

# **$\alpha$ -Olefins Synthesis from Fischer-Tropsch Reaction in a Trickle Bed Reactor**

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## **Abstract**

The influence of solvent on the selectivity of  $\alpha$ -olefin in the product hydrocarbon as a function of carbon number over a 20 wt.% Co on SiO<sub>2</sub> catalyst under the typical reaction conditions of 513 K, 4.5 MPa and H<sub>2</sub>/CO = 2 has been investigated. Hydrocarbons with different carbon numbers and molecular structures, including n-hexane, n-octane, n-decane, n-dodecane, n-hexadecane, iso-octane and decahydronaphthalene, were used as solvents. Although the selected solvents did not obviously affect the catalytic activity or chain growth probability ( $\alpha$ -value), they exhibited remarkable influences on the  $\alpha$ -olefin selectivity. In the case of n-hexane solvent, the  $\alpha$ -olefin content in the product decreased markedly with increasing carbon number of the product. The n-decane solvent gave the highest olefin content. It was independent of carbon number on the C<sub>6</sub>+ product at the level of about 40%. This could be attributed to quicker desorption, diffusion and more suppressed re-adsorption of primary FTS product ( $\alpha$ -olefin).

**Keywords:** Fischer-Tropsch reaction; Solvent;  $\alpha$ -Olefin synthesis; Co/SiO<sub>2</sub> catalyst

## **1. Introduction**

Recently, there is a world-wide increasing interest in the Fischer-Tropsch (FTS) as a method to produce synthetic liquid fuels and chemicals from coal, natural gas or biomass in view of dwindling petroleum reserves. The FTS product spectrum consists of a complex multicomponent mixture of linear and branched hydrocarbons and oxygenated products. The main products are linear paraffins and  $\alpha$ -olefins. Linear  $\alpha$ -olefins are very important chemical intermediate for a number of industrial and consumer products, including polymers, synthesis fluids, surfactants, additives and specialty chemicals [1,2]. For example, C<sub>5</sub>–C<sub>8</sub>  $\alpha$ -olefins are used as the comonomers in ethylene polymerization and the longer chain  $\alpha$ -olefins provide premium synthetic lubricants. Therefore, significant economic benefit can be achieved by increasing the  $\alpha$ -olefin selectivity of the raw FTS products [3].

In general, modern FT synthesis is operated in the gas phase-fixed bed system, in the gas phase-fluidized bed system and in the liquid phase-slurry system. In the gas phase-fixed bed system, catalyst bed and catalyst pores are plugged by a waxy product to suppress the catalytic performances. One can avoid this problem, if the fixed bed is washed with solvent continuously or intermittently during the operation. The continuous washing system is a kind of “trickle bed reactor” system. Therefore, the washing material is a kind of solvent of the reactor. It is expected that the solvent will affect the FTS reaction.

One of the present authors has found that the supercritical solvent affects the FTS reaction to a marked extent [4], especially for the selectivity of olefins [5],  $\beta$ -olefin [6], CO<sub>2</sub> [7], as well as the minimization of waxy product in the catalyst bed. The minimization effect can be attributed to an extraction effect of supercritical hexane (or pentane). The extraordinarily high selectivity of olefin in the super critical fluid (SCF) phase reaction has been explained by the well-balanced extraction of  $\alpha$ -olefin from the catalyst surface and its transfer inside of the catalyst pores [8].

In recent studies of FTS on Ru- and Co-based catalysts, Fan and Fujimoto [9] has introduced a supercritical phase into the conventional gas–solid phase FT process. Results show that the  $\alpha$ -olefin content decreases with an increase in the carbon number, but this phenomenon is more moderate than in the gas phase- or liquid phase-FTS. We deduce that the reaction media will remarkably affect the  $\alpha$ -olefin selectivity due to the different capabilities of extraction and transportation.

In this study, our major aim is to obtain a deeper insight into the effect of solvent on the  $\alpha$ -olefin selectivity and to assist the product distribution towards the desired  $\alpha$ -olefin. For this purpose, we have undertaken a thorough investigation of the effects of solvents. Not only supercritical n-hexane, but also near critical fluids and other kinds of fluids such as n-octane, n-decane, n-dodecane, n-hexadecane, iso-octane and decahydronaphthalene are studied. The effect of carbon chain length, molecular structure or content of solvent on the CO conversion, product distribution and especially on the  $\alpha$ -olefin content in the FTS products, are discussed in details.

