

Development of Precipitated Iron Fischer-Tropsch Catalysts

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ABSTRACT

This report describes research conducted to support the DOE program in indirect coal liquefaction. Specifically, we have developed very active and selective precipitated iron catalysts suitable for converting the coal derived synthesis gas into transportation fuels via Fischer-Tropsch synthesis reaction. At the present time the focus of research is on synthesis, characterization and testing of attrition resistant catalysts for use in slurry bubble column reactors.

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I. EXECUTIVE SUMMARY

Four (alumina or silica) supported catalysts were prepared by conventional impregnation of two commercial supports (silica - Davison grade 952; and alumina - Vista B). Nominal compositions (on mass basis) of synthesized catalysts are: (1) 100 Fe/5 Cu/6 K/139 SiO₂ (2) 100 Fe/10 Cu/6 K/134 SiO₂, (3) 100 Fe/5 Cu/6 K/139 Al₂O₃ and (4) 100 Fe/10 Cu/6 K/134 Al₂O₃. The corresponding weight % of iron (as metal) in the prepared catalysts is about 33.8%.

Reduction behavior of the four supported catalysts was studied by both temperature programmed and isothermal reduction in hydrogen, and by isothermal reduction in CO at 280°C. Also, two precipitated promoted iron catalysts, containing aluminum oxide as a binder, were reduced isothermally in the TGA unit with hydrogen at 240°C and 280°C. One of the two alumina containing catalysts (100 Fe/5 Cu/4.2 K/20 Al₂O₃) was tested in a slurry reactor (run SA-0097), and catalyst samples withdrawn from the reactor at various times on stream were characterized by XRD to determine bulk iron phases in the catalyst.

Two slurry reactor tests were completed during this quarter. The first test (SA-0097) was conducted with alumina containing catalyst with nominal composition 100 Fe/5 Cu/4.2 K/20 Al₂O₃, which was synthesized previously in our laboratory (DOE Contract DE-AC22-85PC80011). The second test (SB-0627) was conducted with one of the silica supported catalysts which was prepared during this quarter: 100 Fe/5 Cu/6 K/139 SiO₂ (Davison silica, grade 952). The performance of these two catalysts was inferior in comparison to our catalysts B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂). Activity of these two catalysts was lower, catalyst deactivation rate was faster, and gaseous hydrocarbon selectivities were higher in comparison to the baseline catalysts B and C.

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; and (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst synthesis. 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 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂). 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) , 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 - July 31, 1997)

The goal of this task is to: (a) provide basic characterization of all catalyst prepared (atomic absorption analysis, surface area, X-ray diffraction); (b) determine bulk iron phases after the pretreatment and during Fischer-Tropsch synthesis in slurry reactors by XRD and Mossbauer spectroscopy (at University of Kentucky); and (c) study reduction behavior of iron FT catalysts by isothermal and temperature programmed reduction (TPR). These studies may lead to activity-structure relationships, and better understanding of the factors which influence catalyst activity, selectivity and longevity.

Task 9 Testing of Alternative Catalysts for Slurry Reactors

Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition resistance properties required for utilization in commercial bubble column slurry reactors. We propose to evaluate the performance of up to three alternative catalysts containing either silica and/or alumina as a binder/support in the STSR tests. Mechanical strength and attrition resistance of these catalysts will be determined in collaboration with other DOE contractors.

Task 10. Characterization of Product Distribution and Data Analysis

The objective of this task is to perform detailed gas chromatographic analysis of selected liquid and wax products collected during the STSR tests (Tasks 3-7), and provide information on the effects of time on stream (catalyst aging), process conditions, pretreatment conditions and/or catalyst promoters on catalyst selectivity (i.e. product distribution).

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

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

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 9 has been initiated. Four (alumina or silica) supported catalysts were prepared by conventional impregnation of two commercial supports (silica - Davison grade 952; and alumina - Vista B). A brief description of catalyst preparation procedure is provided in Appendix A. These four catalysts were characterized by atomic absorption spectroscopy (Huffman Laboratories, Inc.) to verify their elemental

composition. BET surface area and catalyst pore volume of two supports were determined prior to impregnation.

Reduction behavior of the four supported catalysts was studied by both temperature programmed and isothermal reduction in hydrogen, and by isothermal reduction in CO at 280°C. Also, two precipitated promoted iron catalysts, containing aluminum oxide as a binder, were reduced isothermally in the TGA unit with hydrogen at 240°C and 280°C. One of the two alumina containing catalysts (100 Fe/5 Cu/4.2 K/20 Al₂O₃) was tested in a slurry reactor (run SA-0097), and catalyst samples withdrawn from the reactor at various times on stream were characterized by XRD to determine bulk iron phases in the catalyst.

III. 8. 1 Surface Area and Elemental Analysis of Supported Catalysts

The BET surface areas of the calcined supports (air at 500°C for 5 h) were 308 m²/g (Davison silica support) and 195 m²/g (Vista B alumina support), whereas the corresponding pore volumes were 0.7 cm³/g and 0.45 cm³/g (Table 1).

Elemental compositions of the four catalysts prepared by impregnation of the two supports, determined by Huffman Laboratories, Inc., are listed in Table 1. In general, amounts of promoters (Cu and K), relative to metallic iron, are in good agreement with their intended (nominal) amounts. Experimentally determined amounts of silica and alumina are in all cases less than the expected amounts, which is due to experimental errors (incomplete dissolution of these two oxides and errors in their quantification).

III. 8. 2 XRD Measurement Results

Figure 1 illustrates changes in bulk iron phases with time on stream during run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al₂O₃ catalyst. Magnetite (Fe₃O₄) and α-Fe were the major phases (Figure 1-A) in the sample withdrawn immediately after the hydrogen reduction (TOS = 0 h). During Fischer-Tropsch (FT) synthesis magnetite was present (Figure 1-B to 1-E) along with small amounts of ε'-Fe_{2.2}C phase. There are no significant changes in XRD patterns for samples

withdrawn after 4 h (1-B) and 308 h (1-E) on stream, but the catalyst activity decreased continuously with time on stream (Figure 9).

III. 8. 3 Temperature Programmed Reduction (TPR)

TPR studies were performed using 5% H_2 /95% N_2 as reductant. In a typical experiment about 20 mg of catalyst was packed in a quartz reactor and purged with helium to remove the moisture from the catalyst sample. Then the catalyst sample was heated in a flow of 5% H_2 /95% N_2 (flow rate = 40 ml/min) from room temperature to 800°C at a heating rate of 20°C/min. The TPR results (peak positions and degree of reduction) of the four supported catalysts are summarized in Table 2.

Figure 2 illustrates the TPR profiles of 100 Fe/x Cu/ 6 K/y SiO_2 catalysts (where x= 5 & 10; y = 134 & 139) prepared by impregnation of the Davison silica support. Results show that the catalysts were reduced almost completely by the end of final reduction temperature (i.e. 800°C). The peak positions are inconsistent with the catalyst compositions. The peak positions for the catalyst having smaller amount of copper promoter (5 parts) and 139 parts of silica are lower (344°C and 544°C) than the corresponding values (358°C and 560°C) observed for the catalyst having 10 parts of copper and 134 parts of silica. However, the degree of reduction for both the first and second stage of the reduction increases with increasing amount of copper promoter. The degree of reduction values for the first stage of reduction are 21% and 27%, respectively for the catalysts having 5 and 10 parts of copper. Similarly, the total degree of reduction values for these two catalysts are 85% and 102%, respectively. These results are consistent with the expected effect of copper promotion on the reduction of iron oxides.

TPR profiles of 100 Fe/x Cu/ 6 K/y A_2O_3 catalysts (where x= 5 & 10; y = 134 & 139) are shown in Figure 3. The peak positions for the first stage of reduction are 284°C and 339°C for the catalysts having 10 and 5 parts of copper, respectively. These results are consistent with the expected effect of copper promotion on the reduction of iron oxide. However, the peak positions (602°C and 612°C) for the second stage of reduction are inconsistent with the promotional effect of copper. The degree of reduction values (Table 2) for the first stage of reduction ($Fe_2O_3 \rightarrow$

Fe₃O₄) are 20% and 26% for the catalysts having 5 and 10 parts of copper, respectively, whereas the expected degree of reduction corresponding to complete conversion of iron oxide (Fe₂O₃) into magnetite (Fe₃O₄) for these two catalysts is 10.8% and 10.5%, respectively. Total degree of reduction values for these two catalysts are 73% and 103%, respectively. These results clearly show that the addition of copper promotes the reduction of iron.

III. 8. 4 TGA Measurement Results

Isothermal reduction in thermogravimetric analysis (TGA) experiments was conducted using catalyst samples of approximately 20 mg. The catalyst sample was purged with helium (100 cc/min) and temperature was ramped at a rate of 5°C/min from room temperature to 280°C. Then the helium flow was switched to hydrogen (99.995% purity) at 100 cc/min, and the temperature was maintained at 280°C for a total period of about 8 h. The degree of reduction was calculated from the weight loss vs. time data. Results are summarized in Table 3, and Figures 4 - 6.

Figures 4a and 4b illustrate the effect of reduction temperature and catalyst composition on the reduction behavior of precipitated iron catalysts promoted with copper, potassium and aluminum oxide. Degree of reduction of 100 Fe/5 Cu/4.2 K/20 Al₂O₃ catalyst increased sharply during the first 70 minutes of reduction, and then leveled off at both the reduction temperatures (240°C and 280°C). The degree of reduction values (Table 3) at the end of 8 h reduction period are about 59% and 69%, for the reduction temperatures of 240°C and 280°C, respectively.

Degree of reduction of 100 Fe/5 Cu/4.2 K/31.6 Al₂O₃ catalyst increased sharply initially (Figure 4b), and then leveled off at both reduction temperatures (240°C and 280°C). At the end of the reduction period the degree of reduction values are about 28% and 42%, at the reduction temperatures of 240°C and 280°C, respectively. Comparison of the results in Figures 4a and 4b) shows that the reduction is inhibited or retarded by the addition of aluminum oxide, which is indicative of interactions between the metal and alumina.

Degree of reduction of 100 Fe/5 Cu/4.2 K/139 SiO₂ (batch-1) catalyst increased gradually during the first 220 minutes of reduction, and then leveled off with no further increase in

reduction with time (Figure 5). After 8 h of reduction the final degree of reduction is about 43%. The degree of reduction of 100 Fe/10 Cu/4.2 K/134 SiO₂ (batch-1) catalyst increased sharply during the first 50 minutes of reduction, and then leveled off with no further increase in reduction with time. After 8 h of reduction period the final degree of reduction was about 79%. These results clearly show that the addition of copper promotes the reduction of iron.

Reduction behavior of the two alumina supported catalysts is shown in Figure 6. The degree of reduction of 100 Fe/5 Cu/4.2 K/139 Al₂O₃ (batch-1) catalyst this catalyst increased sharply during the first 20 minutes of reduction, time and then continued to increase slowly with time. At the end of 8 h reduction period, the degree of reduction was about 35%. as a function of reduction time.

The reduction behavior of the 100 Fe/10 Cu/4.2 K/134 Al₂O₃ (batch-1) was similar to that of the alumina supported catalyst containing 5 parts of copper. At the end of 8 h reduction period the degree of reduction for this catalyst was about 51%. These results again show that the addition of copper promotes the reduction of iron oxide.

Reduction behavior of the silica and alumina supported catalysts in CO at 280°C is shown in Figures 7 and 8, respectively. The two silica supported catalysts lost about 2% of the initial weight during heating in helium from room temperature to 280°C, due to moisture removal. The weight loss was rapid during the first 100 minutes of exposure to CO. After 200 minutes, both catalysts started to gain weight. Interestingly, the weight loss of both the catalysts is almost the same during the entire reduction period. As shown above (Figure 5) the degree of reduction in hydrogen (at 280°C) of the catalyst having 10 parts of copper was significantly higher than that of the catalyst having 5 parts of copper. Hence, the relatively low weight loss of the catalyst having 10 parts of copper during CO reduction suggests that carburization (formation of iron carbides) and/or carbon deposition are dominant processes from the very beginning of the catalyst exposure to CO.

Alumina supported catalysts (100 Fe/5 Cu/6 K/139 Al₂O₃ and 100 Fe/10 Cu/6 K/134 Al₂O₃) had lost about 6% of the initial weight during heating in helium from room temperature

to 280°C, due to removal of adsorbed moisture. The weight loss was rapid during the first 60 minutes of exposure to CO. After 200 minutes of reduction, the weight remaining began to increase slowly with time. The weight loss during the first 60 minutes of reduction was slightly higher for the catalyst having 5 parts of copper compared to the catalyst having 10 parts of copper. Again, this suggests that carburization and/or carbon deposition are dominant processes on the catalyst having higher copper content.

The observed changes in weight for all four catalysts during the CO reduction are the net result of three competing reactions: (a) reduction of iron oxides; (b) carbon deposition ($2 \text{ CO} \rightarrow \text{CO}_2 + \text{C}\downarrow$); and (c) carbide formation (i.e. carburization). For all four catalysts, the weight loss corresponding to formation of χ -carbide ($\text{Fe}_2\text{O}_3 \rightarrow \chi\text{-Fe}_5\text{C}_2$) is about 14%, whereas the theoretical weight loss for formation of magnetite ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$) is about 2.4%. After 100 minutes of CO reduction, the experimental weight loss was about 6%, suggesting that oxide reduction and carburization are the dominant reactions, and that carburization is incomplete. During the later stages of reduction a gradual increase in weight was observed with all four catalysts. This may suggest that carbon deposition is the dominant reaction, even though the carburization process was not completed.

III. 9 Testing of Alternative Catalysts for Slurry Reactors

The work on this task has begun during this quarter. Two slurry reactor tests were completed during this quarter. The first test (SA-0097) was conducted with alumina containing catalyst with nominal composition 100 Fe/5 Cu/4.2 K/20 Al_2O_3 , which was synthesized previously in our laboratory (DOE Contract DE-AC22-85PC80011). The second test (SB-0627) was conducted with one of the silica supported catalysts which was prepared during this quarter: 100 Fe/5 Cu/6 K/139 SiO_2 (Davison silica, grade 952). Catalyst performance (activity and gaseous hydrocarbon product selectivities) during these two tests is described below.

III. 9. 1 Run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al₂O₃ Catalyst

Approximately 11 g of the catalyst (< 270 mesh in size) was loaded for the test, together with 329 g of Durasyn 164 oil as the initial slurry medium. The catalyst was reduced with hydrogen at 250°C for 4 h, and then tested at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of 0.67 (H₂/CO = 0.67) and gas space velocity of 1.4 NI/g-cat/h (or, 2.5 NI/g-Fe/h). After about 40 h on stream, the CO and syngas conversions reached 67% and 63%, respectively, and then started to decline slowly (Figure 9). At 160 h, the CO and syngas conversions were 62% and 60%, respectively. The H₂/CO usage ratio increased with time from 0.56 (at 30 h) to 0.62 at 160 h on stream (Figure 9). Methane selectivity increased with time from 4.4% at 13 h to 6.7%. Gaseous hydrocarbon selectivities (C₁+C₂ and C₂-C₄ hydrocarbons) followed the same trend (Figure 10).

Upon increasing the reaction pressure and space velocity to 2.17 MPa (300 psig) and 2.1 NI/g-cat/h (3.6 NI/g-Fe/h), respectively, the catalyst continued to deactivate with time (Figure 9). At 300 h the CO and syngas conversions were 52% and 51%, respectively, and the usage ratio increased to 0.65 (lower water-gas-shift activity). Methane, and other gaseous hydrocarbon selectivities decreased initially, but at the end of the testing period (~300 h) approached the corresponding values observed at the end of testing at 1.48 MPa (Figure 10). At 300 h on stream, methane, C₁+C₂ and C₂-C₄ hydrocarbon selectivities were: 6%, 11.4%, and 21.4%, respectively. Major events for run SA-0097 are summarized in Table 4.

III. 9. 2 Run SB-0627 with 100 Fe/5 Cu/6 K/139 SiO₂ Catalyst

For this slurry reactor test, 15 grams of catalyst (45-63 μm in diameter) was loaded initially to the reactor together with 323 g of Durasyn 164 oil as the initial slurry medium. The catalyst was reduced with CO diluted with helium (see Table 5 for the reduction conditions), and then tested at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of H₂/CO = 0.67, and gas space velocity of 1.4 NI/g-cat/h (or 4.1 NI/g-Fe/h).

After initial 20 h on stream, the catalyst activity started to decline as shown in Figure 11. The CO and syngas conversions at 20 h were about 68% each, and the usage ratio, 0.66, was nearly the same as the H₂/CO molar feed ratio (0.67). At the end of testing at these process conditions (~150 h on stream), the CO and syngas conversions were: 55.5% and 58%, respectively, whereas the usage ratio increased to 0.74. After 150 h of testing at baseline conditions the reaction pressure and gas space velocity were increased simultaneously to 2.17 MPa (300 psig) and 2 NI/g-cat/h (5.8 NI/g-Fe/h). The bed residence (contact) time at the new process conditions is the same as at the baseline conditions, and the resulting conversions are expected to be the same (for a first order reaction). Initial conversions were the same, as expected, but the catalyst continued to deactivate with time (Figure 11). At 300 h on stream, the CO and syngas conversions were: 37% and 41%, respectively, whereas the usage ratio increased further to 0.83.

