CHAPTER III

KINETIC MODEL DEVELOPMENT FOR THE MODIFIED FISCHER-TROPSCH REACTION

Incorporation of alkenes with the synthesis gas (hydrogen and carbon monoxide) was used in the study of the reaction mechanism for the Fischer-Tropsch synthesis [234]. It was also involved in the production of aldehydes by the Oxo process [234]. Nevertheless, little work has been done on studying the kinetics of incorporation of ethylene in the heterogeneous FTS. In this chapter, a reaction mechanism for the modified Fischer-Tropsch synthesis will be rationalized based on common observations of the traditional FTS and theoretical kinetic models (rate equations) will be developed accordingly.

III-1. Definitions.

As in the traditional Fischer-Tropsch synthesis, theoretically, an infinite number of chemical species can simultaneously exist due to an infinite number of reactions occurring in the modified Fischer-Tropsch synthesis system. The definition of the overall modified

Fischer-Tropsch reaction (MFTR), utilized in this kinetic study, is specified as:

$$xH_{2(g)} + yCO_{(g)} + zC_2H_{4(g)} \xrightarrow[Co_3O_4/Al_2O_3]{T,P} \text{Products} \qquad (3.1)$$

Here, x, y and z are the net stoichiometric coefficients for hydrogen, carbon monoxide and ethylene respectively. The products include all possible chemical species, however, diesel fuel may be preferred. When both external (interparticle) and internal (intraparticle) resistances to mass and heat transfer in the reacting system are eliminated, the observed overall reaction becomes the intrinsic reaction.

The catalyst used in the experiments is an impregnated cobalt oxide supported by ALCOA F-1 activated alumina. The details of the molecular and crystallite structures were not investigated. However, some physical and chemical specifications can be determined by various available methods of catalyst characterization. The nature of catalyst active sites, which are responsible for the function and activity of the catalyst is also unknown. It will be postulated that they are the activated surface cobalt atoms.

The activity of the catalyst is referred to as the rate at which the reaction approaches chemical equilibrium [191]. There are many ways of defining the reaction rate, but the most precise description for a heterogeneous catalytic reaction is in terms of the turnover frequency. The turnover frequency is defined as the number of molecules that react per catalytic site per unit time [33]. The rate equation predicts the variation of the turnover frequency as a function of process variables (temperature and total pressure) and composition of components participating in the reaction.

The support in a supported-metal catalyst was thought to be an inert substance which only provided a means of improving the mechanical strength of the metal catalyst. But, it is now generally accepted that the carrier may actually contribute to the activity of the catalyst, or even react with other ingredients in the catalyst to a certain extent [34]. However, in this study, the interaction between the metal (cobalt) and the support (activated alumina) is assumed to be insignificant.

The turnover frequency and the rate equation are the two types of information necessary for understanding the activity of catalyst at the molecular level. Determining a reliable rate equation is the essential goal of chemical kinetics.

III-2. Assumptions.

For reactions between fluid reactants catalyzed by porous solids, a generally accepted mechanism can be described by the following steps [116,117]:

1. Mass transfer of reactants and products by counterdiffusion between the bulk fluid and the outer surface of catalyst particle.
2. Mass transfer of reactants and products by counterdiffusion through the catalyst pores.
3. Adsorption of reactants onto the active sites of the catalyst surface and desorption of products from the catalyst surface.
4. Chemical reaction involving one or more chemisorbed species on the catalyst surface.

The rates of these four types of processes are dependent on widely different factors in addition to the concentration or concentration gradients involved, and so is the relative importance of individual steps in determining the overall rate. In general, step 1, 2 and 4 are strictly consecutive processes and can be studied separately and then combined into a net rate. However, step 3 cannot be separated because active sites are spread all over the pore walls. One or more of these steps may be rate-determining in the sense that it, or they, consume(s) the major portion of the chemical potential available for the overall process to proceed.

For the purpose of developing the intrinsic reaction model for the overall MFTR, steps 1 and 2, i.e., mass transfer processes, are ignored. The justification of these assumptions can be done either by experiments or by theoretical calculations. The details of the kinetics of individual elementary steps will not be emphasized in favor of the development of a plausible and reliable overall reaction rate expression.

The following assumptions regarding the chemisorption step of the modified Fischer-Tropsch reaction will be utilized:

1. All surface active sites are identical, both thermodynamically and kinetically, which befit a uniform surface.
2. There are no significant interactions other than possible reactions between adsorbed species so that concentrations can be used instead of thermodynamic activities.
3. Hydrogen molecules will be dissociatively adsorbed by a pair of dual active sites to form two adsorbed hydrogen atoms.
4. Carbon monoxide perpendicularly adsorbs to one

active site through the carbon end, then either dissociatively releases an oxygen atom and forms a carbide atom or associatively reacts with a neighbor adsorbed hydrogen to form a hydroxyl ligand.

5. Ethylene will either adsorb to a pair of dual active sites horizontally and then split up into two methylene intermediates, or molecularly react with a neighboring adsorbed hydrogen to generate an intermediate ethyl group. The later is assumed to be the rate-determining step (RDS).

6. Molecules of methane and carbon dioxide do not compete with hydrogen, carbon monoxide and ethylene for the active sites as far as chemisorption is concerned.

