Reactions of Olefins Added during Fischer-Tropsch Synthesis over Supported Cobalt Catalyst

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Abstract

The control on product distributions in Fischer-Tropsch synthesis by feeding olefins in the n-paraffin solvent over a 20 wt.% Co/SiO_2 catalyst under the typical reaction conditions of 503K, 2.1MPa, H_2/CO = 2, and co-fed olefins 16 mol% in CO base in a trickle bed reactor has been studied. The selected co-fed olefins include 1-octene, 2-octene and 1-dodecene. Results showed that the addition of 1-octene or 1-dodecene could greatly enhance the selectivity of heavy wax products with a marked increase in CO conversion while suppressing the formation of lighter hydrocarbon product by incorporation of co-fed 1-olefins into chain growth compared to the conventional FT reaction. In the case of co-fed 1-dodecene, disproportionate reaction may occur, which resulted in a symmetrical product distributions and gave a high selectivity in middle distillates in 1-dodecene-added FT reaction. The disproportionate reaction occurred due to the successive demethylation of 1-dodecene and higher hydrocarbons formed by 1-dodecene incorporated with CH_2 species from demethylation of 1-dodecene. The disproportionate reaction of co-fed olefins was competitive with incorporation into chain growth and were controllable by tuning process conditions. The disproportionate reaction was increased with chain length n. When the 2-octene was used as co-fed olefin, the incorporation into chain growth was much less and hydrogenation reaction was also relatively more difficult to occur, which was ascribed to the sterical hindrance.

Keywords: Fischer-Tropsch synthesis; Co/SiO_2 catalyst; Co-fed olefins; Product distribution; Disproportionate reaction; Chain initiation;

1. Introduction

Synthesis gas (syngas), a mixture of H_2 and CO, obtained from natural gas, coal, petroleum, biomass and even from organic wastes is converted to hydrocarbons and H_2O over a heterogeneous Fischer-Tropsch (FT) synthesis catalyst containing a group   metals such as Co, Fe and Ru. In the FT process, CO and H_2 are dissociated at the surface of the catalyst and at first generate CH_x species and H_2O [1]. The CH_3 surface species is regarded as the chain initiator and chain growth occurs by successive incorporation of the monomer CH_2 surface species in a growing alkyl species. Principally two termination reactions are possible, namely α-hydrogenation, yielding a paraffin, or β-dehydrogenation, producing an α-olefin as primary products [2-5]. Such a chain growth mechanism gives a so-called Anderson-Schulz-Flory (ASF) distribution that logarithmic molar product distributions decreases with chain length n, which places a significant limitation on the selectivity of the more valuable products such as diesel and wax. In the early days of FT reasearch, real product distributions often show deviations from ideal ASF distributions. It is widely considered that the occurrence of secondary reactions (reinsertion into the chain growth process, hydrogenolysis and isomerization) gives the most reasonable explanation for these deviations of the ASF distribution [6-10].

Olefin readsorption pathways were examined by the addition of α-olefins to the H_2/CO feed. Co-fed olefins studies have previously shown the reactivity of α-olefins in chain initiation and growth causing an increase in heavier hydrocarbon yield [11,12,13-17], hydrogenolysis shortening long hydrocarbons by successive demethylation [8], as well as their extensive conversion to the corresponding paraffin by secondary hydrogenation

[6,18-20]. To this point, Readsorption reactions of α-olefins in FT synthesis can be utilized to optimize the selectivity to the desired product range. But in the study of readsorption reactions of α-olefins the most important one is to understand how to control and assist the favorable reaction pathways towards the optimal product distribution.

In the recent studies of FTS, we have carried out the FT reaction in a trickle bed reactor to explore the effects of solvent on the performances of FTS [21]. Results show that the selected solvents do exhibit remarkable influences on the α-olefin selectivity. In the case of n-hexane solvent, the α-olefin content in the product decreases markedly with increasing carbon number. The n-decane solvent gives the highest olefin content. It was independent of carbon number on the C_6+ product at the level of about 40%. This phenomenon has been attributed to quicker desorption, diffusion and more suppressed re-adsorption of primary FTS product (α-olefin).

