TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSIS

Contract No. DE-AC22-94PC94055

Quarterly Technical Progress Report No. 10

Covering the Period January 1, 1997 to March 31, 1997

Prepared for

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Date Submitted
May 14, 1997

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Abstract

The goal of the proposed work is the development of iron-based Fischer-Tropsch catalysts that combined high activity, selectivity and life with physical robustness for slurry phase reactors that will produce either low-alpha or high-alpha products. The catalyst that is developed will be suitable for testing at the Advanced Fuels Development Facility at LaPorte, Texas or similar sized plant. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst that is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for

catalysts synthesized in this program for activity, selectivity and aging characteristics.

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1.0 Executive Summary

As part of our effort to develop a robust catalyst for iron-based Fisher-Tropsch synthesis (FTS), we have been testing a series of supported catalysts. Supported iron catalysts are generally thought to be less active and have poorer methane and alkene selectivity than precipitated catalysts because of the acidity of most of the supports used (silica, alumina, etc.). Developing a catalyst with an attrition resistant support that has the activity and selectivity of precipitated catalysts could facilitate catalyst-separation by reducing catalyst fines.

It is clear from these preliminary data that alumina and magnesium aluminate are superior to silica and magnesium silicate as supports for iron FTS catalysts. The best activity and selectivity was obtained with the magnesium aluminate supported catalyst. A comparison of the activity and selectivity of this catalyst with a precipitated iron catalyst operated under similar conditions is shown in Table 2. In general, the precipitated catalyst ($100Fe/3.1Cu/8.1K/5.2SiO_2$) is more active than the $100Fe/6.0Cu/8.0K/260MgAl_2O_4$ catalyst; however, methane, carbon dioxide and C_2-C_4 alkene selectivities are similar.

Future work in this area will be concentrated on other supports such as, zinc aluminate, zirconia and carbon. The iron loading on alumina and magnesium aluminate will also be increased to 30 wt% and 40 wt%; this will increase the efficiency of the catalysts and may improve the activity and selectivity.

2.0 Introduction

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst.

In parallel, work will be conducted to design a high-alpha iron catalyst this is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

The research is divided into four major topical areas: (a) catalyst preparation and characterization, (b) product characterization, (c) reactor operations, and (d) data assessment.

To accomplish the objectives of the project, these topics have been organized into the following technical tasks:

<u>a. Task 1.0</u> Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts

The goal of this task is to identify and optimize procedure for the preparation of iron-based catalysts that combine high activity selectivity and life with physical robustness. Each of the subtasks address an area of considerable uncertainty in the synthesis of catalysts.

1.1 Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Fischer-Tropsch Catalysts

- Role of precursor particle size on activity.
- Role of Cu in precipitated catalysts.
- Define attrition resistance.

1.2 Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts

- Define optimum SiO_2.
- Define optimum Al_2O_3.

1.3 Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity in both Low- and High-Alpha Catalysts.

1.4 Complete the Optimization of the Two Best Low-Alpha, Iron-Based Fischer-Tropsch Catalysts Developed during the Previous Contract.

b. Task 2.0 Definition of Preferred Pretreatment for both Low- and High-Alpha Fischer-Tropsch Catalysts.

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

2.1 Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.

2.2 Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.

2.3 Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.

2.4 Evaluate the Effect of Carbon Deposition during Catalyst Activation on Activity, Selectivity and Aging Characteristics.

<u>c. Task 3.0</u> Catalyst Structure and Characterization.

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM, XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

<u>d. Task 4.0</u> Catalyst Testing.

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

4.1 Verify the Quality of Data Obtained from the CSTR's.

4.2 Measure Catalyst Performance.

4.3 Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.

4.4 Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

3.0 Experimental

3.1 Catalyst Preparation

Four supports were impregnated with $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and KNO_3. The supports used were silica (Grace), alumina (Discovery Chemicals), magnesium silicate (Fisher) and magnesium aluminate. The silica, alumina and magnesium aluminate supports were screened to 60-325 mesh and the magnesium silicate was used as received, 60-100 mesh. Silica, alumina and magnesium silicate were activated at 600°C for 4 h. Magnesium aluminate was prepared by coprecipitating Mg-Al hydroxides from $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (1:2 molar ratio) followed by calcination at 400°C for 16 h and 800°C for an additional 16 h.

The typical impregnation procedure was as follows. The support (86 g) was heated to 100°C while $Fe(NO_3)_3 \cdot 9H_2O$ (125 g), $Cu(NO_3)_2 \cdot 3H_2O$ (3.96 g) and KNO_3 (3.61 g) were melted in an oil bath at 70°C. The melt was slowly added to the support with good mixing. The impregnated support was then calcined at 300°C for 2 h. The impregnation and calcination procedures were repeated resulting in a catalyst with approximately 21-23 wt% Fe. X-ray diffraction shows the iron in the form of α-Fe_2O_3 for all four catalysts. Nominal compositions and BET data for the supports and catalysts are shown in Table 1.

3.2 FTS Conditions

Approximately 40 g of catalyst and 290 g of Ethylflo 164 oil (C_{30}) were loaded into one liter stirred autoclave reactors. The slurry was treated with hydrogen at 120 SLPH at ambient pressure and the temperature was increased to 270°C at 120°C h^{-1}. Hydrogen reduction was carried out for 24 h and then the temperature was lowered to 250°C. The pressure was increased to 1.31 MPa and a catalyst sample was taken. Carbon monoxide flow was started and the hydrogen flow gradually decreased until the total flow rate was 3.1 SL h^{-1}g-Fe^{-1} and the H_2/CO ratio was 0.7. Additional catalysts samples were withdrawn at ~100 h and at the end of the runs.

Task 1. Development of Optimum Promoter Levels for Low- and High-alpha Catalysts.

No additional results to report.

Task 2. Definition of Preferred Pretreatment for Low- and High-Alpha Catalyst

This task is essentially complete.

Task 3. Catalyst Structure and Characterization

No additional results to report.

Task 4. Catalyst Testing

Results and Discussion

Carbon monoxide conversion for each catalyst is shown in Figure 1. The $100Fe/6.0Cu/8.1K/250Al_2O_3$ and $100Fe/6.0Cu/8.0/260MgAl_2O_4$ catalysts had the highest conversions. Both went through a long induction period in which the conversion increased from ~40% to 60%. A reactor upset occurred during the $100Fe/6.0Cu/8.1K/250Al_2O_3$ run in which the hydrogen flow was cut off for 2-8 h; however, within 72 h the conversion had rebounded. The 100Fe/6.0Cu/8.1K/250SiO_2 and 100Fe/6.0Cu/8.1K/260MgOxSiO_2 catalysts had maximum carbon monoxide conversions of 32% and 7%, respectively and had poor stability. Hydrocarbon production rates paralleled the carbon monoxide conversions (Figure 2). The 100Fe/6.0Cu/8.1K/250Al_2O_3 and 100Fe/6.0Cu/8.0K/260$MgAl_2O_4$ catalysts both had maximum values >0.35 g h^{-1}g-Fe^{-1} while the 100Fe/6.0Cu/8.1K/250SiO_2 and 100Fe/6.0Cu/8.1K/260MgOxSiO_2 catalysts were somewhat lower at 0.2 and 0.05 g h^{-1}g-Fe^{-1}, respectively. The low activity obtained with the silica based supports may be due to ineffective reduction during the activation procedure. The induction period seen with the alumina and magnesium aluminate supported catalysts is typical of catalysts that are not reduced adequately during the activation period. The hydrogen reduction characteristics of these catalysts will be examined by thermogravimetric analysis to verify this.

Analysis of liquid samples has not been finished so complete selectivity data are not available. Methane selectivity (Figure 3) was generally below 5% (based on carbon converted to hydrocarbon) for the 100Fe/6.0Cu/8.0K/260$MgAl_2O_4$ and between 5 and 6% for the 100Fe/6.0Cu/8.1K/250Al_2O_3 catalyst. Methane selectivity was substantially higher for the silica (>8%) and magnesium silicate (9-15%) supported catalysts. The alkene selectivity for the C_2, C_3 and C_4 hydrocarbon fractions is shown in Figures 4-6. Ethylene selectivity was higher for the alumina and magnesium aluminate supported catalysts than for the silica and magnesium silicate supported catalysts. The best selectivity was obtained for the 100Fe/6.0Cu/8.0K/260$MgAl_2O_4$ catalyst; the ethylene fraction was stable throughout the run at ~0.76. The 100Fe/6.0Cu/8.1K/250Al_2O_3 catalyst had similar ethylene selectivity initially; however, it decreased to <0.6 by the end of the run. Propene and butene selectivities were similar for all of the catalysts (0.78-0.0.86). Carbon dioxide selectivity for the four catalysts is shown in Figure 7. The 100Fe/6.0Cu/8.1K/250Al_2O_3, 100Fe/6.0Cu/8.0K/260MgAl$_2$O$_4$ and 100Fe/6.0Cu/8.1K/250SiO$_2$ catalysts had high carbon dioxide selectivities (48-50% of the converted carbon) which is an indication that the water-gas shift activity was high. The catalyst with the lowest FTS activity, 100Fe/6.0Cu/8.1K/260MgOxSiO$_2$, also had the lowest carbon dioxide selectivity (~30%).

