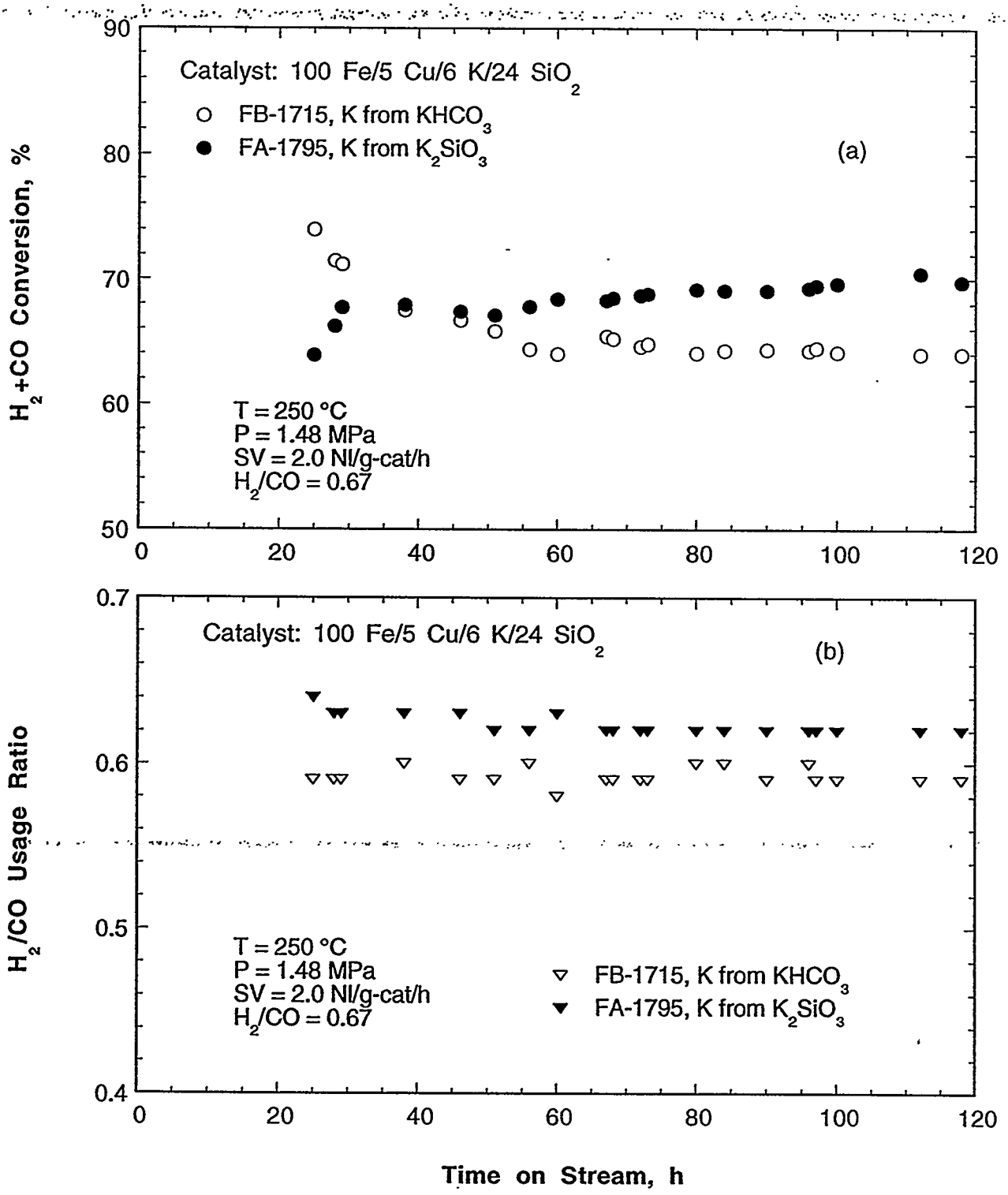

Figure 9. Variations in (a) (H_2+CO) conversion and (b) H_2/CO usage ratio with time on stream in run FA-1795 with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst and comparison with run FB-1715.