For α-olefin-added FT reaction, the adsorption of co-fed α-olefins to catalytic sites should be a reverse process relative to the diffusion of primary α-olefins out of catalyst pores. The easier to diffuse to catalytic sites for the co-fed α-olefins, the more difficult to diffuse out of catalyst pores for the primary α-olefins products. So, we deduce that it is possible to effectively diffuse the added α-olefins onto catalytic sites by choosing suitable accompanying fluids, flow rate of fluid and subsequently to control the reaction pathways for an increasing yield of desired products.

In this study, we have investigated the reaction pathways of co-fed olefins in a trickle bed reactor with 1-octene, 2-octene or 1-dodecene 16.0 mol% in CO base for a more observable effect on the product spectrum of FT synthesis. Based on the obtained results, a modifed secondary reactions network is presented and the speculation on possible mechanisms and optimal control in carbon number distribution are also discussed.

2. Experimental

2.1 Catalyst preparation

The 20 wt.% Co/SiO_2 catalyst was prepared by an incipient impregnation method. The cobalt nitrate was used as the precursor of cobalt and silica gel (Fujisilica Q-15, surface area: 200 m^2 g^{-1}, average pore diameter: 15 nm, pore volume: 1.0 ml g^{-1}) was used as the support. After being dried overnight at 200 ℃, the catalyst was calcined at 473 K for 2 h. The catalyst used in this work was pressed, crushed and sieved to 20~40 mesh size. Some catalyst (1.0 g) was diluted with Q-15 (2.0 g) before loading into the reactor. The catalyst was pretreated at 673 K for 3 h in situ in a flow of hydrogen.

2.2 Reaction procedure and product analysis

The reaction system and operating procedure for FT reaction have been described in earlier publication [21]. The only difference was that the co-fed 1-olefin in the n-paraffin solvent was fed into vaporizer. n-Hexane (T_b 68.8 ℃), n-octane (T_b 125.6 ℃) or n-dodecane (T_b 216.3 ℃) was utilized as the solvent fluids. The typical reaction conditions were: P_{total} = 2.1 MPa, $CO:H_2:Ar$ = 1:2:0.1, W/F_{syngas} = 5 g h mol^{-1}, T = 230 ℃, co-fed 1-octene (T_b 121.3 ℃), 2-octene (T_b 124.5 ℃) or 1-dodecene (T_b 213 ℃) 16 mol% in CO base.

The effluent gaseous products were analyzed with two on-line gas chromatographs (GC). One was equipped with a thermal conductivity detector (TCD) for analysis of CO, CH_4 and CO_2 by using Ar as internal standard while the other one was equipped with a Flame ionization detector (FID) and an Al_2O_3-KCl capillary column for analysis of C_1~C_5 hydrocarbons. The condensed products of 3.5~5.0 h time-on-stream collected in the ice-cooled trap were analyzed offline for C_3~C_{25} hydrocarbons by capillary column GC-17A (Shimadzu).

2.3 Product distribution calculations

We report selectivities on a carbon-atom basis as the percentage of the converted CO that appears as a given product. Hydrocarbon synthesis rates are reported as catalyst-time yield (mmol h^{-1} kgcat^{-1}) and only normal hydrocarbons are included for the product selectivity or carbon flow distribution calculation. To show the effect of co-fed olefin on carbon flow distribution, we compare the assumed conventional FT reaction with olefin-added FT reaction at the same level of CO conversion while the carbon flow distribution of the assumed conventional FT reaction is obtained from the below equation,

$$F = \frac{\varphi_0}{\varphi_C} F_C$$

with F hydrocarbon synthesis rate for assumed conventional FT reaction, φ_0 the CO conversion for olefin-added FT reaction, φ_c the CO conversion for real conventional FT reaction, F_C hydrocarbon synthesis rate for real conventional FT reaction. Carbon flow distribution in Table 4 is calculated to combine the characteristics of original FT reaction, disproportionate reaction of co-fed olefins and chain growth initiated by co-fed olefins.