The main purpose for running these catalysts is to develop a catalyst resistant to attrition. Catalyst samples were removed during the runs and have been Soxhlet extracted to remove accumulated wax. Particle size determination will be obtained by SEM and will be reported in the future.

It is clear from these preliminary data that alumina and magnesium aluminate are superior to silica and magnesium silicate as supports for iron FTS catalysts. The best activity and selectivity was obtained with the magnesium aluminate supported catalyst. A comparison of the activity and selectivity of this catalyst with a precipitated iron catalyst operated under similar conditions is shown in Table 2. In general, the precipitated catalyst (100Fe/3.1Cu/8.1K/5.2SiO$_2$) is more active than the

$100Fe/6.0Cu/8.0K/260MgAl_2O_4$ catalyst; however, methane, carbon dioxide and C_2-C_4 alkene selectivities are similar.

Future work in this area will be concentrated on other supports such as, zinc aluminate, zirconia and carbon. The iron loading on alumina and magnesium aluminate will also be increased to 30 wt% and 40 wt%; this will increase the efficiency of the catalysts and may improve the activity and selectivity.

Table 1

BET Surface Area and Pore Volume of Supports and Catalysts

	Area (m^2g^{-1})	Pore Vol. (cm^3g^{-1})
Silica	284	1.15
Magnesium silicate	231	0.54
Alumina	196	0.43
Magnesium aluminate	71	0.37
100Fe/6.0Cu/8.1K/250SiO_2	N.A.	N.A.
100Fe/6.0Cu/8.1K/260MgOxSiO_2	57	0.22
100Fe/6.0Cu/8.1K/250Al_2O_3	78	0.19
100Fe/6.0Cu/8.1K/260$MgAl_2O_4$	43	0.16

Table 2

Comparison of Activity and Selectivity of Supported and Precipitated Iron FTS Catalysts

	Supported Catalyst	Precipitated Catalyst
Time (h)	240	120
Composition	$100Fe/6.0Cu/8.1K/260MgAl_2O_4$	$100Fe/3.1Cu/8.1K/5.2SiO_2$
Conversion (%)		
CO	62	86
H_2	48	71
$CO+H_2$	56	80
Hydrocarbon ($g\ h^{-1} g\text{-}Fe^{-1}$)	0.37	0.50
Selectivity (mol%, carbon basis)		
CH_4	3.8	3.0
CO_2	48	49
Alkene Selectivity (mol fraction)		
C_2	0.76	0.72
C_3	0.83	0.78
C_4	0.78	0.85

FTS Conditions - 250°C, 1.31 MPa, $H_2/CO = 0.7$, 3.1 SL $h^{-1} g\text{-}Fe^{-1}$

Figure 1. Carbon monoxide conversion for 100Fe/6.0Cu/8.1K/250SiO$_2$ (○), 100Fe/6.0Cu/8.1K/260MgOxSiO$_2$ (□), 100Fe/6.0Cu/8.1K/250Al$_2$O$_3$ (◇) and 100Fe/6.0Cu/8.0K/260MgAl$_2$O$_4$ (△). FTS conditions: 270 °C, 1.31MPa, H$_2$:CO=0.7, 3.1 NL h^{-1} g-Fe^{-1}.

