CHAPTER 2

The Product Distribution and Reaction Mechanisms

2.1 The Product Distribution

2.1.1 Hydrocarbon Products

It is a well known fact that the principal product distribution obtained from a classical Fischer Tropsch catalyst consists of straight chain olefin and parffin hydrocarbons (6,44,91). Herington (55) introduced quantity β_n to describe the probability of obtaining a hydrocarbon chain of n carbon atoms. This quantity is defined as follows:

$$\beta_n = \frac{\text{rate of chain termination}}{\text{rate of chain propagation}} = \frac{1-\alpha_n}{\alpha_n} \qquad 2.1.1$$

where α_n is the probability of producing a n+1 carbon chain from a n carbon chain. For a given product distribution

$$\beta_n = \frac{\phi_n}{\sum\limits_{n+1}^{\infty} \phi_i} \qquad 2.1.2$$

where ϕ_n is the molar amount of carbon length n. Friedel and Anderson (47) developed the following relation to model hydrocarbon chain length in the FT synthesis

$$\phi_n = \phi_x \, \alpha^{n-x} \quad \text{for} \quad n \geqslant x \qquad 2.1.3$$

where ϕ is the molar amount of a hydrocarbon chain containing n or x carbon atoms, and α was found to be independent of hydrocarbon chain length.

Recently Madon (73) has shown that the Friedel-Anderson relation can be transformed into the well known Schulz-Flory (Most Probable) Product

Weight Distribution (45,108) shown in equation 2.1.4. The abbreviation SF will be used for this distribution. This transformation is obtained solely by assuming that the molecular weight of the insertable carbon monomer is constant and independent of chain length during the synthesis process.

$$w_n = n \, \alpha^{n-1} (1 - \alpha)^2 \qquad \qquad 2.1.4$$

w_n is the weight fraction of product hydrocarbon of

carbon chain length n

The functional dependency of weight fraction on chain length can set some strict restrictions on selectivities towards gasoline or diesel range hydrocarbon products. As shown by Madon (73) the maximum weight fraction of hydrocarbon product n, $w_{n_{max}}$ is given by the relation shown below.

$$w_{n,max} = 4n \, \frac{(n-1)^{n-1}}{(n+1)^{n+1}} \qquad \qquad 2.1.5$$

Indeed, if the FT synthesis were limited to the above hydrocarbon distribution the economic viability of this process would be severely limited. Although most investigators have reported product distributions compatable with the Schulz-Flory model (6,8,56,74,39) there have been a fair number of reported product distributions which show substantial deviations (48,86,27). These non Schulz-Flory distributions generally lack the long tailing of the high molecular

weight products. Madon (73) has suggested that the growth probability (α_n) may decrease with increasing carbon number and is dependent on the nature of the catalytic site. Nijs and Jacobs (87) have developed a model which relates the hydrocarbon chain length distribution with the particle size distribution for a given catalyst. Indeed, the product distribution may be affected by the structural nature of the catalyst especially when one considers the improved olefin and C_5-C_{12} selectivity in zeolite catalysts (27).

A major draw back to the SF model is that it does not consider chain branching. Anderson et al. (8) extended the model to account for the isomer distribution (Equation 2.1.6). The isomers generally produced are methyl branched and the extent of isomerization slowly increases with increasing hydrocarbon chain length (8). The modelling equation assumes that branching can only occur on either the end carbon (bonded to surface) or the penultimate carbon.

$$\phi_n = 2\phi_2 \, g_n(f) \, \alpha^{n-2}$$
<div align="right">2.1.6</div>

where $g_n(f)$ is the isomer distribution function for a hydrocarbon chain of n carbon atoms.

The major drawback to this model is that it predicts branched isomers at all conversions. Recent results indicate that the extent of chain branching decreases with decreasing H_2/CO ratios and increasing pressure (82).

