

ALPHA-OLEFIN SELECTIVITY DURING CONVENTIONAL AND SUPERCRITICAL FISCHER-TROPSCH SYNTHESIS.

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ABSTRACT

Fischer-Tropsch synthesis was studied on a precipitated iron catalyst (Ruhchemie LP 33/81) in a fixed bed reactor at several different temperatures (235°C, 250°C and 265°C) and synthesis gas feed compositions ($H_2/CO = 0.67, 1$ or 2) under both supercritical (propane as a supercritical fluid) and conventional ($P = 1.5$ MPa) operating conditions. It was found that the supercritical operation results in enhanced selectivity of α -olefins relative to conventional (normal) operation. Both total olefin content and α -olefin selectivity decreased with either increase in conversion or H_2/CO molar feed ratio, whereas olefin selectivities were essentially independent of reaction temperature.

INTRODUCTION

Alpha olefins are used as chemical intermediates for a number of important industrial and consumer products. The even-numbered carbon alpha olefins (C_4, C_6 and C_8) are used as comonomers for ethylene and propylene polymerization, whereas the higher molecular weight olefins are used in plasticizers, household detergents and sanitizers [1]. Linear C_{10} olefins and others provide premium value synthetic lubricants. Alpha olefins are produced in significant quantities during conventional Fischer-Tropsch synthesis (FTS) in fixed bed and fluid bed reactors at Sasol in South Africa, and recently Sasol has built a large scale commercial plant for production of 1-pentene and 1-hexene utilizing raw streams from fluid bed FTS reactors [2]. The purification process employed by Sasol entails a series of distillation steps to separate desired alpha olefins from other products. Significant economic benefits can be achieved by increasing the alpha olefin content of FTS products and thus reducing the cost of product separation.

Fischer-Tropsch synthesis in supercritical fluids provides means to accomplish this objective. In recent studies of FTS, on silica supported cobalt-lanthanum and/or alumina supported ruthenium catalysts, in a supercritical n-hexane Fujimoto and co-workers [3-4] have demonstrated certain advantages of this operation, including higher olefin selectivity, relative to gas phase and liquid phase (trickle bed) operation. Lang et al. [5] studied FTS on a precipitated iron catalyst (Ruhchemie LP 33/81), and found that supercritical operation results in enhanced selectivity of 1-olefins (α -olefins) relative to conventional FTS, but it does not have significant effect on catalyst activity and hydrocarbon product distribution.

Here, we report results from a comprehensive study with the Ruhchemie LP 33/81 catalyst, which was used originally in Arge fixed bed reactors at Sasol [6], over a wide range of process conditions. At a given reaction temperature and feed composition, gas space velocity was varied to achieve different levels of syngas conversion. Variations in residence time allow us to distinguish primary and secondary reaction steps that control olefin selectivity.

EXPERIMENTAL

Experimental equipment and procedures have been described previously [5]. Experiments were conducted in a conventional downflow fixed bed reactor (1.3 cm inside diameter, 40 cm³ effective bed volume for supercritical FTS, and 1 cm inside diameter, 27 cm³ effective bed volume for conventional FTS) embedded in an aluminum block with a two-zone heater. Carbon monoxide, hydrogen, carbon dioxide, and C_5 - hydrocarbons were analyzed by on-line gas chromatography. Condensed C_5+ hydrocarbons, collected for 6-8 h after reaching steady-state at a given set of reaction condition, were analyzed using gas chromatography [5]. Premixed synthesis gas (Iweco, Inc. >99.7% purity) containing approximately 5% of argon as an internal standard, was used as the feed. Propane (Phillips 66 Co., >99% purity) was pumped from a liquid propane dip tube tank using a diaphragm metering pump (American Lewa, Inc.; Model FCMK-1). Olefin selectivities reported here are based on the analysis of gas phase (C_2 - C_5 hydrocarbons) and liquid phase products (C_6 - C_{15} hydrocarbons).