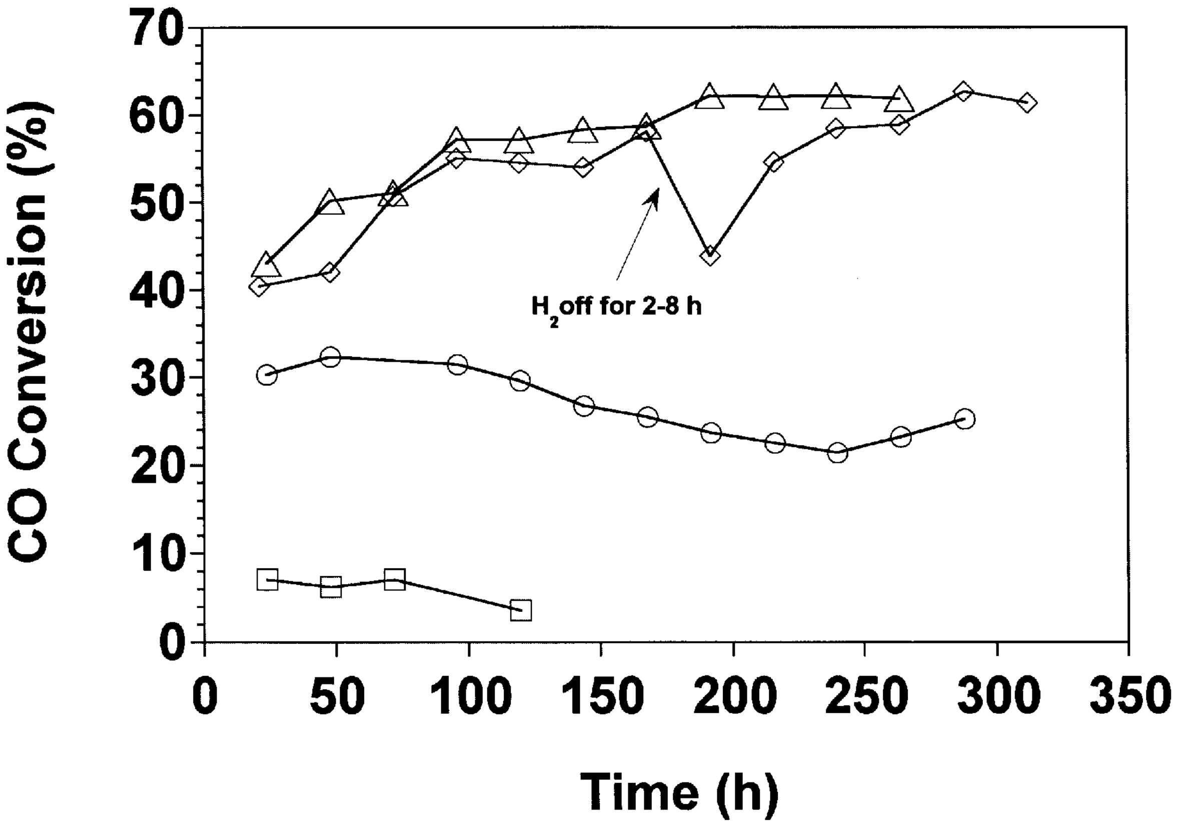

Figure 2. Hydrocarbon production rate for 100Fe/6.0Cu/8.1K/250SiO_2 (○), 100Fe/6.0Cu/8.1K/260MgOxSiO_2 (□), 100Fe/6.0Cu/8.1K/250Al_2O_3 (◇) and 100Fe/6.0Cu/8.0K/260$MgAl_2O_4$ (△). FTS conditions: 270 °C, 1.31MPa, H_2:CO=0.7, 3.1 NL h^{-1} g-Fe^{-1}.

