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Chain-Limiting Operation of Fischer-Tropsch Reactor

Technical Progress Report

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ABSTRACT

The use of pulsing to limit the chain growth of the hydrocarbon products of the Fischer-Tropsch (FT) synthesis in order to to maximize the yield of diesel-range (C_{10}-C_{20}) products was examined on three high-chain-growth-probability ($\alpha \geq 0.9$) FT catalysts. On a Co-ZrO_2/SiO_2 FT synthesis catalyst the application of H_2 pulsing causes significant increase in CO conversion, and only an instantaneous increase in undesirable selectivity to CH_4. Increasing the frequency of H_2 pulsing enhances the selectivity to C_{10}-C_{20} compounds but the chain-growth probability $\boldsymbol{\alpha}$ remains essentially unaffected. Increasing the duration of H_2 pulsing results in enhancing the maximum obtained CO conversion and the instantaneous selectivity to CH_4. An optimum set of H_2 pulse parameters (pulse frequency and duration) is required for maximizing the yield of desirable diesel-range C_{10}-C_{20} products.

On a high-$\boldsymbol{\alpha}$ Fe/K/Cu/SiO_2 FT synthesis catalyst H_2 pulsing enhances the yield of C_{10}-C_{20} but at the same time decreases the catalyst activity (CO conversion) and increases the selectivity to CH_4. On the other hand, pulsing with CO also increases the yield of C_{10}-C_{20} but has no impact on the selectivity to CH_4 or CO_2 and decreases catalytic activity only moderately.

In contrast to these catalysts, H_2 pulsing on a high-$\boldsymbol{\alpha}$ Ru/alumina FT synthesis catalyst has only minimal effect on activity and product distribution, showing enhanced activity towards methanation and water-gas-shift at the expense of FT synthesis. However, these observations are based on experiments performed at a significantly lower reaction pressure (ca. 26 atm) and higher reaction temperature (210-250°C) than those commonly used for supported-Ru FT catalysts (typically 100-1000 atm, 160-170°C).

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EXECUTIVE SUMMARY

Objective

The objective of this research project is to limit the chain growth of Fiscer-Tropsch (FT) products by removing the growing hydrocarbons from the catalyst surface. The present research work focuses on investigating the effect of pulsing on the activity and product distribution of high-α FT synthesis catalysts, in an attempt to limit chain growth to C_{20} hydrocarbons, thus maximizing the desirable diesel-range C_{10}-C_{20} yield.

This investigation involves periodic substitution of the reactant (H_2+CO) flow by an equal flow of a selected "pulse" gas (typically H_2) and monitoring the resulting changes in productivity and product distribution of a particular FT synthesis catalyst. The evaluation of various FT catalysts is based on maximizing the C_{10}-C_{20} product yield. Optimization of the pulse sequence characteristics (frequency, duration, gas type, and gas concentration) is also within the scope of this research.

Summary of Results

Four materials were examined for evaluating the chain-limiting concept on FT synthesis in terms of activity and product selectivity. These were:

- a high-purity, low-surface-area (0.2-m^2/g) α-alumina (SA 5397, Norton), which was an "inert" material and was also used for diluting the other examined FT catalysts,
- a high-α (~0.9) 25pbw Co-18pbw Zr-100pbw SiO_2 catalyst, synthesized at RTI,
- a very-high-α (~0.95) Fe/K/Cu/SiO_2 catalyst, synthesized by the Hampton University, RTI, University of Pittsburgh team under another DOE contract (DE-FG22-96PC96217), and
- a very-high-α (0.95 or more) 0.5wt% Ru/alumina catalyst (synthesized at North Carolina State University, in sub-contract to RTI).

Preliminary FT synthesis runs were performed on the α-alumina catalyst at 208 and 270°C, so as to establish a "blank" activity in the absence of a metal-supported FT catalyst. This α-alumina catalyst exhibited no measurable activity for FT synthesis at 208°C and 270°C; thus, its presence did not contribute to the activity measurements for the other examined catalysts.

The chain-limiting concept was examined on the Co-ZrO_2/SiO_2 FT synthesis catalyst using a series of pulse runs of varying pulse gas, pulse frequency, and pulse duration. "Blank" pulse runs (i.e., involving a switch between two feed streams of the same composition) had no effect on the progress of FT synthesis in terms of activity and product distribution. Pulsing with an inert gas (N_2) gave only minimal variations in catalyst activity (as measured by CO conversion) and product yield for FT reaction.

Pulsing with reactant gas H_2 resulted in a significant increase in CO conversion, along with an enhanced reaction exotherm, while only instantaneously increasing the selectivity to CH_4. The activity decreased gradually until the next pulse, indicating a tendency to return to its steady-state value, whereas the selectivity to CH_4 is quickly restored to its steady-state value. Thus, H_2 pulsing increases catalytic activity while only briefly increasing the formation of CH_4.

An increase in the H_2 pulse frequency enhanced the selectivity to C_{10}-C_{20} compounds (while maintaining or slightly decreasing the selectivity to CH_4), but the chain-growth probability α remained essentially unaffected. Increasing the H_2 pulse duration increased the maximum

obtained CO conversion as well as the instantaneous selectivity to CH_4. The extent of the CH_4 formation appears to be correlated to the increase in H_2 concentration as caused by pulsing. The FT reaction, however, appears to have a different dependence on H_2 concentration, since it progressed within a different time frame. An optimum set of pulse parameters (pulse frequency and duration) is required for maximizing the yield of desirable (diesel-range) C_{10}-C_{20} products.

The effect of pulsing was also examined on a high-α Fe/K/Cu/SiO_2 FT catalyst at different reaction conditions than those applied for the Co-ZrO_2/SiO_2 catalyst (moderately higher reaction temperature, and a H_2:CO ratio of 0.67). Pulsing with H_2 increased the C_{10}-C_{20} yield but also caused a significant decrease in catalyst activity (CO conversion) and an undesirable increase in the selectivity to CH_4. Pulsing with CO also enhanced the C_{10}-C_{20} yield and had no measurable effect on the selectivity to CH_4 and CO_2, while causing only a moderate decrease in CO conversion. Pulsing with a 24%CO_2/N_2 gas mixture had essentially no effect on the catalyst activity or product distribution (α-value, C_{10}-C_{20} yield).

In contrast, H_2 pulsing had only minimal effect on the activity and product distribution of the examined 0.5% Ru/alumina FT synthesis catalyst, which exhibited enhanced activity towards methanation and water-gas-shift reactions. This could be due to a lower reaction pressure (ca. 26 atm) and higher reaction temperature compared to those commonly used for supported-Ru FT catalysts (typically 100-1000 atm, 160-170°C). Application of another reduction procedure produced a better-activated catalyst, exhibiting the same activity at lower temperatures, along with lower selectivity to undesirable compounds CH_4 and CO_2.

Publications/Presentations

1. Two-page abstract entitled "*Fischer-Tropsch Synthesis on a Co-ZrO₂/SiO₂ Catalyst: Effect of H₂ Pulsing*", submitted for presentation in the 17th North American Catalysis Society Meeting, to be held in Toronto, Canada, on June 3-8, 2001 (see Appendix I).

2. Six-page camera-ready manuscript entitled "*Effect of Periodic Pulsed Operation on Product Selectivity in Fischer-Tropsch Synthesis on Co-ZrO₂/SiO₂*", submitted for oral presentation and publication in the Proceedings of the 6th Natural Gas Conversion Symposium, to be held in Girdwood, Alaska, on June 17-21, 2001 (see Appendix II).

Keywords

Chain-limiting
Cobalt
Diesel
Fischer-Tropsch synthesis
Iron
Pulsing
Ruthenium

1. INTRODUCTION

The Fischer-Tropsch synthesis (FTS) can convert solid fuel- or natural gas-derived syngas ($CO+H_2$) to liquid fuels and high-value products. The extensively reviewed Fischer-Tropsch (FT) reaction [1-3] produces a non-selective distribution of hydrocarbons (C_1-C_{100+}) from syngas. FT catalysts are typically based on Group-VIII metals (Fe, Co, Ni, and Ru), with Fe and Co most frequently used. The product distribution over these catalysts is generally governed by the Schultz-Flory-Anderson (SFA) polymerization kinetics [4].

Currently there is significant commercial interest in producing diesel-fuel range middle distillates (C_{10}-C_{20} paraffins) from natural gas-derived syngas [5]. Increasing the selectivity of FTS to desired products such as diesel (C_{10}-C_{20}) or gasoline (C_5-C_{11}) by altering the SFA distribution is economically attractive. Use of bifunctional catalysts (FT-active metals on zeolite, e.g. ZSM-5) to produce high-octane gasoline-range hydrocarbons (explored in the past 2 decades), has been economically unsuccessful [6-9]. The zeolite cracking activity lowers the chain-growth probability (α), producing gasoline-range products in excess of 48 wt% of the total hydrocarbon, but it also produces a significant amount of undesirable C_1-C_4 gases (Figure 1).

The present emphasis has shifted towards maximizing the yield of high-cetane C_{10}-C_{20} products from FTS. Increased worldwide demand for low-sulfur diesel has further stressed the importance of development of zero-sulfur FT-diesel products. An alternative approach to the use of bifunctional catalysts to alter selectivity is periodic FT reactor operation (pulsing) [3]. It entails alternatively switching between two predetermined input compositions over the FT catalyst to promote time-average rate, selectivity, and catalyst life [10-12]. Periodic pulsing of H_2 has been examined so as to limit chain growth by removing the growing hydrocarbon chain from the catalyst surface [13-15]. Experimental studies have shown the potential to alter the SFA distribution [16,17]; they were performed, however, at conditions of limited industrial interest.

The chain-limiting concept using pulsing to maximize diesel yield is shown in a plot of carbon number vs. mole fraction (Fig. 1). The slope of the curve is determined by the chain-growth probability, α. Periodic operation on a high-α catalyst may result in removal of the growing chain from the surface at the desired C_{10}-C_{20} length, thereby maximizing diesel yield without increasing the dry gas.

The objective of this study is to investigate the effect of pulsing on the activity and product distribution of high-α FT synthesis catalysts, in an attempt to maximize the C_{10}-C_{20} product yield.

Figure 1.1. Product distribution (α-plot) for FT synthesis

2. EXPERIMENTAL

2.1. Reaction Set-Up

The reaction system consisted of the gas-feed, a fixed-bed reactor, and a sampling/analysis system for the liquid and gaseous products. The feed system blended CO/Ar, H_2, N_2, or other premixed gases in desired concentrations. The feed streams enter through the top of the reactor. Mass flow controllers (from Brooks) were used to control the flow rate of the feed streams. They operated in a fail-closed mode in order to stop the flow of the feed gases to the reactor in the event of a power/controller failure.

A time-programmable interface system (Carolina Instrumentation Co.) was used to control a series of actuated valves, so that a (reactant or inert) flow opened / closed automatically and independently of the others. Appropriate periodic switch of these valves offered the capability to perform various pulsing-type experiments with this configuration. Pulse time could be varied from 1 min to 48 hours. All valves automatically switched to their respective fail-safe position (N_2 open, all others closed) in the event of power failure.

A stainless-steel 3/8-in o.d. (0.305-in i.d.) downflow reactor was enclosed in a three-zone programmable furnace. A 90-μm sintered stainless-steel frit, held in place by a welded cap, was placed at the bottom of the reactor. It supported the catalyst bed and prevented the removal of catalyst fines from the catalyst bed into the liquid product stream. A "dual-profile" internal bed thermocouple measured the bed temperature at two points: 1 inch from the top of the bed and 3 inches from the bottom of the bed.

The liquid products were collected and separated into a wax trap (waxes) maintained at 140°C and a water trap (oil + water) maintained at 25°C. Two sets of these traps, positioned in parallel, enabled continuous operation. A Kammer back-pressure-control valve, located down-stream of the traps, controlled the reactor and trap pressure.

An on-line GC-Carle (TCD) analyzed the permanent gases (H_2, CO_2, Ar, N_2, CH_4, CO). Argon was used as internal standard. An on-line GC-FID (100-m Petrocol column, ramped from –25 to 300°C) analyzed the light hydrocarbons (C_1-C_{15}). A third off-line GC-FID (15-m SPB-1 capillary column, 0.1-μm, ramped from 50 to 350°C) analyzed the composite wax and oil collected from the wax and water traps, respectively.

2.2. Catalytic Materials

The following catalysts were examined in terms of their activity and product selectivity with respect to the application of various pulse schemes:

a) a high-purity, low-surface-area (0.2-m^2/g) α-alumina (SA 5397, Norton), which was also used for diluting the other examined FT catalysts,

b) a high-**α** (~0.9) 25pbw Co-18pbw Zr-100pbw SiO_2 catalyst, synthesized at RTI,

c) a very-high-**α** (~0.95) Fe/K/Cu/SiO_2 catalyst, synthesized by the Hampton University, RTI, University of Pittsburgh team under another DOE contract (DE-FG22-96PC96217), and

d) a potentially very-high-**α** (0.95 or more) 0.5wt% Ru/alumina catalyst (synthesized by Henry Lamb at North Carolina State University, in sub-contract to RTI).

3. RESULTS AND DISCUSSION

3.1. FT Reaction on α-Alumina

A preliminary FT reaction run was performed on a low-surface-area (~0.2 m^2/g) high-purity α-alumina sample (SA 5397, Norton). This alumina was used for diluting the other examined FT catalysts included in this report. The objective of this experiment was to establish a "blank-run" activity in the absence of a metal-supported FT catalyst.

The reactor was loaded with 17.7 cc (28.32 g) of α-alumina. The sample was reduced *in-situ* under H$_2$ at 350°C for 14 h, and was cooled and pressurized to ca. 300 psig (19.4 atm). The FT reaction was started by feeding a 10%Ar/CO gas mix, thus establishing the following base reaction conditions:

> Syngas (H$_2$ + CO)=50%, H$_2$:CO=2:1 (i.e., 33.3% H$_2$ and 16.7% CO)
> Inerts (N$_2$ + Ar)=50% (1.7% Ar, 48.3% N$_2$)
> P=300 psig, F=200 scc/min, SV=6000 h^{-1}.

The reaction temperature was stabilized at 208°C, thus allowing the reaction to reach a "pseudo-steady state". Under these reaction conditions a moderate (<10%) CO conversion is observed initially (Figure 3.1.1). Then, the α-alumina shows no FT activity, thus establishing a true "blank" run at 208°C.
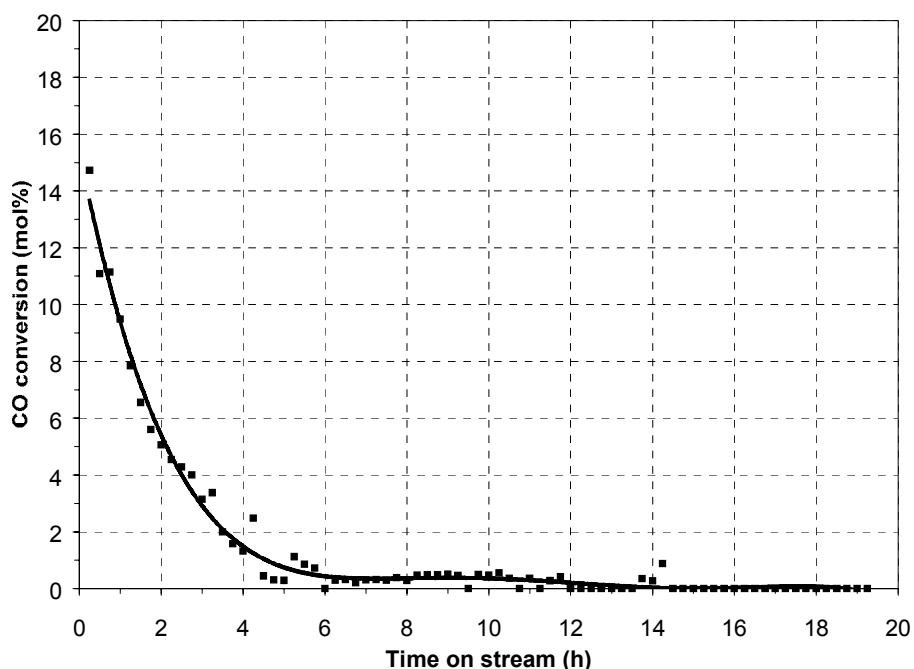
Figure 3.1.1. CO conversion on α-alumina @208°C;
P=300 psig; SV=6000 h^{-1}.

The reaction T was then gradually increased to 270°C (maximum temperature for Fe-FT reaction). The observed CO conversion also remains essentially zero at this reaction temperature. After 4 hours on stream a 1-min H_2 pulse per 1 hour was applied, so as to establish any background activity when pulses are used. Pulse runs involved substituting the reactant feed flow (H_2+CO/Ar) with an equal molar flow of a pulse gas. The total molar flow and the reaction pressure were kept constant between base and pulse runs. Seventeen such H_2 pulses (in a period of 17 hours) were applied. The effect on the outlet H_2:CO ratio is shown in Figure 3.1.2.

Due to the 15-min analysis time of the permanent gases (H_2, CO_2, Ar, N_2, CH_4, CO), only 4 data points could be obtained for every 1-hour pulse cycle. In order to better observe the effect of a given pulse, a "delay time" is defined as the time difference between the end of a pulse and the following GC data point. The need for applying a delay time arises from the fact that a step change in the reactant feed cannot be instantaneously detected due to the dead volume of the reaction/analysis system. A delay time of 5 min was used, i.e., the first 1-min H_2 pulse was completed at 4 hours and 55 min on stream and the next data point was obtained at 5 hours on stream, as shown in Figure 3.

The results of Fig. 3.1.2 indicate that the applied H_2 pulses cause an increase in the outlet H_2:CO ratio (up to ca. 2.4), but this ratio is moderately quickly restored to a value of ca. 2. A minimal reactor pressure variation (ca. 3 psi, i.e., ca. 1% of the measured pressure) is observed during each pulse. The measured CO conversion is also essentially zero throughout this run, thus establishing a zero-activity baseline for the FT reaction at 270°C even under a typical H_2 pulse sequence.
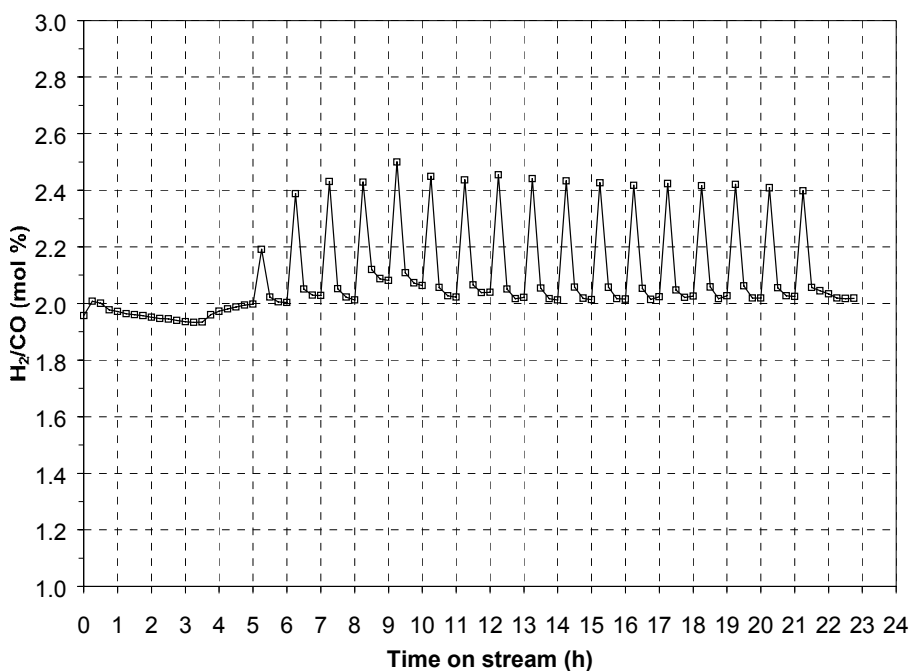
Figure 3.1.2. Effect of H_2 pulse (1 min per 1 hour) on outlet H_2:CO ratio @270°C; P=300 psig; SV=6000 h^{-1}.

3.2. FT Reaction on 25pbw Co-18pbw Zr-100pbw SiO$_2$

A 25pbw Co-18pbw Zr-100pbw SiO$_2$ catalyst was synthesized by sequential incipient wetness impregnation of a high-purity, high-surface-area (144-m^2/g) silica support (XS 16080, Norton) [18]. The support (crushed and sieved to a particle size of 100-150 μm) was degassed in vacuum and heated to 80°C. A zirconium tetrapropoxide (Zr(OCH$_2$CH$_2$CH$_3$)$_4$) solution in 1-propanol (Aldrich) was used for the incipient wetness impregnation, performed in two steps. After each impregnation step, the product was dried (120°C, 2 h) and calcined in air (500°C, 1 hour). The produced material had a nominal loading of 18pbw Zr/silica.

Cobalt was impregnated on the zirconia/silica support using a cobalt nitrate hexahydrate precursor (Co(NO$_3$)$_2$.6H$_2$O, Aldrich). The hexahydrate was dissolved in water and the formed solution was added in a controlled manner to the zirconia/silica support, forming the catalyst with a nominal composition of 25pbw Co-18pbw Zr-100pbw SiO$_2$. Finally, the catalyst was calcined in air at 350°C for 1 hour.

The surface area of the Co-ZrO$_2$/SiO$_2$ catalyst was measured (by BET method) to be 102±3 m^2/g. Its pore volume was estimated at 0.40±0.01 cc/g (by mercury porosimetry). Its crystalline structure was examined by X-ray diffraction (XRD). The predominant phase was Co$_3$O$_4$, with no other Co-O or Zr-O crystalline phases or cobalt silicate present in the diffraction pattern.

A physical mixture of 2 cc (1.55 g) of the calcined Co-ZrO$_2$/SiO$_2$ catalyst and 10 cc (15.91 g) of a low-surface-area (0.2 m^2/g) α-alumina (SA5397, Norton) was loaded into the reactor. The catalyst was reduced *in-situ* under H$_2$ at 350°C for 14 h, and was cooled and pressurized to ca. 300 psig (19.4 atm). The FT reaction was initiated by feeding a 10%Ar/CO gas mix, thus establishing the following base reaction conditions:

> Syngas (H$_2$ + CO)=50%, H$_2$:CO=2:1 (i.e., 33.3% H$_2$ and 16.7% CO)
> Inerts (N$_2$ + Ar)=50% (1.7% Ar, 48.3% N$_2$)
> P=300 psig, F=200 scc/min, SV=6000 h^{-1}.

The reaction temperature was increased (by 0.5°C/h or less) to 220°C and was stabilized at this value, thus allowing the reaction to reach a "pseudo-steady state". Pulse runs involved substituting the reactant feed flow (H$_2$+CO/Ar) with an equal molar flow of a pulse gas. The total molar flow and the reaction pressure were kept constant between base and pulse runs.

A "blank" pulse run (i.e., switching between two equal flows of H$_2$/CO/Ar reactant mix) was performed in order to identify the possible effect of the periodic pressure disturbance (directly related to the applied pulse) due to non-ideal switching of the actuated valves. This run produces no measurable variation on CO conversion, H$_2$:CO ratio, or product distribution (α-value, C$_{10}$-C$_{20}$ yield), as seen in Table 3.2.1. Therefore, pulse runs involving no variations in the feed composition have no effect on measurements of the progress of the FT reaction.

Table 3.2.1. Effect of "blank" pulse on the performance of Co-ZrO$_2$/SiO$_2$ @220°C.

Run type	Pulse gas	T (°C)	X(CO) (%)	S(CH$_4$) (mol%)	Alpha (-)	Y(CH$_4$) (cc/cc/h)	Y(C$_{10}$-C$_{20}$) (cc/cc/h)
Base run	-	220	13.0	14.5	0.89	0.014	0.025
Blank pulse	H$_2$+CO/Ar	220	13.0	15.0	0.89	0.014	0.021

Table 3.2.2. Effect of inert (N2) pulse on the performance of Co-ZrO2/SiO2 @224°C.

Run type	Pulse gas	T (°C)	X(CO) (%)	S(CH$_4$) (mol%)	Alpha (-)	Y(CH$_4$) (cc/cc/h)	Y(C$_{10}$-C$_{20}$) (cc/cc/h)
Base run	-	224	15.0	14.5	0.89	0.016	0.027
Inert pulse	N$_2$	224	15.0	14.5	0.89	0.018	0.022
Base run	-	224	15.5	14.0	0.88	0.017	0.027

A 1-min N$_2$ (inert) pulse per 1 hour (i.e., substituting the H$_2$/CO/Ar flow, which is 51.7% of the total, with an equal flow of N$_2$ for 1 min every hour) was applied so as to examine the effect of inert pulsing on the reaction progress. The N$_2$ pulse gives only minimal variations in activity (CO conversion) or product selectivity (α-value, CH$_4$ yield, C$_{10}$-C$_{20}$ yield) as shown in Table 3.2.2, implying that short (1-min) disruptions in reactant flow do not substantially affect the FT reaction.

In contrast to the inert pulse, a 1-min H$_2$ (reactant) pulse causes significant variations in CO conversion and CH$_4$ selectivity. Effects of varying the H$_2$ pulse frequency (1-min H$_2$ per 1, 2, and 4 hours) on the CO conversion and the C$_1$ (CH$_4$ and CO$_2$) selectivity are shown in the composite plots of Figures 3.2.1 and 3.2.2, respectively. These plots are composed of 10-hour segments of a series of sequential runs (typically lasting 48 hours, so as to collect sufficient amounts of oil + wax for the analysis), starting and ending with a base (no pulse) run. The data points correspond to measurements of the reactor effluent gas every 15 minutes.

A 1-min H$_2$ pulse per 1-hour (10-20-hour segment in Figs. 3.2.1 and 3.2.2) causes a significant increase in CO conversion (from 16% to ca. 30%). The measured temperature of the catalyst bed also increases to 226°C, indicating a strong reaction exotherm. The conversion of CO decreases *gradually* until the next H$_2$ pulse. A less-pronounced increase in CO conversion is also observed for the 1-min H$_2$ pulse per 2-h and 4-h runs. The observed decrease in CO conversion after the pulse indicates that the activity tends to return to its steady state (comparing also the base runs before and after the 3 pulse runs). The measured changes in CO conversion cannot be attributed to variations in the inlet CO concentration since the conversion was based on comparing the inlet and outlet *ratios* of CO to the inert Ar (fed at a fixed ratio from a single gas cylinder).

The selectivity to CH$_4$ is observed to increase *instantaneously* after each H$_2$ pulse (from 13-14% to ca. 20% for all examined pulse runs). It is then quickly restored to its base value (Fig. 3.2.2). Thus, H$_2$ pulsing increases catalytic activity while only briefly increasing the undesirable formation of CH$_4$.

The effect of varying H$_2$ pulse frequency on the desired C$_{10}$-C$_{20}$ yield vs. the undesired CH$_4$ yield is shown in Figure 3.2.3. Pulse frequencies of 1, 0.5, and 0.25, h^{-1} correspond to a 1-min H$_2$ pulse per 1, 2, and 4 hours, respectively. The zero pulse frequency corresponds to the average of the two no-pulse (base) runs before and after the 3 pulse runs.

Both C$_{10}$-C$_{20}$ and CH$_4$ yields increase with H$_2$-pulse frequency (and so does the yield of C$_{21+}$), obviously due to the enhancement in catalytic activity caused by the pulsing (Fig. 3.2.1). As seen in Fig. 3.2.3, the effect of the 1-min H$_2$ pulse per 1 hour compared to the (average) base run is to increase the C$_{10}$-C$_{20}$ yield by ca. 57%, while the CH$_4$ yield only increased by ca. 34%.
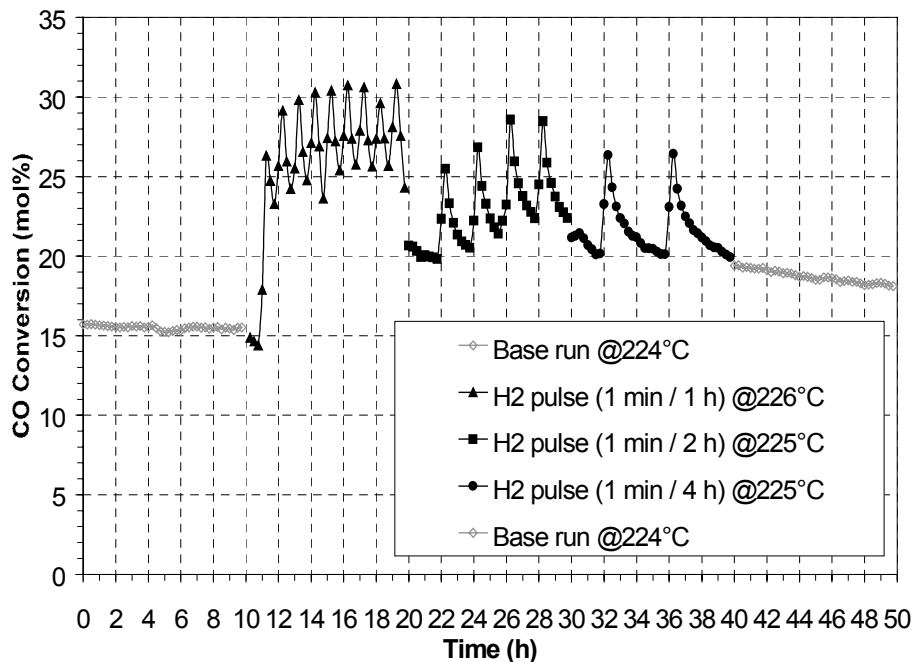
Figure 3.2.1. Effect of H_2 pulse frequency on CO conversion of Co-ZrO$_2$/SiO$_2$ @300 psig and 6000 h^{-1}.
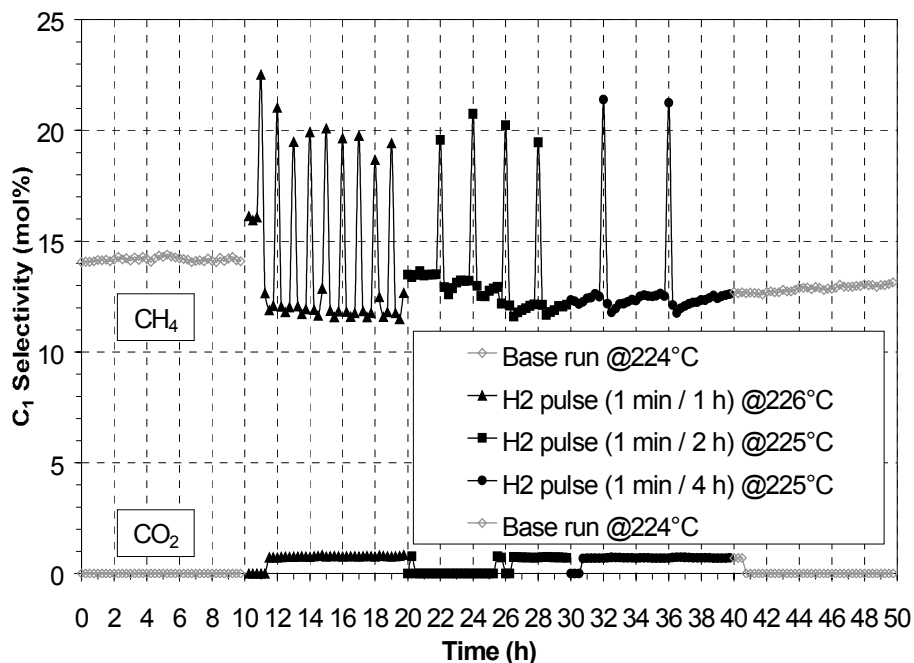
Figure 3.2.2. Effect of H_2 pulse frequency on C_1 selectivity of Co-ZrO$_2$/SiO$_2$ @300 psig and 6000 h^{-1}.
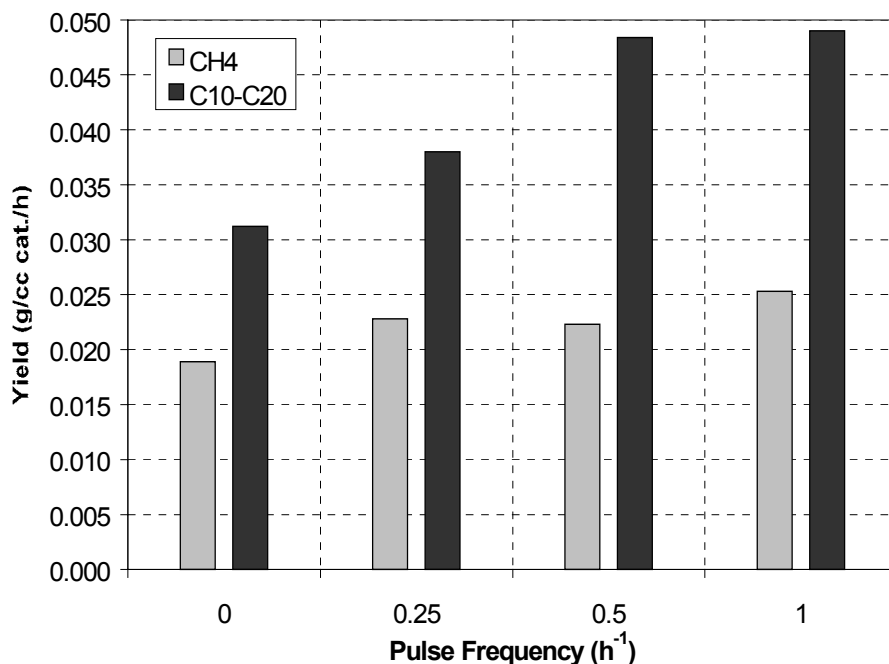
Figure 3.2.3. Effect of H_2 pulse frequency on product yield of Co-ZrO$_2$/SiO$_2$ @300 psig and 6000 h^{-1}.

Although this comparison entails a temperature change (from 224°C to 226°C), the increase in the C_{10}-C_{20} yield is more than what could be accounted for solely by a 2°C increase in reaction temperature.

The CH_4 selectivity in the pulse runs (13-14% on molar basis) is lower than that of the base runs (15.5%), whereas the selectivity to C_{10}-C_{20} and C_{21+} compounds is higher (28-32% vs. 27%, and 23-24% vs. 20%, respectively). The α-values of the pulse runs (based on the molar fractions of C_{10}-C_{65} products) are found to be essentially identical to that of the base runs (0.890±0.005). Thus, the applied H_2 pulsing apparently does not alter the SFA distribution.

Within the examined pulse frequency range, the greater difference between the yields of the desirable C_{10}-C_{20} and the undesirable CH_4 is obtained at the *intermediate* pulse frequency of 0.5 h^{-1} (1-min H_2 per 2 hours). Also, upon extrapolating to higher H_2-pulse frequencies, we could expect a stronger reaction exotherm and thus an increase in reaction temperature, which is known to cause a shift in FTS product distribution to lower molecular weight compounds and to enhance the methanation reaction [4]. Higher pulse frequencies would thus tend to increase the CH_4 yield much more than the C_{10}-C_{20} yield. An optimum H_2-pulse frequency (depending on catalyst and reaction conditions) would therefore be required for maximizing the C_{10}-C_{20} yield without substantially increasing the CH_4 yield.

Another series of H_2-pulse runs on the Co-ZrO$_2$/SiO$_2$ catalyst examined the effect of H_2-pulse duration on the outlet H_2:CO ratio, the activity, and product distribution, by varying the pulse duration (1, 2, 4-min of H_2) at a fixed pulse frequency (0.5 h^{-1}). The results of this study are given in the plots of Figures 3.2.4, 3.2.5, and 3.2.6, respectively, composed of superimposed 10-hour segments of sequential runs (typically lasting 48 hours), starting and ending with a base (no pulse) run.

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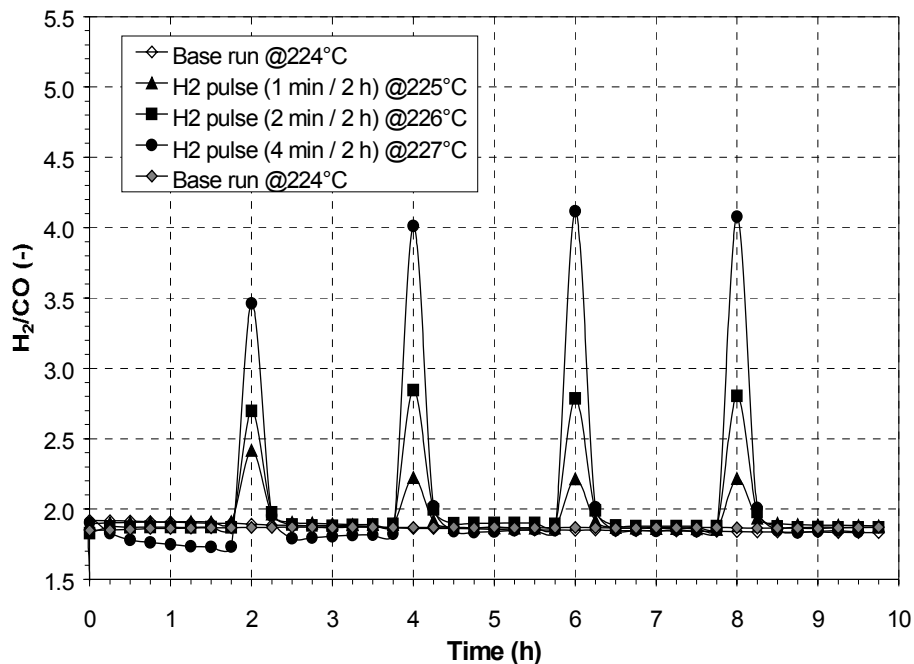
Figure 3.2.4. Effect of H_2 pulse duration on outlet H_2:CO ratio of Co-ZrO$_2$/SiO$_2$ @300 psig and 6000 h^{-1}.
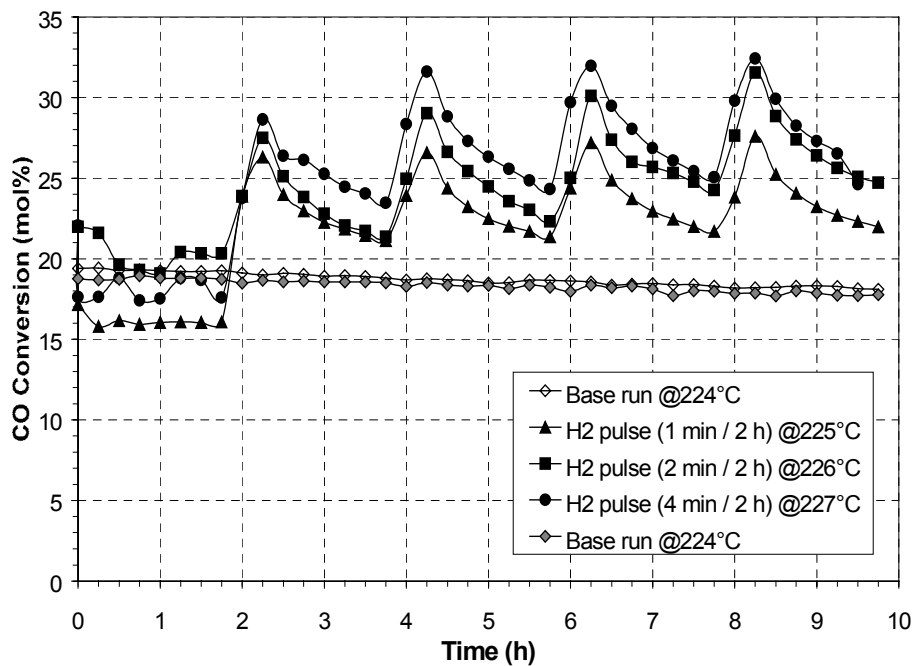
Figure 3.2.5. Effect of H_2 pulse duration on CO conversion of Co-ZrO$_2$/SiO$_2$ @300 psig and 6000 h^{-1}.
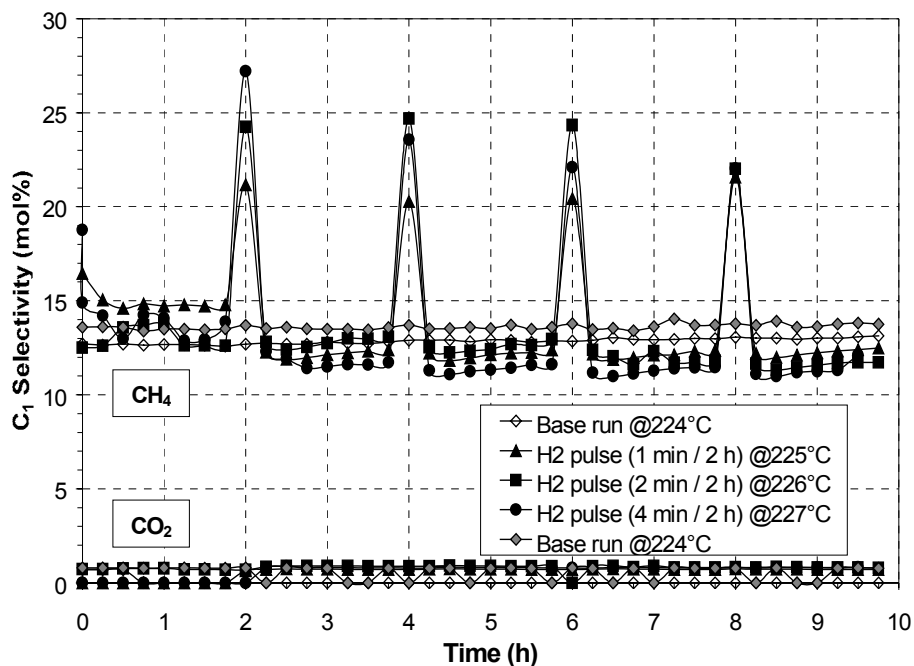
**Figure 3.2.6. Effect of H_2 pulse duration on C_1 selectivity
of Co-ZrO$_2$/SiO$_2$ @300 psig and 6000 h^{-1}.**

As seen in Fig. 3.2.4, an increase in the H_2 pulse duration (1 min, 2 min, 4 min) increases the outlet H_2:CO ratio (from a base value of 1.9 to 2.2, 2.8, and 4.1, respectively). However, this ratio is very quickly (within 20 min, as indicated by the 2nd data point after each pulse) restored to its base value of 1.9. Thus there appears to be no impact of the system "dead" volume (from the catalyst bed to the GC sample loop) on the measured parameters within the examined pulse duration (4 min or less).

As expected, application of a H_2 pulse causes an increase in the measured CO conversion (Fig. 3.2.5). An increase in the H_2 pulse duration (1 min, 2 min, 4 min) increases the maximum obtained CO conversion (from a base value of 18.5% to 27%, 31%, and 32%, respectively). The measured temperature of the catalyst bed also increases (from 224°C to 227°C) indicating a strong reaction exotherm. The conversion of CO decreased *gradually* until the next H_2 pulse (in clear contrast to the observed rapid decrease in the outlet H_2:CO ratio, Fig. 3.2.4). The observed decrease in CO conversion after the pulse indicates that the activity tends to return to its steady state (comparing also the base runs before and after the 3 pulse runs).

The selectivity to CH_4 is observed to increase *instantaneously* after each H_2 pulse and to eventually stabilize to a common maximum value (from 12-14% to ca. 22% for all 3 examined pulse runs). It is then quickly restored to its base value (Fig. 3.2.6). On the other hand, the CO_2 formation remains very low (selectivity below 1%) for both base and pulse runs. The similar time-dependence of the measured outlet H_2:CO ratio and selectivity to CH_4 (Figs. 3.2.4 and 3.2.6) imply a correlation between the increase in H_2 concentration (caused by pulsing) and the extent of the methane formation reaction. The FT reaction, however, appears to have a different dependence on the inlet H_2 concentration compared to the undesirable CH_4 formation, since it progresses within a different time-frame (Fig. 3.2.5).

The effect of the H_2 pulse duration on the product distribution of the Co-ZrO_2/SiO_2 catalyst is shown in the form of the logarithm of the molar fraction of the hydrocarbon products (C_1-C_{65}) vs. the corresponding carbon number (α-plot) in Figure 3.2.7. Only the α-plots produced by the initial base run and two H_2 pulse runs are shown for purposes of clarity. A straight line with a slope that corresponds to $\alpha = 0.9$ is also shown for comparison.

The produced curves of Fig. 3.2.7 appear to be almost overlapping, indicating only minor variations in the product distribution between base and pulse runs, as well as between two pulse runs of different H_2 pulse duration (1 min vs. 2 min). The slopes of these curves (based on the molar fractions of the C_{10}-C_{65} range) are very similar to each other and to that of the $\alpha = 0.9$ curve. Indeed, the α values of these runs (as well as those of the other base and pulse runs not included in the graph of Fig. 3.2.7) are equal to 0.890±0.005. Therefore, the applied variable-duration H_2 pulsing apparently does not alter the SFA distribution, similar to the applied variable-frequency H_2 pulsing.

The effect of varying H_2 pulse duration on the desired C_{10}-C_{20} yield vs. the undesired CH_4 yield is shown in Figure 3.2.8. The zero pulse duration corresponds to the average of the two no-pulse (base) runs before and after the 3 pulse runs. Both C_{10}-C_{20} and CH_4 yields increase with H_2-pulse duration (and so does the yield of C_{21+}), obviously due to the enhancement in catalytic activity caused by the pulsing (Fig. 3.2.5). As seen in Fig. 3.2.8, the effect of the 4-min H_2 pulse per 2 hours compared to the (average) base run is to increase the C_{10}-C_{20} yield by ca. 45%, while the CH_4 yield only increased by ca. 28%. This comparison entails a temperature change (from 224°C to 227°C); however, the increase in the C_{10}-C_{20} yield is more than what could be accounted for solely by a 3°C increase in reaction temperature.
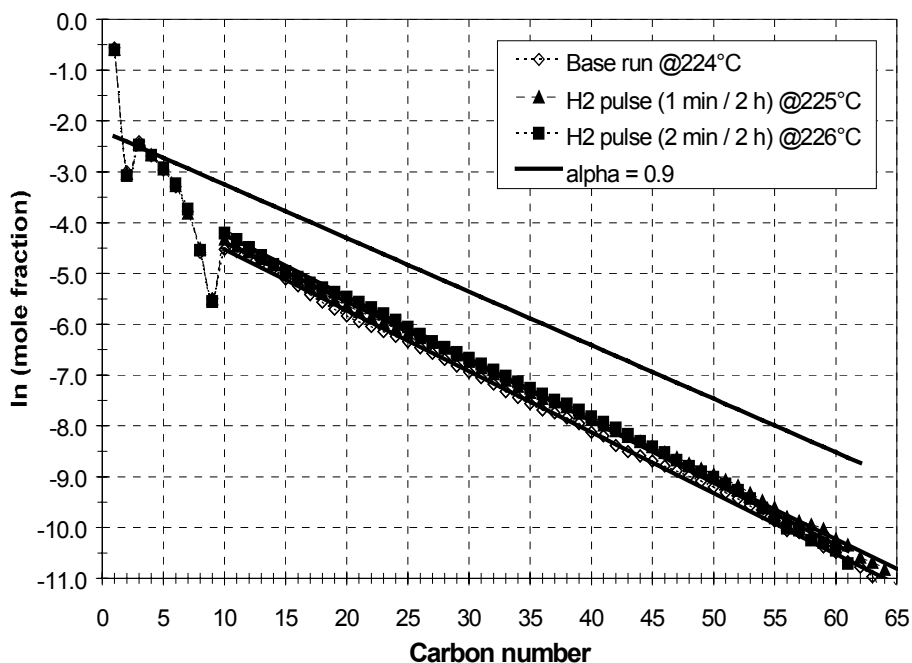
Figure 3.2.7. Effect of H_2 pulse duration on product distribution (α-plot) of Co-ZrO_2/SiO_2 @300 psig and 6000 h^{-1}.
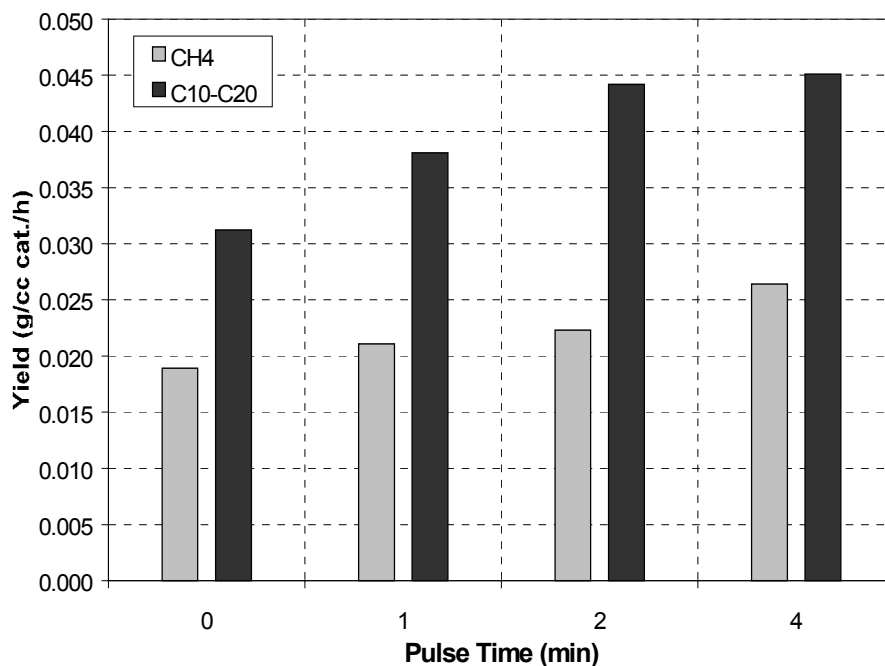
Figure 3.2.3. Effect of H_2 pulse duration on product yield of Co-ZrO$_2$/SiO$_2$ @300 psig and 6000 h^{-1}.

Within the examined pulse duration range, the greater difference between the yields of the desirable C_{10}-C_{20} and the undesirable CH_4 is obtained at the *intermediate* pulse duration of 2-min H_2 per 2 hours. In addition, upon extrapolating to higher H_2-pulse duration, we could expect a stronger reaction exotherm and thus an increase in reaction temperature, which is known to cause a shift in FTS product distribution to lower molecular weight compounds and to enhance the methanation reaction [4]. Higher pulse duration would thus tend to increase the CH_4 yield much more than the C_{10}-C_{20} yield, in a similar manner to the effect of increasing pulse frequency. Therefore, an optimum set of both H_2-pulse parameters (pulse frequency and pulse duration) would be required for maximizing the formation of diesel-range FT products.

Additional experiments included studying the effect of pulsing (at 1 min per 1 hour) with a pulse gas other than H_2 (namely, 50%H_2/N_2 and 24%CO_2/N_2). The dilute-H_2 pulse had minimal impact on CO conversion and C_{10}-C_{20} yield compared to the full H_2 pulse. The CO_2 pulse had a minimal effect on CO conversion and a positive effect on the selectivity to CH_4 (from 18% to 24%), resulting in low C_{10}-C_{20} yield. Despite some increased uncertainty on the obtained data, the effect of CO_2 pulsing appears to be not promising (or minimal at best).

A final set of experiments involved changing reaction conditions by lowering the H_2+CO molar flow (or partial pressure) to 16.7% instead of the standard 50%, and adding 10% steam. A 1-min H_2 pulse per 1 hour run was performed under these new reaction conditions. The addition of steam caused a decrease in both CO conversion (from 32.55 to 23.5%) and selectivity to CH_4 (from 14% to 9%). The applied H_2 pulse restored partially both CO conversion (29%) and CH_4 selectivity (13%). Due to increased difficulty in collecting and analyzing the wax product, these experiments (i.e., pulsing in the presence of steam) should be repeated.

3.3. FT Reaction on Fe/K/Cu/SiO$_2$ catalyst (HPR-43)

The effect of pulsing on the FT synthesis activity and product distribution of a very-high-α (~0.95) Fe/K/Cu/SiO$_2$ catalyst, synthesized by the Hampton University, RTI, University of Pittsburgh team under another DOE contract (DE-FG22-96PC96217), was examined. A series of runs were performed after establishing a "pseudo-steady state" at appropriate reaction conditions, including H$_2$, 24%CO$_2$/N$_2$, and CO pulses. The objective of this series of runs was to examine the effect of various pulsing types on the FT reaction activity and the C$_{10}$-C$_{20}$ yield of the Fe/K/Cu/SiO$_2$ catalyst (denoted as HPR-43).

A physical mixture of 3 cc (3.04 g) of catalyst HPR-43 and 9 cc (14.41 g) of a low-surface-area (0.2 m^2/g) α-alumina (SA5397, Norton) was loaded into the 3/8 in o.d. stainless steel reactor, between two beds of the α-alumina.

The catalyst was reduced *in-situ* under a reactant (H$_2$+CO/Ar) gas mixture (H$_2$:CO=0.67, CO:Ar=9) at 280°C for 8 hours, it was cooled to 112°C and was then gradually pressurized to ca. 300 psig (19.4 atm), establishing the following base reaction conditions:

> Reactants: CO=24.75%, H$_2$=16.5% (H$_2$:CO=0.67, H$_2$+CO=41.25%)
> Inerts: Ar=2.75% (CO:Ar=9), N$_2$=56%
> P=300 psig, F=300 scc/min, SV=6000 h^{-1}.

The reaction temperature was increased so as to start the FT reaction, and was stabilized at 231°C, allowing the reaction to reach a "pseudo-steady state". Pulse runs involved substituting the reactant (H$_2$+CO/Ar) feed flow (44% of total molar flow) with an equal molar flow of a pulse gas, namely H$_2$, 24% CO$_2$/N$_2$, or CO. The total molar flow and reaction pressure was maintained constant between base and pulse runs. A single pulse sequence of 1 min per 1 hour was applied in all cases.

Effect of H$_2$ pulse at 231°C

After establishing a "pseudo-steady state" at 231°C and 298±2 psig, a 1-min H$_2$ pulse per 1 hour was applied. One 8-hour run was performed under these conditions. The reactant feed was then returned to its standard composition (base run) and the catalyst attained a new "pseudo-steady state" at 230°C.

The effect of the H$_2$ pulse on the outlet H$_2$:CO ratio, CO conversion, and C$_1$ (CH$_4$/CO$_2$) selectivity vs. time-on-stream is shown in Figures 3.3.1, 3.3.2, and 3.3.3, respectively. The last 8 hours of the initial base run are shown as the first 8 hours (0-8 h) in these figures. The 8-hour H$_2$-pulse run is shown next (8-16 h), followed by the first 8 hours of the new base run (16-24 h). The data points correspond to measurements of the reactor effluent gas every 15 minutes.

Due to the 15-min analysis time of the permanent gases (H$_2$, CO$_2$, Ar, N$_2$, CH$_4$, CO), only 4 data points can be obtained for every 1-hour pulse cycle. In order to better observe the effect of a given pulse, a "delay time" is defined as the time difference between the end of a pulse and the following GC data point. The need for applying a delay time arises from the fact that a step change in reactant feed cannot be instantaneously detected due to the dead volume of the reaction/analysis system. A delay time of 5 min was used, i.e., the first 1-min H$_2$ pulse was applied at 8 hours and 55 min (55 min after starting the pulse run), and the next data point was obtained at 9 hours on stream (Figs 3.3.1, 3.3.2, and 3.3.3).
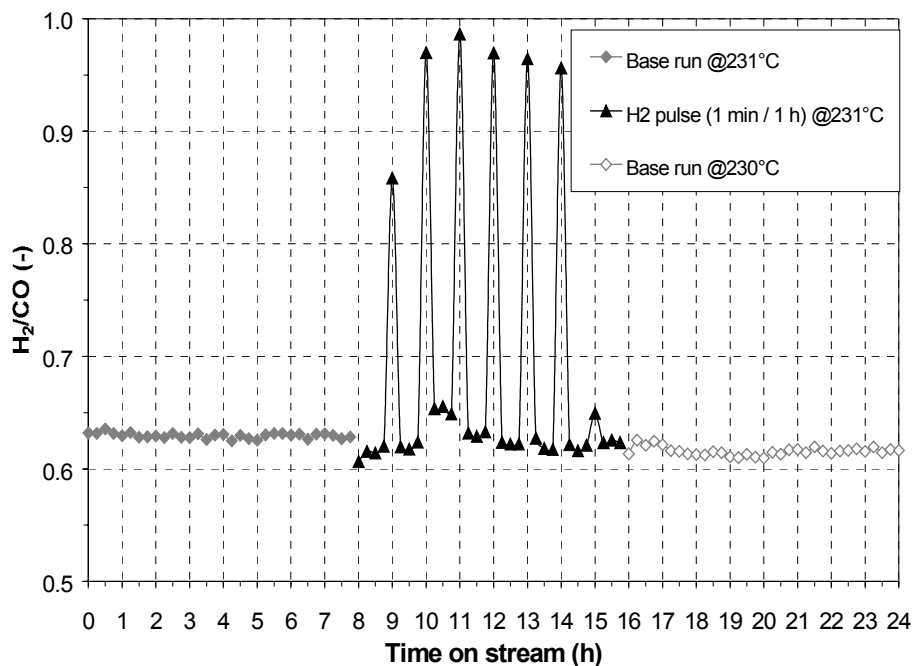
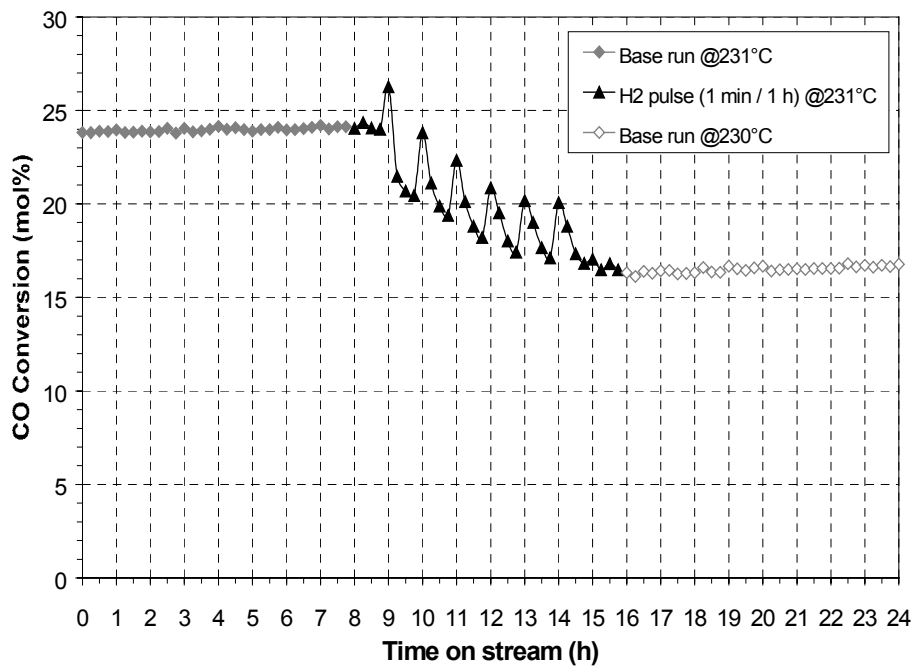**Figure 3.3.1. Effect of H$_2$ pulse on outlet H$_2$:CO ratio of HPR-43 @300 psig and 6000 h^{-1}.**

Figure 3.3.2. Effect of H$_2$ pulse on CO conversion of HPR-43 @300 psig and 6000 h^{-1}.

14
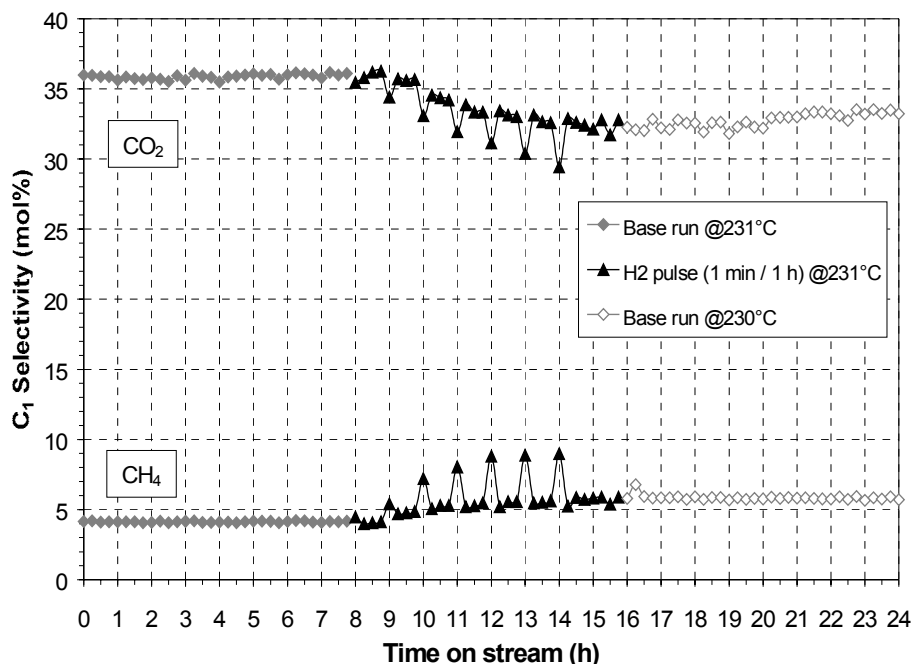
Figure 3.3.3. Effect of H$_2$ pulse on C$_1$ selectivity of HPR-43 @300 psig and 6000 h^{-1}.

The 1-min H$_2$ pulse per 1 hour increases the outlet H$_2$:CO ratio from 0.63 (base run) to ca. 0.95±0.05 (at 5 min after the pulse), but this ratio is quickly restored (after 20 min) to its original value (Fig. 3.3.1). As seen in Fig. 3.3.2, the H$_2$ pulse causes a significant decrease in CO conversion, from ca. 24% (initial base run) to ca. 17% (final base run). The corresponding decrease in CO productivity is from ca. 350 cc/cc cat./h to ca. 250 cc/cc cat./h. The H$_2$ pulse also decreases the selectivity towards CO$_2$ (from ca. 36% down to ca. 33%) and increases the selectivity towards CH$_4$ (from ca. 4% to ca. 6%) (Fig. 3.3.3).

The effect of H$_2$ pulse on the product distribution of HPR-43 at 231°C is presented in the form of the logarithm of the molar fraction of the products vs. the corresponding carbon number (α-plot) in Figure 3.3.4. The product distribution curves for the base run before and after the H$_2$ pulse run are also shown for comparison. The H$_2$ pulse is found to slightly decrease the α-value (from 0.95 to 0.94) while increasing the C$_{10}$-C$_{20}$ weight fraction (from 13.6/15.2% up to 19.8%) and the corresponding yield of this product fraction (from 0.016 g/cc cat./h up to 0.022 g/cc cat./h). Therefore, the H$_2$ pulse has a positive effect on the C$_{10}$-C$_{20}$ yield but also causes a decrease in catalyst activity and an undesirable increase in the selectivity towards CH$_4$.

Effect of 24%CO$_2$/N$_2$ pulse at 230°C

After the base run at 230°C (the results of which are shown in Figs. 3.3.1 to 3.3.4) a 1-min 24%CO$_2$/N$_2$ pulse was applied. With respect to the base runs before and after this pulse, there was essentially no effect on CO conversion (18%) and selectivity to CH$_4$ (5%) or CO$_2$ (35%). The effect of the CO$_2$ pulse on product distribution (compared to that of the base runs before and after the pulse) is shown in Figure 3.3.5. There is no measurable effect of the CO$_2$ pulse on the product distribution as well (α=0.94) or the C$_{10}$-C$_{20}$ yield.

Figure 3.3.4. Effect of H₂ pulse on product distribution of HPR-43 @300 psig and 6000 h⁻¹.

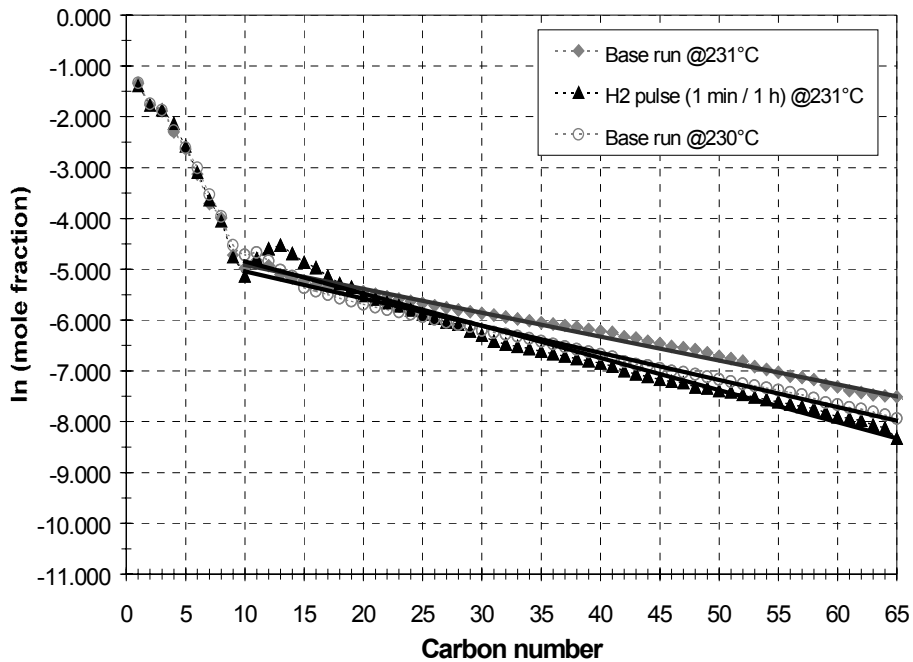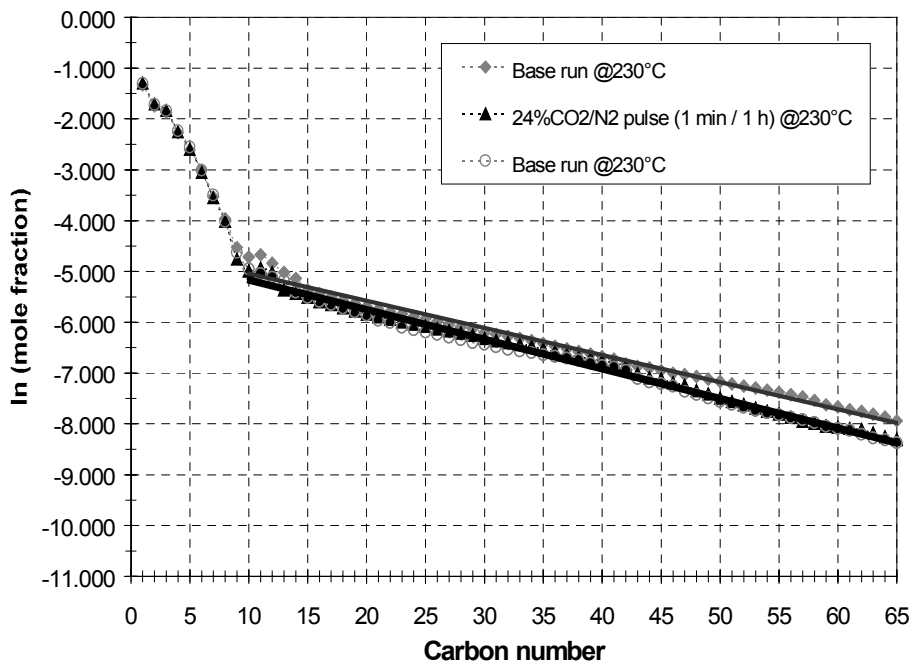**Figure 3.3.5. Effect of 24%CO₂/N₂ pulse on product distribution of HPR-43 @300 psig and 6000 h⁻¹.**

Effect of CO pulse at 246/253°C

At the reaction temperature of 230°C the temperature distribution within the catalyst bed appears to be essentially uniform (difference of ca. 1°C or less between the top and bottom of catalyst bed). However, upon heating up the bed to higher temperatures, an increase in this deviation between top and bottom bed T was observed. After a slow heating process, a new "pseudo-steady state" was established at 246°C (bottom bed T) / 253°C (top bed T).