A precipitated iron catalyst synthesized by Ruhchemie AG (Oberhausen - Holten, Germany) was used in this test. The nominal catalyst composition is 100 Fe/5 Cu/4.2 K/25 SiO₂ (on mass basis), and the preparation procedure is described elsewhere [6]. Catalyst was calcined in air at 300°C for 5 h, and then crushed and sieved to 32/60 mesh size (0.48 mm in diameter). About 3.5 g of catalyst was diluted 1:6 by volume with glass beads of same size prior to loading into the reactor. The catalyst was reduced with hydrogen at 220°C, ambient pressure and a flow rate of 5100 cm³/min (linear superficial velocity of 150 cm/s) for 1 h.

Following reduction, the catalyst was tested initially at baseline process conditions (1.5 MPa, 250°C, 2 L (NTP)/g-cat-h, $H_2/CO = 0.67$). After 67 h of conventional FTS at the baseline conditions the total pressure was increased to 5.5 MPa using propane as a balance gas (run FA-1724), while keeping the partial pressure and the flow rate of syngas at the baseline conditions. Since the reaction pressure and temperature (5.5 MPa and 250°C, respectively) are well above the critical pressure and temperature of the propane (4.19 MPa and 96.7°C, respectively), this is

referred to as supercritical FTS. Between 70 and 700 h on stream the catalyst was tested under different sets of process conditions. In another test (run FB-1644) the Ruhrchemie catalyst was evaluated under similar process conditions as those used in run FA-1724, but without supercritical propane (conventional FTS).

RESULTS AND DISCUSSION

Olefin Selectivities - Effect of gas residence time

Effects of gas residence time (i.e. gas hourly space velocity (GHSV) defined as the total volumetric (NTP) feed flow rate of synthesis gas and propane per unit bed volume, ca. 40 cm³) and carbon number on total olefin selectivity ((1-olefin + 2-olefin)/(1-olefin + 2-olefin + n-paraffin)) and 2-olefin selectivity (2-olefin/(1-olefin + 2-olefin)) are illustrated in Figures 1a and 1b, respectively. Data shown in Figure 1 were obtained at 250°C with H₂/CO = 0.67, GHSV = 330 - 1340 h⁻¹ and correspond to syngas conversions of 75 to 34% (periods 2-4 in Table 1). Results obtained at gas hourly space velocities of 680 and 1340 h⁻¹ were nearly identical, whereas the residence time effect was clearly observed at the gas space velocity of 330 h⁻¹. Ethylene selectivity was significantly higher at the two higher gas space velocities, whereas the increase of total olefin selectivity at higher carbon numbers was much smaller. Selectivity of 2-olefins decreased (i.e. 1-olefin selectivity increased) with increase in GHSV. The same trends were observed in experiments with different syngas feed compositions (H₂/CO = 0.93 and 2.03). From these observations it is concluded that 1-olefins, and to a smaller extent n-paraffins and 2-olefins, are the primary products of FTS. These conclusions are consistent with those from previous studies with iron FT catalysts [6-8]. At the present time there is no consensus whether some of n-paraffins and 2-olefins are formed by secondary hydrogenation and isomerization reactions, respectively, on sites where chain growth cannot take place, or as primary products following secondary readsorption of 1-olefins on FTS sites [9-11]. Upon readsorption, 1-olefin becomes a reaction intermediate which can either continue to grow and terminate as a longer chain 1-olefin, n-paraffin or 2-olefin, or be terminated to n-paraffin or a 2-olefin of the same carbon number.

Shapes of curves in Figure 1, reflect carbon number (molecular weight) effect on secondary reactions. Ethylene is more reactive than other low molecular weight 1-olefins, and thus its selectivity is low. Decrease in olefin content with increase in carbon number has been attributed to their greater adsorptivity [9], higher solubility in the liquid phase resulting in higher 1-olefin concentrations [8], and/or diffusion enhanced 1-olefin readsorption [10,11]. Madon et al. [10,11] proposed that larger 1-olefins spend longer times in a catalyst pore, due to their lower diffusivities, and this in turn increases probability for their readsorption on FTS active sites before exiting the pore. The increase in 2-olefin selectivity with increase in carbon number (Fig. 1b) or with increase in bed residence time (lower gas space velocity) is due to the same factors mentioned above. Longer residence time of high molecular weight 1-olefins either in the catalyst pores or in the reactor itself, increases probability for secondary 1-olefin readsorption followed by termination as 2-olefin on FTS and/or different type of sites.

