Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled for further activity to report.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

Concentration Profile of Fischer-Tropsch Products in Catalyst Pores

INTRODUCTION

It has been generally agreed that a simple polymerization mechanism can be used to describe the distribution of Fischer-Tropsch (FT) synthesis product. On a catalyst surface, a FT chain growth intermediate can either propagate to form another intermediate of one higher carbon number or terminate to produce an oxygenate, paraffin, or olefin of same carbon number. The path of termination to olefin is reversible because olefin can adsorb reversibly (readsorb) on chain growth sites and initiate chain growth. The propagation probability (α value) of each surface intermediate has been assumed to be a constant independent of carbon number, producing the so-called Anderson-Schultz-Flory distribution (single α distribution). The experimental observation of a two, or more α distribution, or more precisely, the α value is an increasing function of carbon number, resulted in different models being proposed to explain this phenomenon. One of the prevailing models is the diffusion enhanced olefin readsorption model which describes the effect of diffusion limited removal of olefins from catalyst pores (1). Since olefin termination is reversible and its diffusivity decreases rapidly with increasing carbon number, the higher olefin should have a longer residence time and higher fugacity in the pores of the catalyst pellet. As a result, accumulation of these heavy hydrocarbons in the catalyst pores leads to olefin diffusion limitation, which enhances olefin readsorption and hence the two α observation.

In other words, this model relies on increased hydrocarbon concentration with carbon number in catalyst pores which might be resulted from internal diffusion limitation. The pore concentration of a hydrocarbon component relative to its surface concentration (relative concentration) must increase with carbon number to contribute to the two α distribution. It is obvious that in the presence of internal diffusion limitation of hydrocarbon products, the concentration of a hydrocarbon component in the catalyst pores must be significantly higher than that at the catalyst surface. However, the hydrocarbon concentration profile in the catalyst pores was not demonstrated and the existence of internal diffusion limitation of hydrocarbons was not verified by either simulation or experimental data. Also, this model ignored the existence of vapor-liquid equilibrium of hydrocarbon products in a typical reactor.

It is therefore of interest to examine the conditions under which product diffusion limitation might exist in catalyst pores. The FT reaction is simulated in a CSTR reactor whose modeling and simulation has been reported previously (2).

Fischer-Tropsch Reaction

The major product of the Fischer-Tropsch reaction consists of a spectrum of paraffins and olefins. For simplicity of discussion, it is assumed that CO and H_2 react stoichiometrically to produce exclusively paraffins and water following a single α ASF distribution. Thus the FT reaction can be written as

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + H_2O \qquad (n = \frac{1}{1-\alpha}) \qquad 1)$$

and the hydrogen reaction rate is assumed to follow

$$(-r_H) = k_H C_H \qquad 2)$$

Based on Equations (1) and (2) and the single α assumption, the production rate of each individual hydrocarbon component (i) can be expressed as

$$r_i = (1-\alpha)\alpha^{i-1} r_{HC} = \frac{(1-\alpha)^2}{(3-\alpha)}\alpha^{i-1} k_H C_H = k_i C_H \qquad 3)$$

where

$$k_i = \frac{(1-\alpha)^2}{(3-\alpha)}\alpha^{i-1} k_H \qquad 4)$$

is the production rate constant of hydrocarbon component i and is a function of α.

Mass Transfer in Catalyst Pores

Assuming that the catalyst pellet is spherical, the steady state concentration profiles of hydrogen and a hydrocarbon component i in the catalyst pores can be described using the following equations, respectively,

$$\frac{C_H}{C_{H,s}} = \left(\frac{R_p}{r}\right)\frac{\sinh(\phi_H r / R_p)}{\sinh(\phi_H)} \qquad 5)$$

$$\frac{C_i}{C_{i,s}} = 1 + \left(\frac{\phi_i}{\phi_H}\right)^2\left(1 - \frac{C_H}{C_{H,s}}\right) \qquad 6)$$

where

$$\phi_H = R_p \sqrt{\frac{k_H}{D_H}} \qquad 7)$$

$$\phi_i = R_p \sqrt{\frac{k_i}{D_i} \frac{C_{H,s}}{C_{i,s}}} \qquad 8)$$

In the above equations,

C_H, C_i : concentrations of hydrogen and hydrocarbon i in the catalyst pores, respectively

$C_{H,s}$, $C_{i,s}$: concentrations of hydrogen and hydrocarbon i at the catalyst surface, respectively

D_H, D_i : effective diffusivities of hydrogen and hydrocarbon i, respectively

k_H, k_i : rate constants of hydrogen consumption and hydrocarbon i production, respectively

R_p : radius of the catalyst particle

φ_H , φ_i : Thiele modulus of hydrogen and hydrocarbon component i, respectively

φ_i is a measure of the relative scale of reaction and diffusion rates in the catalyst pores. For large φ_i, the diffusion rate is slower than the reaction rate and hence the effect of internal diffusion on total observed rate is significant or even controlling. For the same catalyst pellet, the effective diffusivity D_i is calculated using the following correlation (1):

$$D_n = D_0 e^{-0.3n} \qquad 9)$$

where D_0 is a constant and n is the carbon number. It is seen from equation (6) that the relative concentration of component i depends on its Thiele modulus and hydrogen concentration distribution in the catalyst pores. Also it is seen that the surface concentration is important in determining the

Thiele modulus and, thus the pore concentration. When vapor-liquid separation is considered, the surface concentration of each component at the catalyst surface is the same as its bulk liquid concentration in a CSTR, the latter can be obtained with model simulation.

Reactor Modeling And Simulation

The CSTR modeling and simulation for FT synthesis has been reported in detail elsewhere (2). Briefly speaking, the CSTR is assumed to operate at constant temperature and pressure without catalyst deactivation. Reaction product is separated into liquid and vapor, which are assumed to be in thermodynamic equilibrium following Roult's law under the reaction conditions. For simplicity of simulation, it is further assumed that hydrocarbon products are linear paraffins from C_1 to C_{100} and that they follow single α ASF distribution. The vapor pressure of each paraffin is calculated using Equation (10), obtained from literature (3). In this equation, the unit for vapor pressure is atm and the unit for temperature is Kelvin.

$$P_i^s = 176.0452\exp\left(-427.218\left(\frac{1}{T} - 1.029807\times10^{-3}\right)(i-1)\right) \qquad 10\,)$$

Since CO and H_2O are not of interest in this work, they are assumed to be insoluble in the reactor liquid. Because of their actual magnitude, this assumption has little impact on the compositions that are calculated. However, H_2 is considered soluble in hydrocarbon liquid since it is critical in evaluating the product Thiele modulus as reflected in Equation (8). The hydrogen solubility in reactor liquid is calculated based on the following formula for Henry's law constant (4)

$$H = 2.291\times10^7 \exp(-1.2326 + 583/T) \qquad 11\,)$$

in which H is in kPa cm^3/mol and T in Kelvin.

Two conditions are selected to illustrate the hydrocarbon product distribution in catalyst pores. Condition A consists of pressure 20 atm, temperature 230 ºC, CO conversion 60%, and single α value 0.85. Condition B consists of pressure 20 atm, temperature 200ºC, CO conversion 60%, and single α value 0.75.

RESULTS AND DISCUSSION

As shown in Equation (8), the Thiele modulus of a hydrocarbon component essentially depends on its concentration at the catalyst surface. Due to the complexity of Fischer-Tropsch reaction, many researchers have assumed that the products are in a single phase, either vapor or liquid phase, when developing their models. With this assumption, the product concentration at the catalyst surface should also follow a single α distribution under steady state. Thus the Thiele modulus of hydrocarbon product is inversely proportional to its effective diffusivity and must increase with carbon number. As a result, internal diffusion limitation always has to occur starting from some carbon number and then become larger and larger. This is probably why the two alpha product distribution was attributed exclusively to the effect of internal diffusion limitation of hydrocarbon products (1).

In fact, the assumption of single phase product oversimplified the problem by ignoring the effect of vapor-liquid-equilibrium in a typical FT reactor. Figure 1 shows the steady state liquid composition in a CSTR reactor. Under the conditions simulated in this work, the hydrocarbon concentration increases with carbon number to a maximum and then decreases. This feature is important in understanding why the internal diffusion limitation does not necessarily exist in catalyst pores. Applying the liquid concentration in Figure 1 to Equation (8), the Thiele modulus of each hydrocarbon component can be calculated. Figures 2 shows the Thiele modulus of each hydrocarbon component relative to that of C_2. φ_i/φ_2 decreases with carbon number until about C_{24}, then increases.

This value becomes higher than unity only when the carbon number is higher than 30. This phenomenon indicates that the hydrocarbon diffusion in catalyst pores does not become more and more difficult as expected with the assumption of single phase product. In fact, it is just the opposite; it becomes relatively easier with increasing carbon number for lighter components. When there is no diffusion limitation for C_2, there is also no diffusion limitation for higher hydrocarbons until at least C_{30}. Even if the removal of C_2 is diffusion limited, it is not necessarily for higher hydrocarbons to have diffusion limitation because the effect of internal diffusion become less and less significant. This eliminates the cornerstone assumption of the model that requires stronger product diffusion limitation with increasing carbon number.

Of course, for carbon numbers higher than 30, there might be diffusion limitation starting with some hydrocarbon component. These heavy hydrocarbons tend to accumulate in catalyst pores until they have enough driving force to transfer the products out of the pores. However, this issue should not affect the total FT product distribution since olefins of these high carbon numbers typically are not produced from catalyst surface. The accumulation of heavy hydrocarbons in catalyst pores may lead to internal diffusion limitation of reactants and catalyst deactivation, but this should not cause the two α distribution.

It therefore can be concluded that, in the presence of VLE, the internal diffusion limitation of products does not necessarily exist and, even if it exists, should not be responsible for the two alpha product distribution in FT reactions.

Figure 3 shows the relative concentration profile of several hydrocarbon components in the catalyst pores under Condition A and φ_H=1.0 (efficiency 94%). For carbon number lower than 20, the higher the hydrocarbon, the lower its relative concentration in the catalyst pores, indicating that the effect of internal diffusion is less significant with increasing carbon number. This is, in fact, the same result as has been discussed above when analysis is made in terms of Thiele modulus.

Figure 4, plotted with volumetric average concentration of C_2 vs. hydrogen Thiele modulus, shows that the effect of internal diffusion of C_2 increases with φ_H. When there is no internal diffusion limitation of hydrogen, e.g., $\varphi_H < 0.2$, there is also no internal diffusion limitation of C_2. Of course there is no diffusion limitation for other hydrocarbons up to about C_{35} as has been discussed previously (Figures 2 and 3). With the same catalyst efficiency (same φ_H), the significance of product diffusion is affected by reaction conditions. When the catalyst efficiency is only 80% ($\varphi_H = 2.0$), the average concentration of C_2 in catalyst pores can be only 6% higher than its surface concentration under Condition B, while it is 37% higher under Condition A.

CONCLUSION

Due to the effect of VLE in the Fischer-Tropsch reactor, the relative concentration of a hydrocarbon product in the catalyst pores decreases with increasing carbon number until about C_{20} under steady state. The impact of internal diffusion of a product is significant only when there is internal diffusion limitation of reactants, and this significance decreases with increasing carbon number. Therefore, it can be deduced that the two alpha product distribution in FT reactions is not due to the effect of product diffusion limitation, even if it exists under some reaction conditions.

LITERATURE CITED

1. Iglesia, E., Reyes, S.C., and Soled, S.L; Reaction-transport selectivity models and the design of Fischer-Tropsch catalysts; "Computer-Aided Design of Catalysts and Reactors," (E. R. Becker and C. J. Pereira, Eds.), Marcel Dekker, Inc., 1992.
2. Zhan, X. and B.H. Davis, B.H.; Two-alpha Fischer-Tropsch product distribution. A role for vapor-liquid-equilibrium?, submitted to Petroleum Science and Technology
3. Caldwell, L. and van Vuuren, D.S.; On the formation and composition of the liquid phase in Fischer-Tropsch reactors; Chem. Eng. Sci., 41 (1986) 89-96.
4. Deckwer, W.D.; "Bubble Column Reactors", John Wiley and Sons, 1992.

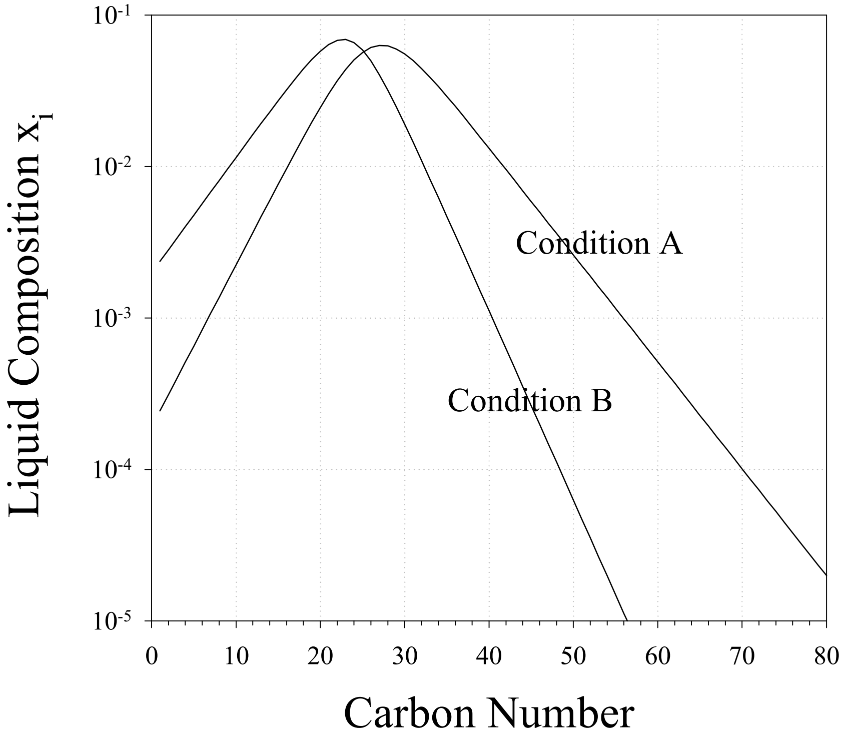

Figure 1. Liquid Composition in the CSTR Reactor.

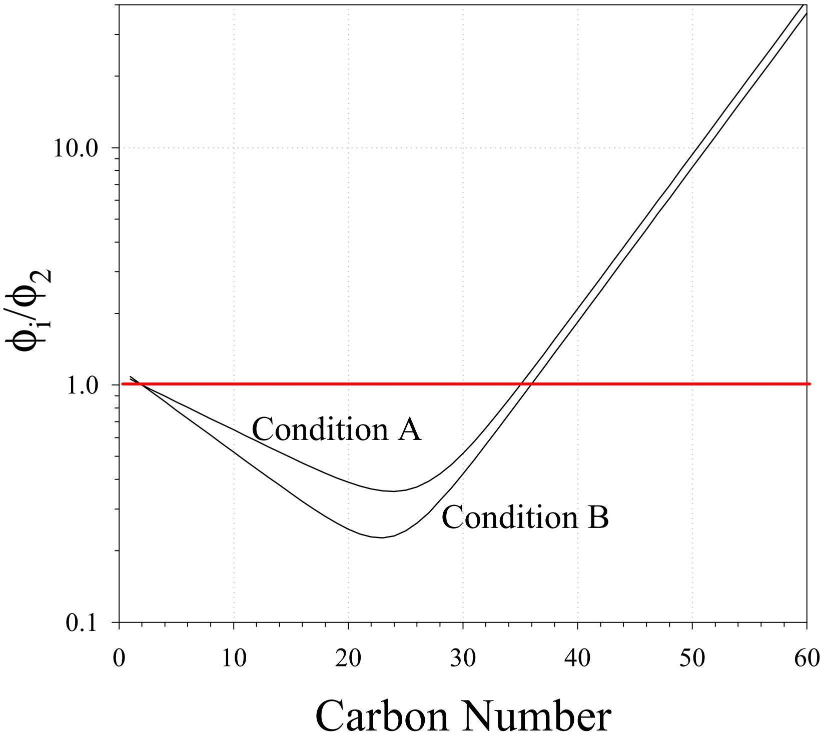

Figure 2. Relative Thiele Modulus of Hydrocarbon Products in Catalyst Pores.

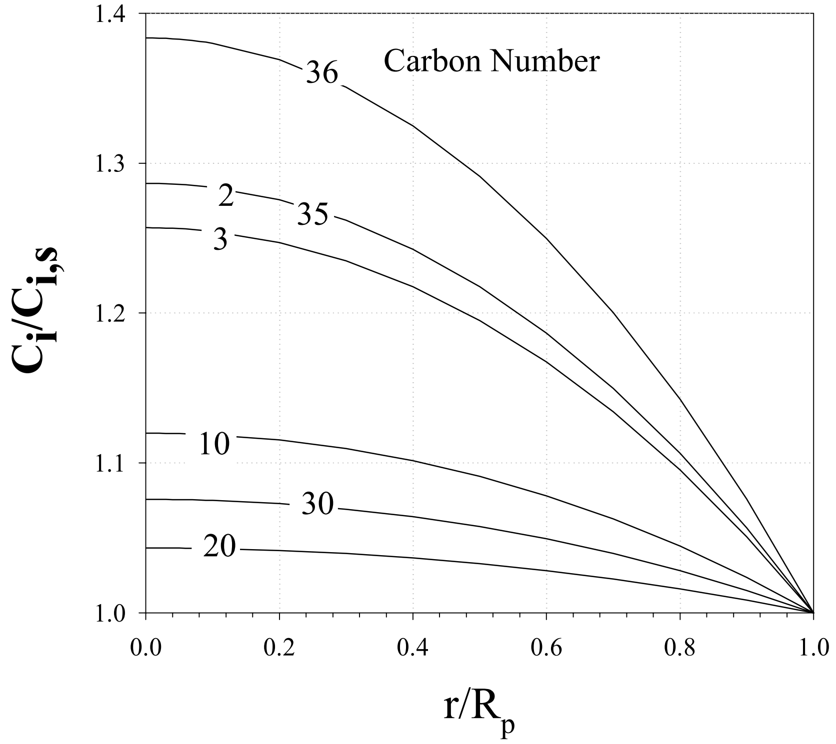

Figure 3. Hydrocarbon Concentration Profile in Catalyst Pores at Condition A with $\phi_H = 1.0$ ($\eta_H = 94\%$).

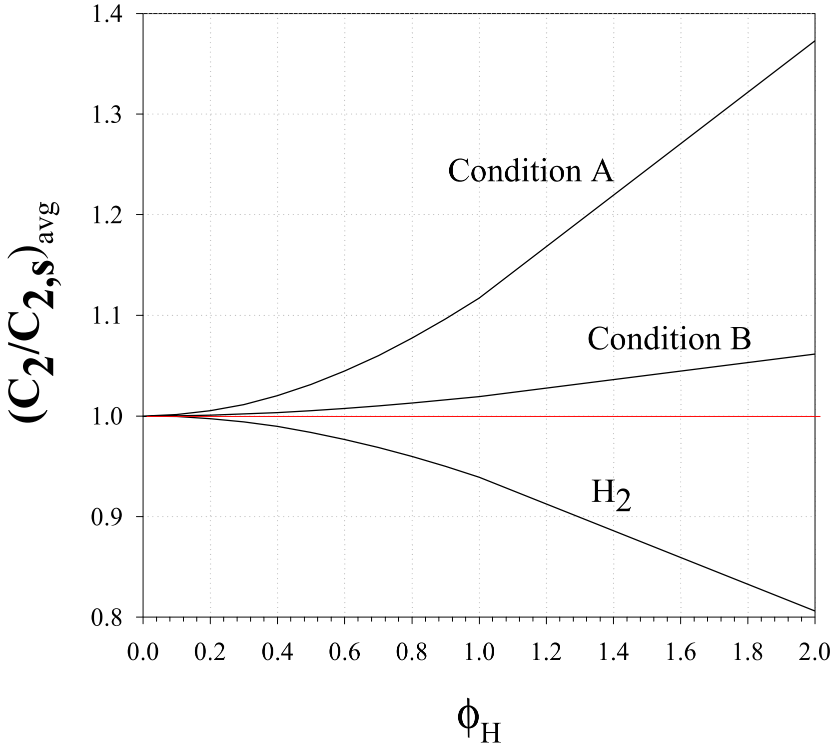

Figure 4. Effect of Hydrogen Thiele Modulus on Average Concentration of C_2 in Catalyst Pores.