Simulation of the C-Number Distribution In the Fischer-Tropsch Synthesis

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Abstract

It was studied the reactions of co-fed 1-decene during Fischer-Tropsch synthesis on Co/SiO$_2$ catalyst in a trickle bed reactor with n-paraffin solvent. Addition of a small amount of 1-decene could greatly enhance the selectivity of diesel range while suppressing the formation of light hydrocarbon products. However, inner olefin or cyclic olefin showed no effects. Products distribution in 1-decene-added FT reaction suggested that the hydrogenolysis, cracking or oligomerization-cracking reactions of co-fed 1-decene, which are competitive with chain growth, occurred depending on the process conditions. The possibility of the practical use of this system was also discussed.

Keywords: Fischer-Tropsch synthesis, Co/SiO$_2$ catalyst, co-fed a-olefin, trickle bed Reactor

Introduction

For a long period of time the carbon-number distribution of the Fisher-Tropsch Synthesis (FTS) product has been simulated by the Anderson-Schuluz-Flory (ASF) distribution which is based on the concepts that (1) the chain growth probability is independent on the c-number of the intermediate, and (2) products are never subjected

to the secondary reactions which change the c-number. However, many researches have shown that the real products distribution deviate from that of AFS plot. It is widely considered that the occurrence of the deviation of the real data from the ideal data can be attributed to the secondary reactions (reinsertion into the chain growth process, hydrogenolysis and isomerization) gives the most reasonable explanation for these deviations [1-7].

Olefin re-adsorption and reaction pathways were examined by the addition of 1-olefin to the H_2/CO feed. Studies on the co-fed olefins have previously shown that the reaction of 1-olefins in the chain initiation and growth cause an increase in the heavier hydrocarbon yields[8-16], the hydrogenolysis shorten the chain of long hydrocarbons by successive demethylation, as well as their extensive conversion to the corresponding paraffin by secondary hydrogenation[17]. To this point, the reaction of re-adsorbed in FTS can be utilized for controlling the carbon number (c-number) distribution towards desired products.

It is well known that the FTS products contains fairly large amount of olefins (mainly α-olefin), its contents decreases with increasing c-number of the products and usually the C_{20}+ products contains little olefins[18]. One of the present authors has demonstrated that the contents of olefin is high and almost independent on the c-number of the FTS products over C_4-C_{25} in the reaction under supercritical n-hexane solvent[19] or in the trickle bed reaction with n-paraffin solvent. The phenomenon has been attributed to the quick extraction of 1-olefin from the active site and the quick transfer of it out of the catalyst pores, which minimize the successive hydrogenation of 1-olefins[19,20].

On the basis of experimental results, a new reaction network including the reactive 1-olefin was presented. Also we added some new experimental data on the effect of added olefin under a variety of conditions[21]. In addition to that, we proposed a new basic reaction model to express the carbon number distribution and analyzed it by the simulation method as 1-olefin was added in the n-paraffin solvent on FTS[22]. In this paper, we added some new experimental data and showed the latest simulation results.

2. Experimental

2.1 Catalyst preparation

The 20 wt.% Co/SiO_2 catalyst was prepared by an incipient wetness method. The cobalt nitrate was used as the precursor of cobalt and a commercially available silica gel (Fujisilica Q-15, surface area: 200 m^2/g, average pore diameter: 15 nm, pore volume: 1.0 ml/g) was used as the support. The apparent dispersion of Co was about 3%. After being dried overnight at 393K, 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. The 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. The detail and the catalyst has been written elsewhere [19][20].

2.2 Reaction procedure and product analysis

The configuration of reactor for the conventional or olefin-added FT reaction is shown in Fig.1. Syngas ($CO/H_2/Ar=1/2/0.1$) and solvent (or co-fed olefin in the 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 the reactor passed through an ice-cooled condenser, where the solvent and FT products

were condensed continuously, and uncondensed products with unreacted syngas were depressurized and led to an online gas chromatograph. n-Hexane (T_b,68.8 ℃), n-octane (T_b, 125.6 ℃), n-nonane(T_b, 150.7℃) or n-dodecane (T_b, 216.3 ℃) was utilized as the solvent fluids. 1-octene (T_b 121.3 ℃), 2-octene (T_b 124.5 ℃) or 1-decene (T_b 172 ℃) was selected as the co-fed olefin. The temperature of the vaporizer is 240℃. Typical reaction conditions were: P_{total} = 2.1 MPa, W/F_{syngas} = 5 g/(h/mol) , F_{syngas} = 81 ml/min, T = 230 ℃, Mole ratio of co-fed olefin to CO = 0.16, $F_{co\text{-}fed\ olefin}$ = 1.1-mmol/h.

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 other one was equipped with a flame ionization detector (FID) 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 using a GC-17A (SHIMADZU) capillary column for C_3~C_{25} hydrocarbons. The chain growth probability (α) of the products was defined by the ASF plot, in which the carbon number extended from C_4 to C_{20}. The c-number simulation was conducted by the REX file supplied by Optience Corporation.

2.3 Product distribution calculations

We have reported that the product selectivity on the carbon-atom basis is presented as the percentage of the converted CO that appears as a given product. Hydrocarbon synthesis rates are reported as the space-time yield (mmol/(h・kg−cat)) and mainly normal hydrocarbons are calculated for the product selectivity or c-number flow distribution[20]. In order to show the effect of co-fed olefin on the c-number

distribution, we compare results of the conventional FT reaction with those of the

olefin-added system reaction at the same level of CO conversion by multiplying a factor,

which equals the ratio of the CO conversion of the olefin-added FT reaction to that of

the conventional reaction.

$$F = \frac{\varphi_0}{\varphi_C} F_C \quad \text{(eq.1)}$$

F: the 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

Fc: the hydrocarbon synthesis rate for real conventional FT reaction

Production rate of each product was calculated to combine the characteristics of

original FT reaction, that is the chain degradation by demethylation and the chain

growth initiated by co-fed olefins. Liu et al [14] proposed one method of this calculation.

We proposed another approach of reaction network [22] and also showed it in the later

section.

3. Results and discussion

3.1 Reactions of added 1-olefin in the FTS system

(a)Effect of co-fed 1-olefin on the carbon number distribution

To proceed the reactions of co-fed 1-olefins, they must diffuse through reaction

media and be adsorbed onto the catalytic sites. Therefore, the low flow rate of solvent

will facilitate the diffusion of co-fed 1-olefin onto catalytic sites and increase the

residence time of co-fed 1-olefin in the catalyst bed, which was favorable for the

secondary reactions such chain growth, chain degradation and hydrogenation. Here, we used a low flow rate of n-dodecane as solvent fluids to study the effect of co-fed 1-decene on the carbon number distribution. As displayed in Table 1 and Fig. 2, we can see that the CO conversion was increased and the lighter hydrocarbon products in C_1-C_9 range was surprisingly suppressed by about 40% as shown in Fig.2 compared to the FT reaction with different amount of added 1-decene and without olefin addition with the same CO conversion level, which is ascribed to the promoted chain growth initiated by co-fed 1-decene. As a result, the disproportionate reaction occurred with increasing added olefin to a larger extent.

As displayed in Table 1 and Fig.3, we also can see that the formation of lighter hydrocarbon products in C_1-C_9 range is suppressed and high 1-olefin selectivity under the low pressure reaction condition. However, the CO conversion in 1.0 MPa is lower than that in 2.1MPa. These results suggest that the high pressure of 2.1 MPa and co-fedding much volume of 1-olefin is the suitable reaction condition to suppress the products in C_1-C_9 and to promote the formation of higher products with high 1-olefin selectivity.

As displayed in Table1 and Fig.4, we also can see that the formation of lighter hydrocarbon products in C_1-C_9 range is suppressed and high 1-olefin selectivity under the co-fedding much volume of 1-olefin and the high pressure of 2.1 MPa.
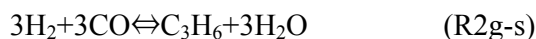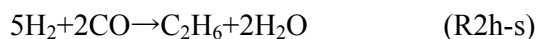
(b)Effect of the chemical structure of added olefin on the carbon number distribution
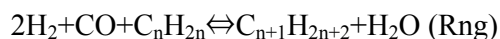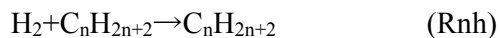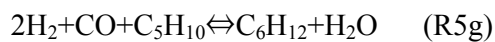
Effects of added C_8 olefins (1-octene, 2-octene and cyclo-octene) on the product distribution are shown in Fig. 5. One can see that the co-fed 1-octene promoted the CO conversion by about 9% as well as the formation of higher hydrocarbon and suppressed

the C_7- hydrocarbon products by about 40%. For co-fed 2-octene, the promotion of CO

conversion or carbon number distribution appeared to some extent as shown in Fig. 5

but its level was much smaller than that of 1-octene, which was ascribed to the harder

incorporation into chain growth probably caused by steric hindrance of

secondary-positioned alkyl group ($R-C^*H-CH_3$ in Fig.6) compared to the co-fed

1-octene. The co-fed cyclo-octene on the product distribution showed as in Fig.5 almost

no   effect. Based on this result, we assume that the structure of cyclo-octene makes the

stronger steric hindrance on the chain growth (pathway ②), and the chain degradation

(pathway ③) shown in Fig. 6.

3.2 Trials on the simulation of c-number distribution

We have shown reaction network as Fig.6 where CH_2 species play important roles in

chain growth and chain degradation. But we could not measure CH_2 species on the

catalyst directly. Therefore, we proposed new simplified reaction model by using

molecular reactions to identify as follows: (which contain the carbene species)

$3H_2+CO \rightarrow CH_4$ $\qquad\qquad$ (R1)

$5H_2+2CO \rightarrow C_2H_6+2H_2O$ $\qquad$ (R2h-s)

$3H_2+3CO \Leftrightarrow C_3H_6+3H_2O$ $\qquad$ (R2g-s)

$H_2+C_3H_6 \rightarrow C_3H_8$ $\qquad\quad$ (R3h)

$2H_2+CO+C_3H_6 \Leftrightarrow C_4H_8+H_2O$ $\quad$ (R3g)

$H_2+C_4H_8 \rightarrow C_4H_{10}$ $\qquad\quad$ (R4h)

$2H_2+CO+C_4H_8 \Leftrightarrow C_5H_{10}+H_2O$ $\quad$ (R4g)

$H_2+C_5H_{10}\rightarrow C_5H_{12}$ (R5h)

$2H_2+CO+C_5H_{10}\Leftrightarrow C_6H_{12}+H_2O$ (R5g)

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$H_2+C_nH_{2n+2}\rightarrow C_nH_{2n+2}$ (Rnh)

$2H_2+CO+C_nH_{2n}\Leftrightarrow C_{n+1}H_{2n+2}+H_2O$ (Rng)

Reaction model for calculation is shown schematically in Fig7. We adopted Langmuir-Hinselwood-Hougen-Watson (LHHW) as reaction equations. The details of this model and its assumptions are shown in the paper [22].

We applied new model to simulate the data in Table1. Results are shown in Figs 8, 9 ,10 and 11. In Fig.8, in comparison with the experimental data, it can be seen from the calculated data that the amount of $C_{11}+$ product increased while the amount of C_9- product is decreased. Then the c-number distribution jumps from C_9 to C_{11} when a small amount of 1-decene is added to the FTS system (5% to CO in carbon base). Also, the CH_4 formation was suppressed. These phenomena agreed well with those of the experimental data. In addition to that, other simulation data in Figs9, 10 and 11 also expressed c-number behavior well.

The details of the calculated parameters of this model will be shown in the next paper.

4. Conclusions

1. Added 1-olefin promoted the chain growth as well as the chain degradation.

2. The chain growth of olefins was obvious only for 1-olefin and 2-olefin or cyclo-olefin showed much smaller effects on the disproportion, probably because of the steric hindrance.

3. We proposed new reaction model and simulated both olefin-added and conventional FTS by using the same rate parameters.

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Table 1 experimental data for the simulation [a]

Added Olefin	Solvent (n-C12) (ml/min)	Olefin (C10H20) (c-mmol/hr-kg)	Temperature (°C)	Pressure (MPa)	CO conversion (%)	Selectivity (%)			α
						CH4	CO2	1-olefin	
No	0.323	0	230	2.1	64.3	8.6	0	10.1	0.89
Added	0.323	3,600	230	2.1	65.2	7.3	0	12.1	–
Added	0.323	11,000	230	2.1	77.7	5.5	0.8	16.9	–
No	0.323	0	230	1.0	32.7	12.2	0	7.8	0.86
Added	0.323	3,600	230	1.0	33.4	9.8	0	10.5	–
No	0.104	0	230	2.1	66.6	7.4	0	12.3	0.91
Added	0.104	11,000	230	2.1	70.6	4.8	0	15.9	–