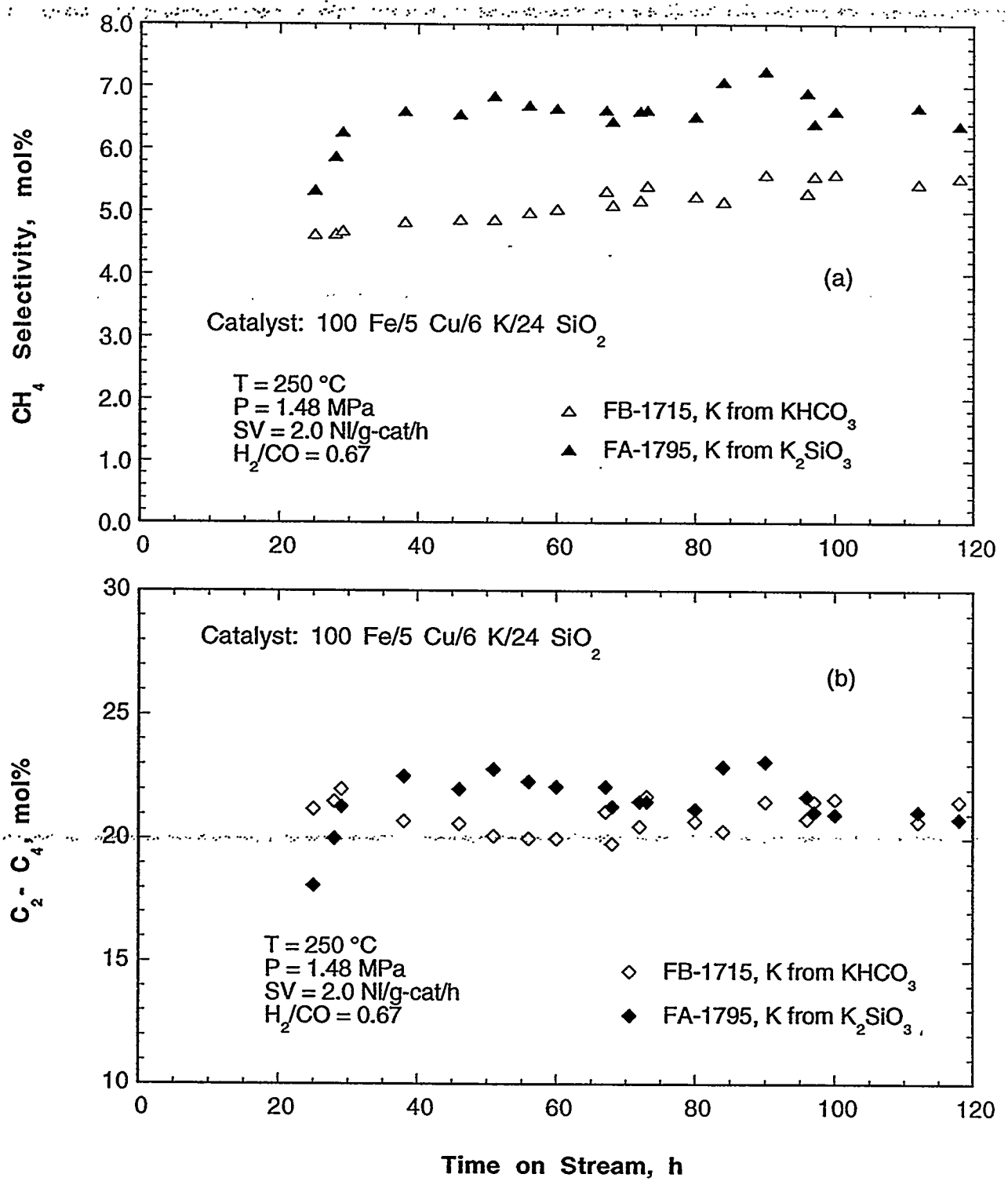

Figure 10. Variations in (a) methane and (b) (C_2-C_4) selectivity with time on stream in run FA-1795 with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst and comparison with run FB-1715.

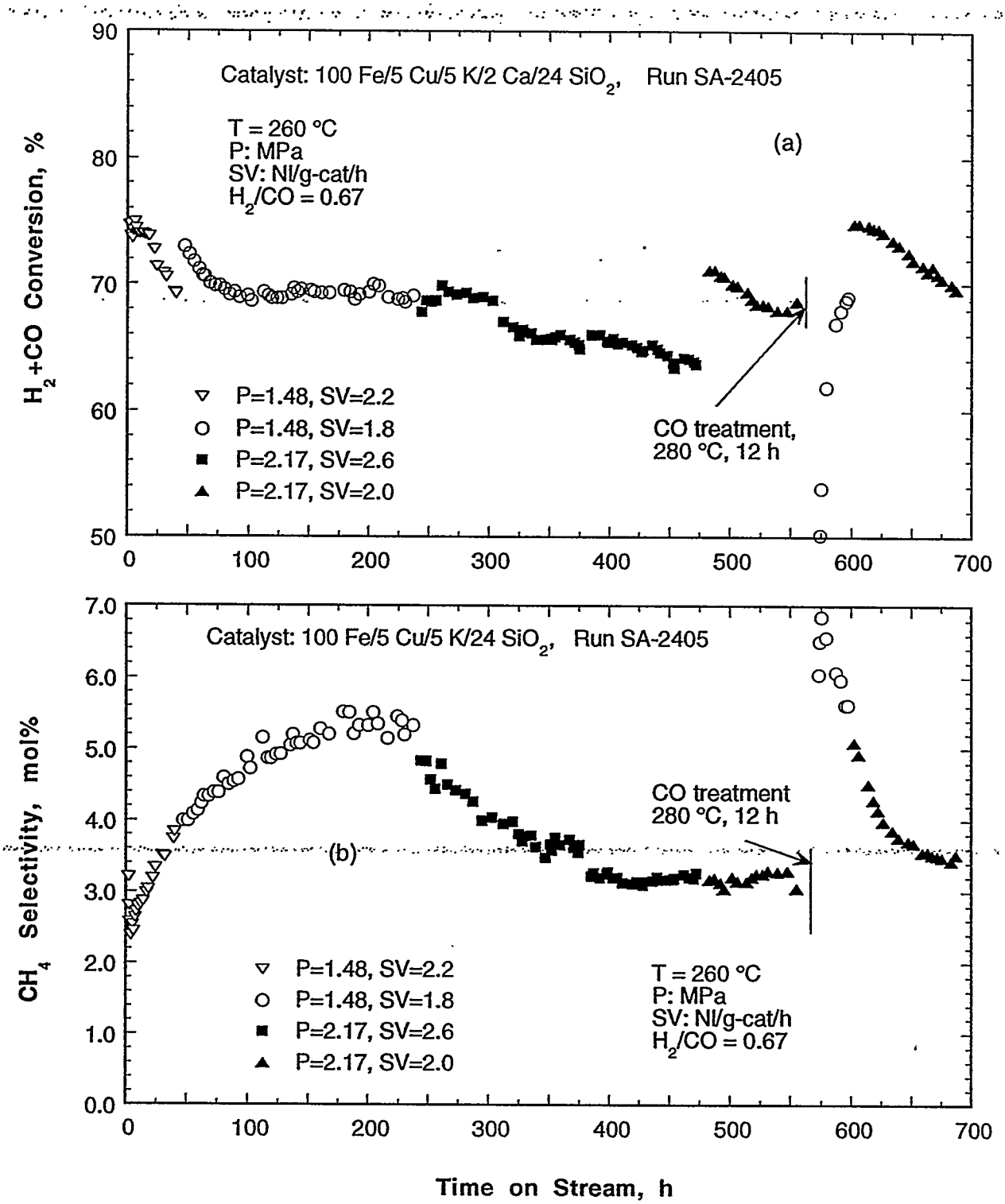

Figure 11. Variations in (a) (H_2+CO) conversion and (b) methane selectivity with time on stream in run SA-2405 with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst.

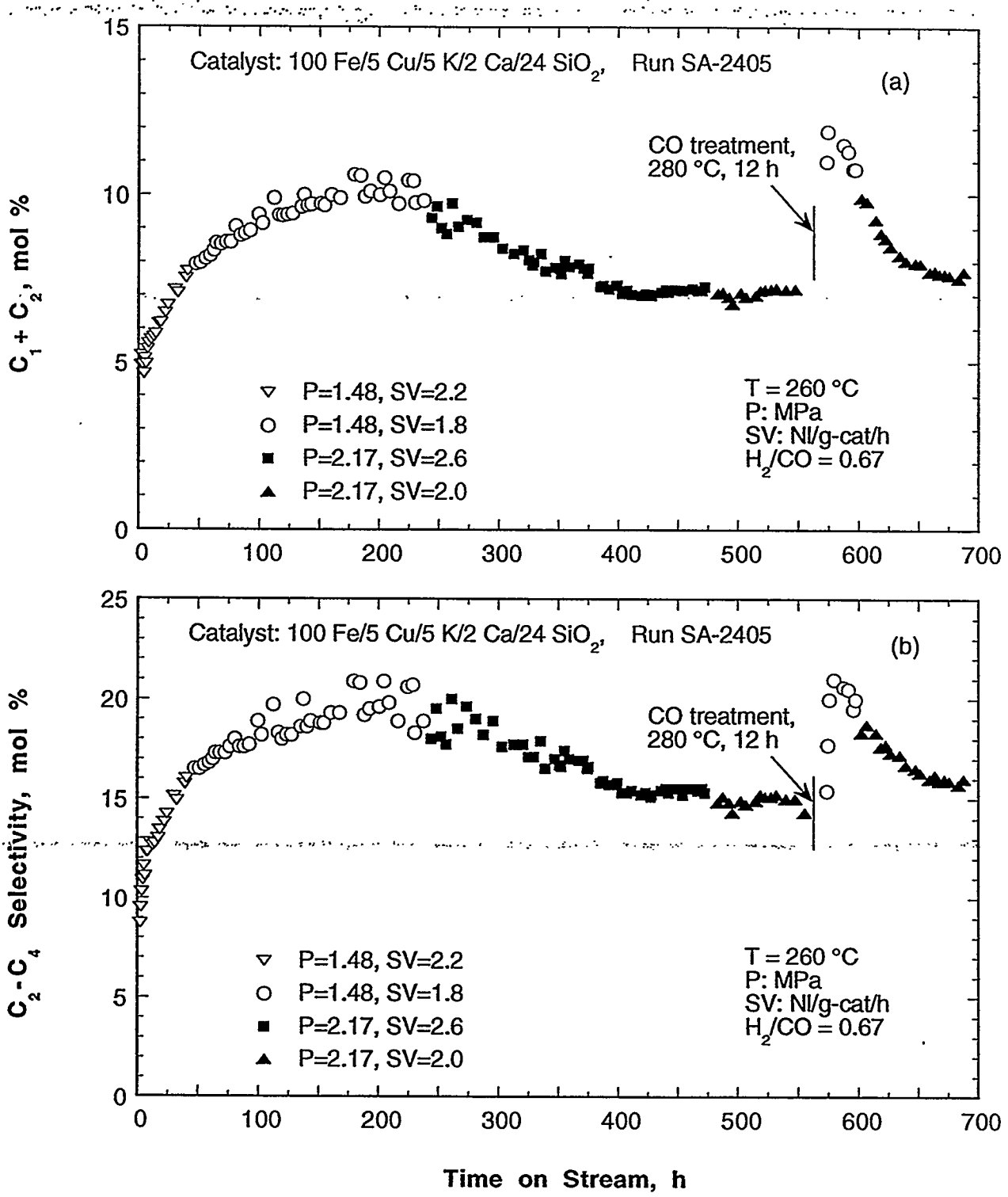

Figure 12. Variations in (a) (C_1+C_2) and (b) (C_2-C_4) hydrocarbon selectivity with time on stream in run SA-2405 with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst.

