Catalysis Letters Vol. 108, Nos. 1–2, April 2006 (© 2006)
DOI: 10.1007/s10562-006-0022-1

Selective synthesis of higher linear α-olefins over cobalt Fischer–Tropsch catalyst

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Received 23 October 2005; accepted 7 January 2006

An efficient approach for *more* selective synthesis of higher linear α-olefins was achieved by utilizing suitable reaction media in FTS reaction. About 41.4% average α-olefins content in C_5–C_{25} fractions was obtained at $W/F_{(CO+H_2)} = 5$ g-cat h mol^{-1} in n-C_{10} solvent, which is markedly higher than the value (2.5%) obtained in 85% N_2 + 15% n-C_6.

KEY WORDS: FTS reaction; solvent; α-olefins synthesis; Co/SiO_2 catalyst.

1. Introduction

Higher linear α-olefins are valuable products and intermediates, which are used in a myriad of commercial products, including polymers, synthesis fluids, surfactants, additives and specialty chemicals [1,2]. For example, C_5–C_8 α-olefins are used as comonomers in polyethylene products and the longer chain α-olefins provide premium value synthetic lubricants. Significant economic benefit, therefore, can be achieved by increasing the α-olefin selectivity in Fischer–Tropsch synthesis (FTS) products [3,4].

It is well accepted that the FTS reaction is a surface-catalyzed stepwise growth process that uses CHx monomers formed by the hydrogenation of CO [3, 5–8]. Figure 1 illustrates the concept of chain growth pathways in the FTS. At each stage of growth, adsorbed hydrocarbon groups have the option of desorbing to form primary linear α-olefins, or of being hydrogenated to form n-paraffins products or of adding another CH_2 monomer to continue the chain growth. The primary α-olefins, however, can readsorb on the active sites and initiate secondary reactions (hydrogenation, etc), which results in the decrease of olefin to paraffin ratio with the chain length. Therefore, if α-olefins can escape from the particles before being readsorbed and hydrogenated to paraffins, the olefin to paraffin ratio of the FTS will increase.

It has been found that the α-olefin content of products in the near-critical or supercritical phase FTS is always higher than that in conventional gas phase FTS [9–15]. Enhanced diffusion and desorption rates of α-olefins in the near-critical or supercritical phase contribute to the increased α-olefins selectivity. In the present study, we have attempted a more selective synthesis of higher linear α-olefins during FTS through choosing a suitable solvent.

2. Experimental

The experiments were carried out in a fixed bed reactor, detailed information of which has been reported in our early publication [16]. The catalyst used was a silica supported cobalt catalyst (composition: $Co:SiO_2$ = 20:80 by weight; particle size: 20–40 mesh; BET surface area: 131 m^2/g; pore volume: 0.56 cm^3/g), which was prepared by incipient wetness impregnation method. The amount of catalyst loaded was 1 g, which was diluted in 2 g of glass beads. Each reaction was conducted for 6 h. During the reaction process, the gaseous compounds were analyzed on-line by two coupled gas chromatographs (CO, CO_2 and CH_4 were analyzed by GC with a thermal conductivity detector and light hydrocarbons (C_1–C_6) were analyzed by

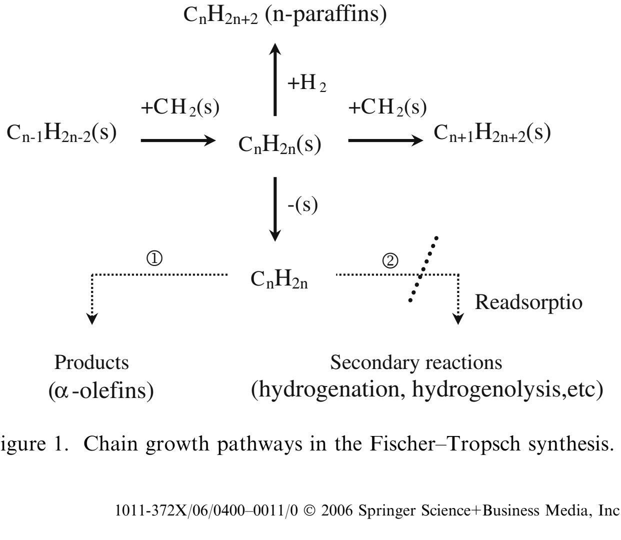

Figure 1. Chain growth pathways in the Fischer–Tropsch synthesis.

