

Development of Precipitated Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
for the Period 1 April 1997 – 30 June 1997

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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 with 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 were characterized by BET surface area measurements. The surface areas of all four catalysts are between 94 and 136 m²/g, whereas the surface areas of alumina and silica support are 213 and 252 m²/g, respectively. The decrease in surface area of the supports is due to pore filling and blocking during the impregnation of supports with iron and promoters.

During the current reporting period one slurry reactor test (SB-2337) was performed with an alumina supported catalyst with nominal composition 100 Fe/5 Cu/9 K/139 Al₂O₃, which was synthesized in our laboratory during the last quarter. The performance of this catalyst 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 the alumina supported catalyst was lower, and its catalyst deactivation rate was higher than that of the baseline catalysts B and C. The work on testing of alternative catalyst has been completed.

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 (January 1 - June 30, 1997)

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 (June 1 - August 31, 1997)

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 continued during this quarter. Characterization of supported catalysts (prepared by impregnation) by BET surface area has been completed. We were not able to characterize used catalysts from run SB-0627 due to technical problems with our X-ray diffractometer (Scintag XDS 2000). A new chiller for the

XRD machine was installed, and the instrument was calibrated with standards, however, the instrument was not working properly (intermittent power losses during X-ray scans). After consultations with the Scintag's Service Department, a new X-ray tube was ordered

III.8.1 Surface Areas of Supported Catalysts

The BET surface area of the supports and supported catalysts has been determined by using nitrogen adsorption at 77K in Pulsechemisorb 2705 Micromeritics instrument. Prior to the nitrogen adsorption measurements, the catalyst samples were degassed at 200°C in helium flow for 2.5 h. From the amount of nitrogen adsorbed and the amount of catalyst sample used the BET surface areas were calculated.

The BET surface areas of the supports and supported catalysts (calcined at 300°C for 5 h) are summarized in Table 1. The BET surface area of both the silica containing catalysts (100 Fe/5 Cu/6 K/139 SiO₂ and 100 Fe/10 Cu/6 K/134 SiO₂) is about 94 -103 m²/g-cat. Similarly, the BET surface areas of alumina containing catalysts (100 Fe/5 Cu/6 K/139 Al₂O₃ and 100 Fe/10 Cu/6 K/134 Al₂O₃) varied from 94 to 136 m²/g-cat. Comparing the surface areas of supports and the impregnated catalysts it appears that the surface areas of both the supports (252 m²/g for silica and 213 m²/g for alumina) is reduced to about 94-136 m²/g-cat after the impregnation of support with iron, copper, and potassium. The decrease in surface area of the supports may be attributed to the pore filling or pore blocking of part of the meso pores during the impregnation step.

III.9 Testing of Alternative Catalysts for Slurry Reactors

The work on this task began during the previous quarter (1 January 1997 -31 March 1997). During the current reporting period one slurry reactor test (SB-2337) was performed with an alumina supported catalyst with nominal composition 100 Fe/5 Cu/9 K/139 Al₂O₃, which was synthesized in our laboratory during the last quarter. Catalyst performance (activity and gaseous hydrocarbon product selectivities) during the slurry test is described below.

III.9.1 Run SB-2337 with 100 Fe/5 Cu/9 K/139 Al₂O₃ Catalyst

Approximately 15 g of the catalyst (45 - 63 μm particle size range) was loaded for the slurry test, together with 316 g of Durasyn 164 oil as the initial slurry medium. The catalyst was reduced with a mixture of CO and helium (1:5 by volume) at 280°C for 8 h, 4000 cm^3/min and then tested at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of 0.67 ($\text{H}_2/\text{CO} = 0.67$) and gas space velocity of 1.3 NL/g-cat/h (or 4.1 NL/g-Fe/h). After about 32 h on stream, the CO and syngas conversions reached 48% and 47%, respectively, and then started to decline (Figure 1a and 1b). At 236 h on stream, the CO and syngas conversions were about 19%. The H_2/CO usage ratio was in the range of 0.60 to 0.70 throughout the run (Figure 1c).