Although the details of the hydrogenation process are not fully understood, it seems reasonable to propose that carbon atoms from the dissociation of CO can react with adsorbed hydrogen to form methylidyne, methylene and methyl intermediates consecutively. The methylene ligands are assumed to be the dominating intermediate species. The water-gas shift reaction is also assumed to take place as soon as there are enough adsorbed-H_2O species generated and they are in a close neighborhood of adsorbed-CO species. To further simplify the derivation of the rate equation, it is also supposed that the chain propagation rate is independent of chain length and that all branching and double bond formation will happen at the carbon atom next to the end carbon. Finally, it is assumed that wherever a product is formed, a desorption can be written and this desorption reaction is also a termination step.

III-3. Mechanism.

The lack of knowledge of the nature of the catalytic surface in the past has frequently led to much difficulties in determination of a reliable rate equation. This situation is being changed as a result of rapid progress made recently in surface science, which is founded on the physical examination of the surface by an increasing number of new spectroscopic methods. Recent catalytic research performed on the single crystals in ultrahigh vacuum chambers has resulted in understanding the kinetics of the elementary steps, i.e., adsorption, surface reaction and desorption [12,37,38,41,42,129,148,149,153,154,209,245], and applying this knowledge to catalytic reactions on microscopic clusters at normal pressure [68]. Furthermore, for the first time, the overall kinetics of a few catalytic reactions on well-defined surfaces has become quantitatively reproducible [34]. Even with the flourishing of current progress in catalysis research, not even the simplest catalytic reaction is yet known with regard to the details of its true mechanism [191].

III-3.1. Chemisorption.

There are two types of adsorption: physical adsorption (or physisorption) and chemical adsorption (or chemisorption) [117]. Physisorption results from physically attractive forces such as dipole-dipole interaction and induced dipoles and are similar to those causing the condensation of a vapor. Chemisorption, however, involves electron transfer and chemical bond formation between the adsorbate and the adsorbent. As a gas molecule strikes the surface of a single crystal solid, it can be either elastically scattered or physically adsorbed. The latter is always a precursor of chemisorption. It is believed that chemisorption of one or more of the reactants is involved as an intermediate step in the overall reaction [117].

Cobalt catalysts have been promising candidates for production of fuels and chemicals via Fischer-Tropsch synthesis. Early investigations of hydrogen and carbon monoxide adsorptions on cobalt were aimed at estimating the metal surface area [4,5,119,200,244]. Gupta, Viswanathan and Sastri [104,188] initiated a systematic study of the interaction between hydrogen and carbon monoxide adsorptions on cobalt catalysts and concluded that neither hydrogen nor carbon monoxide adsorption is rate determining in the hydrocarbon synthesis.

It is now generally accepted that the hydrogen molecule is first physisorbed and then dissociated on most transition metals [15,20,52-54,57-59,172,181, 215,216,228-230,246,247,250].
There is no sufficient evidence to distinguish the difference between the bridge mode and atop mode of hydrogen adsorption. Hydrogen atoms are hydridic and electron transfer occurs from metal to hydrogen to form bonding. Under certain circumstances, hydrogen atoms chemisorbed on a supported metal can migrate to the support which then serves as a reservoir for the hydrogen atom [32,147,199]. The mechanism of this spillover is yet unclear.

The first step of carbon monoxide adsorption is also physisorption, followed by a rapid conversion to chemisorption. Sufficient evidence from studies of ultraviolet photoelectron spectroscopy (UPS) and infrared spectroscopy (IRS) have shown that carbon monoxide is most likely bonded to the surface of transition metals perpendicularly through the carbon end of the molecule [3,17,30,43,63,143,144]. The cobalt-carbon bond may be formed with either a single metal atom giving rise to linear bonding or may be shared between two or more metal atoms to produce a bridge bonding [10,135,207].

Two components contribute to the metal-carbon bond. The first arises from an overlap of the occupied 5σ orbital of CO and unoccupied metal d_{z^2} and s orbitals. This results in the donation of electrons from the molecule of carbon monoxide to the metal atom. The second component comes from the backdonation of electrons from occupied metal d_{xz} and d_{yz} orbitals to the unoccupied $2\pi^*$ orbitals of CO. Since $2\pi^*$ orbitals are antibonding with respect to the C-O bond and backdonation into those orbitals leads to weakening of the C-O bond, this makes the C-O bond more susceptible to hydrogenation and/or other reactions.

Dissociative chemisorption of CO is also known to occur on the surface of many transition metals and most likely proceeds via a molecularly adsorbed state. Cobalt actually locates on the borderline between associative adsorption and dissociative adsorption of transition metals at room temperature in the periodic table. It was noted that the trend of dissociative adsorption parallels the increase in the separation between the 1π and 4σ states of molecularly adsorbed CO and it was concluded that stretching of the C-O bond is a prerequisite for dissociation [18].

For a metal on an oxide support, the carbon of the CO could be coordinated with one or more of the metal atoms, and the oxygen with a metal or metalloid atom in the oxide support. This type of CO adsorption may be related to the strong metal-support interactions. The effect of supports on CO dissociation has not yet been studied systematically, but it is believed that the effect can be significant [183].