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another GC with a flame ionization detector). The liquid product was analyzed off-line by capillary column GC-17A (SHIMADZU). *n*-Hexadecane was used as the internal standard for the analysis of liquid products. After each reaction, residual products remaining within the catalyst were extracted by *n*-hexane and analyzed by GC.

3. Results and discussion

Four different solvents: 85% N_2 + 15% *n*-C_6 (by mole), *n*-C_6, 75% *n*-C_6 + 25% *n*-C_{10} and *n*-C_{10} were used in this work. Here *n*-C_6 and *n*-C_{10} denoted *n*-hexane and *n*-decane, respectively. In terms of the Antoine vapor pressure equation, which gives good correlation with experimental values [17], the calculated values of the vapor pressure of *n*-C_6 and *n*-C_{10} at 240 °C are 2.98 MPa and 0.41 MPa, respectively. The critical constants were 234.3 °C and 2.97 MPa for *n*-C6 and 344.7 °C and 2.11 MPa for *n*-C_{10}. Therefore, under the reaction conditions: $T = 240$ °C, $P_{\text{total}} = 4.5$ MPa, Solvent:Feed gas = 3.5:1 (by mole), 85% N_2 + 15% *n*-C_6 is at gas phase, *n*-C_6 is at supercritical phase, 75% *n*-C_6 + 25% *n*-C_{10} and *n*-C_{10} are at gas–liquid phase. The reaction performance of the FTS reaction in these four different solvents at $W/F_{(CO+H_2)} = 5$ g-cat h mol^{-1} is summarized in table 1. It can be seen that CO conversion and CO_2 selectivity had little change irrespective of the solvent. Higher CH_4 selectivity and *lower chain growth probability factor* α were observed in 85% N_2 + 15% *n*-C_6, which may be ascribed to the higher catalyst bed temperature in the gas phase than those in supercritical or gas–liquid phase [18]. The α-olefin content of FT products in the different solvents, however, was obviously different, which is shown in figure 2. The average α-olefin content of the products in the C_5–C_{25} fraction varied in the order: 2.5% (85% N_2 + 15% *n*-C_6) < 16.5% (*n*-C_6) < 31.8% (75% *n*-C_6 + 25% *n*-C_{10}) < 41.4% (*n*-C_{10}). It should also be noted that α-olefin content in the products in *n*-C_{10} solvent was almost constant across the range of C_{10}–C_{25} fractions irrespective of the chain length of the products and *the selectivity was stable with time on stream* [20].

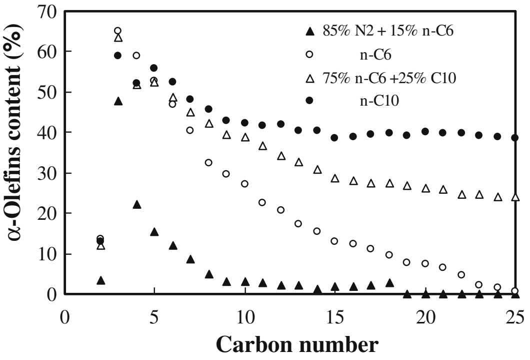

Figure 2. α-Olefins content of FT products in different solvent. Reaction conditions: $T = 240$ °C, $P_{\text{total}} = 4.5$ MPa,$W/F_{(CO+H_2)} = 5$ g-cat h mol^{-1}, Feed gas: $H_2/CO = 2$, $P_{\text{reaction media}}:P_{\text{syngas}} = 3.5:1$.