Methane and gaseous hydrocarbon selectivities as a function of time on stream are shown in Figure 12. General trend of the data is that gaseous hydrocarbon selectivity increased with time on stream. At the end of the test (~300 h) methane, C₁+C₂ and C₂-C₄ hydrocarbon selectivities were: 7.5%, 15.5%, and 33.5%, respectively. Major events for run SB-0627 are summarized in Table 5.

In summary, the performance of these two catalysts was inferior in comparison to our catalysts B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂). The activity of these two catalysts was lower, catalyst deactivation rate was faster, and gaseous hydrocarbon selectivities were higher in comparison to the baseline catalysts B and C.

III. 10 Characterization of Product Distribution and Data Analysis

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

Plans for the Next Quarter

During the next quarter we plan to continue with work on : (a) testing of alternative catalysts, and (b) characterization of catalysts from slurry reactor tests conducted under Task 9.

APPENDIX A

Catalyst Preparation

During the reporting period we have completed the preparation of four supported catalysts (~ 50 g each) using incipient wetness method. The supports (silica - Davison grade 952; and alumina - Vista B) were sieved and calcined at 500°C in air for 5 h prior to impregnation. Catalysts containing iron, copper and potassium on silica or alumina were prepared by impregnation with aqueous solutions containing desired amounts of ferric nitrate, copper nitrate and potassium bicarbonate in successive steps. The total volume of impregnating solution (which contains the calculated amounts of promoters) was about 95 ml in each catalyst preparation. However, the amount of impregnating solution consumed in each impregnation step was different and varied with the support. For example during the preparation of silica supported catalysts we were able to complete the preparation of catalysts in three impregnation steps, whereas seven impregnation steps were used in preparation of alumina supported catalysts. After each impregnation step the sample was vacuum dried at 100°C for about 2 h. After the final impregnation and drying for 12 h in vacuum the catalyst was calcined in air at 300°C for 5 h. Various steps in the catalyst preparation are shown in Figure A1. Nominal compositions (on mass basis) of synthesized catalysts are: (1) 100 Fe/5 Cu/6 K/139 SiO₂ (2) 100 Fe/10 Cu/6 K/134 SiO₂, (3) 100 Fe/5 Cu/6 K/139 Al₂O₃ and (4) 100 Fe/10 Cu/6 K/134 Al₂O₃. The corresponding weight % of iron (as metal) in the prepared catalysts is about 33.8%.

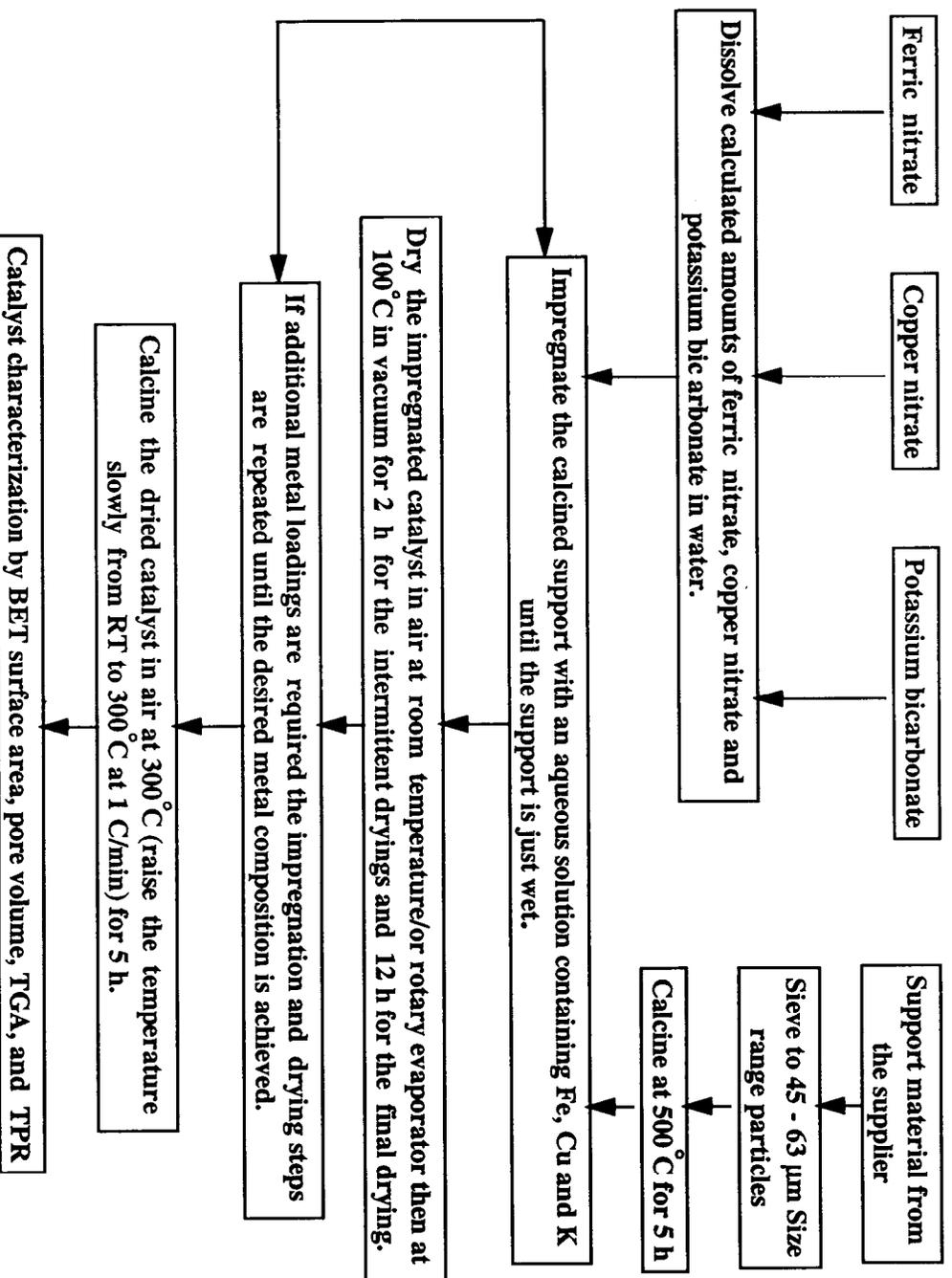


Figure A1. Steps in preparation of alumina or silica supported catalysts

Table 1. Physical properties of calcined supports and impregnated catalysts

Catalyst Nominal Composition	Catalyst Composition by AAS**	BET Surface* area, m ² /g	Pore Volume*, cm ³ /g
Silica (Davison, Grade 952)	-	308	0.70
Alumina (Vista B)	-	195	0.45
100 Fe/5 Cu/6 K/139 SiO ₂ , batch-1	100 Fe/5.0 Cu/5.6 K/125 SiO ₂		
100 Fe/10 Cu/6 K/134 SiO ₂ , batch-1	100 Fe/8.9 Cu/5.7 K/122 SiO ₂		
100 Fe/5 Cu/6 K/139 Al ₂ O ₃ , batch-1	100 Fe/4.8 Cu/5.7 K/119 Al ₂ O ₃		
100 Fe/10 Cu/6 K/134 Al ₂ O ₃ , batch-1	100 Fe/8.3 Cu/5.4 K/97 Al ₂ O ₃		

* Calcined in air at 500°C for 5 h.

** Determined by Huffman Laboratories, Inc.

Table 2. Effect of copper, alumina and silica addition on the TPR profiles of iron oxide catalysts prepared by impregnation .

Sample	Reduction Temperature Range, C	Peak Position, °C		Degree of Reduction, (%) (#)	
		First Stage	Second Stg.	First stage	Total*
100 Fe/5 Cu/6 K/139 SiO ₂ batch-1	RT to 800	344	544	21	85
100 Fe/10 Cu/6 K/134 SiO ₂ batch-1	RT to 800	358	560	27	102
100 Fe/5 Cu/6 K/139 Al ₂ O ₃ batch-1	RT to 900	339	602	20	73 (80)*
100 Fe/10 Cu/6 K/134 Al ₂ O ₃ batch-1	RT to 900	284	612	26	103 (109)*

* The %degree of reduction are for the temperature range of RT to 800°C and the values in the parenthesis represent the %degree of reduction values calculated for the reduction temperature range of RT to 900°C.

Sample wt = 20 mg, reducing gas = 5%H₂/95%N₂, flow rate = 40 cc/.min, ramp = 20°C/min, temperature range = room temperature to 800 - 900°C.

Table 3. Summary of the TGA isothermal reduction experiments with iron oxide catalysts.

Catalyst	Reduction Temperature, C	% Degree of Reduction
100 Fe/5 Cu/4.2 K/20 Al ₂ O ₃	240 280	59 69
100 Fe/5 Cu/4.2 K/31.6 Al ₂ O ₃	240 280	28 42
100 Fe/5 Cu/4.2 K/100 SiO ₂ , batch-1	280 240	38 33
100 Fe/5 Cu/6 K/139 SiO ₂ , batch-1	280	43
100 Fe/10 Cu/6 K/134 SiO ₂ , batch-1	280	79
100 Fe/5 Cu/6 K/139 Al ₂ O ₃ , batch-1	280	35
100 Fe/10 Cu/6 K/134 Al ₂ O ₃ , batch-1	280	51

Reduction conditions: Reducing gas = H₂ (100 cc/min), ramping in He = 5°C/min, sample wt = ~ 20 mg, and total reduction time = ~ 8 h. The sample was dried at 280°C in He (100 cc/min) for 30 minutes.

Table 4. Major Events in Run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al₂O₃ Catalyst

TOS (h)	Event
	Slurry loading: 329 g of Durasyn 164 oil, 11.0 g of catalyst (particle size < 325 mesh)
	Catalyst pretreatment: H ₂ , 250 °C, 4 h, 0.8 Mpa, 7500 cm ³ /min
	Slurry sample withdrawal after the pretreatment: 13.9 g slurry, 0.5 g catalyst
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P = 100 psig (1.48 MPa), SV = 2.4 NI/g-Fe/h, (H ₂ /CO) = 0.67
4	Slurry sample withdrawal: 13.6 g slurry, 0.5 g catalyst
24	Slurry sample withdrawal: 9.3 g slurry, 0.4 g catalyst
74	The pressure dropped to 160 psig, then test continued after adjustment
162	Slurry sample withdrawal: 13.1 g slurry, 0.4 g catalyst
163	Change pressure to 2.17 MPa and SV to 3.6 NI/g-Fe/h
308	Slurry sample withdrawal: 9.0 g slurry, 0.3 g catalyst
309	End of run: 235.5 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 194.9 g wax, 2.1 g catalyst

Table 5. Major Events in Run SB-0627 with Catalyst (100 Fe/5 Cu/6 K/139 SiO₂)

TOS (h)	Event
	Slurry loading: 322.6 g of Durasyn 164 oil, 15.0 g of catalyst (45 - 63 μm particle size)
	Catalyst pretreatment: CO diluted with helium (1:8), 280°C, 8 h. 0.8 MPa, 7000 cm ³ /min
	wax withdrawal: 34.8 g after CO reduction.
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P (syngas) = 1.48 MPa, SV(syngas) = 1.4 NI/g-cat/h, (H ₂ /CO) = 0.67
50	wax withdrawal: 53.8 g wax
100	wax withdrawal: 63.6 g wax
150	slurry sample withdrawal: 10.3 g slurry sample, 0.5 g catalyst
	wax withdrawal: 40.2 g wax
	Change process condition to pressure (syngas) = 2.17 MPa, SV (syngas) = 2.0 NI/g-cat/h
179	The power was failed, the stirrer of reactor did not work, the process conditions were recovered after 10 hours.
211	wax withdrawal: 24.3 g wax,
259	wax withdrawal: 19.2 g wax.
306	slurry sample withdrawal: 9.8 g slurry sample, 0.4 g catalyst
306	End of run: 314.3 g slurry recovered from the reactor
	Wax and catalyst removed during the run: 255.1 g wax, 0.9 g catalyst

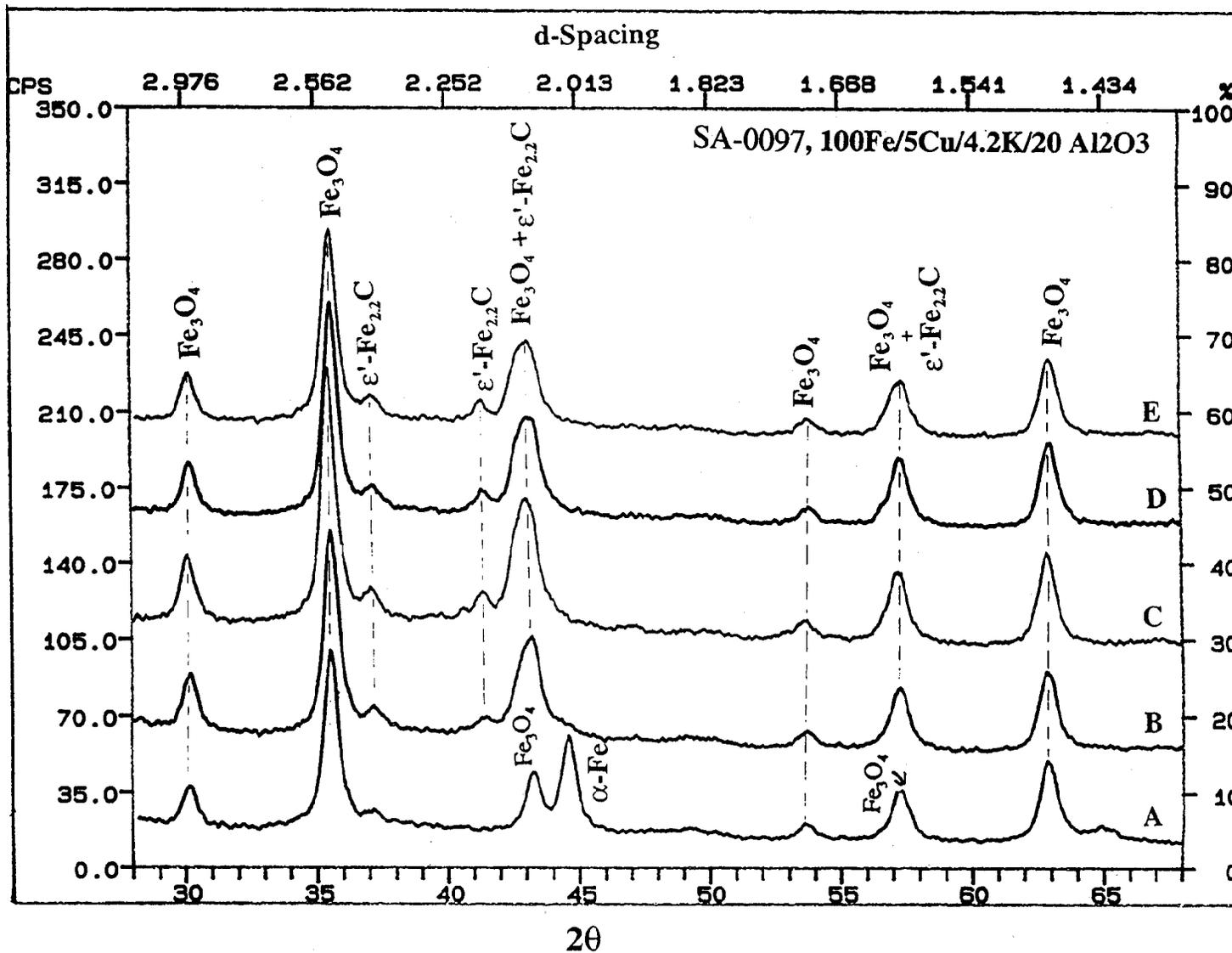


Figure 1. Change in bulk iron phases with time on stream during run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al₂O₃ catalyst: (A) TOS = 0 h; (B) TOS = 4 h; (C) TOS = 24 h; (D) TOS = 162 h; (E) TOS = 308 h.

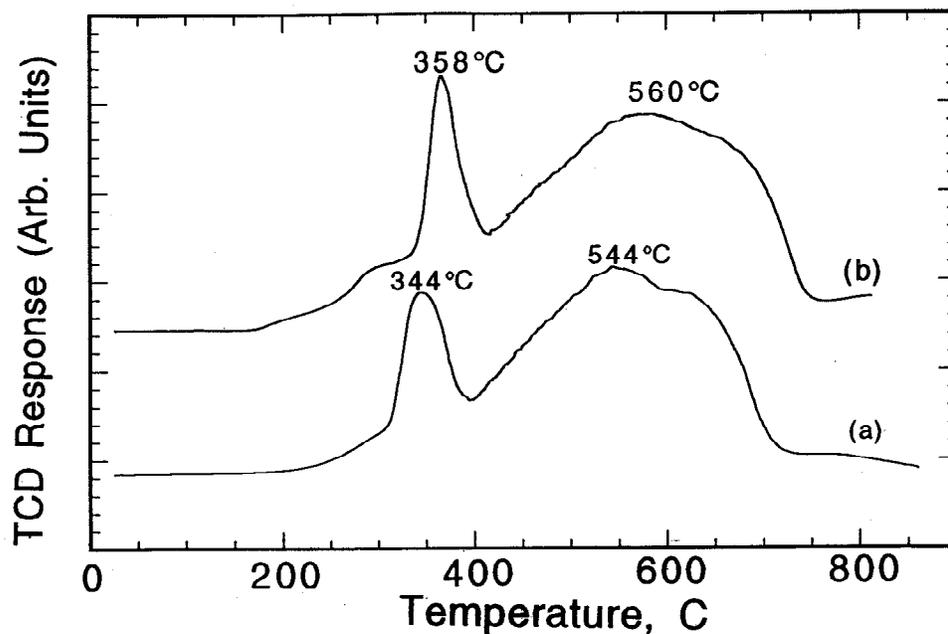


Figure 2. Effect of copper addition on the reduction behavior of silica supported iron catalysts: (A) 100 Fe/5 Cu/6 K/139 SiO₂; and (B) 100 Fe/10 Cu/6 K/134 SiO₂.

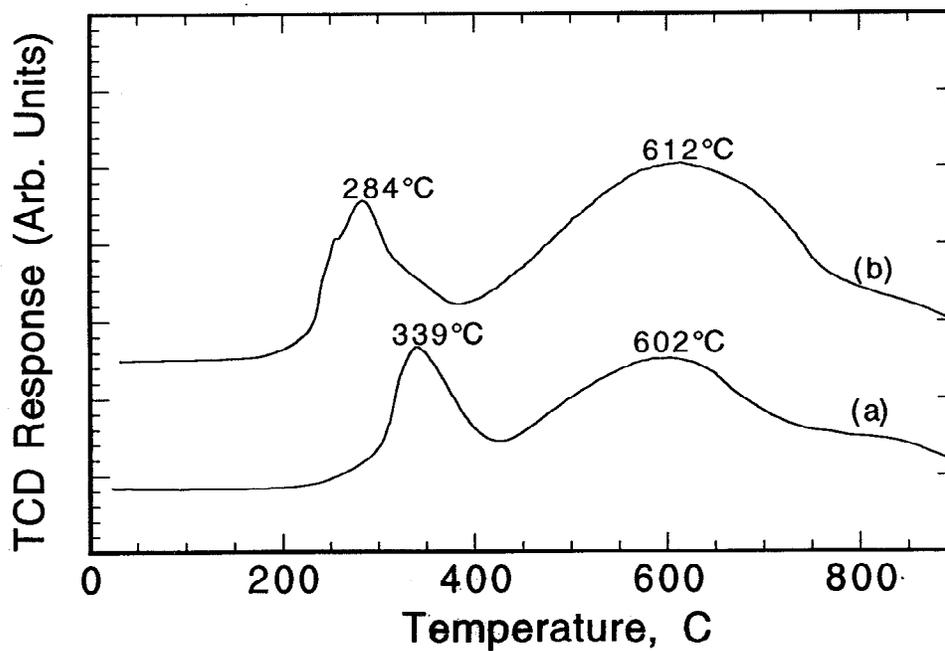


Figure 3. Effect of copper addition on the reduction behavior of alumina supported iron catalysts: (A) 100 Fe/5 Cu/6 K/139 Al₂O₃; and (B) 100 Fe/10 Cu/6 K/134 Al₂O₃.

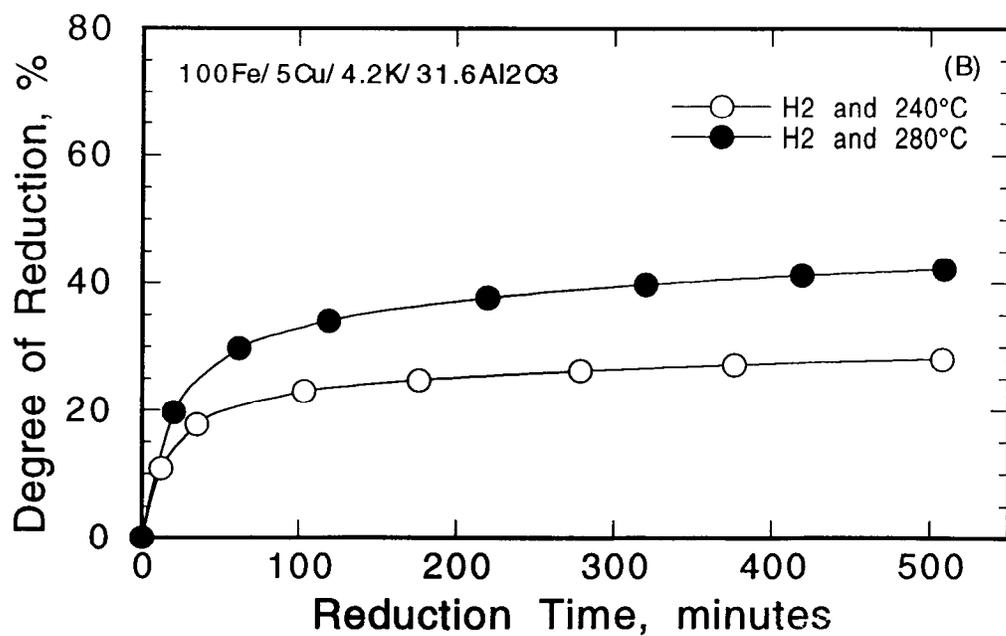
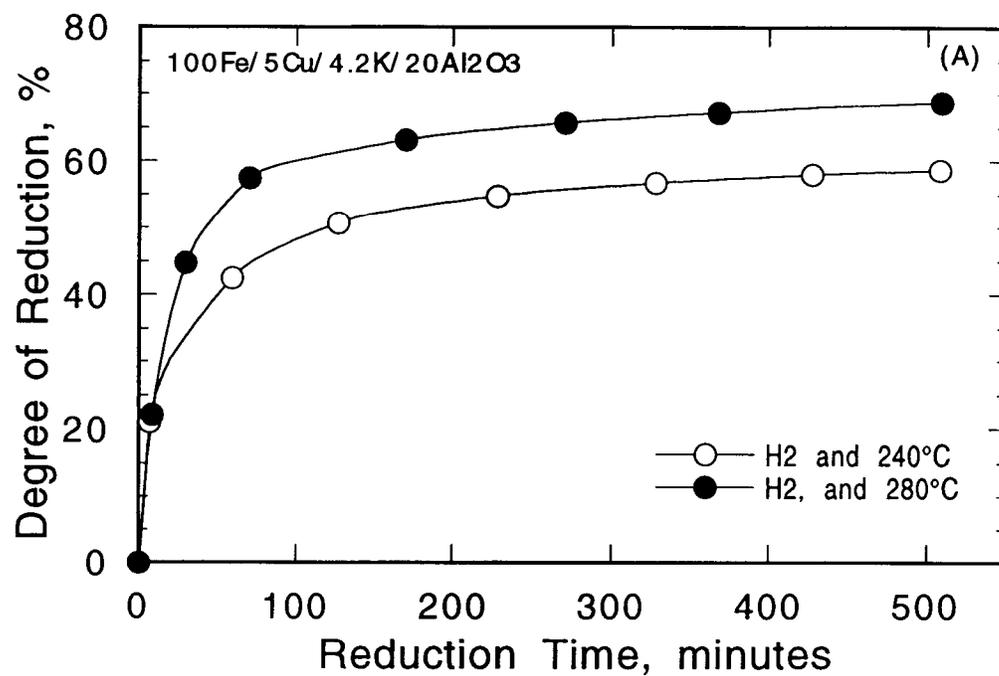


Figure 4. Effect of alumina content and reduction temperature on the reduction behavior of promoted iron oxide catalysts determined by TGA at a H₂ flow rate = 100 ml/min, ramp = 5°C/min until 280°C: (A) 100 Fe/5 Cu/4.2 K/20 Al₂O₃; (B) 100 Fe/5 Cu/4.2 K/31.6 Al₂O₃.

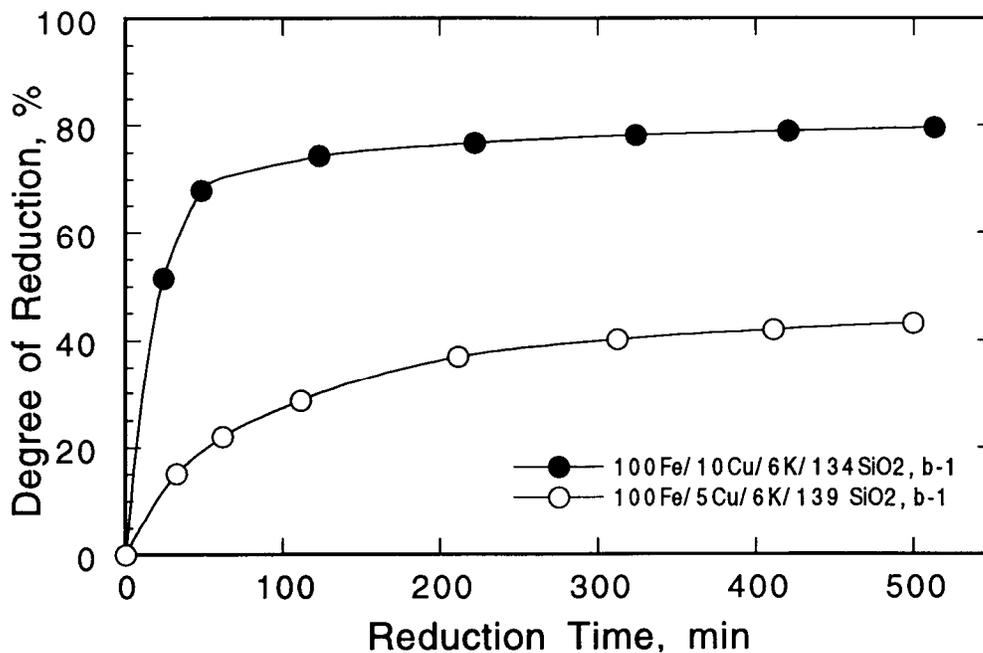


Figure 5. Effect of copper promotion and reduction temperature on the degree of reduction of silica supported iron catalysts determined by TGA at a H₂ flow rate = 100 ml/min, ramp = 5°C/min until 280°C: (-O-) 100 Fe/5 Cu/6 K/139 SiO₂; (-●-) 100 Fe/10 Cu/6 K/134 SiO₂.

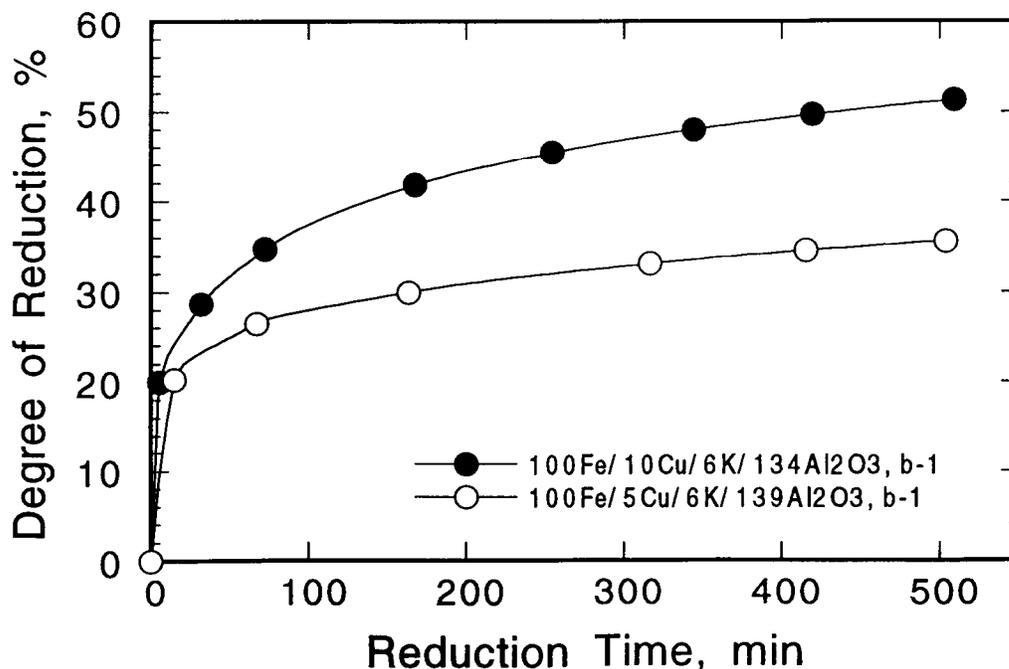


Figure 6. Effect of copper promotion and reduction temperature on the degree of reduction of alumina supported iron catalysts determined by TGA at a H₂ flow rate = 100 ml/min, ramp = 5°C/min until 280°C: (-O-) 100 Fe/5 Cu/6 K/139 Al₂O₃; (-●-) 100 Fe/10 Cu/6 K/134 Al₂O₃.

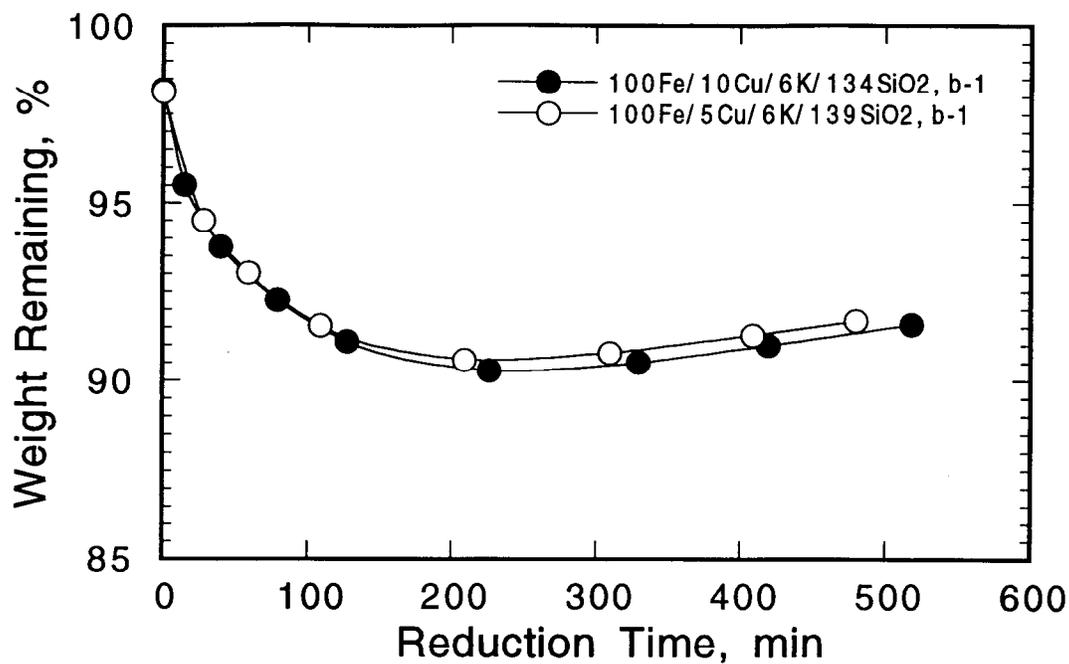


Figure 7. Effect of copper promotion and reduction temperature on the degree of reduction of silica supported iron catalysts determined by TGA at a CO flow rate = 100 ml/min, ramp = 5°C/min until 280°C: (-O-) 100 Fe/5 Cu/6 K/139 SiO₂; (-●-) 100 Fe/10 Cu/6 K/134 SiO₂.

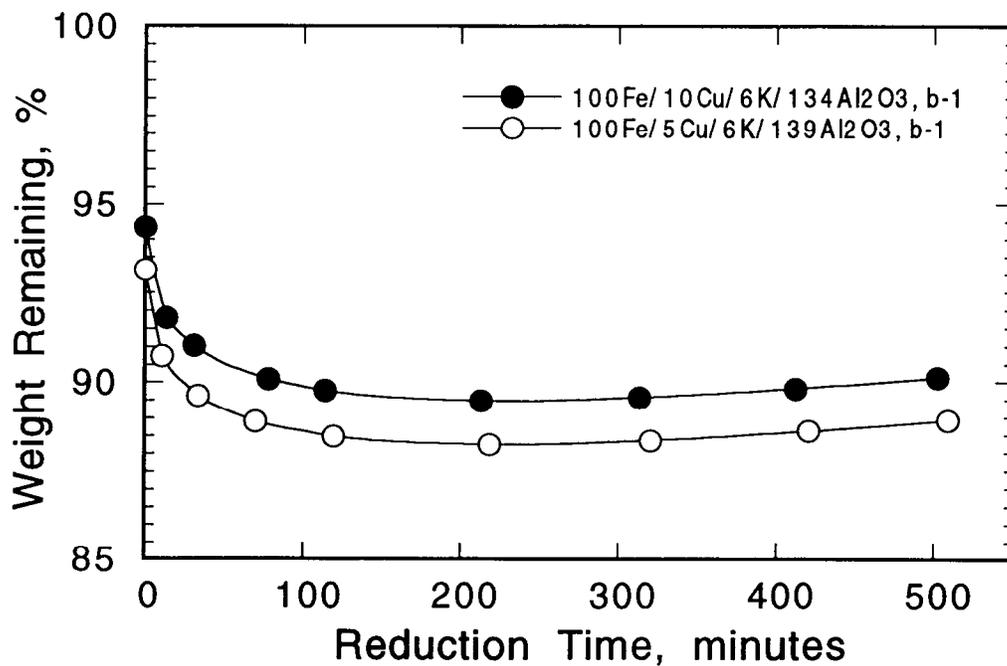


Figure 8. Effect of copper promotion and reduction temperature on the degree of reduction of alumina supported iron catalysts determined by TGA at a H₂ flow rate = 100 ml/min, ramp = 5°C/min until 280°C: (-O-) 100 Fe/5 Cu/6 K/139 Al₂O₃; (-●-) 100 Fe/10 Cu/6 K/134 Al₂O₃.

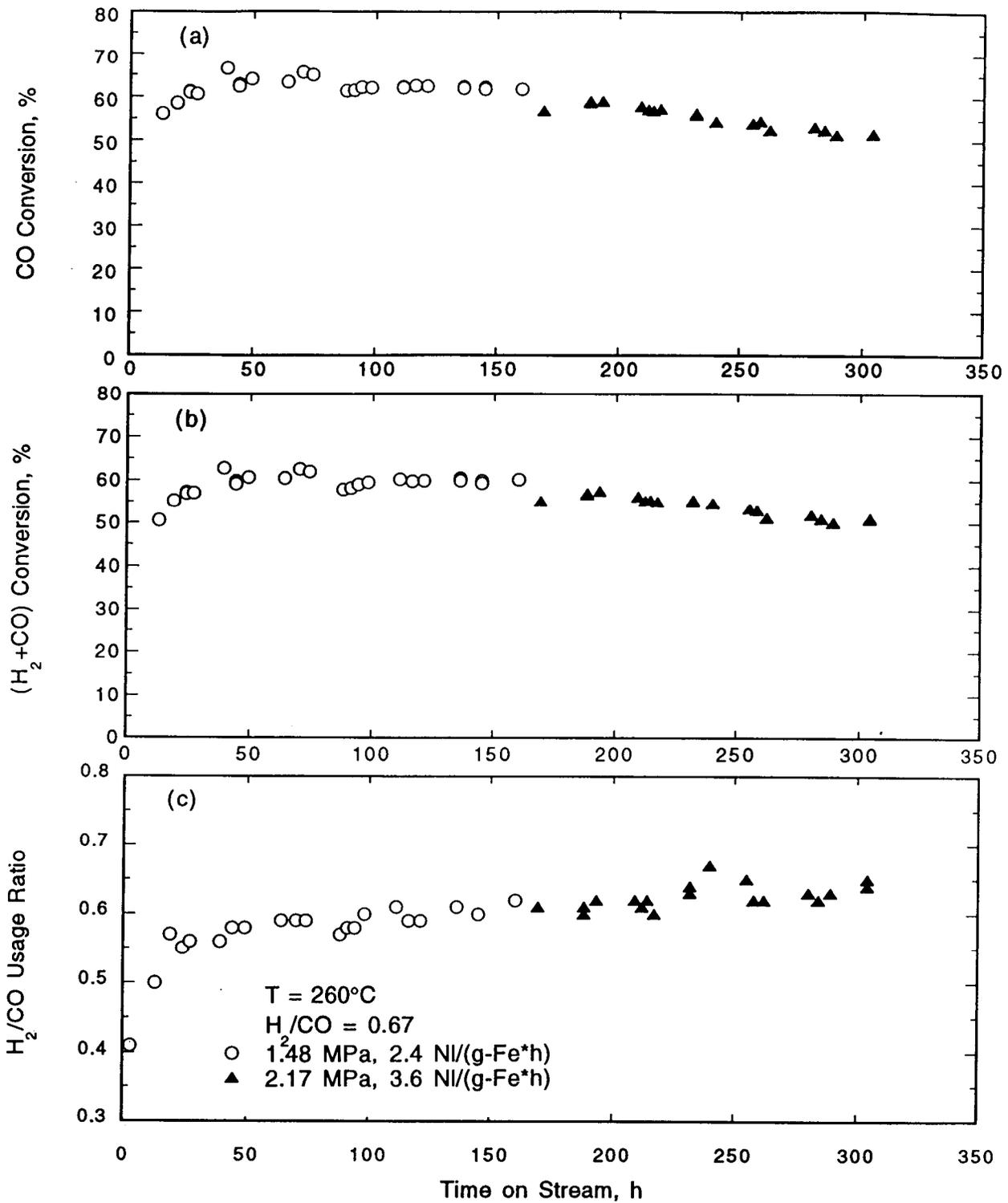


Figure 9. Change in (a) CO conversion, (b) (H₂+CO) conversion, and (c) H₂/CO usage ratio with time on stream in run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al₂O₃ catalyst

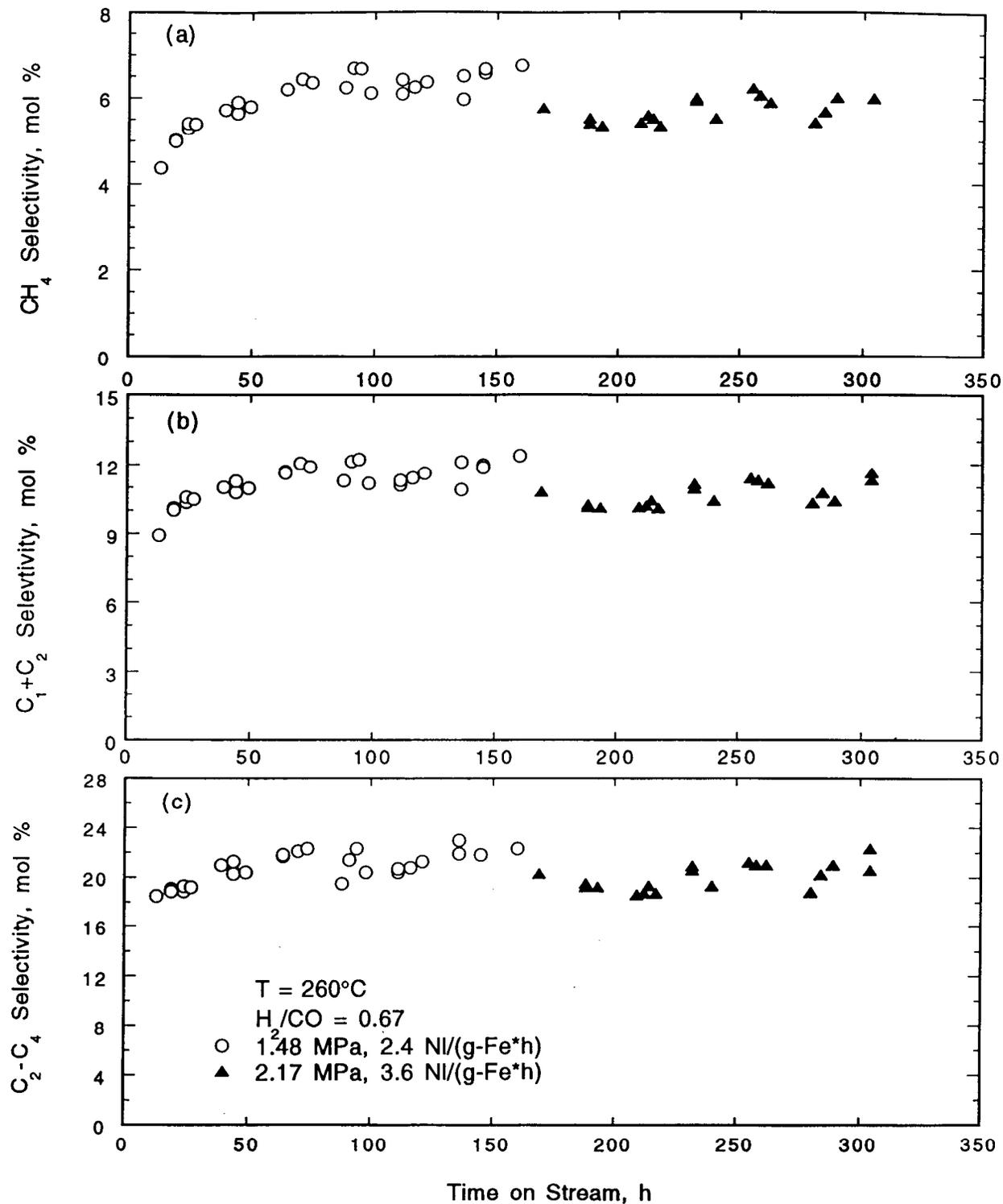


Figure 10. Change in (a) methane selectivity, (b) C₁+C₂ selectivity and (c) C₂-C₄ selectivity with time on stream in run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al₂O₃ catalyst

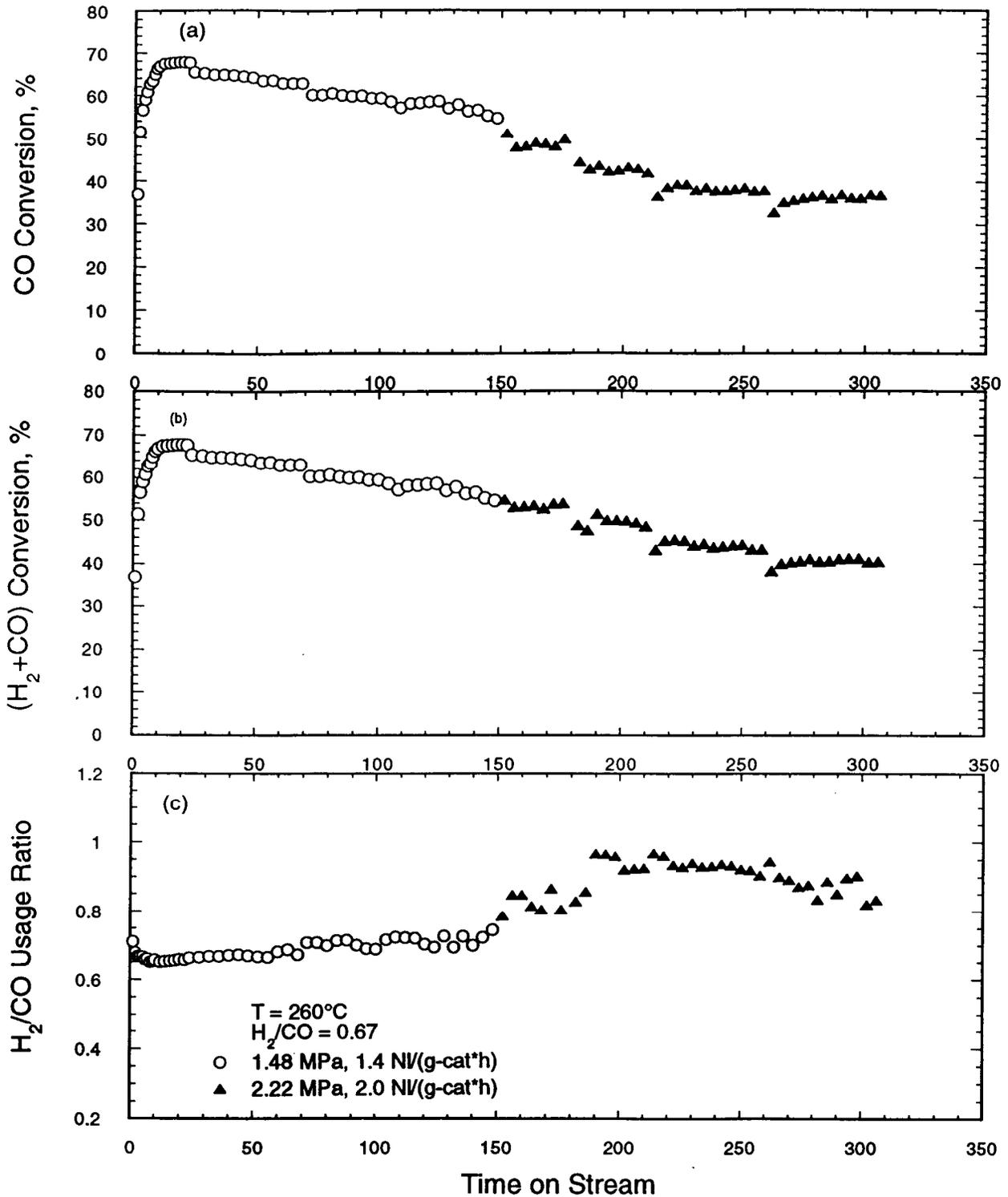


Figure 11. Change in (a) CO conversion, (b) (H₂+CO) conversion, and (c) H₂/CO usage ratio with time on stream in run SB-0627 with 100 Fe/5 Cu/6 K/139 SiO₂ catalyst

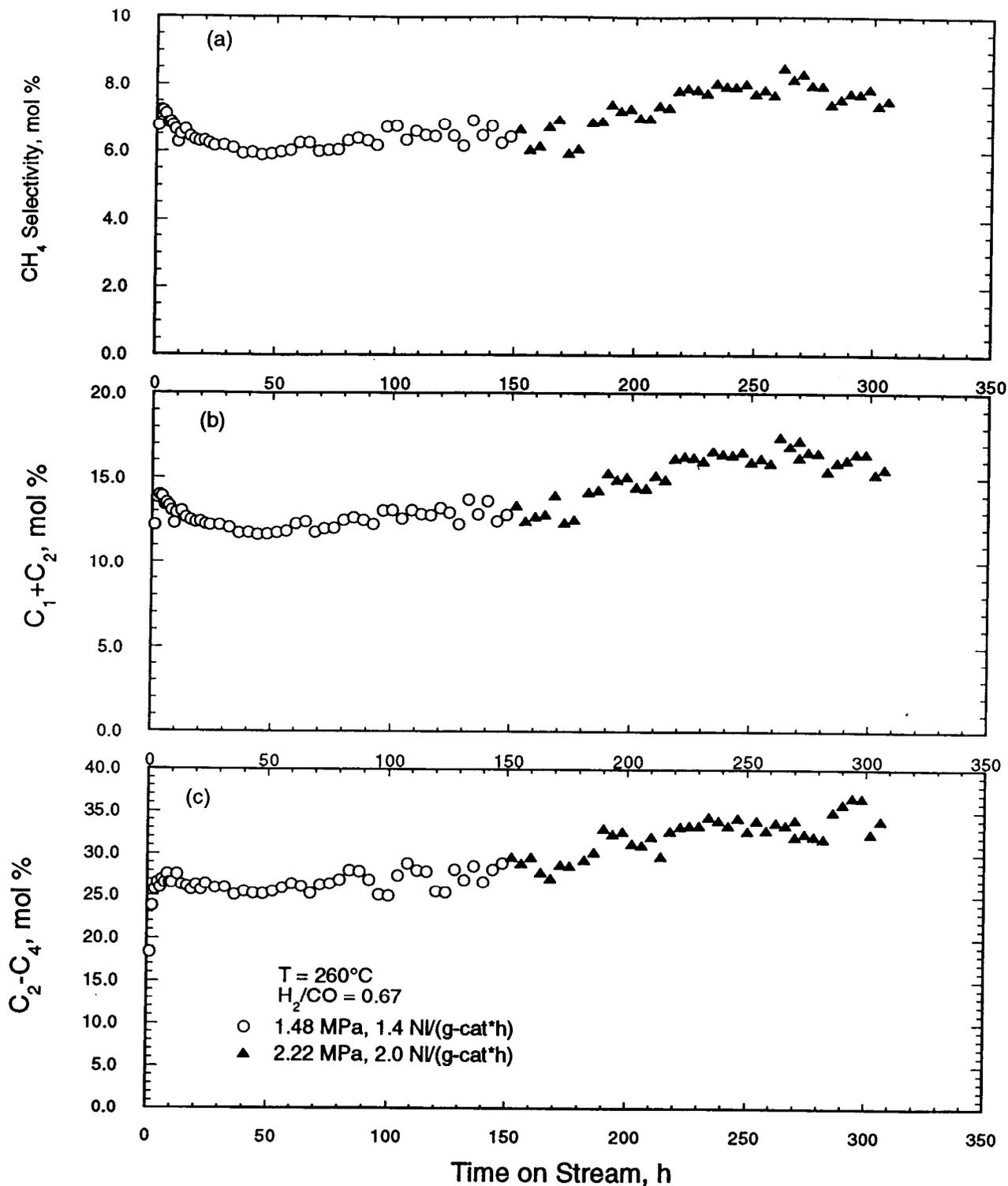


Figure 12. Change in (a) methane selectivity, (b) C₁+C₂ selectivity and (c) C₂-C₄ selectivity with time on stream in run SB-0627 with 100 Fe/5 Cu/6 K/139 SiO₂ catalyst