A recent reference [16] has confirmed that the hydrogen adsorption on cobalt is strongly activated, reversible and dissociative while the adsorption of carbon monoxide is nonactivated and reversible, and the interaction between cobalt metal and supporting alumina is rather strong.

The kinetics of adsorption and desorption processes of H_2 and CO over supported Co have been studied by the technique of the temperature programmed desorption (TPD) since 1975 [60,101,250]. The activation energies for hydrogen adsorption and desorption on 10% Co/Al_2O_3 were reported to be 39 and 144 kJ/mol respectively and the order of desorption was 2 [250]. The activation energy for desorption of CO from single cobalt crystal surface was 103 kJ/mol [41]. Infrared spectroscopic studies have positively identified the existence of both associative linear adsorption and dissociative bridge adsorption of CO on cobalt surface, and the latter is responsible for producing CO_2 [101].

The adsorption of ethylene on transition metal surface has been suggested to produce butyl groups and one molecule of ethylene adsorbed on two metal active sites [172]. Both associative and dissociative chemisorption on nickel were observed [49].

III-3.2. Initiation.

The initiation of reactions are generally occurring among adsorbed species and take place throughout the whole synthsis process. In order for adsorbed species to react, they must be mobile on the surface. CO and H ligands are reported to be extremely mobile on metal cluster compounds [14,218]. For CO or H adsorbed alone on other metal surfaces, the interactions among the adsorbates appear to be repulsive, as indicated by the common observation of decreasing adsorption energy with increasing coverage. The interaction between adsorbed CO and H appears to be slightly attractive on the Fischer-Tropsch catalyst metals [65,99,100,104,155,158, 188,228-230].

The carbide atom from the dissociation of adsorbed CO can react with neighbor adsorbed H atom(s) to form methylidene, methylene and methyl intermediates consecutively [161]. Structural characterization of the methylidyne-containing species shows that the CH unit is bonded through both the carbon and hydrogen atoms and there is a fast exchange of hydrogen between the hydridic state and the protonic state.

Four types of surface carbon have been observed on alumina-supported nickel catalyst in decreasing reactivity toward hydrogen: chemisorbed carbon, bulk nickel carbide, amorphous carbon and crystalline graphitic carbon [153,154]. Both adsorbed carbon and bulk carbide can be easily hydrogenated to methane. Another carbon species has been identified as a surface carbide which can also contribute to the hydrogenation reaction, yet distinguishing between adsorbed carbon and surface carbide is not clear. The amorphous and crystalline carbon species appear to act mainly as poisons to hydrocarbons. The reaction of alkenes with surface intermediates on ruthenium gives evidence of the presence of alkyl and alkylidene groups as intermediates [78,195].

Adsorbed oxygen atoms released from CO disproportionation should react either with two adsorbed hydrogens to form water or with associatively other adsorbed CO to produce carbon dioxide. The former should be the dominant component in the aqueous product of cobalt catalyst.

III-3.3. Propagation.

It was noted that the reaction of methyl iron complexes with CD_2Cl_2 yielded CH_2CD_2 [124]. A similar result was also observed for methyl nickel complex. The formation of CH_2CD_2 was explained by proposing that a CD_2 group inserts into the M-CH bond and that the metal then abstracts a hydrogen atom from the resulting alkyl species.

Methylene groups were observed to be inserted into the nickel-carbon bonds of methyl and ethyl nickel complexes by reacting these complexes with CH_2Cl_2 [240].

Biloen et al. first proposed that the stepwise insertion of methylene segments into the metal-carbon bond of adsorbed alkyl species forms the backbone of chain growth of the synthesis [21].

Further evidence of the role of methylene groups in the chain growth process was recently presented by Brady and Petit [39,40]. It was noticed that passage of a dilute stream of CH_2N_2 over nickel, palladium, iron, cobalt, ruthenium and copper catalysts produced predominantly ethylene and nitrogen. When hydrogen was mixed with the CH_2N_2 mixture, the nature of the products changed markedly. Detailed analyses of the products show that they consisted mainly of normal alkanes and monoolefins with a distribution closely resembling that of conventional Fischer-Tropsch synthesis over the same metals.

Brady and Petit explained their results that in the absence of hydrogen, the CH_2 groups released by the decomposition of CH_2N_2 dimerize to form ethylene. When hydrogen is present on the catalyst surface, then the CH_2 groups can undergo hydrogenation to produce methane. The CH_3 groups formed as a precursor to methane are assumed to act as chain growth centers. Insertion of a CH_2 group into the metal-carbon bond of a CH_3 group produces an ethyl group, and continuation of this type of reaction can eventually give a spectrum of adsorbed alkyl groups.

Alkanes are produced by reaction of the alkyl groups with adsorbed hydrogen, and olefins are produced by elimination of a β-hydrogen atom from the alkyl groups. In the absence of sufficient atomic hydrogen on the catalyst surface, the CH_2 groups recombine to form ethylene rather than adding hydrogen to form CH_3 groups needed to initiate chain growth. On the other hand, if too much atomic hydrogen is available, the extent of chain growth is suppressed.

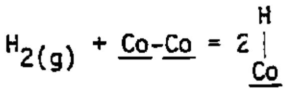
Tanaka et al. also concluded that methylene species are the pivotal precursors for hydrocarbon formation on carbon deposited cobalt catalyst from their experiments using isotopic D_2 to generate CH_2D_2 [210,211]. The propagation of the MFTR is thought to be via the stepwise addition of a methylene ligand to the growing chain one at a time.

III-3.4. Termination.

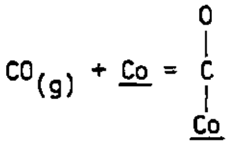
The distinction between the primary product and the secondary one has been somewhat arbitrary in that the primary products are those produced directly by the reactions of a proposed mechanism, while the secondary products are those produced by readsorption and further reaction of the primary products. However, by the principle of microscopic reversibility, if all the reactions including the desorption steps are reversible, then the intermediates produced from the readsorption of stable products would not be distinguishable from those not having undergone desorption and readsorption. Termination steps are considered to be the same as the desorptions of product species from the surface of the adsorbent cobalt by releasing an active site behind.

Following the assumptions made in previous section (III-2), the proposed reaction mechanism with the reaction between ethylene molecules and adsorbed hydrogen atoms being the rate-determining step, for the net MFTR is now summarized in Figure 3.1.

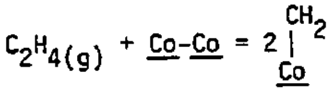
i. Chemisorption



$$H_{2(g)} + \underline{Co}\text{-}\underline{Co} = 2\,\overset{\displaystyle H}{\underset{\displaystyle \underline{Co}}{|}} \qquad (3.2)$$



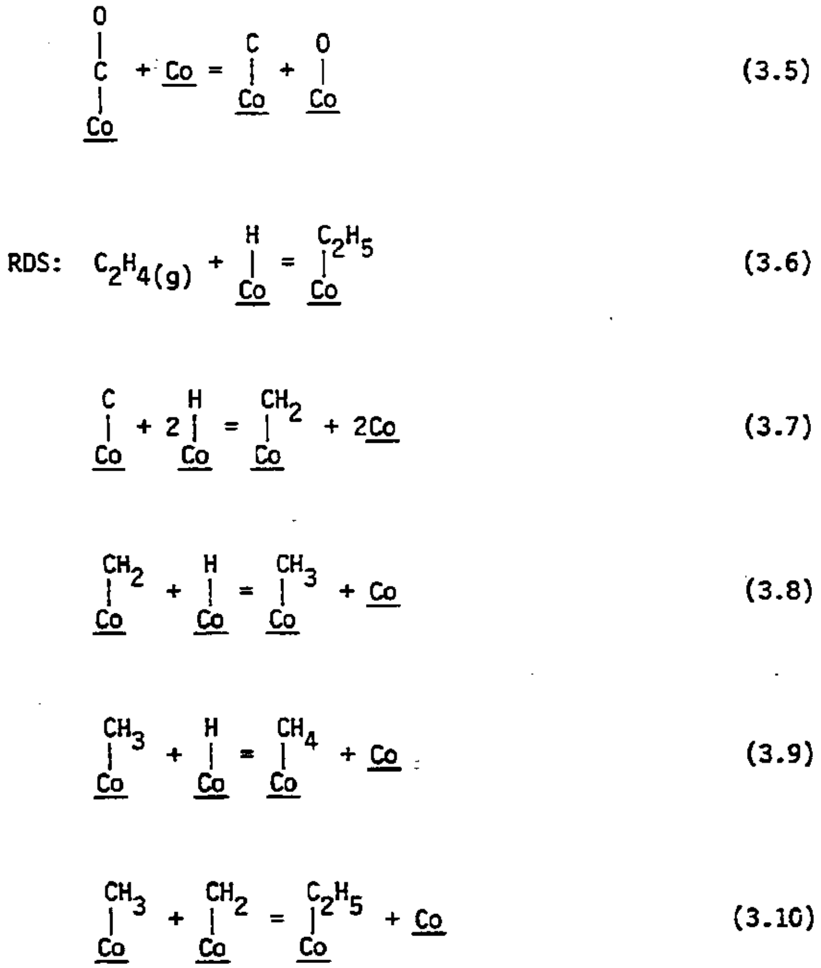
$$CO_{(g)} + \underline{Co} = \overset{\displaystyle O}{\overset{|}{\underset{\underset{\displaystyle \underline{Co}}{|}}{C}}} \qquad (3.3)$$



$$C_2H_{4(g)} + \underline{Co}\text{-}\underline{Co} = 2\,\overset{\displaystyle CH_2}{\underset{\displaystyle \underline{Co}}{|}} \qquad (3.4)$$

Figure 3.1. Summary of the Reaction Mechanism Proposed for the Modified Fischer-Tropsch Reaction (MFTR) Corresponding to Kinetic Model #6.

ii. Initiation



$$\begin{array}{c}O\\|\\C\\|\\\underline{Co}\end{array} + \underline{Co} = \begin{array}{c}C\\|\\\underline{Co}\end{array} + \begin{array}{c}O\\|\\\underline{Co}\end{array} \qquad (3.5)$$

$$\text{RDS:}\quad C_2H_{4(g)} + \begin{array}{c}H\\|\\\underline{Co}\end{array} = \begin{array}{c}C_2H_5\\|\\\underline{Co}\end{array} \qquad (3.6)$$

$$\begin{array}{c}C\\|\\\underline{Co}\end{array} + 2\begin{array}{c}H\\|\\\underline{Co}\end{array} = \begin{array}{c}CH_2\\|\\\underline{Co}\end{array} + 2\underline{Co} \qquad (3.7)$$

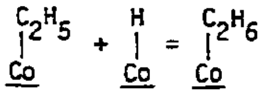
$$\begin{array}{c}CH_2\\|\\\underline{Co}\end{array} + \begin{array}{c}H\\|\\\underline{Co}\end{array} = \begin{array}{c}CH_3\\|\\\underline{Co}\end{array} + \underline{Co} \qquad (3.8)$$

$$\begin{array}{c}CH_3\\|\\\underline{Co}\end{array} + \begin{array}{c}H\\|\\\underline{Co}\end{array} = \begin{array}{c}CH_4\\|\\\underline{Co}\end{array} + \underline{Co} \qquad (3.9)$$

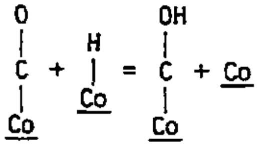
$$\begin{array}{c}CH_3\\|\\\underline{Co}\end{array} + \begin{array}{c}CH_2\\|\\\underline{Co}\end{array} = \begin{array}{c}C_2H_5\\|\\\underline{Co}\end{array} + \underline{Co} \qquad (3.10)$$

Figure 3.1. (Cont'd.)

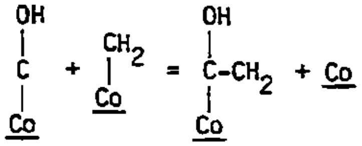
ii. Initiation (Cont'd.)



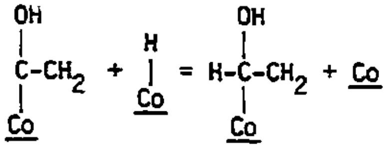
$$\underset{\underline{\mathrm{Co}}}{\mathrm{C_2H_5}} + \underset{\underline{\mathrm{Co}}}{\mathrm{H}} = \underset{\underline{\mathrm{Co}}}{\mathrm{C_2H_6}} \tag{3.11}$$



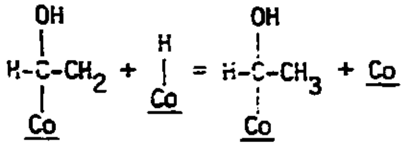
$$\overset{\mathrm{O}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}} + \underset{\underline{\mathrm{Co}}}{\mathrm{H}} = \overset{\mathrm{OH}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}} + \underline{\mathrm{Co}} \tag{3.12}$$



$$\overset{\mathrm{OH}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}} + \underset{\underline{\mathrm{Co}}}{\mathrm{CH_2}} = \overset{\mathrm{OH}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}}\mathrm{-CH_2} + \underline{\mathrm{Co}} \tag{3.13}$$



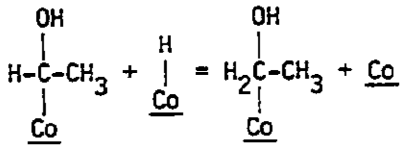
$$\overset{\mathrm{OH}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}}\mathrm{-CH_2} + \underset{\underline{\mathrm{Co}}}{\mathrm{H}} = \mathrm{H-}\overset{\mathrm{OH}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}}\mathrm{-CH_2} + \underline{\mathrm{Co}} \tag{3.14}$$



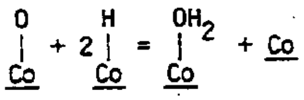
$$\mathrm{H-}\overset{\mathrm{OH}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}}\mathrm{-CH_2} + \underset{\underline{\mathrm{Co}}}{\mathrm{H}} = \mathrm{H-}\overset{\mathrm{OH}}{\underset{\underline{\mathrm{Co}}}{\mathrm{C}}}\mathrm{-CH_3} + \underline{\mathrm{Co}} \tag{3.15}$$

Figure 3.1. (Cont'd.)

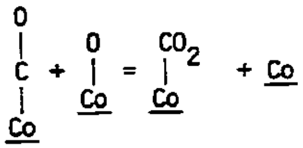
ii. Initiation (Cont'd.)



$$\mathrm{H{-}\overset{\displaystyle OH}{\underset{\displaystyle \underline{Co}}{C}}{-}CH_3} + \overset{\mathrm{H}}{\underset{\underline{\mathrm{Co}}}{|}} = \mathrm{H_2\overset{\displaystyle OH}{\underset{\displaystyle \underline{Co}}{C}}{-}CH_3} + \underline{\mathrm{Co}} \qquad (3.16)$$

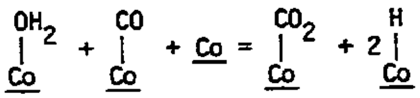


$$\overset{\mathrm{O}}{\underset{\underline{\mathrm{Co}}}{|}} + 2\overset{\mathrm{H}}{\underset{\underline{\mathrm{Co}}}{|}} = \overset{\mathrm{OH_2}}{\underset{\underline{\mathrm{Co}}}{|}} + \underline{\mathrm{Co}} \qquad (3.17)$$



$$\overset{\displaystyle \mathrm{O}}{\underset{\displaystyle \underline{\mathrm{Co}}}{\mathrm{C}}} + \overset{\mathrm{O}}{\underset{\underline{\mathrm{Co}}}{|}} = \overset{\mathrm{CO_2}}{\underset{\underline{\mathrm{Co}}}{|}} + \underline{\mathrm{Co}} \qquad (3.18)$$

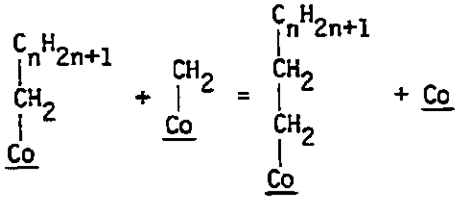
Water-gas shift reaction:



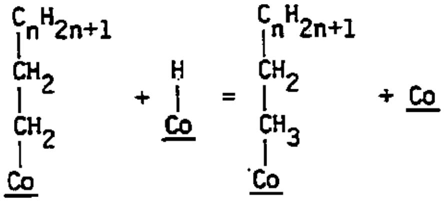
$$\overset{\mathrm{OH_2}}{\underset{\underline{\mathrm{Co}}}{|}} + \overset{\mathrm{CO}}{\underset{\underline{\mathrm{Co}}}{|}} + \underline{\mathrm{Co}} = \overset{\mathrm{CO_2}}{\underset{\underline{\mathrm{Co}}}{|}} + 2\overset{\mathrm{H}}{\underset{\underline{\mathrm{Co}}}{|}} \qquad (3.19)$$

Figure 3.1. (Cont'd.)

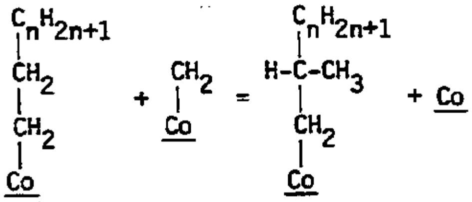
iii. <u>Propagation</u> (for n ≥ 1)



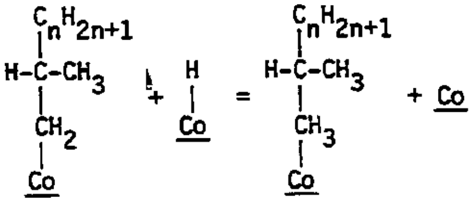
$$C_nH_{2n+1}-CH_2-\underline{Co} + CH_2-\underline{Co} = C_nH_{2n+1}-CH_2-CH_2-\underline{Co} + \underline{Co} \qquad (3.20)$$



$$C_nH_{2n+1}-CH_2-CH_2-\underline{Co} + H-\underline{Co} = C_nH_{2n+1}-CH_2-CH_3-\underline{Co} + \underline{Co} \qquad (3.21)$$



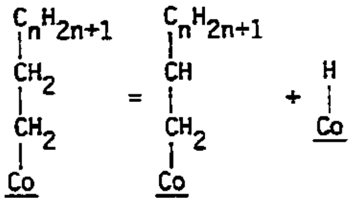
$$C_nH_{2n+1}-CH_2-CH_2-\underline{Co} + CH_2-\underline{Co} = C_nH_{2n+1}-C(H)(CH_3)-CH_2-\underline{Co} + \underline{Co} \qquad (3.22)$$



$$C_nH_{2n+1}-C(H)(CH_3)-CH_2-\underline{Co} + H-\underline{Co} = C_nH_{2n+1}-C(H)(CH_3)-CH_3-\underline{Co} + \underline{Co} \qquad (3.23)$$

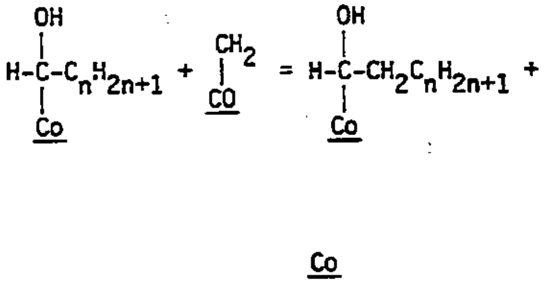
Figure 3.1. (Cont'd.)

iii. Propagation (Cont'd.)



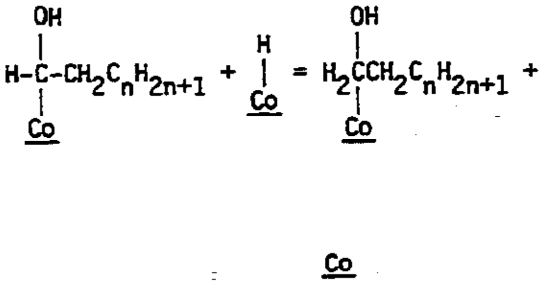
$$C_nH_{2n+1}CH_2CH_2\text{–}\underline{Co} = C_nH_{2n+1}CH(\text{–})CH_2\text{–}\underline{Co} + H\text{–}\underline{Co}$$

(3.24)



$$H\text{–}C(OH)(\underline{Co})\text{–}C_nH_{2n+1} + CH_2\text{–}\underline{Co} = H\text{–}C(OH)(\underline{Co})\text{–}CH_2C_nH_{2n+1} + \underline{Co}$$

(3.25)

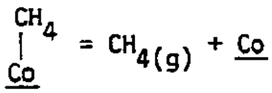


$$H\text{–}C(OH)(\underline{Co})\text{–}CH_2C_nH_{2n+1} + H\text{–}\underline{Co} = H_2C(OH)(\underline{Co})CH_2C_nH_{2n+1} + \underline{Co}$$

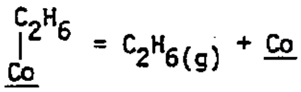
(3.26)

Figure 3.1. (Cont'd.)

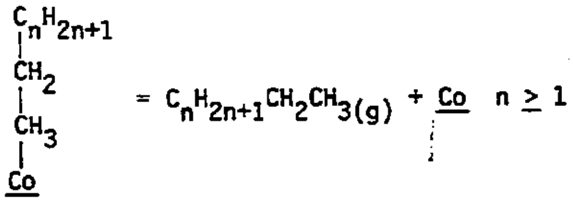
iv. Termination (Desoprtion)



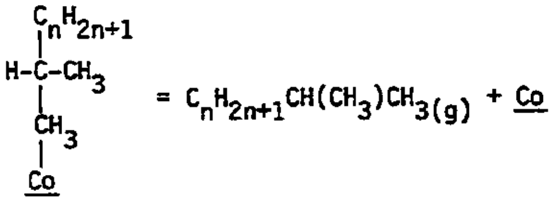
$$\begin{array}{c} CH_4 \\ | \\ \underline{Co} \end{array} = CH_{4(g)} + \underline{Co} \qquad (3.27)$$



$$\begin{array}{c} C_2H_6 \\ | \\ \underline{Co} \end{array} = C_2H_{6(g)} + \underline{Co} \qquad (3.28)$$



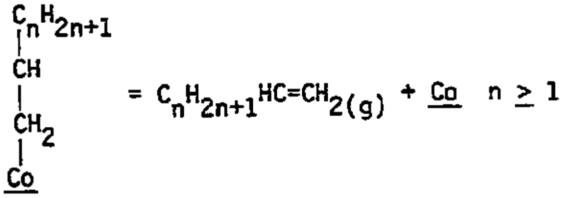
$$\begin{array}{c} C_nH_{2n+1} \\ | \\ CH_2 \\ | \\ CH_3 \\ | \\ \underline{Co} \end{array} = C_nH_{2n+1}CH_2CH_{3(g)} + \underline{Co} \quad n \geq 1 \qquad (3.29)$$



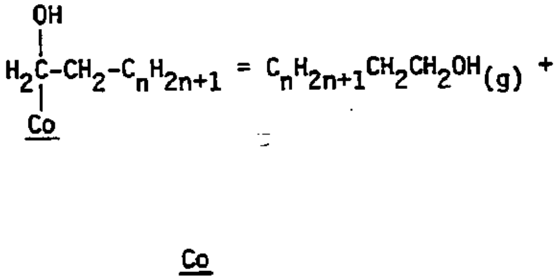
$$\begin{array}{c} C_nH_{2n+1} \\ | \\ H\text{-}C\text{-}CH_3 \\ | \\ CH_3 \\ | \\ \underline{Co} \end{array} = C_nH_{2n+1}CH(CH_3)CH_{3(g)} + \underline{Co} \qquad (3.30)$$

Figure 3.1. (Cont'd.)

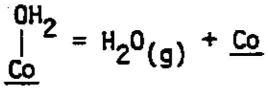
iv. Termination (Cont'd.)



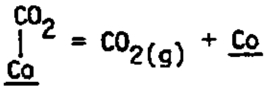
$$\begin{array}{l} C_nH_{2n+1} \\ | \\ CH \\ | \\ CH_2 \\ | \\ \underline{Co} \end{array} = C_nH_{2n+1}HC{=}CH_{2(g)} + \underline{Co} \quad n \geq 1 \qquad (3.31)$$



$$H_2\underset{\underline{Co}}{\overset{OH}{C}}-CH_2-C_nH_{2n+1} = C_nH_{2n+1}CH_2CH_2OH_{(g)} + \underline{Co} \qquad (3.32)$$



$$\underset{\underline{Co}}{\overset{OH_2}{|}} = H_2O_{(g)} + \underline{Co} \qquad (3.33)$$



$$\underset{\underline{Co}}{\overset{CO_2}{|}} = CO_{2(g)} + \underline{Co} \qquad (3.34)$$

Figure 3.1. (Cont'd.)

III-4. Rate Equations (Kinetic Models).

Theoretical rate equations for the overall modified Fischer-Tropsch reaction, based on the mechanism as proposed in the previous section (III-3), for various assumed rate controlling steps are presented in Table 3.1 along with a semi-empirical power law. Details of the derivation for an example case, i.e., the rate-determining steps are the reactions between ethylene molecules and adsorbed hydrogen atoms, is presented in Appendix A. Other rate equations based on the assumed mechanism for different controlling steps can be similarly derived.

Table 3.1. Theoretical Kinetic Models for the Modified Fischer-Tropsch Reaction.

1. Adsorption of hydrogen controlling:

$$r = \frac{a e^{\frac{-E}{RT}} \{p_2 - (\frac{1}{K}) \prod_{i \neq 2} p_i^{\nu_i}\}}{\{1 + (\frac{K_2}{K}) \prod_{i \neq 2} p_i^{\nu_i} + \sqrt{K_3 p_3} + \sqrt{K_4 p_4} + \sum_i K_i' p_i\}^2} \qquad (3.35)$$

2. Adsorption of carbon monoxide controlling:

$$r = \frac{a e^{\frac{-E}{RT}} \{p_3 - (\frac{1}{K}) \prod_{i \neq 3} p_i^{\nu_i}\}}{\{1 + (\frac{K_3}{K}) \prod_{i \neq 3} p_i^{\nu_i} + \sqrt{K_2 p_2} + \sqrt{K_4 p_4} + \sum_i K_i' p_i\}^2} \qquad (3.36)$$

3. Adsorption of ethylene controlling:

$$r = \frac{a e^{\frac{-E}{RT}} \{p_4 - (\frac{1}{K}) \prod_{i \neq 4} p_i^{\nu_i}\}}{\{1 + (\frac{K_4}{K}) \prod_{i \neq 4} p_i^{\nu_i} + \sqrt{K_2 p_2} + \sqrt{K_3 p_3} + \sum_i K_i' p_i\}^2} \qquad (3.37)$$

Table 3.1. (Cont'd.)

4. General surface reaction controlling:

$$r = \frac{ae^{\frac{-E}{RT}}K_2K_3K_4(p_2p_3p_4 - \frac{1}{K}\prod_i p_i^{\nu_i})}{\{1 + \sqrt{K_2p_2} + \sqrt{K_3p_3} + \sqrt{K_4p_4} + \sum_i K_i'p_i\}^4} \tag{3.38}$$

5. Net surface reaction among molecular ethylene and adsorbed species controlling:

$$r = \frac{ae^{\frac{-E}{RT}}K_2^2K_3K_4p_2^2p_3p_4}{(1 + \sqrt{K_2p_2} + \sqrt{K_3p_3})^3(1 + K_2p_2 + K_3p_3 + K_4p_4 + \sum_i K_i'p_i)^3} \tag{3.39}$$

6. Reaction between ethylene molecule and adsorbed hydrogen atom controlling:

$$r = \frac{ae^{\frac{-E}{RT}}(p_4\sqrt{K_2p_2} - \frac{K_6'K_{11}'K_{28}'p_{28}}{\sqrt{K_2p_2}})}{1+\sqrt{K_2p_2}+\frac{K_3^2K_5p_3^2}{K_{18}'K_{34}'p_{34}}+K_3p_3+\sqrt{K_4p_4}+\frac{K_9K_{27}'p_{27}+K_{18}'K_{34}'p_{34}}{\sqrt{K_2p_2}}+(1+\frac{K_{18}'+K_2K_{19}'p_2}{K_3p_3})K_{34}'p_{34}+\sum_i K_i'p_i} \tag{3.40}$$

Table 3.1. (Cont'd.)

7. Irreversible reaction betwwen ethylene molecule and adsorbed hydrogen atom controlling:

$$r = \frac{a e^{\frac{-E}{RT}} p_4 \sqrt{K_2 p_2}}{1+\sqrt{K_2p_2}+\frac{K_3^2K_5p_3^2}{K'_{18}K'_{34}p_{34}}+K_3p_3+\sqrt{K_4p_4}+\frac{K_9K'_{27}p_{27}+K'_{18}K'_{34}p_{34}}{\sqrt{K_2p_2}}+(1+\frac{K'_{18}+K_2K'_{19}p_2}{K_3p_3})K'_{34}p_{34}+\sum_i K'_ip_i} \qquad (3.41)$$

8. Desorption of ethane controlling:

$$r = \frac{e^{\frac{-E}{RT}} K(\prod_{i\neq 28} p_i^{-\nu_i} - \frac{p_{28}}{K})}{1 + \sqrt{K_2p_2} + \sqrt{K_3p_3} + \sqrt{K_4p_4} + \sum_i K'_ip_i} \qquad (3.42)$$

9. Semi-empirical power law:

$$r = a e^{\frac{-E}{RT}} p_2^x p_3^y p_4^z \qquad (3.43)$$

Notations for Table 3.1.

a	preexponential factor,
E	activation energy, kJ/kmol,
K	equilibrium constant for rate-determining step,
K_j	equilibrium constant for step j, j = 2, 3 and 4 represent the adsorption steps for hydrogen, carbon monoxide and ethylene,
K_i'	equilibrium desorption constant for product species i, i = 27, 28 and 34 represent methane, ethane and carbon dioxide,
p_i	partial pressure of component i, kPa, i = 2, 3, 4, 27, 28 and 34 represent hydrogen, carbon monoxide, ethylene, methane, ethane and carbon dioxide,
R	gas constant, 8.314 kJ/mol-°K,
r	net reaction rate, g-mol of (H_2+CO+C_2H_4) disappeared per hour per gram of catalyst,
T	reaction temperature, °K,
x	order of the net reaction with respect to hydrogen,
y	order of the net reaction with respect to carbon monoxide,
z	order of the net reaction with respect to ethylene,
ν_i	net stoichiometry coefficient for component i in the overall reaction, +1 for products and -1 for reactants.