2.1.2. Oxygenated Products

As stated earlier, the FT process can yield straight chain primary

alcohols and esters (112,91). At 10 atm a bulk iron catalyst can produce 10 to 30% of the total liquid products as alcohols and esters. Higher pressure will increase this yield. Under similar conditions cobalt will only produce about 1% in oxygen-containing liquid products (91).

Henrici-Olivé and Olivé (55) presented the alcohol product distribution data of Kagan et. al (59) in terms of the SF relation and found that these products obey the SF distribution model. Kellner and Bell (62) recently investigated the formation of oxygenated products using a supported Ru catalyst under differential reaction conditions. They found that acetaldehyde was the principle oxygenated product with a silica support while methanol was the principle oxygen containing product with alumina.

2.2 Reaction Mechanisms

Since the mid 1970's most research efforts have been aimed at elucidating the mechanism of the synthesis process. There are many excellent review articles in this area (6,20,80,91,103,123) and the discussion presented here will only deal with a limited number of investigations in order to highlight the major "mechanistic viewpoints". Any disparities in the amount of material presented for each proposed mechanism reflects the current research emphasis.

There are several proposed mechanisms in the literature which explain the observed product distribution and have experimental justification via such techniques as radioactive labeling, high resolution product and mass balance analysis and surface spectroscopy. All the popular mechanisms currently available in the literature can be grouped into three distinct groups as shown below:

1) Carbidic intermediate - the CO decomposes on the catalytic surface, and hydrogenates to methylene species which "polymerize" and/or hydrogenate to form the hydrocarbon products

2) Oxygen-containing intermediate - Chemisorbed CO reacts with hydrogen to form an enolic and/or alcoholic intermediate. Condensation and elimination involving terminal OH groups leads to hydrocarbon products.

3) Carbidic intiation/CO insertaion - CO decomposition leads to an active chain initiator which grows via CO insertion and subsequent hydrogenation into products.

Comparing the three catagories of proposed mechanisms one immediately identifies the major difference among them is the intermediate pathway of the reactant CO. Is the C-H bond formed before the C-O bond is broken? Experimental results supporting all three mechanisms will be presented. Before presenting the investigations involved with these mechanisms a quick historical overview should be given.

Mechanism 1 was the principal belief from the original discovery of the synthesis mechanism until the 1950's, at which time mechanism 2 totally dominated the literature. During the early to mid 1970's mechanism 3 developed and mechanism 2 was solely displaced by mechanism 1. At the start of the 1980's it seems that mechanism 1 is again dominant but there is still continual experimental support for mechanisms 2 and 3.

The careful reader will note that the results presented and along with their "mechanistic implications" are based over a wide variety of catalyst and reaction conditions. Comparison between different investigations must be done prudently and with reservation since

different reaction mechanisms may prevail under different conditions and with different catalysts. Additionally many studies, especially those carried out under ultrahigh vacuum, are at conditions far different than those employed in normal FT synthesis.

2.2.1 The Carbidic Intermediate

Fischer and Tropsch (45) suggested that the formation and subsequent hydrogenation of metal carbides resulted in the formation fo hydrocarbon products. Craxford and Rideal (20) assumed that the active catalytic surface is first hydrogenated into one large polymethylene monomer which is then hydrocracked into products. Later investigators (107,112) point out that the products of hydrocracking are significantly different than the products of the FT synthesis. In fact Schulz and Achtsnit (107) have shown that negligible cracking occurs under FT conditions over a bulk Fe catalyst. The carbide intermediate still receives support from two basic sources:

1) an adsorbed carbon species (C_{ads} or $(CH_x)_{ads}$) has been found to be active in the synthesis process on Ni, Co and Ru catalyst,

2) Fe catalysts are known to carburize under reaction conditions. It has been found that reduced iron metal (3,4,84,100,117) or iron oxide (6,70,67) are not very active catalysts and that the hydrocarbon production rate increases as the catalyst undergoes carburization. It would seem that the iron carbide formed during exposure to the feed gas plays some role in hydrocarbon production. Kryukov et al. (68) precarburized an iron catalyst with radioactive carbon monoxide and found labeled carbons in the hydrocarbon products. In fact the radioactivity in the higher molecular weight products was higher than that calculated assuming one labeled carbon in each growing chain. Therefore more than

one labeled carbidic carbon is present in a given chain supporting the surface polymerization model. Since ninety-nine percent of the radioactive carbon did not react to yield products the authors conclude that the carbide may not be an important intermediate. Similar results were obtained by Kummer et al. (70). These results support the fact that the carbide intermediate may not be the principle reaction pathway. Biolen and Sachtler (20) note that the carbides used by Kummer et al. (70) were formed at much higher temperatures than typical FT conditions. This same argument could be applied to the work of Kryukov et al. (68). Additionally both of these studies were conducted with bulk Fe catalyst with very low dispersions. If the bulk carbide is considered to be a stable phase during the synthesis the small amount of labeled carbon found in the product stream may only reflect the small surface area of the catalyst and suggest that larger catalytic surface areas might yield a higher labeled carbon fraction in the products.

In the 1950's the carbide intermediate mechanism was losing its predominance and being replaced with the hypothesis of an oxygen containing intermediate. This was mainly due to the pioneering work of Dr. P.H. Emmett (71,53,54), which will be discussed in a subsequent section.

In the mid 1970's when a renewed research effort in the FT process began to take place, the carbidic intermediate developed some strong experimental support. Wentrcek, Wood, and Wise (125) performed a classical experiment which provided convincing evidence that the surface carbide may be the only reaction intermediate on Al_2O_3 supported nickel at 1 atmosphere. In their investigations, CO was pulsed over the catalyst at 250°C and disproportionated to C_{ads} and CO_2. By knowing the amount of CO pulsed into the reactor and measuring the amount of CO_2 at

the outlet the surface average of C_{ads} and CO_{ads} was determined. The amount of CH_4 formed via introduction of pure H_2 pulses corresponded to the amount of adsorbed carbon rather than the amount of adsorbed CO. In a pure H_2 environment the C_{ads} species is the far more reactive species. Transition metals decompose CO into an adsorbed carbon which can be readily hydrogenated. The authors (97) could not obtain any relative rate data for the hydrogenation of C_{ads} or CO_{ads} but "suggest" that the C_{ads} is more reactive.

Araki and Ponec (9), using Ni films, disproportionated ^{13}CO and then passed a CO/H_2 mixture continuously over the catalyst. They observed $^{13}CH_4$ prior to the formation of $^{12}CH_4$ and $^{12}CO_2$, and concluded that the hydrocarbon products are formed via a carbidic intermediate rather than by the direct hydrogenation of adsorbed CO. Biloen and Sachtler (20) point out that the catalyst has a very high $^{13}C_{ads}$ surface coverage prior to the introduction of the CO/H_2 mixture. The presence of ^{13}C in the initial products may be a manifestation of the high surface coverage since the relative rates based on the two possible reactions (equations 2.2.1 and 2.2.2) can be influenced by the initial surface concentration of $^{13}C_{ads}$

$$CO_{ads} \xrightarrow{H^2} CH_4 + H_2O \text{ (or } CO_2) \qquad\qquad 2.2.1$$

$$^{13}C_{ads} \xrightarrow{H^2} {}^{13}CH_4 \qquad\qquad 2.2.2$$

Indeed this argument is also valid for the previously mentioned experiments of this type (125,97).

The investigations involving preadsorbed carbon (9,97,125) were conducted at low pressures ($\approx$1 atm) where methane was the predominant

product. A small difference in reaction order compounded with an artificially induced surface composition may give kinetic observations which are inappropriate under normal synthesis conditions of pure CO/H_2 feed and pressures greater than 1 atmosphere.