It is generally accepted that the α-olefin content of the FT products decreases with the increase of the carbon chain length due to the readsorption and secondary reactions of olefins [19]. This phenomenon indicates that the primary α-olefin products can be more effectively removed from the catalyst bed in *n*-C_{10} solvent. The introduction of solvent into the FT process can be used to improve heat transfer across the catalyst bed and for *in-situ* extraction of heavier products. Since the FT products over Cobalt catalyst consist mostly of linear paraffins and α-olefins, it is reasonable that *n*-C_6 solvent has higher solubility and extraction capability for FT products than 85% N_2 + 15% *n*-C_6 solvent according to the principle of like dissolves in like. That α-olefin content in *n*-C_{10} solvent is higher than that in *n*-C_6, may be caused by two main aspects. On the one hand, *n*-C_{10} has a longer carbon chain than *n*-C_6, so the former has higher affinity for heavy aliphatic hydrocarbons than the later, which results in the more effective extraction of α-olefins from catalyst surface in *n*-C_{10} solvent. On the other hand, under the reaction conditions, the vapor pressure of *n*-C_{10} is only about 0.41 MPa and about 88% *n*-C_{10} is in the condensed liquid phase. Therefore, when the primary α-olefin is extracted from the catalyst surface, the α-olefin is surrounded by *n*-C_{10} molecule and dissolved in the liquid phase solvent, which may retard the possibility of readsorption and secondary reactions. Furthermore, we investigated the residual ratio of the products in different solvent. The residual ratio herein was defined as the percentage of extracted products divided by the total amount of products (extracted products plus effluent products). The result is listed in table 2. The highest and lowest residual ratios were observed in 85% N_2 + 15% *n*-C_6 and *n*-C_{10},

Table 1
Reaction performances of the FT reaction in the different solvent

Reaction media	85% N_2 + 15% *n*-C_6	*n*-C_6	75% *n*-C_6 + 25% *n*-C_{10}	*n*-C_{10}
CO conv.%	44.5	46.9	42.6	41.5
CH_4 sel.%	13.0	8.5	9.5	9.7
CO_2 sel.%	1.2	1.5	1.2	1.2
α	0.78	0.85	0.89	0.88

Reaction conditions: $T = 240$ °C, $P_{\text{total}} = 4.5$ MPa,$W/F_{(CO+H_2)} = 5$ g-cat h mol^{-1}, Feed gas: $H_2/CO = 2$, $P_{\text{reaction media}}:P_{\text{syngas}} = 3.5:1$.

Table 2
Residue ratio of FT products in the different solvent

Reaction media	85% $N_2 + 15\%$ n-C_6	n-C_6	75% n-C_6 + 25% n-C_{10}	n-C_{10}
Effluent products, C-mmol/h kg-cat, (a)	15559	17456	16548	17247
Extracted products, C-mmol/h kg-cat, (b)	1385	982	624	167
Residual ratio (%) 100*b/(a + b)	8.2	5.3	3.4	1.0

Reaction conditions: $T = 240$ °C, $P_{\text{total}} = 4.5$ MPa, $W/F_{(CO+H_2)} = 5$ g-cat h mol^{-1}, Feed gas: $H_2/CO = 2$, $P_{\text{reaction media}}:P_{\text{syngas}} = 3.5:1$.

respectively. This result is also consistent with the above explanation that n-C_{10} has higher extraction capability for heavier FT products.

In addition, similar experiments were also carried out at $W/F_{(CO+H_2)} = 10$ g-cat h mol^{-1}. CO conversion were 86.5% for in n-C_6 solvent and 83.3% for in n-C10 solvent. The average α-olefin content in the C_2–C_{25} fractions in n-C_{10} (18.5%) was also higher than that in n-C_6 (3.2%).

As the effect of purity of solvent itself on the α-olefin selectivity, the major impurities of different solvent are iso-paraffins. For n-C_6 or n-C_{10} solvent, the normal paraffin content is more than 99.0%. This effect can be negligible due to the very low concentrations of iso-paraffins. Moreover, the existence of iso-paraffins in the solvent decreases the selectivity of α-olefin [20], which is contrary to our reported results. Therefore, we can conclude that the changes in the α-olefin selectivity are not caused by trace solvent impurities.

A more thorough investigation of the effects of solvent systems on the α-olefin selectivity and the proposed explanation based on the model of the α-olefin diffusion in the different reaction phase will be discussed in [20],

4. Conclusions

In summary, *more* selective synthesis of higher linear α-olefins during FTS has been achieved by choosing suitable reaction media. 41.4% average α-olefin content in the C_5–C_{25} fractions was obtained at $W/F_{(CO+H_2)} = 5$ g-cat h mol^{-1} in n-C_{10} solvent, which is markedly higher than the value (2.5%) that obtained in 85% $N_2 + 15\%$ n-C_6.

Acknowledgments

This study was entrusted from Nippon Oil Corporation as a part of NEDO-ATL Project (New Energy and Industrial Technology development Organization, Asphalt to Liquid Project).

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