3. Results and discussion

The main products of FT synthesis are linear paraffins and linear α-olefins. Secondary reactions can occur when primary α-olefins desorb from a site and interact with another catalytic site before leaving the reactor. In general, possible secondary reactions of α-olefins was listed by Novak et al. [6,22] as 1. hydrogenation to give n-paraffins, 2. isomerization, 3. cracking and hydrogenolysis, 4. insertion into growing chains, mostly effective for C_2H_4 and C_3H_6, and 5. readsorption and initiation of hydrocarbon chains. However, the most important secondary reactions are hydrogenation (pathway   ), reinsertion (pathway   ), and hydrogenolysis (pathway   ) as shown in Fig. 1. Hydrogenation will convert an olefin into a paraffin. This changes the paraffin to olefin ratio, but has no direct impact on the growth probability. Reinsertion of an α-olefin into the chain growth process, on the other hand,
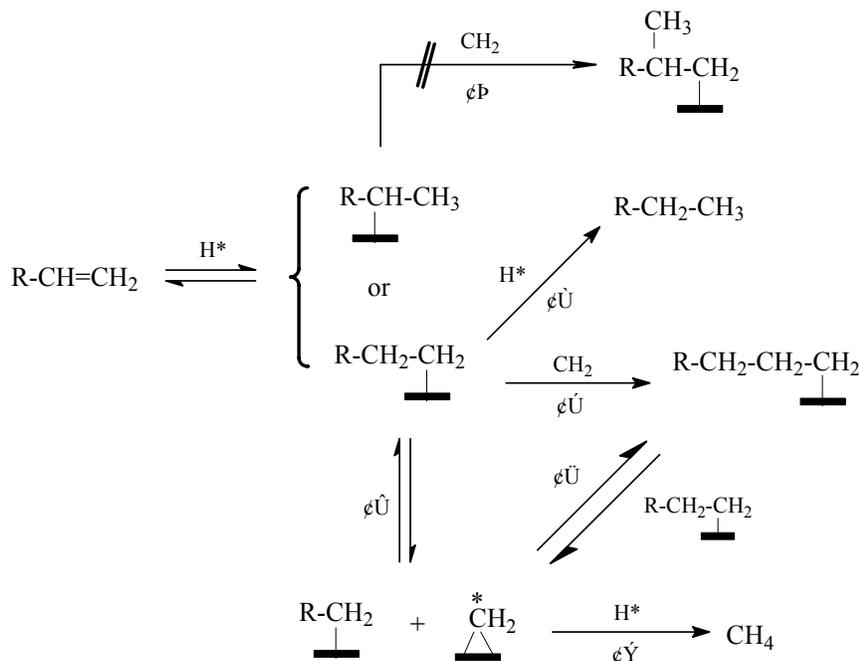
Fig. 1. Scheme of the reaction network of co-fed 1-olefins.

reverses the termination via β-dehydrogenation and will thus affect the carbon number distribution to favor the formation of heavier hydrocarbon. Hydrogenolysis of olefins will reverse the growth process and thus lead to a decrease in chain growth probability (α value).

Table 1
Influence of solvent in the olefin-added FT reaction

Added olefin	Solvent	CO conversion (%)	Selectivity (%)			$R_1 : R_2 : R_3$ (%) [a]	α
			CH_4	CO_2	1-olefin		
No addition	$n\text{-}C_6$	46.5	9.0	0	7.5	-----	0.86
1-dodecene	$n\text{-}C_6$	48.2	7.7	0	11.6	80.2:2.8:17.0	-----
No addition	$n\text{-}C_9$	55.3	8.0	0	19.2	-----	0.89
1-dodecene	$n\text{-}C_9$	66.8	5.7	0	26.6	66.1:22.8:11.1	-----

