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Mechanistic double ASF product distribution study of Fischer–Tropsch synthesis on precipitated iron catalyst

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ABSTRACT

Product distributions of iron based catalyst represented by double ASF distributions characterized by two growth probabilities. Based on enol mechanism and double ASF distributions the complete set of elementary reactions is given. By using mechanistic kinetic studies of Fischer–Tropsch reaction, the chain growth probabilities (α_1 and α_2) for double ASF distributions are formulated. Fe–Cu–La catalyst was prepared by co-precipitation procedure, and steady-state FTS reaction rates were measured in a continuous spinning basket reactor. The experimental results for low carbon monoxide conversions have been satisfactorily fit with the double ASF model. But for higher carbon monoxide conversions deviate substantially because the FTS reaction highly depends on the hydrogen formed by the WGS as the carbon monoxide conversion increases.

1. Introduction

Fischer–Tropsch synthesis (FTS) has attracted increasing interest as an important route for indirect coal liquefaction and gas to liquid (GTL) process (Anderson, 1984; Davis, 2005). The use of iron-based catalysts is attractive due to their high FTS activity as well as their water–gas shift (WGS) reactivity, which helps to make up the deficit of H_2 in the syngas derived from coal gasification (Dry, 2002, 2004).

The products of the FTS are primarily linear hydrocarbons distributed over a wide range of carbon numbers. In the Anderson–Schulz–Flory (ASF) distribution model, the formation of hydrocarbon chains was assumed as a stepwise polymerization procedure and the chain growth probability was assumed to be independent of the carbon number (Davis, 2009; Dry, 1999). However, significant deviations from the ideal ASF distribution have been observed in many studies (Nakhaei Pour et al., 2008; Gaube and Klein, 2008). Many literatures reported that for both iron and cobalt catalysts, product distributions can be represented by superposition of double ASF distributions characterized by two growth probabilities (Gaube and Klein, 2008, 2010; Huff and Satterfield, 1984; Pour et al., 2008, 2010a).

The mechanistic kinetic studies for iron catalysts are based on the formation of the monomer species as the rate-determining step in the consumption of synthesis gas (Teng et al., 2006; Visconti et al., 2007; Pour et al., 2010b, 2012). In this approach, all the mechanistic steps in which the CO and H_2 are consumed and lead to the final products are considered jointly (Nakhaei Pour et al., 2010a; Yang et al., 2003). Based mechanistic kinetic studies of FTS reaction on iron catalysts the growth probabilities for two ASF distributions can be formulated.

In this work the chain growth probabilities of the FTS reaction are developed by Langmuir–Hinshelwood–Hougen–Watson (LHHW) modeling in gradientless reactor over Fe/Cu/La/Si catalyst. The concept two ASF distributions are used for prediction of products distribution of iron catalyst in FTS reaction using developed mechanistic chain growth probabilities. Based on enol mechanism and two ASF distributions the complete set of elementary reactions is given. By using the experimental data, the FTS kinetics model are estimated and discriminated separately.

2. Product distribution model

In this work the carbon number distribution of Fischer–Tropsch products on iron catalyst was studied by use of a modified Anderson–Schulz–Flory (ASF) distribution with two chain growth

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Table 1
Elementary reactions for proposed models.

Model	Reaction steps	Elementary reaction
FT	1	$CO + s \leftrightarrow COs$
	2	$COs + H_2 \leftrightarrow H_2COs$
	3	$H_2COs + H_2 \leftrightarrow CH_2s + H_2O$
	4	$H_2 + 2s \leftrightarrow 2Hs$
	5	$CH_2s + Hs \leftrightarrow CH_3s + s$
	6 rate determining step	$CH_3s + Hs \rightarrow CH_4 + 2s$
	7	$CH_3s + CH_2s \leftrightarrow C_2H_5s + s$
	8 rate determining step	$C_2H_5s + Hs \rightarrow C_2H_6 + 2s$
	9 rate determining step	$C_2H_5s + s \rightarrow C_2H_4 + Hs + s$
	10	$CH_3s + C_{n-1}H_{2n-3}s \leftrightarrow C_nH_{2n}s + s \quad n \le \zeta$
	11	$C_nH_{2n}s + Hs \leftrightarrow C_nH_{2n+1}s + s \quad n \le \zeta$
	12 rate determining step	$C_nH_{2n+1}s + Hs \rightarrow C_nH_{2n+2}+2s \quad n \le \zeta$
	13 rate determining step	$C_nH_{2n+1}s + s \rightarrow C_nH_{2n} + Hs + s \quad n \le \zeta$
	14	$CH_3s + C_{n-1}H_{2n-3}s \leftrightarrow C_nH_{2n}s + s \quad n > \zeta$
	15	$C_nH_{2n}s + Hs \leftrightarrow C_nH_{2n+1}s + s \quad n > \zeta$
	16 rate determining step	$C_nH_{2n+1}s + Hs \rightarrow C_nH_{2n+2}+2s \quad n > \zeta$
	17 rate determining step	$C_nH_{2n+1}s + s \rightarrow C_nH_{2n} + Hs + s \quad n > \zeta$

probabilities. The modified ASF distribution with two chain growth probabilities method was proposed by Donnelly et al. (1988) and is used to characterize the carbon number distribution of FTS where independent ASF distributions with different chain growth probabilities are superimposed.

$$x_i = A\alpha_1^{i-1} + B\alpha_2^{i-1} \tag{1}$$

The most important double ASF distribution aspect is α_1 and α_2 hydrocarbon chain as following:

$$\frac{R_{C_nH_{2n+2}} + R_{C_nH_{2n}}}{R_{C_{n-1}H_{2n}} + R_{C_{n-1}H_{2n-2}}} = \alpha_1 \quad n \le \xi \tag{2}$$

$$\frac{R_{C_nH_{2n+2}} + R_{C_nH_{2n}}}{R_{C_{n-1}H_{2n}} + R_{C_{n-1}H_{2n-2}}} = \alpha_2 \quad n > \xi \tag{3}$$

which RC_nH_{2n} is olefin rate, RC_nH_{2n+2} is linear paraffin rate with n carbon, and α is a factor of hydrocarbon chain growth probability ($0 < \alpha < 1$). For deriving the Langmuir–Hinshelwood–Hougen–Watson (LHHW) for growth probabilities (α_1 and α_2) presented in Table 1, enol theory is utilized to initiate the hydrocarbon chain reaction. In this complete set of elementary reactions, the breakdown of normal ASF is considered. The concentration of the surface intermediate species such as [Hs], $[C_nH_{2n+1}s]$, $[CH_3s]$, and[s] must be determined to achieve rate equations by applying quasi-equilibrium condition for elementary reactions and then according to the partial pressure of CO, H_2, and H_2O.

$$[CH_3s] = \frac{K_1K_2K_3K_4^{\frac{1}{2}}K_5P_{H_2}^{\frac{3}{2}}P_{CO}}{P_{H_2O}}[s] \tag{4}$$

$$[Hs] = \left(K_4P_{H_2}\right)^{1/2}[s] \tag{5}$$

By applying steady state condition according to the partial pressure of CO, H_2, and H_2O, the concentration of the surface intermediate $[C_nH_{2n+1}s]$ can be determined and then solve above equations. Therefore, for $[C_nH_{2n+1}s]$ when $n \le \xi$, can be defined:

$$-d[C_nH_{2n+1}s]/dt = 0 \quad n \le \xi \tag{6}$$

By applying steady state condition:

$$\begin{aligned} & k_{11}[Hs][C_nH_{2n}s] - k_{-11}[C_nH_{2n+1}s][s] - k_{12}[C_nH_{2n+1}s][Hs] \\ & - k_{13}[C_nH_{2n+1}s][s] \\ & = 0 \quad n \le \xi \end{aligned} \tag{7}$$

Then by rearranging:

$$\frac{[C_nH_{2n+1}s]}{[C_{n-1}H_{2n-3}s]} = \frac{k_{11}K_{10}[CH_3s][Hs]}{k_{-11}[s]^2 + k_{12}[Hs][s] + k_{13}[s]^2} = \alpha_1 \ \ n \le \xi \tag{8}$$

According to the above equation, ratio of adjacent carbon species concentrations may be assumed to be the same as probability factor of hydrocarbon chain growth. Probability factor of hydrocarbon chain growth is attained by replacing (4) and (5) equations in (8) as following:

$$\alpha_1 = \frac{k_{11}K_1K_2K_3K_4K_5K_{10}\frac{P_{H_2}^2P_{CO}}{P_{H_2O}}}{k_{-11} + k_{12}K_4^{1/2}P_{H_2}^{1/2} + k_{13}} \quad n \le \xi \tag{9}$$

Also, for $[C_nH_{2n+1}s]$ when $n > \xi$, can be defined:

$$-d[C_nH_{2n+1}s]/dt = 0 \quad n > \xi \tag{10}$$

By applying steady state condition:

$$\begin{aligned} & k_{15}[Hs][C_nH_{2n}s] - k_{-15}[C_nH_{2n+1}s][s] - k_{16}[C_nH_{2n+1}s][Hs] \\ & - k_{17}[C_nH_{2n+1}s][s] \\ & = 0 \quad n > \xi \end{aligned} \tag{11}$$

Then by rearranging:

$$\frac{[C_nH_{2n+1}s]}{[C_{n-1}H_{2n-3}s]} = \frac{k_{15}K_{14}[CH_3s][Hs]}{k_{-15}[s]^2 + k_{16}[Hs][s] + k_{17}[s]^2} = \alpha_2 \quad n > \xi \tag{12}$$

According to the above equation, ratio of adjacent carbon species concentrations may be assumed to be the same as probability factor of hydrocarbon chain growth. Probability factor of hydrocarbon chain growth is attained by replacing (4) and (5) equations in (12) as following:

$$\alpha_2 = \frac{k_{15}K_1K_2K_3K_4K_5K_{14}\frac{P_{H_2}^2P_{CO}}{P_{H_2O}}}{k_{-15} + k_{16}K_4^{1/2}P_{H_2}^{1/2} + k_{17}} \quad n > \xi \tag{13}$$

It is important to notice that two growth probabilities α_1 and α_2 not independent parameters in double ASF model. Instead, we note that at the break point on ASF diagram, the contributions of each term in Equation (1) are equal.

$$A\alpha_1^{i-1} = B\alpha_2^{i-1} \quad i = \zeta \tag{14}$$

It is now possible to obtain kinetic rate equations for proposed models according to the above assumptions. In break point, i illustrate as ζ and necessarily is not an integral carbon number. In this model A and B were not assumed to correspond directly to the fractions of products produced from α_1 and α_2, respectively. Instead the sum of the mole fractions overall carbon numbers is unity:

$$\sum_{i=1}^{\infty} x_i = \sum_{i=1}^{\infty}\left[A\alpha_1^{(i-1)} + B\alpha_2^{(i-1)}\right] = 1 \tag{15}$$

Methane and ethene does not obey the ASF equation and after removing C_1 and C_2 products to fit theoretical distributions to data leads to: