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Reaction behavior of Fischer-Tropsch synthesis in supercritical *n*-hexane media

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Abstract : The reaction performance of supercritical Fischer-Tropsch synthesis in a fixed bed reactor was studied in this work. *n*-hexane was used as supercritical media. Three kinds of Co catalysts : impregnated catalyst, sprayed catalyst and bimodal catalyst were tested. Under the same Co content condition, the catalytic activity of the sprayed catalyst was similar with that of the bimodal catalyst, but higher than that of the impregnated catalyst. CO conversion over the sprayed catalysts was remarkably higher than that over the impregnated catalysts. Higher lighter fractions selectivity and lower 1-olefins content of FT products were observed over the sprayed catalysts. At the similar CO conversion conditions, however, the 1-olefins content over the sprayed catalyst was similar with that over the impregnated catalyst. For impregnated catalyst, CO conversion increased obviously from 8.3% to 43.6% when Co content increased from 5% to 15%. CH₄ selectivity for 5% Co catalyst was lower about 2.0% ~ 3.0% than those of 10%, 15% and 20% Co catalysts. 1-Olefin content of products over 5% Co catalyst was obviously higher than those over 10%, 15% and 20% Co catalysts.

Key words : Fischer-Tropsch synthesis ; supercritical phase ; *n*-hexane ; cobalt catalyst

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The increasing demand for high quality and environmentally friendly transportation fuels together with the improvement of Fischer-Tropsch synthesis (FTS) technology in the last years has renewed the interesting of using coal/natural gas as a potential source of hydrocarbons^[1~3]. Recently, some researchers have introduced a supercritical fluid (SCF) into the FTS. Due to the unique properties of the SCF (e. g. gas-like transport property, liquid-like solvent power and heat capacities), it has been found that the supercritical FTS has shown some characteristics such as effective removal of reaction heat, quick diffusion of reactant gas and in situ extraction of heavy hydrocarbons (wax) from the catalyst surface^[1,4~7].

In our early studies, we have investigated the supercritical FTS in the different reactor system. The effects of mass transfer of reactant and products, reaction conditions, solvent type etc on the reaction behavior of FTS have been studied in detail^[5,8,9]. The objective of this work is to study the influences of catalyst preparation method and metal loading on the reaction behavior of supercritical FTS.

1 Experimental

1.1 Catalyst preparation The cobalt catalysts used were prepared by incipient wetness impregnation method (catalyst was denoted as I-xCo, I represents impregnation and x represents weight percentage of

Co in the catalyst) and spray method (catalyst was denoted as S-xCo, S represents spray). The support was a commercially silica gels (Fuji davisin ID gel, 15 nm average pore diameter, 1.0 cm³/g pore volume and 200 m²/g surface area). For comparison, some bimodal Co catalysts (the catalyst was denoted as B-xCo, B represents bimodal) were also tested in this study.

1.2 Reaction apparatus and procedure The reaction apparatus flow sheet for the FTS has been shown in elsewhere^[9]. The flow sheet of the reactor system was similar to that of a conventional, pressurized, downflow fixed bed reactor system, except that a preheating vaporizer and an ice-cooled high-pressure trap were set upstream and downstream of the reactor, respectively. Feed gas (H₂: CO: Ar of 2: 1: 0.1) and supercritical solvent were introduced into the system vaporizer by a Brooks 5850E mass flow controller and a high-pressure liquid pump (JP-H2, Japan) and then entered into the reactor concurrently. The effluent gas and liquid of the reactor passed through an ice-cooled trap, where the solvent, liquid hydrocarbons and wax were condensed continuously, and uncondensed products with unreacted syngas were expanded and then introduced to on-line gas chromatograph.

Each reaction was conducted for 6 h. The amount of the catalyst loaded and the mean diameter of the

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catalyst were 1 g and 530 μm respectively. A typical reaction conditions were $t = 240\text{ }^\circ\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$ and $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h}/\text{mol}$. Argon was used as the internal standard in the feed gas.

Gaseous compounds were analyzed on-line by two-coupled gas chromatographs. CO , CO_2 and CH_4 were analyzed by using an activated charcoal column with a thermal conductivity detector (TCD). Light hydrocarbons ($\text{C}_1 \sim \text{C}_6$) were analyzed by using an $\text{Al}_2\text{O}_3\text{-KCl}$ capillary column with a flame ionization detector (FID). A capillary column (DB-2881) with a FID was used for the analysis of the liquid compounds. The n -hexadecane was used as the internal standard for liquid products. The chain growth probability (α) of the products was defined by the Anderson-Schulz-Flory plot, in which the carbon number extended from C_5 to C_{25} ^[10].

1.3 Choice of the solvent Choice of the solvent for supercritical phase FTS was based on the following criteria^[11]:

(1) the critical temperature and pressure are slightly lower than the reaction temperature and pressure;

(2) the solvent should not be poisonous to the catalysts and should be stable under the reaction conditions;

(3) the solvent should have a high affinity for aliphatic hydrocarbons in order to extract the wax from the catalyst surface and reactor.

According to these criteria and the reaction conditions used in this study, n -hexane ($n\text{-C}_6\text{H}_{14}$) was selected as the supercritical fluid. The critical value of n -hexane is listed in Table 1.

Table 1 Critical values of n -hexane

Solvent	Critical temperature $t/^\circ\text{C}$	Critical pressure p/MPa	Critical density $/\text{kg} \cdot \text{m}^{-3}$
n -hexane	234.3	2.97	233

2 Results and discussion

To investigate the effect of preparation method on the catalytic behavior of catalysts, two impregnated catalysts and two sprayed catalysts were tested at the same reaction conditions. The results were summarized in Table 2, Figure 1 and Figure 2. It can be seen from Table 2 that, under the same Co content condition, CO conversion over the sprayed catalysts was remarkably higher than that over the impregnated catalysts. For the sprayed catalysts, the active metal Co is located preferentially near outer pellet surfaces, which may lead to the higher synthesis rates. It is sur-

prised that CO_2 selectivity over the sprayed catalysts was only about half of that over the impregnated catalysts. CO_2 is the product of water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) from the primary by-product water of FT reactions. This result indicates that the removal of water from the sprayed catalyst surface should be easier than that from the impregnated catalysts, which impresses the occurrence of WGS reaction over the sprayed catalyst. Although CH_4 selectivity over S-20Co catalyst was slightly higher than the other three catalysts, the influence of preparation method on CH_4 selectivity was not obvious. For the same Co content of catalysts, the higher lighter fractions selectivity (Figure 1) and lower 1-olefins content of FT products (Figure 2) were observed over the sprayed catalysts. At the similar CO conversion conditions, however, the 1-olefins content over the sprayed catalyst (S-10Co) was similar with that over the impregnated catalyst (I-20Co). It is generally agreed that the 1-olefins, primary products of FT reactions, can be readsorbed on the active sites and take place the secondary reactions (hydrogenation etc), which have significant influences on the product distribution of the FTS. The above results, at least to some extent, indicates that the 1-olefins content of the

Table 2 Reaction performances of FT reaction over the different catalysts

Catalyst No.	I-20Co	I-10Co	S-20Co	S-10Co
Preparation method	impregnation		spray	
Cobalt cont. $w/\%$	20	20	10	10
CO conv. $x/\%$	44.5	67.0	28.5	40.3
CH_4 sel. $s/\%$	8.3	9.9	8.1	7.5
CO_2 sel. $s/\%$	0.9	0.4	0.5	0.2

reaction conditions: $t = 240\text{ }^\circ\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$, $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h}/\text{mol}$

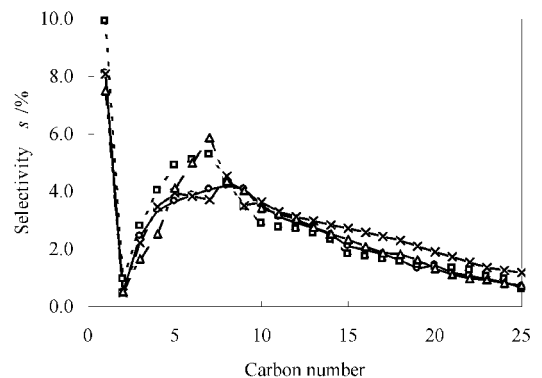


Figure 1 Selectivity of products over the different catalysts
 $t = 240\text{ }^\circ\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$,
 $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h}/\text{mol}$
 ○ I-20Co; □ S-20Co; × I-10Co; △ S-10Co