Reaction conditions: 20 wt.% Co/SiO_2 (Q-15), T = 230 ℃, P = 2.1 MPa, $W/F_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, added olefin: 1-dodecene, 16.0 mol% in CO base; $F_{(Solvent+1\text{-}dodecene)}$ = 1.42 ml/min, $F_{1\text{-}dodecene}$ = 0.04 ml/min; [a] $R_1 : R_2 : R_3$ = (hydrogenation or shift to internal double bond olefin) : unreacted : other reactions.
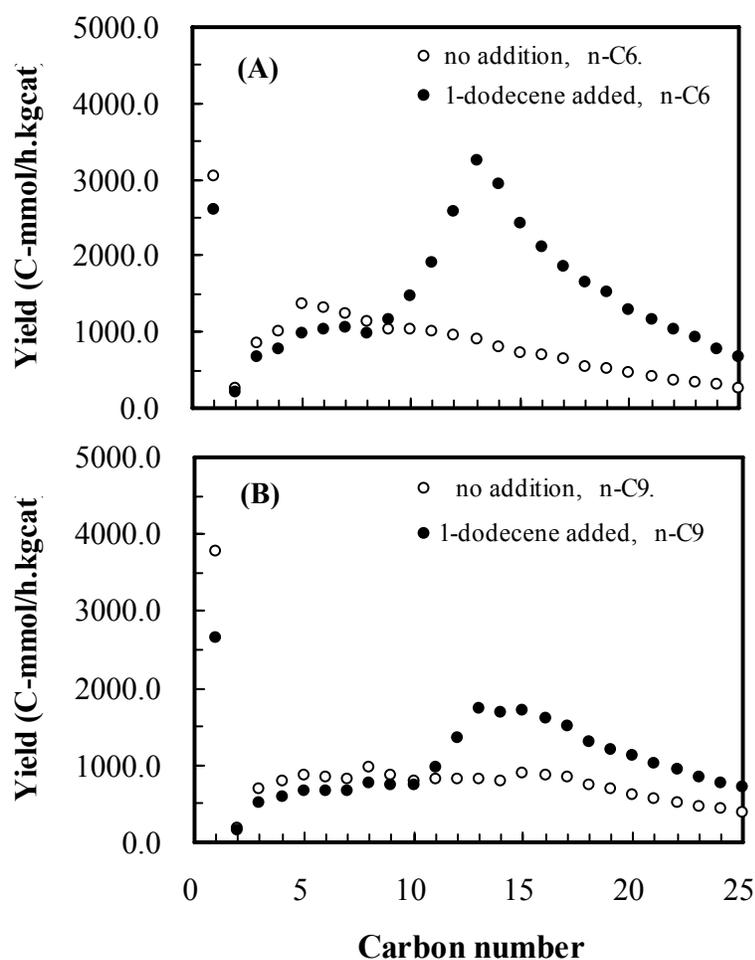
Fig. 2. Effect of solvent on the carbon number distribution in olefin-added FT reaction.

To obtain more insight into the role of secondary reactions on the carbon number distribution and assist the reactions towards the optimal product distributions. We have carried out the co-fed olefins studies accompanied by solvent fluids with syngas feed. As shown in Table 1 and Fig. 2, one can see that co-fed 1-dodecene can increase the CO conversion (Table 1), especially in n-nonane solvent, and suppress the yield of lighter hydrocarbon products (Fig. 2) and promote the yield of heavier hydrocarbons, which is because the CH_2 species was consumed for chain growth initiated by co-fed 1-dodecene so that the original FT reaction starting from CH_3 species and following a consecutive CH_2 species insertion was suppressed. A quite interesting phenomenon was obtained that the product distribution in the 1-dodecene-added FT reaction exhibited symmetry. This phenomenon was more clear in n-hexane reaction media. Since the 1-dodecene was utilized as co-fed olefins, the yield of C_{12-} in 1-dodecene added FT reaction should be lower than that in the conventional FT reaction. However, in n-hexane reaction media, the yield of C_{11},C_{10} or C_9 was obviously higher than that in the conventional FT reaction, which is due to the successive demethylation (pathway ③ in Fig. 1) of co-fed 1-dodecene resulting in a increase in corresponding hydrocarbon products. The formed CH_2 species may be incorporated with co-fed 1-dodecene to yield the higher hydrocarbons than C_{12} as shown pathway ④ in Fig. 1, which is so-called disproportionate reaction. We have experimentally evidenced this reaction in the absence of syngas and will report and discuss it in detail in a subsequent paper. Disproportionate reaction is directly responsible for the symmetrical product distributions and high yield in middle distillates. Under the same reaction conditions, the n-hexane solvent gives a lower syngas partial pressure than that in the n-nonane solvent due to the lower boiling point and relatively much vaporized. The low syngas partial pressure will promote the disproportionate reaction of co-fed 1-dodecene and be unfavorable for the incorporation into chain growth. The disproportionate reaction of co-fed 1-dodecene is competitive with incorporation into chain growth and are controllable by tuning process conditions. Seen from Table 1, the hydrogenation was the main pathway for co-fed 1-dodecene and the unreacted co-fed 1-dodecene was much higher in n-nonane solvent due to the more liquid phase appeared to suppress the co-fed 1-dodecene diffusion onto catalytic surface.

