[Review Paper]

Fischer-Tropsch Synthesis in Supercritical Phase

Li FAN, Kohshiroh YOKOTA, and Kaoru FUJIMOTO*

Dept. of Applied Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

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Fischer-Tropsch synthesis in supercritical phase was developed and its reactional behavior and mass transfer phenomenon were analyzed by both experimental and simulation methods. The same reaction apparatus and catalysts were used for both gas-phase reaction and liquid-phase F-T reactions to correctly compare characteristic features of diffusion dynamics and the reaction itself, in various reaction phases. Efficient transportation of reactants and products to the inside of catalyst bed and pellet, quick heat transfer and *in situ* wax extraction from catalyst by supercritical fluid were accomplished and deactivation of the catalyst was suppressed. As an application of this process, wax can be produced effectively in the supercritical phase reaction, especially in the case when heavy olefin is added to the supercritical fluid.

1. Introduction

The Fischer-Tropsch synthesis reaction (F-T) conducted in the solid-catalyzed gas-phase reaction system, which has been commercially operated or will be operated in several countries, is inevitably accompanied by local overheating of catalyst surface as well as by production of heavy wax. Local overheating of catalyst may lead to the deactivation of catalyst and also to the increase in methane selectivity. Heavy wax may plug micropores of the catalyst and the catalyst bed itself, resulting in catalyst deactivation as well.

The slurry-phase F-T reaction process, on the other hand, in which a slurry, composed of fine powdery catalyst and mineral oil, is used as a reaction medium, has been developed to overcome defects of the gas-phase process¹⁾. The diffusion of synthesis gas in the micropores of the catalysts is, however, so slow in the slurry phase that overall reaction rate is markedly lower than that in the gas-phase reaction^{2),3)}. Further, the concentration of solid catalyst particles in slurry medium is limited to low level (<20 wt%), in order to maintain slurry fluidity. Other disadvantages of the slurry reactors are: the accumulation of high molecular weight products in the reactor during operation, and the *in situ* separation of fine catalyst particles from the heavy products.

It was known that a supercritical fluid has a

unique characteristic in its molecular diffusion and its solubility parameter⁴⁾. The present authors developed F-T synthesis reaction in the supercritical phase, and compared its reaction performance with those in the liquid phase and gas phase, both experimentally and theoretically. It will be reported here that the supercritical phase F-T reaction shows unique characteristics such as quick diffusion of reactant gas, effective removal of reaction heat, and *in situ* extraction of high molecular weight hydrocarbons (wax).

2. Experimental

2. 1. Preparation of Catalyst

Alumina-supported ruthenium catalysts were prepared by impregnating γ -alumina (Aerosil, 200 m²/g) with ruthenium chloride from its aqueous solution. Composition of the catalysts was Ru: 2 and Al₂O₃: 98 by weight. The catalyst precursors were dried overnight at 120°C in an air oven, and were then calcined at 450°C for 2 h to form a supported metal oxide^{5),6)}. The catalysts were reduced in hydrogen flow at 150°C and 300°C for 1 h, respectively, and at 400°C for 2 h in series and then passivated. They were reduced again at 400°C for 2 h *in situ* before catalytic reaction.

Silica-supported cobalt catalysts were prepared from cobalt nitrate (Co(NO₃)₂), lanthanum nitrate (La(NO₃)₃) and commercially available SiO₂ gel (Fuji Davison, ID gel, 270 m²/g) by conventional method of impregnation. The composition of

* To whom correspondence should be addressed.

the catalyst was Co:La:SiO₂ 20:6:87 by weight. The catalyst precursor was dried in air at 120°C and then calcined at 450°C for 3 h to form supported metal oxides. It was then exposed to hydrogen at 400°C for 12 h. The mean pore diameter of the catalyst was 8.7 nm.

The fused iron catalyst is a commercially available iron catalyst for ammonia synthesis. The composition of the catalyst is Fe:Ca:Al:Si:K 83.5:2.1:1.5:0.4:0.5 by weight. The catalyst tablets were crushed to a suitable size and then reduced with hydrogen at 450°C for 14 h before reaction.