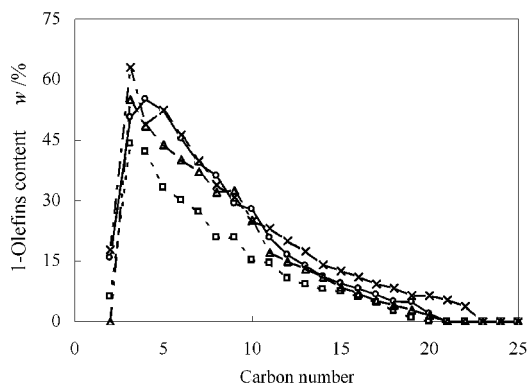


Figure 2 1-Olefins content of FT products over the different catalysts

$t = 240\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$,
 $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h}/\text{mol}$

○ I-20Co ; □ S-20Co ; × I-10Co ; △ S-10Co

products decreases with increasing CO conversion was due to the inefficiency removal of 1-olefins from the catalysts surface.

Furthermore, the reaction performance of FTS over the impregnated catalyst was also compared with that over the bimodal catalysts prepared using different pore diameter SiO_2 support. The results are summarized in Table 3 and Figure 3. Under the same conditions, the bimodal catalyst (B-20Co1) got higher catalytic activity than the impregnated catalyst (I-20Co). At the same time, higher CH_4 selectivity was observed on the bimodal catalyst. From Table 3, it also can be seen that the activities and selectivities of the bimodal catalysts were obviously different from one another, depending on the pore diameter of SiO_2 support. CO conversion increased with the decrease of pore diameter of SiO_2 support. It is clear from the data that the chain growth probability of the bimodal catalysts increased with the increase in the pore diameter of SiO_2 support. It can be seen from Figure 3 that the products distribution of the B-20Co3 (50 nm) catalyst was wider and the proportion of the heavy hydrocarbons was high. On the other hand, the catalyst supported on small pore diameter SiO_2 (B-20Co1) tended to produce relatively lighter hydrocarbons. The increased chain growth probability occurring on the catalyst with larger pore size might be attributed to the larger cobalt particle size as well as the larger pore size of the catalyst. The result is similar with the result obtained on the ruthenium catalyst in our early research^[12].

The effect of metal loading of the catalyst was also studied in this work. Figure 4 shows the changes of CO conversions, CH_4 and CO_2 selectivity with Co loading over the impregnated catalysts. CO conver-

Table 3 Reaction performances of FT reaction over the different Co catalysts

Catalyst No	I-20Co (15 nm)*	B-20Co1 (15 nm)	B-20Co2 (30 nm)	B-20Co3 (50 nm)
Cobalt cont. w / %	20	20	20	20
CO conv. x / %	44.5	66.52	55.64	44.48
CH_4 sel. s / %	8.3	11.60	8.69	7.33
CO_2 sel. s / %	0.9	1.09	0.96	1.10
Chain growth probability	0.83	0.80	0.82	0.83

* 15 nm, 30 nm and 50 nm represent the average pore diameter of SiO_2 supports.

reaction conditions : $t = 240\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$, $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h}/\text{mol}$.

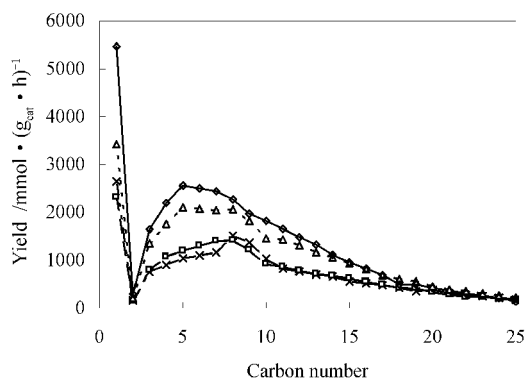


Figure 3 Products distribution of FT process over different 20% Co catalysts

$t = 240\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$,
 $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h}/\text{mol}$

× I-20Co ; □ B-20Co3 ; △ B-20Co2 ; ◇ B-20Co1

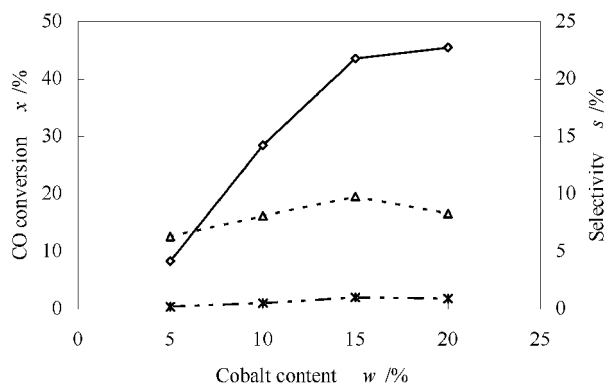


Figure 4 Effect of Co loading of impregnated catalysts on CO conversion, CH_4 and CO_2 selectivities

$t = 240\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$,
 $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h}/\text{mol}$

◇ CO conv. ; △ CH_4 sel. ; * CO_2 sel.

sion increased obviously from 8.3% to 43.6% when Co content increased from 5% to 15%. The value of CO conversion, however, just changed from 43.6%

to 45.5% when Co content increased from 15% to 20%. In principle, the activity of reduced Co catalysts should be proportional to the concentration of surface Co^0 sites. The result thus reflects the inverse trends of Co dispersion and extent of reduction when increasing Co loading. The similar phenomenon has been observed over other Co catalysts reported by other researchers^[3]. It also can be seen from Figure 4 that CH_4 selectivity of 5% Co catalyst was lower about 2.0% ~ 3.0% than those of 10%, 15% and 20% Co catalysts. The values of CO_2 selectivity were not higher than 1% in the four runs, but CO_2 selectivity of 5% Co catalyst was as low as 0.2%, which is only one fifth of that of 15% Co catalyst. Similar change trends of CO conversion, CH_4 and CO_2 selectivity with Co loading were also observed over the sprayed catalysts. These results indicate that the increase of Co loading of the catalyst not only improve the conversion of CO, but also increase the formation of CH_4 and water gas shift reaction.

The effect of Co metal loading on hydrocarbon distribution and 1-olefin content of products were shown in Figure 5 and Figure 6, respectively. It can be seen from Figure 5 that higher lighter hydrocarbon fractions selectivity was obtained over the I-5Co catalyst. In general, the influence of Co loading at range of 10 to 20 on the hydrocarbon selectivity and 1-olefin content of products was not obviously. 1-Olefin content of products over I-5Co catalyst, however, was higher than those over the other three catalysts. This is reasonable because the formation rate of 1-olefin product decreases with the decrease of Co loading. Assuming the removal rate of 1-olefin from the catalyst surface under same W/F conditions, then with the decrease of the formation rate of 1-olefin product,

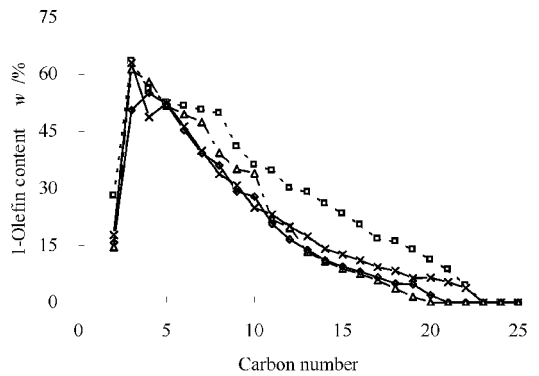


Figure 6 1-Olefins content of FT products over different Co loading catalysts
 $t = 240\text{ }^\circ\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$,
 $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h/mol}$
 □ I-5Co; × I-10Co; △ I-15Co; ◆ I-20Co

the percent of 1-olefin removed effectively from the catalyst surface in total 1-olefin products increases.