To proceed the reactions of co-fed 1-olefins, these added 1-olefins must diffuse through reaction media and be adsorbed onto the catalytic sites. Once the 1-olefins was adsorbed on the surface of catalyst, which route of hydrogenation, disproportionate reaction or incorporation into chain growth as the important process will depend on the catalyst, reaction conditions and 1-olefins itself. Even if the liquid phase media was disadvantageous for the diffusion of co-fed 1-dodecene, it was feasible to facilitate the diffusion of co-fed 1-dodecene onto catalytic sites and increase the residence time of co-fed 1-dodecene in the catalyst bed by decreasing flow rate of solvent and the liquid phase media will give higher syngas partial pressure, which was favorable for the incorporation of 1-dodecene into chain growth and for

Table 2
Effect of co-fed 1-dodecene on the FT reaction performances

Added olefin	CO conversion (%)	Selectivity (%)			α
		CH_4	CO_2	1-olefin	
No addition	65.4	7.7	0	13.5	0.85
1-dodecene	77.4	5.1	0.8	19.4	-----

Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15), T = 230 ℃, P = 2.1 MPa, W/F$_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-dodecene, 16.0 mol % in CO base; F$_{n-dodecane}$ = 0.29 ml/min, F$_{1-dodecene}$ = 0.04 ml/min;
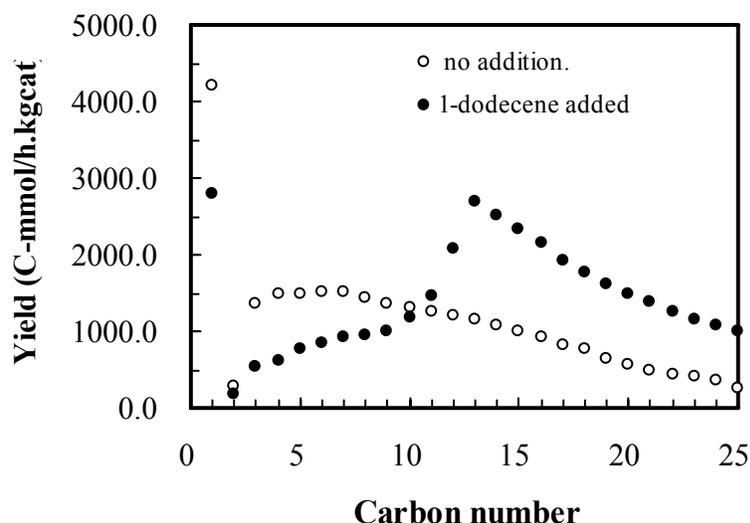
Fig. 3.   Effect of co-fed 1-dodecene on the carbon number distribution control.

suppression of disproportionate reaction. It was especially worthy to note that complete liquid phase reaction media was unfavorable for syngas diffusion into catalyst pores inside and products diffusion out of the catalyst channel so that the chain growth probability (α value) was decreased. Here, we used a low flow rate of n-dodecane as solvent fluid to carry out the co-fed 1-dodecene studies. As displayed in Table 2 and Fig. 3, one can see that the CO conversion was increased about 12% and the lighter hydrocarbon products in C_1-C_{11} range was surprisingly suppressed about 40% (Table 4 (a)) compared to the conventional FT reaction under the same CO conversion level, which is ascribed to the largely released diffusion limitation through the reaction media and promoted chain growth initiated by co-fed 1-dodecene. As a result, the disproportionate reaction occurred to a limited extent.

