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Supercritical-phase process for selective synthesis of wax from syngas: Catalyst and process development

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Abstract

Cobalt-based catalysts which showed high activity and wax selectivity even at a relatively low-reaction temperature such as 210°C were studied. Lanthanum and nickel additions to the catalysts were investigated. Both these additions could promote Co-based catalyst activities. Structure factors concerning these additions were discussed. Calcination temperature effect as well as loading amount influence were also investigated for these catalysts. Addition of a small amount of middle olefins into a supercritical-phase or liquid-phase Fischer–Tropsch (FT) reaction medium could significantly promote the carbon-chain growth and greatly enhance the selectivity of waxy products, with increased CO conversion while suppressing methane and CO_2 selectivity. Hydrocarbon products exhibited anti-Anderson–Schultz–Flory (anti-ASF) distribution. The influences of reaction conditions, catalyst pore size, and catalyst calcination temperature, were studied for the supercritical-phase FT reaction where middle olefin was co-fed. This phenomenon was not observed in the gas-phase reaction and liquid-phase reaction conducted in the trickle bed. But the liquid-phase reaction conducted in the batch-type reactor exhibited the same olefin addition effect.

Keywords: Olefin addition; Supercritical phase; Fischer–Tropsch synthesis; Metal catalyst; Transport effect

1. Introduction

Wax is widely used in many fields, such as adhesives and cosmetics. Especially, the wax produced by Fischer–Tropsch (FT) synthesis has been recognized for its high quality and stability as FT wax contains no aromatics and is sulfur-free.

Selective synthesis of waxy hydrocarbons through FT reaction is not easy. The foremost problem is that the FT products obey the Anderson–Schultz–Flory (ASF) distribution. The other problem is the operating difficulty as the wax can easily block the catalyst bed and reactor itself. For the latter problem, the present authors applied supercritical-phase hexane or pentane to the FT reaction system to improve its mass and heat transfers [1,2]. It is found that the problem of catalyst deactivation due to wax deposition can be solved in the supercritical-phase FT reaction. As an extension and a new aspect of this previous work, we want to investigate the feasibility of applying this technique to wax synthesis from syngas. In order to solve the first problem, we tried two approaches: catalyst development and process modification. This paper will be divided into two parts.

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Firstly, the catalysts which can enhance the selectivity of waxy products will be studied. Of course, it is known that selected reaction parameters, such as low-reaction temperature, high partial pressure of syngas, high-reaction pressure, low H_2/CO ratio in feed gas may favor the carbon-chain growth. We aim at the intrinsic influence from catalyst structure. Addition of second or third metal composition is expected to enhance wax selectivity and/or CO conversion. These catalysts should show high CO conversion and high chain growth probability. Secondly, modification of FT catalysts is not sufficient to completely release the restriction of ASF distribution. Here, we report that the addition of 1-olefins with long carbon chains into accompanying fluids in the supercritical-phase or liquid-phase FT reaction markedly promotes carbon-chain growth, decreasing the formation rate of light hydrocarbons and increasing the selectivity of heavy hydrocarbons (i.e., more than C_{20}). The products thus formed do not obey the ASF distribution. Naturally, the catalysts reported in the first part were employed.

2. Experimental

Impregnated Co–La catalyst or Co catalysts on SiO_2 gel were prepared by the incipient-wetness method from metal nitrate aqueous solution. Multiple metal components were impregnated onto the catalyst support simultaneously from their nitrate aqueous solution. Detailed procedures concerning the catalyst preparation are described in our previous report [3,4]. A Ru/Al_2O_3 catalyst was also prepared, from $RuCl_3$ aqueous solution, by a method similar to that of the Co catalyst. The catalysts were calcined in air for 1 h at specified temperatures. Fresh Co-based catalysts were prepared by hydrogen reduction at 400°C for 12 h before reaction. Catalyst pellets (1 g) of 20–40 mesh size were mixed with quartz sand (4 g) before loading. Also, 2 g of glass beads were loaded to the upstream of the catalyst bed.

Supercritical fluid *n*-pentane (T_c 196.6°C, P_c 33.3 bar) was utilized as the reaction medium or the extraction solvent after the gas-phase reaction. The experimental apparatus for the supercritical-phase reaction was a fixed bed flow-type, similar to the one used in our previous work [2]. It should be noted that this reaction apparatus can be used either for the gas-phase reaction or the liquid-phase reaction (trickle bed) if the reaction medium is changed. Accumulated products, extracted by the supercritical fluid in the ice-trap, were analyzed hourly. Liquid-phase reaction was conducted in trickle-bed and batch-type reactors, respectively. As already mentioned, trickle-bed liquid-phase reaction utilized the same reaction apparatus as in the supercritical phase, with n-$C_{13}H_{28}$ as the accompanying material. In the liquid-phase reaction conducted in batch-type reactor, n-$C_{13}H_{28}$ was also employed as the liquid reaction medium in the autoclave. Fresh catalyst powder suspended in the liquid medium was prepared in a dry box without exposure to air.

Gaseous products were analyzed with on-line gas chromatographs. CO and CO_2 were analyzed by using an activated charcoal or a molecular sieve column equipped with a thermal conductivity detector (TCD). Light hydrocarbons were analyzed by a Porapak-Q column with a flame ionization detector (FID). Hydrocarbons dissolved in the solvent were analyzed by a Silicone SE-30/Uniport-B column with FID. Capillary columns (OV-1 or OV-1701 bonded) as well as a high-temperature gel permeation chromatograph (GPC) (Walters, 860/V2.2) were used for precision analysis of the products. Wax selectivity was calculated as the weight percentage of C_{21}–C_{45} hydrocarbons in C_1–C_{45} hydrocarbons.

The standard reaction conditions were $P(\text{total})=45$ bar, $P(CO+H_2)=10$ bar, $P(\text{balance material})=35$ bar, $CO/H_2=1/2$, $W/F(CO+H_2)=9\ \text{g h mol}^{-1}$, $T=210$–240°C. Argon was employed as an internal standard with a concentration of 3% in the feed gas.

3. Results and discussion

3.1. Reaction performances of the FT catalysts

3.1.1. Effect of metal loading on Co-based catalysts

Table 1 shows the supercritical-phase reaction performance as the Co loading increased. As cobalt-to-silica weight ratio increased from 10:100 to 40:100, CO conversion increased notoriously from 28 to 70% even when the reaction temperature was only 210°C. But the chain growth probability and the selectivity of wax (C_{20+}) did not show a meaningful change if the

Table 1
Supercritical-phase reaction performances of Co/SiO_2 catalysts with different Co loadings [a]

Weight ratio of Co/SiO_2	CO conversion (%)	α	C1 selectivity (%)	Wax selectivity (%)
10:100	28.3	0.85	3.8	29.2
20:100	35.8	0.92	3.1	42.9
25:100	33.9	0.92	4.9	42.9
35:100	53.0	0.92	4.7	42.9
40:100	70.1	0.90	3.3	33.3

[a] 210°C, $CO/H_2=1/2$, $W/F=9$ g h mol^{-1}, partial pressure of the supercritical fluid: 35 bar.

metal/support ratio was higher than 20:100. As these catalysts were prepared by the incipient-wetness method, Co loading could not be enhanced further here. It is considered that Co was at well-dispersion state even on a high Co-loading catalyst. As wax synthesis should be conducted at low-reaction temperature, a catalyst which can show adequate activity at low-reaction temperature is favored.

3.1.2. Promoting effect of lanthanum oxide and nickel for Co-based catalysts

Fig. 1 where reaction temperature is 230°C, shows the effect of addition of various amounts of La into the 10 wt% Co catalyst. It is clearly found that addition of 3 wt% La exhibited a most remarkable promoting effect. CO conversion increased from 33 to 44% when 3 wt% La was added. But CO conversion dropped to 36% when the amount of La addition was increased to 10 wt%. Addition of La up to 10 wt% showed a lower promoting effect than in case of addition up to 3 wt%. In any La-added catalyst, the chain growth probability was similiar to that of a nonaddition Co/SiO_2 catalyst. As 3 wt% addition of La into Co/SiO_2 catalyst can enhance the activity, obviously this catalyst may be used for a low-temperature reaction with sufficient catalytic activity. It should be noted that here lanthanum existed in the form of La_2O_3 as it cannot be reduced in H_2 at temperatures below 500°C [5].

Further, nickel was added to Co–La/SiO_2 catalyst. In Fig. 2 the supercritical-phase reaction performances of the catalysts with different Ni contents are compared. At the temperature of 240°C, addition of Ni exhibited further enhancement in CO conversion, while keeping similar high chain growth

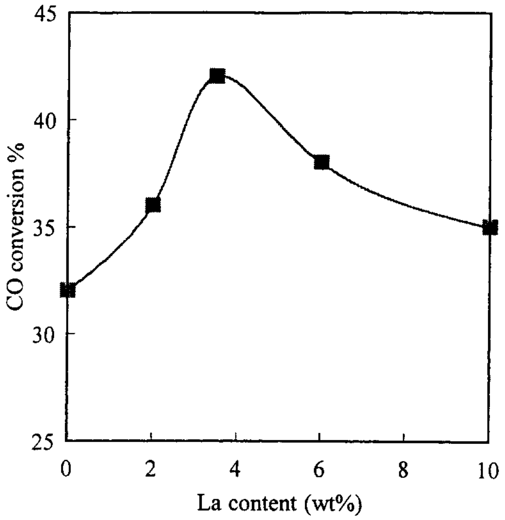

Fig. 1. Influence of amount of lanthanum addition on the activity of Co/SiO_2 catalysts. 230°C, 6 bar, $W/F=10$ g h mol^{-1}, $H_2/CO=2$, Co loading: 10 wt%.

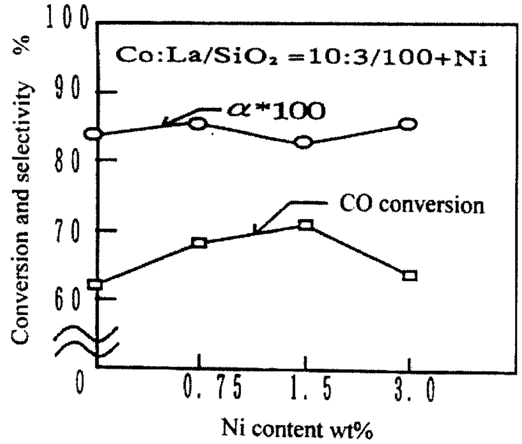

Fig. 2. Effect of the amount of the added nickel on the activity of Co–La/SiO_2 catalysts. 45 bar (syngas 10 bar+pentane 35 bar), 240°C, $W/F=9$ g h mol^{-1}, supercritical phase.

Table 2
Effect of addition of La into Co/SiO_2 catalysts in supercritical-phase reaction [a]

Weight ratio of Co–La/SiO_2 (a:b:100)	CO conversion (%)	α	C1 selectivity (%)	Wax selectivity (%)
20:0	35.8	0.92	3.1	42.9
20:3	37.5	0.94	4.4	53.1
20:6	23.9	0.92	5.7	42.9
25:0	33.9	0.92	4.9	42.9
25:3	19.8	0.93	4.6	48.0
25:6	24.7	0.91	3.6	38.0
35:0	53.0	0.92	4.7	42.9
35:9	30.7	0.91	4.9	38.0

[a] 210°C, CO/H_2=1/2, W/F=9 g h mol^{-1}, partial pressure of the supercritical fluid: 35 bar.

probability. As the reaction temperature here was high, the chain growth probability could be increased further if the reaction temperature was lowered. In fact, when the Co–La catalyst with 1.5 wt% Ni addition was used for supercritical-phase reaction at 210°C, chain growth probability increased to as high as 0.924. Fig. 2 shows that 1.5 wt% Ni addition gave most favorable results.

Based on these findings, it is interesting to investigate the effect of addition of La onto the high Co-loading catalysts. Listed in Table 2 is the comparison of the supercritical-phase reaction performances of these catalysts at 210°C. For the catalyst whose Co/SiO_2 ratio was 20:100, La addition of 3 wt% gave the most appropriate values: the highest CO conversion as well as the highest chain growth probability (0.94). Consequently, its wax selectivity was as high as 53.1%. It is promising that even at 210°C, CO conversion reached 37.5% while chain growth probability was 0.94. It is inferred that a certain amount of La can improve decomposition of the adsorbed CO on Co site.

It is clearly demonstrated in Table 2 that the promoting effect of La could not appear for the catalysts whose Co loadings were more than 25%. This means that La addition was not necessary for these catalysts. It is revealed by TPR and IR that adsorbed CO on a La-modified Co catalyst is in the more active state than on monometallic Co catalyst because of the larger Co crystal [6]. It is considered that for the low Co-loading catalysts, La can promote the decomposition of adsorbed CO on Co to increase the overall catalytic activity. But for high Co-loading catalysts, Co content was so high that only Co was enough to increase the activity. In other words, La addition effect was negligible for high Co-loading catalysts because of the strong effect of Co. La could make the Co particle grow to decrease metal dispersion, as indicated above. This phenomenon might strongly decrease the metal dispersion for high Co-loading catalysts, resulting in low catalytic activities of these catalysts.

Concerning Co–La–Ni/SiO_2 catalysts, from EDS and TEM observations, it is clear that Co and nickel existed at the same spot, while La was located around Co–Ni aggregates (K. Yoshii and K. Fujimoto, unpublished data). As already mentioned, La could improve the cleavage of the CO bond of the adsorbed CO on Co to increase catalyst activity. Ni seemed to be able to promote the hydrogenation of the carbides derived from CO cleavage to initiate the chain growth process. As a result, Ni could increase CO conversion while keeping chain growth probability.

3.1.3. Calcination temperature effect on FT catalysts

Three types of catalysts were studied through calcination temperature variation, and the results have been compared in Table 3. The same change trend appeared for each catalyst type, if the reaction conditions were the same. High calcination temperature favored large carbon-chain growth probability (high α value) but low CO conversion. Reversely, low-calcination temperature led to enhanced CO conversion but suppressed carbon-chain growth probability. The metal dispersion decreases and the metal crystal becomes larger if the supported catalyst calcines at a higher temperature. It can be concluded that large metal crystals intrinsically showed high carbon-chain

Table 3

Calcination temperature effect on Ru- or Co-based catalysts for supercritical-phase FT synthesis [a]

Catalyst (composition)	Calcination temperature (°C)	Reaction temperature (°C)	Syngas partial pressure (bar)	CO conversion (%)	α value
Ru/Al_2O_3 (2:100)	450	220	10	16.5	0.96
Ru/Al_2O_3 (2:100)	120	220	10	45.8	0.95
Ru/Al_2O_3 (2:100)	400	240	21	38.1	0.96
Ru/Al_2O_3 (2:100)	120	240	21	58.0	0.88
Cu/SiO_2 (40:100)	450	210	10	70.1	0.90
Cu/SiO_2 (40:100)	300	210	10	76.7	0.90
Cu/SiO_2 (40:100)	150	210	10	84.0	0.89
Co–La/SiO_2 (25:3:100)	450	220	10	25.8	0.92
Co–La/SiO_2 (25:3:100)	300	220	10	35.9	0.90
Co–La/SiO_2 (25:3:100)	150	220	10	49.1	0.84

[a] $CO/H_2=1/2$, $W/F=10$ g h mol^{-1}, partial pressure of the supercritical fluid: 35 bar.

growth probability. As variation of calcination temperature can control both the chain growth probability and CO conversion through reverse trend, selection of a suitable calcination temperature in the catalyst preparation is critical for the production of high-molecular-weight hydrocarbon. As mentioned subsequently, in the supercritical-phase FT reaction, added long-chain olefin can enhance wax selectivity remarkably. The catalysts calcined under different temperatures were employed and it was found that Co-based catalysts calcined at 300°C gave the highest wax selectivity from among similar catalysts calcined between 120 and 450°C.

3.2. Co-fed olefins in the supercritical-phase FT reaction

3.2.1. Anti-ASF distribution of the hydrocarbon products

A new reaction approach, different from the classical FT reaction, should be developed to overcome ASF constraints in order to enhance heavy hydrocarbon selectivity. Significant research has been conducted to investigate the effect of light olefin addition, such as ethylene or propylene, to synthesis gas on the behavior of the FT reaction [7–12]. Their effect on the carbon-chain growth is, however, very weak, as the chain growth probability remains nearly the same. For example, only the formation rate of the C3 fraction increases in the ethylene-added FT reaction. Also, hydroformylation reaction often occurs with the addition of these light olefins.

The present authors found that when small amounts of middle olefins such as 1-tetradecene ($C_{14}H_{28}$) or 1-hexadecene ($C_{16}H_{32}$) were added to the supercritical n-pentane fluid, the product distributions in the olefin-added systems were very flat, in marked contrast with the ones in the supercritical-phase FT reaction without olefin addition. The selectivities for hydrocarbons lower than C_{14} were higher in the FT reaction without olefin addition. The reverse was true, however, for heavy products with carbon numbers higher than 14; the selectivity to waxy products was noticeably enhanced in the olefin-added reactions. Another remarkable phenomenon was the suppression of methane and carbon dioxide formation in the olefin-added FT reactions. Similarly, co-fed olefin effect was observed for 1-heptene as well as 1,7-octadiene [3].

The essential prerequisite for the occurrence of this process is the rapid diffusion of these heavy olefins added to the catalyst pores to reach the metal sites, as well as the effective diffusion of the heavy products released from the interior active sites to the outer catalyst surface, both of which can be realized in the supercritical phase.

The added 1-olefins could arrive at metal sites by the aid of accompanying supercritical fluid and adsorb onto the active sites as alkyl radicals to initiate the carbon-chain growth; such chains should be indistinguishable from other carbon chains formed directly from synthesis gas. These new alkyl radicals would consume extra methylene to initiate new carbon-chain propagation centers. Because methylene species are involved in chain growth with the added 1-olefins as well, the selectivity of methane, which is formed mainly from methylene hydrogenation, decreases. Also, due to increased consumption of the adsorbed methylene species, CO adsorption and cleavage of CO to carbide on the metal site, as well as hydrogenation of carbide to methylene species is accelerated. Experimentally, the CO conversion increased with 1-olefin addition. The acceleration in this direction may contribute to the suppressed CO_2 selectivity as well, in the olefin-added reaction, as CO_2 is the by-product from CO through the water-gas shift reaction, this side-reaction being suppressed by the competitive main reaction.

It is considered that two ASF distributions existed simultaneously for the olefin-added FT reaction. One was the original chain growth starting from CO and hydrogen, distributed from C1 to a higher carbon number. The other, which was more important, was the compulsive added-olefin-initiated chain growth process, distributed from the carbon number of the added olefin to a higher carbon number. The overall hydrocarbon distribution in the olefin-added reaction combined the contributions from these two different ASF distributions, resulting in the anti-ASF distribution.

3.2.2. *Effect of the reaction conditions*

Reaction temperature should have a strong influence on the carbon-chain growth process. High temperature is not favorable to carbon-chain growth, whereas low temperature limits the reactivity of CO which in turn reduces the formation rate of methylene. Carbon-chain growth will not be accelerated if the surface concentration of methylene is limited.

Compared in Table 4 are the 1-$C_{16}H_{32}$ addition reaction performances at 220 and 240°C respectively. When the temperature was elevated from 220 to 240°C, CO conversion increased from 51.4 to 75.6%. The selectivity of heavy hydrocarbons of the reaction at 240°C was higher than that at 220°C while the CO_2 selectivity showed the same trend. Higher CO conversion contributed partly to the enhancement of CO_2 selectivity through water-gas shift reaction and it should be the main reason for the increased selectivity of long-chain hydrocarbon products. In Fig. 2, both cases show flat hydrocarbon distribution scattering from C6 to C30, but the formation rate of each fraction in this area was higher for the reaction at 240°C.

In Table 4 and Fig. 3, the amount of the added olefin (1-$C_{16}H_{32}$) was varied and its effect was compared. When the amount of the added olefin decreased from 4 to 2% (CO base), the formation rate of the fractions between C6 and C30 correspondingly

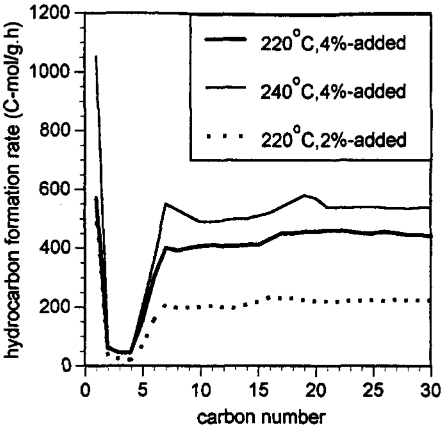

Fig. 3. Influence of the reaction temperature and amount of the added olefin in the olefin-added supercritical-phase FT reactions: 1-hexadecene addition; standard reaction conditions; and Co:La/SiO_2=25:3/100.

Table 4
Influence of reaction conditions in the olefin-added FT reaction in supercritical phase [a]

Added olefin	Reaction temperature (°C)	Added olefin amount in CO base (%)	CO conversion (%)	CO_2 selectivity (%)	CH_4 selectivity (%)	C_{20+} yield (%)
No-addition	220	0	49.1	1.0	6.1	19.4
α-C16	220	4	51.4	0.5	3.1	37.0
α-C16	240	4	75.6	2.0	3.2	45.0
α-C16	220	2	47.9	0.2	3.0	33.1

[a] Co:La/SiO_2=25:3/100, 45 bar (syngas 10 bar+*n*-C5 35 bar), supercritical fluid: *n*-C5, *W*/*F*=9.0 g h mol^{-1}, amount of added olefin: 4 mol% in CO base.

dropped to half. It can thus be inferred that the added olefin predominantly determines the surface concentration of the total olefin, at least under the existing reaction conditions. The possibility of the carbon-chain growth process initiated by the added olefins was remarkably higher than that of the intrinsic FT chain growth. It is evident that the added olefins are involved effectively in the chain growth reaction with the help of supercritical-phase *n*-pentane fluid.

3.2.3. Co-based catalyst calcined at different temperatures

From the foregoing discussion it is seen that calcination temperature of FT catalysts exerts a strong influence on chain growth probability, olefin percentage in the products, and CO conversion. For the olefin-added supercritical-phase FT reaction here, Co/SiO_2 catalysts were also significantly affected by the calcination temperature, as listed in Table 5. In each case, CO conversion was higher than 70% even when the reaction temperature was only 210°C. 150°C-calcined Co/SiO_2 catalyst showed CO conversion of 84.6%. Higher calcination temperature resulted in lower CO conversion. As already discussed, supported Co crystals became larger at a higher calcination temperature. Consequently, the dispersion of Co decreased and the total metal surface was reduced. This is the principal reason for the enhanced CO conversion at a lower calcination temperature. Of course, it should be pointed out that the high CO conversions realized here were partly attributable to the added long-chain olefin in supercritical fluid.

Concerning the wax (C_{20+}) yield, high selectivity was obtained in each case. 300°C-calcined Co/SiO_2 gave the highest wax selectivity, which is considered to be the best balance between carbon-chain growth probability and CO conversion, which were the main factors as CO conversion mainly determines the surface concentration of methylene while carbon-chain growth probability is controlled predominantly by metal crystalline size. For 150°C-calcined catalyst, CO conversion was very high, determining the high concentration of methylene on the catalyst surface, because CO_2 selectivity was very low and nearly the same in each case. But its carbon-chain growth probability was lower, which was intrinsically decided by its smaller Co crystal size. Wax selectivity was limited by the metal crystal size. Reversely, on 450°C-calcined catalyst, CO conversion was lower although its metal crystal size was larger. As a result the surface concentration of methylene was comparatively lower and its wax formation rate was limited as well, although its larger Co crystal size was favorable to chain propagation. As a compromise effect, the catalyst calcined at a moderate temperature such as 300°C showed highest wax selectivity.

We understand that the foregoing explanation is a qualitative elucidation. A quantitative model, including the influence from diffusion of olefin, and synthesis gas, desorption and secondary reaction of hydrocarbons, is necessary to clarify the results in detail, which will be reported in a subsequent paper.

3.2.4. Catalyst pore size effect in olefin-added reactions

Table 6 shows the investigation of catalyst pore size effect on the olefin-added supercritical-phase FT reactions. In order to eliminate the influence of different metal particle sizes of different catalysts, Co loading was adjusted to ensure that the same amount of metal was deposited on the specific surface area (0.0036 g metal/m^2). Co loading was different for each catalyst due to their different specific surface areas. For the catalyst with 150 Å average pore size, CO conversion was as high as 96%, partly due to its large surface area.

Table 5
Effect of calcination temperature on the olefin-added FT reaction in supercritical phase [a]

Catalyst	Calcination temperature (°C)	CO conversion (%)	CO_2 selectivity (%)	CH_4 selectivity (%)	C20 up yield (%)
Co/SiO_2	450	70.1	1.6	3.3	23.6
Co/SiO_2	300	76.7	1.4	2.1	33.6
Co/SiO_2	150	84.6	1.3	2.1	31.5

[a] Co/SiO_2=40/100, 210°C, 45 bar (syngas 10 bar+*n*-C5 35 bar), added olefin: 1-hexadecene, supercritical fluid: *n*-C5, W/F=9.0 g h mol^{-1}, amount of added olefin: 4 mol% in CO base.

Table 6
Effect of catalyst pore size on the reaction performance of supercritical-phase FT synthesis [a]

	Pore diameter (Å)	Co loading (by weight) (%)	CO conversion (%)	CO_2 selectivity (%)	C_{20}^{+} selectivity (%)
Catalyst 1	150	40	96	10	36.85
Catalyst 2	300	29	93	6	41.73
Catalyst 3	500	20	73	0	49.49

[a] Reaction conditons: T=210°C, P(total)=4.5 MPa, $P(CO+H_2)$=1.0 MPa, CO/H_2=1/2, P(pentane)=3.5 MPa, 4 mol%(CO base) 1-tetradecene added, W/F=15 g h mol^{-1}.