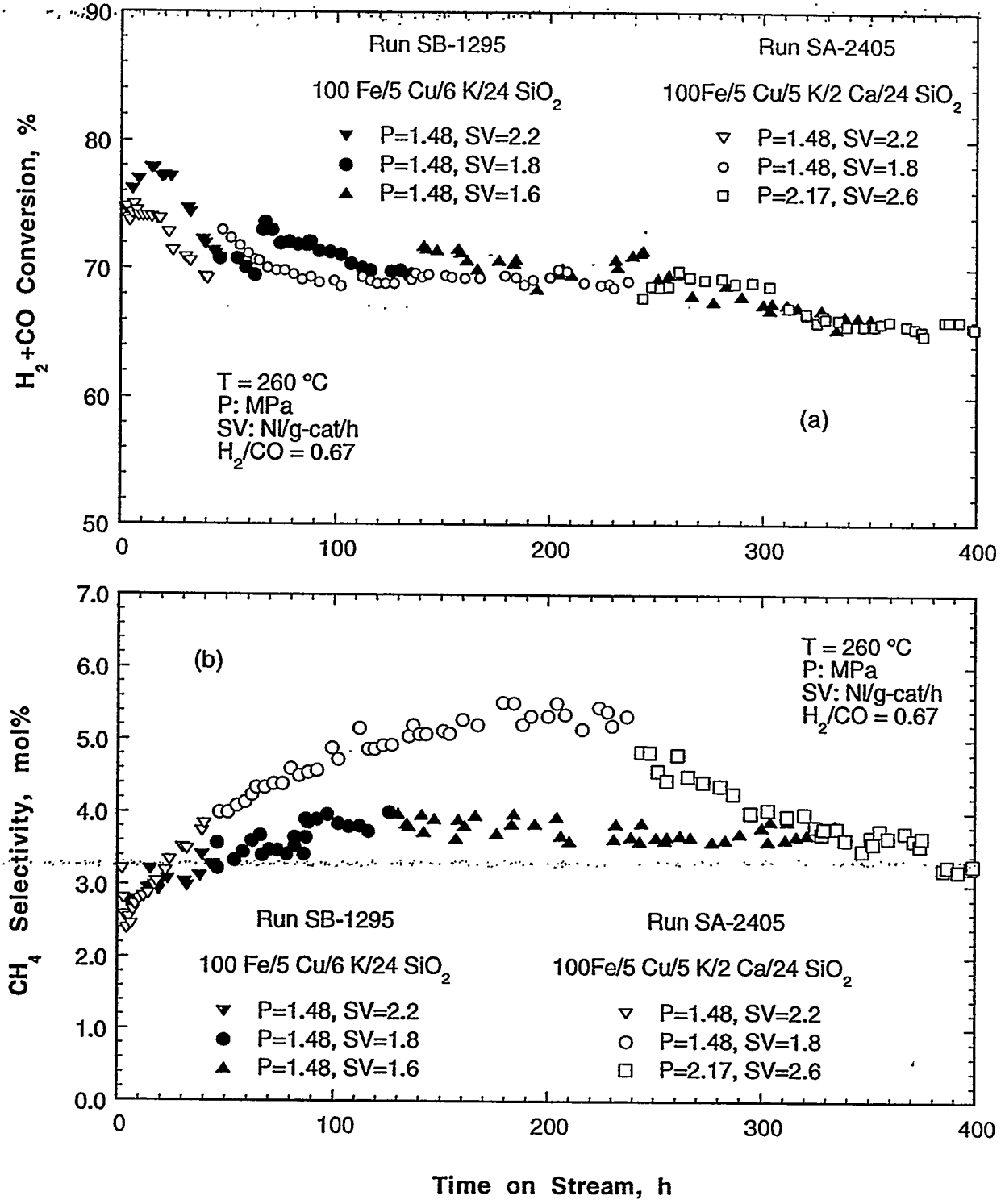

Figure 13. Comparison of (a) (H_2+CO) conversion and (b) methane selectivity with time on stream between runs SB-1295 (100 Fe/5 Cu/6 K/24 SiO_2 catalyst) and SA-2405 (100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst).