More recent investigations (18,19) involved the deposition of submonolayer amounts of ^{13}C on SiO_2 supported Ni, Co and Ru catalyst. Following deposition, a batch mixture of a $3/1$ $H_2/^{12}CO$ feed gas was contacted with the catalyst at pressures greater than one atmosphere in order to monitor the radioactivity in the C_2^+ hydrocarbon products. Upon repeated contact of the feed mixture on the same catalyst it was found that the amount of $^{13}CH_4$ produced corresponded to the surface concentration of $^{13}C_{ads}$ on the catalytic surface. The adsorbed species ^{13}C and ^{12}CO were found to be kinetically equivalent for both methane and the higher molecular weight hydrocarbons. The authors assume that identical catalytic sites are used for both the C_{ads} and CO_{ads} species, i.e.,

$$\theta_{12_{CO_{ads}}} + \theta_{13_{C_{ads}}} = 1 \qquad 2.2.3$$

where θ_x is the fraction of sites occupied by species x. Rapid oxygen scrambling between the ^{12}C and ^{13}C atoms which could account for the kinetic observations was was found to be less than 3% in the CO/H_2 environment and the rate of scrambling in a H free environment was found to be very low.

The authors (20) conclude that both the $^{13}C_{ads}$ and $^{12}CO_{ads}$ are rapidly converted into a common reaction intermediate CH_x which is then converted to methane and/or higher carbon number hydrocarbons. This reaction sequence is shown below in equation (2.2.4).

$$^{13}C_{ads} \searrow \quad \nearrow ^{12,13}CH_4$$
$$^{12,13}CH_x$$
$$^{12}CO_{ads} \nearrow \quad \searrow ^{12,13}-CH_2^-$$

2.2.4
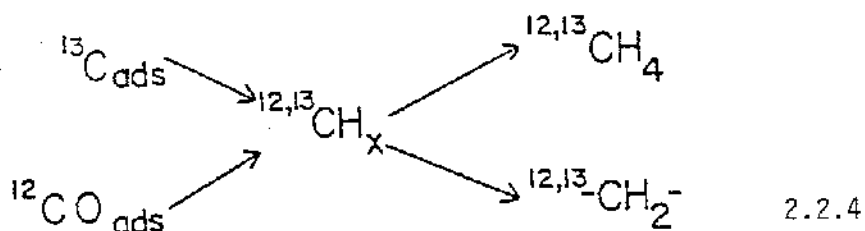
Some carbon chains contained more than one ^{13}C atom again supporting some type of surface methylene polymerization step.

The carbidic carbon intermediate is further supported from the work of Pichler and Schulz (92). They introduced a labeled α olefin $^{14}CH_2 = CH - C_{14}H_{29}$ into a CO/H_2 feed over a Co catalyst at one atmosphere and found radioactivity in carbon chains containing less than 16 carbon atoms. In terms of the overall product distribution only 6.3% of the ^{14}C atoms occurred in the $C_n > 16$ fraction while 14.3% occurred in product chains of 15 carbons or less. The remaining ^{14}C atoms in the parent compound which was predominantly hydrogenated. The authors conclude that the presence of radioactivity in the hydrocarbon fraction of 15 carbon atoms or less strongly supports the transfer of a $(CH_x)_{ads}$ species to growing chains.