At these reaction conditions, the effect of a 1-min CO pulse per 1 hour on the outlet H_2:CO ratio, the CO conversion, and the CH_4/CO_2 selectivity vs. time-on-stream is shown in Figures 3.3.6, 3.3.7, and 3.3.8, respectively. The last 12 hours of the base run before the CO pulse are shown as the first 12 hours (0-12 h) in these figures. The 24-hour CO-pulse run is shown next (12-36 h), followed by the first 12 hours of the new base run (36-44 h).

The outlet H_2:CO ratio decreases from ca. 0.7 to ca. 0.5 as a result of the CO pulse (Fig. 3.3.6). As seen in Fig. 3.3.7, the applied CO pulse causes a decrease in CO conversion (from ca. 45% prior to the pulse run down to ca. 41% after the pulse run) as well as in CO productivity (from ca. 670 scc/cc cat./h to ca. 610 scc/cc cat./h). On the other hand, no measurable effect of the CO pulse run on CH_4 and CO_2 selectivity prior to and after the pulse run was observed (Fig. 3.3.8).

The effect of CO pulse on the product distribution of HPR-43 at 246/253°C is shown in the α-plot of Figure 3.3.9. The CO pulse has only minimal effect on the measured α-value (from 0.94 to 0.93), while increasing the C_{10}-C_{20} weight fraction (from 17.1/16.7% up to 21.7%) and the corresponding yield of this fraction (from 0.045/0.041 g/cc cat./h up to 0.053 g/cc cat./h). Therefore, the CO pulse benefits the C_{10}-C_{20} yield without increasing the CH_4 or CO_2 selectivity.

Figure 3.3.6. Effect of CO pulse on outlet H_2:CO ratio of HPR-43 @300 psig and 6000 h^{-1}.
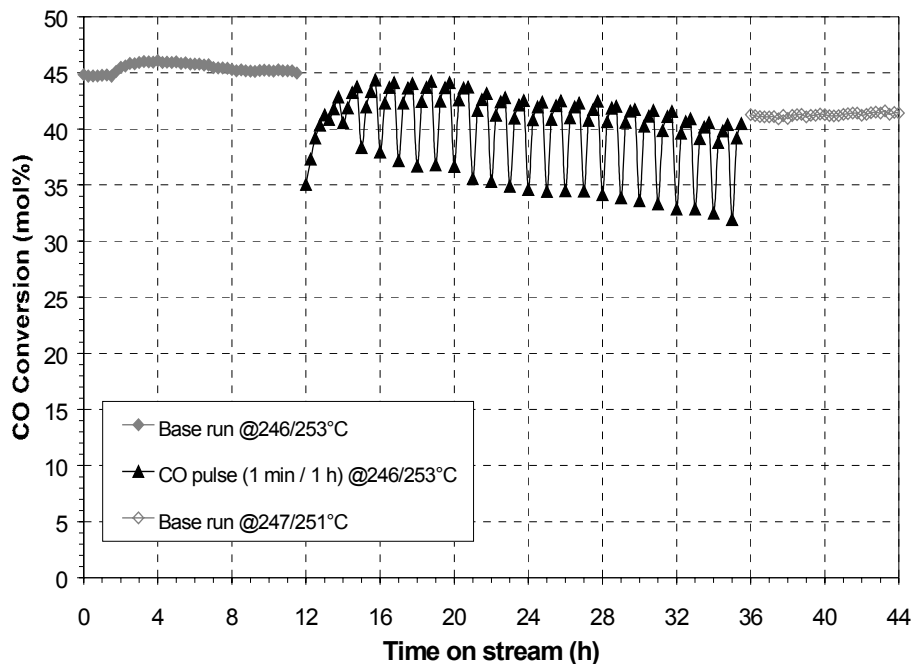
Figure 3.3.7. Effect of CO pulse on CO conversion of HPR-43 @300 psig and 6000 h^{-1}.
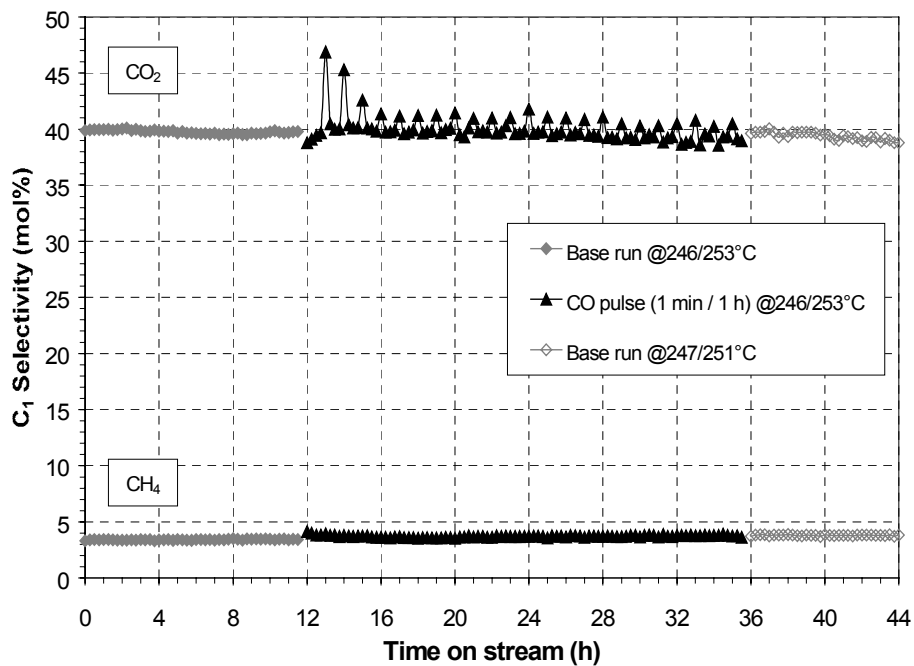
Figure 3.3.8. Effect of CO pulse on C$_1$ selectivity of HPR-43 @300 psig and 6000 h^{-1}.

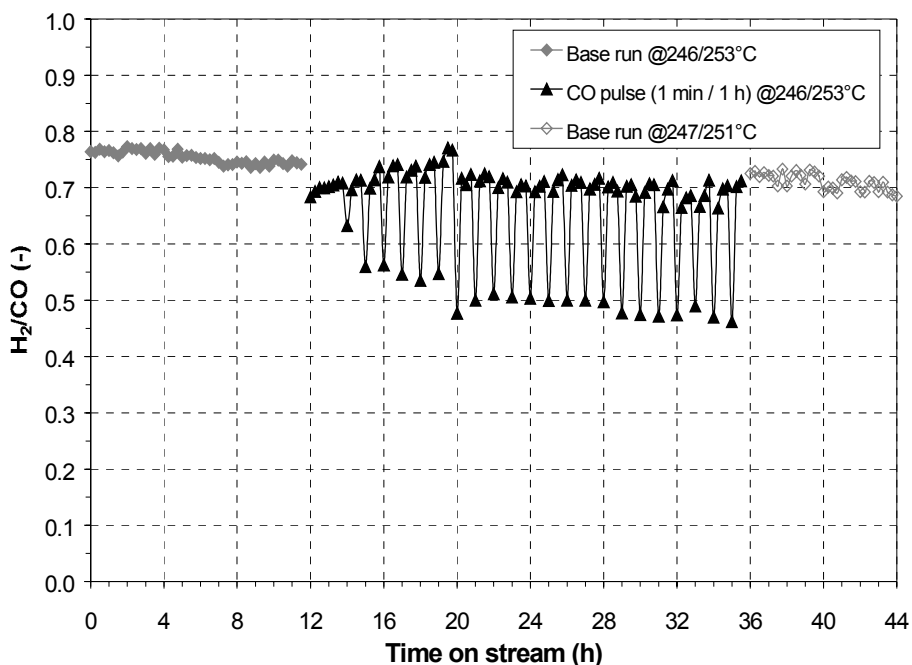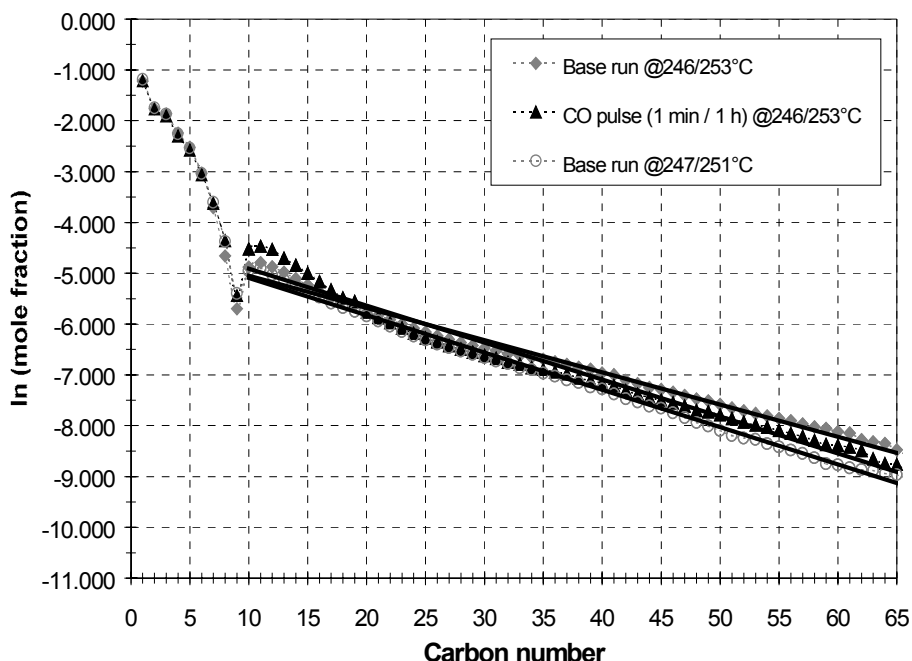**Figure 3.3.9. Effect of CO pulse on product distribution of HPR-43 @300 psig and 6000 h^{-1}.**

Effect of H₂ and CO pulse at elevated temperatures

A 1-min H_2 pulse per 1 hour was applied for a period of 24 hours after the reaction system had reached a new "pseudo-steady state" at 262/272°C. The measured CO conversion decreased from ca. 51% prior to the pulse run to ca. 40% after the pulse run (the corresponding CO productivity was ca. 750 and ca. 600 scc/cc cat./h, respectively). Also, an increase in the selectivity to CH_4 was observed (from ca. 4.5% to ca. 5.5%), whereas there was no measurable variation in the CO_2 selectivity.

A 1-min CO pulse per 1 hour was then applied for 24 hours after reaching a new "pseudo-steady state" at 261/271°C. In good qualitative agreement with previous observations, the CO conversion decreased moderately (from ca. 42% to ca 38.5%) as a result of the CO pulse, whereas the CH_4 and CO_2 selectivity remained constant (ca. 5% and 42%, respectively). Consequently, the observed effect of the H_2 and the CO pulse appears to be applicable throughout the examined reaction temperature range (i.e., from ca. 230°C to ca. 270°C).

3.4. Fixed bed (RTI) and CSTR data (Syntroleum Corp.) of catalyst HPR-43

Syntroleum Corp. performed a CSTR run of FT reaction on catalyst HPR-43. All tests were run at GHSV=2300 h^{-1}, 300 psig, and H_2:CO feed ratio of 0.67, using 10 cc of catalyst in paraffin wax. Because of equipment limitations, the tests were run at 232°C for the first 310 hours; then the temperature was increased to 260°C for an additional 218 hours. Figure 3.4.1. shows the results. The CO productivity at 232°C is ca. 350 cc CO/cc cat/h (corresponding to 25% CO conversion) and remains steady after the first 24 hours. When the temperature was increased to 260°C the conversion initially increases and then decreases to the previous level. This may be due to loss of catalyst from the reactor – possibly due to buildup of wax.
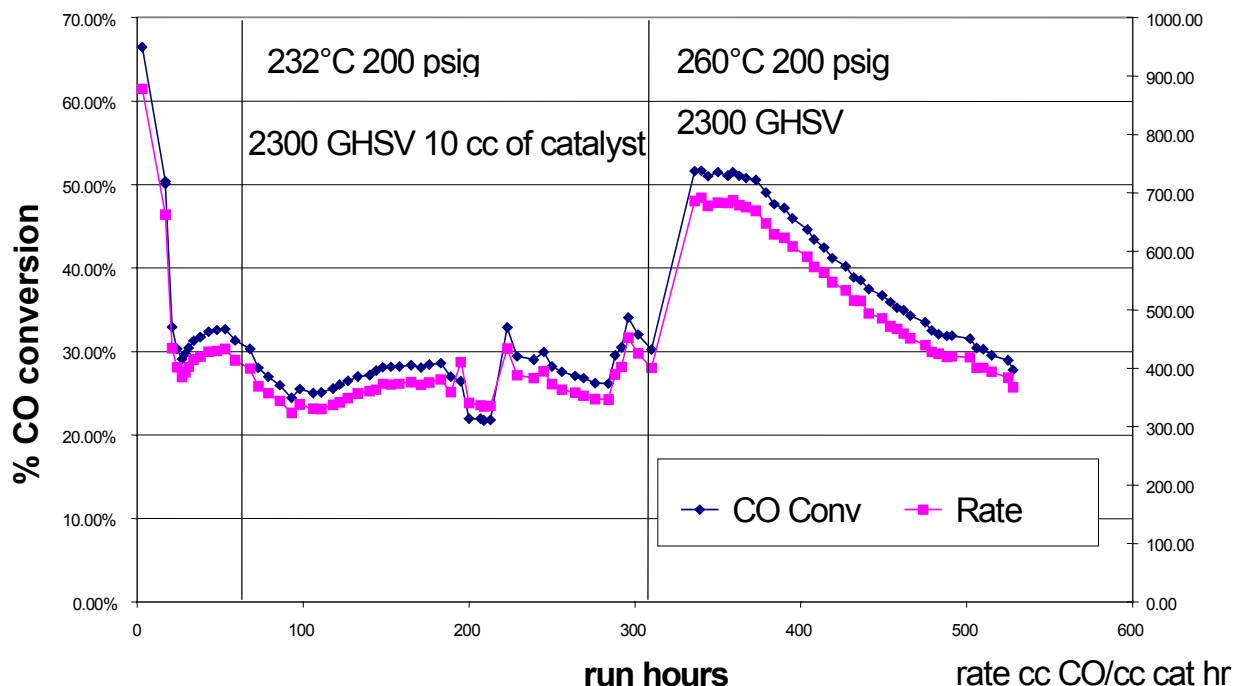
**Figure 3.4.1. % CO conversion and rate (cc CO / cc cat/h)
from CSTR run of RTI catalyst HPR-43.**

A comparison between the fixed bed data (obtained by RTI) and the CSTR data (obtained by Syntroleum) on catalyst HPR-43 is presented in Table 3.4.1.

Table 3.4.1. Fixed bed and CSTR data of catalyst HPR-43.

	Fixed bed		CSTR	
CO (%)	24.8		56.7	
H_2 (%)	16.5		38.4	
N_2 + Ar (%)	58.7		4.9	
SV (h^{-1})	6000		2300	
T (°C)	231	258	230	260
P (psig)	300	300	200	300
CO productivity (cc/cc/h)	350	650	350	800
Alpha (-)	0.95	0.92	0.94	-
Water (g/cc/h)	0.05	0.036	0.022	0.008
Oil + Wax (g/cc/h)	0.07	0.1	0.1	0.13
CH_4 selectivity (mol%)	4.0	4.0	2.2	2.1
C_{10}-C_{20} yield (g/cc/h)	0.016	0.051	-	-

3.5. FT Reaction on 0.5%Ru/Al$_2$O$_3$

A 0.5wt%Ru/Al$_2$O$_3$ catalyst was synthesized (by Henry lamb at North Carolina State University, in sub-contract to RTI) using the incipient wetness impregnation method on a high-purity CATAPAL alumina. After drying, the catalyst was reduced (*without prior calcination*) in 7%H$_2$/Ar at 300°C and was then passivated in air at room temperature. The actual Ru loading (determined by elemental analysis) was 0.5wt%.

A physical mixture of 2 cc (1.77 g) of the reduced Ru/Al$_2$O$_3$ catalyst and 10 cc (16.02 g) of a low-surface-area (0.2 m^2/g) α-alumina (SA5397, Norton) was loaded into the reactor. The catalyst was reduced *in-situ* under H$_2$ at 300°C for 8 h, and was cooled and pressurized to ca. 400 psig (26.2 atm). The FT reaction was started by feeding a 3.3%Ar/33.3%CO/63.4%H$_2$ reactant mixture, thus establishing the following base reaction conditions:

H$_2$=63.4%, CO=33.3% (H$_2$:CO=1.9)
Inert (Ar)=3.3% (Ar:CO=0.1)
F=100 scc/min, SV=3000 h^{-1}, P=26 atm (typical operating pressure: 100-1000 atm).

The reaction temperature was increased slowly to 245°C (typical operating T: 160°C). However, the reaction did not actually reach a "pseudo-steady state"; the CO conversion was found to increase at a very slow rate (from ca. 12% to ca. 18% in a period of 66 hours) and the measured bed temperature was 243°C (bottom) and 252°C (top). Despite not attaining steady state, this isothermal run was followed by a pulse run, involving substitution of the reactant feed flow (H$_2$/CO/Ar) with an equal molar flow of a pulse gas (H$_2$). The total molar flow and the reaction pressure were kept constant between base and pulse runs. A pulse sequence of 1 min per 1 hour was applied. The time-on-stream data on the outlet H$_2$:CO ratio, the CO conversion, and selectivity to CH$_4$/CO$_2$ are shown in Figures 3.5.1, 3.5.2, and 3.5.3, respectively.

