Primary And Secondary Reactions Of The Fisher-Tropsh Synthesis

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ABSTRACT

Fischer-Tropsch synthesis is a surface-catalyzed polymerization reaction. It is primarily a basic reaction that produces saturated (paraffins) and unsaturated (olefins) linear hydrocarbons (HCLCs).

Keywords: Hydrocarbons, polymers, polymerization, catalysts, surface adsorption, reaction, desorption, carbon dioxide, hydrogen.

The Fischer-Tropsch synthesis is a surface-catalyzed polymerization reaction. It is primarily a basic reaction that produces saturated (paraffins) and unsaturated (olefins) linear hydrocarbons (KWST). According to the equation. (R 2.1)5, carbon monoxide and hydrogen form a methylene group –(CH2)– and water/carbon dioxide. The methylene group participates in the chain growth of hydrocarbons, while water is the main by-product of the polymerization reaction.

$$\mathrm{CO} + 2\,\mathrm{H_2} \longrightarrow -(\mathrm{CH_2})- + \mathrm{H_2O} \qquad \Delta_\mathrm{R} H^\circ_{300} = -165{,}0\,\mathrm{kJ\,mol^{-1}} \qquad (\mathrm{R}\,2.1)$$

The reaction equations for the synthesis of paraffins to form hydrocarbons with a C number/chain length j are derived from Eq. (R 2.2) and from olefins according to Eq. (R 2.3) [1].

$$j\mathrm{CO} + (2j+1)\mathrm{H_2} \longrightarrow \mathrm{C}_j\mathrm{H}_{2j+2} - + j\mathrm{H_2O} \qquad (\mathrm{R}\,2.2)$$

$$j\mathrm{CO} + 2j\mathrm{H_2} \longrightarrow \mathrm{C}_j\mathrm{H}_{2j} - + j\mathrm{H_2O} \qquad (\mathrm{R}\,2.3)$$

In addition to the formation of KWST, the water gas shift reaction (WGS) according to equation (R 2.4) is one of the most important (side) reactions of FTS, which was discovered in 1780 by Felice Fontana (1730- . 1805) [2].

$$\mathrm{H_2O} + \mathrm{CO} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2} \qquad \Delta_\mathrm{R} H^\circ_{300} = -39{,}8\,\mathrm{kJ\,mol^{-1}} \qquad (\mathrm{R}\,2.4)$$

This is very rare for cobalt catalysts under FTS conditions. Iron catalysts exhibit WGS activity [3], as magnetite (Fe_3O_4) is the most active phase of WGS [4]. WGS is of particular interest when using substoichiometric synthesis gas, such as that obtained from coal or biomass (H2/CO = 0.7–1.0) [5]. Subsequent side reactions include methanation according to equation (R 2.5) or alcohol formation according to equation (R 2.6). Another side reaction is the Boudoir reaction (R 2.7), named after Octave

L. Boudoir (1872–1923), which describes the formation of solid carbon and carbon dioxide from carbon monoxide [82].

$$3\,H_2 + CO \longrightarrow CH_4 + H_2O \qquad (R\,2.5)$$

$$2\,jH_2 + CO \longrightarrow C_jH_{2j+2}O + (j-1)\,H_2O \qquad (R\,2.6)$$

$$2\,CO \rightleftharpoons CO_2 + C \qquad (R\,2.7)$$

Reaction mechanism of Fischer-Tropsch synthesis

The exact mechanistic processes in the Fischer-Tropsch synthesis are still controversial today [6]. The dependence on the catalyst and the parallel operation of different mechanisms are discussed; a more in-depth comparison of the approaches can be found in Pöhlmann [7]. All the mechanisms presented are based on the following four elementary steps [8]:

1. **surface adsorption,**
2. **chain initiation reaction**
3. **chain growth reaction**
4. **chain termination reaction and product desorption**

2 Theoretical foundations and data

In addition to a number of other reaction mechanisms, for example, the vinylene mechanism according to Rytter et al. [9], three mechanisms have emerged for FTS. These are the carbide mechanism proposed by Fischer and Tropsch [10], the condensation mechanism according to Anderson et al. [10], and the CO injection mechanism by Pichler and Schulz [11]. The elementary steps of a typical CO injection mechanism are shown in Figure 1. The individual steps of the three mechanisms are compared below. The first step of all reaction mechanisms is the surface adsorption of the reactants on the catalyst. All approaches assume dissociative chemisorption of H_2, so that individual hydrogen atoms are bound to the surface. The chemisorption of CO is also the same for all approaches. In the carbide mechanism, the oxygen atom also reacts with hydrogen, leaving only the surface-bound carbon; after chemisorption, dissociation of CO is assumed, with the oxygen atom being present as a bound surface species to support the oxygen reaction [12]. After adsorption on the surface, the chain initiation reaction proceeds as follows,. This forms a monomer based on a polymerization reaction. For the carbide mechanism, the bound carbon is hydrogenated to CH_3 with the help of hydrogen via the intermediates CH and CH_2. In the CO insertion mechanism, this occurs.

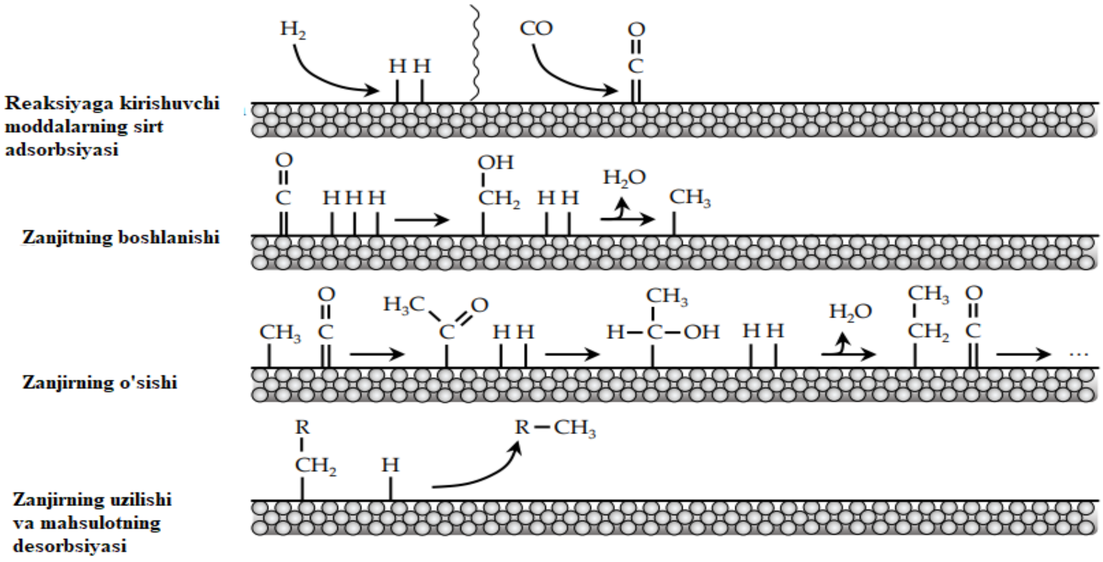

Figure 1: A visual representation of the four steps of the CO injection mechanism for the synthesis of oxygenated hydrocarbons using FTS. See the graph between the CO injection mechanism, the condensation mechanism, and the carbide mechanism.