Ekerdt and Bell (43) showed that cyclohexene introduced in a feed mixture of CO/H_2 will react to form alkyl cyclohexenes and alkyl cyclohexanes. The authors suggest that these results can be attributed to a reaction between the cyclohexene with either adsorbed alkyl and/or alkylidine species. These results were obtained at one atmosphere over a Ru/SiO_2 catalyst with CO_2/H_2 feed ratios of 1/3 and less. Tamaru (115) introduced a small amount of $^{12}CH_2 = ^{12}CH_2$ into a $^{13}CO/H_2$ feed mixture and detected propylene containing only one labeled carbon $(^{13}C^{12}C_2H_6)$. The fact that no propylene contained one or three ^{12}C atoms indicates that ethylene is not a source of CH_2 intermediates.
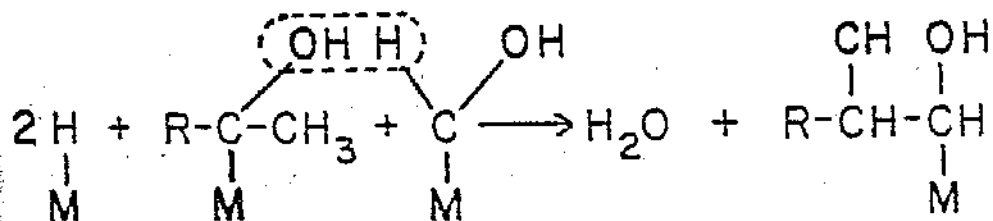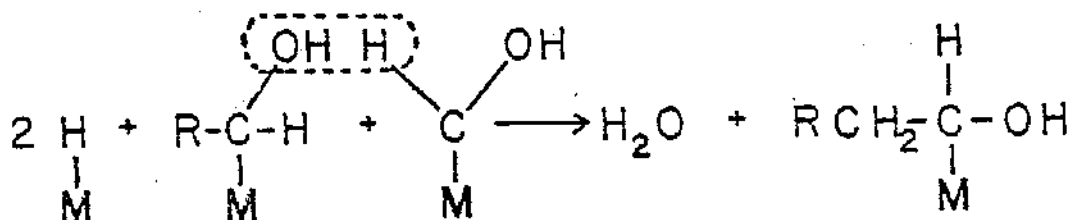
The presence of a surface carbidic intermediate (methylene group) is shown to be present in the work of Brady and Petit, reviewed by Bell (16). They passed a dilute stream of CH_2N_2 over Ni, Pd, Co, Fe and Ru catalyst. In the absence of H_2 the products were ethylene and nitrogen. However when H_2 was mixed with the CH_2N_2 reactant they observed a product mixture of straight chain hydrocarbons resembling that normally obtained in the synthesis. In a subsequent study (25) it was found that the addition of CH_2N_2 to a CO/H_2 feed shifted the product distribution towards higher molecular weight products. Using labeled ^{13}CO with CH_2N_2 resulted in a product distribution consistent with the one predicted assuming a growth model involving the combination of $-CH_2-$groups.

2.2.2 Oxygen-containing Intermediate

The introduction of a hydrocarbon or oxygen containing compound in addition to the synthesis gas is not a recent method in the investigation of the Fischer Tropsch reaction mechanism. Through the 1950's Emmett performed some classical experiments in the use of radioactive isotopes in the study of the synthesis mechanism (53,54,71). It was found that ethylene can act as a chain initiator but to a lesser extent than a primary alcohol. Using an iron catalyst, the amount of ethylene incorporated into higher molecular weight products decreased with increasing pressure.

Kummer et al. (70) performed FT reaction studies on various carbided catalysts. Pichler (91) reviewed these results and concludes that the activity of these catalysts was too low to justify them as possible intermediates. The oxygen-containing intermediate started appearing in the literature (112) about this time. Kummer and Emmett

(71) and Hall et al. (53) introduced labelled ethylene and various

alcohols into a feed gas using an iron catalyst. They found that the

primary alcohols were incorporated to a greater extent than ethylene, and

no degradation of alcohols into surface $-CH_2-$ groups was observed.

Also they concluded (53) that the alcohols form a different type of

adsorbed complex than that of ethylene. The mechanism involving adsorbed

alcohols can be shown as follows

$$2\ \underset{M}{H} + R-\underset{M}{\overset{\overline{OH\ H}}{C}}-H + \underset{M}{\overset{OH}{C}} \longrightarrow H_2O + RCH_2-\underset{M}{\overset{H}{\underset{|}{C}}}-OH$$

$$2\ \underset{M}{H} + R-\underset{M}{\overset{\overline{OH\ H}}{C}}-CH_3 + \underset{M}{\overset{OH}{C}} \longrightarrow H_2O + R-\overset{CH}{\underset{|}{CH}}-\underset{M}{\overset{OH}{\underset{|}{CH}}}$$

This mechanism as given by Hall et al. (53,54) does not differentiate

between CO or H_2 being the reductant in the dehydration step.

Methanol showed the greatest activity in both initiating chains and

entering into them, however, not to the extent it should if it were

indeed the basic building block (53,54). Introduction of 1-propanol

resulted in about 50% of the alcohol being incorporated into higher

molecular weight products including significant amounts of isobutene and

isobutane (54). The addition of propionaldehyde resulted in a labeled

carbon distribution similar to that of 1-propanol implying this compound

forms the same adsorbed complex as 1-propanol. For the ethylene and

alcohol feed mixtures there was negligible hydrocracking at both 1 and

7.5 atmospheres. The propionaldehyde exhibited a small amount of hydrocracking.

Kummer and Emmett (71) added labeled ketene ($^{14}CH_2CO$) to a reaction mixture (about 1.5%) and found that the $^{14}CH_2$ group did not incorporate into any growing chain at 1 atmosphere. More recent investigations using higher ketene concentrations over supported catalysts at one atmosphere have shown that insertion of the $-CH_2-$ group does occur (96).

Nijs and Jacobs (87) have performed pulsed and continuous FT reactions over various supported catalyst completely covered with ^{13}C via the ^{13}CO disproportionation reaction. They worked at relatively high pressure (7-15 atm), high CO conversion (25-35%) and used a feed ratio of 2/3 in CO/H_2. The catalyst employed included Co on kieselghur and Ru on aerosil. On the initially clean metal surface they found methane and Co_2 to be the initial products. Upon subsequent pulses they found a drop in the amount of these compounds while the rate of formation of heavier hydrocarbons increased. The CO conversion was initially high and decreased to a constant level. The authors propose that the CO_2 initially produced reacts with H_2 to produce H_2O via the reverse water gas shift reaction. The H_2O formed combines with the adsorbed C to form an adsorbed enol complex which is the intermediate in carbon chain growth.

$$\underset{M}{C} \; + \; H_2O \longrightarrow \underset{M}{\overset{H \quad OH}{C}}$$
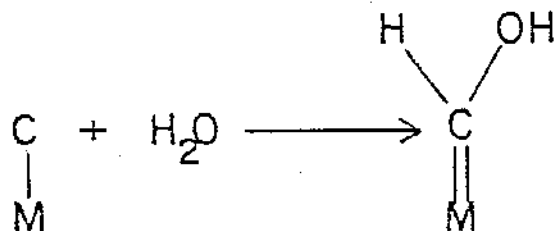
2.2.6

The addition of steam into the feed gas accelerated the time needed to reach a steady state product distribution confirming the fact that water plays some role in the transient behavior of the catalytic surface. The authors (87) conclude that there are two intermediates on a FT catalyst, a carbide and an adsorbed enol. The former is responsible for the production of methane while the latter is involved in the growth of hydrocarbon chains.

2.2.3 Carbidic Iniation/CO Insertion

The previously mentioned mechanisms can not explain some rather basic experimental phenomena associated with the FT product distribution. The carbidic intermediate mechanism can not explain the production of oxygen-containing products nor readily account for the relatively small amount of branched isomers. As Ponec (95) points out the alcoholic intermediate mechanism does not readily explain why alcohols cannot enter into chain growth via a dehydrocondensation reaction.

Hall et al. (54) point out that labeled ethylene affects the product distribution differently than that of labeled primary alcohols. Indeed there may be parallel reaction networks at work over the wide range of catalyts and conditions under which the Fischer Tropsch synthesis occurs. However, if one is to assume a common mechanism for the synthesis process the carbidic initiation/CO insertion model can explain the above inconsistancies in the previous two mechanisms.

Wender et al. (124) first introduced the concept of CO insertion into a growing hydrocarbon chain. Pichler and Schultz (92,93) suggested that initially the CO inserted into a metal-hydrogen bond and chain growth proceeded via CO insertion into a metal-alkyl bond (equation