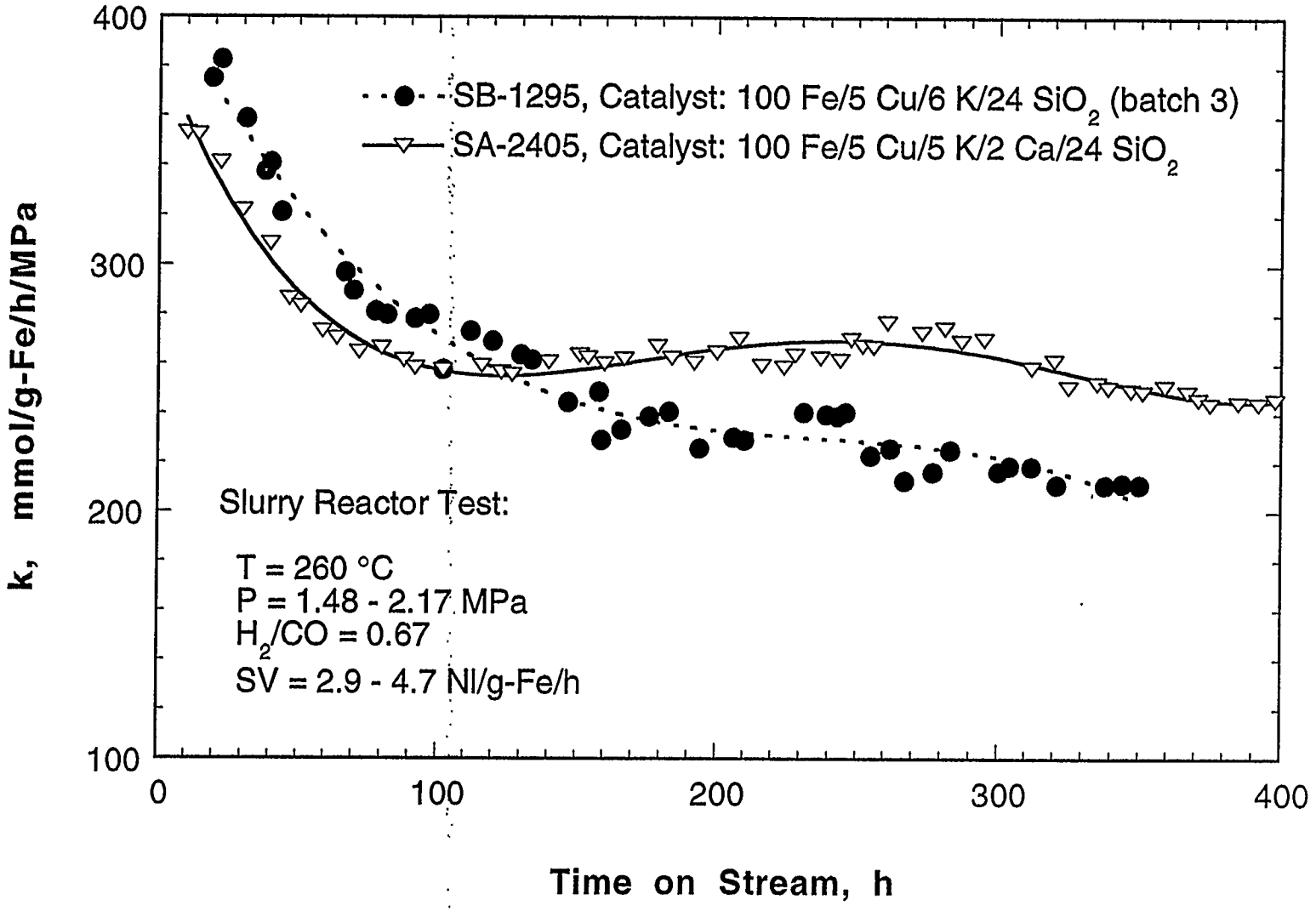

Figure 14. Comparison of an apparent first order reaction rate constant between runs SB-1295 and SA-2405.