## 2. Experimental

### 2.1 Catalyst preparation

Twenty weight percent Co/SiO<sub>2</sub>, as FTS catalyst, was prepared from Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and commercially available SiO<sub>2</sub> (Fujisilicia Q-6, Q-15 and Q-50) by an incipient wetness impregnation method [10]. The catalyst precursor was dried in air at 393 K for 12 h and then calcined at 473 K for 2 h to form the supported metal oxide. The calcined catalyst was crushed and sieved to 20–40 mesh size. Some catalyst (1.0 g) was diluted with Q-30 up to a constant volume of 5.7 cm<sup>3</sup> before loading into the reactor. The catalyst was reduced in situ in a hydrogen flow at 400 °C for 3 h.

### 2.2 Reaction procedure and product analysis

The reactor flow diagram for FTS was similar to that of a conventional, pressurized, fixed-bed flow reactor system. The only difference was that a preheating vaporizer and an ice-cooled high pressure trap was vertically set upstream and downstream of the reactor, respectively, as described in [9]. The temperature of the vaporizer is 240 °C. Syngas (CO:H<sub>2</sub>:Ar = 1:2:0.1) and solvent were fed to the vaporizer by a mass flow controller and a high pressure liquid pump, and then entered into the reactor concurrently. The effluent gas and liquid from reactor passed through an ice-cooled trap, where the solvent and FT products were condensed continuously, and uncondensed products with unreacted syngas were depressed and led to an online gas chromatograph. Each reaction was conducted for 6 h. Standard operating conditions of T = 240 °C, P<sub>total</sub> = 4.5 MPa, W/F<sub>(CO+H<sub>2</sub>)</sub> = 5.0 g-cat h mol<sup>-1</sup>, F<sub>solvent</sub> = 1.42 ml min<sup>-1</sup> and CO:H<sub>2</sub>:C<sub>10</sub> (n-decane) = 1:2:6.4 (mole ratio) were applied. The effluent gas was analyzed online with two gas chromatographs. One was equipped with a TCD detector for analysis of CO, CH<sub>4</sub> and CO<sub>2</sub> while the other one was equipped with a FID detector for analysis of C<sub>1</sub>–C<sub>5</sub> hydrocarbons. When the reaction reached the steady state after ca. 2.5 h, the condensed products of 3-5.5 h time-on-stream collected in the ice-cooled trap were analyzed offline using a GC-17A (SHIMADZU) capillary column for C<sub>3</sub>–C<sub>25</sub> hydrocarbons. The chain growth probability ( $\alpha$ ) of the products was defined by the Anderson-Schulz-Flory plot, in which the carbon number extended from C<sub>4</sub> to C<sub>20</sub>.

## 3. Results and discussion

### 3.1 Effect of carbon chain length of solvent

To investigate the effect of carbon chain length of solvent on the FTS, we used one of five different chain length normal paraffins: n-hexane, n-octane, n-decane, n-dodecane or n-hexadecane, as reaction media. The FTS reaction performance over Co/SiO<sub>2</sub> catalyst in these solvents under the operating conditions of T = 240 °C, P<sub>total</sub> = 4.5 MPa, W/F<sub>(CO+H<sub>2</sub>)</sub> = 5.0 g-cat h mol<sup>-1</sup>, and H<sub>2</sub>/CO = 2 is shown in Table 1 and Fig. 1. Data show that there are no significant differences in the CO conversion, CH<sub>4</sub> selectivity,  $\alpha$ -value and the selectivity of olefins (mostly  $\alpha$ -olefin) in C<sub>2</sub>–C<sub>5</sub> light hydrocarbons or in the product selectivity when using n-paraffin with 6-16 carbon atoms as solvent. However, higher  $\alpha$ -olefins are strongly

dependent on the selected solvent. In the case of n-hexane solvent, the olefin content decreased obviously with increasing carbon number. However, the n-decane solvent gives the highest  $\alpha$ -olefin content, which is independent of carbon number at the level of about 40%. For n-octane, n-dodecane and n-hexadecane reaction media, the olefin content is similar to n-decane as solvent but slightly decreased with increasing carbon number.

**Table 1**

Effect of carbon chain length of solvent on the FT reaction performances

Solvent	CO conversion (%)	Selectivity (%)		$\alpha$
		CH <sub>4</sub>	CO <sub>2</sub>	
n-Hexane	68.9	9.3	1.3	0.86
n-Octane	66.4	9.6	2.1	0.87
n-Decane	65.8	8.8	1.3	0.88
n-Dodecane	64.2	8.7	1.7	0.86
n-Hexadecane	56.4	9.1	1.6	0.87

Reaction conditions: 20 wt.% Co/SiO<sub>2</sub> (Q-15), T = 240 °C, P<sub>total</sub> = 4.5 MPa, W/F<sub>(CO+H<sub>2</sub>)</sub> = 5.0 g-cat·h·mol<sup>-1</sup> and F<sub>solvent</sub> = 1.42 ml/min.

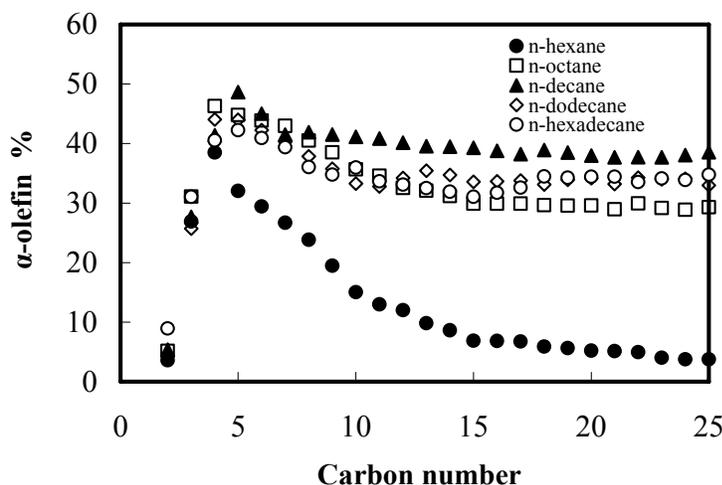


Fig. 1. Effect of carbon chain length of solvent on the  $\alpha$ -olefin selectivity.

### 3.2 Effect of molecular structure of solvent

The FTS over cobalt catalyst results in a product which is the mixture of n-paraffin and  $\alpha$ -olefin. Since the affinity between different molecules is related with the molecular structure, we select branched paraffin (iso-octane) and cyclic paraffin (decahydronaphthalene) as solvent to identify their effect on the FT reaction performance compared to normal paraffin solvent. Table 2 shows that similar results for CO conversion, CH<sub>4</sub> selectivity, CO<sub>2</sub> selectivity and chain growth factor  $\alpha$  were obtained even if the FT reaction was carried out in the solvent with different molecular structure. However, as shown in Fig. 2, the  $\alpha$ -olefin content in the product with C<sub>5+</sub> hydrocarbons is lower for branched or cyclic molecular structure reaction media compared to the content in the n-paraffin solvent with the same carbon number.

**Table 2**

Effect of molecular structure of solvent on the FT reaction performances

Solvent	CO conversion. (%)	Selectivity ( % )		$\alpha$
		CH <sub>4</sub>	CO <sub>2</sub>	
n-Octane	66.4	9.6	2.1	0.87
2,2,4-Trimethylpentane	67.7	9.4	2.1	0.87
n-Decane	65.8	8.8	1.3	0.88
Decahydronaphthalene	65.6	8.9	1.9	0.85

Reaction conditions: 20 wt.% Co/SiO<sub>2</sub> (Q-15), T = 240 °C, P<sub>total</sub> = 4.5 MPa, W/F<sub>(CO+H<sub>2</sub>)</sub> = 5.0 g-cat·h·mol<sup>-1</sup> and F<sub>solvent</sub> = 1.42 ml/min.