For its high Co loading this catalyst gave a high wax selectivity of 36.85%. When the pore size increased from 150 to 500 Å, it is interesting to note that CO_2 selectivity decreased from 10% to 0. For the catalyst of 500 Å average pore size, wax selectivity was nearly 50% with a conversion of 73%. It should be noticed here that the effect of metal particle size was negligible due to the catalyst preparation and the difference of these reaction performances arose because of mass transfer efficiency of syngas and the produced hydrocarbons within catalyst micropore [2,3,13]. Demonstrated in Fig. 4 are catalysts with larger pores exhibiting more heavy hydrocarbons. It is clear that large catalyst pores favor carbon-chain growth. Co-fed 1-olefins can diffuse inside a larger catalyst pore more efficiently to initiate and take part in a new carbon-chain growth process. Also, wax thus formed can go out of a larger catalyst pore more effectively so as to reduce the possibility of secondary hydrocracking.

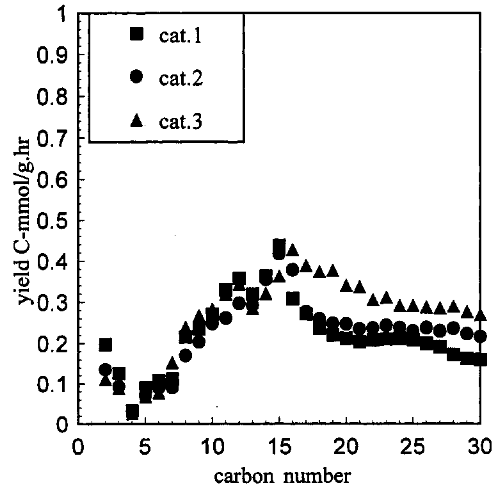

Fig. 4. Product distributions of catalysts with different pore sizes: co-fed reaction. The same reaction conditions as in Table 6.

3.2.5. *Added olefins in gas-phase FT reaction*

1-heptene-added FT reaction was conducted under gas phase using the same apparatus for the supercritical-phase reaction. Nitrogen was used as the reaction medium for the gas-phase reaction. Fig. 5 shows the product distribution of the gas-phase FT reaction whether or not 1-heptene was added. Although the formation rate of heavy hydrocarbon product increased slightly in the heptene-added case, no remarkable change occurred in its product distribution profile compared to the conventional FT reaction. Meanwhile, added 1-heptene did not affect the chain growth probability, as also reported by Iglesia et al. [13], where light 1-olefin (C_2–C_5) was added to the gas-phase FT reaction.

In this reaction, CO conversion increased slightly from 7.2 to 8.1%, and methane selectivity decreased from 22.2 to 11.4% when 1-heptene was fed. This changing trend was similar, to some extent, to what

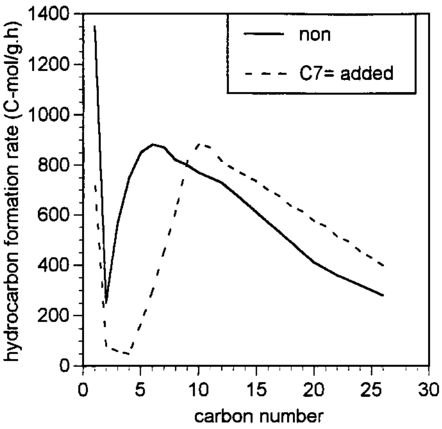

Fig. 5. Hydrocarbon distribution in the gas-phase FT reaction with 1-heptene addition. Standard reaction conditions, total pressure: 45 bar (syngas 10 bar+N_2 35 bar), the amount of added olefin is 4 mol% (CO base).

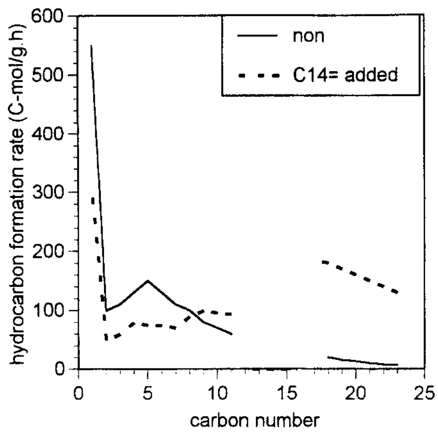

Fig. 6. Different product distributions in the batch-type liquid-phase FT reaction with or without 1-tetradecene addition. Standard reaction conditions: 10 bar, Co:La/SiO_2=10:3/100. Reaction medium: *n*-tridecane. The amount of added olefin is 8 mol% (CO base).

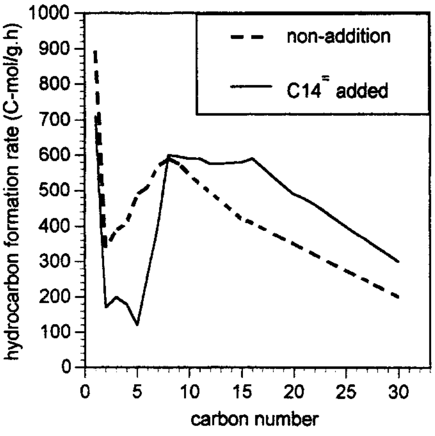

Fig. 7. Different product distributions in the trickle-bed liquid-phase FT reaction with or without 1-tetradecene addition. Standard reaction conditions: 10 bar, Co:La/SiO_2=10:3/100. Reaction medium: *n*-tridecane. The amount of added olefin is 4 mol% (CO base).

happened in the olefin-added supercritical phase. But this promotional effect derived from the added olefin was not obvious here, which could be partly accounted for the slow desorption of the heavy hydrocarbons from catalyst surface to gas phase.

3.2.6. Added olefins in the liquid-phase FT reaction: different reactor

Liquid-phase reaction was conducted in trickle-bed reactor and batch-type reactor, respectively. Liquid-phase FT reaction in a batch-type reactor, where *n*-tridecane was employed as a reaction medium, showed a very flat hydrocarbon product distribution when 8 mol% of 1-tetradecene was added to the reaction medium compared to CO in the feed gas, as displayed in Fig. 6. Although the overall catalytic activity was not so high, which is characteristic of the liquid-phase FT reaction, the accelerated carbon-chain growth was clearly observed because of 1-tetradecene addition. As in the supercritical-phase reaction, the product distribution changed drastically. High solubility and affinity of heavy hydrocarbons including tetradecene in the tridecane medium under reaction conditions, and their effective diffusion realized inside the catalyst powder suspended in tridecane medium, should contribute mainly to the enhanced carbon-chain growth. When 1-tetradecene was added, CO conversion was enhanced slightly from 7.2 to 8.1% and methane selectivity was remarkably suppressed from 22.2 to 11.4%.

As for the trickle-bed type reaction, CO conversion increased from 45.2 to 50.9%, accompanied by a slight decrease of methane selectivity from 5.1 to 4.4% when 4 mol% of 1-tetradecene was added to the reaction medium compared to CO in the feed gas. More importantly, change of the hydrocarbon distribution resulting from olefin addition was not obvious, as displayed in Fig. 7, which just shows a very slight decrease in methane selectivity. It is inferred that diffusion efficiency of the added olefin was not very high in liquid-phase reaction. For trickle-bed reaction, consequently, the contact time of the added olefin was so low that it could not contribute to the carbon-chain growth effectively. Similiarly, Hanlon and Satterfield [14] studied olefin addition effect on Fe catalyzed FT reaction conducted in a continuous-flow slurry-phase reactor. But most of the added olefins were hydrogenated to paraffins or isomerized to 2-olefins, leading to the same chain growth probability [14]. In case of the batch-type reaction, longer contact time of the added olefin could compensate the low diffusion efficiency inside the liquid reaction medium, to realize the behavior of the anti-ASF product distribution in supercritical-phase reaction.

4. Conclusions

Co-based catalysts which showed high activity and wax selectivity even at a relatively low-reaction temperature such as 210°C were developed. La and Ni addition to the catalysts remarkably enhanced catalyst activities. Structure factors concerning these additions were discussed. Moderate calcination temperature of the catalysts and high loading amount of Co favored wax formation by increasing both CO conversion and chain growth probability. Addition of middle 1-olefin into the supercritical-phase or the batch-tpye liquid-phase FT reactions could promote carbon-chain growth remarkably and the selectivity of waxy products was enhanced to a great extent, while suppressing the formation of methane, carbon dioxide and light hydrocarbons. ASF distribution regulation was not observed in these systems. This effect was not available in the gas-phase reaction and trickle-bed liquid-phase FT reaction.

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