Methane selectivity increased from 1.7 to 5.2% during the first 6 hours of the test, and then decreased to about 3.5% after 24 h on stream and stabilized at about 3.5 -3.9% between 24 and 236 h on stream (Figure 2a). Gaseous hydrocarbon selectivities (C_1+C_2 and C_2-C_4 hydrocarbons) followed the same trend (Figure 2b & 2c). Although the catalyst selectivity was satisfactory, the catalyst deactivation rate was too high. Run was terminated after 237 h. Major events for run SB-2337 are summarized in Table 2.

Concluding Remarks on Slurry Reactor Tests with the Alternative Catalysts

Three slurry reactor tests were completed for this task. Two tests: SA-0097 (Quarterly Report for January 1 - March 31, 1997) and SB-2337 were conducted with alumina containing catalysts with nominal compositions 100 Fe/5 Cu/4.2 K/20 Al₂O₃ (SA-0097) and 100 Fe/5 Cu/9 K/139 Al₂O₃ (SB-2337). In the third test, SB-0627 (Quarterly Report for January 1 - March 31, 1997) silica supported catalyst with nominal composition 100 Fe/5 Cu/6 K/ 139 SiO₂ was used. Comparison of results from these three tests is shown in Figure 3 (catalyst activity) and Figure 4 (selectivity of gaseous hydrocarbons).

The maximum CO and (H_2+CO) conversions were about 70 % in runs SA-0097 and SB-0627 and about 50 % in run SB-2337. Catalyst deactivation was the most rapid in run SB-2337 with the alumina supported catalyst, which had high potassium content (9 parts of K by weight

per 100 parts of Fe by weight). The alumina containing catalyst 100 Fe/5 Cu/4.2 K/20 Al₂O₃ (SA-0097) was the most stable. Catalyst deactivation was more rapid during testing at 2.17 MPa in runs SA-0097 and SB-0267.

Silica supported catalyst had relatively high methane selectivity (about 7-8 mol%), whereas the lowest methane selectivity was obtained in run SB-2337. The latter is consistent with high potassium content of this catalyst. Alumina containing catalyst (SA-0097) has methane selectivity between 5 and 6 mol%, which is high in comparison to our catalyst B with nominal composition (100 Fe/5 Cu/6 K/24 SiO₂). The latter catalyst has a similar composition, except that it contains silica instead of alumina, but its methane selectivity is about 3-4 mol%. Gaseous hydrocarbon selectivities in runs SA-0097, SB-0627 and SB-2337 follow the same trends as methane selectivity.

In general, the performance of all three alternative catalysts was inferior in comparison to our baseline catalysts B (100 Fe/5 Cu/6 K/ 24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂).

III. 10 Characterization of Product Distribution and Data Analysis

The work on this task has been initiated in June. Liquid products and wax produced from previous slurry reactor tests are analyzed to obtain information on product distribution of high molecular weight hydrocarbons.

Plans for the Next Quarter

During the next quarter we plan to continue with work on: (a) characterization of catalysts from slurry reactor tests conducted under Task 9; (b) analysis of high molecular weight products (liquids and wax); and (c) preparation of final report for this contract.

Table 1 Summary of BET surface areas of supports and supported catalysts

Catalyst or Support*	Surface area, m ² /g
Silica (Davison, grade 952)	252 245
Alumina (Vista B)	213 213
100 Fe/5 Cu/6 K/139 SiO ₂	100 103
100 Fe/10 Cu/6 K/134 SiO ₂	94 94
100 Fe/5 Cu/6 K/139 Al ₂ O ₃	136 136
100 Fe/10 Cu/6 K/134 Al ₂ O ₃	94 95

* Samples were degassed at 200 °C in He flow (50 cm³/min) for 2.5 hours.

Table 2. Major Events in Run SB-2337 with Catalyst (100 Fe/5 Cu/9 K/139 Al₂O₃)

TOS (h)	Event
	Slurry loading: 316.4 g of Durasyn 164 oil, 14.74 g of catalyst (45 - 63 μ m particle size)
	Catalyst pretreatment: CO diluted with helium (1.5), 280°C, 8 h, 0.8 MPa, 4000 cm ³ /min
	wax withdrawal 41.79 g after CO reduction.
0	Initiate synthesis gas flow, achieve process conditions: T = 260°C, P (syngas) = 1.48 MPa, SV (syngas) = 1.3 Ni/g-cat/h, (H ₂ /CO) = 0.67
50	wax withdrawal 17.98 g wax
76	slurry sample withdrawal 14.28 g slurry sample, 0.64 g catalyst
122	wax withdrawal 10.01 g wax
144	slurry sample withdrawal 12.09 g slurry sample, 0.54 g catalyst.
237	slurry sample withdrawal 8.51 g slurry sample, 0.38 g catalyst
237	End of run 301.5 g slurry recovered from the reactor
	Wax and catalyst removed during the run 288.3 g wax, 13.2 g catalyst

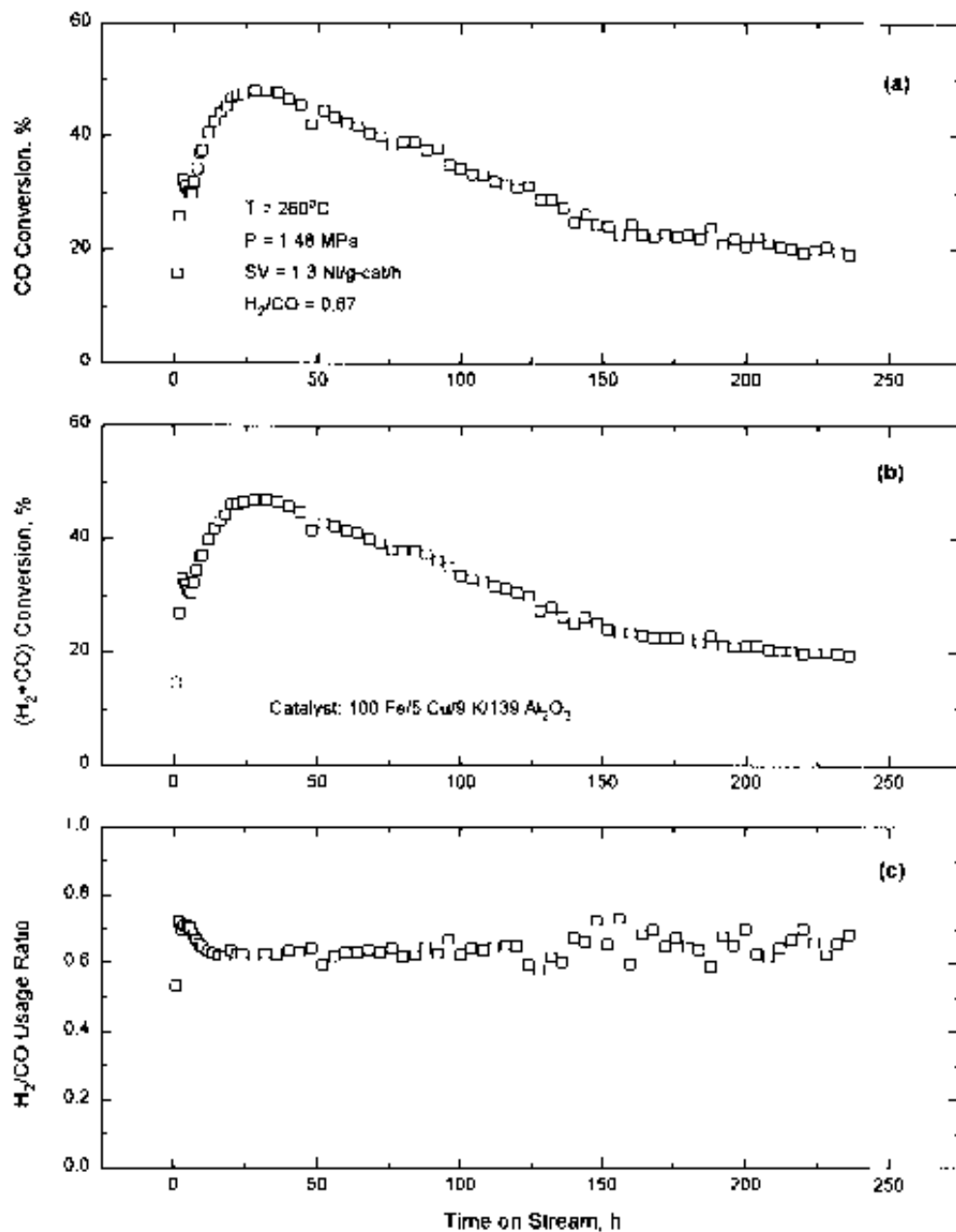


Figure 1. Change in (a) CO conversion, (b) $(\text{H}_2 + \text{CO})$ conversion and (c) H_2/CO usage ratio with time-on-stream in run SB-2337 with the 100 Fe/5 Cu/9 K/139 Al_2O_3 catalyst.

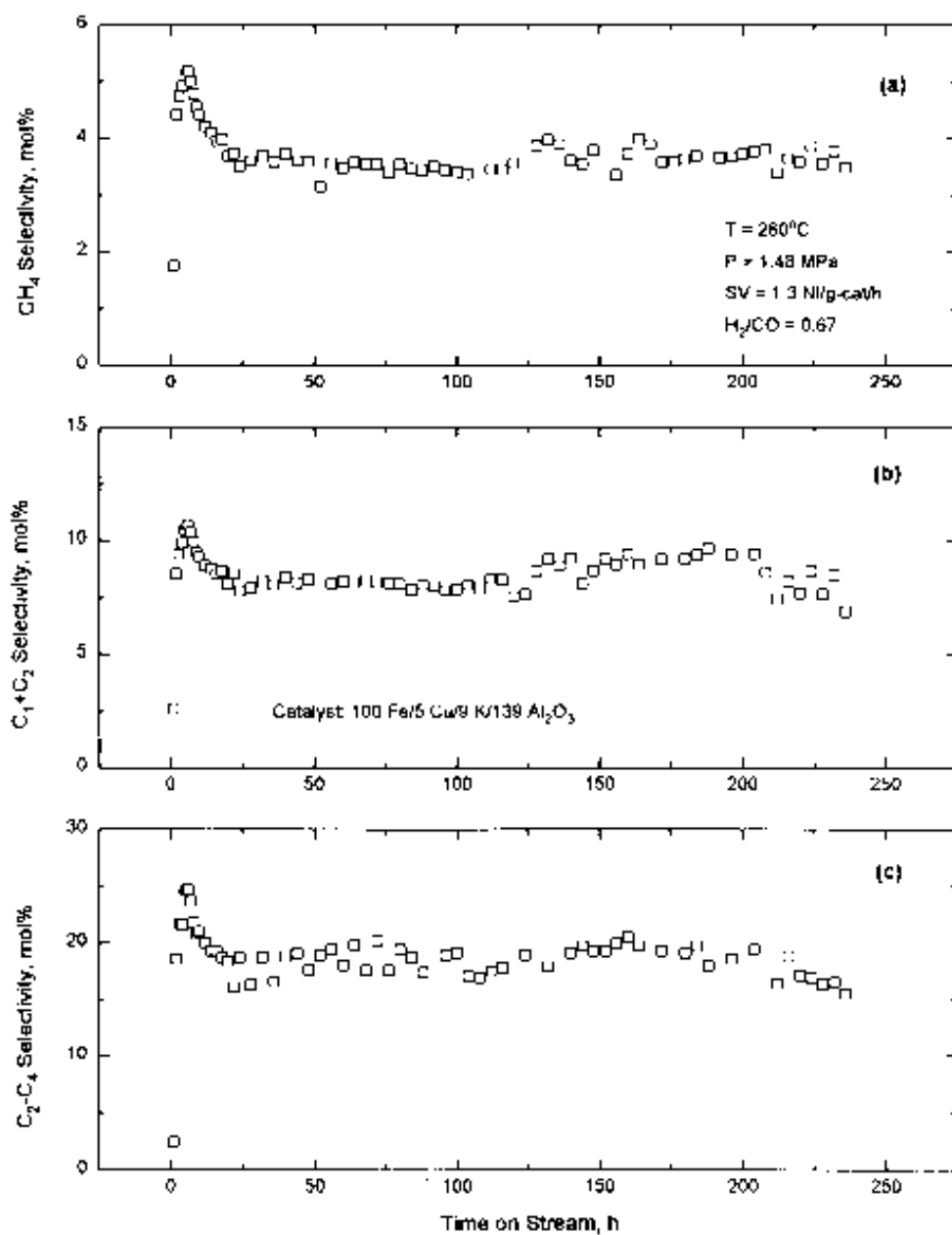


Figure 2. Change in (a) methane selectivity, (b) C₁+C₂ selectivity and (c) C₂-C₄ selectivity with time-on-stream in run SB-2337 with the 100 Fe/5 Cu/9 K/139 Al₂O₃ catalyst.

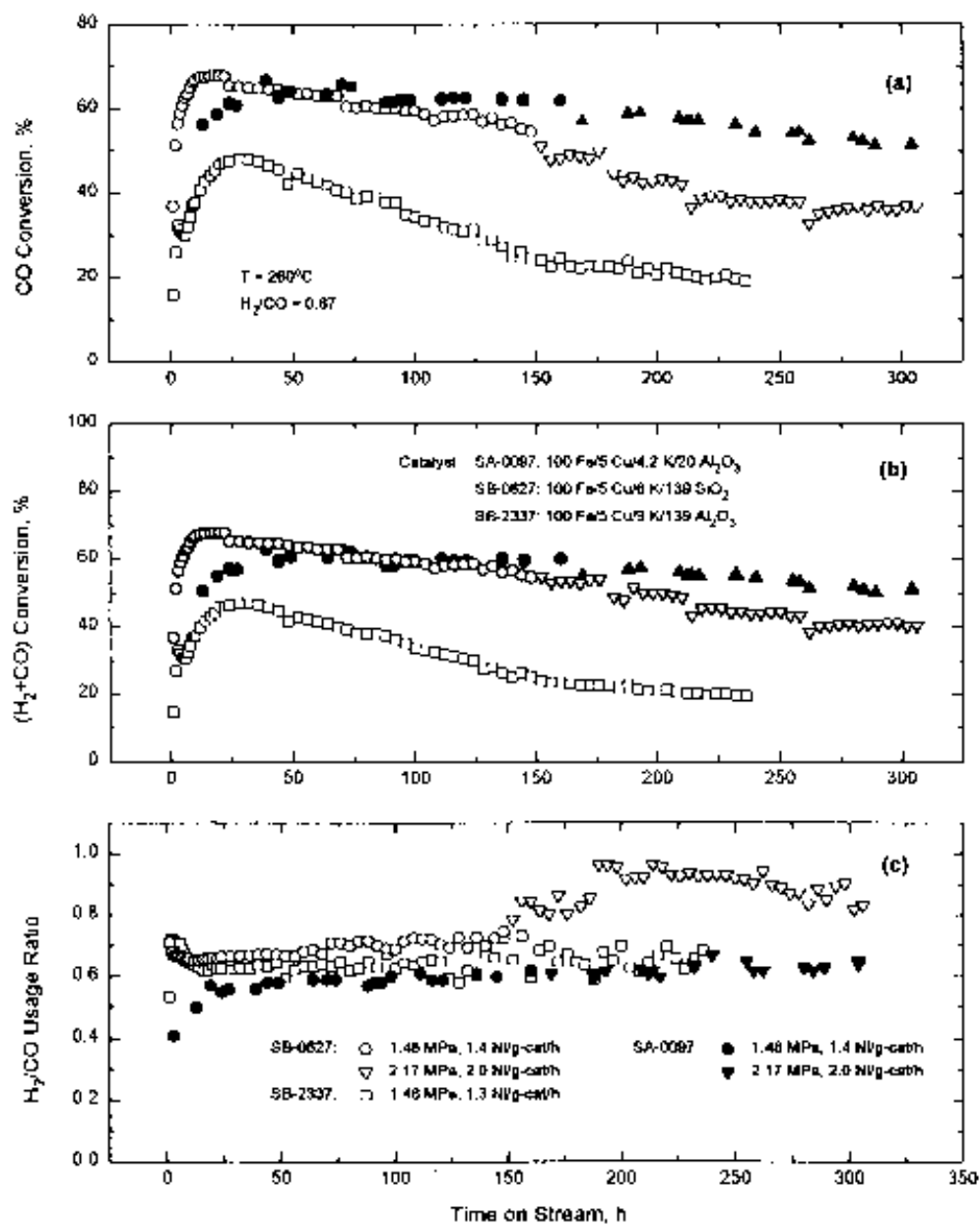


Figure 3. Comparison of (a) CO conversion, (b) $(\text{H}_2 + \text{CO})$ conversion and (c) H_2/CO usage ratio among three tests with the alternative catalysts.

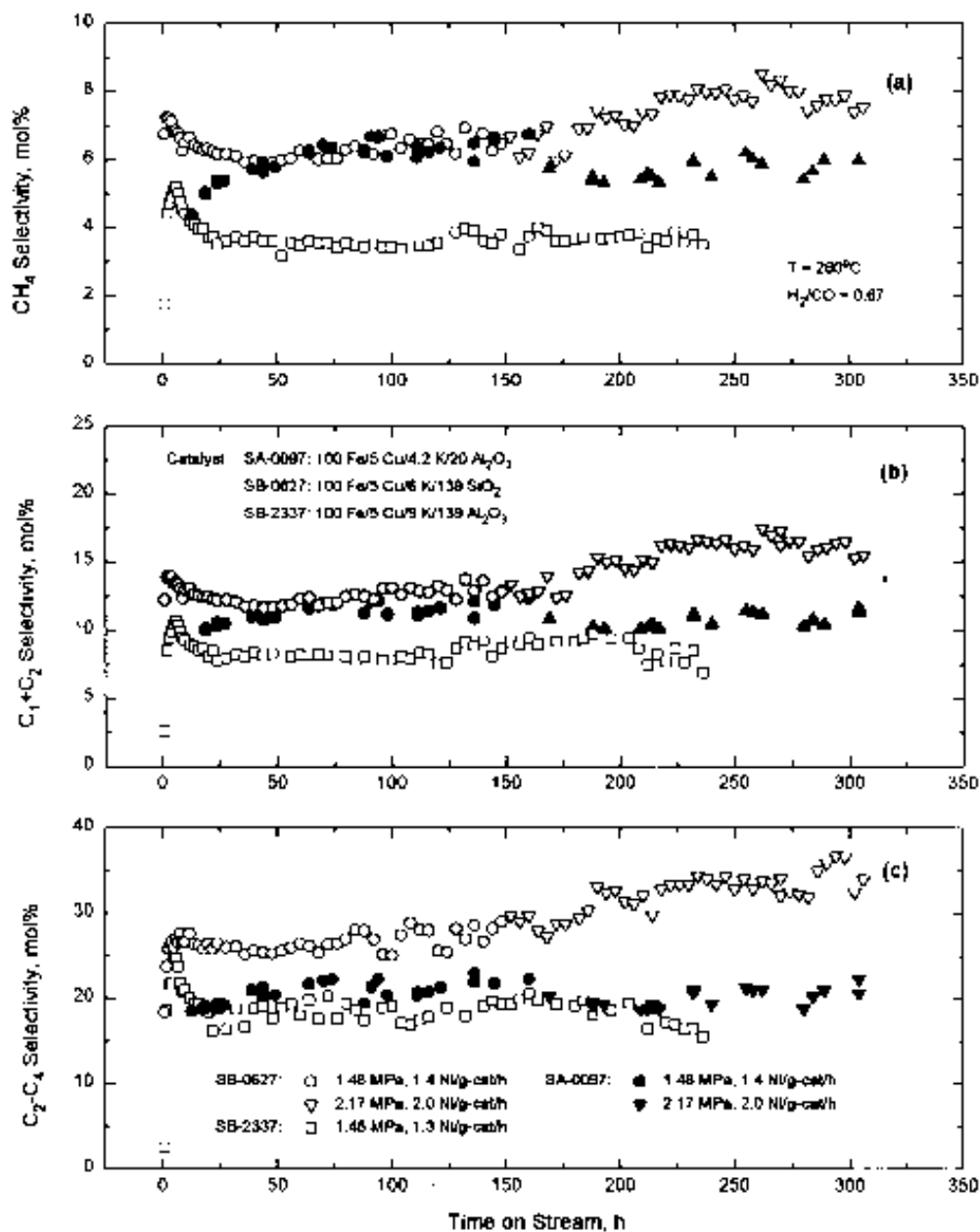


Figure 4. Comparison of (a) methane, (b) C₁+C₂ selectivity and (c) C₂-C₄ selectivity among three runs with three tests with the alternative catalysts.