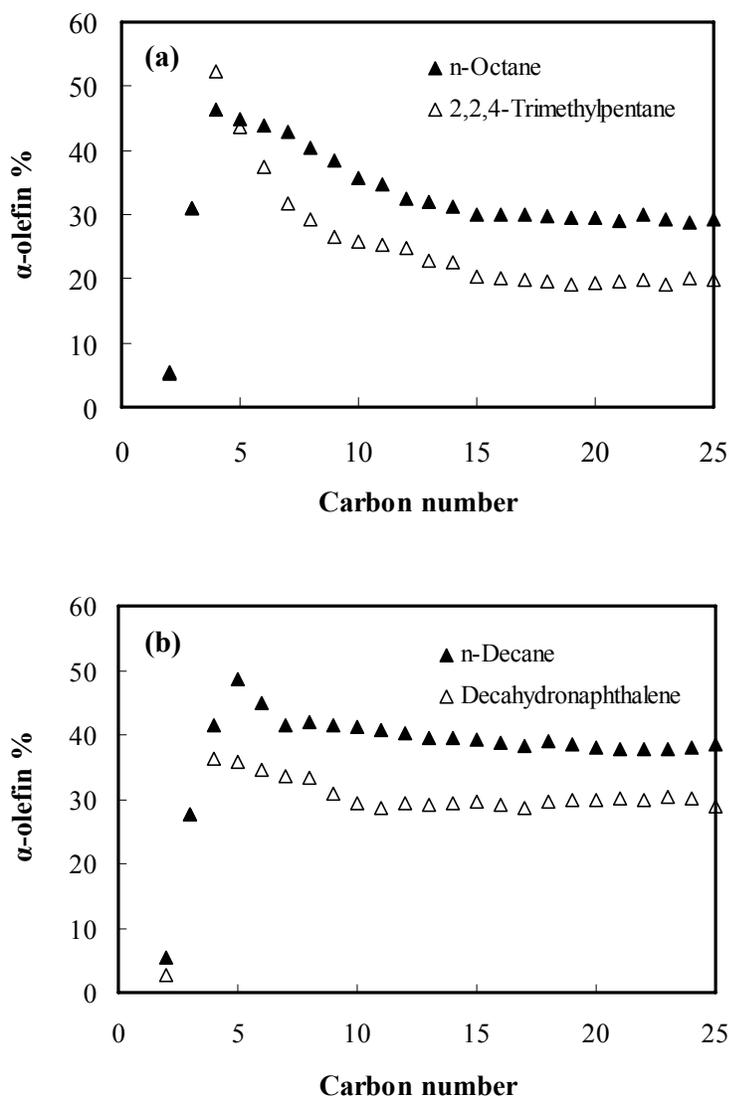


Fig. 2. Effect of molecular structure of solvent on the  $\alpha$ -olefin selectivity: (a) n-octane and 2,2,4-trimethylpentane, and (b) n-decane and decahydronaphthalene.

### 3.3 Effect of flow rate of solvent

The effect of flow rate of solvent on the FT reaction performance is given in Table 3. One can see that the CO conversion is increased with the decreasing n-decane flow rate and that the chain growth factor  $\alpha$  was unchanged. The higher CO conversion is due to the FTS becoming nearer to a gas phase reaction with decreasing solvent flow rate and longer residence time because of the low flow of gaseous solvent. From Fig. 3, it is clear that the  $\alpha$ -olefin content in  $C_5+$  product gradually decreased under low n-decane flow rate.

**Table 3**

Effect of flow rate of n-decane solvent on the FT reaction performances

Solvent	Flow rate ( ml·min <sup>-1</sup> )	CO conversion ( % )	Selectivity ( % )		$\alpha$
			CH <sub>4</sub>	CO <sub>2</sub>	
n-Decane	0.20	80.1	9.7	1.3	0.87
n-Decane	0.46	74.5	9.9	0.5	0.86
n-Decane	1.42	65.8	8.8	1.3	0.88

Reaction conditions: 20 wt.% Co/SiO<sub>2</sub> (Q-15), T = 240 °C, P<sub>total</sub> = 4.5 MPa, W/F<sub>(CO+H<sub>2</sub>)</sub> = 5.0 g-cat·h·mol<sup>-1</sup>.

