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Development of Precipitated Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
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NOTICE

PATENT STATUS

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I. EXECUTIVE SUMMARY

Two slurry reactor tests were completed in continuation of our studies on the effect of pretreatment conditions on catalyst activity and selectivity. Exceptionally good performance was obtained in run SA-2186, using the new pretreatment developed at Texas A&M University (TAMU). During testing at 260°C, 2.17 MPa, 5.7 Nl/g-Fe/h and $H_2/CO = 0.67$ (210 - 520 h on stream) the CO and syngas conversions were 80-87% and 76-85%, respectively, whereas methane and C_1+C_2 hydrocarbon (HC) selectivities were low (2.2 -2.9 mol% and 5.5-6.5 mol%). The catalyst space-time-yield (productivity) was estimated to be 0.92 g HC/g-Fe·h. This is significantly higher than obtained previously (under similar conversions and selectivities) in our laboratory and elsewhere. For example, the catalyst productivity in Rheinpreussen demonstration unit was 0.49 g HC/g-Fe·h, whereas the highest productivity achieved at TAMU was 0.72 g HC/g-Fe·h (run SA-0946, Quarterly Report for April 1 - June 30, 1996).

In run SB-2486 the catalyst was heated in helium to reaction temperature of 260°C, and then the synthesis gas with H_2 : CO molar feed ratio of 2:3 was introduced at 1.48 MPa and 2.3 Nl/g-cat/h. Initial activity of the catalyst, which had not been pretreated, was low, and increased during the first 50 h on stream. However, after that the catalyst deactivated with time on stream. Gaseous hydrocarbon selectivities were very low initially (first 20 h on stream), and then increased with time on stream. For example, at 20 h on stream, methane, C_1+C_2 and C_2-C_4 hydrocarbon selectivities were: 1.9 mol%, 4.1 mol%, and 8.6 mol%, respectively, whereas at 195 h the corresponding values were: 2.4, 5.2 and 10.6 mol%.

The work on catalyst characterization by temperature programmed and isothermal reduction on a variety of iron catalysts, with different amounts of promoters, has been continued. These studies are complementing our work on Task 6, and provide additional insights into the effect of pretreatment procedures on the reduction behavior of iron catalysts.

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

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

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

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

III. 6 Task 6. Pretreatment Effect Research

Work on the pretreatment effect research has continued in this quarter. Two slurry reactor tests were completed with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from batch 4. Detailed description of the individual test results is given below, followed by comparison of results using different pretreatment procedures.

III. 6. 1 Run SA-2186 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

Twelve grams of the catalyst (< 270 mesh in size) was loaded for the test, together with 313 g Durasyn 164 oil as the initial slurry medium. A new pretreatment procedure was employed. Details of this procedure will not be disclosed at the present time, since it is considered to be potentially patentable. Major events are summarized in Table 1.

Following the reduction, the catalyst was tested at 260°C, 1.48 MPa, syngas molar feed ratio of 0.67 (H_2/CO = 0.67) and gas space velocity of 2.3 Nl/g-cat/h. Catalyst activity, measured by CO conversion and (H_2+CO) conversion is shown in Figures 1a and 1b,

respectively. Both conversions increased gradually with time on stream during the first 20 h and then stabilized at about 80 - 82%, CO conversion, and 76 - 78% for (H_2+CO) conversion. The usage ratio (Figure 1c) decreased from 0.62 to 0.58 at 20 h and then remained stable at these conditions. After 20 h on stream, methane selectivity (Figure 2a) varied between 2.9 and 3.3 mol%, C_1+C_2 hydrocarbon selectivity was between 6.6 and 7.8 mol% (Figure 2b), and C_2-C_4 hydrocarbon selectivity varied between 14 and 16 mol% (Figure 2c).

At 209 h on stream, the reaction pressure and gas space velocity were increased to 2.17 MPa and 3.4 Nl/g-cat/h (5.7 Nl/g-Fe/h). After 20 hours at these conditions, the CO and syngas conversions were about 79% and 76%, respectively, and then increased with time reaching 87% (CO) and 83% (syngas conversion) at about 500 h on stream. The catalyst space time yield at these process conditions corresponding to the (H_2 + CO) conversion of 80% is estimated to be 0.92 (g hydrocarbons produced/g-Fe·h), based on assumed hydrocarbon yield of 200 gHC produced/Nm^3 of (H_2 + CO) converted. The latter value has been typically obtained in our laboratory with precipitated iron catalysts (the stoichiometric amount is 208 gHC produced/Nm^3 of (H_2 + CO) converted). This is the highest catalyst productivity obtained in our laboratory, and is significantly higher than that obtained in the two most successful bubble column slurry reactor operations at comparable conversions and low methane selectivities (Mobil's work, and Kölbel's Rheinpreussen demonstration plant unit). In Mobil's study (Kuo, 1985) the catalyst productivity of 0.39 (g hydrocarbons produced/g-Fe·h) was achieved at 257°C, 1.48 MPa, 2.3 Nl/g-Fe/h and H_2/CO = 0.73 (syngas conversion of 82%, methane selectivity of 2.7 wt%), whereas Kölbel et al. (1955) obtained 0.49 (g hydrocarbons produced/g-Fe·h) at 268°C, 1.2 MPa, 3.1 Nl/g-Fe/h and H_2/CO = 0.67 (syngas conversion of 89%, methane + ethane selectivity of 3.2 wt%). For comparison, we achieved the catalyst productivity of 0.92 (g hydrocarbons produced/g-Fe·h) at 260°C, 2.17 MPa, 5.7 Nl/g-Fe/h and H_2/CO = 0.67 (syngas conversion of 80%, methane selectivity of 2.4 mol%. The latter corresponds to approximately 2.7 wt%). Two main reasons for higher catalyst space-time-yield (productivity) obtained in the present study relative to the

previous ones are: (1) the use of higher reaction pressure, and (2) higher intrinsic activity of our catalyst.

Gaseous hydrocarbon selectivities were initially decreasing during testing at 2.17 MPa with $H_2/CO = 0.67$ (210-400 h), and at about 400 h started to increase . For example at 400 h on stream, methane, C_1+C_2 and C_2-C_4 hydrocarbon selectivities were 2.3, 5.5 and 12.1 mol%, respectively, whereas at 500 h on stream, the corresponding values were 2.5, 6.4 and 14.6 mol%, respectively.

In general, this has been the most successful FT test conducted in our laboratory.

III. 6. 2 Run SB-2486 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

About 15 grams (< 270 mesh in size) of catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from batch 4, and 309 g of Durasyn 164 oil were loaded for the test. The catalyst was heated in helium at 0.8 MPa to the desired reaction temperature of 260°C over a period of 3.5 h, and then exposed to the synthesis gas at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of $H_2/CO = 0.67$ and space velocity of 2.3 Nl/g-cat/h. Initial activity of the catalyst, which had not been pretreated, was low, and increased during the first 50 h, as evidenced by increase in the CO and syngas conversions (Figures 3a and 3b). At 50 h on stream the CO and syngas conversions were 65% and 61%, respectively. During the next 50 h of testing, the catalyst deactivated slowly with time, and at 195 h the CO and syngas conversions were approximately 54% and 50%, respectively. Initially, the usage ratio was about 0.62 (at 4 h), and it decreased to 0.56 at 195 on stream (Fig. 3c).

Gaseous hydrocarbon selectivities were very low initially (first 20 h on stream), and showed increase with time on stream (Figure 4). For example, at 20 h on stream, methane, C_1+C_2 and C_2-C_4 hydrocarbon selectivities were: 1.9 mol%, 4.1 mol%, and 8.6 mol%, respectively, whereas at 195 h the corresponding values were: 2.4, 5.2 and 10.6 mol%.

Between 196 and 213 h on stream, the gas space velocity was changed to 1.8 Nl/g-cat/h, whereas the other process conditions were kept constant. At 213 h the space velocity was

decreased further to 1.4 Nl/g-cat/h, in attempt to obtain higher conversions. At 220 h the CO and syngas conversions were 70% and 65.5%, respectively. However, the catalyst continued to deactivate with time, and at 314 h the CO and syngas conversions were only 60% and 56%, respectively. During testing at the gas space velocity of 1.4 Nl/g-cat/h, gaseous hydrocarbon selectivities were fairly stable, in spite of catalyst deactivation. The test was terminated at 315 h, due to relatively low catalyst activity and high deactivation rate.

III. 6. 3 Comparison of Pretreatment Procedures

So far, we have employed seven pretreatment procedures with the catalyst C from batch 4 in slurry reactor tests. They are: (1) baseline procedure with hydrogen at 240°C for 2 h (runs SB-2145 and SA-1665); (2) reduction with hydrogen at 250°C for 4 h (run SB-3425); (3) reduction with hydrogen at 280°C for 8 h (run SA-0376); (4) CO activation at 280°C for 8 h (runs SA-0946 and SB-1486); (5) syngas activation at 280°C for 8 h (run SA-1626); (6) TAMU activation (SA-2186) and (7) no pretreatment (SB-2486). Comparison of the hydrogen pretreatment procedures (1 -3) was given in the Quarterly Technical Progress Report for January 1 - March 31, 1996, and the comparison of pretreatment procedures (2) to (5) was given in the last quarterly report (April 1 - June 30, 1996). The latter comparison is updated here with inclusion of the last two tests (pretreatments 5 and 6).

Effect of pretreatment procedures on syngas conversion during the first 100 h of synthesis is shown in Figure 5. Hydrogen reductions (runs SB-3425 and SA-0376) and TAMU activation procedure (SA-2186) result in rapid achievement of steady state activity, whereas the syngas (SA-1276), CO (SA-0946) and no pretreatment (SB-2486) require longer time to achieve the steady state activity.

Activity comparison, in terms of the apparent reaction rate constant for first order reaction in hydrogen, is given in Figure 6. Initially, the TAMU activation procedure resulted in the highest activity (k = 400 mmol/g-Fe/MPa), followed by the hydrogen reduction at 250°C for 4 h (k = 360 mmol/g-Fe/MPa), the CO and syngas activated catalysts (k = 280 mmol/g-Fe/MPa) ,

whereas the catalyst reduced with hydrogen at 280°C for 8 h and the catalyst which was not pretreated were the least active (k = 240 mmol/g-Fe/MPa). Activity of the CO and syngas catalysts increased with time during the first 100 h on stream, whereas the activity in other tests remained fairly stable (this follows the same trend as the syngas conversion in Figure 5). Catalyst activity in runs SA-0946 and SA-2186 remained high and stable up to 400 h on stream (at different gas space velocity and/or reaction pressure), whereas the catalysts in the other four tests deactivated with time on stream (Figure 6). The catalyst in run SA-2186 (TAMU activation procedure) was the most active and stable at all times (10 - 400 h on stream).