3 Conclusions

The reaction performance of supercritical phase FTS in a fixed bed reactor was studied in this work. *n*-hexane was used as supercritical media. Three kinds of Co catalysts: impregnated catalysts, sprayed catalysts and bimodal catalysts were tested.

Under the same Co content condition, the catalytic activity of the sprayed catalyst was similar with that of the bimodal catalyst, but higher than that of the impregnated catalyst. CO conversion over the sprayed catalysts was remarkably higher than that over the impregnated catalysts. It is surprised that CO_2 selectivity over the sprayed catalysts was only about half of that over the impregnated catalysts. The influence of preparation method on CH_4 selectivity was not obvious. For the same Co content of catalysts, the higher lighter fractions selectivity and lower 1-olefins content of FT products were observed over the sprayed catalysts. At the similar CO conversion conditions, however, the 1-olefins content over the sprayed catalyst (S-10Co) was similar with that over the impregnated catalyst (I-20Co).

CO conversion increased obviously from 8.3% to 43.6% when Co content increased from 5% to 15%. The value of CO conversion, however, just changed from 43.6% to 45.5% when Co content increased from 15% to 20%. CH_4 selectivity of 5% Co catalyst was lower about 2.0% ~ 3.0% than those of 10%, 15% and 20% Co catalysts. The values of CO_2 selectivity were not higher than 1% for all the catalysts, but CO_2 selectivity of 5% Co catalyst was only 0.2%. 1-olefin content of products over I-5Co

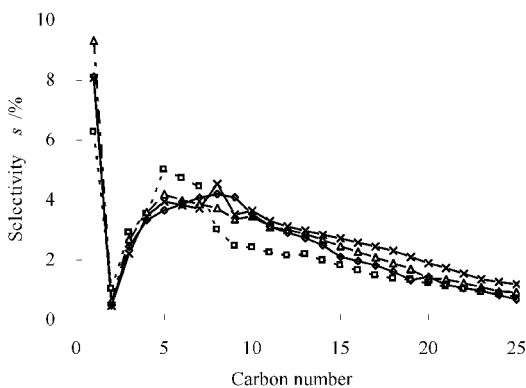


Figure 5 Selectivity of products over different Co loading catalysts
 $t = 240\text{ }^\circ\text{C}$, $p_{\text{total}} = 4.5\text{ MPa}$, $p_{\text{solvent}} = 3.5\text{ MPa}$,
 $W/F_{(\text{CO}+\text{H}_2)} = 5\text{ g}_{\text{cat}} \cdot \text{h/mol}$
 □ I-5Co; × I-10Co; △ I-15Co; ◆ I-20Co

catalyst was higher than those over I-10, I-15 and I-20Co catalysts.

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在超临界正己烷介质中的 F-T 合成反应行为

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摘要 : 在固定床反应器中,以正己烷为超临界介质,研究了三种 Co 催化剂(浸渍、喷雾干燥、双模催化剂)上的 F-T 合成反应行为。在相同的 Co 质量分数下,喷雾干燥催化剂和双模催化剂的活性接近,都高于浸渍催化剂。在喷雾干燥催化剂上 CO 的转化率显著高于浸渍催化剂。喷雾干燥催化剂 F-T 产物中具有高的低碳选择性和低的 1-烯烃质量分数,然而在相近的 CO 转化率下,喷雾干燥和浸渍催化剂具有类似的 1-烯烃质量分数。对于浸渍催化剂,当 Co 质量分数从 5% 增加到 15%, CO 转化率从 8.3% 增加到 43.6%。含 Co5% 的催化剂比质量分数为 10%、15%、20% 催化剂的甲烷选择性低 2.0% ~ 3.0%, 但产物中 1-烯烃的质量分数明显要高。

关键词 : F-T 合成; 超临界相; 正己烷; 钴催化剂

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