**Figure 3.5.1. Effect of H$_2$ pulse on outlet H$_2$:CO ratio
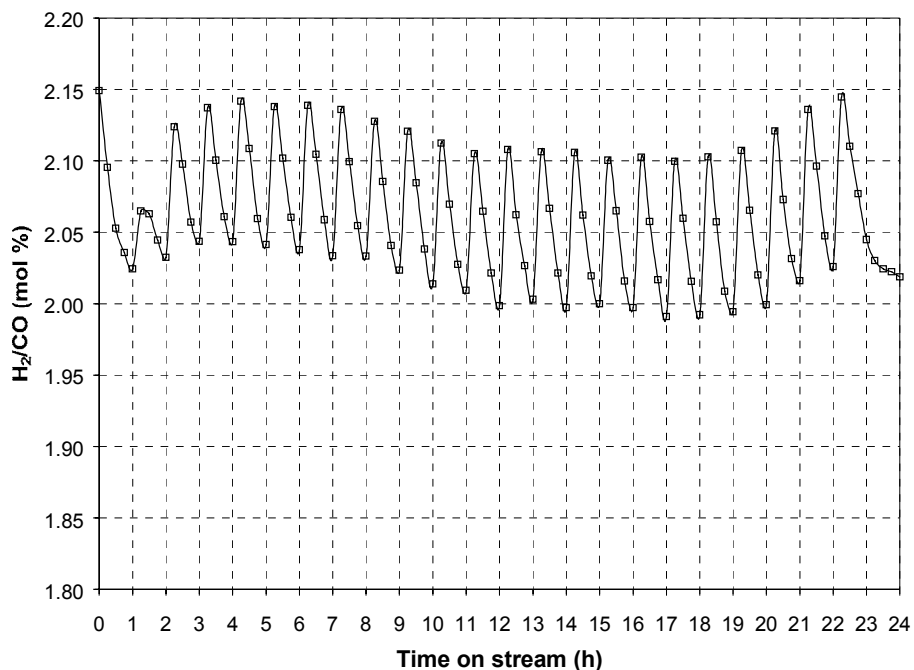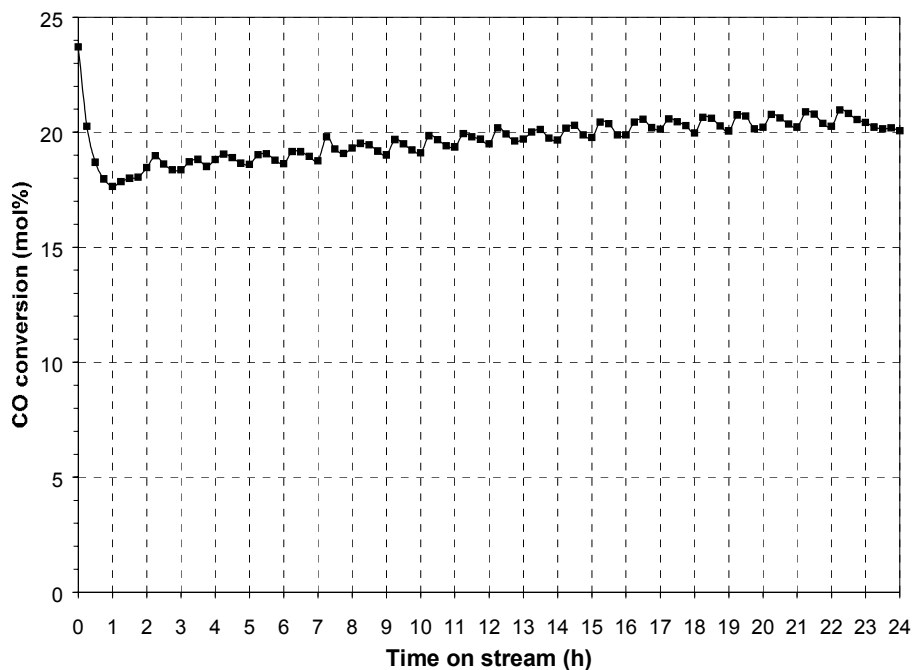of Ru/Al$_2$O$_3$ @400 psig and 3000 h^{-1}.**

Figure 3.5.2. Effect of H₂ pulse on CO conversion of Ru/Al₂O₃ @400 psig and 3000 h⁻¹.
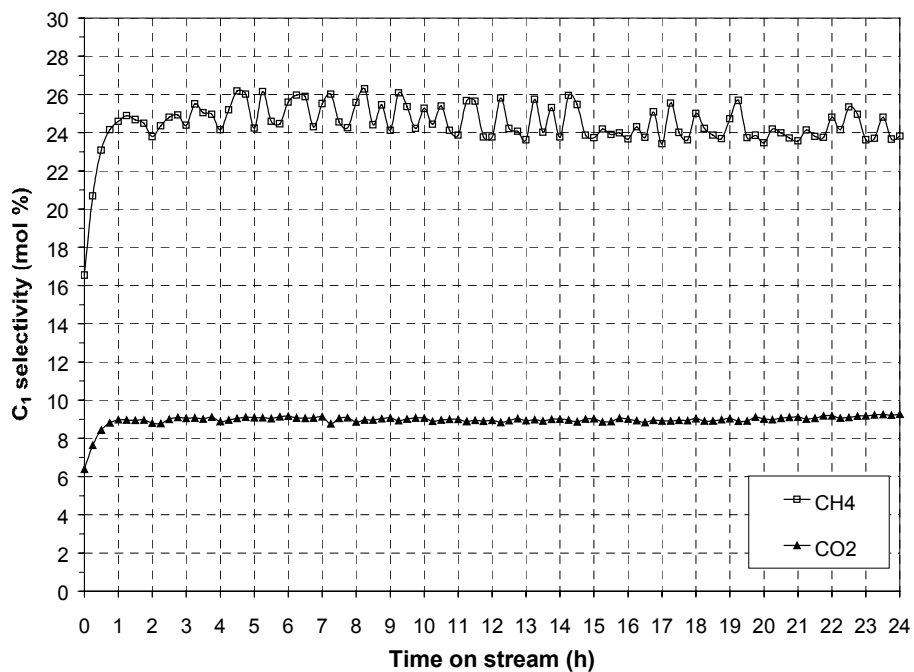
Figure 3.5.3. Effect of H₂ pulse on C₁ selectivity of Ru/Al₂O₃ @400 psig and 3000 h⁻¹.

The applied H_2 pulse increases the outlet H_2:CO ratio only moderately (from ca. 2.0 to ca. 2.1), in a time-pattern similar to that observed for the other examined FT catalysts (Fig. 3.5.1). The CO conversion increases from ca. 18% to ca. 20% during the 24-hour run; however, this increase in activity is apparently not associated with the application of the H_2 pulse, since it matches with that observed for the isothermal run (increase by ca. 6% in almost 3 days). Indeed, each applied H_2 pulse has only minimal positive effect on CO conversion (increase of only 1%, Fig. 3.5.2). The selectivity to CH_4 and CO_2 is very high (ca. 24% and ca. 9%, respectively), with small fluctuations (mainly for CH_4) due to the applied pulse sequence. Therefore, the H_2 pulse has only a minimal effect on the activity and C_1 selectivity of the Ru/alumina catalyst, which appears to show high methanation (product CH_4) and water-gas-shift (product CO_2) activity.

The poor FT synthesis performance of the Ru/alumina catalyst could be due to insufficient reduction of Ru at 300°C. In order to examine this hypothesis, after the pulse run the reactor was depressurized gradually, the catalyst was reduced again *in-situ* under H_2 at 350°C for 8 hours, it was cooled to 115°C and pressurized back to 400 psig under the H_2/CO/Ar reactant mixture. The catalyst was then heated from 115°C to 215°C by 15°C/h. Due to an error in the controller program, after reaching the target temperature of 215°C the bed was cooled back to the initial temperature of 115°C. The heating process was repeated and the bed temperature was stabilized at 214°C (bottom) and 219°C (top), establishing a new "base" reaction condition. The variation in CO conversion with time-on-stream is shown in the composite plot of Figure 3.5.4, composed of two 14-hour segments of the two heat-up processes.

The CO conversion curves for the two activation runs are essentially identical (Fig. 3.5.4), suggesting that there is no effect of applying these procedures on catalyst activity. The effect of temperature on the rate of CO disappearance (calculated from the measured CO conversion assuming differential plug-flow reactor conditions) is shown in Figure 3.5.5.
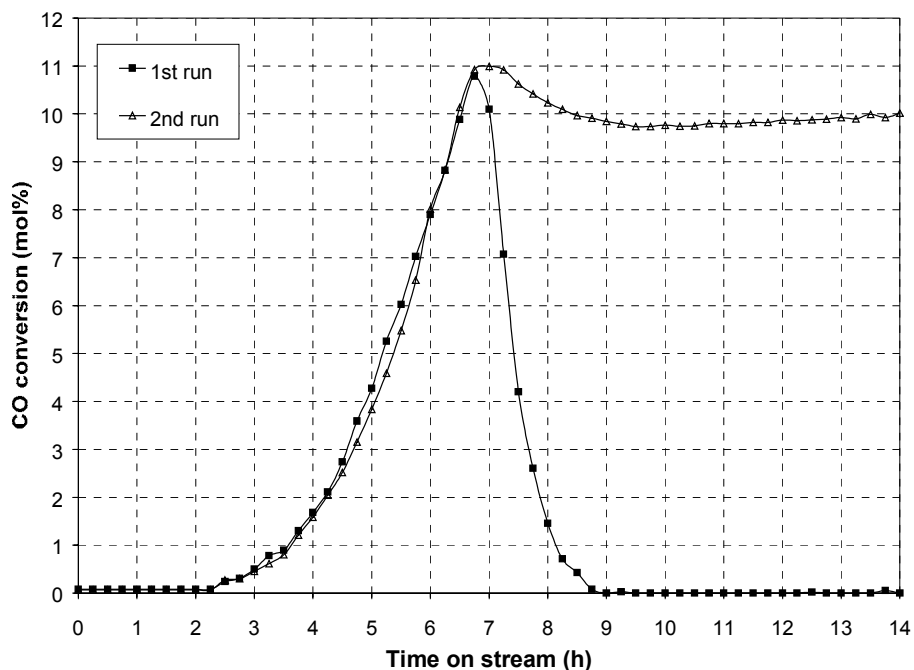
Figure 3.5.4. Effect of activation process on CO conversion of Ru/Al$_2$O$_3$ @400 psig and 3000 h^{-1}.
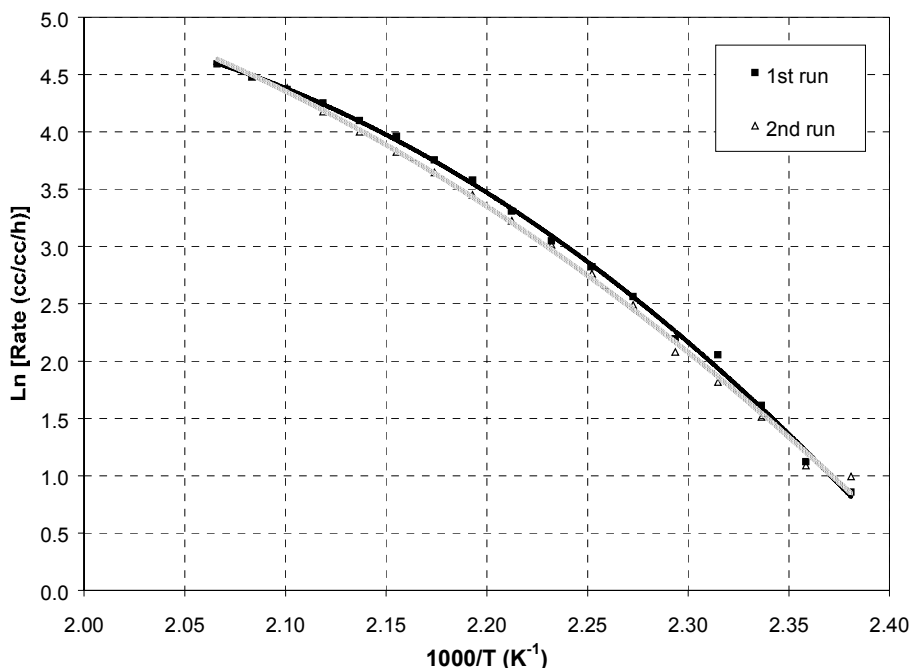
Figure 3.5.5. Effect of temperature on rate of CO consumption of Ru/Al$_2$O$_3$ @400 psig and 3000 h^{-1}.

The Arrhenius-type plots of Fig. 3.5.5 present the dependence of the experimentally determined rate of reaction (rate of CO consumption) on the reciprocal temperature of reaction (the "bottom" bed temperature was used). The slope of these curves provides a measurement for the apparent energy of activation for the overall reaction on the Ru/alumina catalyst, under the examined reaction conditions. The curvature of the plots in Fig. 3.5.5 implies a shift between two regimes with a different reaction-controlling (rate-determining) step. Based on the low-T data (7 last points) of these curves the obtained apparent energy of activation is:

$$E_{a\ (low-T)} = 125 \pm 5\ \textbf{kJ/mol}.$$

On the other hand, the high-T data (first 5 points) give the apparent activation energy of:

$$E_{a\ (high-T)} = 65 \pm 7\ \textbf{kJ/mol}.$$

The decrease in the apparent activation energy with increasing reaction temperature is a clear indication of a transition from a kinetics-controlled reaction (at low-T) to a diffusion-controlled reaction (at high-T) under the examined conditions. More specifically, for a 1st order reaction (1st order dependence of the reaction rate on the concentration of CO) the apparent activation energy under diffusion-control is close to one half of that under kinetics-control. The numerical values of the two apparent activation energies in this experiment appear to be in good agreement with this prediction. Therefore, the obtained data imply a pseudo-1st order dependence of the overall FT reaction on the concentration of CO.

After the second activation procedure, the bed temperature was stabilized at 214/219°C, thus allowing the reaction to reach a new "pseudo-steady state". The measured conversion was ca. 11% (in comparison to 12%-18% at 243/252°C), indicating a clear activation of the catalyst, with still a tendency for minor increase in activity with time on stream. The outlet H_2:CO ratio dropped to ca. 1.9 (compared to ca. 2.0 prior to the activation). The most important difference, however, in the measured parameters before and after the activation, was the strong suppression of the selectivity to CH_4 (ca. 14% instead of ca. 24%) and CO_2 (ca. 4% instead of ca. 9%). This shift in selectivity from the undesired C_1 compounds to the desired FT reaction hydrocarbon products is apparently related to the lower reaction temperature while maintaining a reasonable conversion of CO (which in turn suggests a better activation of the catalyst).

Following this "base" run a 1-min H_2 pulse per 1 hour was applied, so as to compare the effect of H_2 pulsing between the runs prior to and after the activation. The time-on-stream response of the CO conversion and the CH_4/CO_2 selectivity are given in Figures 3.5.6 and 3.5.7, respectively. The CO conversion increases by 1% (from 11% to 12%) in the 24-hour duration of the run. Again, this minor increase in activity is due to the continuous activation of the catalyst by the strong reaction exotherm, rather than the applied H_2 pulse sequence. Each H_2 pulse has only minimal positive effect on the measured CO conversion (Fig. 3.5.6). The selectivity to CH_4 shows a minor increase with each H_2 pulse (ranging between 12% and 14%), and the selectivity to CO_2 remains essentially constant at 4% (Fig. 3.5.7).

Therefore, the H_2 pulsing appears to have only minimal impact on the activity and selectivity of the Ru/alumina catalyst even after the second reduction. The catalyst is significantly better activated after applying the second reduction procedure, resulting in exhibiting the same activity at lower reaction temperatures, which in turn suppresses the selectivity to undesired compounds CH_4 and CO_2.
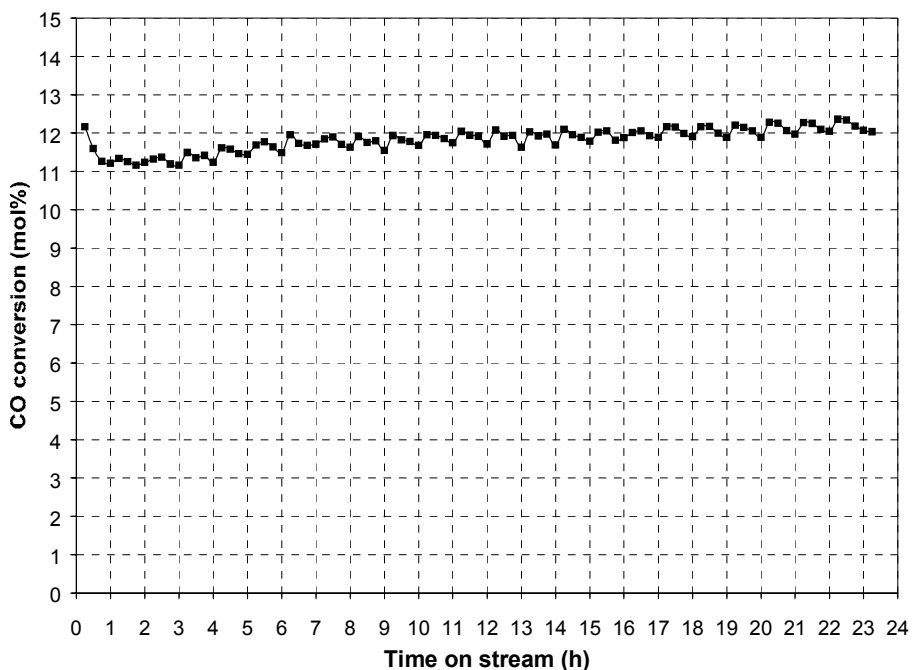
Figure 3.5.6. Effect of H_2 pulse on CO conversion of Ru/Al$_2$O$_3$ @400 psig and 3000 h^{-1}.
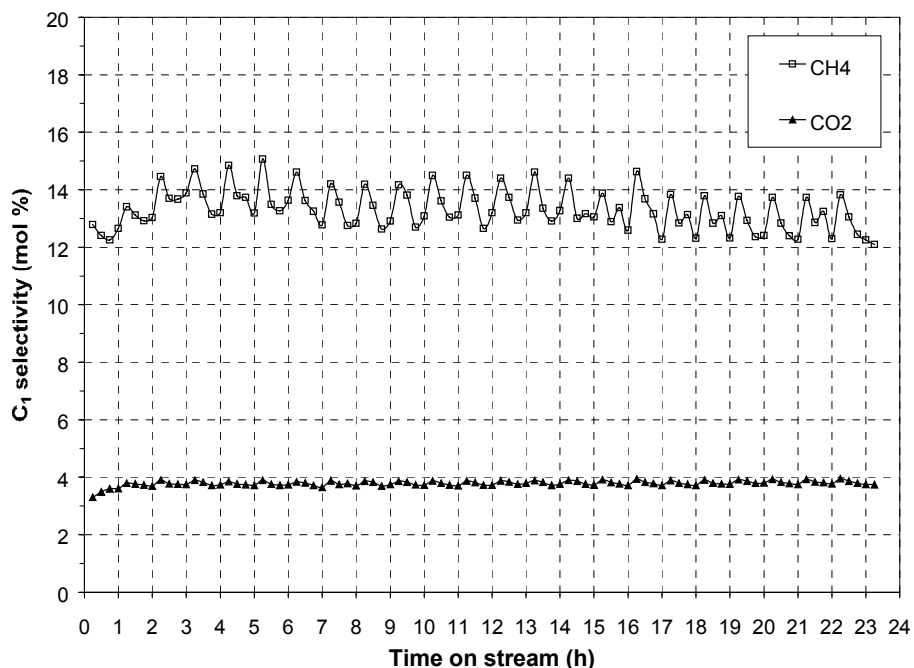
Figure 3.5.7. Effect of H$_2$ pulse on C$_1$ selectivity of Ru/Al$_2$O$_3$ @400 psig and 3000 h^{-1}.

The analysis of the wax for the base run at 214/219°C resulted in obtaining a hydrocarbon product distribution with a chain growth factor **α** of ca. 0.74, which is clearly a very low value for the given type of catalyst. The molar selectivity to the C$_{10}$-C$_{20}$ compound range was ca. 24%. Due to difficulties in the collection of the wax sample for the H$_2$ pulse run the corresponding product analysis involved a large degree of uncertainty. Based on the C$_{10}$-C$_{30}$ product fraction the obtained **α** value was ca. 0.80, while the selectivity to C$_{10}$-C$_{20}$ was ca. 19%. The observed increase in the **α** value for the H$_2$ pulse run could not be positively attributed to the pulsing itself, since a follow-up base run at the same temperature (214/219°C) also gave a higher **α** value (ca. 0.79). Despite the significant uncertainty associated with these values, the observed chain growth is overall much lower than that expected for the Ru/alumina catalyst based on literature references. It is quite possible that the reaction pressure for this experiment (400 psig) is not high enough for this catalyst to show significant FT reaction activity.

4. CONCLUSIONS

Based on the presented results the following conclusions can be drawn:

The α-alumina used for diluting the examined catalysts shows no measurable activity for FT synthesis at temperatures up to 270°C, thus its presence does not affect the activity of the examined catalysts.

"Blank" pulse runs (i.e., runs involving no variations in feed composition) have no effect on measurements of the progress of the FT reaction (conversion, selectivity). "Inert" (N_2) pulsing shows only minimal variations in activity (CO conversion) or in product selectivity (α-value, CH_4 yield, and C_{10}-C_{20} yield) for FT synthesis.

Hydrogen pulsing causes significant increase in CO conversion on a Co-ZrO_2/SiO_2 FT synthesis catalyst, along with an observed enhanced reaction exotherm. Then, the CO conversion decreases gradually until the next H_2 pulse, indicating that the catalyst activity tends to return slowly to its steady-state value. The selectivity to undesirable CH_4 increases instantaneously after each H_2 pulse on the Co-ZrO_2/SiO_2 catalyst, but it is quickly restored to its steady-state value. Thus, H_2 pulsing increases catalytic activity while only briefly increasing the formation of CH_4.

An increase in the H_2 pulse frequency has a positive effect on the selectivity to C_{10}-C_{20} and C_{21+} compounds (while maintaining or slightly decreasing the selectivity to CH_4) but the chain-growth probability α remains essentially unaffected. An increase in the H_2 pulse duration increases the maximum obtained CO conversion and the instantaneous selectivity to CH_4.

The extent of the CH_4 formation reaction appears to be correlated to the increase in H_2 concentration as caused by pulsing. The FT reaction, however, appears to have a different dependence on H_2 concentration, since it progresses within a different time frame. An optimum set of both H_2 pulsing parameters (pulse frequency and pulse duration) is required for maximizing the yield of (diesel-range) C_{10}-C_{20} FT products.

Hydrogen pulsing has a positive effect on the C_{10}-C_{20} yield of a high-α $Fe/K/Cu/SiO_2$ FT catalyst. However, it also causes a significant decrease in catalyst activity (CO conversion) and an undesirable increase in the selectivity to CH_4. Pulsing with CO also has a positive effect on the C_{10}-C_{20} yield and no measurable effect on the selectivity to CH_4 and CO_2, and causes only a moderate decrease in CO conversion. Pulsing with a $24\%CO_2/N_2$ gas mixture has essentially no effect on catalytic activity or product distribution (α-value, C_{10}-C_{20} yield).

Hydrogen pulsing has only minimal effect on the activity and C_1 selectivity of a Ru/alumina FT synthesis catalyst, which appears to show enhanced methanation and water-gas-shift activity. A second reduction procedure produces a better-activated catalyst, showing the same activity at lower temperatures, along with lower selectivity to undesirable compounds CH_4 and CO_2. Still there is only minimal impact of H_2 pulsing on the catalyst performance even after the second reduction.

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APPENDICES

Appendix I.

Two-page abstract entitled "*Fischer-Tropsch Synthesis on a Co-ZrO$_2$/SiO$_2$ Catalyst: Effect of H$_2$ Pulsing*", submitted for presentation in the 17th North American Catalysis Society Meeting, to be held in Toronto, Canada, on June 3-8, 2001.

Appendix II.

Six-page camera-ready manuscript entitled "*Effect of Periodic Pulsed Operation on Product Selectivity in Fischer-Tropsch Synthesis on Co-ZrO$_2$/SiO$_2$*", submitted for oral presentation and publication in the Proceedings of the 6th Natural Gas Conversion Symposium, to be held in Girdwood, Alaska, on June 17-21, 2001.

APPENDIX I

Fischer-Tropsch Synthesis on a Co-ZrO$_2$/SiO$_2$ Catalyst: Effect of H$_2$ Pulsing

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Introduction

Currently there is significant commercial interest in producing diesel-fuel-range middle distillates (C$_{10}$-C$_{20}$ paraffins) from natural-gas-derived syngas by Fischer-Tropsch (FT) synthesis. Increasing the selectivity of the FT reaction to diesel (C$_{10}$-C$_{20}$) or gasoline (C$_5$-C$_{11}$) products by altering the Shultz-Flory-Anderson (SFA) distribution is economically attractive. Use of bifunctional (FT-active metal on zeolite) catalysts to produce gasoline-range hydrocarbons has been economically unsuccessful [1-2]; the enhanced cracking activity of the zeolite lowers the chain-growth probability **α**, thus producing increased amounts of undesirable C$_1$-C$_4$ gases.

The present emphasis has shifted towards maximizing the yield of zero-sulfur high-cetane C$_{10}$-C$_{20}$ products from FT synthesis. Among various approaches, periodic pulsing of H$_2$ or other gases has been examined so as to limit chain growth on a high-**α** FT catalyst by removing the growing chain from the catalyst surface [3-5], thus maximizing the C$_{10}$-C$_{20}$ yield (Figure 1). Experimental studies have shown the potential to alter the SFA distribution [6,7]; however, they were conducted under conditions of limited industrial interest. The scope of this study is to investigate the effect of H$_2$ pulsing on the activity and product distribution of a high-**α** (~0.9) Co/ZrO$_2$/SiO$_2$ FT synthesis catalyst, in an attempt to maximize the C$_{10}$-C$_{20}$ product yield.
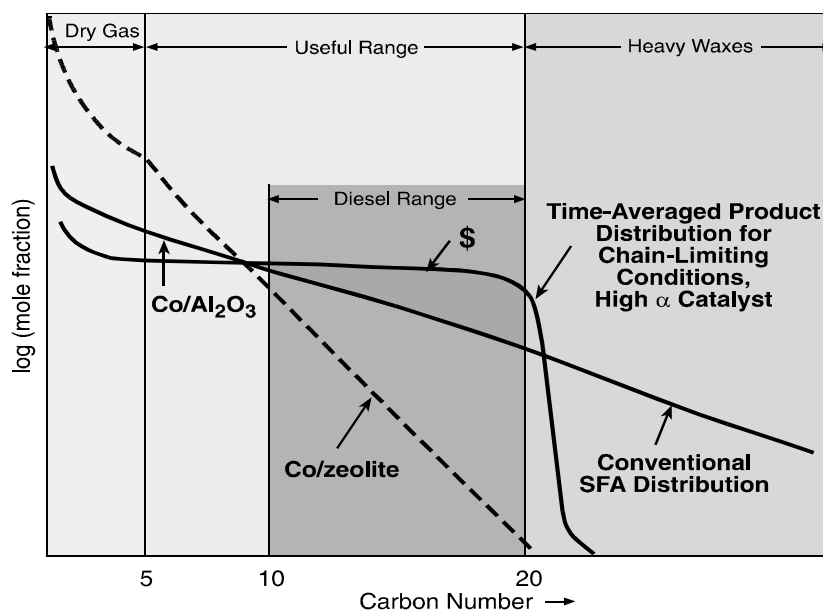

Figure 2. Product distribution (**α**-plot) for FT synthesis

Experimental

A 25%Co-18%Zr/SiO$_2$ catalyst was synthesized by sequential incipient wetness impregnation of a high-purity, high-surface-area silica (XS16080, Norton) with Zr tetrapropoxide and Co nitrate [8]. A mixture of 2 cc of the calcined Co-Zr/SiO$_2$ catalyst and 10 cc of a low-surface-area α-alumina (SA5397, Norton) was loaded into a 0.305-in stainless steel down-flow reactor. The catalyst was reduced *in-situ* in H$_2$ at 350°C and was cooled and pressurized to approximately 300 psig. The feed was 33.3% H$_2$, 16.7% CO (H$_2$:CO=2:1), 1.7% Ar (internal standard), balance N$_2$, at 6000 h^{-1} space velocity. Pulse runs involved substituting the reactant feed flow with an equal molar flow of a pulse gas, thus maintaining the total molar flow and pressure between base and pulse runs.

Results

Runs with a "blank" pulse (i.e., switching between two equal flows of H$_2$+CO/ Ar) indicated no effect on CO conversion or product distribution (**α**-value, C$_{10}$-C$_{20}$ yield). A 1-min N$_2$ pulse per 1 hour gave only minimal variation in activity (CO conversion) and product selectivity. On the other hand, a 1-min H$_2$ pulse per 1 hour resulted in a significant increase in CO conversion at 225°C. The measured CO conversion after the pulse was observed to gradually decrease before the next pulse. The CH$_4$ selectivity also increased substantially (due to the excess of H$_2$) but was quickly restored to its base value. Thus H$_2$ pulsing increased the desired CO productivity while only instantaneously increasing the undesired CH$_4$ selectivity.

The effect of varying H$_2$ pulse frequency (1-min H$_2$ per 1, 2, and 4 hours) on the activity and product yield of the Co-ZrO$_2$/SiO$_2$ catalyst is given in Table 1. Both CH$_4$ yield and C$_{10}$-C$_{20}$ yield increase with H$_2$-pulse frequency. An optimum set of pulse parameters (pulse frequency, pulse duration) appears to be required for maximizing the C$_{10}$-C$_{20}$ yield.

Table 1. Effect of H$_2$ pulse frequency on product yield @225°C, P=300 psig

Frequency (h^{-1})	Alpha (-)	CH$_4$ (wt%)	CH$_4$ yield (g/cc cat/h)	C$_{10}$-C$_{20}$ (wt%)	C$_{10}$C$_{20}$ yield (g/cc cat/h)
0 (no pulse)	0.887	17.0	0.0189	28.2	0.0312
0.25	0.892	15.8	0.0228	26.4	0.0380
0.5	0.885	14.3	0.0223	31.0	0.0484
1	0.890	15.4	0.0253	29.7	0.0490

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Effect of periodic pulsed operation on product selectivity in Fischer-Tropsch synthesis on Co-ZrO$_2$/SiO$_2$

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The effect of H$_2$ pulsing on the activity and product distribution of a high-α ($\sim$0.9) Co/ZrO$_2$/SiO$_2$ Fischer-Tropsch (FT) synthesis catalyst was investigated in an attempt to maximize the diesel-range product yield. H$_2$ pulsing increases CO conversion significantly but only temporarily; catalyst activity decreases gradually towards its steady state. Increasing H$_2$-pulse frequency has a positive effect on the yield of both CH$_4$ (undesirable) and C$_{10}$-C$_{20}$ (desirable) products. An optimum H$_2$-pulse frequency is apparently required in order to maximize the yield of diesel-range FT products without substantially increasing the CH$_4$ yield.

1. INTRODUCTION

The Fischer-Tropsch synthesis (FTS) can convert solid fuel- or natural gas-derived syngas (CO+H$_2$) to liquid fuels and high-value products. The extensively reviewed Fischer-Tropsch (FT) reaction [1-3] produces a non-selective distribution of hydrocarbons (C$_1$-C$_{100+}$) from syngas. FT catalysts are typically based on Group-VIII metals (Fe, Co, Ni, and Ru), with Fe and Co most frequently used. The product distribution over these catalysts is generally governed by the Schultz-Flory-Anderson (SFA) polymerization kinetics [4].

Currently there is significant commercial interest in producing diesel-fuel range middle distillates (C$_{10}$-C$_{20}$ paraffins) from natural gas-derived syngas [5]. Increasing the selectivity of FTS to desired products such as diesel (C$_{10}$-C$_{20}$) or gasoline (C$_5$-C$_{11}$) by altering the SFA distribution is economically attractive. Use of bifunctional catalysts (FT-active metals on zeolite, e.g. ZSM-5) to produce high-octane gasoline-range hydrocarbons (explored in the past 2 decades), has been economically unsuccessful [6-9]. The zeolite cracking activity lowers the chain-growth probability (α), producing gasoline-range products in excess of 48 wt% of the total hydrocarbon product; however, it also produces a significant amount of undesirable C$_1$-C$_4$ gases (Figure 1).

The present emphasis has shifted towards maximizing the yield of high-cetane C$_{10}$-C$_{20}$ products from FTS. Increased worldwide demand for low-sulfur diesel has further stressed the importance of development of zero-sulfur FT-diesel products. An alternative approach to the use of bifunctional catalysts to alter selectivity is periodic FT reactor operation (pulsing) [3]. It entails alternatively switching between two predetermined input compositions over the FT catalyst to promote time-average rate, selectivity, and catalyst life [10-12]. Periodic pulsing of H$_2$ has been examined so as to limit chain growth by removing the growing

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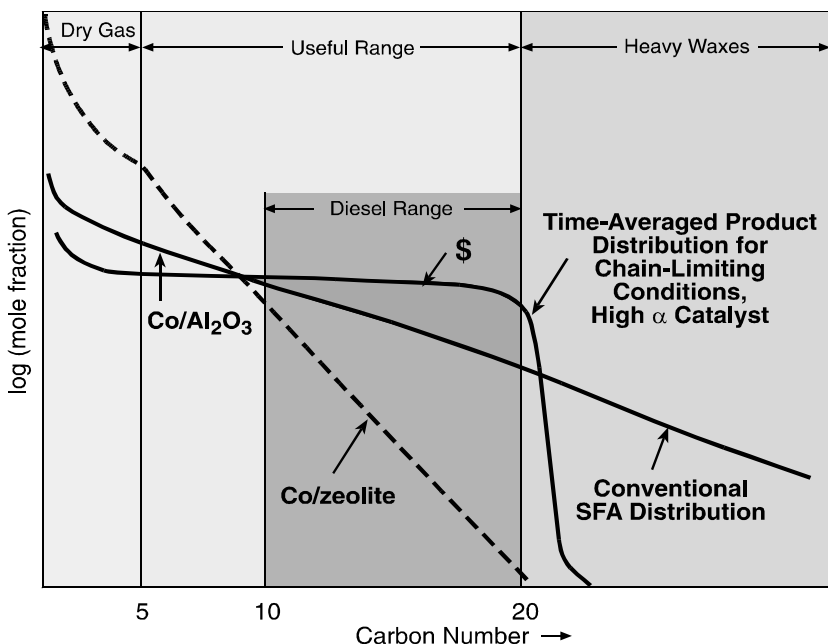
Figure 3. Product distribution (**α**-plot) for FT synthesis

hydrocarbon chain from the catalyst surface [13-15]. Experimental studies have shown the potential to alter the SFA distribution [16,17]; they were performed, however, at conditions of limited industrial interest.

The chain-limiting concept using pulsing to maximize diesel yield is shown in a plot of carbon number vs. mole fraction (Fig. 1). The slope of the curve is determined by the chain-growth probability, **α**. Periodic operation on a high-**α** catalyst may result in removal of the growing chain from the surface at the desired C_{10}-C_{20} length, thereby maximizing diesel yield without increasing the dry gas. Thus, the objective of this study is to investigate the effect of H_2 pulsing on the activity and product distribution of a high-**α** (~0.9) $Co/ZrO_2/SiO_2$ FT synthesis catalyst, in an attempt to maximize the C_{10}-C_{20} product yield.

2. EXPERIMENTAL

2.1. Catalyst synthesis and characterization

A 25%Co-18%Zr/SiO$_2$ catalyst was synthesized by sequential incipient wetness impregnation of a high-purity, high-surface-area (144-m^2/g) silica support (XS 16080, Norton) [18]. The support (crushed and sieved to a particle size of 100-150 μm) was degassed in vacuum and heated to 80°C. A zirconium tetrapropoxide ($Zr(OCH_2CH_2CH_3)_4$) solution in 1-propanol (Aldrich) was used for the incipient wetness impregnation, performed in two steps. After each impregnation step, the product was dried (120°C, 2 h) and calcined in air (500°C, 1 hour). The produced material had a nominal loading of 18%Zr/silica.

Cobalt was impregnated on the zirconia/silica support using a cobalt nitrate hexahydrate precursor ($Co(NO_3)_2.6H_2O$, Aldrich). The hexahydrate was dissolved in water and the formed solution was added in a controlled manner to the zirconia/silica support, forming the catalyst with a nominal composition of 25%Co-18%Zr/SiO$_2$. Finally, the catalyst was calcined in air at 350°C for 1 hour.

The surface area of the $Co-ZrO_2/SiO_2$ catalyst was measured (by BET method) to be 102±3 m^2/g. Its pore volume was estimated at 0.40±0.01 cc/g (by mercury porosimetry). Its crystalline structure was examined by X-ray diffraction (XRD). The predominant phase was Co_3O_4, with no other Co-O or Zr-O crystalline phases or cobalt silicate present in the diffraction pattern.

2.2. Reaction set-up

The reaction system consisted of the gas-feed, a fixed-bed reactor, and a sampling/ analysis system for the liquid and gaseous products. The feed system blended CO/Ar, H_2, N_2, or other premixed gases in desired concentrations. A time-programmable interface system (Carolina Instrumentation Co.) was used to control a series of actuated valves, so that a (reactant or inert) flow opened / closed automatically and independently of the others. Appropriate periodic switch of these valves offered the capability to perform various pulsing-type experiments with this configuration.

A stainless-steel 3/8-in o.d. (0.305-in i.d.) downflow reactor was enclosed in a three-zone programmable furnace. The liquid products were collected and separated into a wax trap (waxes) maintained at 140°C and a water trap (oil + water) maintained at 25°C. Two sets of these traps, positioned in parallel, enabled continuous operation. A Kammer back-pressure-control valve, located downstream of the traps, controlled the reactor and trap pressure.

An on-line GC-Carle (TCD) analyzed the permanent gases (H_2, CO_2, Ar, N_2, CH_4, CO). Argon was used as internal standard. An on-line GC-FID (100-m Petrocol column, ramped from −25 to 300°C) analyzed the light hydrocarbons (C_1-C_{15}). A third off-line GC-FID (15-m SPB-1 capillary column, 0.1-μm, ramped from 50 to 350°C) analyzed the composite wax and oil collected from the wax and water traps, respectively.

2.3. Reaction procedure

A physical mixture of 2 cc (1.55 g) of the calcined Co-ZrO_2/SiO_2 catalyst and 10 cc (15.91 g) of a low-surface-area (0.2 m^2/g) α-alumina (SA5397, Norton) was loaded into the reactor. The catalyst was reduced *in-situ* under H_2 at 350°C for 14 h, and was cooled and pressurized to ca. 300 psig (19.4 atm). The FT reaction was started by feeding a 10%Ar/CO gas mix, thus establishing the following base reaction conditions:

Syngas (H_2 + CO)=50%, H_2:CO=2:1 (i.e., 33.3% H_2 and 16.7% CO)
Inerts (N_2 + Ar)=50% (1.7% Ar, 48.3% N_2)
P=300 psig, F=200 scc/min, SV=6000 h^{-1}.

The reaction temperature was increased (by 0.5°C/h or less) to 224°C and was stabilized at this value, thus allowing the reaction to reach a "pseudo-steady state". Pulse runs involved substituting the reactant feed flow (H_2+CO/Ar) with an equal molar flow of a pulse gas. The total molar flow and the reaction pressure were kept constant between base and pulse runs.

3. RESULTS AND DISCUSSION

A "blank" pulse run (i.e., switching between two equal flows of H_2/CO/Ar reactant mix) was performed in order to identify the possible effect of the periodic pressure disturbance (directly related to the applied pulse) due to non-ideal switching of the actuated valves. This run produced no measurable variation on CO conversion, H_2:CO ratio, or product distribution (**α**-value, C_{10}-C_{20} yield). Therefore, pulse runs involving no variations in feed composition have no effect on measurements of the progress of the FT reaction.

A 1-min N_2 (inert) pulse per 1 hour (i.e., substituting the H_2/CO/Ar flow, which is 51.7% of the total, with an equal flow of N_2 for 1 min every hour) was applied so as to examine the effect of inert pulsing on the reaction progress. The N_2 pulse gave only minimal variations in activity (CO conversion) or product selectivity (**α**-value, CH_4 yield, C_{10}-C_{20} yield), implying that short (1-min) disruptions in reactant flow do not substantially affect the FT reaction.

In contrast to the inert pulse, a 1-min H_2 (reactant) pulse caused significant variations in CO conversion and CH_4 selectivity. Effects of varying the H_2 pulse frequency (1-min H_2 per 1, 2, and 4 hours) on the CO conversion and the C_1 (CH_4 and CO_2) selectivity are shown in the composite plots of Figures 2a and 2b, respectively. These plots are composed of 10-hour segments of a series of sequential runs (typically lasting 48 hours, so as to collect sufficient amounts of oil + wax for the analysis), starting and ending with a base (no pulse) run. The data points correspond to measurements of the reactor effluent gas every 15 minutes.

A 1-min H_2 pulse per 1-hour (10-20-hour segment in Figs. 2a and 2b) caused a significant increase in CO conversion (from 16% to ca. 30%). The measured temperature of the catalyst bed also increased to 226°C, indicating a strong reaction exotherm. The conversion of CO decreased *gradually* until the next H_2 pulse. A less-pronounced increase in CO conversion was also observed for the 1-min H_2 pulse per 2-h and 4-h runs. The observed decrease in CO conversion after the pulse indicates that the activity tends to return to its steady state (comparing also the base runs before and after the 3 pulse runs). The measured changes in CO conversion cannot be attributed to variations in the inlet CO concentration since the conversion was based on comparing the inlet and outlet *ratios* of CO to the inert Ar (fed at a fixed ratio from a single gas cylinder).

The selectivity to CH_4 was observed to increase *instantaneously* after each H_2 pulse (from 13-14% to ca. 20% for all examined pulse runs). It was then quickly restored to its base value (Fig. 2b). Thus, H_2 pulsing increases catalytic activity while only briefly increasing the undesirable formation of CH_4.
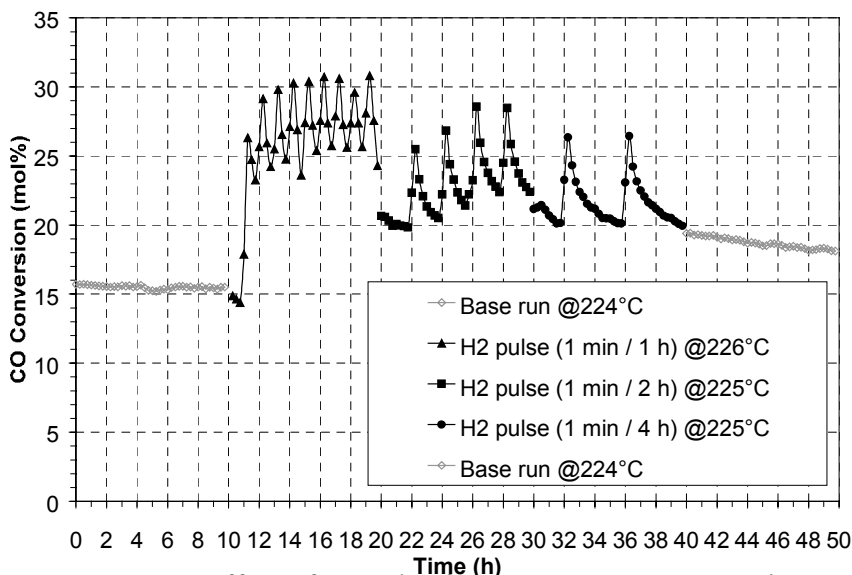

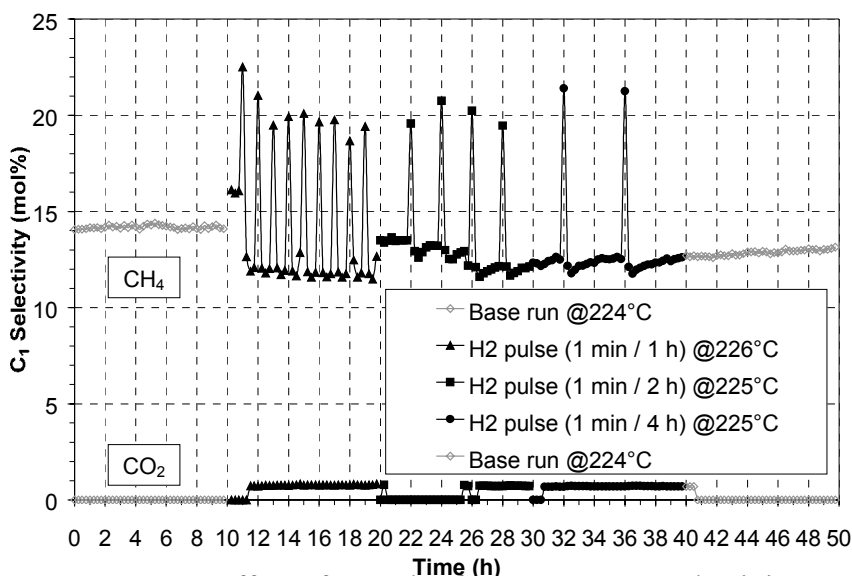**Figure 2a.** Effect of H_2 pulse frequency on CO conversion

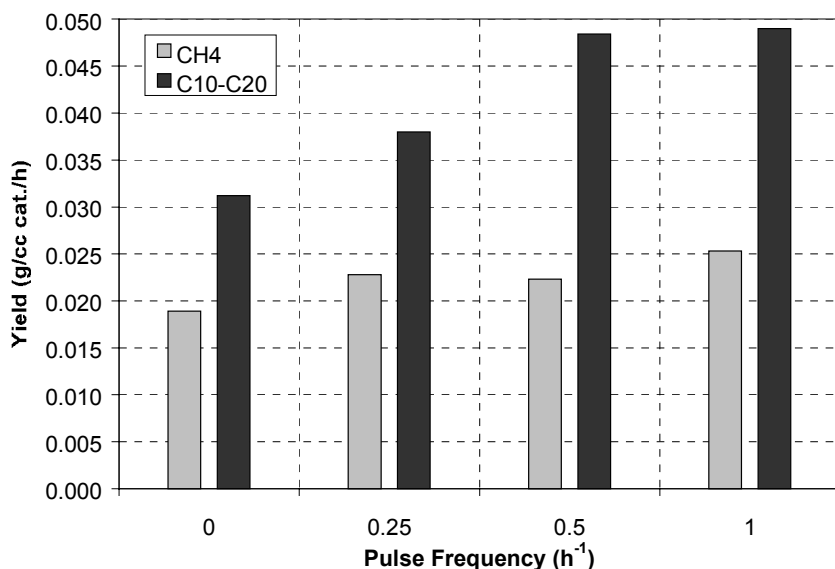**Figure 2b.** Effect of H_2 pulse frequency on C_1 selectivity

Figure 3. Effect of H$_2$ pulse frequency on product yield

The effect of varying H$_2$ pulse frequency on the desired C$_{10}$-C$_{20}$ yield vs. the undesired CH$_4$ yield is shown in Figure 3. Pulse frequencies of 1, 0.5, and 0.25, h^{-1} correspond to a 1-min H$_2$ pulse per 1, 2, and 4 hours, respectively. The zero pulse frequency corresponds to the average of the two no-pulse (base) runs before and after the 3 pulse runs.

Both C$_{10}$-C$_{20}$ and CH$_4$ yields increase with H$_2$-pulse frequency (and so does the yield of C$_{21+}$), obviously due to the enhancement in catalytic activity caused by the pulsing (Fig. 2a). As seen in Fig. 3, the effect of the 1-min H$_2$ pulse per 1 hour compared to the (average) base run was to increase the C$_{10}$-C$_{20}$ yield by ca. 57%, while the CH$_4$ yield only increased by ca. 34%. Although this comparison entails a temperature change (from 224°C to 226°C), the increase in the C$_{10}$-C$_{20}$ yield is more than what could be accounted for solely by a 2°C increase in reaction temperature. The CH$_4$ selectivity in the pulse runs (13-14% on molar basis) is lower than that of the base runs (15.5%), whereas the selectivity to C$_{10}$-C$_{20}$ and C$_{21+}$ compounds is higher (28-32% vs. 27%, and 23-24% vs. 20%, respectively). The α-values of the pulse runs (based on the molar fractions of C$_{10}$-C$_{65}$ products) are found to be essentially identical to that of the base runs (0.890±0.005). Thus, the applied H$_2$ pulsing apparently does not alter the SFA distribution.

Within the examined pulse frequency range, the greater difference between the yields of the desirable C$_{10}$-C$_{20}$ and the undesirable CH$_4$ is obtained at the *intermediate* pulse frequency of 0.5 h^{-1} (1-min H$_2$ per 2 hours). Also, upon extrapolating to higher H$_2$-pulse frequencies, we could expect a stronger reaction exotherm and thus an increase in reaction temperature, which is known to cause a shift in FTS product distribution to lower molecular weight compounds and to enhance the methanation reaction [4]. Higher pulse frequencies would thus tend to increase the CH$_4$ yield much more than the C$_{10}$-C$_{20}$ yield. An optimum H$_2$-pulse frequency (depending on catalyst and reaction conditions) would therefore be required for maximizing the C$_{10}$-C$_{20}$ yield without substantially increasing the CH$_4$ yield.

Another series of H$_2$-pulse runs on the Co-ZrO$_2$/SiO$_2$ catalyst examined the effect of H$_2$-pulse duration on activity and product distribution, by varying the pulse duration (1, 2, 4-min of H$_2$) at a fixed pulse frequency (0.5 h^{-1}). The results of this study (not included here) are qualitatively similar to those of the variable-pulse-frequency study presented here: higher H$_2$-pulse duration causes an increase in both C$_{10}$-C$_{20}$ and CH$_4$ yield, and the greater difference between these yields is obtained at the *intermediate* pulse duration of 2 min. Consequently, optimization of the pulse duration is also important in maximizing the formation of diesel-range FT products.

4. CONCLUSIONS

In contrast to "blank" or inert (N_2) pulsing, pulsing with H_2 has a significant impact on the activity and selectivity of the examined $Co-ZrO_2/SiO_2$ catalyst. H_2 pulsing causes significant increase in CO conversion, along with an observed enhanced reaction exotherm. Then, the CO conversion decreases gradually until the next H_2 pulse, indicating that the catalyst activity tends to return slowly to its steady state, as measured in base (no-pulse) runs. On the other hand, the selectivity to CH_4 increases instantaneously after each H_2 pulse, and gets quickly restored to its steady-state value.

Increasing H_2-pulse frequency has a positive effect on the yield of both CH_4 and $C_{10}-C_{20}$. The selectivity to $C_{10}-C_{20}$ and C_{21+} compounds increases with H_2 pulsing compared to the base runs, but the chain-growth probability **α** is essentially unaffected. An optimum set of H_2-pulse parameters (frequency and duration) appears to be needed to maximize the $C_{10}-C_{20}$ yield without substantially increasing the CH_4 yield.

5. ACKNOWLEDGEMENTS

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