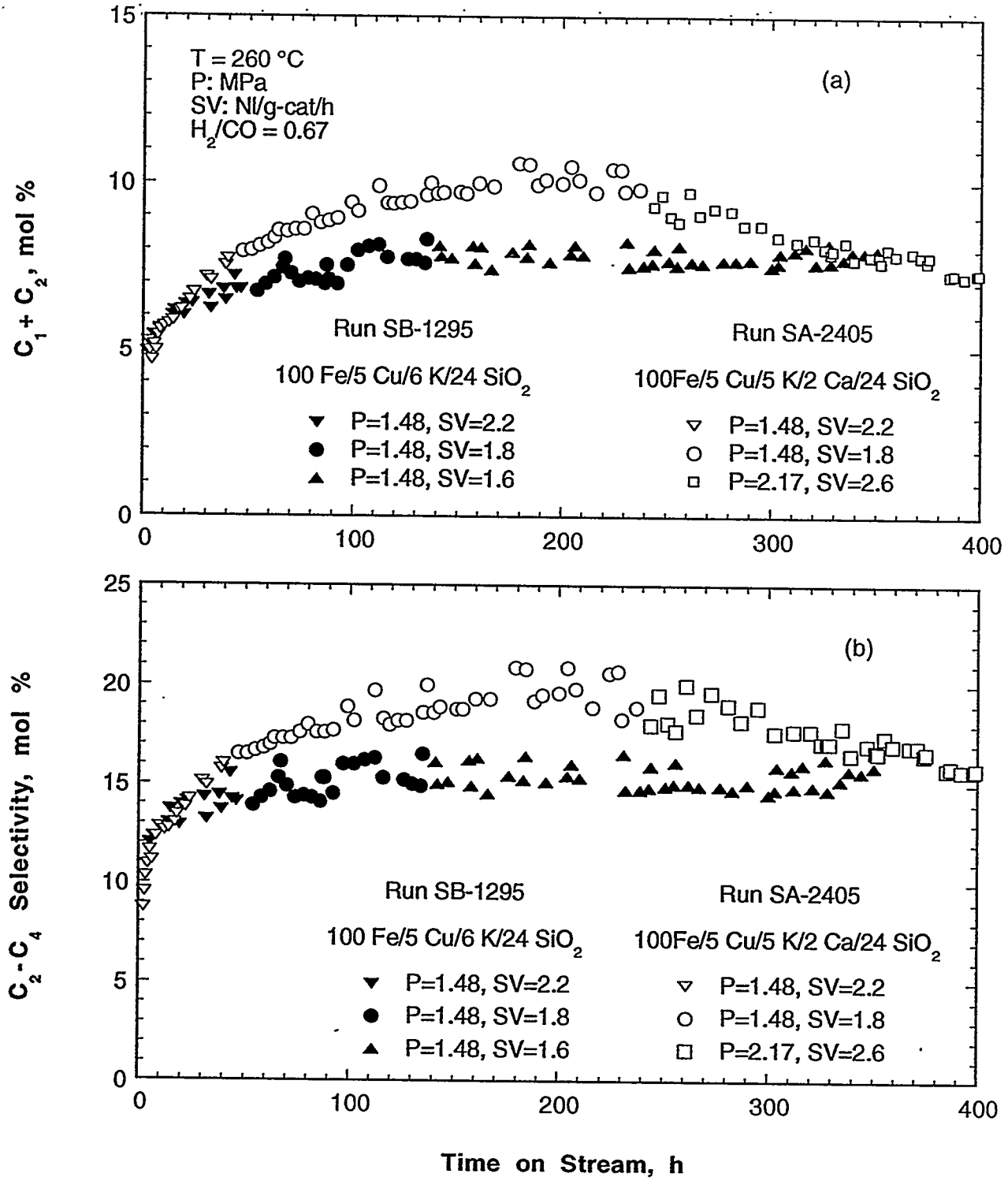

Figure 15. Comparison of (a) (C_1+C_2) and (b) (C_2-C_4) hydrocarbon selectivity with time on stream between runs SB-1295 (100 Fe/5 Cu/6 K/24 SiO_2 catalyst) and SA-2405 (100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst).