SUPERCRITICAL PHASE FISCHER-TROPSCH SYNTHESIS: PRODUCT CONTROL

R.Prasert(a,b),N. Tsubaki(b),
X.-H. Li(a), K. Asami(a) and Kaoru Fujimoto(a)

(a) Faculty of Environmental Engineering
University of Kitakyushu
Fukuoka, 808-0135, Japan
(b) Faculty of Engineering
Toyama University
Gofuku, 630-8555, Japan

Introduction

The Fischer-Tropsch synthesis (F-T) reaction conducted in the solid-catalyzed gas phase reaction system, which has been commercially operated or will be operated in several counties, 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 the catalyst deactivation.

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 and has been developed to overcome defects of the gas phase process[1]. The process has also some defect such as the diffusion of synthesis gas in the micropores of the catalyst.

It was known that a supercritical fluid has a unique characteristic in its molecular diffusion and its solubility parameter[2]. The present authors developed F-T reaction in the supercritical phase and compared its reaction performance with those in the liquid and gas phases, both experimentally and theoretically. In summary, 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). And these characteristics can be utilized to realize a new process where wax is selectively synthesized[3].

Experimental

Reaction apparatus 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. 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 down-flow-type trickle bed. The balance materials were nitrogen for the gas phase reaction, n-hexadecane and nitrogen for the liquid phase reaction. 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℃ in the supercritical phase reaction.

Supercritical fluid was selected under the criteria that follows:

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 stable under the reaction conditions.
3. It has a high affinity for aliphatic hydrocarbons to extract wax from catalyst surface and reactor.

n-Hexane (C_6H_{14}), with critical temperature, *Tc*, and critical pressure, *Pc*, at 233.7℃ and 29.7 bar, respectively, was chosen as the supercritical solvent. In wax synthesis experiments where reaction temperature was low, *n*-pentane (*Tc*, 196.6℃; *Pc*, 33.3 bar) was used alternatively as the supercritical fluid. The standard reaction conditions were *T*= 240℃, *P* (total) = 45 bar, *P* ($CO+H_2$) = 10 bar, *P* (balance gas) = 35 bar, CO/H_2 = 1:2, W/F ($CO+H_2$) = 10g of catalyst h/mol. Argon was used as internal standard with concentration of 3% in the feed gas.

Results and Discussion

Table 1 summarized the reaction behavior of Ru/Al_2O_3 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 was much smaller than that in the gas phase reaction, but similar to that in the liquid phase reaction. Furthermore, the carbon chain growth probability in the supercritical phase or in the gas phase reaction was higher than that in the liquid phase[4]. This revealed that the CO/H_2 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 phase, which will be discussed later.

Table 1 Phase effect on Ru catalyst

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

Ru/Al_2O_3, standard reaction conditions; (a) the amount of total effluent products and (b) the amount of total extracted products after reaction.

It is well known that at the steady state of the gas phase reaction, catalyst micropores were filled with liquid hydrocarbons. But the average viscosity of this kind of liquid hydrocarbons was low due to the dilution effect of the co-existing nitrogen. High diffusion rates in the gas phase reaction could be realized.

Carbon balance was calculated as the percentage of the carbon amount of effluent and extracted products in the carbon amount of the inlet feed gas. From **Table 1**, it is clear that about 10% carbon stayed inside the catalyst pellet even after extraction by the supercritical extraction after reaction, indicating that these carbon species formed a coke-like structure at hot spots during gas phase reaction.

F-T wax, owing to its merits such as high melting point, high hardness value, low viscosity, as well as being nitrogen-, sulfur-, and aromatic-free, has been highly favored. It can be used, not only directly, in many fine chemical fields such as cosmetics, packing materials and adhesives, but also as feedstock for producing different-sized hydrocarbon products ranging from kerosene to aviation fuels. It is extremely difficult to selectively synthesize waxy hydrocarbons through T-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[3]. What was shown in **Figure 1** is the F-T product distribution profile for a 4 mol% (CO base) addition of 1-tetredecene 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 the addition of olefin. The selectivities for hydrocarbons lower than C_{14} were higher in the F-T reaction without the 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 in the olefin-added F-T reactions was the suppression of methane formation. Similar behaviors were observed for the addition of 1-heptene.

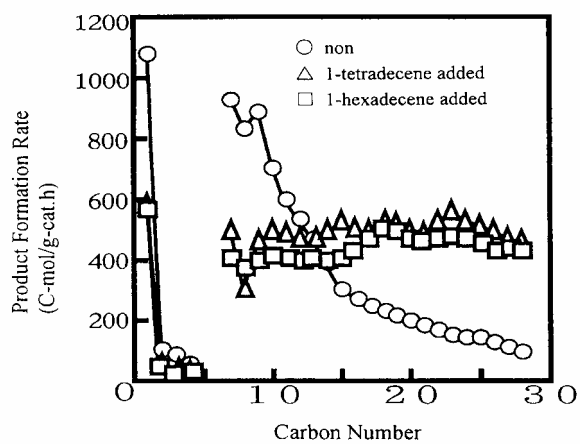

Figure 1. Addition of heavy olefins into supercritical phase F-T reactions: anti-ASF distribution Co-La/SiO_2 catalyst, T=220℃, P(*n*-pentane)=3.5 MPa, P(CO+H_2)=1.0 MPa, W/F(CO+H_2)=9 g-cat. h/mol; added olefin amount/4%(CO base) supercritical fluid/*n*-pentane.

The characteristics of the olefin-added reaction systems are listed in **Figure 2**. Methane selectivity in any olefin-added reaction was lower than half 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, CO_2 selectivity in all F-T reactions with heavy olefin addition was lower than that in the olefin-free 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 prerequisites for the occurrence of this process are the rapid diffusion of these added olefins inside the catalyst pores to reach the metal sites and the effective diffusion of the produced heavy products from the interior active sites to the outer catalyst surface. Both of them can be realized only in the supercritical phase.

The added 1-olefins could arrive at metal sites by the aid of the accompanying supercritical fluid adsorb onto the active sites as alkyl radials 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. Since methylene species are involved in the 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, adsorption and cleavage of CO to carbide on the metal site, as well as the 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 CO_2 selectivity as well as in the olefin-added reaction, as CO_2 is the by-product from CO through the water-gas shift reaction.

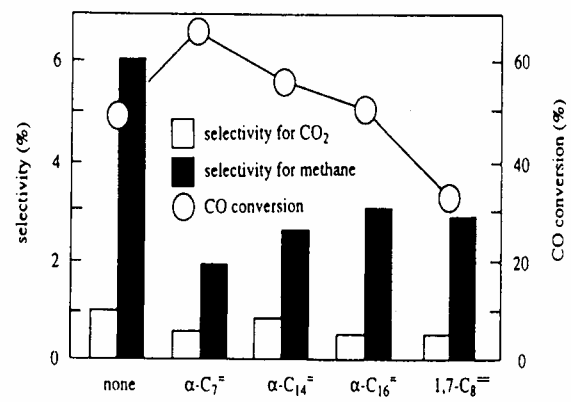

Figure 2. Reaction performance of the supercritical phase F-T reaction with addition of various long-chain olefins.

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 **Figure 2**. 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 H_2 adsorption onto the metal site. This may be the reason for the lower CO conversion in the case of the addition of 1,7-octadiene and the relatively low CO conversion for the addition of 1-$C_{16}H_{32}$.

References

1. Koelbel H.; Ralek M., Catal.Rev.-Sci. Eng. **1980**, 21, 225
2. Debenedetti P.G.; Reid R.C., **1986**, 32, 2034
3. Fujimoto K.; Ohdan K.;Yoshii K. Jpn. Kokai Tokkyo Koho **1992,** 1992-181293, **1993**,1993-138534, **1993**,1993-138535
4. Yokota K.; Fujimoto K., Fuel, **1989**, 68, 255