Methane selectivities of hydrogen reduced and unpretreated catalyst increased during the first 100 h of synthesis and then became stable, whereas methane selectivities of the syngas and CO activated catalysts exhibited the opposite trend, i.e. they decreased with time, and TAMU activation procedure resulted in stable selectivity. Initially (first 20 h on stream) methane selectivities increased in the following order: No pretreatment (2 mol%) < hydrogen and TAMU reduced catalysts (~3 mol%) < CO activated catalyst (3.6 - 4%) < syngas activated catalyst (5.8 - 6%). After 300 h on stream methane selectivity increased in the following order: CO activated catalyst ≈ TAMU activated ≈ no pretreatment (~2.5 mol%) < hydrogen reduced catalysts (3.6 - 3.8 mol%) < syngas activated catalyst (4 mol%). During testing at 2.17 MPa methane selectivity of the CO activated catalyst (SA-0946) and TAMU activated catalyst was low (2.2 - 2.8 mol%).

Based on the above data the TAMU activation procedure (run SA-2186) resulted in the best long term performance: high and stable activity over a long period of time, low methane and gaseous hydrocarbon selectivities. As stated earlier (section III. 6. 1 of this report), the highest catalyst productivity (0.92 g hydrocarbons produced/g-Fe·h) was achieved using this activation procedure, while maintaining the desired selectivity (well within the DOE's performance targets). This is the best performance to date relative to catalysts developed for high wax production ("high alpha" catalysts) in our laboratory or anywhere else. The performance of the CO activated catalyst was also superior relative to other catalysts developed

for high wax production : catalyst productivity of 0.72 g hydrocarbons produced/g-Fe·h, and hydrocarbon selectivity within the DOE's performance targets.

III. 7 Task 7. Calcination Effect Research

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

III. 8 Task 8 Catalyst Characterization

Work on catalyst characterization in support of Task 6 has continued. Results from characterization studies by XRD, TPR and TGA are described in the following sections.

III. 8. 1 XRD Measurement Results

Figure 8 illustrates changes in bulk iron phases with time on stream during run SA-1626 (Quarterly Report April - June, 1996) with catalyst C (100 Fe/3 Cu/4 K/16 SiO2 from batch-4). Iron carbide (ε'-$Fe_{2.2}C$) and small amounts of magnetite (Fe_3O_4) were found (Figure 8-A) in the sample withdrawn immediately after the syngas (H_2/CO = 0.67, 280°C, 100 psig, 750 Nml/min for 8 h) pretreatment (TOS = 0 h). During FT synthesis additional iron carbides were formed (Figure 8-B to 8-D), and magnetite was also present in small quantities (TOS = 137 to 403 h). At the end of run (TOS = 403 h) iron carbide was the most dominant phase.

Figure 9 illustrates changes in bulk iron phases with time on stream during run SB-2486 with catalyst C (100 Fe/3 Cu/4 K/16 SiO2 from batch-4). Only two broad peaks were found (Figure 9-A) in the sample withdrawn immediately after heating in He at 260°C indicating either that the sample is amorphous in nature or the particle is too small to be detected by X-rays. During FT synthesis (Figure 9-B to 9-F) magnetite was the dominant phase, with small amounts of iron carbide phase (ε'-$Fe_{2.2}C$). Activity of this catalyst was low relative to catalysts activated in hydrogen, CO or syngas prior to FT synthesis (section III. 6. 3 of this report).

Results of XRD measurements of several catalysts (catalysts B, C and Ruhrchemie) after different pretreatments in the TGA/DTA apparatus are summarized in Table 3. After the pretreatment the catalyst were carefully passivated by introducing controlled amounts of oxygen,

and then placed in the XRD instrument and/or the BET apparatus. The BET surface areas of hydrogen reduced catalysts at 250°C are about 100 m^2/g whereas, the syngas and the CO reduced samples (at 280°C) have BET areas in the range of 53 to 83 m^2/g.

Metallic iron (α-Fe) was the only crystalline phase found in hydrogen reduced catalysts B, C and Ruhrchemie (reductions at 240°C to 280°C for 8 h). Catalyst B reduced in hydrogen first at 250°C for 4 h (baseline reduction procedure), and then exposed to syngas at 260°C ($H_2/CO = 0.67$) for 4 h, contains ε'-$Fe_{2.2}C$. This phase was also found in the catalyst C reduced in hydrogen first at 240°C for 2 h (baseline reduction procedure), and then exposed to syngas at 260°C ($H_2/CO = 0.67$) for 6 h. These two pretreatments simulate pretreatment conditions employed in slurry reactors, followed by FTS at 260°C (baseline reaction temperature in slurry reactor tests). Results show that ε'-$Fe_{2.2}C$ phase is formed rapidly under the reaction conditions. On the other hand when the catalysts B and C are exposed to syngas directly at 260°C for 8 h, the χ-carbide (χ-Fe_5C_2) phase is formed (see Table 4). XRD results from run SB-2486 shown in Figure 9, indicate that after 51 h on stream, the used catalyst is predominantly in the form of magnetite, ε'-$Fe_{2.2}C$ being present in a smaller amount. This means that either χ-carbide is not formed at all in the slurry reactor under the reaction condition studied, or that it was converted to magnetite and ε'-carbide during the first 50 h of synthesis.

After the reduction of catalysts B and C with CO or syngas ($H_2/CO = 0.67$) at either 260°C or 280°C the χ-Fe_5C_2 phase was the only phase detected by XRD.

III. 8. 2 Temperature Programmed Reduction (TPR)

Figure 10 illustrates the effect of reductant ($5\%H_2/95\%N_2$) flow rate on the TPR profiles of unpromoted iron oxide sample. Results show that increasing reductant flow rate causes a decrease in the peak positions for both stages of iron reduction. The increase in reductant flow rate also causes a decrease in the overall intensity of the TPR peaks. These results demonstrate that the reduction behavior of iron oxide is dependent on the reductant flow rate. It is interesting

to note the existence of the third peak at 905°C in one of the profiles, indicating that the reduction is incomplete even at temperatures up to 1000°C.

The effect of silica addition on the reduction behavior of iron oxide is shown in Figure 4. Unpromoted iron oxide has two dominant peaks (Figure 4-A) at about 392°C and 620°C corresponding to reduction of Fe_2O_3 to Fe_3O_4 to Fe. The addition of silica retards the onset of iron reduction for both stages, and the peak positions shift to the right with the increasing amount of silica. The addition of silica also causes the broadening of the low temperature peak (4-B and 4-C). The broadening of these peaks may be an indication of better dispersion of iron oxide particles in the silica promoted samples.

Figure 12 illustrates the effect of potassium addition on the TPR profiles of iron oxide samples. The addition of small amount of potassium (0.2 parts) to the iron oxide sample did not affect the peak positions during the temperature programmed reduction of iron oxide. However, at higher potassium contents (>1.0 parts) positions of both reduction peaks shifted significantly to higher values. These results demonstrate that potassium plays a significant role in controlling the reduction behavior of iron catalysts.

III. 8. 3 TGA Measurement Results

Figure 13 shows the effect of reduction temperature (240°C to 280°C) on the reduction behavior of catalyst C (100 Fe/3 Cu/4 K/16 SiO2, batch-4) in the TGA unit under isothermal conditions in pure hydrogen. The degree of reduction of the catalyst C at 280°C in hydrogen increased with time up to 100 minutes and then leveled off with further increase in reduction time. The degree of reduction was about 65% after the first 100 minutes of reduction, and about 80% at the end of reduction (after ~ 450 minutes in hydrogen). Reductions at 240°C and 250°C resulted in a lower final degree of reduction of about 60%.

Figure 14 shows the effect of reduction temperature (250°C and 280°C) on the reduction behavior of catalyst B (100 Fe/5 Cu/6 K/24 SiO2, batch-3) in the TGA unit under isothermal conditions in pure hydrogen. As expected the final degree of reduction was higher at higher

reduction temperature (80% at 280°C vs. 60% at 250°C). The reduction behavior of the Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2) at 280°C was very similar to that of catalyst B reduced at 250°C. Apparently, the catalyst B (synthesized in our laboratory) is more easily reducible than the Ruhrchemie catalyst.

Figure 15 illustrates the weight loss behavior of catalysts B, C and Ruhrchemie in CO at 250°C and/or 280°C under isothermal conditions (in TGA unit). Note that catalysts had lost about 3-4% of initial sample weight during the heating in helium (from room temperature to a reduction temperature) due to removal of moisture. The weight loss is rapid during the first 100 minutes of exposure to CO. The resulting weight loss may be due to three different reactions occurring on the catalyst surface/or in the bulk. The possible reactions are reduction of iron oxide, carbon deposition (via Boudoudart reaction) and carbide formation (i.e. carburization). However, the sharp weight losses (> 13%) suggest that the reduction process is predominant during the first 100 minutes of reduction. During the later stages of CO exposure the catalyst weights did not change much and this may be an indication for the competitiveness of all the three reactions (reduction, carbon deposition and carbide formation) occurring simultaneously. However, the catalyst B started to gain weight after 100 minutes of reduction at 280°C, which suggests that carbon deposition and/or carbide formation were predominant reactions.

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 continue : (a) with reaction studies under Task 6 , and (b) with characterization of catalysts at various stages of usage (Task 8).

Table 1. Major Events in Run SA-2186 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst (batch 4)

TOS (h)	Event
	Slurry loading: 314 g of Durasyn 164 oil, 12.0 g of catalyst (particle size< 270 mesh)
	Slurry sample withdrawal after the pretreatment: 10 g slurry, 0.4 g catalyst
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P = 1.48 MPa, SV = 2.34 Nl/g-cat/h, (H_2/CO) = 0.67
85	Slurry sample withdrawal: 14 g slurry, 0.5 g catalyst
164	Slurry sample withdrawal: 13 g slurry, 0.5 g catalyst
209	Change SV to 3.43 Nl/g-cat/h and P to 2.17 MPa
258	Slurry sample withdrawal: 16 g slurry, 0.5 g catalyst
351	Slurry sample withdrawal: 28 g slurry, 0.7 g catalyst
450	Slurry sample withdrawal: 27 g slurry, 0.5 g catalyst
450	mass flow meter failure, stopped flow for some time
517	Slurry sample withdrawal: 27 g slurry, 0.5 g catalyst
518	End of run: 552 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 928 g wax, 3.2 g catalyst

Table 2. Major Events in Run SB-2486 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst (batch 4)

TOS (h)	Event
	Slurry loading: 309 g of Durasyn 164 oil, 15.0 g of catalyst (particle size< 270 mesh)
	Slurry sample withdrawal before synthesis gas initiation: 13 g slurry, 0.6 g catalyst
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P = 1.48 MPa, SV = 2.34 Nl/g-cat/h, (H_2/CO) = 0.67
51	Slurry sample withdrawal: 12 g slurry, 0.6 g catalyst
147	Slurry sample withdrawal: 15 g slurry, 0.7 g catalyst
196	Change SV to 1.8 Nl/g-cat/h
213	Change SV to 1.4 Nl/g-cat/h
260	Slurry sample withdrawal: 14 g slurry, 0.7 g catalyst
314	Slurry sample withdrawal: 13 g slurry, 0.6 g catalyst
315	End of run: 240 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 563 g wax, 2.6 g catalyst

Table 3

Summary of BET Surface area and XRD Measurements of Reduced and Passivated Samples from catalyst C (100Fe/3Cu/4K/16SiO2, batch-4) and catalyst B (100Fe/5Cu/6K/24SiO2, batch-3).*

Catalyst Id	Reduction Conditions	Single-Point BET** Surface Area, m^2/g	Phases found in the Reduced and Passivated Samples			
			α-Fe	Fe_3O_4	ε'-$Fe_{2.2}C$	χ-Fe_5C_2
$100Fe/3Cu/4K/16SiO_2$	reduced in H_2 at 240°C for 8 h	-	+			
$100Fe/3Cu/4K/16SiO_2$	reduced in H_2 at 250°C for 8 h	116	+			
$100Fe/5Cu/6K/24SiO_2$	reduced in H_2 at 250°C for 8 h	109	+			
Ruhrchemie catalyst	reduced in H_2 at 280°C for 8 h	-	+			
$100Fe/3Cu/4K/16SiO_2$	in H_2 at 240°C for 2 h, in syngas at 260°C for 6h	-			+	
$100Fe/5Cu/6K/24SiO_2$	in H_2 at 250°C for 4 h, in syngas at 260°C for 4h	-			+	
$100Fe/3Cu/4K/16SiO_2$,	reduced in syngas at 280°C for 8 h	53				+
$100Fe/5Cu/6K/24SiO_2$	reduced in syngas at 280°C for 8 h	83				+
$100Fe/3Cu/4K/16SiO_2$	reduced in syngas at 260°C for 8 h	-				+
100Fe/5Cu/6K/24SiO	reduced in syngas at 260°C for 8 h	-				+
$100Fe/3Cu/4K/16SiO_2$	reduced in CO at 260°C for 8 h	-				+
$100Fe/5Cu/6K/24SiO_2$	reduced in CO at 260°C for 8 h	-				+
$100Fe/3Cu/4K/16SiO_2$	reduced in CO at 280°C for 8 h	-				+
$100Fe/5Cu/6K/24SiO_2$	reduced in CO at 280°C for 8 h	82				+

* Passivated under controlled conditions at room temperature.

** Degassed the samples at 200°C for 1.5 h prior to the N_2 adsorption measurements.

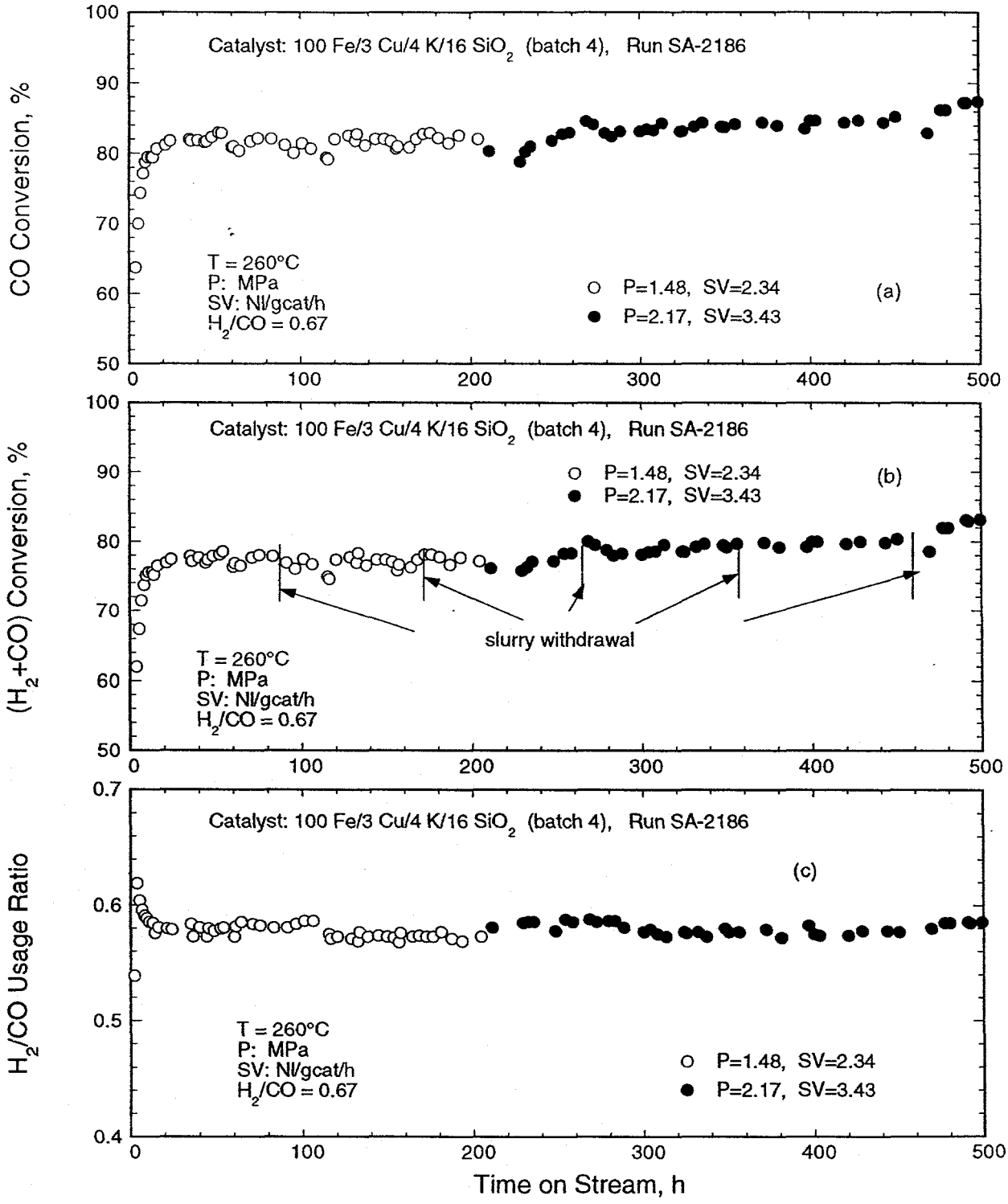

Figure 1. Change in (a) CO conversion, (b) (H_2+CO) conversion, and (c) H_2/CO usage ratio with time on stream in run SA-2186 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

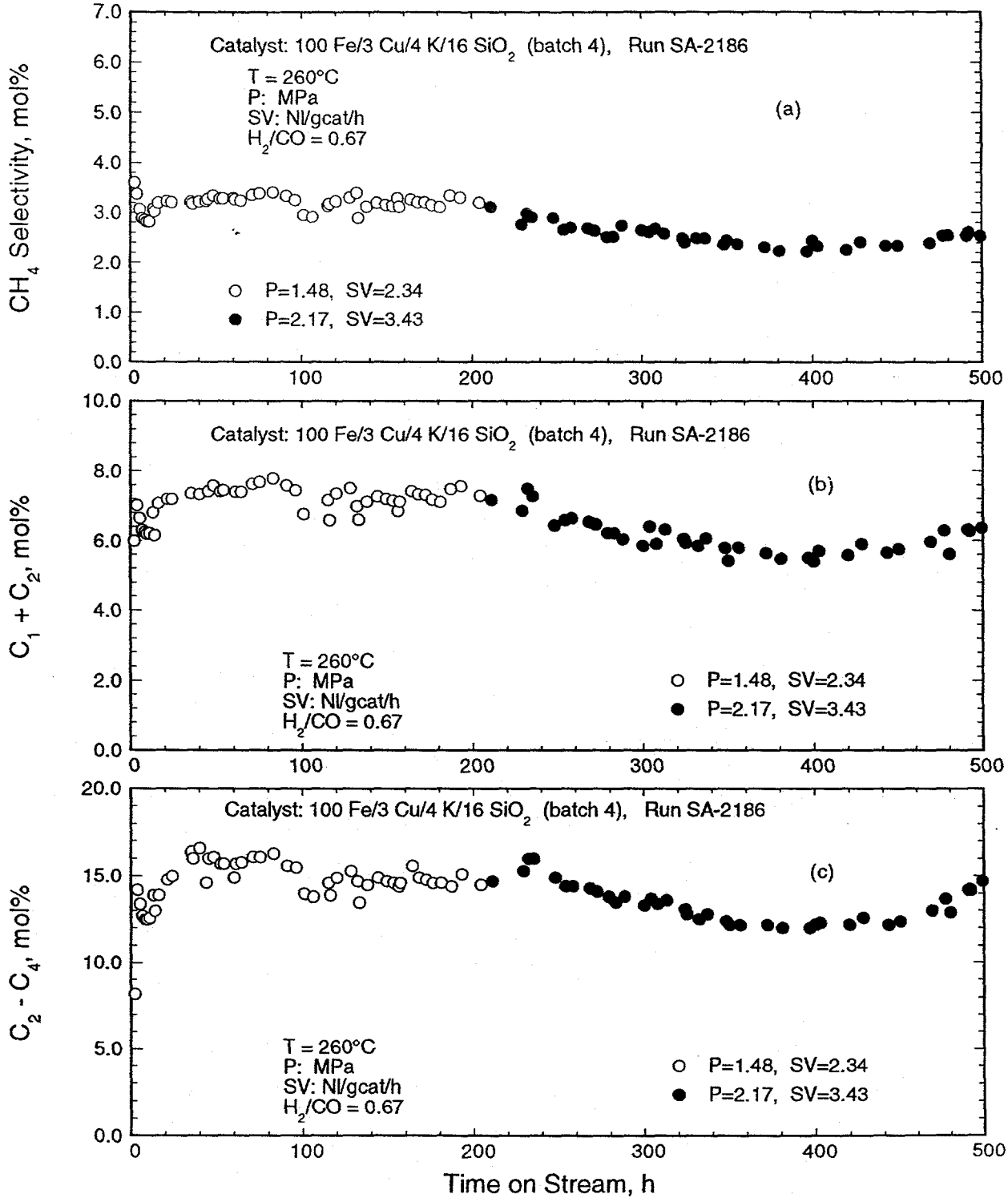

Figure 2. Change in (a) CH_4 selectivity, (b) C_1+C_2 selectivity, and (c) C_2+C_4 selectivity with time on stream in run SA-2186 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

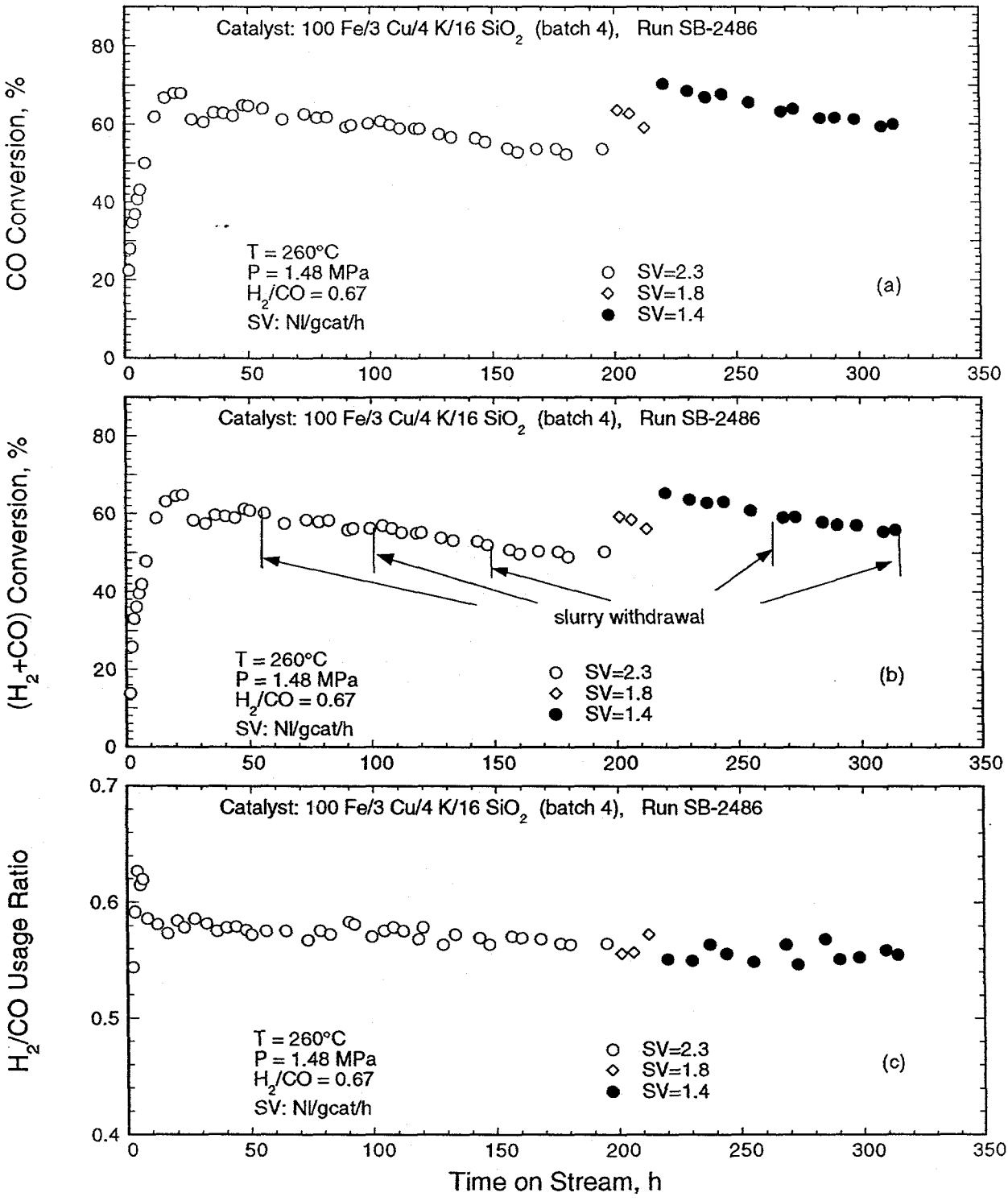

Figure 3. Change in (a) CO conversion, (b) (H_2+CO) conversion, and (c) H_2/CO usage ratio with time on stream in run SB-2486 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

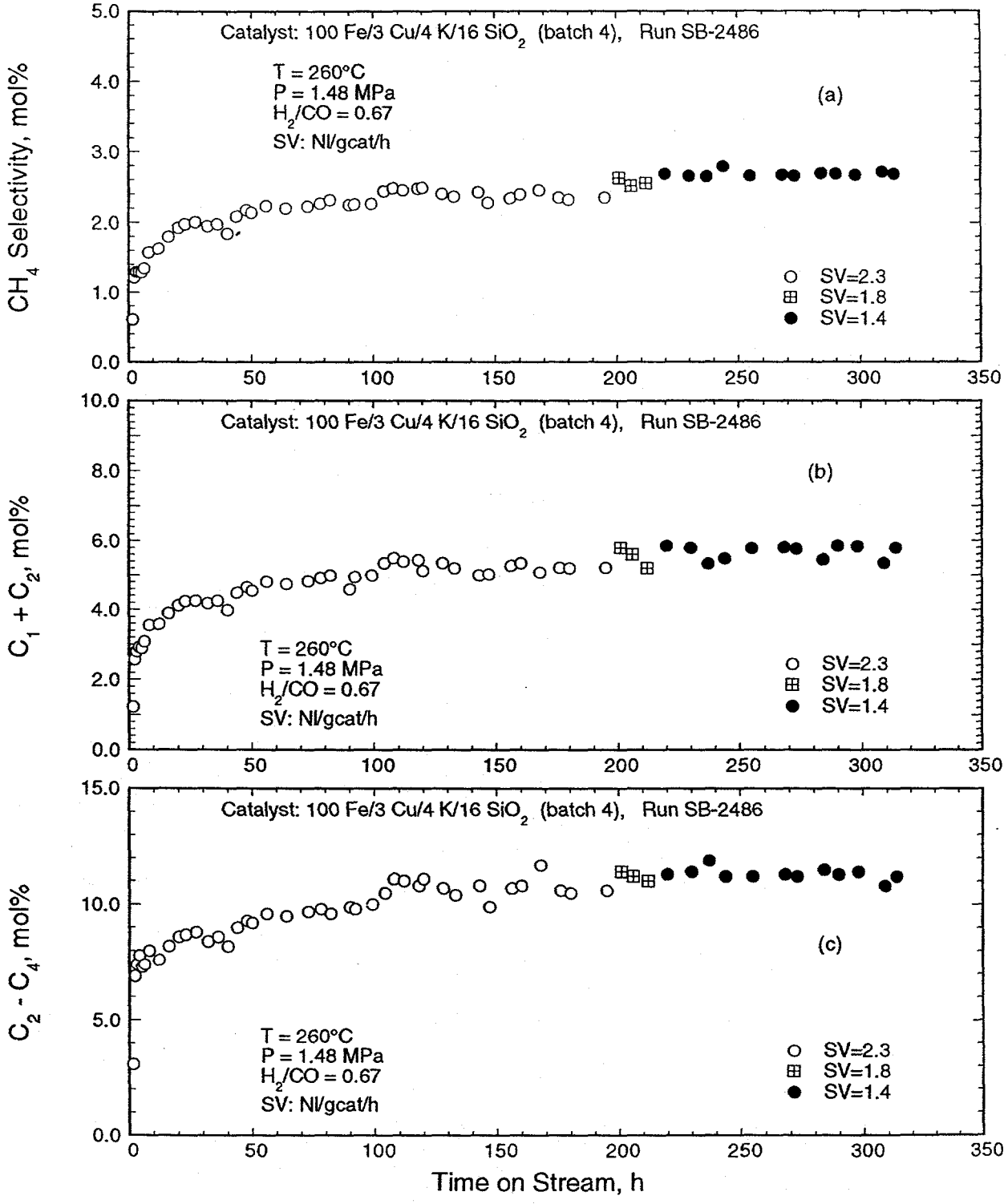

Figure 4. Change in (a) CH_4 selectivity, (b) C_1+C_2 selectivity, and (c) C_2+C_4 selectivity with time on stream in run SB-2486 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