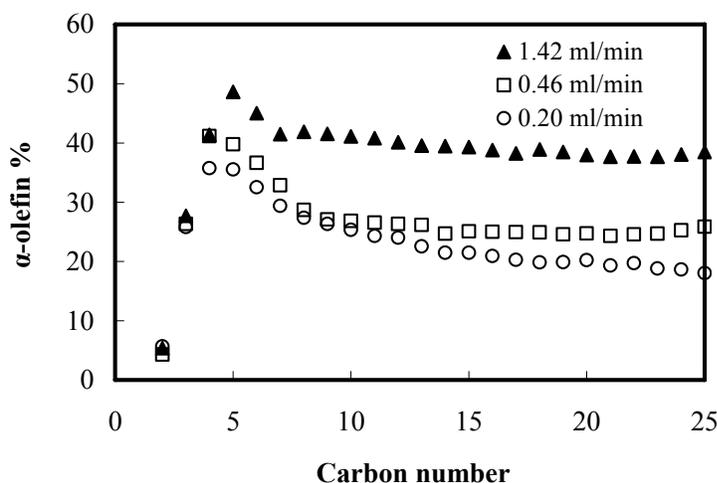


Fig. 3. Effect of flow rate of n-decane solvent on the  $\alpha$ -olefin selectivity.

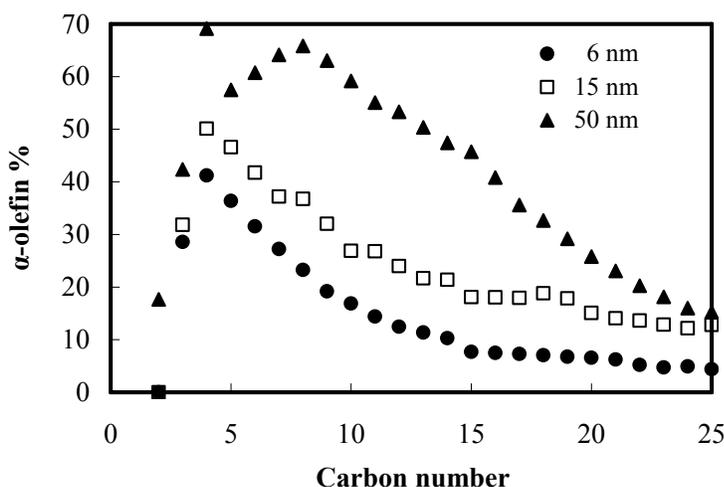
### 3.4 Effect of pore size

Table 4 shows the investigation of catalyst pore size effect on the FTS reaction performances. For the catalyst with 60 nm average pore size, CO conversion was highest up to 75.5% and gave the lowest olefin selectivity. When the pore size increased from 60 to 500 nm, the CH<sub>4</sub> selectivity decreased from 10.1% to 4.9%. For the catalyst of 500 nm average pore size, the olefin selectivity was much higher than for a small pore catalyst. Table 4 and Fig. 4 show that catalysts with larger pores exhibit higher olefin selectivity and chain growth probability, lower CH<sub>4</sub> and CO<sub>2</sub> selectivity. This is mainly because the FTS products can go out of the catalyst pores more quickly so as to minimize the secondary hydrogenation or hydrocracking. These effects will be discussed in the next section.

**Table 4**Effect of pore size of SiO<sub>2</sub> support on the FT reaction performances

Catalyst (20 wt. %)	Pore diameter (nm)	CO conversion. (%)	Selectivity ( % )		$\alpha$
			CH <sub>4</sub>	CO <sub>2</sub>	
Co/Q-6	6	75.5	10.1	1.1	0.86
Co/Q-15	15	58.2	7.2	0.2	0.87
Co/Q-50	50	22.8	4.9	0	0.88

Reaction conditions: 20 wt.% Co/SiO<sub>2</sub>, T = 230 °C, P<sub>total</sub> = 4.5 MPa, W/F<sub>(CO+H<sub>2</sub>)</sub> = 5.0 g-cat·h·mol<sup>-1</sup> and F<sub>n-hexane</sub> = 1.42 ml/min.

Fig. 4.  $\alpha$ -Olefin selectivity versus pore size of SiO<sub>2</sub> support.

### 3.5 Discussion

In accordance with the results above, one can conclude that the properties of solvent have a remarkable effect on the  $\alpha$ -olefin selectivity in C<sub>5</sub>+ hydrocarbons. This phenomenon is ascribed to the differences of solubility and diffusion limitation of primary FTS products (n-paraffin and  $\alpha$ -olefin) in different solvents. The most important chain growth mechanism for the hydrocarbon formation on cobalt [11] catalyst is reported to be the surface carbide mechanism by CH<sub>2</sub> insertion [12–14]. The termination of a growing alkyl species can take place by abstraction of hydrogen to an  $\alpha$ -olefin or by addition of a CH<sub>3</sub> species or hydrogen to form an n-paraffin. The primary  $\alpha$ -olefins, however, are subjected to the catalytic sites and lead to secondary reactions like hydrogenation to n-paraffins, insertion into chain growth, hydrogenolysis, isomerization and cracking before leaving the catalyst bed [15,16]. It is generally accepted that secondary reactions of  $\alpha$ -olefin result in a decrease of olefin selectivity due to preferential physisorption of longer hydrocarbons and increase of the solubility and slow diffusion. Therefore, the interfacial effects of reactive  $\alpha$ -olefins near the gas-wax and wax-catalyst surfaces are important. In the following section, we will discuss how the solvent affects the secondary reactions of the primary  $\alpha$ -olefin and assists the product distribution towards the desired  $\alpha$ -olefin. Fig. 5 gives a schematic representation of the  $\alpha$ -olefin concentration profile on a catalyst with a wax layer [17]. In general, there seems

to be a static liquid phase wax-layer between the catalyst surface and the bulk phase in the conventional gas phase reaction, since the interaction of the wax and the bulk gas phase is quite weak. Steady state production of  $\alpha$ -olefin results in a concentration gradient over the wax film, which depends on the film thickness and the solubility and diffusivity of products with chain length or carbon number  $n$ . At the wax-catalyst interface,  $n$ -dependent physisorption will take place. As a result, the  $\alpha$ -olefin selectivity decreases with the chain length due to the higher re-adsorption rate and slow transportation for later secondary reactions. However, in the case of the solvent utilization, the wax layer can be destroyed to some extent by the extraction of solvent, even supercritical solvent. It makes it easier for the desorbed  $\alpha$ -olefin passing through the wax layer and entering bulk solvent to suppress the secondary reactions.

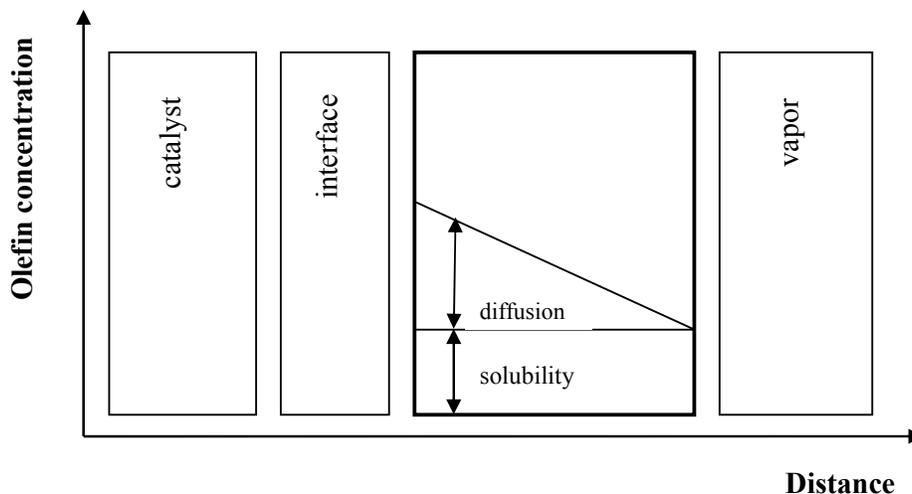


Fig. 5. Schematic  $\alpha$ -olefins concentration profile on a wax-coated catalyst

### 3.5.1 Effect of molecular structure of solvent

According to inter-molecular affinity, the normal paraffin with longer chain should have higher dissolving capability for wax or  $\alpha$ -olefin with straight chain than corresponding branched or cyclic hydrocarbon. To reduce the thickness of wax layer and extract  $\alpha$ -olefin into the solvent, therefore, one needs the selectivity of  $\alpha$ -olefin in normal paraffin solvent to be higher than in branched or cyclic molecular structure solvent with the same carbon number. It is especially important to note that the differences of boiling point between the different molecular-structured solvent with the same carbon number, resulting in different gas to liquid ratios, will affect the evaluation of the effect of molecular structure. However, as shown in Fig. 2, the cyclic decahydronaphthalene as solvent gives lower  $\alpha$ -olefin selectivity than even the ndodecane solvent. Thus, we can deduce the conclusion above.