2. 2. Apparatuses for Reaction and Product Analysis

The configuration of reactor for the supercritical-phase reaction was similar to that of a conventional, pressurized, fixed-bed flow reactor system. The only difference was that a vaporizer and an ice-cooled high pressure trap were set upstream and downstream of the reactor, respectively, as shown in **Fig. 1**. For the purpose to compare characteristic features of the gas-phase, liquid-phase and supercritical-phase reactions, these three kinds of reactions were conducted in this fixed bed reactor. The liquid-phase reaction was operated in a downflow-type trickle bed. The balance materials were nitrogen for the gas-phase reaction, *n*-hexadecane and nitrogen for the liquid-phase reaction⁷⁻⁹.

Reaction temperature was defined as the highest temperature of the catalyst bed, measured by a thermocouple placed along the center of the catalyst bed. Temperature profiles of the catalyst bed were distributed within 1-2°C, in the supercritical phase reaction.

Detailed analytical methods were listed in our previous report^{10,11}. Gel permeation chromatograph (GPC), as well as capillary columns, were employed for the precise analysis of the products. After each reaction, residual products remaining within catalyst and reactor were extracted by *n*-hexane at 250°C (10°C higher than the reaction temperature), 35 bar, accompanied by N₂ gas of 10 bar. The supercritical fluid extraction after the reaction was conducted for 1 h, after which these products were also determined with a chromatograph.

The measurement of the pore distribution of the catalysts was conducted with a mercury porosimeter (Shimadzu 9200). X-Ray diffraction (XRD) measurements were conducted with a Rigaku Rotaflex instrument using CuK α irradiation (40 kV, 100 mA)¹².

The catalyst effectiveness factor determined from experiment was defined as the ratio of catalyst activity of specified pellet size to that of well-

Fig. 1 Reaction Apparatus for Fischer-Tropsch Synthesis

Table 1 Phase Effect on Ru Catalyst

Reaction phase	Gas	Supercritical	Liquid
CO conversion [%]	44.7	39.0	28.0
Effluent products (a) [C-mmol/g-cat.h]	10.8	12.8	8.82
Extracted products (b)	3.0	0.2	0.5
Residual ratio 100b/(a+b) [%]	22	2	5
Chain growth probability	0.94	0.95	0.85
Carbon balance [%]	90	99	96

Ru/Al₂O₃, standard reaction conditions.

crushed catalyst (pellet radius: 0.1 mm)¹³.

2. 3. Supercritical Solvent and Reaction Conditions

Supercritical fluid was selected under the criteria as follows⁹:

- 1) Its critical temperature and pressure are slightly lower than the typical reaction temperature and pressure.
- 2) It should not poison the catalysts and should be stable under the reaction conditions.
- 3) It has a high affinity for aliphatic hydrocarbons to extract wax from catalyst surface and reactor.

N-Hexane (C₆H₁₄), which critical temperature and critical pressure are 233.7°C and 29.7 bar, respectively, was chosen as the supercritical solvent. The standard reaction conditions were *T*=240°C, *P*(total)=45 bar, *P*(CO+H₂)=10 bar, *P*(balance gas)=35 bar, CO/H₂=1/2, *W*/*F*(CO+H₂)=10 g of catalyst h mol⁻¹. Argon was used as internal standard with concentration of 3% in the feed gas.

3. Reaction Performances in Three Reaction Phases

In **Table 1** is summarized the reaction behavior of Ru/Al₂O₃ catalyst. The rate of CO conversion

in the supercritical phase reaction was higher than that in the liquid phase reaction, but lower than that in the gas phase reaction. This suggests that the diffusion of synthesis gas in the supercritical phase was faster than that in the liquid phase, but slower than that in the gas phase. The amount of products extracted from the catalyst bed after the supercritical phase reaction was much smaller than that in the gas phase reaction, but similar to that in the liquid phase reaction. Further, the carbon chain growth probability in the supercritical phase or in the gas phase reaction was higher than that in the liquid phase. This revealed that the CO/H₂ ratio inside the catalyst pores in the supercritical phase reaction was similar to that in the gas phase reaction, because of the effective molecular diffusion in the supercritical phase⁹, which will be discussed later.

Shown in Fig. 2 is the carbon number distribution of the products. In the supercritical phase reaction and the gas phase reaction, the carbon number distribution of the total products (including the effluent and the extracted products) extended to more than 40, which was the characteristic feature of the Ru catalyst. On the contrary, the product distribution in the liquid phase reaction was limited within the carbon number of 35. The carbon number distributions of the extracted products were flat and independent of the carbon number for both the supercritical phase reaction and the liquid phase reaction, whereas the extracted products from the gas phase reaction was characterized by its high carbon number compared with its effluent products⁹. This should be regarded as the effect of the *in situ* extraction of the products, occurred in the supercritical phase reaction and liquid phase reaction.

4. Diffusion Behavior of Synthesis Gas

4.1. Temperature Characteristics of the Catalysts in Three Reaction Phases

The data in Fig. 3, which show the Arrhenius plots for ruthenium-catalyzed reactions in the three reaction phases, showed that the reaction rate fell in the following order: gas phase > supercritical phase > liquid phase.

Apparent activation energies were 23 kcal/mol for the gas-phase reaction, 21 kcal/mol for the supercritical-phase reaction and 17 kcal/mol for the liquid-phase reaction. These results lead to the conclusion that the mass transfer efficiency in the supercritical-phase reaction is higher than that in the liquid-phase reaction and is close to that in the gas-phase reaction.

The lower catalytic activity and the smaller

Ru/Al₂O₃ catalyst, standard reaction conditions.

Fig. 2 Hydrocarbon Distribution of F-T Reaction Product in Various Reaction Phase

Co-La/SiO₂ catalyst, standard reaction conditions, W/F(CO+H₂)=3 g-cat.h/mol.

Fig. 3 Arrhenius Activation Energy of F-T Reaction in Various Phase

apparent activation energy in the liquid phase reaction should be attributed to the lower rate of synthesis gas diffusion inside the catalyst particles compared to the rate of the surface reaction, because the activation energy of diffusion should be fairly smaller than intrinsic reaction activation energy¹⁰. As a result, the reactant concentrations inside the catalyst particles were so low that the effectiveness factor of the catalyst had dropped.

4.2. Simulation of the Diffusion of Reactants in Various Reaction Phases

A theoretical model was suggested by the present

Ru/Al₂O₃ catalyst, standard reaction conditions.

Fig. 4 The Reaction Temperature Effect on the Calculated or Experimental Catalyst Effectiveness Factors

authors to describe the reactant behavior in Fischer-Tropsch reaction¹²⁾. It is applied to gas phase, liquid phase and supercritical phase, respectively.

The change of effectiveness factor with the variation of reaction temperature in three phases, as well as experimental data, are displayed in Fig. 4. For all cases, the simulated data agreed precisely with the experimental data. Considering Arrhenius activation energy measurement results shown in Fig. 3, it could be concluded that the low apparent activation energy for the liquid-phase reaction should be attributed to the low and small change of catalyst effectiveness factor of liquid phase reaction with the change in the reaction temperature, as shown in Fig. 4. As the intrinsic diffusion activation energy is generally much lower than intrinsic activation energy of reaction itself, the apparent activation energy would be decreased in case the reactant diffusion became a rate-determining step.

Shown in Fig. 5, the computed concentration profiles of synthesis gas inside catalyst particle ($Dp=1$ mm) are compared for three reaction phases. It is found that significant concentration profiles were formed inside the catalyst particles, especially for the liquid phase reaction. The concentration of synthesis gas dropped most rapidly inside the catalyst pellet for the liquid phase reaction, indicating that most interior part of the catalyst pellet was free from the reaction. As a result, the catalyst effectiveness factor was 0.18 for liquid phase reaction, and 0.74, 0.56 for gas phase and supercritical phase, respectively.

Ru/Al₂O₃ catalyst, standard reaction conditions, $Dp=1$ mm, ϕ : Thiele modulus, η : catalyst effectiveness factor.

Fig. 5 Synthesis Gas Concentration Profiles Inside the Catalyst Pellet in Various Phase

5. Diffusion and Reaction of the Products

In the F-T synthesis reaction, 1-olefins are produced as the primary products and are subjected to various secondary reactions such as hydrogenation, C-C chain propagation and hydrocracking^{14,15)}.

Shown in Fig. 6 is comparison of the olefin content in the products in each reaction phase on a Ru/Al₂O₃ catalyst. Olefin content in the products decreased in each reaction phase with an increase in the carbon number of the products. The decrease in the olefin content with increasing carbon number should be attributed to the increase

Ru/Al₂O₃ catalyst, standard reaction conditions.

Fig. 6 Olefin Distribution in Hydrocarbon Products of F-T Reaction in Various Phase

in the hydrogenation rate relative to diffusion rate with increasing carbon number. This is due to the longer residence time on the catalyst surface derived from the slower diffusion rate of these olefins.

Although the mass transfer rate in the supercritical fluid is lower than that in the gas phase, the olefin content in the produced hydrocarbons in supercritical-phase reaction was much higher than that in the gas-phase reaction. It means that the fine balance, between the rates of the product desorption from the catalyst surface and its transfer from the catalyst pores, is the characteristic feature for the effective overall transfer of the products in the supercritical phase reaction. The olefins, therefore, were extracted and transported by the supercritical fluid out of the catalyst particles quickly before it was readsorbed and hydrogenated. On the other hand, the primary products, especially those of high molecular weight, in the gas-phase reaction, hardly desorbed to the gas phase flow medium and had to be subjected to

Ru/Al₂O₃ catalyst, *R_p*: pellet radius, syngas pressure: 10 bar, *n*-hexane pressure: 35 bar, 240°C, *W/F*=10 g-cat.h/mol.

Fig. 7 Catalyst Pellet Size Influence on the Olefin Content in the Supercritical Phase F-T Reaction

hydrogenation, resulting in their low olefin contents. In the liquid-phase reaction, the low olefin content was mainly due to the slow diffusion of these olefins inside the catalyst pores, filled with liquid reaction medium, and enhanced possibility of successive hydrogenation, even if these primary olefins desorbed fast enough from catalyst surface.

As introduced above, the supercritical fluid showed effect, not only on the diffusion of the reactant, but also on the desorption of adsorbed species. In Fig. 7 is given the influence of different size of catalyst particles on the olefin contents in supercritical-phase reaction. It was found that the change of catalyst particle size showed little effect on the olefin content in the product. It appears to be concluded that the supercritical fluid showed more obvious effect on the desorption of olefins and perhaps the diffusion rate was higher than the adsorption rate of the produced olefins, at least here under the experimental condition.

As shown in Fig. 8, the olefin content of the product was affected by the contact time (*W/F*). When contact time was increased, olefin content decreased, but its level is much higher than that of the product from the gas-phase reaction. The low olefin content in products from the gas-phase reaction, especially the higher molecular weight portion, can be attributed to their slow desorption from the catalyst surface and the resultant secondary hydrogenation.

In general, the rate of removal of 1-olefins from the catalyst bed is controlled by intraparticle diffusion (pore residence time) and contact time (bed residence time). In the gas-phase reaction, as micropores of the catalyst pellets are filled with

Ru/Al₂O₃ catalyst, standard reaction conditions.

Fig. 8 Contact Time Effect on the Olefin Content in the Supercritical Phase and Gas Phase F-T Reaction

hydrocarbon products, intraparticle diffusion dominates the removal rate of larger reactive molecules, contact time has no effect on the pore residence time and on the readsorption of larger 1-olefins but controls the residence time of hydrocarbons outside liquid-filled pores. As a result, the effect of contact time on readsorption is most apparent for light olefins in the gas-phase F-T reaction. But in the supercritical phase F-T reaction, because of high diffusion rate and high density of the supercritical fluid and its quick *in situ* extraction for waxy product, the content of both light and heavy olefins is controlled by the contact time^{12), 13)}.

6. Heat Transfer and Extraction Behavior in the Reactions

Shown in Fig. 9 are the temperature profiles of the catalyst bed in three reaction phases. Solid lines indicate the temperature profiles of the catalyst bed, and dotted lines indicate the profiles of the fluidized sand bath for heating the reactor.