Under the same conditions, we studied the co-fed 1-octene or 2-octene effect on the product distributions control during FT synthesis and the obtained results were shown in Table 3 and Fig. 4. One can see that the co-fed 1-octene can also increase the CO conversion about 9.4% (Table 3) and suppress the lighter hydrocarbon products in C_1-C_7 range about 40% (Table 4 (b)) while promoting the yield of heavier hydrocarbon products

Table 3
Effect of co-fed olefin molecular strucrue on the FT reaction performances

Added olefin	CO conversion (%)	Selectivity (%)			$R_1 : R_2 : R_3$ (%) [a]	α
		CH_4	CO_2	1-Olefin		
No addition	53.1	7.9	0	10.4	------	0.89
1-octene	62.5	3.8	0	15.3	94.2 : 4.0 : 1.8	-----
2-octene	50.2	7.6	0	11.6	64.4 : 31.4 : 4.1	----

Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15), T = 230 ℃, P = 2.1 MPa, W/F$_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-octane, added olefin:16.0 mol% in CO base; F$_{(n-octane+co-fed olefin)}$ = 0.33 ml/min, F$_{co-fed olefin}$ = 0.03 ml/min; [a] R$_1$: R$_2$: R$_3$ = (hydrogenation or shift to internal double bond olefin) : unreacted : other reactions.
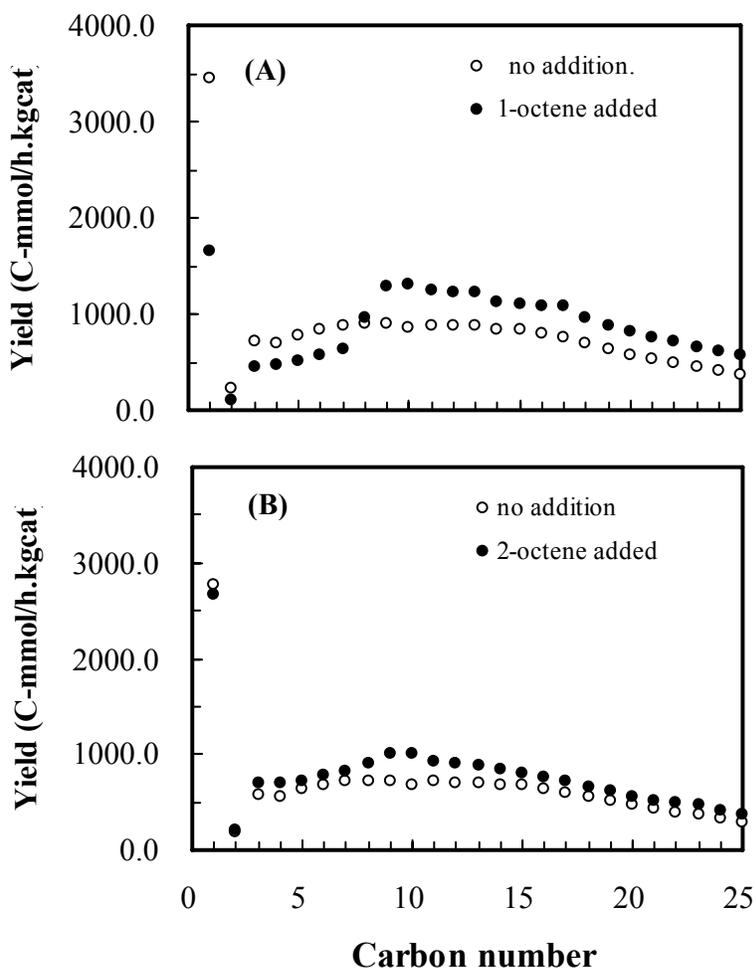
Fig. 4.   Effect of co-fed olefin molecular structure on the carbon number distribution control.

(Fig. 4 (A)). The disproportionate reaction of co-fed 1-octene was much less since the yield in C_7 was also obviously suppressed compared to the conventional FT reaction. This disproportionate reaction of co-fed 1-olefins increased with chain length n may be governed by thermodynamics. For co-fed 2-octene, the CO conversion (Table 3) or carbon number distribution (Fig. 4(B)) has no obvious difference compared to the conventional FT reaction, which is ascribed to the more difficult incorporation of co-fed 2-octene into chain growth caused by sterical hindrance compared to the co-fed 1-octene. As shown in Table 3, the hydrogenation reation for co-fed 2-octene was also more difficult to proceed compared to the co-fed 1-octene.

The carbon flow distributions for the conventional or olefin-added FT reaction are compiled in Table 4 (a) and (b). Seen from these data, it was quite clear that the co-fed 1-octene or 1-dodecene could effectively incorporate with CH_2 species into heavy wax products. Conversion of syngas into heavy wax product (C_{25}+) is 10 wt.% higher than that in the conventional FT reaction. The chain growth initiated by co-fed 1-octene or 1-dodecene to consume some CH_2 species from syngas was terminated as diesel range hydrocarbons to a relatively less extent. When using 1-dodecene as co-fed olefin, the disproportionate reaction resulted in a much higher selectivity in middle distillates mainly from co-fed 1-dodecene.

Table 4
Carbon flow distribution in olefin-added FT reaction

(a)

Added olefin	Solvent	$F_{(solvent+ 1-dodecene)}$ (ml/min)	CO conv. (C-mol h^{-1} kg cat^{-1})	C_1-C_{11} products (C-mol h^{-1} kg cat^{-1})		C_{13}-C_{25} products (C-mol h^{-1} kg cat^{-1})			R_4^{b} (%)	R_5^{b} (%)
				R_1^{a}	R_2^{a}	R_1^{a}	R_2^{a}	R_3^{a}		
No addition	n-nonane	1.42	47.1	11.45	----	8.57	----	----		
1-dodecene	n-nonane	(1.38+0.04)	47.1	8.66	0.42	9.50	0.05	6.6	2.0	3.9
No addition	n-dodecane	0.33	54.4	17.2		8.9	----	----		
1-dodecene	n-dodecane	(0.29+0.04)	54.4	10.2	1.1	10.2	0.1	12.0	2.4	10.5

(b)

Added olefin	Solvent	$F_{(solvent+1-octene)}$ (ml/min)	CO conv. (C-mol h^{-1} kg cat^{-1})	C_1-C_7 products (C-mol h^{-1} kg cat^{-1})		C_9-C_{25} products (C-mol h^{-1} kg cat^{-1})			R_4*^{c} (%)	R_5*^{c} (%)
				R_1^{a}	R_2^{a}	R_1^{a}	R_2^{a}	R_3^{a}		
No addition	n-octane	0.33	43.9	7.6	----	11.8	----	----		
1-octene	n-octane	(0.30+0.03)	43.9	4.4	----	11.9	----	4.7	0.4	7.0

Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15), T = 230 ℃, T = 2.1 MPa, W/F$_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, F$_{syngas}$ = 81 ml/min, co-fed 1-olefins: 16.0 mol% in CO base;
[a] R_1: carbon from CO;
[a] R_2: carbon from the demethylation of 1-octene or 1-dodecene;
[a] R_3: carbon directly from co-fed 1-octene or 1-dodecene reacted with CH$_2$ species;
[b] R_4(R_5): carbon yield decrease in C_1-C_{11} products converted to C_{13}-C_{25} (C_{25+}) products in the percentage of CO conv.;
[c] R_4*(R_5*): carbon yield decrease in C_1-C_7 products converted to C_9-C_{25} (C_{25+}).

4. Conclusion

1. Effective control of carbon number distribution in FTS has been demonstrated with co-fed 1-olefins (1-octene or 1-dodecene) in a trickle bed reactor. Addition of 1-octene or 1-dodecene (16 mol% in CO base) in the n-paraffin solvent could greatly enhance the selectivity of heavy wax (about 3.9~10.5% of total CO conversion) and middle distillates (about 0.4~2.4% of total CO conversion) directly from syngas, with about 10% increase in CO conversion while suppressing the formation of lighter hydrocarbon products at about 40% compared to the conventional FT reaction under the same CO conversion level.

2. In the case of co-fed 1-dodecene, the disproportionate reaction occurred, which resulted in a symmetrical product distributions and gave a much higher selectivity in middle distillates in 1-dodecene added FT reaction.The disproportionate reaction of co-fed olefins was competitive with incorporation into chain growth and were controllable by tuning process conditions. Compared to the co-fed 1-dodecene, the disproportionate reaction of co-fed 1-octene in the n-octane solvent was much less.

3. The incorporation of 2-octene into chain growth could be made negligible and hydrogenation reaction was also relatively more difficult to occur.

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