CHAPTER II

OVERVIEW OF THE FISCHER-TROPSCH SYNTHESIS

II-1. Brief History of the Fischer-Tropsch Synthesis.

The formation of methane from hydrogenation of carbon monoxide over reduced nickel and cobalt catalysts at atmospheric pressure and temperatures between 200 and 300 °C was first reported by Sabatier and Senderens in 1902 [6]. In 1921, Patart reported the production of methanol from carbon monoxide and hydrogen [206]. Badische Anilin and Soda Fabrik patented their processes of hydrogenation of carbon monoxide under high pressure (100 to 200 atmospheres) and temperatures of 300 to 400 °C on alkalized oxides of cobalt and osmium in the preparation of hydrocarbons and oxygenates in 1913 [6], and using zinc oxide for the synthesis of methanol in 1923 [234]. Franz Fischer and Hans Tropsch then developed the Synthol process in 1922 [206], in which the reaction between carbon monoxide and hydrogen occurred at lower pressures ranging from 100 to 150 atmospheres and at temperatures of 400 to 450 °C in the presence of an alkalized iron turnings. This produced a mixture of mostly oxygenates, such as alcohols, aldehydes, ketones, acids and small portions of saturated and unsaturated hydrocarbons [206].

In a later experiment in 1925 [206], Fischer found that as the reaction pressure was lowered to about 7 atmospheres, the distribution of oxygenated and non-oxygenated hydrocarbon products was reversed. In 1929, Smith, Hawk and Golden at the U.S. Bureau of Mines experimented with the incorporation of ethylene in the synthesis over a cobalt catalyst that resulted in significantly increasing the yield of oxygenated compounds which were later identified by Otto Roelen to be primarily propionaldehyde [234]. The discovery of the ZnO and Cr_2O_3-based catalysts represented a decisive step in the selective synthesis of alcohols from CO and H_2 [164]. These early results led to numerous studies for producing various products from synthesis gas containing hydrogen and carbon monoxide. Three distinct lines were developed: the synthesis of paraffinic and olefinic hydrocarbon mixtures, the synthesis of low and high alcohols and the synthesis of aldehydes [164].

The first commercial plants utilizing Fischer-Tropsch technology went on stream in Germany in 1936 [197]. During World War II, a total of nine plants were operating in Germany based on a medium pressure cobalt catalyzed process [110]. At the peak of production in 1943, the German plants were producing ca. 600,000 tons/yr of hydrocarbons consisting of gasoline (46%) and diesel oil (23%) fractions [197]. After the war, the German plants were closed, but research of Fischer-Tropsch technology continued worldwide, especially in Germany, Britain, and the United States. The emphasis was on more easily accessible iron catalysts and improved reactor designs for better heat removal [206].

In the early fifties, the great euphoria over cheap petroleum from oil exploded in the Middle East, USA and Europe, resulting not only in the shut down of coal mines, but also in demoralizing the interest in synthetic fuels [110,176]. The only exception was the start up of a large commercial Fischer-Tropsch plant in Sasolburg, South Africa in 1955 belonging to the South African Coal, Oil and Gas Corporation, later changed to South African Synthetic Oil, Ltd. (SASOL) [75]. The plant (now called SASOL I) uses a Lurgi coal gasification process to produce the synthesis gas from coal and then the Fischer-Tropsch synthesis in both fixed-bed and circulating fluid-bed reactors to manufacture hydrocarbons which are upgraded for gasoline and diesel fuels [76].

Following the 1973 oil embargo, research activity on the Fischer-Tropsch synthesis resurged [110,239]. A great deal of work has been done on searching for better catalysts such as ruthenium, molybdenum, tungsten and manganese of non-conventional Group VIII metals, bimetallic alloys, novel promoters and supporters for the catalysts [197]. One example of the result of the intensive investigations was that a new competitive process for converting methanol to an aromatic gasoline and C_2 to C_4 olefins using so-called shape-selective catalyst (ZSM5) was developed by Mobil in 1976 [157]. The second SASOL plant came on stream in 1980 and a third in 1984 [77]. Annual production capacity was estimated to be around 2 million tons [140]. The worldwide economic recession in 1982, however, sharply slowed down all synthetic fuel ventures [8].

II-2. Fischer-Tropsch Chemistry.

The classical Fischer-Tropsch synthesis (FTS) has been described as the reaction between hydrogen and carbon monoxide in the presence of Group VIII metals to produce a variety of aliphatic hydrocarbons and alcohols of predominantly straight carbon chains in the range of C_4 to C_{17} [206]. An even more inclusive description of Fischer-Tropsch synthesis defines it to be the following reactions [6]:

$$(2n+1)H_2 + nCO = C_nH_{2n+2} + nH_2O \qquad (2.1)$$

$$(n+1)H_2 + 2nCO = C_nH_{2n+2} + nCO_2 \qquad (2.2)$$

$$2nH_2 + nCO = C_nH_{2n} + nH_2O \qquad (2.3)$$

$$nH_2 + 2nCO = C_nH_{2n} + nCO_2 \qquad (2.4)$$

$$2nH_2 + nCO = C_nH_{2n+1}OH + (n-1)H_2O \qquad (2.5)$$

$$(n+1)H_2 + (2n-1)CO = C_nH_{2n+1}OH + (n-1)CO_2 \qquad (2.6)$$

A modern view claims that all the reactions in the Fischer-Tropsch synthesis can be reduced to two types, as below [185]:

$$2H_2 + CO = (-CH_2-) + H_2O \qquad (2.7)$$

$$H_2 + 2CO = (-CH_2-) + CO_2 \qquad (2.8)$$

$$H_2O + CO = H_2 + CO_2 \qquad (2.9)$$

$$H_2O + 3CO = (-CH_2-) + 2CO_2 \qquad (2.10)$$

The reaction type 2.7 is generally promoted by cobalt catalysts while reaction type 2.8 is affected by iron catalysts. The water-gas shift (reaction 2.9) allows for adjusting the CO/H_2 ratio in the synthesis gas. Systematic study of the role of the water-gas shift reaction in the Fischer-Tropsch synthesis resulted in the discovery of another type of hydrocarbon synthesis from carbon monoxide and steam in 1949 and was named the Kolbel-Engelhardt synthesis, i.e., reaction type 2.10, [8]. Other competing reactions include decomposition of carbon monoxide (Boudouard reaction) [223]:

$$2CO = C + CO_2 \qquad (2.11)$$

coke deposition:

$$H_2 + CO = C + H_2O \qquad (2.12)$$

carbide formation:

$$xM + C = M_xC \qquad (2.13)$$

Reaction of the synthesis to produce methane and oxidation of the catalyst also may be involved [223]. Typical carbides are Fe_3C, Co_2C and Ni_3C and they are unstable with respect to the metals and carbon [6].

The dissociation energy of stable hydrogen molecule is 431.4 kJ/mol [110]. About 80 percent of this bond energy is due to the resonance of electrons between the electronic orbits of the two atoms, i.e., H:H. A contribution of about 5 percent is due to the unstable resonance between H+-:H and H-:H+ structures [206]. The remaining 15 percent is attributed to complicated interactions. Hydrogen is soluble in most metals and the solubility increases with temperature. There is some evidence that hydrogen atoms might be hydridic when bonded to a transition metal [57]. The chemisorption of hydrogen on many metals can occur as low as -100 °C [206].

Carbon and oxygen have 4 and 6 valence electrons (L shells) respectively. The resonance among $:C^{+}\;:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$, $:C::\overset{\cdot\cdot}{O}:$ and $:\overset{-}{C}:::\overset{+}{O}:$ contributes roughly the same to the normal state of the molecule [206]. The heat of atomization of carbon monoxide is 965.9 kJ/mol [160]. In the presence of metals, carbon monoxide reacts in a number of ways. At low temperatures, many metals such as cobalt, nickel, iron and copper tenaciously chemisorb carbon monoxide. From room temperature to about 200 °C, carbonyls such as $Fe(CO)_5$, $Ni(CO)_4$ and $[Co(CO)_4]_2$ are formed. These carbonyls are liquids which boil below 50 °C and decompose at atmospheric pressure at temperatures below 150 °C [206]. At temperatures from 150 to 250 °C, carbon monoxide reacts with iron, cobalt and nickel to form carbides such as Fe_2C, Co_2C and Ni_3C. At temperatures between 250 and 350 °C, these carbides decompose to metal and carbon or lower carbides. Above 300 °C, carbon monoxide can decompose on these metals to produce chiefly free carbon and carbon dioxide [206].

The contribution of a C-C bond to a double bond of C=C in alkenes of average bond energy of 146 kcal/mol is 63 kcal/mol. The reaction of this weak bond with a normal single bond to produce a molecule containing two new single bonds is generally a thermodynamically favorable process. The most characteristic way in which ethylene reacts is by addition to its double bond. For example, hydrogen, in the presence of a catalyst, e.g., Ni or Cu, will add to it yielding ethane. More commonly, the attacking reagent is an acid, either a proton donor or an electron acceptor. These acids add rapidly across the bond of ethylene, even in the absence of any catalyst. Ethylene can be strongly adsorbed at 0 °C by copper. Pure nickel is known to chemisorb ethylene so strongly that the surface of nickel is poisoned. Ethylene is only slightly physically adsorbed by iron [85,132].

II-3. Thermodynamics.

The thermodynamics of the hydrogenation of carbon monoxide have been discussed by Smith [201] and Myddleton [163] for a relatively few compounds in the product. The first comprehensive thermodynamic study of the Fischer-Tropsch synthesis was summarized in the book by Storch et al. [206] and later revised in the series of reviews of catalysis edited by Emmett [6]. Important conclusions were drawn as follows:

1. The synthesis of hydrocarbons from H and CO is strongly exothermic, evolving some 146 to 176 kJ per mole of CO converted under usual reaction conditions [110].
2. The formation of methane has the the most negative Gibbs free energy change of any corresponding hydrocarbons [7].
3. Reactions producing carbon dioxide are more thermodynamically favorable than corresponding reactions producing water [206].
4. In the range of temperature and pressure at normal ranges, all types of hydrocarbons, except acetylene, are thermodynamically possible [6].
5. Any amount of ethylene can be incorporated with a hydrogen-carbon monoxide mixture at all Fischer-Tropsch temperatures [6].

6. The production of alcohols, with the least feasible methanol, from the hydrogenation of carbon monoxide under usual reaction conditions is thermodynamically possible [6].
7. Hydrogenation of carbon dioxide to produce hydrocarbons and/or alcohols, except for acetylene and methanol, is possible thermodynamically under most synthesis conditions [6].

Anderson et al. [7] recently have calculated the equilibrium conversions for a few simple straight chain paraffins, olefins, acetone, aldehydes, carboxylic acids and alcohols and further concluded that the free energy changes are usually adequate for forming hydrocarbon and simple oxygenate molecules with only a few exceptions such as acetylene and formaldehyde from the hydrogenation of carbon oxides. For the production of specific hydrocarbon molecules other than methane, selective catalysts are required.

The equilibrium constants for the formation of hydrocarbons of varying chain length also depend on the length of the carbon chain. Below 400 °C, the formation of higher hydrocarbons is more favored than the lower ones since the equilibrium constant increases with the carbon number [110]. For most reactions, the equilibrium constants are greater than unity below 350 °C, but become thermodynamically unfavorable above 450 °C [67]. A more recent study of the thermodynamics of the Fischer-Tropsch synthesis by Ahmad and Wojciechowski took aromatics into account and concluded that the direct synthesis of aromatics can be thermodynamically favorable at temperatures around 650 °K [2].

The study of the chemical thermodynamics of the Fischer-Tropsch synthesis has been incomplete mainly due to the complex nature of the reaction, since, for every hydrocarbon molecule, there are many possible reactions. Most studies are based on simplified overall reaction stoichiometry for a particular type of product. The actual Fischer-Tropsch synthesis is governed by a large number of parallel primary reactions (e.g. formation of hydrocarbons and alcohols), secondary reactions (e.g. isomerization) and side reactions (e.g. water-gas shift reaction, Boudouard reaction and possible Kolbel-Engelhardt reactions), resulting in a system too complex to perform a rigorous equilibrium composition study. Nevertheless, the incomplete thermodynamic studies do provide clues for appropriate operating conditions for desired products.

II-4. Mechanism.

The definition of the mechanism for a simple reaction is the path that the molecules follow in going from reactant to product. For a complex reaction system, it becomes a network of paths and the emphasis is shifted to an explanation of the observed rate rather than the identification of a possible path. Since 1926, many efforts have been made to identify the mechanism in the desire to understand how catalyst composition and reaction conditions govern the the products formed. Many review articles about the mechanism of the Fischer-Tropsch reactions can be found in recent literature [18,19,22,23,161,183] in addition to the book by Anderson [6,8,206]. According to Rofer-DePoorter, only five complete mechanisms have been postulated [183]. These are: (1) Fischer/Tropsch mechanism [6,206], (2) Storch/Golumbic/Anderson mechanism [6,166,206], (3) Pichler/Schulz mechanism [173,193], (4) Henrici-Olive/Olive mechanism [107], and (5) Ponec mechanism [174,175,220]. All of the five mechanisms overlap to some extent.

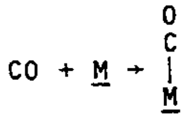
II-4.1. Fischer/Tropsch Mechanism.

Fischer and Tropsch hypothesized that CO reacts with the metal of the catalyst to form a bulk carbide which then evolves methylene groups upon reaction with hydrogen

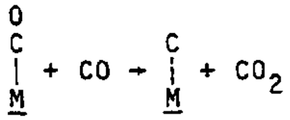
[6,206]. The methylene groups then polymerize to form the products. This mechanism was later detailed by Craxford and Rideal [62]. However, these authors suggested that only surface carbides are involved in the reaction. Part of the justification for carbides as the intermediates was that metal carbides react with acidic aqueous solutions to give similar products to the ones from Fischer-Tropsch synthesis. Both versions of the carbide theory were subjected to criticism [8]. Recent findings that hydrogenation of metal carbides yields only methane have cast doubts on the carbide mechanism [95,177]. The analysis of tracer experiments in which metal carbide layers containing ^{14}C reacts with synthesis gas led to the conclusion that the carbide mechanism could account for only a minor role in the formation of products [139]. Allowance was made, however, for the possibility of chemisorbed carbon atoms as intermediates.

The major shortcoming of the carbide mechanism is that it does not explain the formation of oxygenated products. A variant of the carbide mechanism proposed that methylidyne groups, rather than methylene groups, are the primary carbon-carbon bond formers [127]. Recent evidence on surface intermediates gives new likelihood to some of the reactions proposed in the carbide mechanism, particularly the recombination of hydrocarbon intermediates to form carbon bonds [39,40]. The elementary steps proceed as follows:

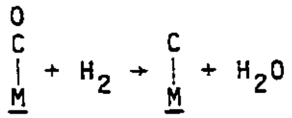
Initiation



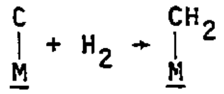
$$CO + \underline{M} \rightarrow \begin{array}{c} O \\ C \\ | \\ \underline{M} \end{array} \qquad (2.14)$$



$$\begin{array}{c} O \\ C \\ | \\ \underline{M} \end{array} + CO \rightarrow \begin{array}{c} C \\ | \\ \underline{M} \end{array} + CO_2 \qquad (2.15)$$

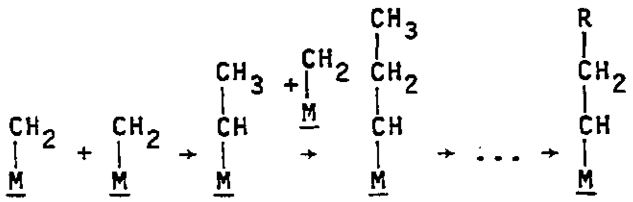


$$\begin{array}{c} O \\ C \\ | \\ \underline{M} \end{array} + H_2 \rightarrow \begin{array}{c} C \\ | \\ \underline{M} \end{array} + H_2O \qquad (2.16)$$



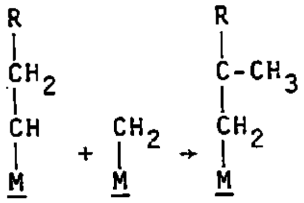
$$\begin{array}{c} C \\ | \\ \underline{M} \end{array} + H_2 \rightarrow \begin{array}{c} CH_2 \\ | \\ \underline{M} \end{array} \qquad (2.17)$$

Propagation



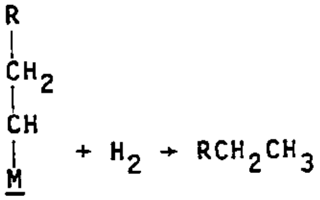
$$\begin{array}{c} CH_2 \\ | \\ \underline{M} \end{array} + \begin{array}{c} CH_2 \\ | \\ \underline{M} \end{array} \rightarrow \begin{array}{c} CH_3 \\ | \\ CH \\ | \\ \underline{M} \end{array} + \begin{array}{c} CH_2 \\ | \\ \underline{M} \end{array} \rightarrow \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH \\ | \\ \underline{M} \end{array} \rightarrow \ldots \rightarrow \begin{array}{c} R \\ | \\ CH_2 \\ | \\ CH \\ | \\ \underline{M} \end{array} \qquad (2.18)$$

Branching

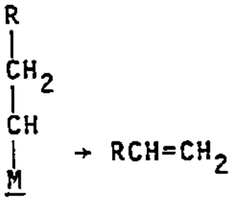


$$\begin{array}{l} R \\ | \\ CH_2 \\ | \\ CH \\ | \\ \underline{M} \end{array} + \begin{array}{l} CH_2 \\ | \\ \underline{M} \end{array} \rightarrow \begin{array}{l} R \\ | \\ C-CH_3 \\ | \\ CH_2 \\ | \\ \underline{M} \end{array} \qquad (2.19)$$

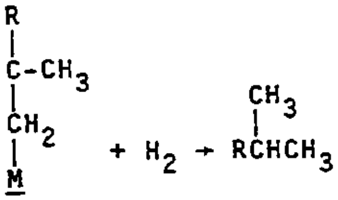
Termination



$$\begin{array}{l} R \\ | \\ CH_2 \\ | \\ CH \\ | \\ \underline{M} \end{array} + H_2 \rightarrow RCH_2CH_3 \qquad (2.20)$$



$$\begin{array}{l} R \\ | \\ CH_2 \\ | \\ CH \\ | \\ \underline{M} \end{array} \rightarrow RCH{=}CH_2 \qquad (2.21)$$



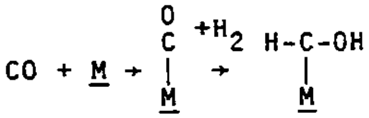
$$\begin{array}{l} R \\ | \\ C-CH_3 \\ | \\ CH_2 \\ | \\ \underline{M} \end{array} + H_2 \rightarrow R\overset{\begin{array}{c} CH_3 \\ | \end{array}}{C}HCH_3 \qquad (2.22)$$

II-4.2. Storch/Golumbic/Anderson Mechanism.

This mechanism accounted for the formation of oxygenated products by making a hydroxycarbene intermediate, M=CHOH, responsible for carbon-carbon bond formation [6]. It was also postulated that the condensation of two M=CHOH groups followed by hydrogenation is the carbon-carbon bond-forming step [166,206]. Condensation of more hydrogenated species, M-CH(R)OH, with M=CHOH gave methyl branching [6,206]. Similar mechanisms were proposed by Edius [79], and Nijs and Jacobs [167].

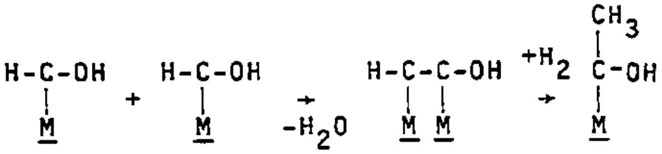
The difficulty in justification of this mechanism is that the hydroxycarbene species M=C(R)OH has never been observed. In addition, no condensation reactions resembling those of reactions shown in the mechanism have been observed in organometallic compounds. Blyholder et al. studied the interaction of alcohols on Fe, Co and Ni by infrared spectroscopy and found no enolic species [26-31]. A hydroxycarbene may be an intermediate in the reductions of CO to methane and acyls to alkyls. The mechanism can be summarized as follows:

Initiation

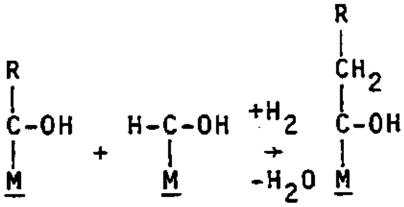


$$CO + \underline{M} \rightarrow \begin{array}{c} O \\ C \\ | \\ \underline{M} \end{array} \xrightarrow{+H_2} \begin{array}{c} H-C-OH \\ | \\ \underline{M} \end{array} \qquad (2.23)$$

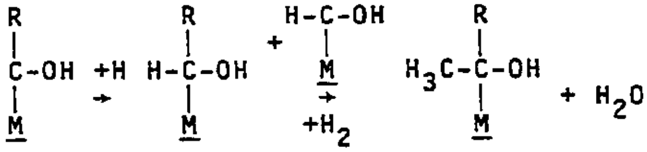
Propagation



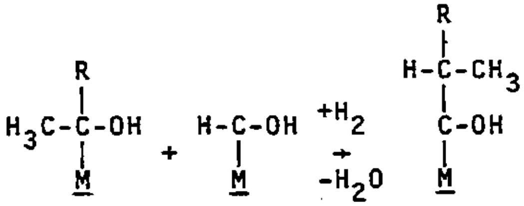
$$\begin{array}{c} H-C-OH \\ | \\ \underline{M} \end{array} + \begin{array}{c} H-C-OH \\ | \\ \underline{M} \end{array} \xrightarrow[-H_2O]{} \begin{array}{c} H-C-C-OH \\ |\quad | \\ \underline{M}\ \underline{M} \end{array} \xrightarrow{+H_2} \begin{array}{c} CH_3 \\ | \\ C-OH \\ | \\ \underline{M} \end{array} \qquad (2.24)$$



$$\begin{array}{c} R \\ | \\ C-OH \\ | \\ \underline{M} \end{array} + \begin{array}{c} H-C-OH \\ | \\ \underline{M} \end{array} \xrightarrow[-H_2O]{+H_2} \begin{array}{c} R \\ | \\ CH_2 \\ | \\ C-OH \\ | \\ \underline{M} \end{array} \qquad (2.25)$$

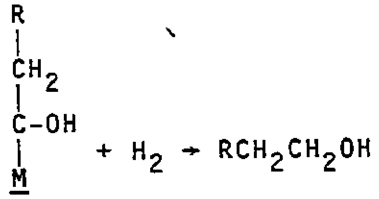


$$\begin{array}{c} R \\ | \\ C-OH \\ | \\ \underline{M} \end{array} \xrightarrow{+H} \begin{array}{c} R \\ | \\ H-C-OH \\ | \\ \underline{M} \end{array} + \begin{array}{c} H-C-OH \\ | \\ \underline{M} \end{array} \xrightarrow[+H_2]{} \begin{array}{c} R \\ | \\ H_3C-C-OH \\ | \\ \underline{M} \end{array} + H_2O \qquad (2.26)$$

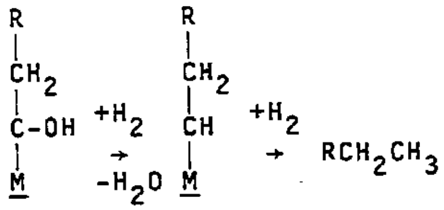


$$\begin{array}{c} R \\ | \\ H_3C-C-OH \\ | \\ \underline{M} \end{array} + \begin{array}{c} H-C-OH \\ | \\ \underline{M} \end{array} \xrightarrow[-H_2O]{+H_2} \begin{array}{c} R \\ | \\ H-C-CH_3 \\ | \\ C-OH \\ | \\ \underline{M} \end{array} \qquad (2.27)$$

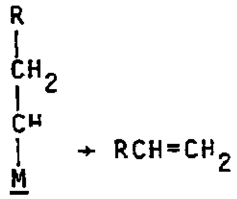
Termination



$$\begin{array}{l} R \\ | \\ CH_2 \\ | \\ C{-}OH \\ | \\ \underline{M} \end{array} + H_2 \rightarrow RCH_2CH_2OH \qquad (2.28)$$



$$\begin{array}{l} R \\ | \\ CH_2 \\ | \\ C{-}OH \\ | \\ \underline{M} \end{array} \xrightarrow[-H_2O]{+H_2} \begin{array}{l} R \\ | \\ CH_2 \\ | \\ CH \\ | \\ \underline{M} \end{array} \xrightarrow{+H_2} RCH_2CH_3 \qquad (2.29)$$

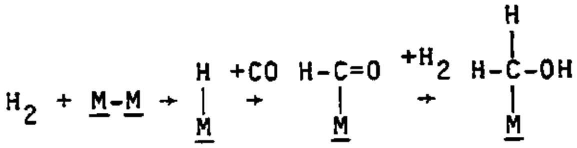


$$\begin{array}{l} R \\ | \\ CH_2 \\ | \\ CH \\ | \\ \underline{M} \end{array} \rightarrow RCH{=}CH_2 \qquad (2.30)$$

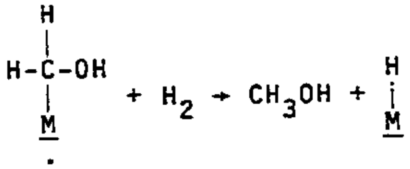
II-4.3. Pichler/Schulz Mechanism.

Pichler and Schulz have presented a detailed version of invoking C-C bond formation by the CO-insertion into an alkyl-metal bond analogous to those reactions in homogenous organometallic chemistry which takes chain growth into account [173,193]. Hydrocarbon radicals are considered as the intermediates. Methyl branches are produced in several different ways, including the incorporation of propylene, migration of a methyl radical, and migration of the point of attachment of a hydrocarbon radical to the metal via a π-bonded intermediate. In the production of oxygenated molecules, the oxygen in the final growth step is not eliminated. The proposed mechanism proceeds as follows:

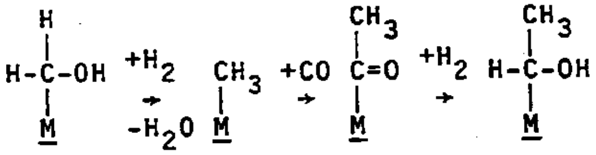
Initiation



$$H_2 + \underline{M}\text{-}\underline{M} \rightarrow \begin{matrix}H\\|\\\underline{M}\end{matrix} \xrightarrow{+CO} \begin{matrix}H\text{-}C{=}O\\|\\\underline{M}\end{matrix} \xrightarrow{+H_2} \begin{matrix}H\\|\\H\text{-}C\text{-}OH\\|\\\underline{M}\end{matrix} \qquad (2.31)$$

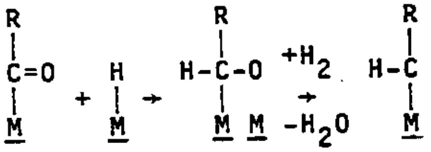


$$\begin{matrix}H\\|\\H\text{-}C\text{-}OH\\|\\\underline{M}\end{matrix} + H_2 \rightarrow CH_3OH + \begin{matrix}H\\|\\\underline{M}\end{matrix} \qquad (2.32)$$



$$\begin{matrix}H\\|\\H\text{-}C\text{-}OH\\|\\\underline{M}\end{matrix} \underset{-H_2O}{\xrightarrow{+H_2}} \begin{matrix}CH_3\\|\\\underline{M}\end{matrix} \xrightarrow{+CO} \begin{matrix}CH_3\\|\\C{=}O\\|\\\underline{M}\end{matrix} \xrightarrow{+H_2} \begin{matrix}CH_3\\|\\H\text{-}C\text{-}OH\\|\\\underline{M}\end{matrix} \qquad (2.33)$$

Propagation



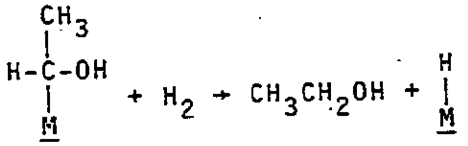
$$\begin{matrix}R\\|\\C{=}O\\|\\\underline{M}\end{matrix} + \begin{matrix}H\\|\\\underline{M}\end{matrix} \rightarrow \begin{matrix}R\\|\\H\text{-}C\text{-}O\\|\quad\\\underline{M}\ \underline{M}\end{matrix} \underset{-H_2O}{\xrightarrow{+H_2}} \begin{matrix}R\\|\\H\text{-}C\\|\\\underline{M}\end{matrix} \qquad (2.34)$$

II-4.4. Henrici-Olive/Olive Mechanism.

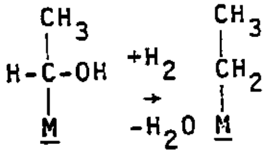
Henrici-Olive and Olive have proposed another reaction scheme based on individual steps well established in the homogeneous catalysis literature [107]. Such individual steps are coordination of CO and olefins, oxidative addition and reductive elimination, insertion, as well as β-H transfer. The insertion of coordinated CO into a metal alkyl bond present at the same transition metal center is one of the key reactions in homogeneous catalysis. Oxidative addition of H_2 leads to the intermediate (II) which can undergo two alternative reactions, giving either the alcohol by reductive elimination, or the alkyl group by H_2O elimination.

The alkyl-metal compound can either add CO and thus contribute to the chain propagation or, by β-H transfer, give an α-olefin and a metal hydride which constitutes the kinetic chain. The β-H abstraction can take place as soon as a β-H becomes available, and can also lead to the production of α-olefins as the primary products of the Fischer-Tropsch synthesis. In the Pichler/Schulz scheme, it was assumed that the intermediate formaldehyde and higher aldehydes are μ-bonded to two neighboring metals. This type of complex bonding has been observed thus far for a ziconium complex only, where the formaldehyde complexes of higher transition metals show μ-bonding to only one metal center. No hydroxymethyl intermediate is formulated. Moreover, the formation of the product of α-olefins was assumed to take place by a rearrangement of the carbene ligand which lacks organometallic support. The propagation step in the proposed mechanism proceeds as follows:

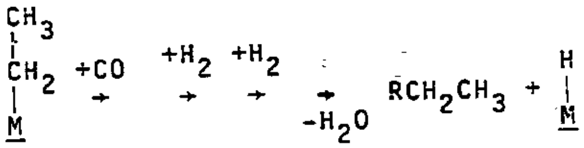
Propagation



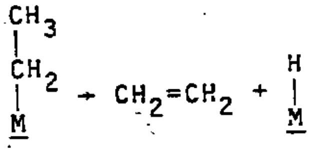
$$\begin{array}{c} CH_3 \\ | \\ H-C-OH \\ | \\ \underline{M} \end{array} + H_2 \rightarrow CH_3CH_2OH + \begin{array}{c} H \\ | \\ \underline{M} \end{array} \tag{2.35}$$



$$\begin{array}{c} CH_3 \\ | \\ H-C-OH \\ | \\ \underline{M} \end{array} \xrightarrow[-H_2O]{+H_2} \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ \underline{M} \end{array} \tag{2.36}$$



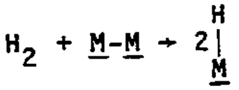
$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ \underline{M} \end{array} \xrightarrow{+CO} \xrightarrow{+H_2} \xrightarrow{+H_2} \xrightarrow[-H_2O]{} RCH_2CH_3 + \begin{array}{c} H \\ | \\ \underline{M} \end{array} \tag{2.37}$$



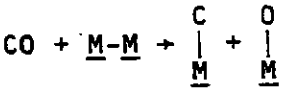
$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ \underline{M} \end{array} \rightarrow CH_2=CH_2 + \begin{array}{c} H \\ | \\ \underline{M} \end{array} \tag{2.38}$$

II-4.5. Ponec Mechanism.

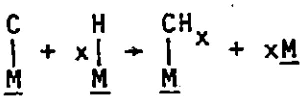
Ponec and his co-workers have postulated a hybrid mechanism in which CO is dissociated on the surface to give up carbon atoms followed by hydrogenation to form CH_x species that can react with adsorbed undissociated CO by alkyl migration to form carbon-carbon bonds, and then with hydrogenation of the resulting acyl intermediates to form alkyls [174,175,220]:



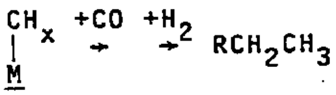
$$H_2 + \underline{M}\text{-}\underline{M} \rightarrow 2\begin{array}{c}H\\|\\\underline{M}\end{array} \tag{2.39}$$



$$CO + \underline{M}\text{-}\underline{M} \rightarrow \begin{array}{c}C\\|\\\underline{M}\end{array} + \begin{array}{c}O\\|\\\underline{M}\end{array} \tag{2.40}$$



$$\begin{array}{c}C\\|\\\underline{M}\end{array} + x\begin{array}{c}H\\|\\\underline{M}\end{array} \rightarrow \begin{array}{c}CH_x\\|\\\underline{M}\end{array} + x\underline{M} \tag{2.41}$$



$$\begin{array}{c}CH_x\\|\\\underline{M}\end{array} \xrightarrow{+CO} \xrightarrow{+H_2} RCH_2CH_3 \tag{2.42}$$

The network character of elementary reaction steps in the Fischer-Tropsch synthesis makes it difficult to separate one path from another, because many paths have common intermediates. Evidence from simplified conditions of low pressures and single crystal metal surfaces have been incorporated into the mechanism insofar as it represents elementary reactions. This kind of evidence is most available for the adsorption of H_2 and CO and for the formation of CO_2 and H_2O. The adsorption steps are generally supported by evidence from surface science and complex chemistry considerations.

The product-forming reactions are the most poorly supported section of the entire mechanism and almost all the evidence comes from complex chemistry. The product-forming reactions are also the most difficult to study because both the forward and reverse reactions on surfaces are complicated by the presence of the other intermediates of the synthesis. Much more information must be collected before a definitive mechanism for the Fischer-Tropsch synthesis can be put forth.

II-5. Kinetics.

The complexity of the Fischer-Tropsch reaction coupled with a large number of variables has made it rather difficult to formulate a general equation for the overall kinetics. Most rate equations obtained are based on specific catalysts under defined conditions.

Anderson and his coworkers [6] at U.S. Bureau of Mines were able to fit their experimental data of kinetic study of the Fischer-Tropsch synthesis on a Co-ThO$_2$-kieselguhr at atmospheric pressure to the concentration of growing chain based on the model of desorption of growing chain in the form of :

$$r = \frac{abp_{H_2}^2 p_{CO}}{1 + bp_{H_2}^2 p_{CO}} \qquad (2.43)$$

where a is the product of effective surface area times the rate of desorption, b is the equilibrium constant for the formation of the chain, p_{H_2} is the partial pressure of hydrogen and p_{CO} is the partial pressure of carbon monoxide.

In his kinetic experiment on a Co-ThO$_2$-MgO-kieselguhr catalyst with H_2/CO ratio = 2 at atmospheric pressure, Brotz proposed the following reaction rate expression [90]:

$$r = \frac{kp_{H_2}^2}{p_{CO}} \tag{2.44}$$

Yang et al. [241] studied the hydrogenation of carbon monoxide over Co-Cu-Al_2O_3 catalyst and found that a simple rate equation first order in hydrogen and inverse square-root order in carbon monoxide adequately fitted their data:

$$r = \frac{kp_{H_2}}{\sqrt{p_{CO}}} \tag{2.45}$$

The kinetics of the Fischer-Tropsch synthesis over a cobalt/alumina catalyst was also studied by Rautavuoma and van der Baan [178,179]. They proposed a model in which the initiation proceeds via carbon dissociation and formation of a CH_2-surface intermediate in which the formation of this intermediate is the rate determining step:

$$r = \frac{k p_{H_2} \sqrt{p_{CO}}}{(1 + \sqrt{K_{H_2} p_{H_2}} + \sqrt{K_{CO} p_{CO}})^3} \qquad (2.46)$$

The chain growth was thought to proceed via the addition of the same CH_2-groups to the growing chains.

Methanation is thought to be the simplest form of the synthesis and has been subjected to kinetic studies in the anticipation that it can provide some sort of clue to the explanation of the synthesis [221,222]. Recent study of methanation over Co/Al_2O_3 by Agrawal et al. [1] has resulted in the following rate expressions for different regimes of pseudo-steady state:

$$r = \frac{k p_{CO} \sqrt{p_{H_2}}}{(1 + K_{CO} p_{CO})^2} \qquad (2.47)$$

The kinetics of the Fischer-Tropsch reactions are only slightly better known than the thermodynamics. However, a general valid rate equation for the FTS can not be written. Each type of catalyst and each individual process variation contributes to a unique variety of kinetics that, in general, cannot be extrapolated or interpolated. Although mass transfer plays an obvious role in the Fischer-Tropsch synthesis kinetics, the role appears to be restricted to pore diffusion to a rather shallow depth. Mass transfer through adhering hydrocarbon film is claimed not to be a rate-limiting feature.

Despite great differences between the numerical data available, the consensus is that the Fischer-Tropsch reactions are about first order and the reaction rate is amazingly low as compared with that of other reactions in the field of heterogeneous catalysis. Most investigators are now aware that the number of active sites cannot be equalized to the number of surface metal atoms, as determined by selective chemisorption of CO, H_2 of O_2. The reasons are manifold. Yates et al. have shown that more than one CO can be coordinated to a surface metal atom [246]; the same may be true for hydride ligands. Hydrogen spillover has suggested that hydrogen can migrate to the support. Furthermore, there is increasing evidence that only metal atoms at specially exposed sites (steps, kinks) are catalytically active, namely, strong metal-support interaction or structure-sensitivity may exist for some catalysts.