The maximum temperature rise in the catalyst bed at a similar CO conversion level (*ca.* 60%)

The reactor was heated by the fluidized sand bath; CO conversion was the same (see Table 2), Co-La/SiO₂ catalyst.

Fig. 9 Temperature Profiles along the Catalyst Bed in Three Phases

was in the following order: liquid phase (10°C) < supercritical phase (13°C) < gas phase (18°C). In Table 2 are shown the integrated areas of the temperature profiles, which indicate that the resistance to heat transfer in each fluid medium was liquid phase (1) (relative value) < supercritical phase (1.6) < gas phase (2.4). These data suggest that heat transfer in the supercritical phase was more effective than in the gas phase and was close to that in the liquid phase.

It is brought to attention that in the area where pressure and temperature are slightly higher than the critical values, the thermal conductivity of the fluid increases drastically by 5 or 6-fold compared to that of the conventional gas¹⁶⁾. The results shown in Fig. 9 are consistent with these general aspects of the supercritical fluid.

Model experiments were conducted to recognize the wax extraction occurring in the reaction. As shown in Fig. 10, little wax was extracted in the gas phase model experiment. In both the supercritical phase and the liquid phase model experiments, however, the effusion of wax began quickly and ended within 1 h; 80% of total wax was extracted in both phases. It should be also noted that the effusion ended in a shorter time in the supercritical phase experiment than in the liquid phase experiment. This suggests that not only does wax extraction occur in the supercritical phase, but the

Table 2 Phase Effect on Heat Transfer^{a)}

Reaction phase	Contact time [g-cat.h/mol]	CO Conversion [%]	Relative integrated area of the profiles
Gas	15	57	2.4
Supercritical	20	57	1.6
Liquid	25	64	1.0

a) Reaction conditions: Pressure total, 4.5 MPa, CO+H₂, 1.0 MPa. Balance materials, 3.5 MPa. Temperature, 240°C.

17 wt% paraffin wax on silica support, standard reaction conditions.

Fig. 10 Model *in situ* Extraction Experiment

extracted wax also moves more quickly in the supercritical phase than in the liquid phase.

When the same experiment was conducted under 10 kg/cm² of *n*-octane (below its critical pressure), although the amount of extracted wax was the same as that in the supercritical phase or the liquid phase experiment, a longer time was necessary and the maximum extraction rate of wax was lower. Since the mass transfer rate should be adequate in the *n*-octane vapor, the poor extraction result in this system is probably caused by the poor solubilizing capability of *n*-octane vapor. Effective extraction of wax in the supercritical phase reaction may be attributed to its high solubilizing characteristics which arises from its high density.

7. Catalyst Design: Effect of Pore Size and Pellet Size

Ru/Al₂O₃ catalysts with different pore sizes were prepared by pH-swing method described in detail in our previous report¹². In Fig. 11 are shown the CO conversion, the dispersion of ruthenium determined by hydrogen adsorption, and the chain-growth probability as a function of catalyst pore diameter. It is clear from the data in Fig. 11 that with the increase in the pore diameter, the chain-growth probability increased while the Ru dispersion decreased. The high ability of carbon-carbon bond formation of the large pore catalyst should be attributed to its large Ru particles. A mathematical model has been already set up which predicted that the propagation of the carbon-carbon chain occurred more easily when the ruthenium particle size became larger¹⁷. Further one of the present authors proved the feasibility of this model in the gas phase reaction⁹. The increased chain-growth probability occurring on the catalyst of larger pore size might be attributed to the larger ruthenium particle size, as well as the larger and uniform pore size. The

Ru/Al₂O₃ catalyst, standard reaction conditions.

Fig. 11 Pore Size Effect on CO Conversion, Chain Growth Probability, and Metal Dispersion (H/Ru) in the Supercritical Phase F-T Reaction

dispersion of the supported ruthenium metal and the pore size of the catalyst show their close relationship with the propagation of the carbon chain, even in the case of supercritical phase reaction. Based on this consideration, it may be regarded that the supercritical fluid (*n*-hexane) should show little effect on the reaction mechanism which is applied to the gas phase reaction.

Using the method determining effectiveness factor set up in our previous report¹², it is found that the effectiveness factor of the small pore catalyst is so low that the catalyst activity remains very low even though its reaction rate constant is the highest. This signifies that the inner surface of this kind of catalyst is hardly utilized. On the other hand, the effectiveness factor for the larger pore catalyst shows a higher value, but its reaction rate constant is not significantly high because of the lower specific surface area of Ru metal. As a result, the activity of the catalyst having the largest pore size is not the highest, and those of catalysts having moderate pore size are supreme, attributed to this compromise effect. This theoretic result is consistent with the experimental results, as shown in Fig. 12.

Shown in Fig. 13 are the olefin contents in the products from catalysts with different pore sizes. Among the light C₂ to C₁₀ hydrocarbons, there is little difference. The olefin content in the product was still as high as 40% for the C₂₀ hydrocarbon, in case of the large pore (33.5 nm) catalyst, even though the catalytic activity was still high, while the olefin content in the product from a smaller

Ru/Al₂O₃ catalyst, standard reaction conditions.

Fig. 12 Simulated and Experimental Results on the Relationship between the F-T Reaction Rate and the Catalyst Pore Size in the Supercritical Phase Reaction

Standard reaction conditions.

Fig. 13 Catalyst Pore Size Effect on the Olefin Percentage in the Supercritical Phase Reaction on Ru/Al₂O₃ Catalyst

pore (11.4 nm) catalyst decreased remarkably with increasing carbon number of the product and reached zero at around C₂₀. For a specific catalyst, light olefin content was high, while the olefin percentage decreased as carbon number increased, with the exception that the content of ethylene was remarkably low.

The high olefin content of product from catalyst with the largest pore size is understandable because a relatively more effective mass transfer occurred for the higher molecular weight product. As a result, the degree of secondary hydrogenation reaction was suppressed. It was reported that the

dispersion of ruthenium metal showed little influence on the olefin-to-paraffin ratio in low carbon number products in the gas-phase F-T synthesis reaction¹⁸. The differences in the metal dispersion of the catalysts here, therefore, are presumed not to be important in determining the olefin content in the products in a supercritical-phase F-T reaction.

Recently, it was reported that in a liquid phase reaction conducted in continuous stirred tank reactor, the higher solubility of larger olefins in the slurry increased their reactor residence time and enhanced their chances of undergoing secondary reactions¹⁹. Some researches showed that in gas-phase F-T reaction, 1-olefin (primary product) readsorption and surface chain initiation took place as secondary reactions^{20,21}. Further, readsorption of 1-olefins increased with molecular size because the rate of removal of olefins from liquid-filled catalyst pores is decreased, attributed to intraparticle diffusion limitation. Our observations for the supercritical phase F-T reaction seem to be supported by their research. We believe that readsorption of 1-olefins onto F-T-active sites plays a crucial role in the synthesis of high molecular weight hydrocarbons. Heavier 1-olefins remained longer within catalyst pores because of their decreased diffusivities and readsorbed onto Ru sites more easily to receive secondary hydrogenation to form paraffin. Paraffinic products do not undergo any further reaction and exit from the pore unreacted. On the other hand, the pore size effect on the product selectivity behaved by the way of changing the diffusivities of primary 1-olefin products. Relatively more effective diffusion for the olefins within larger catalyst pores leads to high olefin content in the product.

The olefin content for C₂ (ethylene) is obviously lower than those of other light hydrocarbons. Several reports showed that yields for C₂, in some cases including C₃, were low and fall below those predicted by the Schulz-Flory distribution²². In our results, these low values reflect the rapid rate of ethylene readsorption and chain initiation, including their incorporation into growing chains.

8. Wax Production: Addition of Heavy Olefin in the Supercritical Phase

It is extremely difficult to selectively synthesize waxy hydrocarbons through F-T reaction. A main reason is that the F-T products fall in the Anderson-Schultz-Flory (ASF) distribution. Development of a new type of F-T reaction, free from ASF constraint on its product selectivity,

is of great importance for wax production, as modification of the F-T catalyst alone is not enough to increase wax selectivity significantly.

Here, we report that addition of a small amount of heavy 1-olefin into supercritical phase F-T reaction can significantly promote the chain growth and greatly enhance the selectivity of waxy products. As a matter of interest, this phenomenon does not occur in the gas phase reaction^{23)~25)}.

Shown in **Fig. 14** is the F-T product distribution profile for a 4 mol% (CO base) addition of 1-tetradecene or 1-hexadecene into the supercritical *n*-pentane fluid. It is clear from the figure that the product distributions in the olefin-added systems are very flat, in marked contrast with that in the supercritical phase F-T reaction without addition of olefin. The selectivities for hydrocarbons lower than C14 were higher in the F-T reaction without addition of olefin. The reverse was true, however, for heavy products with carbon numbers higher than 14; the selectivity to waxy products was remarkably enhanced in the olefin-added reactions. Another remarkable phenomenon was the suppression of methane formation in the olefin-added F-T reactions.

Similar behaviors were observed for addition of 1-heptene or 1,7-octadiene to the supercritical phase reaction^{24), 25)}.

The characteristics of the olefin-added reaction systems are listed in **Fig. 15**. Methane selectivity in any olefin-added reaction was lower than half of that in the same reaction without addition of olefin. CO Conversion was also higher in the 1-olefin added reactions except for 1,7-octadiene. On the other hand, CO₂ selectivity in all F-T reactions with heavy olefin addition was lower than that in the non-olefin added reaction.

Compared with those in the common supercritical phase reaction, addition of olefins with long carbon chain into the accompanying fluid can accelerate the carbon chain growth. The essential prerequisite for the occurrence of this process is the rapid diffusion of these heavy added olefins inside the catalyst pores to reach the metal sites, as well as the effective diffusion of the produced heavy products 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.

Co-La/SiO₂ catalyst, added olefin amount: 4% (CO base), syngas pressure: 10 bar, *n*-pentane pressure: 35 bar, 220°C, *W/F*=9 g-cat.h/mol.

Fig. 14 Addition of Heavy Olefins into Supercritical Phase F-T Reactions: Anti-ASF Distribution

The same reaction condition as in Fig. 14.

Fig. 15 Reaction Performance of the Supercritical Phase F-T Reaction with Addition of Various Long-chain Olefins

Since 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, attributed 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, are accelerated. Experimentally, the CO conversion increased with addition of 1-olefin. The acceleration in this direction may contribute to the suppressed CO₂ selectivity as well in the olefin-added reaction, as CO₂ is the by-product from CO through the water-gas shift reaction.

It should also be noted that the increase of CO conversion was more noticeable for addition of 1-

olefin with shorter carbon chain (*e.g.* heptene); but enhanced chain growth occurred more effectively for addition of longer-chain 1-olefins, as shown in **Fig. 15**. We believe that if the added olefin had a rather long carbon chain, it would adsorb more strongly on the metal site and would cover a large active area of the catalyst, thereby inhibiting CO adsorption onto the metal site. This may be the reason for the lower CO conversion in the case of addition of 1,7-octadiene and the relatively low CO conversion for addition of 1-C₁₆H₃₂.

9. Conclusions

In the supercritical phase Fischer-Tropsch synthesis reaction, rapid transportation of reactants and products to the inside of catalyst bed and pellet, efficient heat transfer and *in situ* wax extraction from catalyst by supercritical fluid, were accomplished and the life of catalyst was prolonged.

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要 旨

超臨界相における Fischer-Tropsch 合成

範 立, 横田 耕史郎, 藤元 薫

東京大学工学部応用化学科, 113 東京都文京区本郷 7-3-1

気相反応, 液相反応と比較しながら, 超臨界相における Fischer-Tropsch 反応を行った。反応条件, 反応装置, 触媒構造, 溶媒効果および抽出挙動などを調べた。高い反応活性と生産効率, 長い活性寿命, 速い熱伝導速度と物質移動速度, ワックス

に対する強い抽出能力と分離効率などの特徴を備えた超臨界相 Fischer-Tropsch 合成は, 液体燃料およびワックスの合成に優れた反応成績を挙げた。

Keywords

Fischer-Tropsch synthesis, Supercritical phase, Catalyst structure, Mass transfer, Secondary reaction