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# Microwave induced solid-state interactions for the synthesis of Fischer-Tropsch catalysts

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**2010-04-13T09:05:24Z**
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# CHAPTER TWO

## LITERATURE OVERVIEW

## 2.1 THE FISCHER TROPSCH SYNTHESIS (FTS)

The Fischer-Tropsch process is regarded as coal to liquid or gas to liquid technologies. This process has been used in industries ever since its first discovery during 1920's. Liquid fuels can be produced from biogas, coal, natural gas or elephant grass (Tijmensen et al., 2002). Coal can be converted through gasification and methane through steam reforming to a mixture of CO and $H_2$ (synthesis gas).

A typical FT process is given in **figure 2.1**. Synthesis gas ($H_2$ and CO) can also be used for power generation, for making fertilizers, methanol, synthetic natural gas, hydrogen and carbon dioxide.

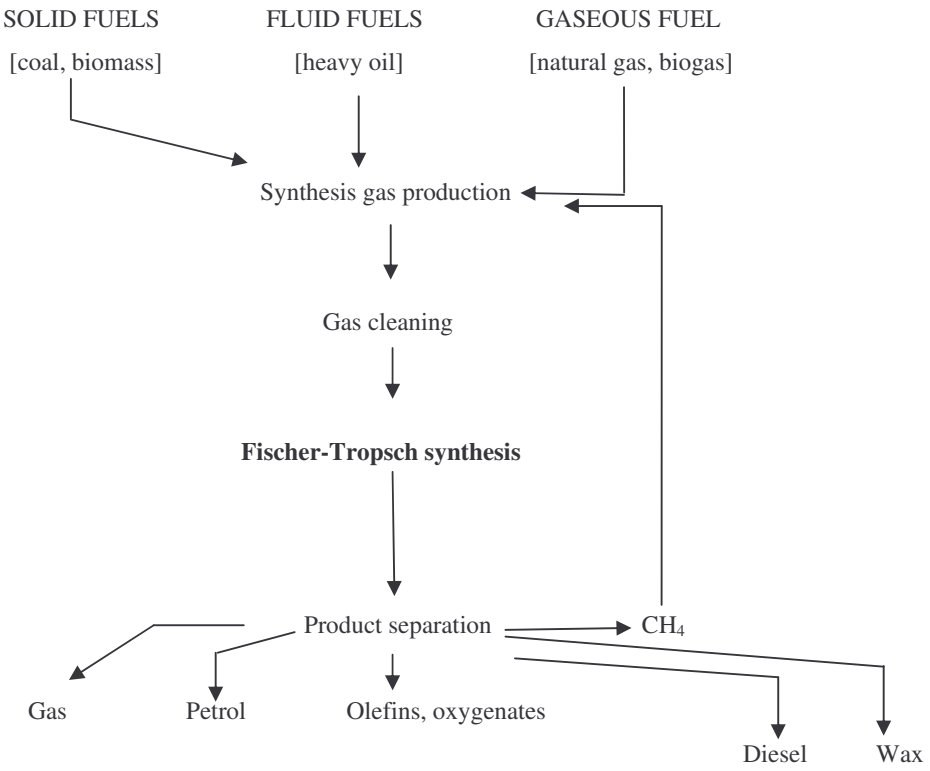


**Figure 2.1:** Process overview for transport fuel and chemicals production via Fischer-Tropsch synthesis (FTS).

There has been growing interest in FT process with the aim of improving catalytic activity and product selectivity. A number of paper publications, patent publications, growing research and development in the process highlight the importance of Fischer-Tropsch synthesis. There is a variety of companies involved in FT such as PetroSA, BP, Exxon, Rentech, Shell, Sasol, Statoil and Syntroleum. It has become important as the planet faces exhaustion of its petroleum reserves in the near future (Datye et al., 1995).

The use of different catalysts and different reaction conditions helps to manipulate the types of products that can be produced. Much research has been done in an attempt to obtain insight into the reaction mechanism of the Fischer-Tropsch synthesis in order to improve selectivity and activity of the catalyst. The product distribution depends on temperature, total pressure, $H_2$:CO ratio and the nature of the catalyst (Dry, 1981; Boudart, 1984; Schulz et al., 1994).

## 2.1.1 THE FISCHER-TROPSCH (FT) REACTIONS

The FT reaction is highly exothermic and the heat removal needs to be efficient in order to avoid temperature increase which would result in the formation of unwanted products (Dry, 2001). The FT reaction can be represented stoichiometrically as follows:

FTS: $2H_2 + CO \rightarrow -(CH_2)- + H_2O \quad \Delta H_{rxn}(250\ ^oC) = -152\ kJ/mol$ (2.1)

Depending on a number of factors, first and foremost the hydrogen to carbon monoxide ratio in the synthesis gas and the type of catalyst employed, paraffin (alkane) formation or olefin formation predominates in the synthesis (Weil et al., 1949). Paraffin formation is normally favoured by relatively high $H_2$:CO ratios and catalyst with high hydrogenating activity whereas the olefin formation takes place at low $H_2$:CO ratios and catalyst with strong CO chemisorption ability.

The stoichiometry of this highly exothermic reaction (2.1) implies a $H_2$:CO usage ratio of 2:1. The FT reaction is a carbon chain building process, where the hydrocarbon chain monomer ($-CH_2-$) groups are attached to the carbon chain. It has been likened to a surface polymerization reaction because it yields a wide range of products of high molecular weight (Thomas, 1996). The hydrocarbons are formed in FTS by insertion of ($-CH_2-$) into metal-alkyl bonds and dehydrogenation. The FT reaction results into a wide range of organic products including branched hydrocarbons and oxygenated compounds such as alcohols, aldehydes and ketones. However, there are some theoretical objections on the $-CH_2-$ as an insertion unit.