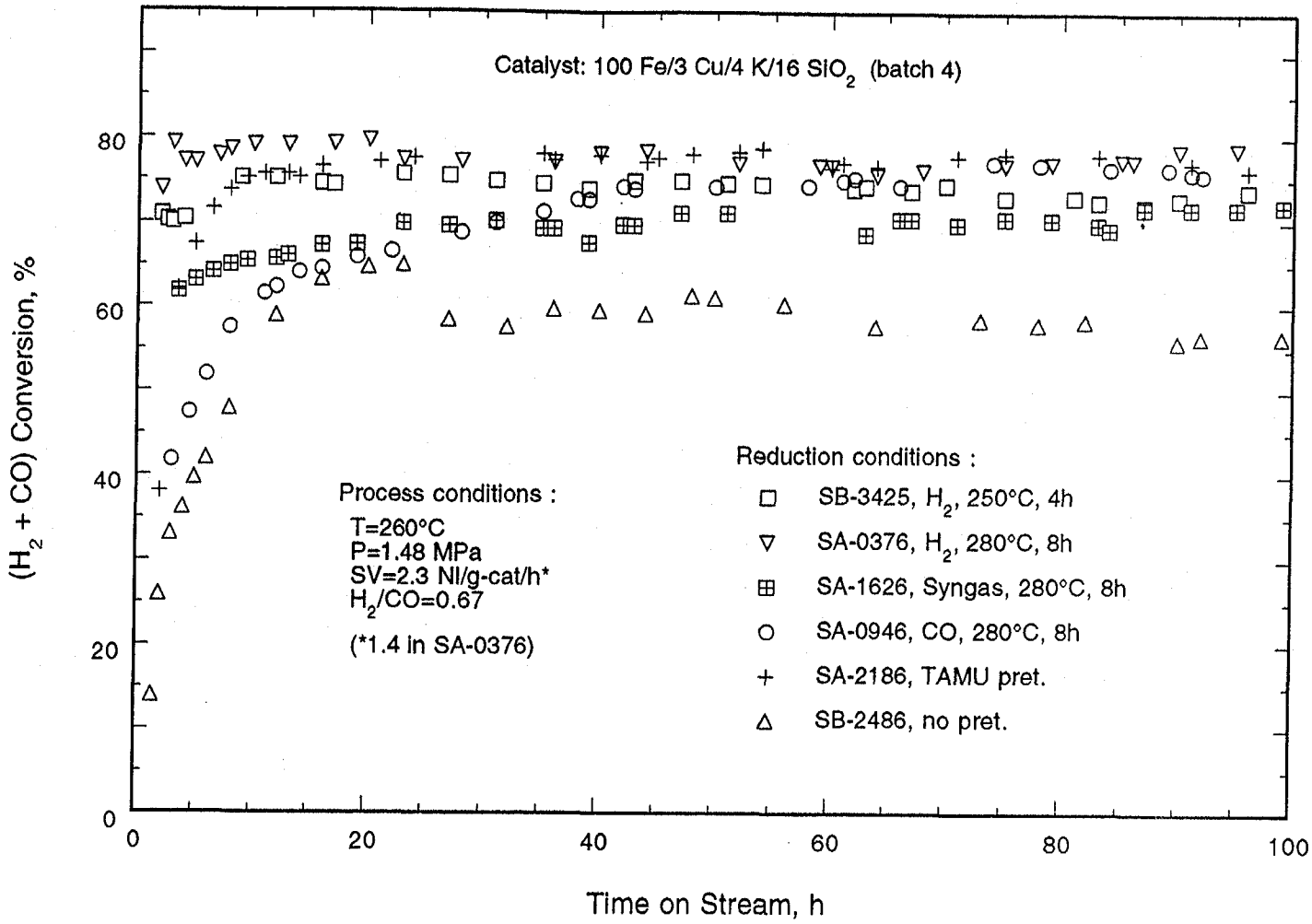

Figure 5. Effect of reducant on (H_2+CO) conversion in STSR tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

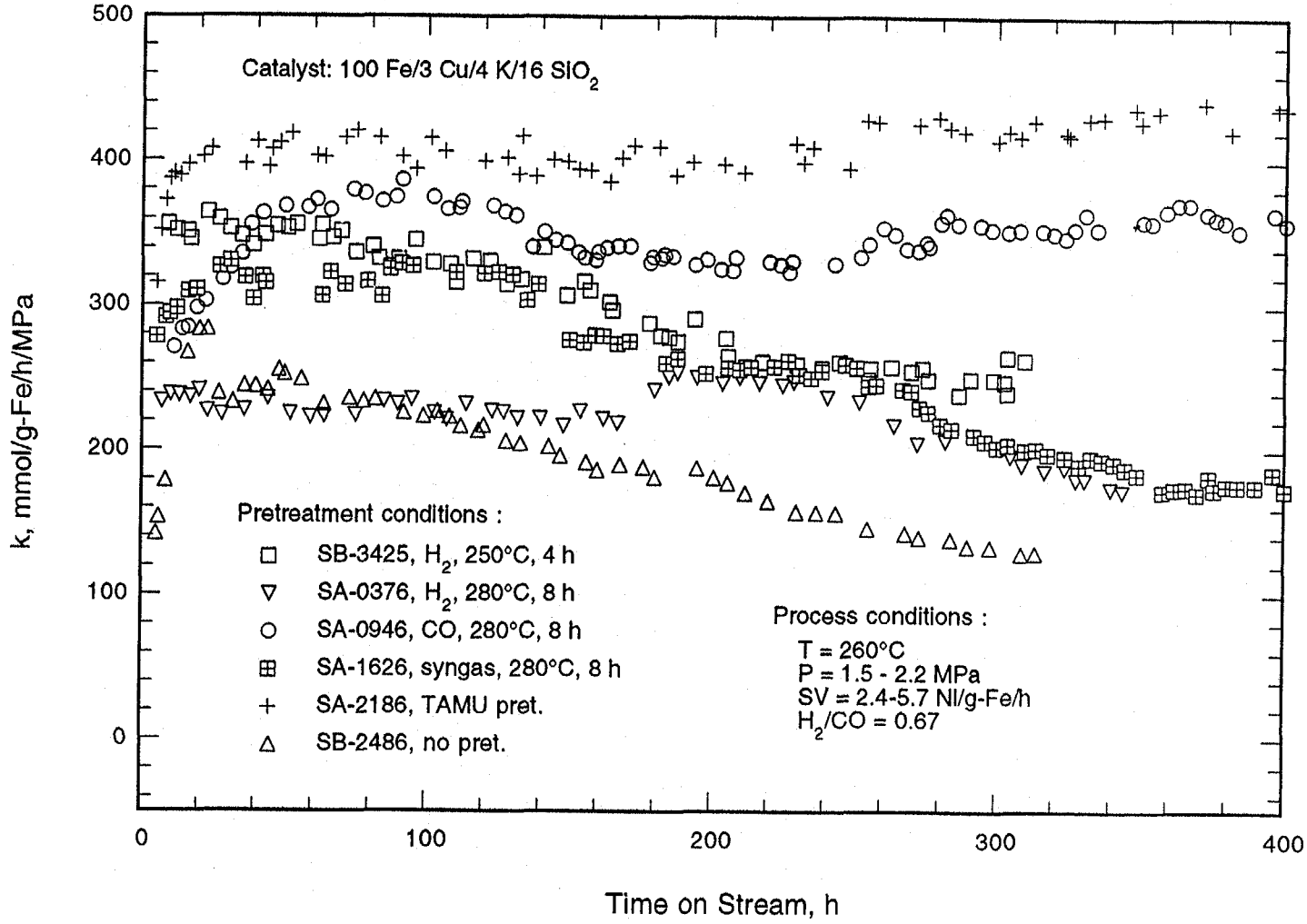

Figure 6. Effect of reducant on apparent first order reaction rate constant in STSR tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

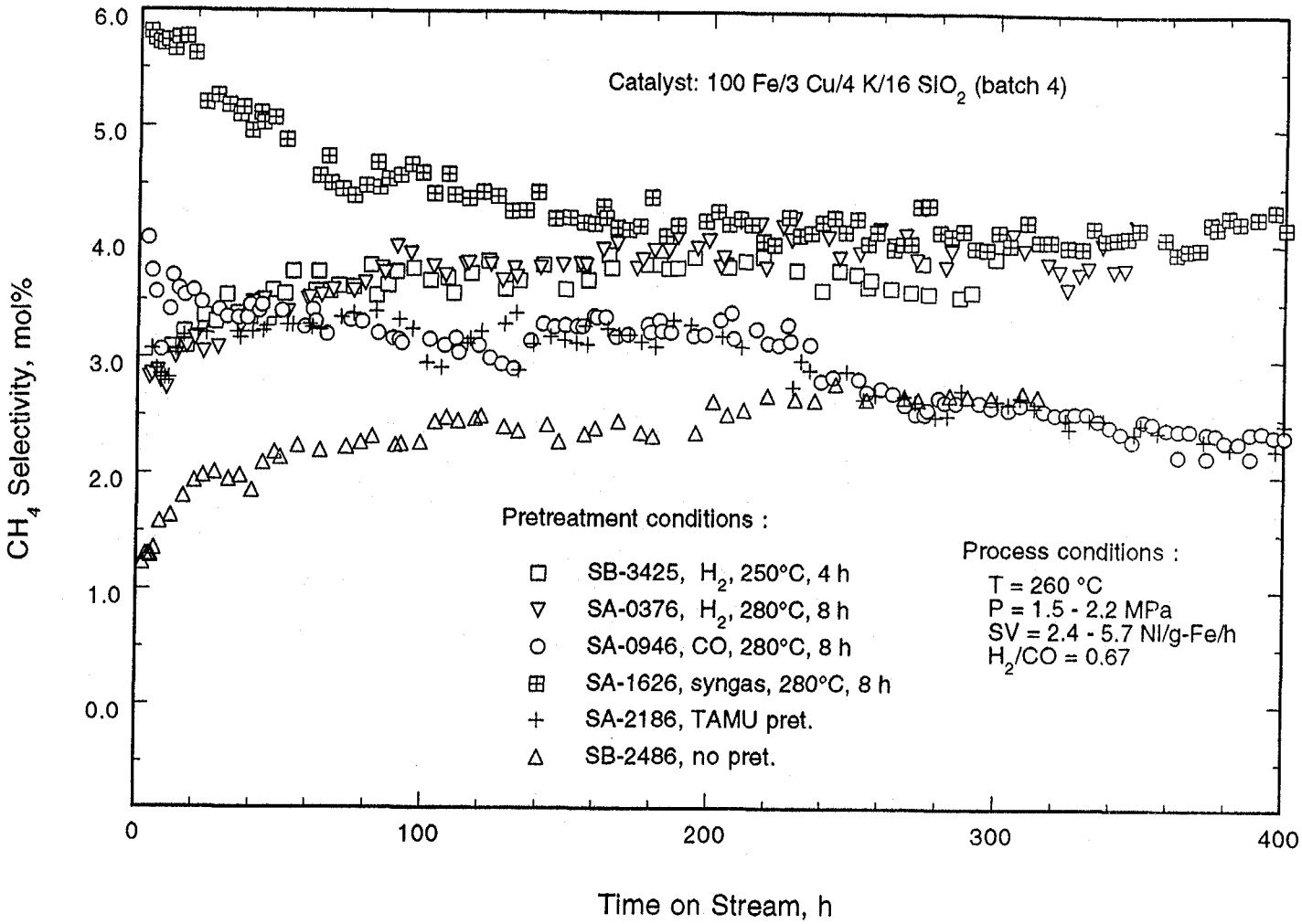

Figure 7. Effect of reducant on methane selectivity in STSR tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

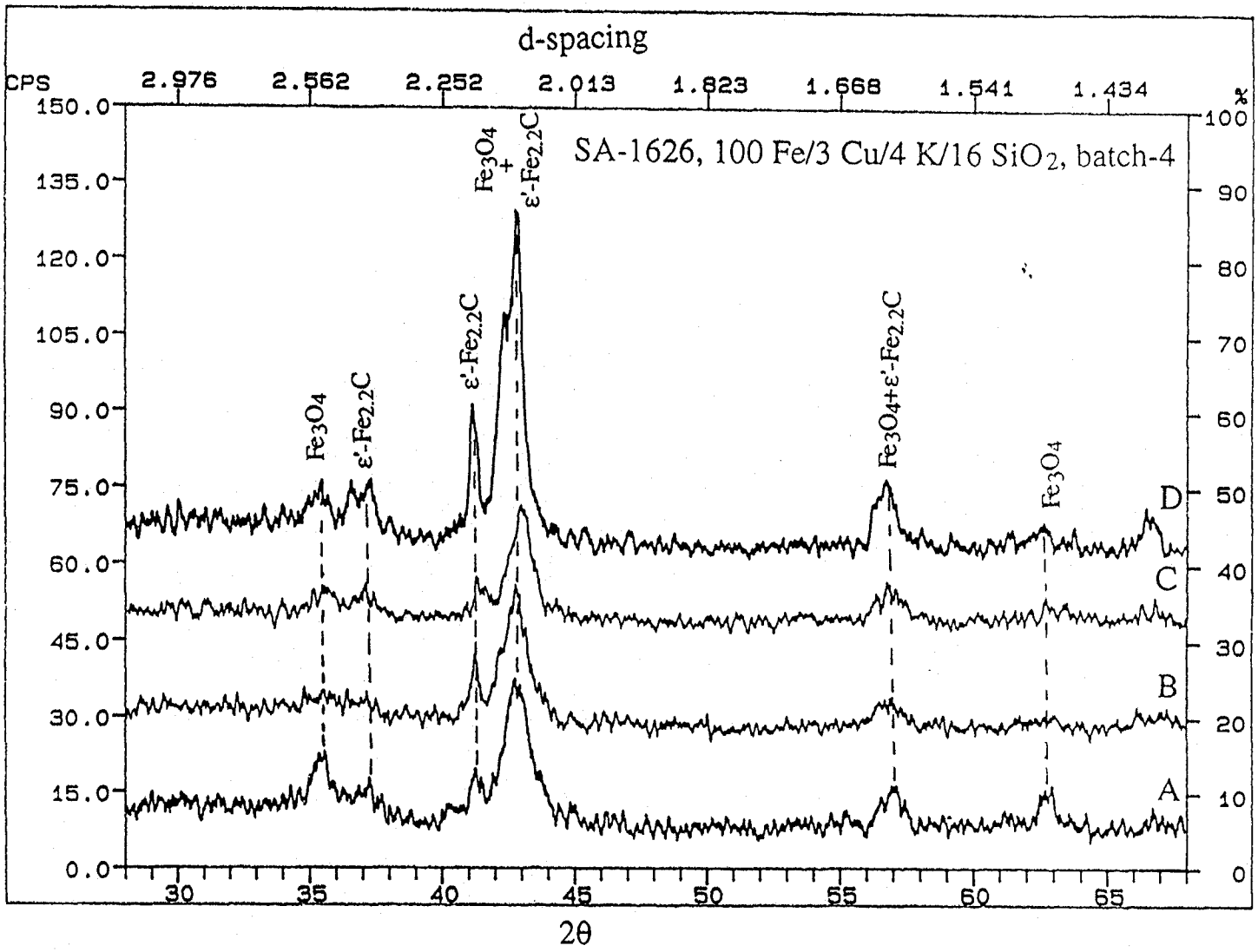

Figure 8 Change in bulk iron phases with time on stream during run SA-1626 with catalyst C (100 Fe/3 Cu/4 K/16 SiO2, batch-4): (A) TOS=0 h; (B) TOS=137 h; (C) TOS=258 h; (D) TOS= 403 h.

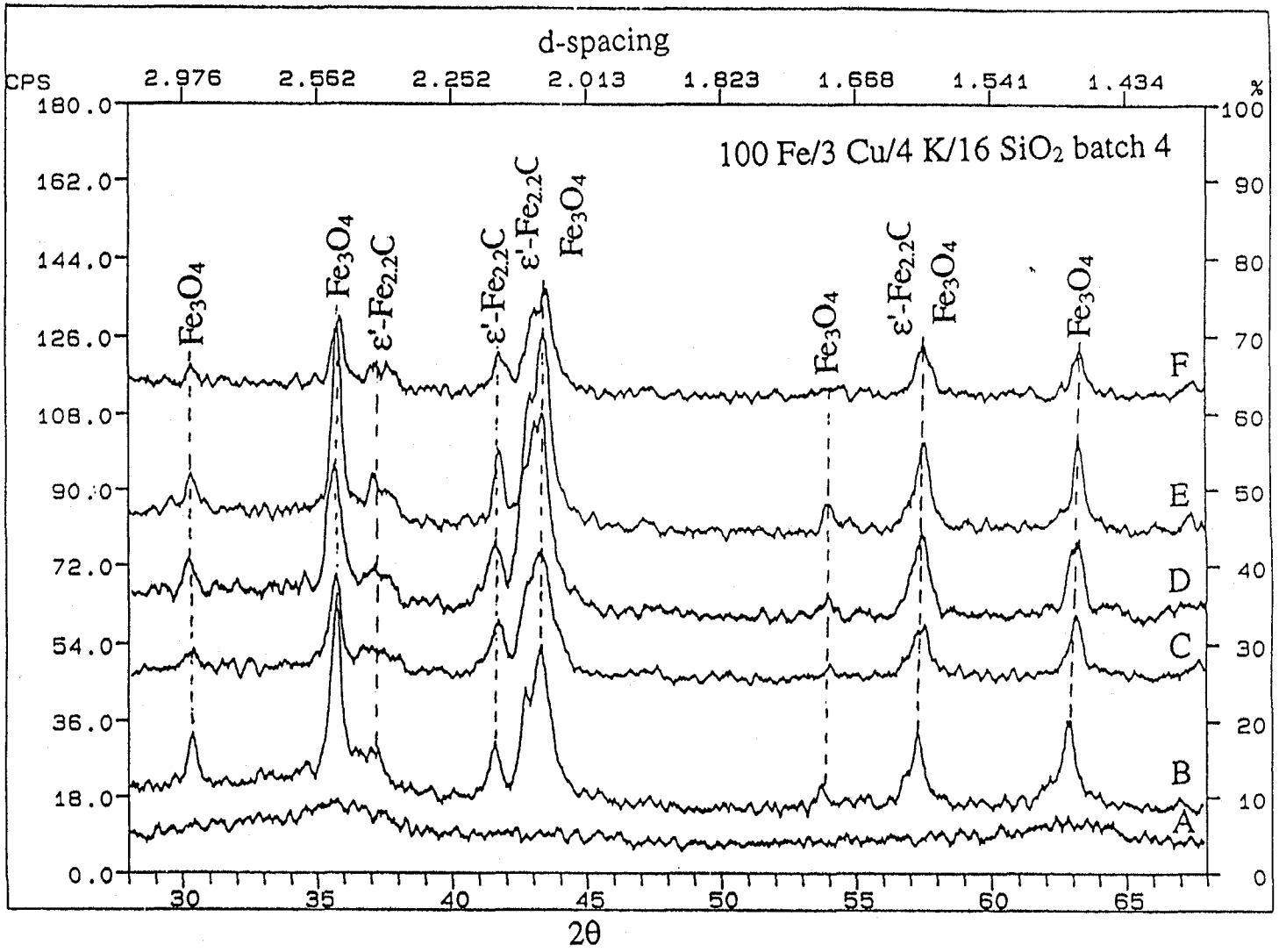

Figure 9 Change in bulk iron phases with time on stream during run SB-2486 with catalyst C (100Fe/3Cu/4K/16SiO2, batch-4): (A) TOS=0 h; (B) TOS=51 h; (C) TOS=100 h; (D) TOS=147 h; (E) TOS=260 h; (F) TOS=315 h.

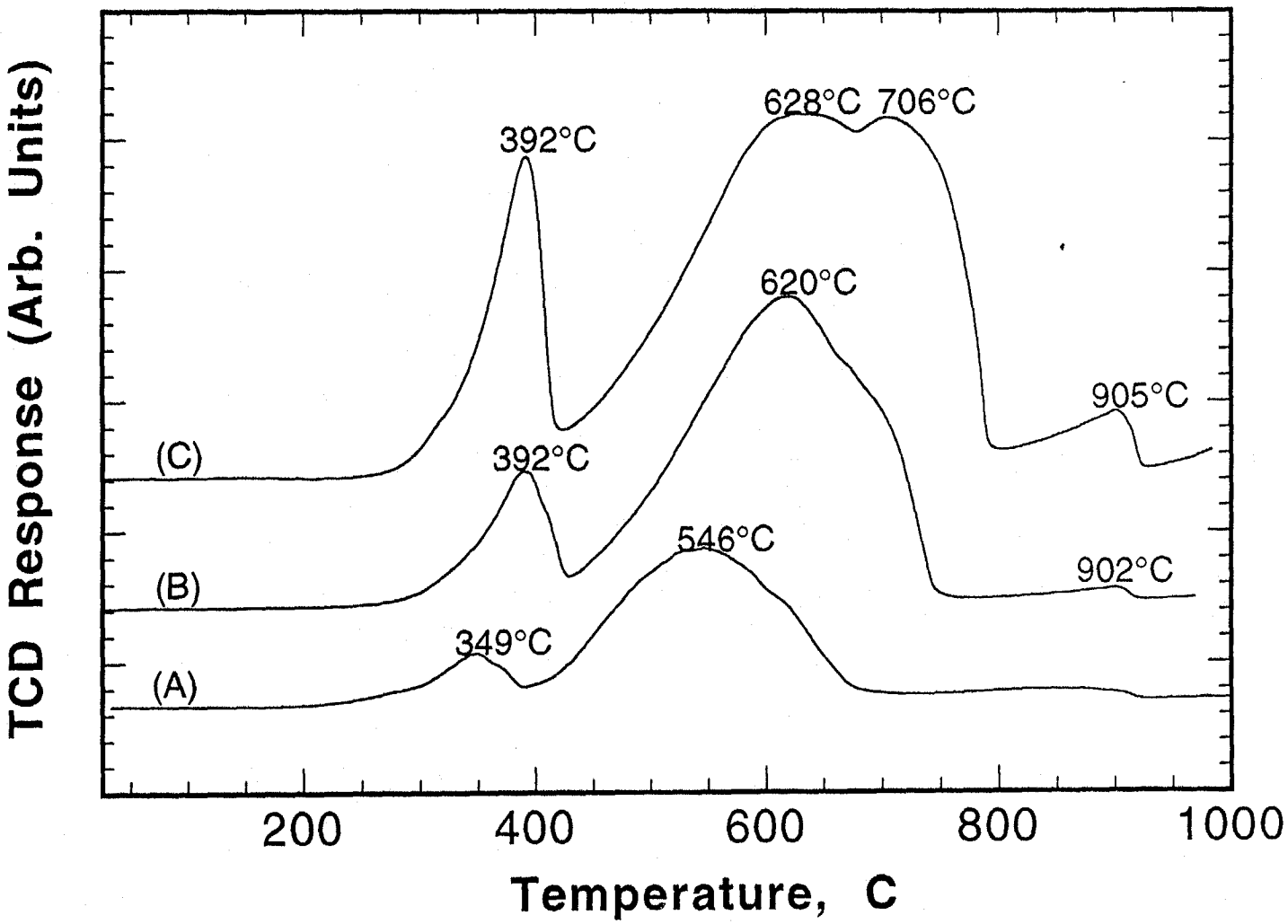

Figure 10 Effect of reductant (5%H_2 and 95%N_2) flow rate on the temperature programmed reduction profiles of iron oxide: (A) 65 ml/min; (B) 40 ml/min ; (C) 20 ml/min.

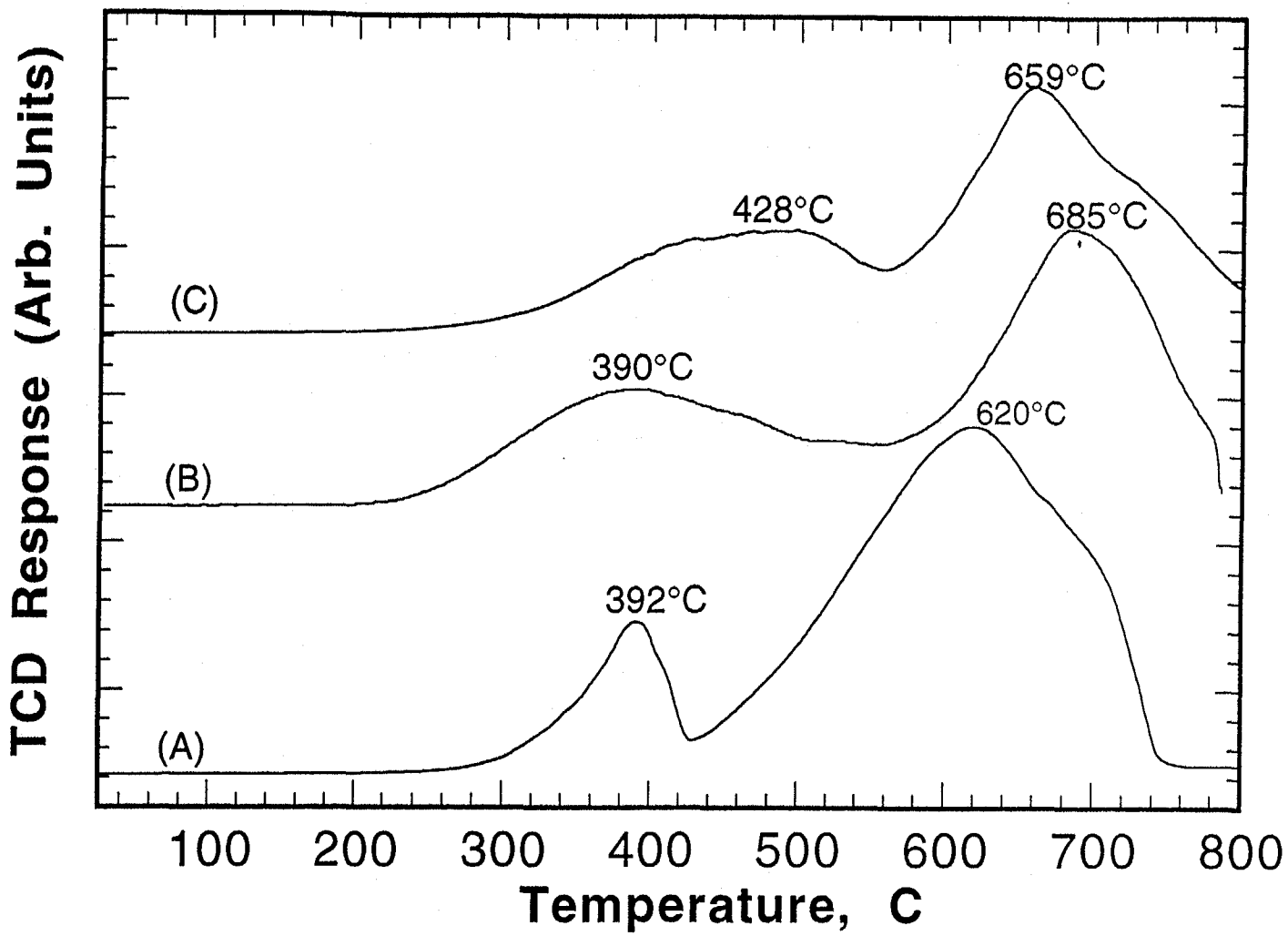

Figure 11 Effect of silica addition on the temperature programmed reduction profiles of iron oxide catalysts: (A) 100Fe (B) 100Fe/16SiO2; (C) 100Fe/24 SiO2.

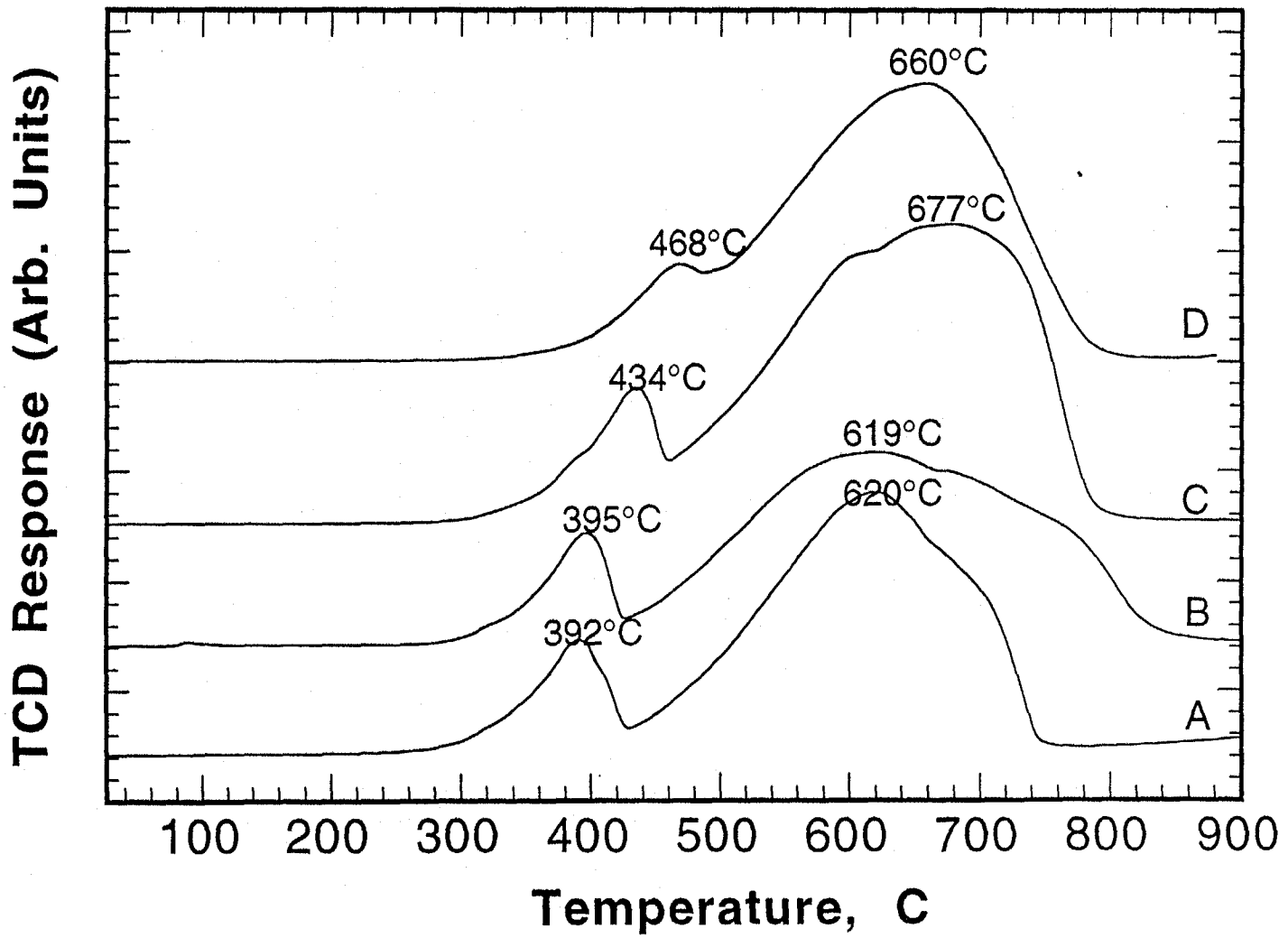

Figure 12 Effect of potassium addition on the temperature programmed reduction profiles of iron oxide catalysts: (A) 100Fe; (B) 100Fe/0.2 K; (C) 100Fe/1.0 K; (D) 100Fe/2.0 K.

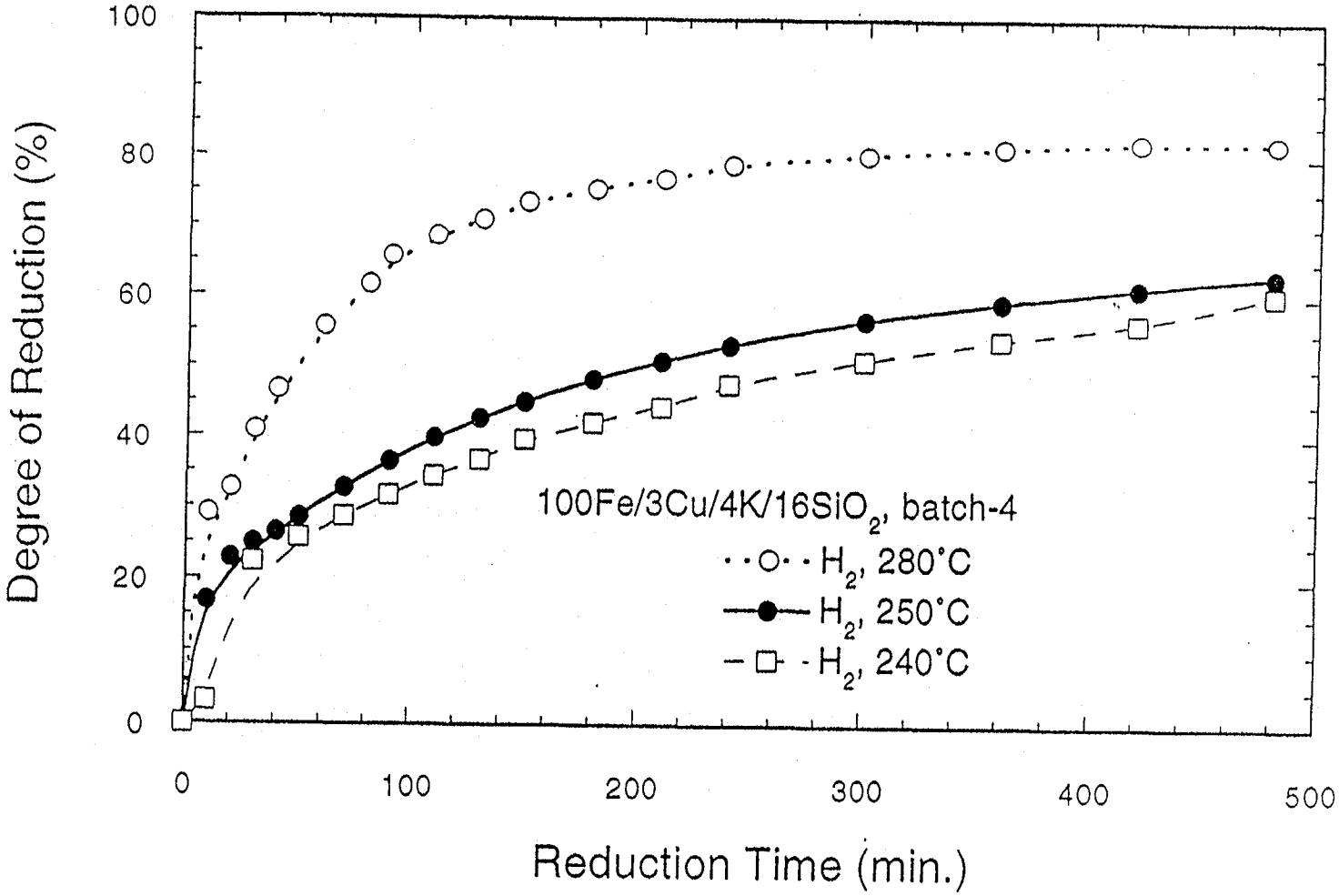

Figure 13 Isothermal reduction of catalyst C (100Fe/3Cu/4K/16SiO2, batch-4) in TGA unit. Reduction conditions: Heating the sample in helium flow (40 ml/min) from room temperature to reduction temperature (i.e 240, 250, and 280°C) at 5°C/min, followed by reduction in pure hydrogen for 8 h, H_2 flow rate = 150 ml/min, and sample weight = ~80 mg.

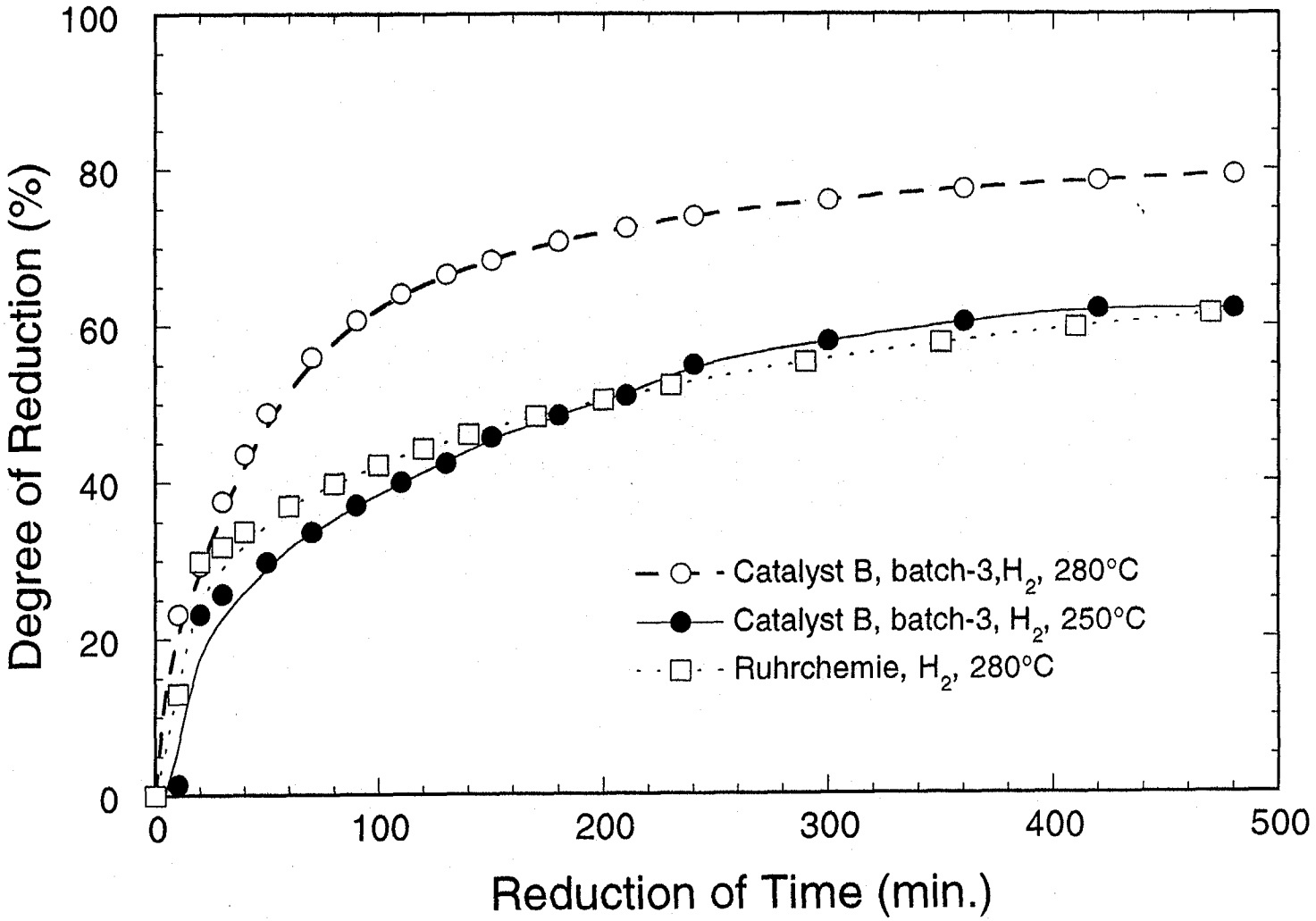

Figure 14 Isothermal reduction of catalyst B (batch-3) and Ruhrchemie catalyst in TGA unit. Reduction conditions: Heating the sample in helium flow (40 ml/min) from room temperature to reduction temperature (i.e 250 or 280°C) at 5°C/min, followed by reduction in pure H_2 for 8 h, H_2 flow rate = 150 ml/min, and sample weight = ~80 mg.

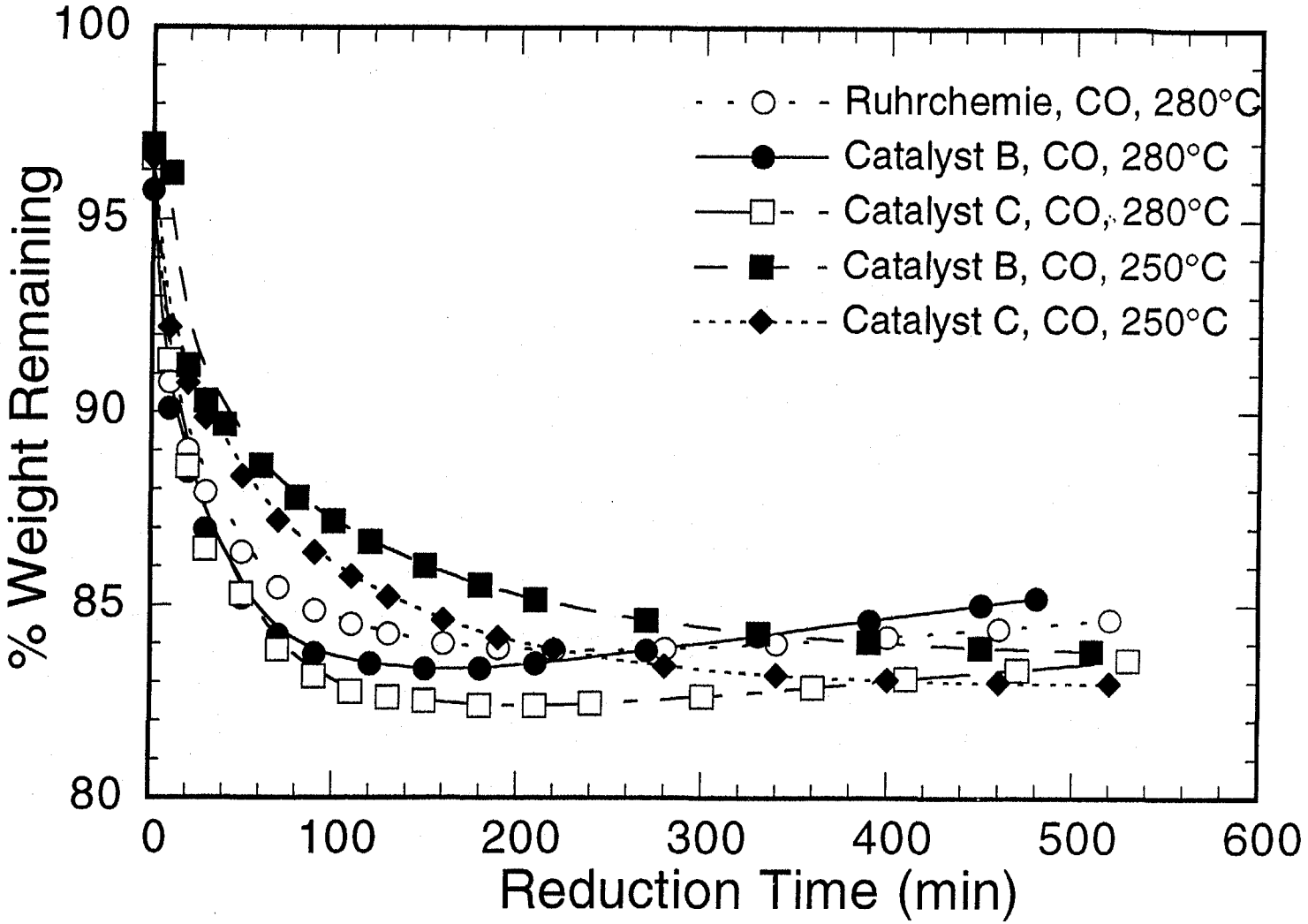

Figure 15 Isothermal reduction of catalysts B, C and Ruhrchemie in TGA unit. Reduction conditions: Heating the sample in helium flow (40 ml/min) from room temperature to reduction temperature (i.e 250 or 280°C) at 5°C/min, followed by reduction in pure CO for 8 h, CO flow rate = 150 ml/min, and sample weight = ~80 mg.