### 3.5.2 Effect of flow rate of solvent

The increasing solvent flow rate can obviously increase the capability of wax extraction and consequently promote the diffusion of  $\alpha$ -olefin. This will result in higher  $\alpha$ -olefin selectivity, as well as an increase in the gaseous flow rate of the syngas plus solvent vapor so as to reduce the residence time in the catalyst bed.

### 3.5.3 Effect of carbon chain length of solvent

The  $\alpha$ -olefin diffusion in the different reaction phase can be summarized as follows: (1)

the re-adsorption-desorption equilibrium of primary  $\alpha$ -olefin shifts markedly to the desorption side in the gas-liquid phase or liquid phase reaction because of stronger in situ extraction of product from the catalyst surface with the liquid phase reaction media. (2) The  $\alpha$ -olefin transfer out of catalyst pores should be lower in the gas-liquid phase than in the supercritical phase but higher than in the liquid phase. (3) The physical re-adsorption rate of  $\alpha$ -olefin is higher in the liquid phase than in the gas-liquid phase due to the slower  $\alpha$ -olefin transportation out of catalyst pores. The dissolving capability of normal paraffin solvent is gradually increased with increasing chain length because of the higher inter-molecular force. This is because the liquid phase content of solvent is gradually increased from n-hexane (supercritical) to n-hexadecane solvent under the operating conditions. As a result, the wax layer in a longer chain normal paraffin solvent should be thinner than in a shorter one. So, the desorbed  $\alpha$ -olefins can be easily diffuse into the bulk solvent. The  $\alpha$ -olefins in longer chain bulk solvents will find it more difficult to be re-adsorbed to catalytic sites for secondary reactions due to reverse diffusion limitation (the diffusion rate of  $\alpha$ -olefin in supercritical phase n-hexane is much quicker than in gas-liquid mixed phase or liquid phase). The normal paraffin solvents used in this study can be divided into three kinds: supercritical phase (n-hexane), liquid phase (n-hexadecane) and gas-liquid mixed phase (others). For the gas-liquid mixed phase, the ratio of liquid phase to gas phase is dependent on the boiling point of solvent. Although the presence of a liquid phase will enhance the desorption rate and will make it relatively more difficult for reactive  $\alpha$ -olefin to be re-adsorbed because the desorbed  $\alpha$ -olefin is dissolved and surrounded by the liquid phase solvent molecules, the pure liquid phase n-hexadecane is slower to flow out of the catalyst pore tunnel compared to the gas-liquid mixed n-decane. Such a longer residence time of solvent inside catalyst pores results in increasing chances for re-adsorption. Therefore, the  $\alpha$ -olefin selectivity in normal paraffin solvents of different chain lengths should have a maximum with the carbon chain length. The highest  $\alpha$ -olefin selectivity and its constant level against carbon number obtained in n-decane solvent should be attributed to the comprehensive effects of the destroyed diffusion limit of primary  $\alpha$ -olefin, the more suppressed re-adsorption in the presence of a liquid phase compared to supercritical phase and the shorter residence time in the catalyst pore tunnel by the transportation of  $\alpha$ -olefin by gas-liquid mixture of n-decane compared to that by liquid phase n-hexadecane.

#### **4. Conclusions**

The influence of solvent on the selectivity of  $\alpha$ -olefin as a function of carbon number over 20 wt.% Co/SiO<sub>2</sub> catalyst under the typical reaction conditions of 513 K, 4.5 MPa and H<sub>2</sub>/CO = 2 has been investigated. Hydrocarbons with various carbon numbers and molecular structures, including n-hexane, n-octane, n-decane, n-dodecane, n-hexadecane, iso-octane and decahydronaphthalene, are used as solvents. The results show that the selected solvents do not obviously affect the catalytic activity or chain growth factor, but do exhibit remarkable influence on the  $\alpha$ -olefin content. In the case of n-hexane solvent, the  $\alpha$ -olefin content decreased markedly with carbon number. The n-decane solvent gives the highest  $\alpha$ -olefin selectivity which is independent of carbon number on the C<sub>6</sub>+ products at the level of about 40%. This result is due to quicker desorption, diffusion and more suppressed re-adsorption for primary  $\alpha$ -olefin. With the solvent of the same carbon number, an n-paraffin gives a higher  $\alpha$ -olefin selectivity than a branched paraffin or a cyclic paraffin.

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