In the CO injection mechanism, the bound CO is first hydrogenated to CH2OH with the elimination of water to CH_3. In the condensation mechanism, CO is hydrogenated to the monomer CHOH. In the chain propagation process, hydrocarbons are formed by the polymerization of monomers on the catalyst surface. In the carbide mechanism, CH_2 reacts with the surface-bound CH_3 to form CH2 - CH_3. This is extended by the subsequent addition of CH_2. In the condensation mechanism, two CHOH react with hydrogen to form COH - CH_3 with the elimination of water. The chain is formed by the subsequent reaction with hydrogen and CHOH with the elimination of water. In the CO injection mechanism, CH_3 first reacts with adsorbed CO to form CO - CH_3, which is then converted to CHOH - CH_3 by hydrogenation. Further hydrogenation and elimination of water produce CH_2 - CH_3, which in turn can react with CO. Instead of chain growth, there is always the possibility that a chain termination reaction occurs and the resulting oligo- or polymer desorbs from the catalyst surface 1. The chain termination reaction can produce paraffins, olefins, alcohols, carboxylic acids, etc., but not all product formations are discussed here. The part of the chain of hydrocarbons that does not participate in the chain termination reaction is abbreviated below as the R radical. In the carbide mechanism and the insertion mechanism, chain termination occurs by the reaction of hydrogen with R-CH_2 to form R-CH_3. Hydrogenation of R-CHOH can also produce alcohols in the insertion mechanism. The "classical" KWST (R - CH3) and alcohols (R - CH_2OH) are formed when water is eliminated in the condensation mechanism. Recent studies have shown that the rate-determining step of the reaction is pressure-dependent [13]. Petsmann et al. observed that at low pressures (less than 2 bar), the chain termination reaction by hydrogenation is the rate-determining step (RDS) [13]. For higher pressures, the reactivation of the active sites by desorption of the bound carbon, together with the dissociation of CO, is considered to be the RDS [14]. Using isotope labeling, various research groups, such as Biloen et al. [14], Bianchi et al. [15] or Govender et al. [16], have provided evidence for a carbide mechanism. On the other hand, chain assembly occurs via oxygen species and therefore via a CO insertion mechanism according to Kummer et al. [17] and Kölbel et al. [18] instead. Density functional theory (DFT) calculations support both a carbide mechanism [19] and a CO insertion mechanism [20]. DFT calculations by Asiaee et al. The carbide mechanism as the main reaction pathway, while the increasing proportion of the liquid phase supports the increasing contribution of the CO incorporation mechanism in addition to the main reaction pathway [21]. There is also an approach to determine or model the reaction mechanism using kinetic approaches [22]. In 1988, Wojciechowski conducted experiments; however, this revealed deviations of more than 40% between the experimental data and the model9 [23], and Marchese et al. [24], still found deviations of more than 25% between the experiment and the model. Therefore, the proof of the reaction mechanism remains in the widely used literature by Schulz [25], van der Laan et al. [26] and Davis [27].

Product distribution of Fischer-Tropsch synthesis

The main reaction of FTS is a polymerization reaction; therefore, the reaction product contains a wide range of hydrocarbons. This product range is independent of the actual reaction mechanism. This polymerization reaction can be described using the Schulz-Flory polymerization [28]. Therefore, the mole fraction xj of a molecule with the number of Cs j can be expressed in terms of the value of a:

$$x_j = \alpha^{j-1} \cdot (1 - \alpha) \qquad (2.1)$$

A simplified illustration of polymerization can be seen in Figure 2.5. It should be noted that this is for simplified illustration only and does not claim to describe the complex reaction mechanism..

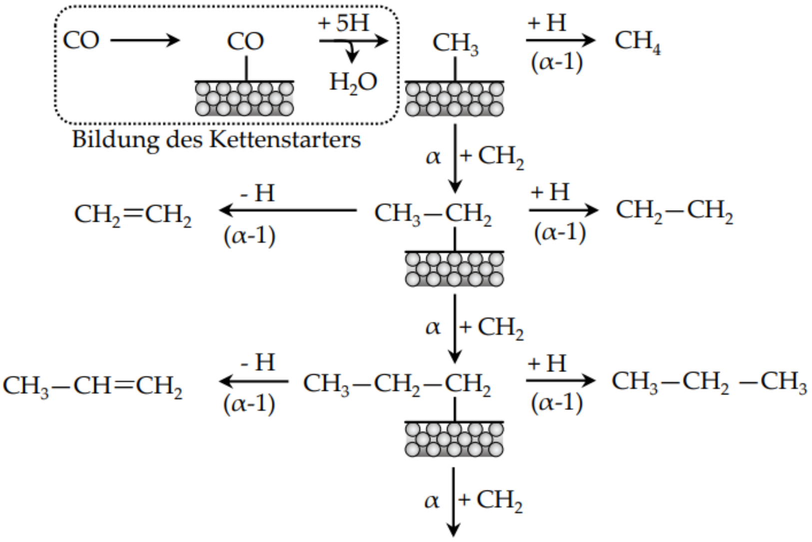

Figure 2: Schematic chain growth in the Fischer-Tropsch synthesis of olefins and paraffins. As can be seen from the figure, three reactions are possible with an adsorbed alkyl group:

1. A chain growth reaction with a chain growth probability of a occurs with the addition of a CH_2 group.

2. The alkyl group is desorbed from the catalyst surface with probability 1-a, forming an olefin/alkene (CjH2j).

3. The alkyl group is desorbed from the catalyst surface with probability 1-a and hydrogenated with hydrogen to form a paraffin/alkane (CjH2j+2).

In addition to the molar fraction, the mass fraction ωC,j is of particular importance and can be calculated from the equation. It describes the mass distribution of carbon atoms throughout the product.

$$\omega_{C,j} = j \cdot \alpha^{j-1} \cdot (1-\alpha)^2 \qquad (2.2)$$

The probability of further chain growth strongly influences the α-mass distribution or the product spectrum. If the α value of the catalyst is changed by changing or modifying the reaction conditions, a significant increase in selectivity to the desired C fraction can be achieved. In practice, deviations from the ideal Anderson-Schulz-Flory distribution are repeatedly observed, for example, the probability of chain growth increases with the number of C [29]. The main deviations that occur can be described in the following three points

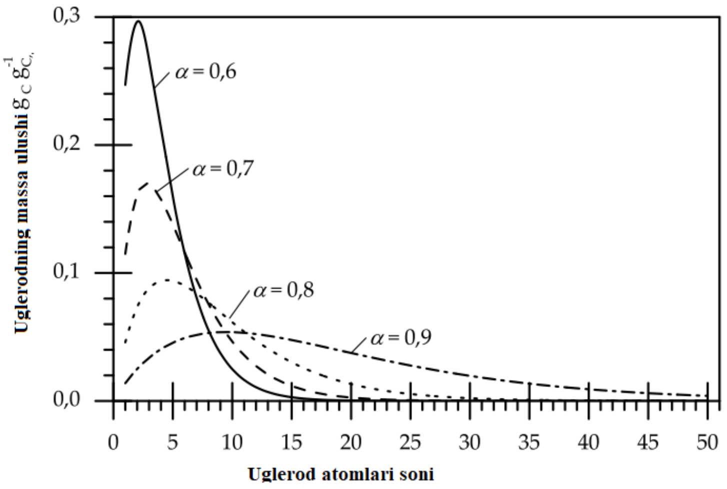

Figure 3: Mass fraction of carbon ωC as a function of the growth probability of an individual hydrocarbon chain.

Methane selectivity

The methane content in the product gas is usually underestimated due to the ASF distribution, especially for technical particles. In many cases, an increasing selectivity for technical particles towards methane and short-chain KWST can be observed. A possible explanation lies in the gradual decomposition of olefins with the release of methane [28]. In addition, according to Ponek, the reason can be found in the active phase catalyzing the formation of CH4 [29].

Ethene selectivity

If the ASF distribution is considered from the point of view of ethene, a lower amount of ethene is often found than predicted by the distribution. This is due to the high reactivity of the ethene molecule. After studying it, it is increasingly involved in chain growth and chain propagation reactions [30]. One attempt to explain the participation in chain growth is that there is a double surface bond in the form CH_2 - CH_2 [52]. This represents a twofold increase in the chain growth probability compared to a single surface bond (CH_2 - CH_3) [52]. This double surface bond is particularly questionable for ethene [31].

Two-Different Chain Growth Probabilities

For iron catalysts, a superposition of two different chain growth probabilities can often be observed in the FTS, as shown by Huff et al. [32]. The mole distribution xj of carbons with number c j follows from equation (2.3) [33]. Use equation to describe the Z factor.

$$x_j = Z(1-\alpha_1)\cdot\alpha_1^{j-1} + (1-Z)(1-\alpha_2)\cdot\alpha_2^{j-1} \qquad (2.3)$$

As an explanation for the occurrence of two different α values, different chain termination mechanisms [33] are used. On the other hand, secondary reactions at the surface can explain the changes in the product distribution, as shown by Kuipers et al. [34].

Determining the chain growth probability(s)

Equation (2.1) can be linearized to equation (2.4) using logarithms. Therefore, the α value can be determined from the experimentally determined molar fraction xj of hydrocarbons.

$$\ln x_j = \ln\left(\frac{1-\alpha}{\alpha}\right) + j\ln\alpha \qquad (2.4)$$

C5+ selectivity is usually determined in parametric studies to provide a qualitative statement about the chain growth potential. This allows for comparison without a full product analysis. The C_5+ selectivity (mass fraction of C_2+ hydrocarbons based on ωC_5+) can be calculated using the equation. (2.5) The chain growth probability, aC_5+ (realistic range 0.6 ≤ a ≤ 0.9), can also be estimated;

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