Effects of gas space velocity and carbon number on olefin selectivities during conventional FTS (run FB-1644) at 1.5 MPa, 250°C, H₂/CO = 0.67 are shown in Figure 2. Qualitative trends are the same as those observed during SFTS (Fig. 1), i.e. the total olefin selectivity increased (Fig. 2a), whereas the 2-olefin selectivity decreased (Fig. 2b), with increase in gas space velocity (decrease in bed residence time). However, the bed residence time effect on selectivity was markedly higher during the conventional FTS, although conversions and nominal gas residence times were similar in both sets of experiments (0.9 - 4.8 min in run FB-1644 vs. 1.3 - 5.1 min in run FA-1792. Residence times were calculated from the ideal gas law, using the arithmetic average of inlet and outlet gas flow rates). Carbon number effect on total olefin and 2-olefin selectivity was also more evident in the case of conventional FTS. Changes in 1-olefin selectivity (1-olefin/(1-olefin + 2-olefin + n-paraffin)) with carbon number, for both modes of operation at syngas conversion of about 80%, are shown in Figure 3. It can be seen that selectivity of C₂ and C₇₊ 1-olefins is significantly higher during supercritical FTS, and this is of potential commercial importance.

Results in Figures 1 and 2 show that gas space velocity has a marked effect on olefin selectivity during conventional FTS, and relatively small effect during SFTS. During conventional FTS the reaction mixture inside the reactor is distributed among two phases : gas and liquid. High molecular weight hydrocarbons (C₈₊) are leaving the reactor preferentially in the liquid phase, the flow rate of which increases along the reactor length. In a fixed bed reactor the residence time of the liquid phase is much longer than that of the gas phase. This increases probability for readsorption of high molecular weight 1-olefins and leads to increased formation of n-paraffins and 2-olefins via secondary reactions. On the other hand during SFTS operation, there is only one phase in the reactor and the residence time of all products, regardless of their molecular weight, is the same.

Carbon number effects, can be explained in terms of diffusion enhanced 1-olefin readsorption. Larger 1-olefins spend longer time in the catalyst pores than smaller ones, due to their lower diffusivities, and this increases probability for secondary 1-olefin readsorption, double bond isomerization and hydrogenation reactions. Ethylene, which has relatively large diffusivity due to its small molecular size, is significantly more reactive than other 1-olefins [9, 10], and its selectivity is low in comparison to C₃-C₆ olefins. Ethylene selectivity during conventional FTS was smaller than during SFTS at comparable bed residence times, i.e. syngas conversions (Figures 1 and 2). However, the pore residence time of ethylene is greater during conventional FTS, because ethylene diffusivity is smaller in the liquid filled pores (conventional FTS), than in the supercritical propane. Also, at a given gas space velocity, the carbon number effect on either the total olefin or 2-olefin selectivity was much more evident during the conventional FTS. In both modes of operation diffusivity decreases with increase in carbon number (molecular weight), but since diffusivities are significantly smaller in hydrocarbon wax than in the supercritical propane, the intraparticle diffusional resistance during conventional FTS is larger and carbon number effect on olefin selectivity is stronger.

Olefin Selectivities - Effect of reaction temperature

The effect of reaction temperature on olefin selectivities during SFTS and conventional FTS (run FB-1644) at a nearly constant syngas conversion was insignificant for temperatures between 235 and 265°C. Results from previous studies with iron FT catalysts showed different types of behavior, i.e. in some cases the olefin selectivity increased with increase in temperature, but on some catalysts either no effect or the opposite trends were observed [8, 9].

Olefin Selectivities - Effect of reactant composition

Figure 4 illustrates the effect of gas feed composition on olefin selectivity during SFTS at 235°C and syngas conversion of about 30% (data from periods 6, 11 and 15 in Table 1). Total olefin selectivity was lower, and 2-olefin selectivity higher when the synthesis gas with H₂/CO = 2.03 was used (representative of syngas obtained from steam reforming or partial oxidation of natural gas). Olefin selectivities were similar in experiments with H₂/CO = 0.67 and H₂/CO = 0.93.

Concentration of surface hydrogen determines chain termination probabilities and olefin content, and it increases with increase in H₂/CO molar feed ratio. High surface concentrations of hydrogen favor termination reactions, and termination to paraffins rather than olefins, as well as secondary 1-olefin isomerization reactions [8, 11].

SUMMARY

Effects of reaction temperature, gas space velocity and feed composition on olefin selectivity were studied in a fixed bed reactor during conventional FTS, and FTS in supercritical propane. It was found that total olefin content decreased and 2-olefin selectivity increased with either decrease in gas space velocity or increase in H₂/CO molar feed ratio, whereas olefin selectivities were essentially independent of reaction temperature.

Results from bed residence time effect studies in both modes of operation indicate that 1-olefins are the dominant primary products of FTS. Selectivity of n-paraffins and 2-olefins increases, whereas 1-olefin selectivity decreases with increase in carbon number, due to secondary reactions of 1-olefins. At high syngas conversions (~80%), selectivities of high molecular weight 1-olefins during SFTS were significantly higher than those obtained during conventional operation. These results indicate that SFTS is a potentially attractive route for synthesis of high molecular weight alpha olefins from the synthesis gas.

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Table I. Process conditions and catalyst activity results in test FA-1724

| Period. # | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|--------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Time on stream, h | 67 | 140 | 164 | 191 | 215 | 239 | 259 | 331 | 352 | 373 | 406 | 428 | 475 | 547 | 571 | 598 | 624 | 691 |
| T, °C | 250 | 250 | 250 | 250 | 235 | 235 | 265 | 265 | 250 | 250 | 250 | 235 | 235 | 250 | 250 | 235 | 235 | 250 |
| SV, L(NTP)/g-cat·h | 2.0 | 2.0 | 3.8 | 1.0 | 0.5 | 2.2 | 7.1 | 1.4 | 2.0 | 5.0 | 2.0 | 3.0 | 1.5 | 1.4 | 4.0 | 2.2 | 0.5 | 2.0 |
| GHSV, h ⁻¹ | 175 | 680 | 1340 | 330 | 288 | 752 | 2480 | 507 | 680 | 1750 | 1234 | 1047 | 529 | 487 | 1413 | 772 | 162 | 681 |
| H ₂ /CO feed ratio | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 2.0 | 2.0 | 2.0 | 2.0 | 0.93 | 0.93 | 0.93 | 0.93 | 0.67 |
| CO conv., % | 48.5 | 48.5 | 32.0 | 74.7 | 62.1 | 26.8 | 29.2 | 77.0 | 43.8 | 34.2 | 92.5 | 48.3 | 77.3 | 70.4 | 26.3 | 26.0 | 75.3 | 33.8 |
| H ₂ + CO conv., % | 43.1 | 50.2 | 34.4 | 75.5 | 65.0 | 29.3 | 32.5 | 76.6 | 46.7 | 22.1 | 60.3 | 30.4 | 51.7 | 64.9 | 27.4 | 27.7 | 69.9 | 35.1 |
| H ₂ /CO usage ratio | 0.82 | 0.73 | 0.79 | 0.69 | 0.74 | 0.82 | 0.85 | 0.66 | 0.78 | 0.95 | 0.98 | 0.90 | 1.03 | 0.78 | 1.01 | 1.06 | 0.79 | 0.73 |
| H ₂ /CO exit ratio | 0.60 | 0.61 | 0.61 | 0.61 | 0.54 | 0.61 | 0.57 | 0.69 | 0.58 | 2.59 | 15.1 | 3.08 | 5.45 | 1.31 | 0.90 | 0.89 | 1.35 | 0.63 |

Notes: Conventional FTS during period 1; SFTS during periods 2 - 18 with P_{total} = 5.5 MPa. Syngas partial pressure P_{H₂+CO} = 0.7 MPa in periods 5 and 11, otherwise P_{H₂+CO} = 1.5 MPa.

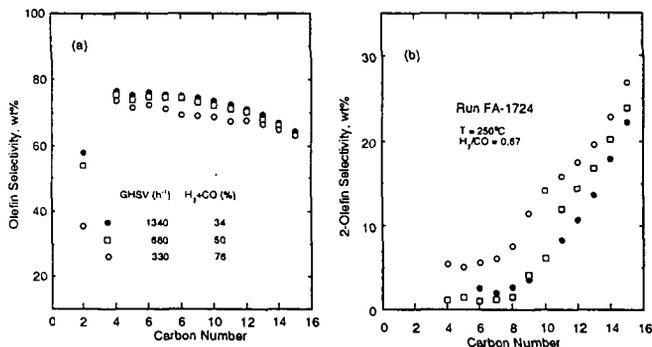


Figure 1. Effect of gas space velocity on: (a) olefin; and (b) 2-olefin selectivity during SFTS at 250°C, H₂/CO = 0.67 and 5.5 MPa (FA-1724).

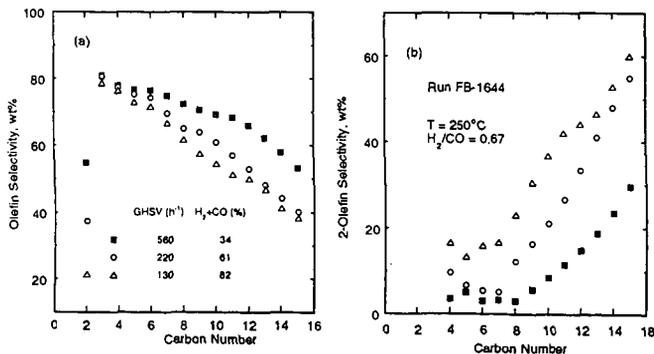


Figure 2. Effect of gas space velocity on: (a) olefin; and (b) 2-olefin selectivity during conventional FTS at 250°C, H₂/CO = 0.67 and 1.5 MPa (FB-1644).

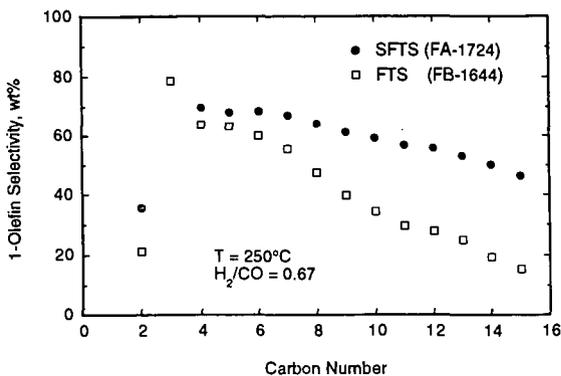


Figure 3. Comparison of α -olefin selectivities during conventional and supercritical FTS at 250°C, $H_2/CO = 0.67$ and syngas conversions of 82% (FB-1644) and 76% (FA-1724).

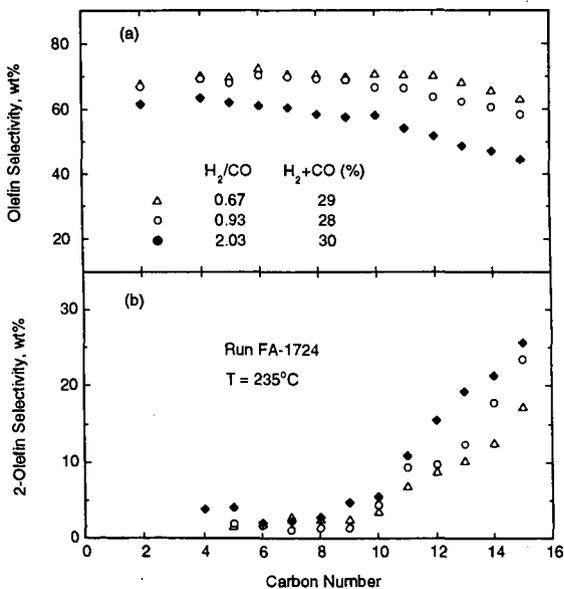


Figure 4. Effect of gas feed composition on: (a) olefin; and (b) 2-olefin selectivity during SFTS at 5.5 MPa and 235°C (FA-1724).