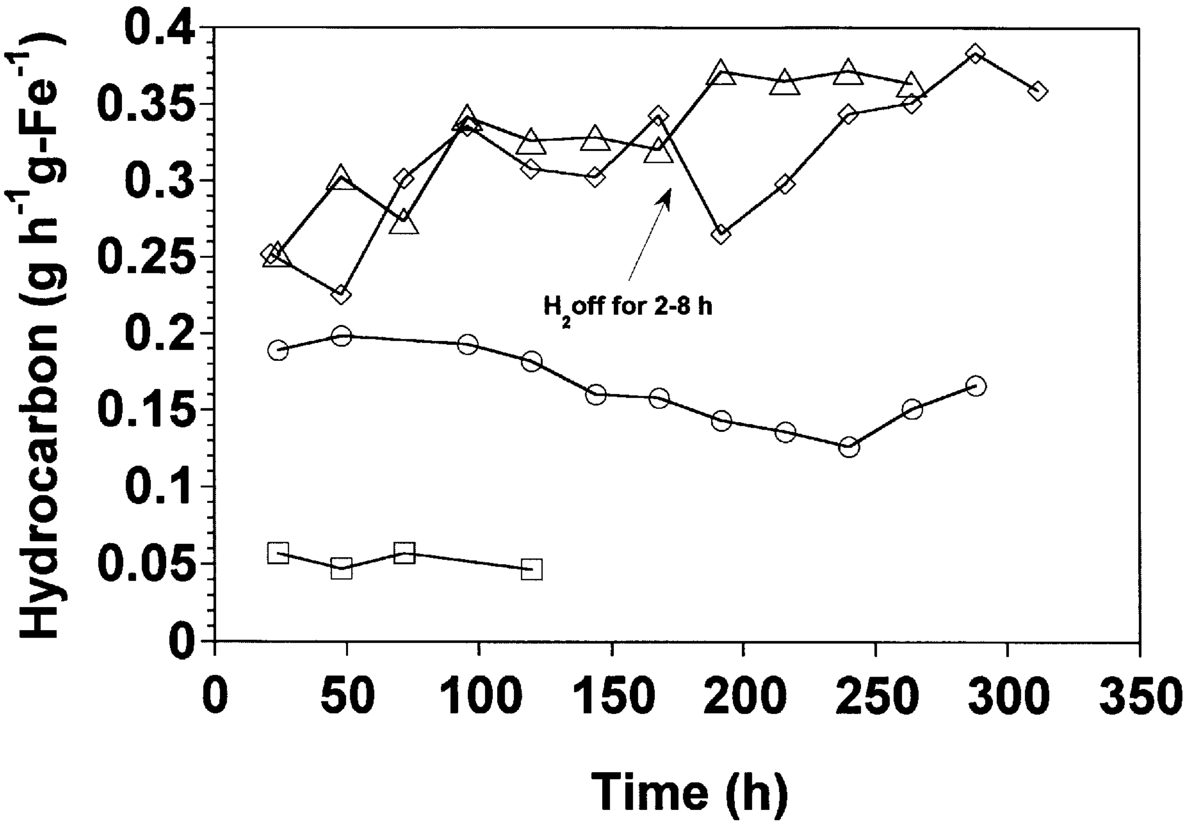

Figure 3. Methane selectivity for 100Fe/6.0Cu/8.1K/250SiO_2 (○), 100Fe/6.0Cu/8.1K/260MgOxSiO_2 (□), 100Fe/6.0Cu/8.1K/250Al_2O_3 (◇) and 100Fe/6.0Cu/8.0K/260$MgAl_2O_4$ (△). FTS conditions: 270°C, 1.31MPa, H_2:CO=0.7, 3.1 NL h^{-1} g-Fe^{-1}.

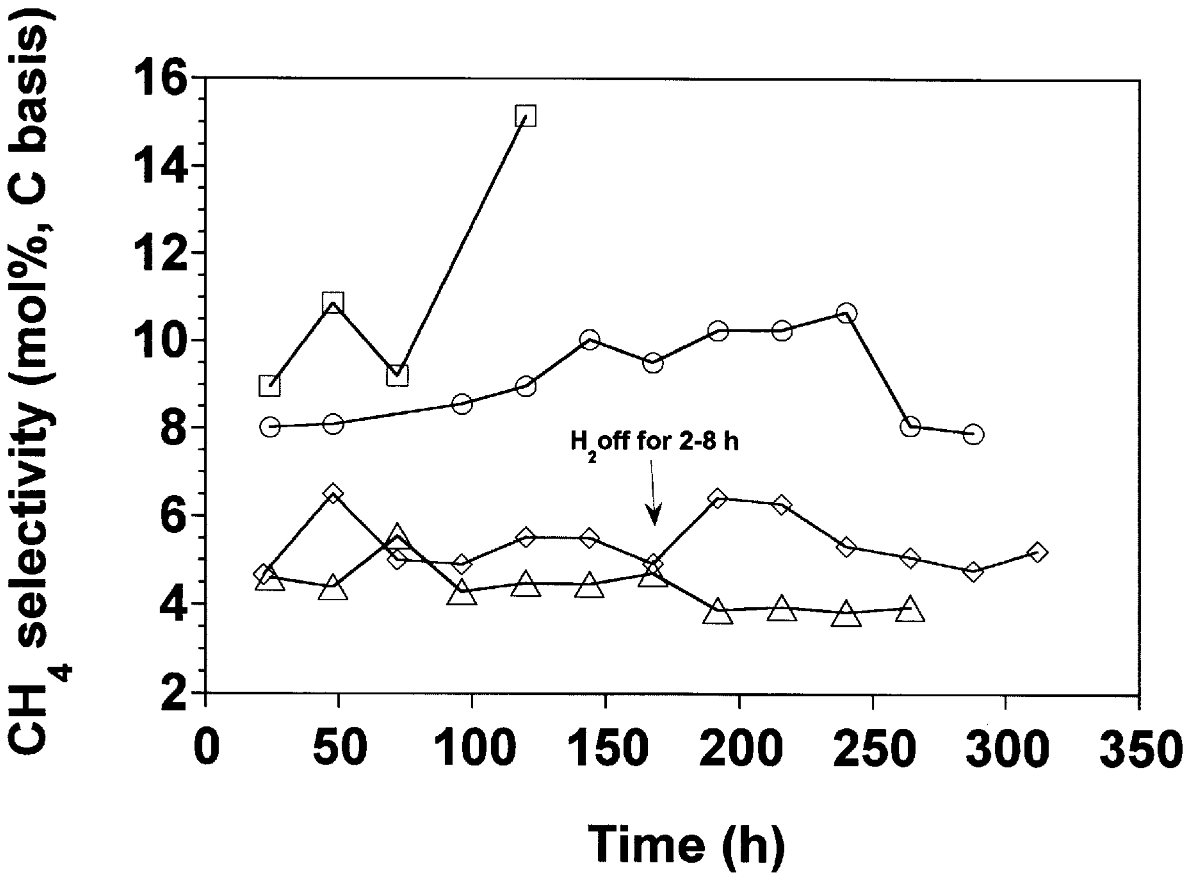

Figure 4. Ethylene selectivity for 100Fe/6.0Cu/8.1K/250SiO$_2$ (○), 100Fe/6.0Cu/8.1K/260MgOxSiO$_2$ (□), 100Fe/6.0Cu/8.1K/250Al$_2$O$_3$ (◇) and 100Fe/6.0Cu/8.0K/260MgAl$_2$O$_4$ (△). FTS conditions: 270 °C, 1.31MPa, H$_2$:CO=0.7, 3.1 NL h^{-1} g-Fe^{-1}.

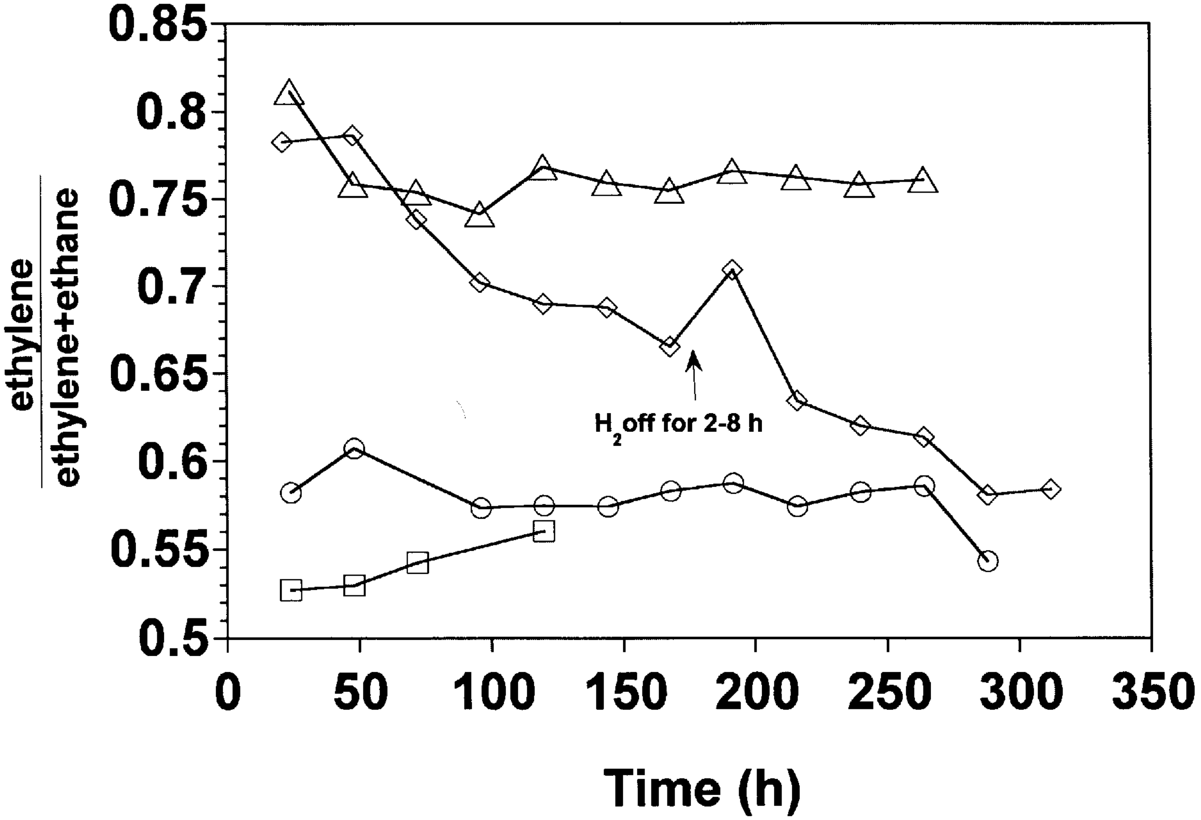

Figure 5. Propene selectivity for 100Fe/6.0Cu/8.1K/250SiO_2 (○), 100Fe/6.0Cu/8.1K/260MgOxSiO_2 (□), 100Fe/6.0Cu/8.1K/250Al_2O_3 (◇) and 100Fe/6.0Cu/8.0K/260$MgAl_2O_4$ (△). FTS conditions: 270 °C, 1.31MPa, H_2:CO=0.7, 3.1 NL h^{-1} g-Fe^{-1}.

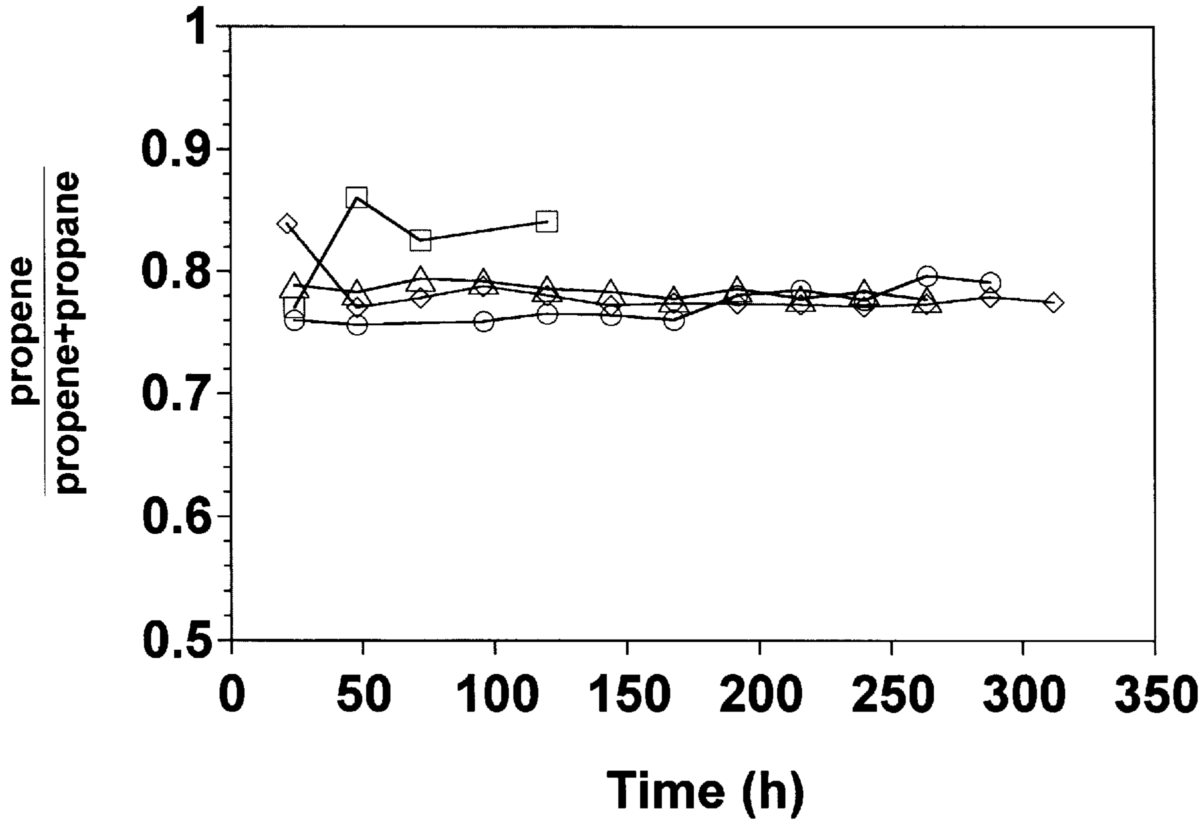

Figure 6. Butenes selectivity for 100Fe/6.0Cu/8.1K/250SiO$_2$ (○), 100Fe/6.0Cu/8.1K/260MgOxSiO$_2$ (□), 100Fe/6.0Cu/8.1K/250Al$_2$O$_3$ (◇) and 100Fe/6.0Cu/8.0K/260MgAl$_2$O$_4$ (△). FTS conditions: 270 °C, 1.31MPa, H$_2$:CO=0.7, 3.1 NL h^{-1} g-Fe^{-1}.