[a] Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15) = 1.0 g, T = 230 ℃, W/F$_{(CO+H2)}$ = 5.0

g-cat·h·mol^{-1}

Mass flow controller

N$_2$

H$_2$

Syngas

P

Vaporizer

Check valve

Solvent

To vent

FID-GC

TCD-GC

P

Condensor

Line heater

Liquid indicator

Reactor

Needle valve

Ice trap
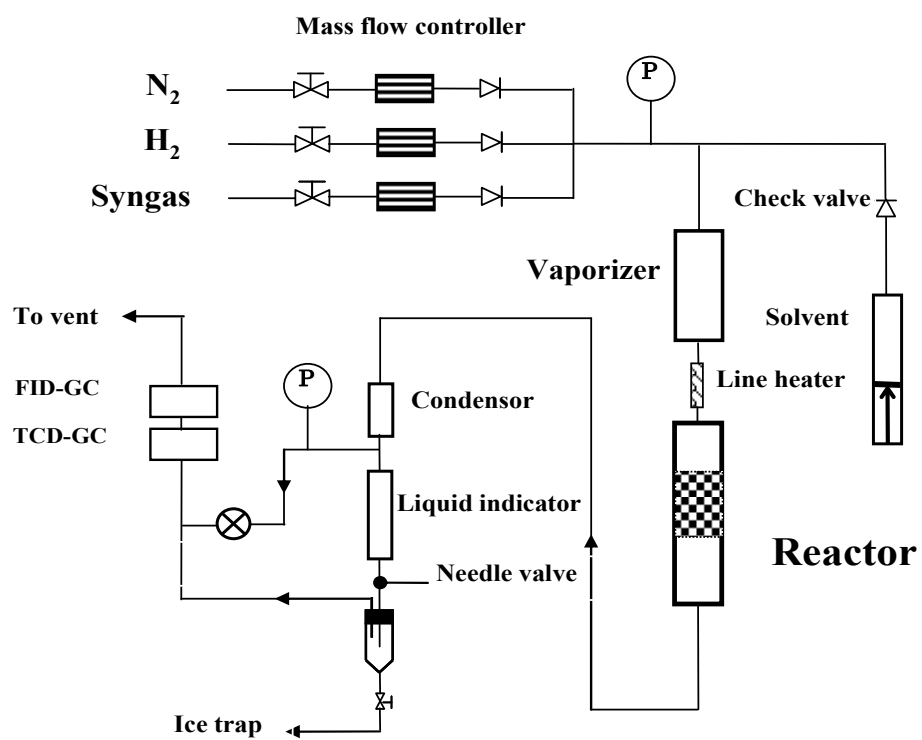
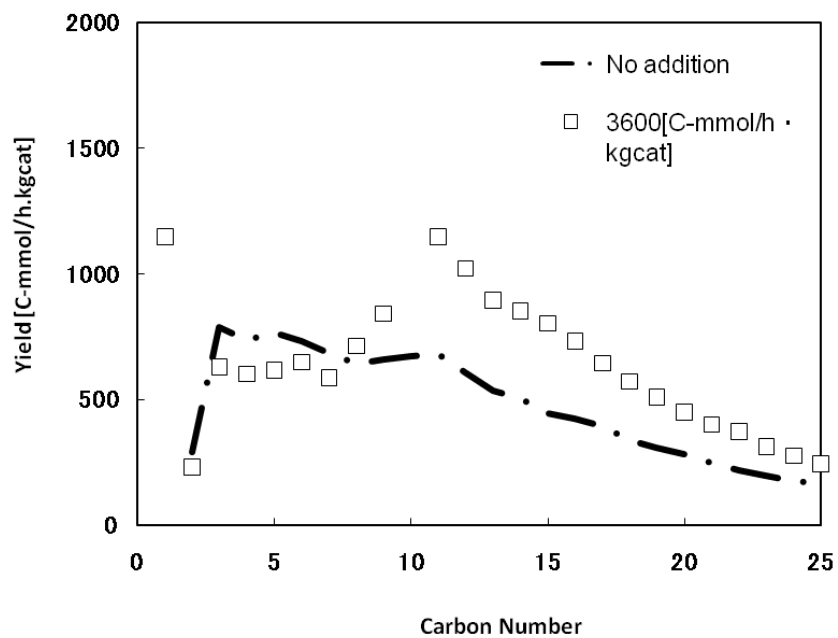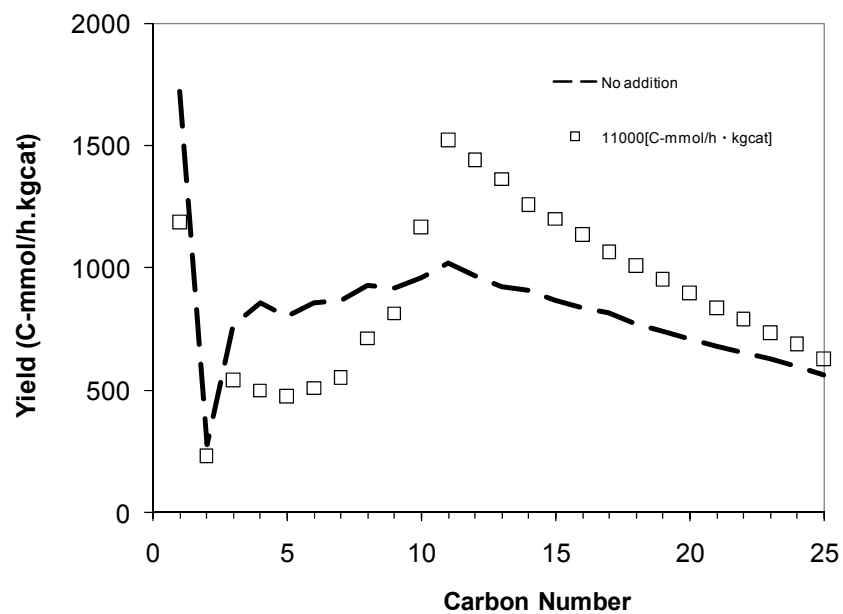Fig.1 Schematic flow diagram of FT synthesis apparatus.
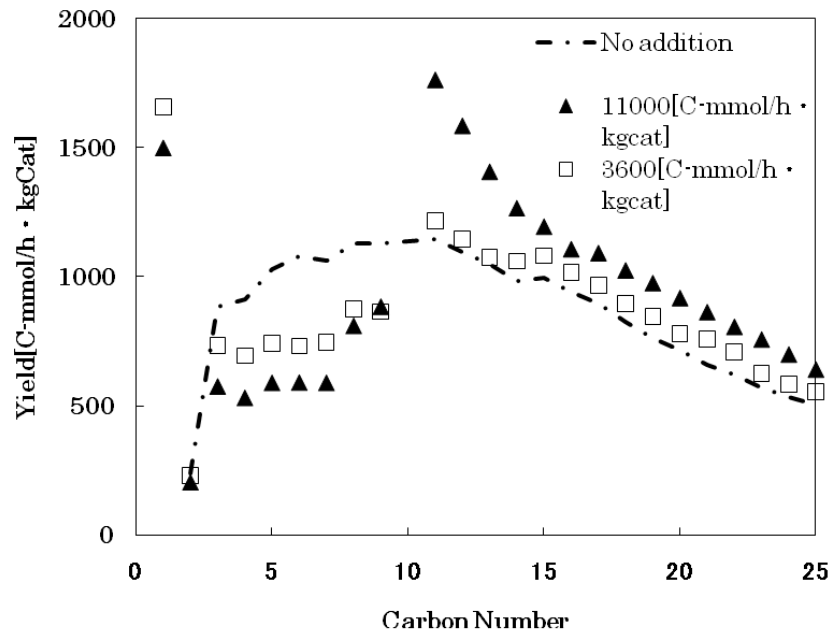
Fig.2. Effect the amount of co-fed 1-decene on the carbon number distribution[b]

Reaction conditions: 20 wt.% Co/SiO_2 (Q-15) = 1.0 g, T = 230 ℃, P = 2.1 MPa,

$W/F_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-decene, $F_{n-dodecane}$ = 0.323 ml/min

[b] CH_4 yield=measurement/2

Fig.3. Effect of co-fed 1-decene on the carbon number distribution[b]

Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15) = 1.0 g, T = 230 ℃, P = 1.0 MPa,

W/F$_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-decene, F$_{n\text{-}dodecane}$ = 0.323 ml/min

[b] CH$_4$ yield=measurement/2

Fig.4. Effect of co-fed 1-decene on the carbon number distribution[b]

Reaction conditions: 20 wt.% Co/SiO_2 (Q-15) = 1.0 g, T = 230 ℃, P = 2.1 MPa,

$W/F_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-decene, $F_{n-dodecane}$ = 0.104 ml/min

[b] CH_4 yield=measurement/2
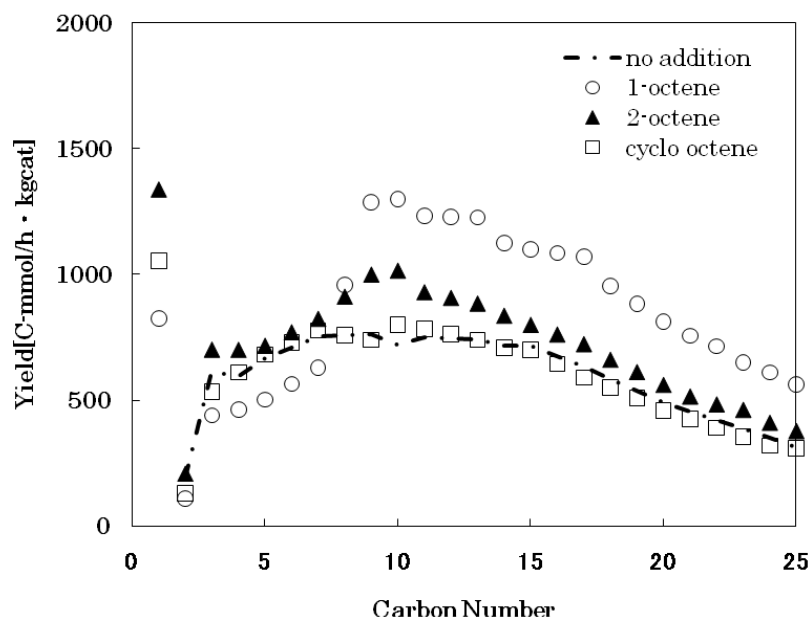
Fig.5. Effect of co-fed olefin molecular structure on the carbon number distribution[b]
control.

Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15) = 1.0 g, T = 230 ℃, P = 2.1 MPa,

W/F$_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-octane, added olefin: 1-octene or 2-octene or

cyclo-octene, F$_{(n-octane+co-fed olefin)}$ = 0.33 -0.34ml/min,F$_{co-fed olefin}$= 11.2 mmol/h

[b] CH$_4$ yield=measurement/2
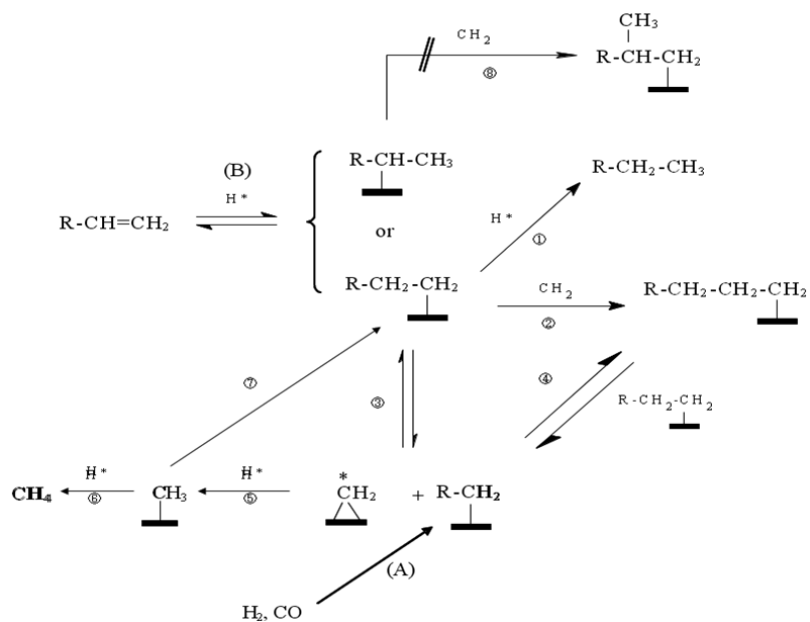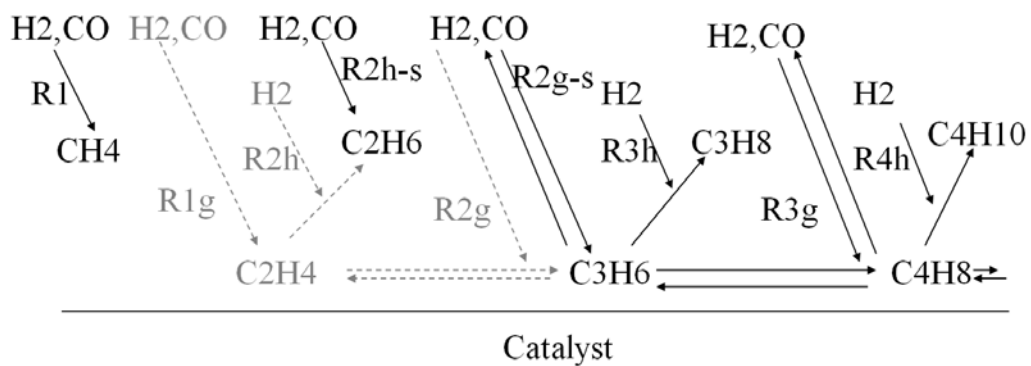
Fig.6. Scheme of the reaction network of co-fed 1-olefins.

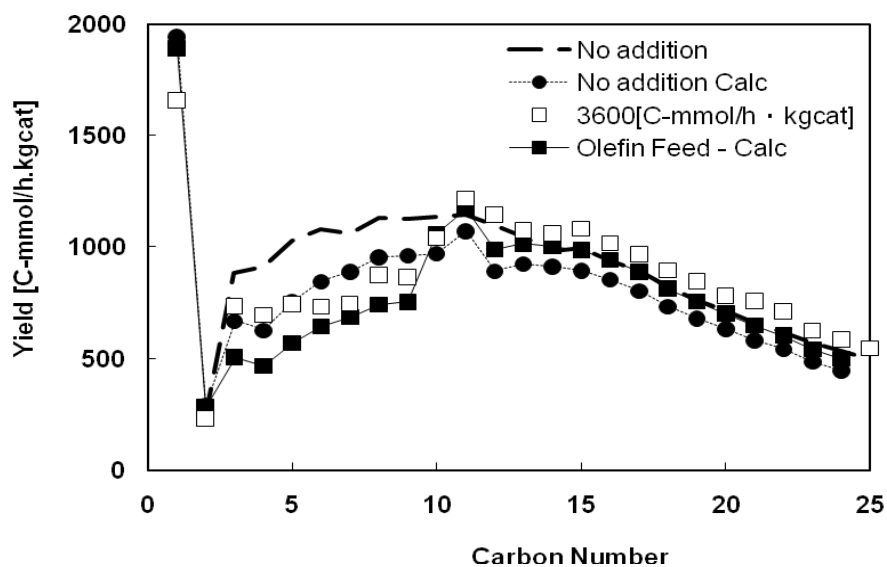
Fig.7. Scheme of the new reaction network.

Fig.8 Experimental data and simulation result [c]

Reaction conditions: 20 wt.% Co/SiO_2 (Q-15) = 1.0 g, T = 230 ℃, P = 2.1 MPa,

$W/F_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-decene; 3600 c-mmol/hr-kg, $F_{n-dodecane}$ = 0.323 ml/min

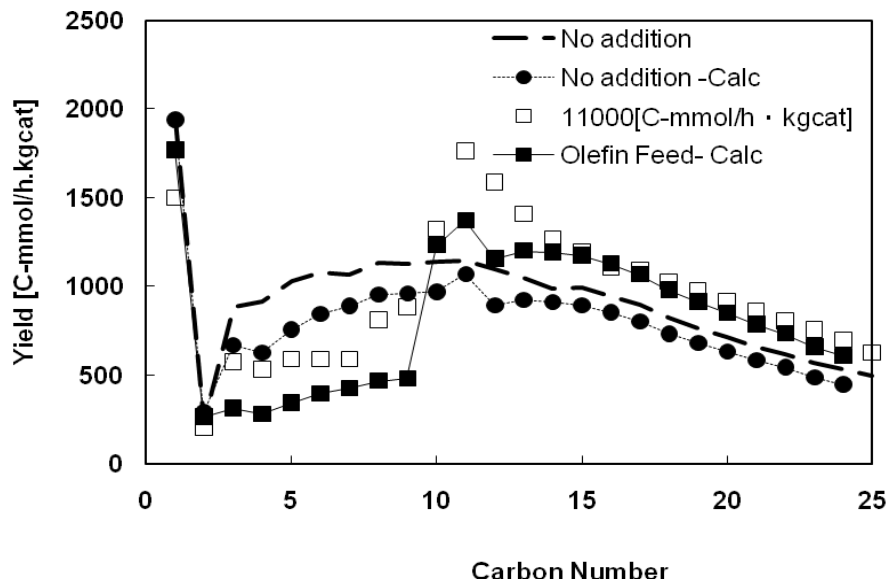[c] CH_4 yield=measurement/2 or calculated value/2

Fig.9 Experimental data and simulation result [c]

Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15) = 1.0 g, T = 230 ℃, P = 2.1 MPa,

W/F$_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-decene; 11000

c-mmol/hr-kg, F$_{n-dodecane}$ = 0.323 ml/min

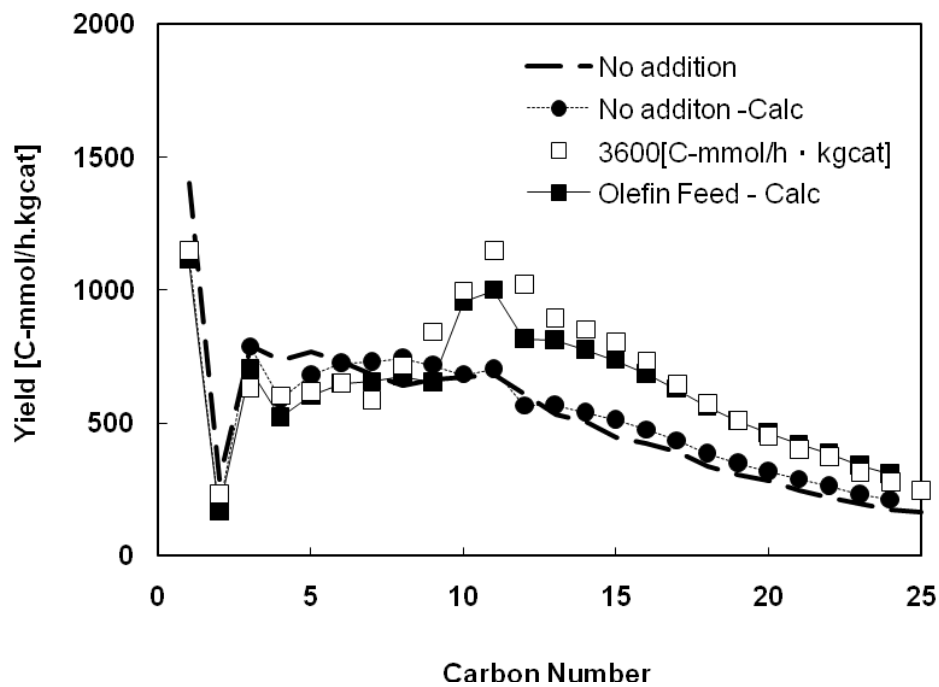[c] CH$_4$ yield=measurement/2 or calculated value/2

Fig.10 Experimental data and simulation result [c]

Reaction conditions: 20 wt.% Co/SiO_2 (Q-15) = 1.0 g, T = 230 ℃, P = 1.0 MPa,

$W/F_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-decene; 3600

c-mmol/hr-kg, $F_{n\text{-}dodecane}$ = 0.323 ml/min

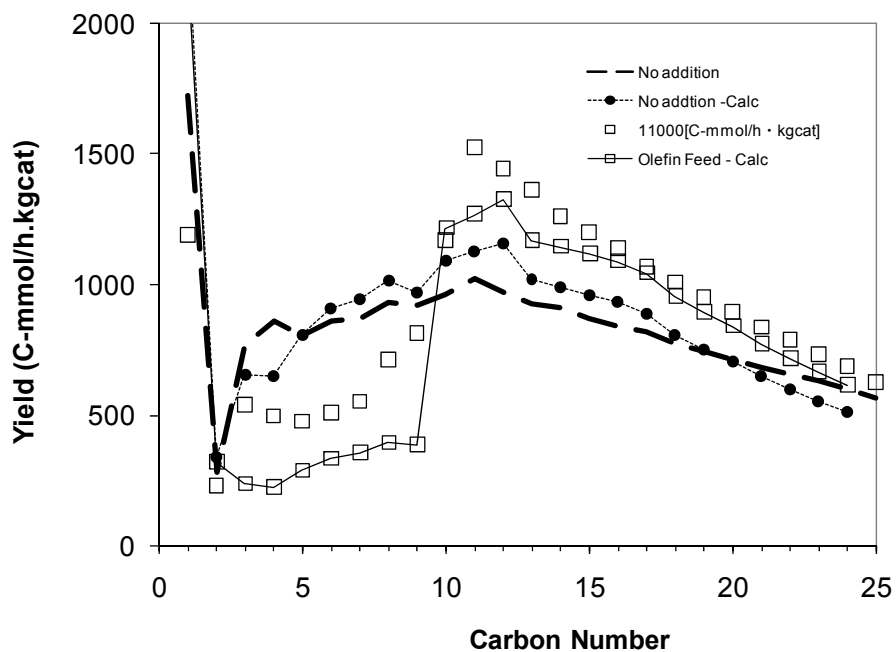[c] CH_4 yield=measurement/2 or calculated value/2

Fig.11 Experimental data and simulation result [c]

Reaction conditions: 20 wt.% Co/SiO$_2$ (Q-15) = 1.0 g, T = 230 ℃, P = 2.1 MPa,

W/F$_{(CO+H2)}$ = 5.0 g-cat·h·mol^{-1}, Solvent: n-dodecane, added olefin: 1-decene; 11000

c-mmol/hr-kg,   F$_{n-dodecane}$ = 0.104ml/min

[c] CH$_4$ yield=measurement/2 or calculated value/2