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Development of Precipitated Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
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Texas Engineering Experiment Station Project 32525-44580

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NOTICE

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TECHNICAL STATUS

This technical report is being transmitted in advance of DOE review and no further dissemination or publication shall be made of the report without prior approval of the DOE Project/Program Manager.

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I. EXECUTIVE SUMMARY

Three slurry reactor tests with Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2) were completed in continuation of our studies on the effect of pretreatment conditions on catalyst activity and selectivity. The primary purpose of these tests was to study the catalyst performance during early periods of FTS after different catalyst pretreatments, and relate the catalyst performance to iron phases determined by X-ray diffraction measurements. Three pretreatment procedures were employed: (1) reduction with hydrogen at 250^{o}C for 4 h (run SB-2886); (2) activation with carbon monoxide diluted in helium at 280^{o}C for 8 h (SB-3316); and (3) no activation (SB-3126).

Hydrogen reduced catalyst was the most active, whereas activity of the CO pretreated catalyst was only slightly higher than that of the unpretreated catalyst. The reason for relatively low activity in run SB-3316 (CO pretreatment) may be related to a loss of Durasyn 164 oil during the run. We removed only 182 g of slurry from the reactor at the end of run SB-3316, and the small volume of slurry in the reactor may have not been sufficient to ensure good contact between the syngas and the catalyst.

After 30 h on stream methane selectivities were as follows : no pretreatment (3.2 mol%), CO activated catalyst (3.6 to 4.5 mol%), and hydrogen activated catalyst (4.5 to 5 mol%). Selectivities of C_2-C_4 hydrocarbons for unpretreated and hydrogen reduced catalyst were similar (about 13-15 mol%), whereas C_2-C_4 hydrocarbon selectivity for the CO reduced catalyst was higher (about 18-20 mol%). Initial gaseous hydrocarbon selectivities of unpretreated catalysts were markedly lower than those of the CO and hydrogen pretreated catalysts, and they increased with time on stream as iron oxides were partially converted to ε'-carbide.

The work on catalyst characterization by isothermal reduction and X-ray diffraction 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 and catalytic 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

Three slurry reactor tests were conducted with Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2). The primary purpose of these tests was to study the catalyst performance during early periods of FTS after different catalyst pretreatments, and relate the catalyst performance to iron phases determined by X-ray diffraction measurements. Detailed description of individual test results is given below, followed by comparison of results using different pretreatment procedures. With these three tests the work on pretreatment effects has been completed.

III. 6. 1 Run SB-2886 with 100 Fe/5 Cu/4.2 K/25 SiO_2 (Ruhrchemie) Catalyst

Approximately 15 g of the catalyst (< 270 mesh in size) was loaded for the test, together with 341 g of Durasyn 164 oil as the initial slurry medium. In this first test of the series, the catalyst was reduced with hydrogen diluted with helium (H_2/He = 1/1) at 250^{o}C, 1.48 MPa,

7,500 cm^3/min for 4 h. These reduction conditions are similar to the ones normally used for our Catalyst B (nominal composition 100 Fe/5 Cu/6 K/24 SiO_2).

Following the reduction, the catalyst was tested at 260^oC, 1.48 MPa (200 psig), syngas molar feed ratio of 0.67 (H_2/CO = 0.67) and gas space velocity of 2.15 Nl/g-cat/h (or, 4.1 Nl/g-Fe/h). After about 12 h on stream, the CO and syngas conversions reached 63% and 61%, respectively, and these values did not change during the next 90 h on stream (Figure 1). Methane selectivity was about 6 mol% initially, and then fluctuated between 4 and 5 mol%, whereas of C_2-C_4 hydrocarbon selectivity was 13 -16 mol% (Figure 2). The H_2/CO usage ratio was stable, at about 0.58-0.59 (Figure 1). Slurry samples were withdrawn from the reactor after 2, 4, 10, 30, 50 and 100 h on stream for catalyst characterization by XRD. Major events for run SB-2886 are summarized in Table 1.

After 100 h on stream the catalyst was tested at different gas space velocities, to obtain data illustrating the effect of conversion on space-time-yield (STY). The syngas conversion varied from 20% (SV = 8.5 Nl/g-cat/h) to 79% (SV = 1.2 Nl/g-cat/h). The STY decreased as conversion increased. For example, the STY at SV = 8.5 Nl/g-cat/h was 0.076 mol (H_2+CO)/g-cat/h, whereas the corresponding value at SV = 1.2 Nl/g-cat/h was 0.042 mol (H_2+CO)/g-cat/h. To check for catalyst deactivation, the baseline conditions were repeated at 171 h on stream (SV = 2.15 Nl/g-cat/h) and the catalyst activity, measured by syngas conversion, has not changed in comparison to values obtained during first 100 h on stream (Figure 1). However, methane and C_2-C_4 selectivities were slightly higher, i.e. 6 and 18 mol%, respectively. The usage ratio was also higher in comparison to the first 100 h on stream, 0.63 instead of 0.58-0.59. The run was terminated voluntarily after 216 h on stream.

III. 6. 2 Run SB-3126 with 100 Fe/5 Cu/4.2 K/25 SiO_2 (Ruhrchemie) Catalyst

For this slurry reactor test, 15 grams of catalyst (< 270 mesh in size) was loaded initially to the reactor together with 303 g of Durasyn 164 oil as the initial slurry medium. After heating to reaction temperature of 260^oC in helium at 0.8 MPa over a period of 3.5 h, the catalyst was

exposed to the synthesis gas at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of H_2/CO = 0.67, and gas space velocity of 2.15 Nl/g-cat/h. Activity of the catalyst, that had not been pretreated, increased gradually and reached steady state value after about 30 h on stream. At this time the CO and syngas conversions were about 40 %, and the H_2/CO usage ratio was about 0.71. During the next 70 h of testing, the catalyst activity was stable (Figure 3). Gaseous hydrocarbon selectivities were rather low. For example, methane selectivity was 3.3 mol%, C_1+C_2 selectivity was 6 mol%, and lumped C_2-C_4 selectivity was less than 14 mol% (Figure 4).

Between 106 and 128 h on stream the feed gas H_2/CO molar feed ratio was 0.75. This did not have effect on the CO and syngas conversions, but the usage ratio increased from 0.71 to 0.75. This has also resulted in higher selectivities of gaseous hydrocarbons. Methane selectivity increased to about 4 mol%, C_1+C_2 selectivity to 8 mol%, and lumped C_2-C_4 selectivity to 16 mol%. After switching to syngas with H_2/CO = 0.67 the usage ratio, and hydrocarbon selectivities returned to previous values, but the catalyst deactivated slowly with time. The test was terminated at 151 h.

III. 6 .3 Run SB-3316 with 100 Fe/5 Cu/4.2 K/25 SiO_2 (Ruhrchemie) Catalyst

About 15 g of catalyst was loaded into the reactor together with 335 g of Durasyn 164 oil as the initial slurry medium. Prior to the test, the catalyst was pretreated with CO diluted with helium at 280°C, 0.8 MPa (100 psig) for 8 h. After the pretreatment, the catalyst was tested under the same baseline conditions as those employed in runs SB-2886 and SB-3126, i.e. 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of H_2/CO = 0.67, and gas space velocity of 2.15 Nl/g-cat/h.

After several hours on streams, the CO and syngas conversion were 38 and 40 % (Figure 5), and then increased slowly reaching about 44 and 47 %, respectively, at the end of the run (100 h on stream). Usage ratio was relatively high in this test. It increased from 0.7 (initially), to 0.81 at the end of the run.

Methane selectivity varied between 3.5 and 4.0 mol% (Figure 6). C_1+C_2 selectivity was between 7 and 10 mol%, and lumped C_2-C_4 selectivity was between 17 and 23 mol%.

III. 6. 4. Comparison of Pretreatment Procedures

We have employed three pretreatment procedures with the Ruhrchemie catalyst in slurry reactor tests. They were: (1) reduction with hydrogen at 250°C for 4 h (run SB-2886); (2) activation with carbon monoxide diluted in helium at 280°C for 8 h (SB-3316); and (3) no activation (SB-3126).

Effect of pretreatment procedures on catalyst activity is shown in Figure 7. Comparisons are made during initial 100 hours of stream, when the catalyst was tested at baseline process conditions (260°C, 1.48 MPa, SV = 2.15 Nl/g-cat/h, and feed H_2/CO ratio of 0.67). Initial activities of the CO pretreated (magnetite and iron carbides - Figure 11) and hydrogen reduced (magnetite - Figure 9) were markedly higher than that of the unpretreated catalyst (amorphous iron oxide - Figure 10). Catalyst activity in all three tests increased with time initially. After hydrogen reduction about 15 h was necessary to achieve the steady state activity, and unpretreated catalyst required longer time (about 32 h), whereas the activity of the CO activated catalyst increased rapidly during the first 4 h of synthesis, and then more gradually. In all three runs the catalyst activity was fairly stable after about 40 h on stream. After 50 h on stream the iron phases in catalyst samples from all three tests were: magnetite and iron carbides (Figures 9-11).

Hydrogen reduced catalyst was the most active, whereas activity of the CO pretreated catalyst was only slightly higher than that of the unpretreated catalyst. The reason for relatively low activity in run SB-3316 (CO pretreatment) may be related to a loss of Durasyn 164 oil during the run. We removed only 182 g of slurry from the reactor at the end of run SB-3316, and the small volume of slurry in the reactor may have not been sufficient to ensure good contact between the syngas and the catalyst.

After 30 h on stream methane selectivities were as follows : no pretreatment (3.2 mol%), CO activated catalyst (3.6 to 4.5 mol%), and hydrogen activated catalyst (4.5 to 5 mol%). Selectivities of C_2-C_4 hydrocarbons for unpretreated and hydrogen reduced catalyst were similar (about 13-15 mol%), whereas C_2-C_4 hydrocarbon selectivity for the CO reduced catalyst was higher (about 18-20 mol%). Initial gaseous hydrocarbon selectivities of unpretreated catalysts were markedly lower than those of the CO and hydrogen pretreated catalysts, and they increased with time on stream as iron oxides were partially converted to ε'-carbide.

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. X-ray diffraction (XRD) measurements of Ruhrchemie catalyst samples withdrawn from slurry reactor runs SB-2886, SB-3126 and SB-3316 at various times on stream were made to determine bulk iron phases in the catalyst. Several measurements were made with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) withdrawn at 403 h on stream from slurry reactor run SA-1276 to study the effects of scan rate (0.1^o/min vs. 1^o/min), and catalyst extraction procedure (extracted vs. unextracted scan) on phase identification. Also, XRD measurements of the reactor wax withdrawn from the reactor at 403 h on stream, through a porous metal filter, were made to determine its crystallinity and potential interference with bulk iron phases in the catalyst samples.

Isothermal reduction studies were conducted with catalysts B and C in TGA unit. Two types of reduction procedures were employed: (a) syngas (H_2/CO = 0.67) reduction at 260°C and 280°C; and (b) hydrogen reduction at 240°C (catalyst C) or 250°C (catalyst B) followed by syngas reduction at 260°C. The latter procedure simulates our baseline reduction procedures with these two catalysts employed in our reaction studies.

III. 8. 1 XRD Measurement Results

Figure 9 illustrates changes in bulk iron phases of the soxhlet extracted Ruhrchemie catalyst samples with time on stream during run SB-2886. Magnetite (Fe_3O_4), and possibly metallic iron (α-Fe) were found (Figure 9-A) in the sample withdrawn from the reactor after the hydrogen reduction (H_2/He = 1/1, 250°C, 1.48 MPa, 750 cm^3/min for 4 h). The most intensive peak of α-Fe has d-spacing of ~2.03 angstroms, which is observed in Figure 9-A, however its magnitude is comparable to the signal noise level, and thus we hesitate to ascribe it to α-Fe phase. During early periods of FT synthesis (up to 10 h on stream) magnetite disappeared slowly (Figures 9-B to 9-E), as evidenced by gradual disappearance of its most intensive peak at about d-spacing of 2.53, whereas relative amount of ε'-carbide (ε'-$Fe_{2.2}C$) phase increased with time (as evidenced by increase of a peak with d-spacing of about 2.1 in Figures 9-B to 9-E). It should be noted that the most intensive peak of ε'-carbide (d = 2.1; relative intensity = 100) overlaps with one of the peaks of magnetite (relative intensity = 20). At longer times on stream (TOS = 50 to 215 h, Figures 9-F to 9-H) both magnetite and iron carbide peaks increased with time.

XRD patterns of unextracted Ruhrchemie catalyst samples withdrawn from the reactor during run SB-3126 at various times on stream are shown in Figure 10. The catalyst was nearly amorphous after heating to the reaction temperature (260°C) in helium at 0.8 MPa over a period of 3.5 h (Figure 10-A). Iron oxides (hematite - Fe_2O_3; and magnetite) and ε'-carbide were found in samples withdrawn from the reactor between 2 and 150 h on stream. Discrimination between hematite and magnetite, in the presence of ε'-carbide and possibly crystalline wax (in samples after 50 h on stream) is difficult. These two iron oxides, have similar d-spacing values at 2θ values of about 35.4, 53.7 and 62.2°. Also, as noted above, one of magnetite peaks (at approximately 2θ = 43°) nearly overlaps with the dominant peak of ε'-carbide. Our interpretation of these results is that during early periods of FT synthesis (up to 23 h on stream) both oxides are present in the catalyst, but with increasing time on stream, magnetite becomes the dominant iron oxide phase. Iron oxide phases were decreasing with time on stream, whereas ε'-carbide increased significantly during FT synthesis (Figures 10-B to 10-G). Carburization,

under the reaction conditions, proceeds rather rapidly, and iron carbide was already found in the sample withdrawn from the reactor after 2 h on stream (Figure 10-B).

Magnetite and iron carbides (ε'-$Fe_{2.2}C$ and χ-Fe_5C_2) were found (Figure 11-A) in the unextracted sample of the Ruhrchemie catalyst withdrawn from the reactor immediately after the CO pretreatment (CO/He = 1/10, 280°C, 0.80 MPa for 8 h). During FT synthesis (Figure 11-B to 11-G), the degree of crystallinity of all iron phases increased with time, and the amount of magnetite increased relative to iron carbides. At the end of the run (Figure 11-G) magnetite and iron carbide phases (ε'-$Fe_{2.2}C$ and χ-Fe_5C_2) were present in significant quantities. In this run we have not observed appearance of new iron phases with time on stream, nor disappearance of any of the iron phases which were formed during the pretreatment.

Figure 12 illustrates the effect of scan speed on XRD patterns of the solvent extracted 100 Fe/3 Cu/4 K/16 SiO_2 catalyst, which was withdrawn from slurry reactor run SA-1276 at 403 h on stream. As can be seen from this figure, the same results were obtained with both scan rates (i. e. ε'- carbide and small amount of magnetite were found in both patterns). However, the signal to noise ratio at high resolution data acquisition (i.e. low scan rate of 0.1^o/min) was lower than that at higher scan rate of 1^o/min. This result shows that the scan rate of 1^o/min is usually adequate for identification of major phases in catalyst.

The effect of presence of reactor wax on identification of bulk iron phases in the catalyst was investigated by using solvent extracted and unextracted catalyst samples in XRD measurements (Figure 13). XRD pattern of the unextracted sample, has a substantial number of peaks due to crystalline reactor wax, some of which overlap with those of bulk iron phases and thus hinder the identification of the latter. For example, the identification of small amount of magnetite in the unextracted catalyst samples is very difficult due to the abundance of crystalline wax, and peak overlaps with wax and/or ε'- carbide. Peak assignments for the unextracted catalyst sample in Figure 13-B, were made on the basis of XRD patterns of pure wax (Figure 14-A) and extracted catalyst sample (Figure 12-A). Experimental values of d-spacings, relative intensities, and corresponding peak assignments of unextracted catalyst sample are listed in

Table 4, together with literature values of d-spacing values and intensities of magnetite and ε'-carbide phases.

Comparison of XRD patterns of unextracted catalyst sample with that of wax filtered from the reactor at the same time on stream is shown in Figure 14. As can be seen a large number of peaks in the XRD pattern of the unextracted catalyst sample, is due to the reactor wax, and there is some peak overlap between the wax and bulk iron phases in the used catalyst.

The above results illustrate difficulties associated with bulk iron phase identification of wax coated catalyst samples. Wax extraction in oxygen free atmosphere, prior to XRD measurements, can alleviate these problems.

III. 8. 2 TGA Measurement Results

Figure 15 illustrates the weight loss behavior of catalyst B (100 Fe/5 Cu/6 K/24 SiO_2, batch-3) and C (100 Fe/3 Cu/4 K/16 SiO_2, batch-4) during syngas ($H_2/CO = 0.67$) reduction at 260^oC and 280^oC in the TGA unit. Both catalysts had lost about 3-4% of the initial sample weight during heating in He flow from room temperature to the reduction temperature, due to removal of moisture. The weight loss was rapid during the first 100 minutes of exposure to syngas. After that the weight remaining began to increase slowly.

The observed behavior is the net result of three competing reactions : (a) reduction of iron oxides; (b) carbon deposition ($2\ CO \rightarrow\ CO_2 + C\downarrow$); and (c) carbide formation (i.e. carburization). For catalysts B and C, the maximum value (i.e., theoretical weight loss) of weight loss corresponding to formation of χ- carbide ($Fe_2O_3 \rightarrow \chi\text{-}Fe_5C_2$) is about 20%, whereas the theoretical weight loss for formation of magnetite ($Fe_2O_3 \rightarrow Fe_3O_4$) is about 3.3 %. After 100 minutes of syngas reduction, the experimental weight loss was between 7 and 13%, suggesting that oxide reduction and carburization are dominant reactions, and that carburization is incomplete. During the later stages of reduction the catalyst weight did not change markedly, which is an indication that all three reactions were occurring simultaneously. However, a

gradual increase in weight was observed in all cases, and this suggests that carbon deposition became the dominant reaction, even though the carbide formation process was not completed.

Figure 16 illustrates the weight loss behavior of catalysts B (100 Fe/5 Cu/6 K/24 SiO_2, batch-3) and C (100 Fe/3 Cu/4 K/16 SiO_2, batch-4) exposed first to hydrogen (at 250^{o}C for 4 h - catalyst B; or at 240^{o}C for 2 h - catalyst C), and then to syngas (H_2/CO = 0.67) at 260^{o}C. Again, the initial weight loss of about 3%, is due to loss of moisture during heating in helium from room temperature to the reduction temperature. During reduction in hydrogen, the weight loss was very rapid during the first 20 minutes, and then continued to increase gradually reaching approximately 10% (catalyst C at 120 minutes) and 13% (catalyst B at 240 minutes). Theoretical weight losses for reduction of Fe_2O_3 to Fe_3O_4, and Fe, are approximately 3.3% and 22%, respectively. Experimental weight losses at the end of hydrogen reduction imply that both catalysts, at this reduction stage, were not completely reduced to metallic iron. Upon the catalysts exposure to syngas, the weight remaining of catalyst B began to increase rapidly (about 2.5% in 100 minutes), and then more slowly, while the catalyst C continued to loose weight initially (about 1% in 100 minutes), but eventually its weight also increased slowly with time. The sharp increase in weight remaining of the catalyst B after exposure to syngas suggests that carburization and carbon deposition are predominant reactions. In the case of catalyst C, reduction of magnetite was the dominant reaction during the first 100 minutes in syngas, whereas carbide formation and carbon deposition were dominant reactions afterwards.

III. 9 Catalyst Testing in a Bubble Column Slurry Reactor

The work on this task has not been initiated. Our request for elimination of this task, due to budget reductions, has been submitted for DOE's approval.

III. 10 Scale-up of Catalyst Synthesis Procedure

The work on this task has not been initiated. Our request for elimination of this task, due to budget reductions, has been submitted for DOE's approval.

Plans for the Next Quarter

During the next quarter we plan to : (a) initiate work on testing of alternative catalysts (pending DOE approval), and (b) continue with characterization of catalysts at various stages of usage (Task 8).

Table 1. Major Events in Run SB-2886 with Ruhrchemie Catalyst

TOS (h)	Event
	Slurry loading: 341 g of Durasyn 164 oil, 15.0 g of catalyst (particle size< 270 mesh)
	Catalyst pretreatment: Heat the slurry in helium flow (750 cm^3/min) up to 250°C, then introduce H_2 diluted with helium (H_2/He = 1/1) at 250°C for 4h (P = 1.48 MPa and total flow rate = 7500 cm^3/min).
	Slurry sample withdrawal: 10 g slurry, 0.4 g catalyst
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
2	Slurry sample withdrawal: 9 g slurry, 0.4 g catalyst
4	Slurry sample withdrawal: 14 g slurry, 0.6 g catalyst
10	Slurry sample withdrawal: 14 g slurry, 0.6 g catalyst
29	Slurry sample withdrawal: 18 g slurry, 0.8 g catalyst
50	Slurry sample withdrawal: 16 g slurry, 0.7 g catalyst
100	Slurry sample withdrawal: 9 g slurry, 0.4 g catalyst
	Change space velocity to SV = 5.0 Nl/(g-cat/h)
123	Change space velocity to SV = 1.4 Nl/(g-cat/h)
142	Change space velocity to SV = 7.0 Nl/(g-cat/h)
145	Change space velocity to SV = 8.5 Nl/(g-cat/h)
165	Change space velocity to SV = 2.15 Nl/(g-cat/h)
188	Change space velocity to SV = 1.2 Nl/(g-cat/h)
216	Slurry sample withdrawal: 14 g slurry, 0.6 g catalyst
216	End of run: 178 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 340 g wax, 4.5 g catalyst

Table 2. Major Events in Run SB-3126 with Ruhrchemie Catalyst

TOS (h)	Event
	Slurry loading: 303 g of Durasyn 164 oil, 15.0 g of catalyst (particle size< 270 mesh)
	Catalyst pretreatment: Heat the slurry in helium flow (750 cm^3/min) up to 260°C and maintain at 260°C for about 4 h.
	Slurry sample withdrawal before synthesis gas initiations: 13 g slurry, 0.6 g catalyst
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
2	Slurry sample withdrawal: 10 g slurry, 0.4 g catalyst
4	Slurry sample withdrawal: 13 g slurry, 0.6 g catalyst
10	Slurry sample withdrawal: 6 g slurry, 0.3 g catalyst
23	Slurry sample withdrawal: 18 g slurry, 0.6 g catalyst
50	Slurry sample withdrawal: 11 g slurry, 0.5 g catalyst
103	Change synthesis gas composition to (H_2/CO) = 0.75
128	Change synthesis gas composition back to (H_2/CO) = 0.67
150	Slurry sample withdrawal: 10 g slurry, 0.5 g catalyst
151	End of run: 91 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 276 g wax, 3.5 g catalyst

Table 3. Major Events in Run SB-3316 with Ruhrchemie Catalyst

TOS (h)	Event
	Slurry loading: 335 g of Durasyn 164 oil, 15.0 g of catalyst (particle size< 270 mesh)
	Catalyst pretreatment: Heat the slurry in helium flow (750 cm^3/min) up to 280°C, then introduce CO diluted with Helium (CO/He = 1/10) at 280°C for 8 h (P = 0.8 MPa and total flow rate 6875 cm^3/min).
	Slurry sample withdrawal: 13 g slurry, 0.6 g catalyst
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
2	Slurry sample withdrawal: 7 g slurry, 0.3 g catalyst
4	Slurry sample withdrawal: 13 g slurry, 0.6 g catalyst
10	Slurry sample withdrawal: 14 g slurry, 0.7 g catalyst
30	Slurry sample withdrawal: 9 g slurry, 0.4 g catalyst
50	Slurry sample withdrawal: 12 g slurry, 0.5 g catalyst
100	Slurry sample withdrawal: 10 g slurry, 0.5 g catalyst
100	End of run: 202 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 182 g wax, 3.6 g catalyst

Table 4 XRD results of wax and catalyst samples from run SA-1276 at 403 h on stream

	Experiment Value			Literature Value			
	d-spacing	Phase	Intensity	Fe_3O_4	Intensity	ε'-$Fe_{2.2}C$	Intensity
1	2.9844	wax	20	2.967	30		
2	2.4853	wax	34				
3	2.3993	ε'-$Fe_{2.2}C$	8			2.385	25
4	2.2646	wax	32				
5	2.2244	wax	27				
6	2.1803	wax, ε'-$Fe_{2.2}C$	36			2.175	25
7	2.1252	wax	49				
8	2.1027	wax, ε'-$Fe_{2.2}C$, Fe_3O_4	100	2.099	20	2.091	100
9	2.0715	wax	17				
10	1.9341	wax	18				
11	1.7289	wax	16				
12	1.6749	wax	14				
13	1.6147	wax, ε'-$Fe_{2.2}C$, Fe_3O_4	18	1.616	30	1.607	13
14	1.5064	Fe_3O_4	7	1.484	40		
15	1.3993	ε'-$Fe_{2.2}C$	8			1.377	16

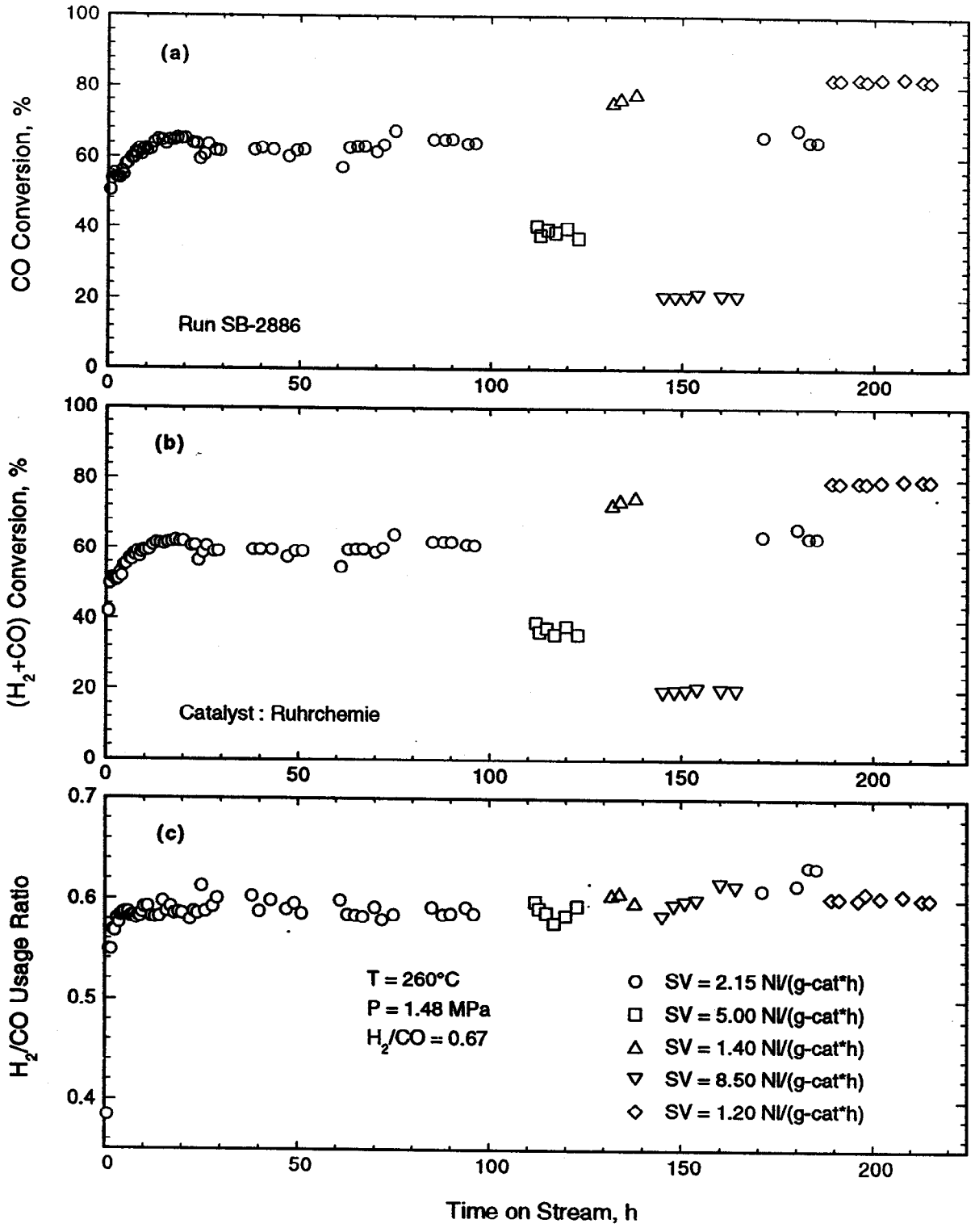

Figure 1. Change in (a) CO conversion, (b) (H_2+CO) conversion, and (c) H_2/CO usage ratio with time on stream in run SB-2886 with Ruhrchemie catalyst.

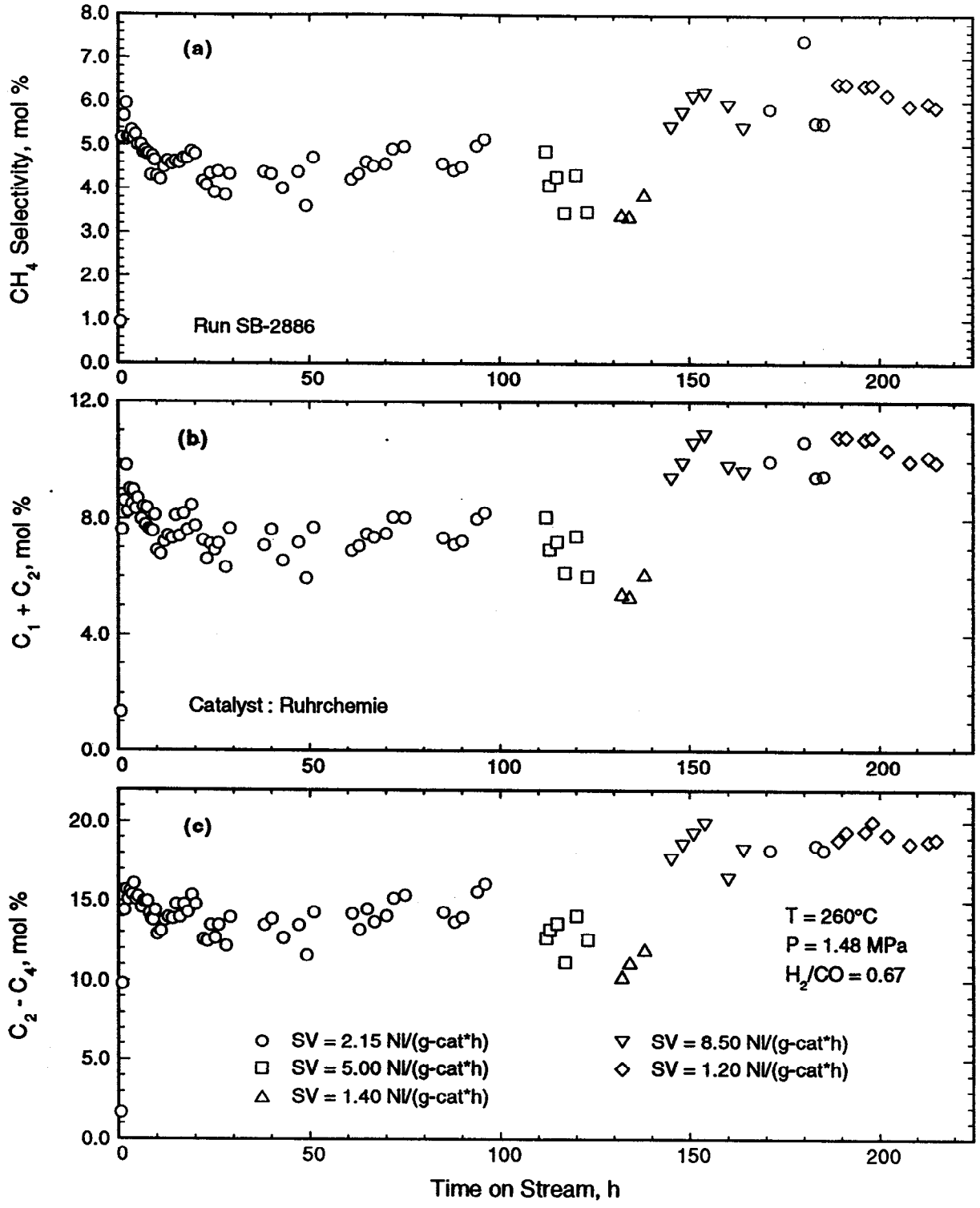

Figure 2. Change in (a) methane selectivity, (b) C_1+C_2 selectivity and (c) C_2-C_4 selectivity with time on stream in run SB-2886 with Ruhrchemie catalyst.

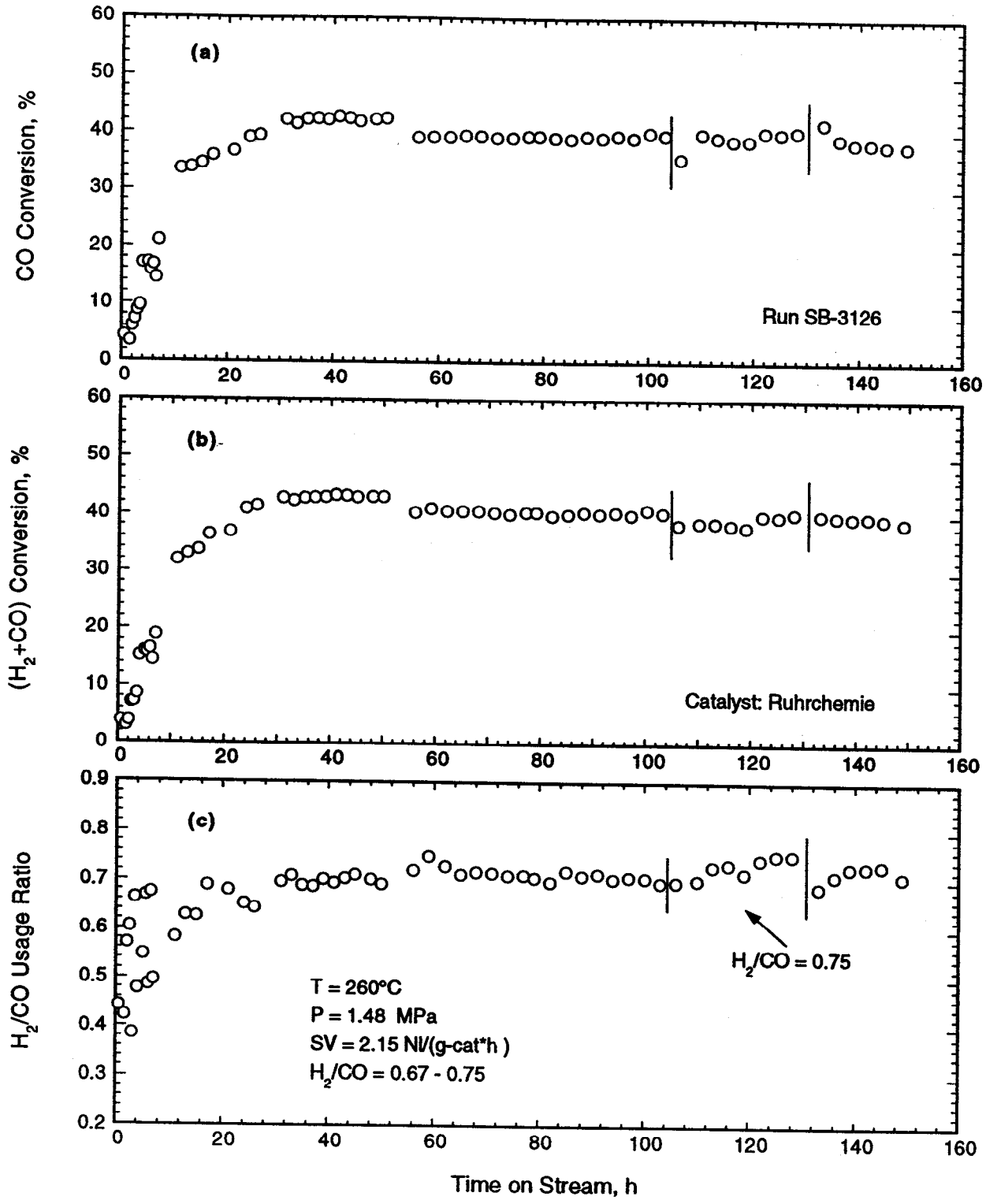

Figure 3. Change in (a) CO conversion, (b) (H_2+CO) conversion, and (c) H_2/CO usage ratio with time on stream in run SB-3126 with Ruhrchemie catalyst.

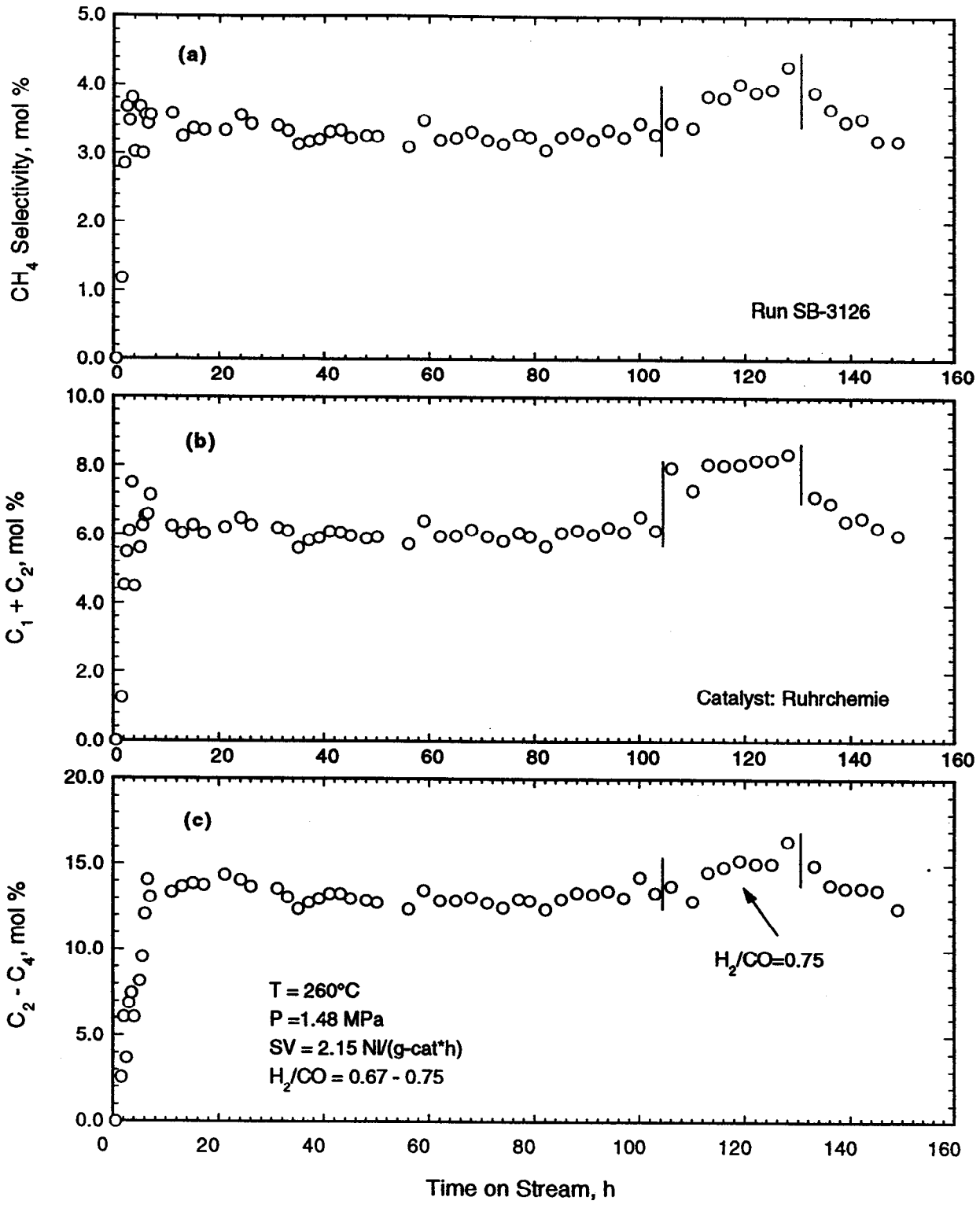

Figure 4. Change in (a) methane selectivity, (b) C_1+C_2 selectivity and (c) C_2-C_4 selectivity with time on stream in run SB-3126 with Ruhrchemie catalyst.

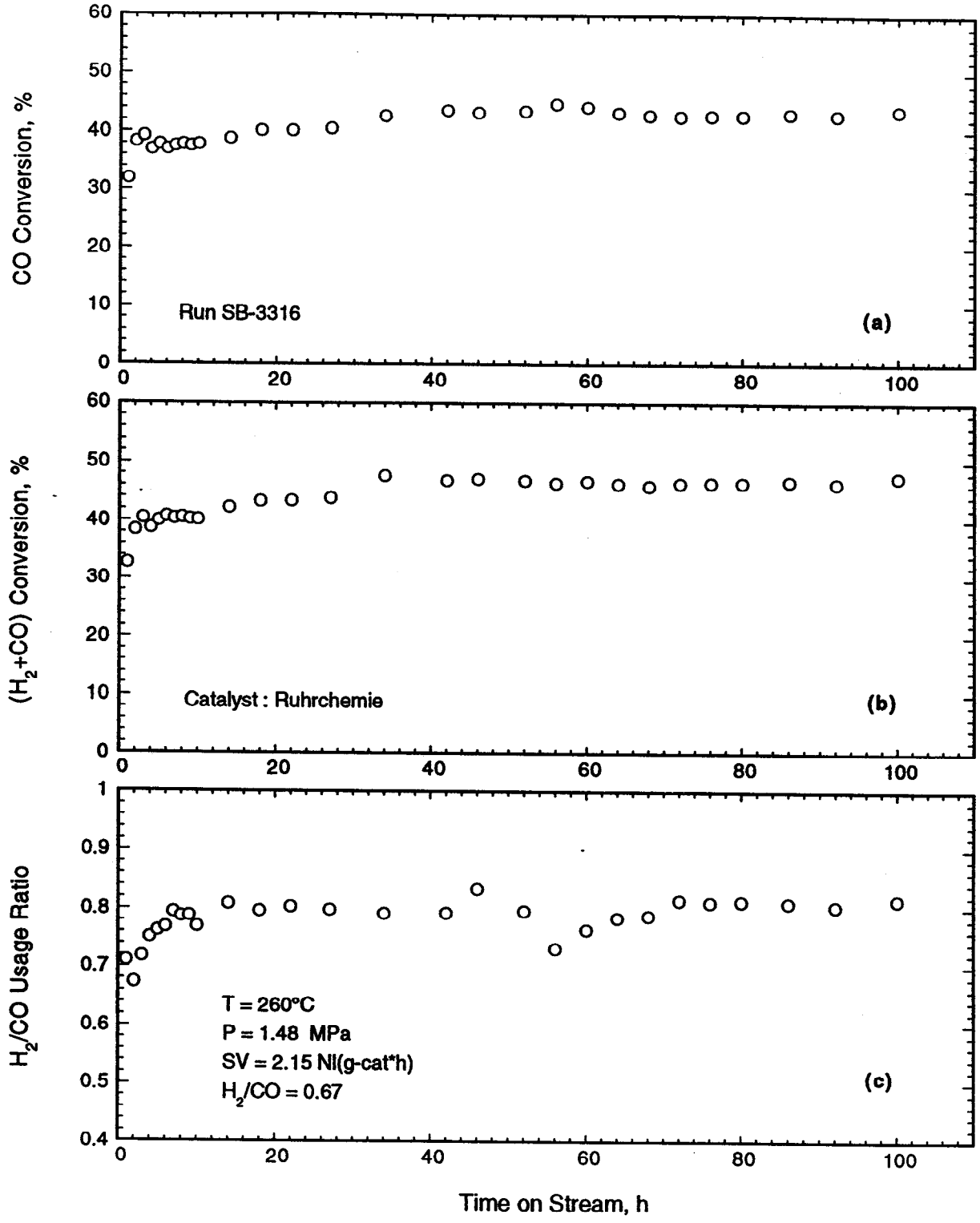

Figure 5. Change in (a) CO conversion, (b) (H_2+CO) conversion, and (c) H_2/CO usage ratio with time on stream in run SB-3316 with Ruhrchemie catalyst.

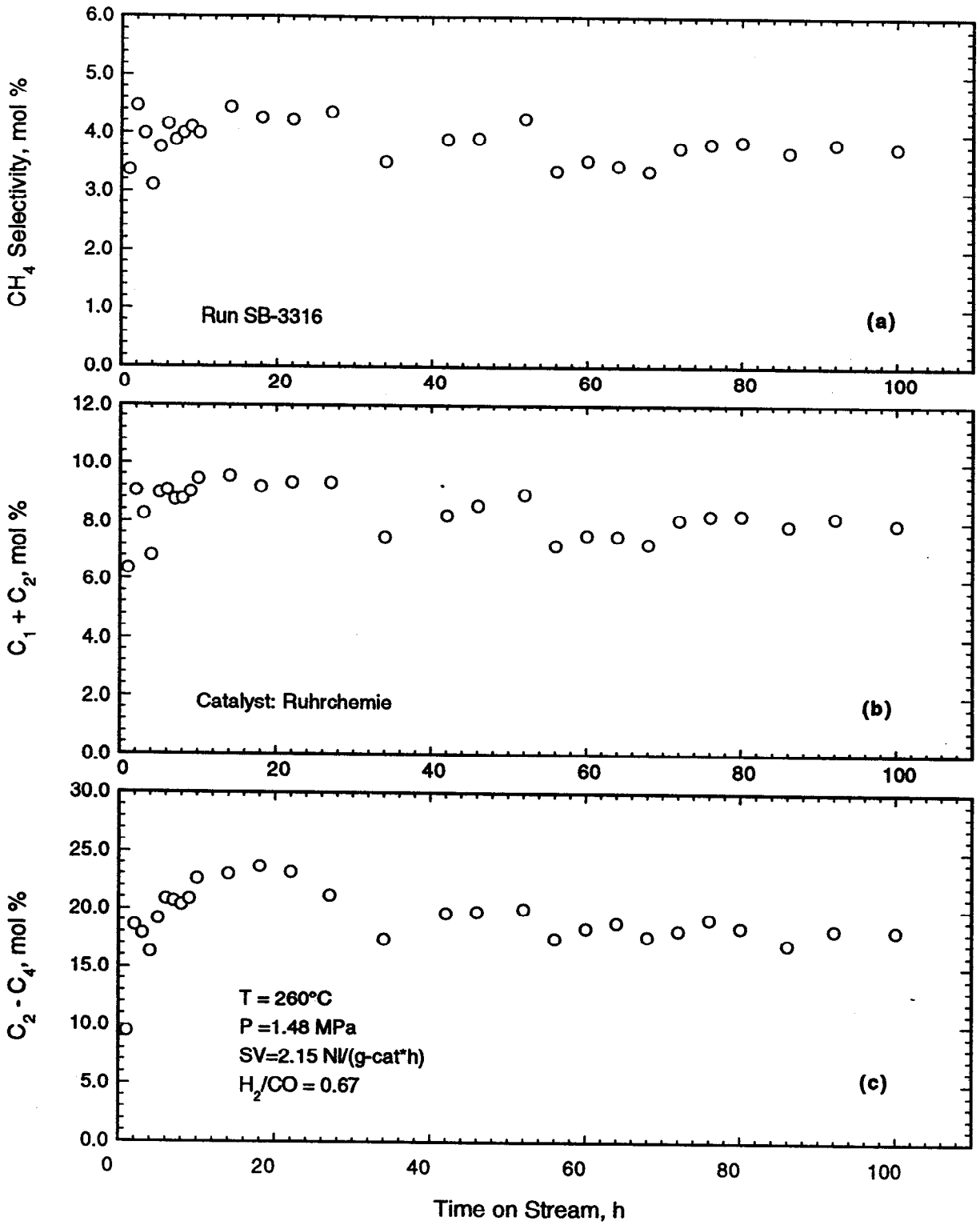

Figure 6. Change in (a) methane selectivity, (b) C_1+C_2 selectivity and (c) C_2-C_4 selectivity with time on stream in run SB-3316 with Ruhrchemie catalyst.

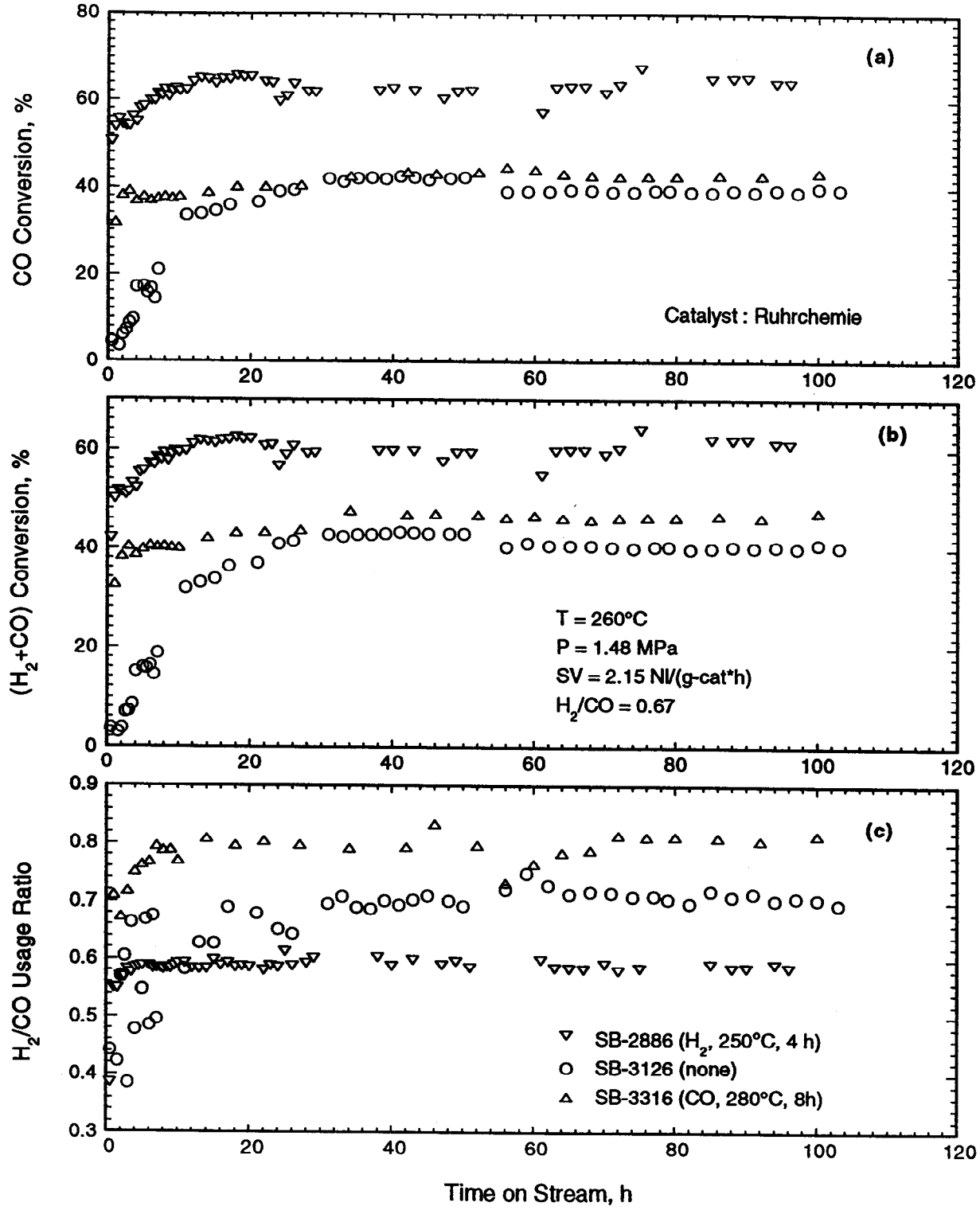

Figure 7 Comparison of (a) CO conversion (b) (H_2+CO) conversion and (c) H_2/CO usage ratio between runs SB-2886, SB-3126 and SB-3316 with Ruhrchemie catalyst.

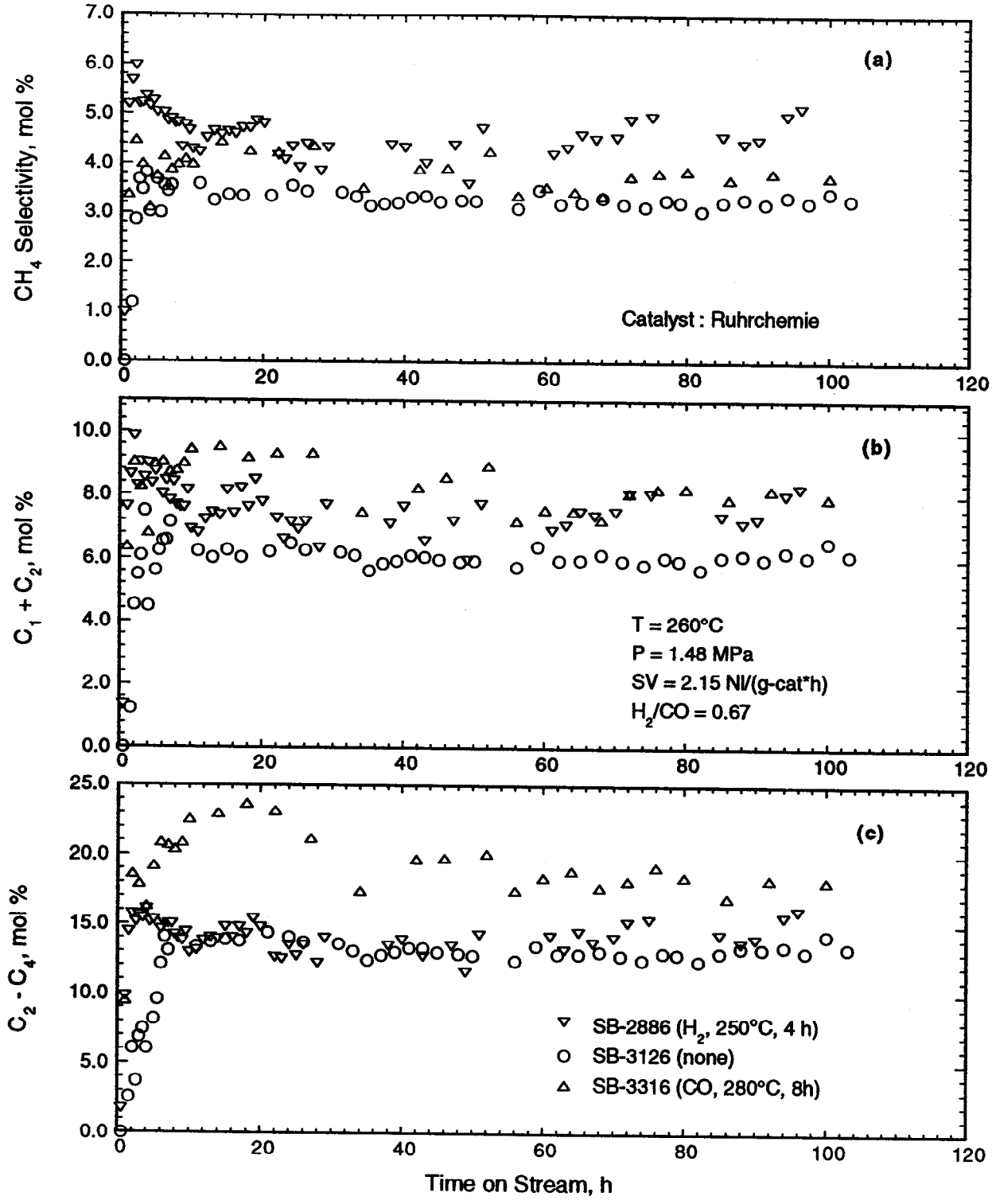

Figure 8. Comparison of (a) methane (b) C_1+C_2 and (c) C1-C4 selectivity between runs SB-2886, SB-3126 and SB-3316 with Ruhrchemie catalyst.

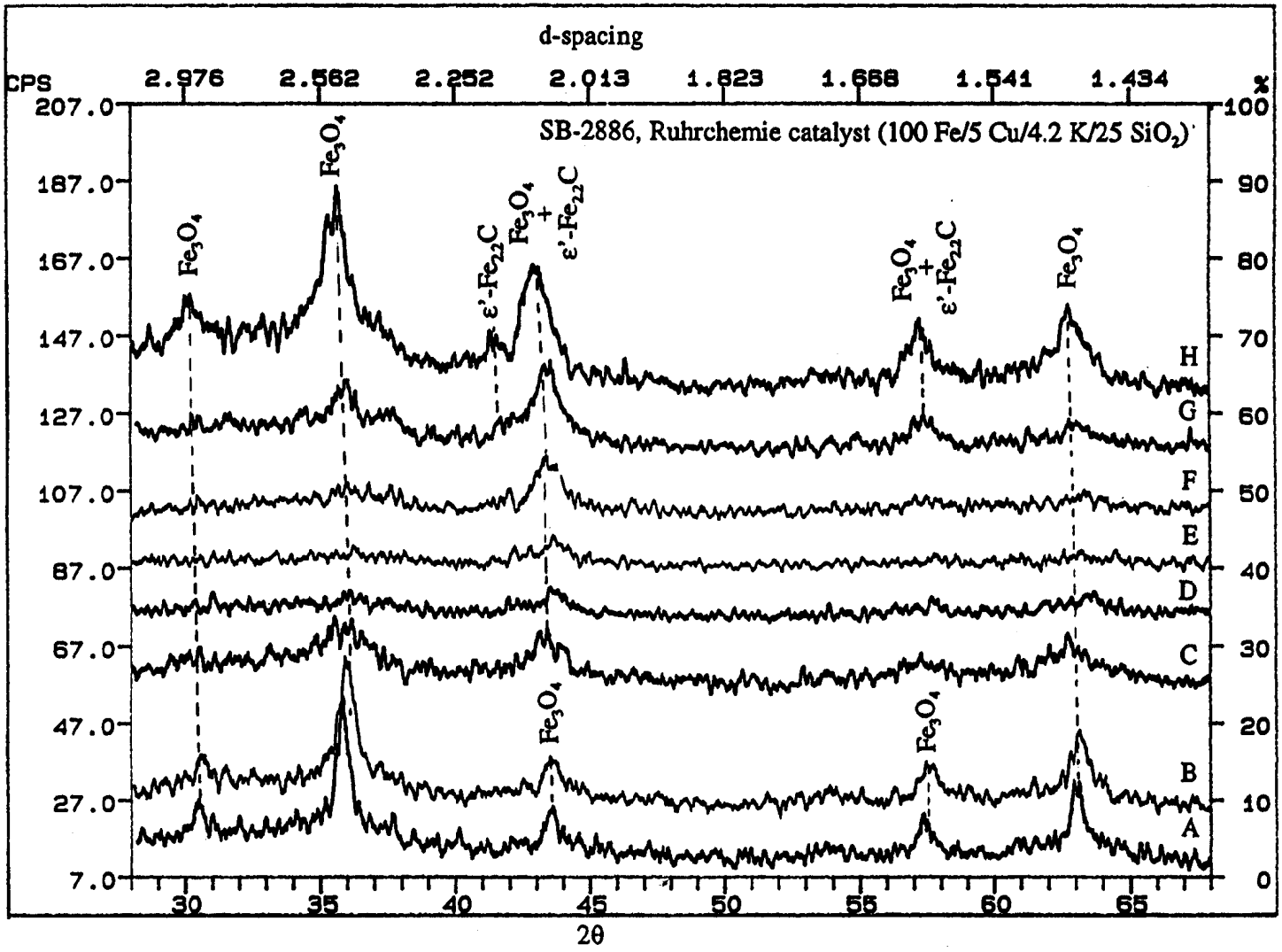

Figure 9. Change in bulk iron phases with time on stream during run SB-2886 with Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2): (A) TOS= 0 h; (B) TOS= 2 h; (C) TOS= 4 h; (D) TOS= 10 h; (E) TOS= 29 h; (F) TOS= 50 h; (G) TOS= 100 h; (H) TOS= 215 h.

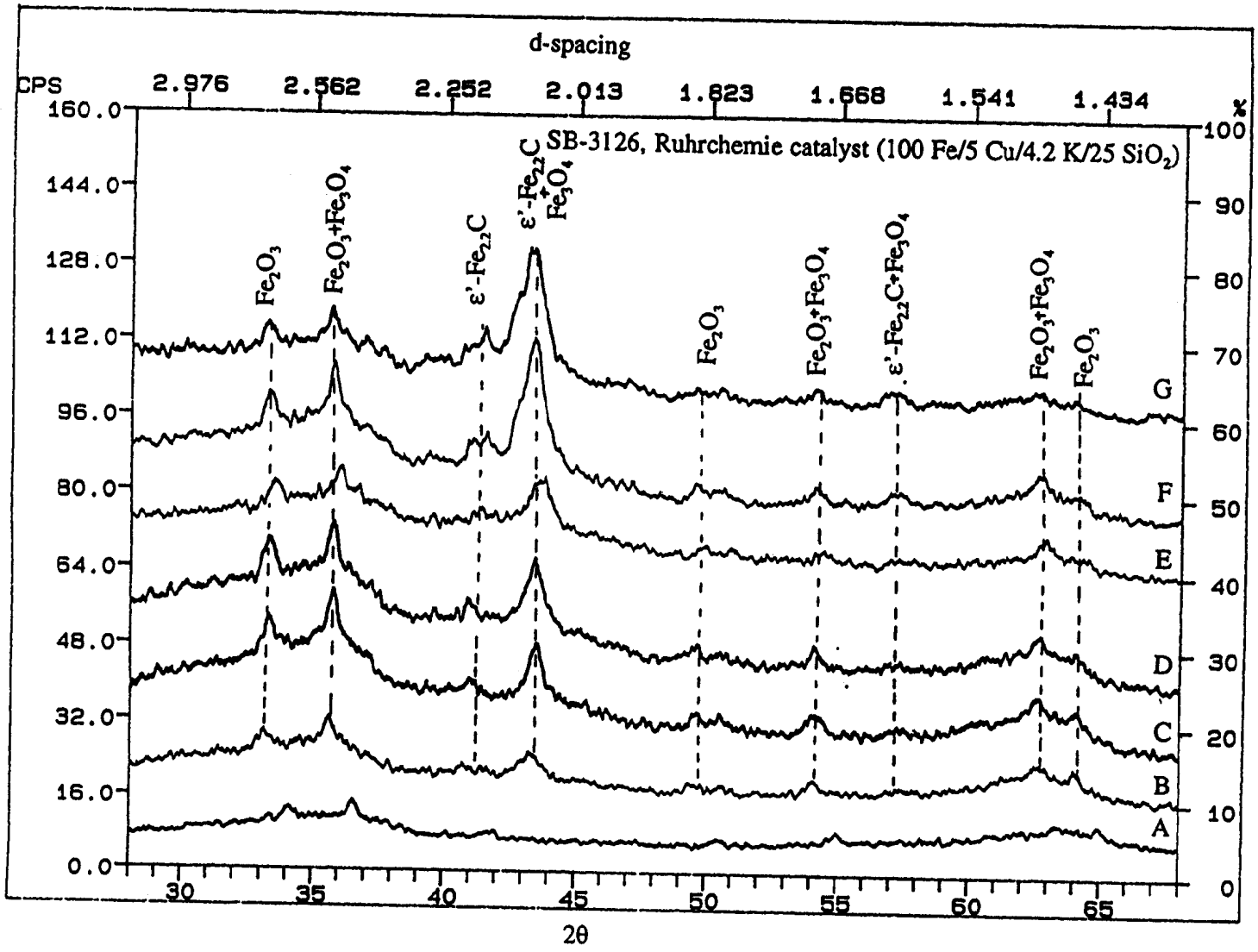

Figure 10. Change in bulk iron phases with time on stream during run SB-3126 with Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2): (A) TOS= 0 h; (B) TOS= 2 h; (C) TOS= 4 h; (D) TOS= 10 h; (E) TOS= 23 h; (F) TOS= 50 h; (G) TOS= 150 h.

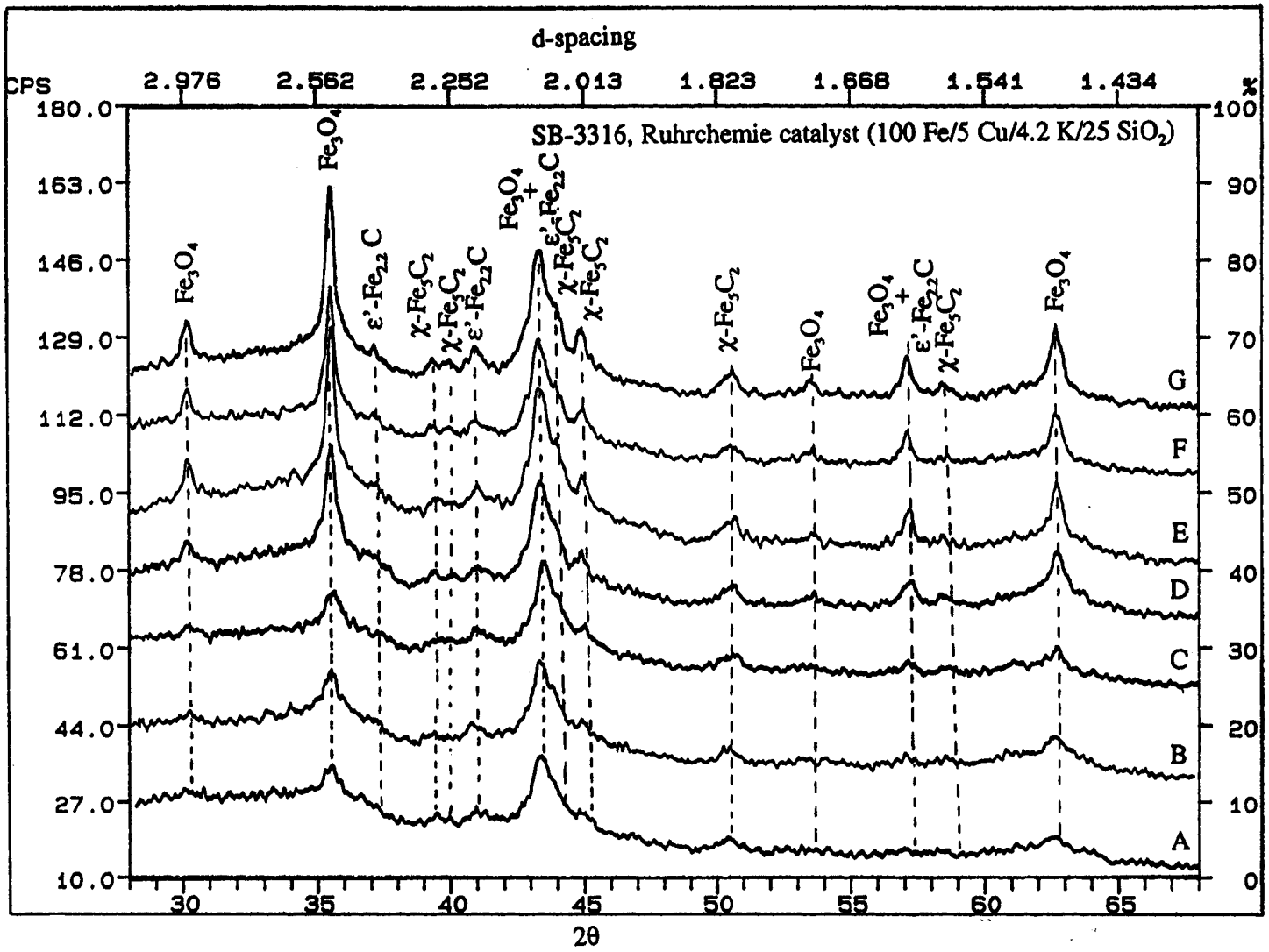

Figure 11. Change in bulk iron phases with time on stream during run SB-3316 with Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2): (A) TOS= 0 h; (B) TOS= 2 h; (C) TOS= 4 h; (D) TOS= 10 h; (E) TOS= 30 h; (F) TOS= 50 h; (G) TOS= 100 h.

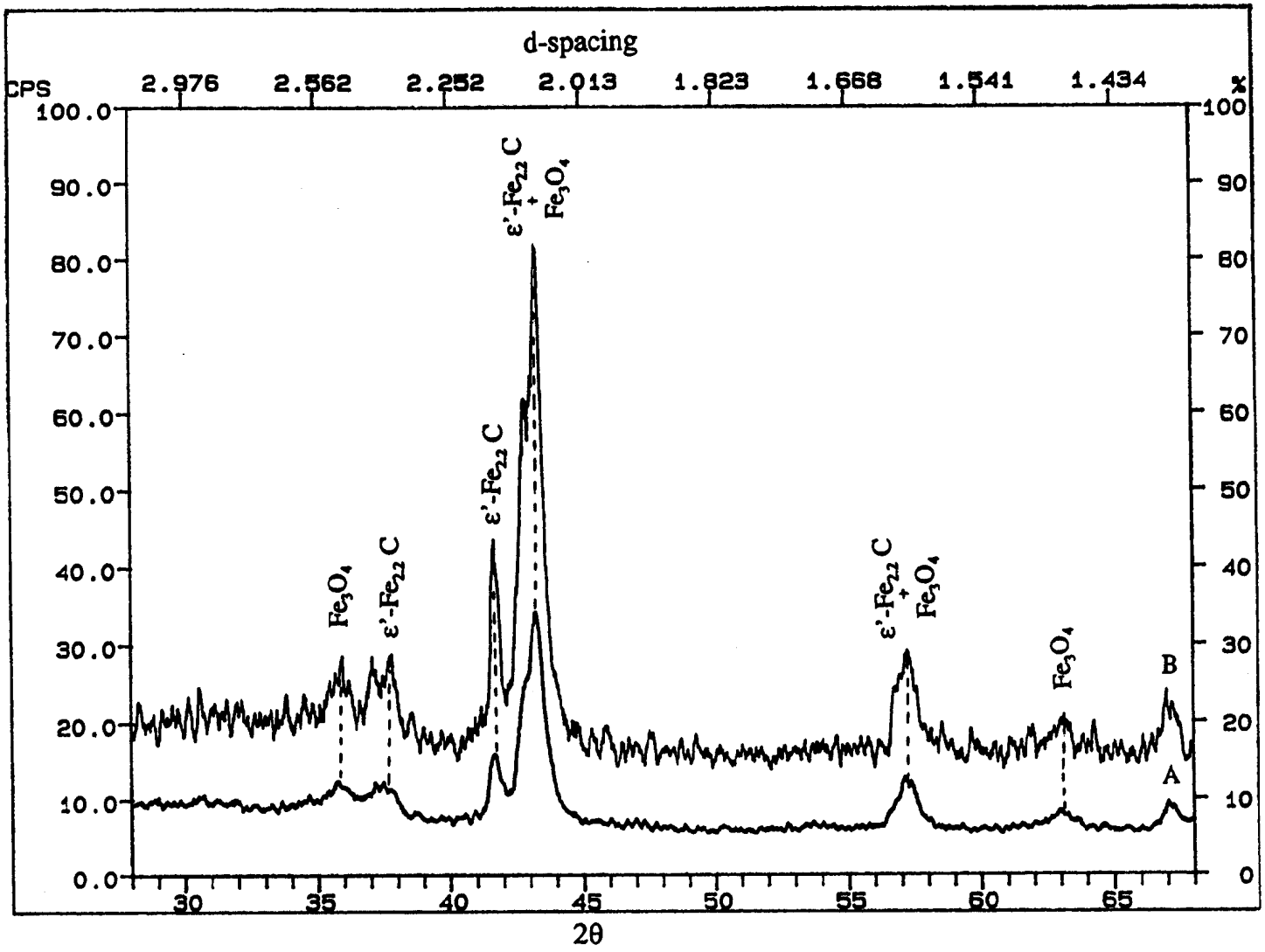

Figure 12. XRD patterns of the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst withdrawn from slurry reactor at TOS = 403 h, (A) scan rate=0.1°/min; (B) scan rate=1°/min

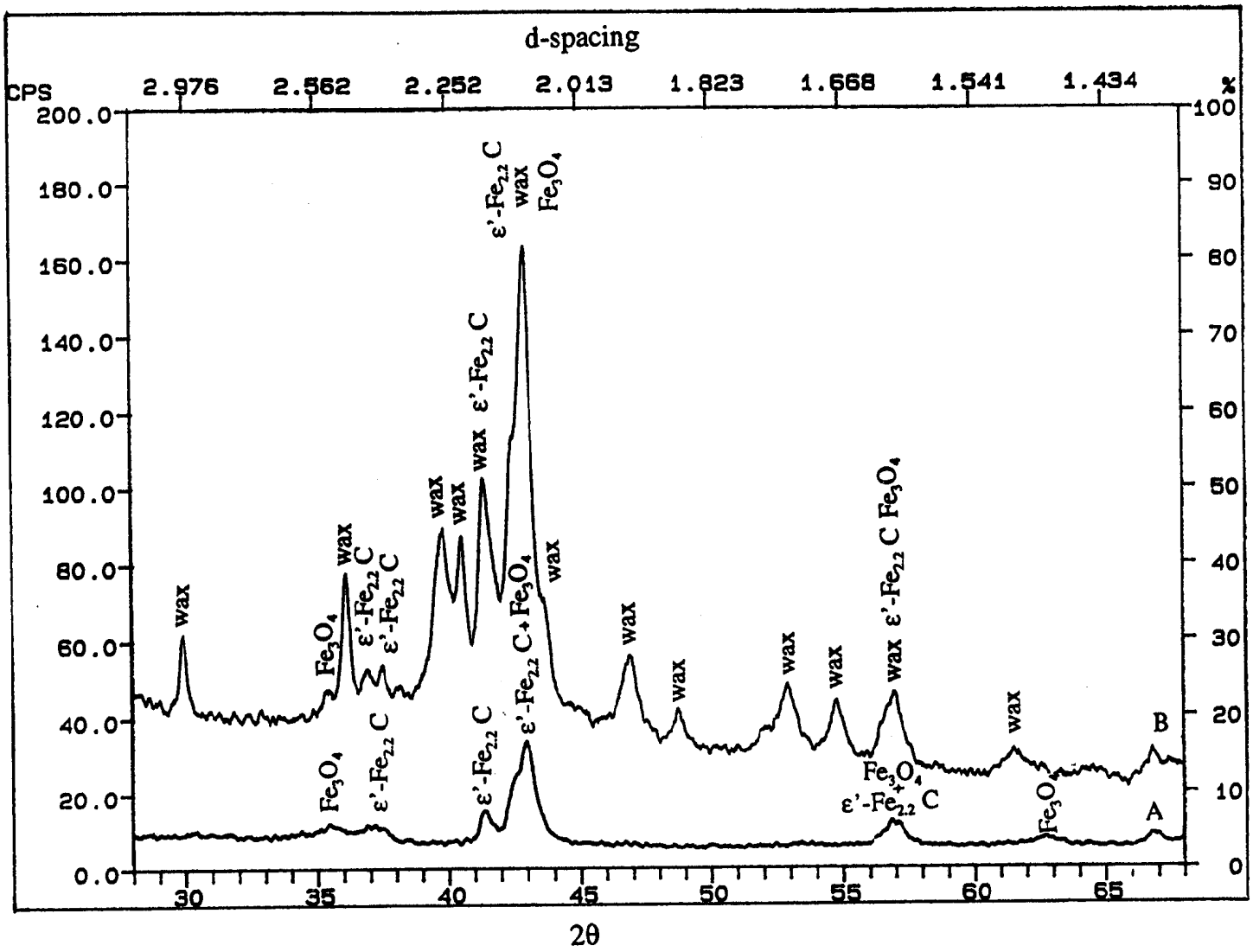

Figure 13. XRD patterns of the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst withdrawn from slurry reactor at TOS = 403 h, (A) extracted sample; (B) unextracted sample. Scan rate=0.1°/min.

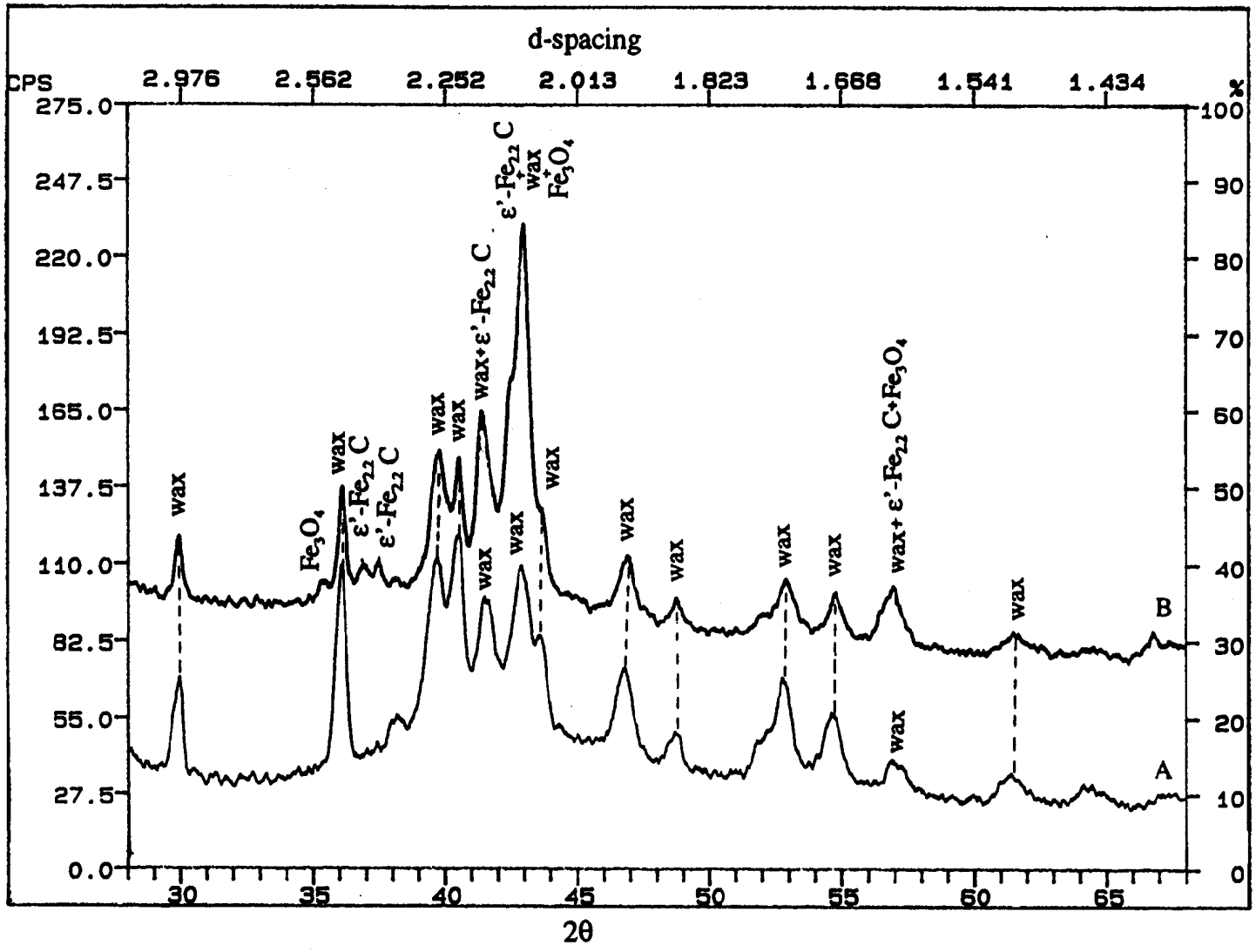

Figure 14. XRD patterns of (A) wax withdrawn from slurry reactor through the filter around TOS=400 h; (B) 100 Fe/3 Cu/4 K/16 SiO_2 catalyst (unextracted) withdrawn from slurry reactor at TOS= 403 h. Scan rate=0.1°/min.

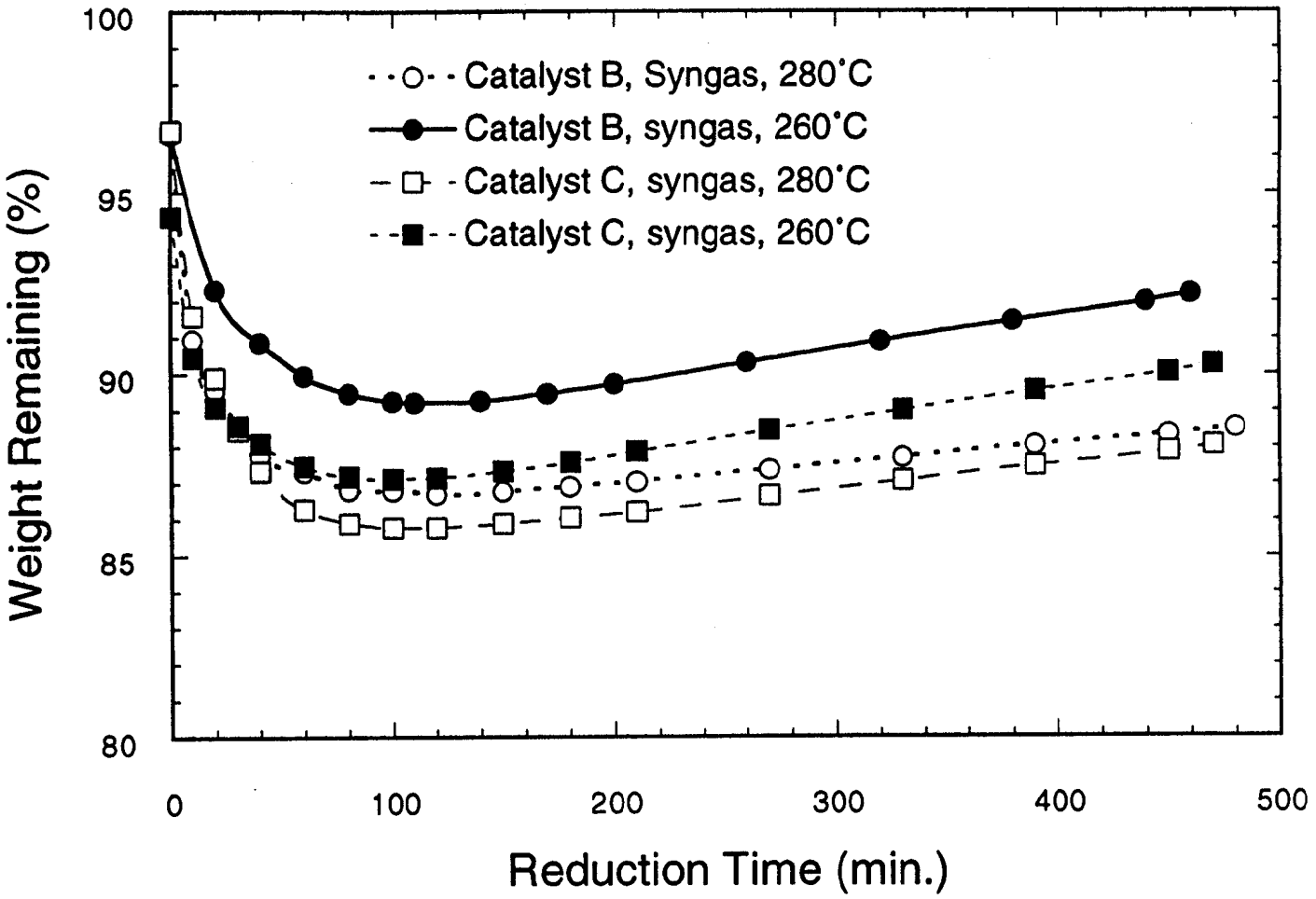

Figure 15. Isothermal reduction of catalysts B and C in TGA unit. Reduction conditions: syngas, flow rate=150ml/min, sample weight=~80 mg, room temperature to 260 or 280°C (in He flow), then maintained at that temperature for 8 hours in syngas flow.

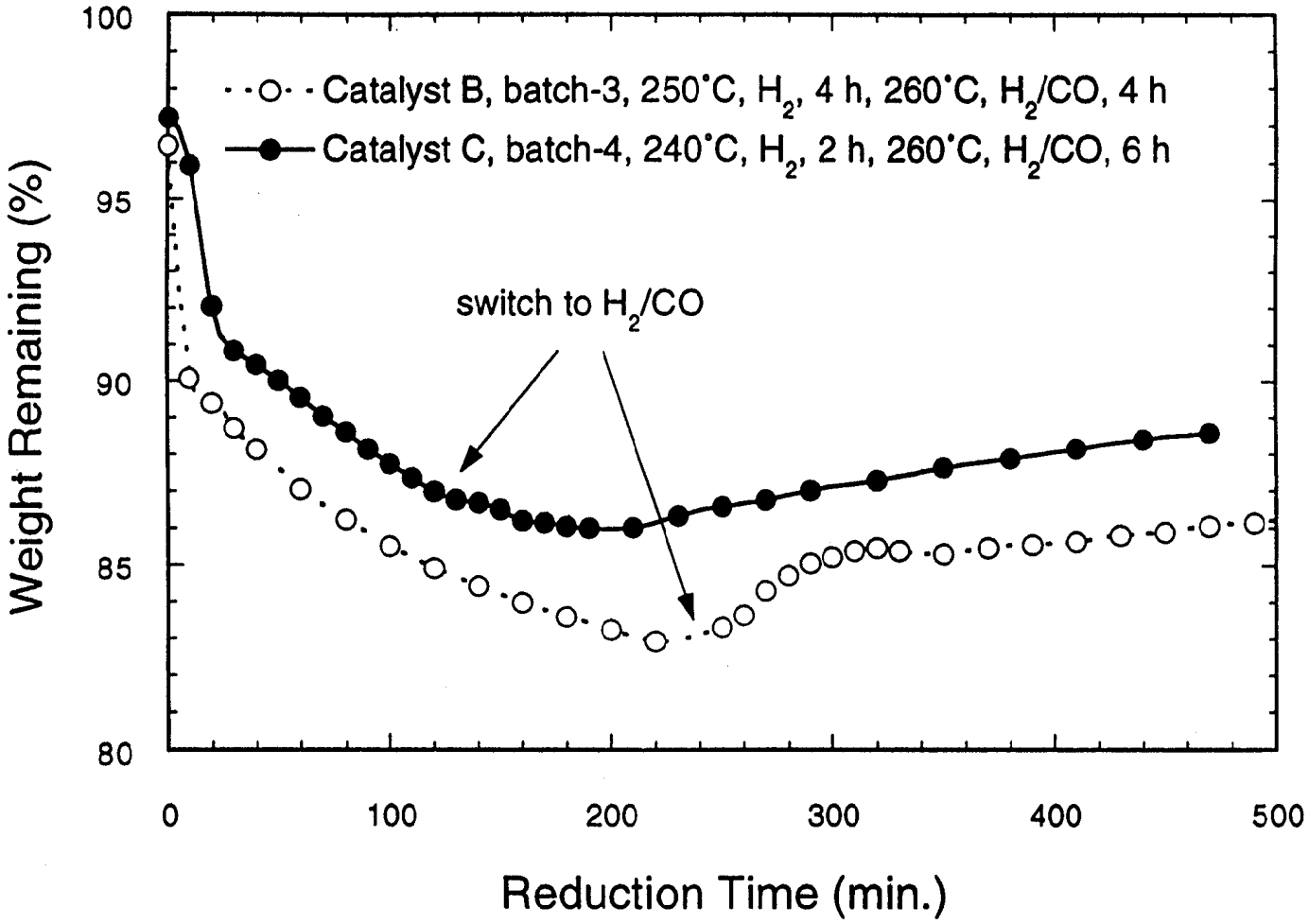

Figure 16. Isothermal reduction of catalysts B and C in TGA unit. Reduction conditions: catalyst B in H2 at 250 °C for 4 h then switched into syngas at 260 °C for 4 h; catalyst C in H2 at 240 °C for 2 h then switched into syngas at 260 °C for 6 h.