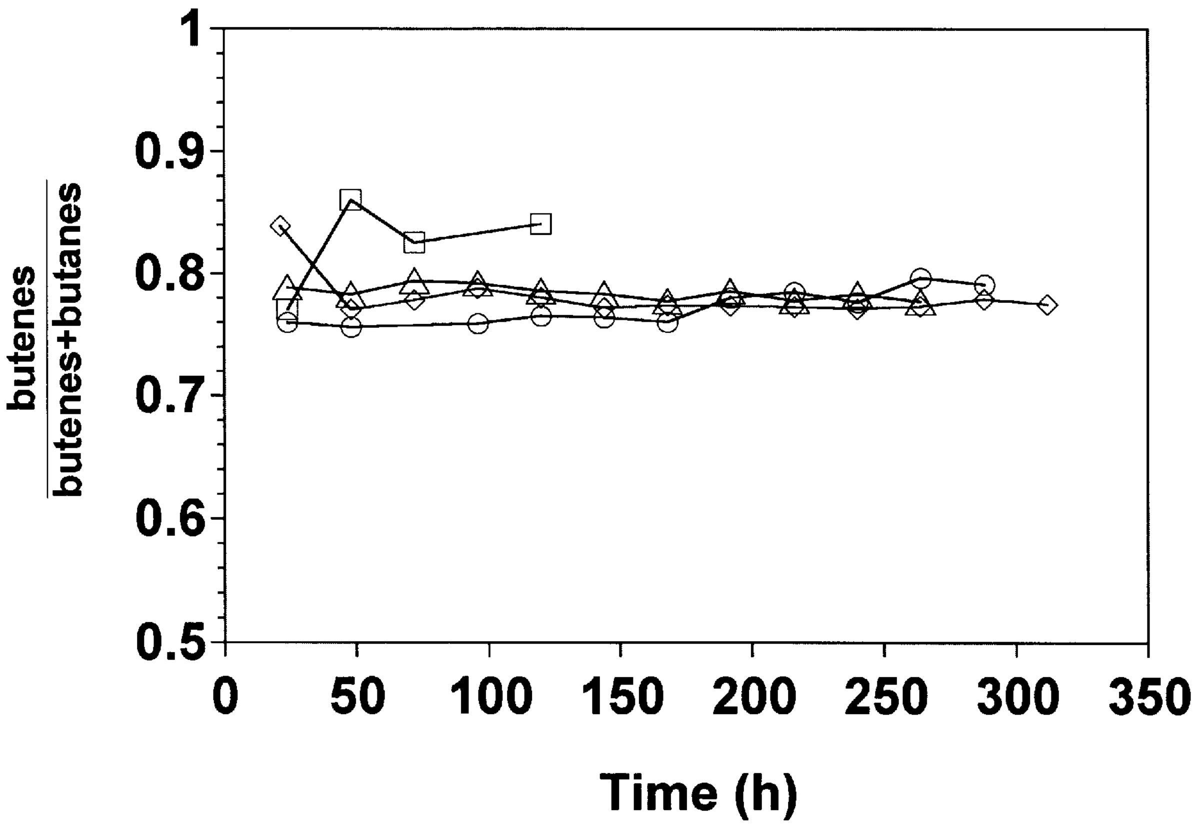

Figure 7. Carbon dioxide selectivity for 100Fe/6.0Cu/8.1K/250SiO$_2$ (○), 100Fe/6.0Cu/8.1K/260MgOxSiO$_2$ (□), 100Fe/6.0Cu/8.1K/250Al$_2$O$_3$ (◇) and 100Fe/6.0Cu/8.0K/260MgAl$_2$O$_4$ (△). FTS conditions: 270 °C, 1.31MPa, H$_2$:CO=0.7, 3.1 NL h^{-1} g-Fe^{-1}.