Depending on the type of catalyst used, side reactions may take place:

WGS: $H_2O + CO \rightarrow CO_2 + H_2 \quad \Delta H_{rxn}(250\ ^oC) = -40\ kJ/mol$ (2.2)

The water gas shift reaction (WGS) is usually catalysed by iron catalyst. Metallic cobalt, nickel and ruthenium are much less active for the water gas shift reaction.

Water, a predominant product in FTS reacts with unreacted CO to form $CO_2$ and $H_2$ by WGS reaction. Synthesis gas with lower $H_2$:CO ratios obtained from coal gasification can be used when iron catalysts are employed in FT process because of its activity towards the WGS reaction. $H_2$, a predominant WGS product, compensates for the insufficient hydrogen of the coal-derived synthesis gas.

$CO_2$ in the FT reaction is mainly produced by the WGS reaction in minor quantities. It can also be produced in small amounts by disproportionation of CO which causes catalyst deactivation due to carbon deposition on active sites present in the FT catalyst surface (Bartholomew, 1991; Dry, 2004b). In this study, $CO_2$ selectivity is low but under high temperature Fischer-Tropsch conditions the water-gas shift reaction is close to equilibrium. In general the $CO_2$ selectivity is relatively low under low temperature FT conditions. Many other iron-based Fischer-Tropsch systems have been reported with up to 40 – 45% $CO_2$ selectivity. WGS reaction can also results in catalyst deactivation on the catalyst surface. Reactions (2.2 and 2.3) are main side reactions in FTS (Bartholomew, 1991).

Boudouard: $2CO \rightarrow CO_2 + C \quad \Delta H_{rxn}(250\ ^{o}C) = -173\ kJ/mol$ (2.3)

In general, the Fischer-Tropsch synthesis yields predominantly linear hydrocarbons (alkenes and alkanes). Oxygen-containing organic compounds (alcohols, aldehydes, ketones and carboxylic acids (Anderson, 1984) are produced in lesser amounts (Dry, 2004). The product spectrum is affected by secondary reactions because oxygenated compounds and olefins can readsorb on the surface of the catalyst and experience secondary reactions such as double bond shift or hydrogenation (Claeys and Schulz, 1999). If hydrogenation of olefins occurs, n-paraffin products dominate in the product spectrum.

Pichler and Roelen discovered that oxygenated compounds can be formed from hydroformylation of olefins during FTS (Pichler and Roelen, 1957).

Branched hydrocarbons are formed via olefin re-adsorption on the catalyst surface which then undergoes secondary reactions with respect to cobalt-based catalysts. Iron-based catalysts tend to form larger amounts of both branched hydrocarbons and

oxygenates than cobalt does. Both these variables were found to increase with increasing potassium promoter in the catalyst (Schulz et al., 1994).

## 2.2 FISCHER-TROPSCH REACTION MECHANISMS

### 2.2.1 INTRODUCTION

Different mechanisms have been suggested for the formation of hydrocarbons on the surface of FT catalysts (Anderson, 1984; Fischer and Tropsch, 1926). Herrington and other researchers describe the FTS as a chain polymerisation reaction (Herrington, 1946); Anderson et al., 1951) which produces various oligomers regularly distributed along the carbon number range and the product spectrum is described by a chain polymerisation kinetic model (Herrington, 1946; Anderson et al., 1951).

There is a general agreement that the products are formed by hydrogenation of CO to generate the methylene monomer (Anderson et al., 1951; Anderson et al., 1958). On the other hand, the nature of this monomer is still debated. The product distribution tends to obey the Anderson-Schulz-Flory (ASF) chain length statistics, though many researchers have reported deviations from the ASF theory (Pichler et al., 1967, Madon et al., 1981, Huff et al., 1984, Iglesia et al., 1991). This indicates that the ASF theory is not always true. The only aspect of the ASF-theory is the chain length independent chain growth probability (Schulz et al. (1990)).

It is widely accepted that the FT reaction may be viewed as a polymerization of methylene species (Fischer and Tropsch, 1926). The catalyst employed in FT reaction must be able to dissociatively adsorb CO and $H_2$ on the surface. The initiation of FT reaction involves adsorption and dissociation of CO on the catalyst surface, this is followed by the reaction of hydrogen with the surface carbon atoms leading to the formation of surface methyne and methylene ($\bullet CH_2$) (Fernandes, 2005).

All the proposed mechanisms have in common the following key steps: reactant adsorption, chain initiation, chain growth (propagation), chain growth termination, product desorption, re-adsorption of reactive products and further reactions.

However, there are two major mechanisms which were suggested to explain the FT propagation and termination mechanisms: the alkyl mechanism and the alkenyl mechanism (Overett et al., 2000).

## 2.2.2 ALKYL MECHANISM

Fischer and Tropsch were the first researchers to propose the involvement of surface methylene (Fischer and Tropsch, 1926). Pettit, Brady, Biloen and their collaborators developed this concept and they proposed an 'alkyl mechanism' (**figure 2.2**) in which surface methylene and surface hydrogen react to form a surface methyl and the chain growth occurs by the insertion of a surface methylene into the M-C bond of the surface alkyl (**figure 2.2**). Termination of the chain growth occurs by means of β-hydride elimination from the surface alkyl to give α-olefins (Biloen et al., 1979; Brady III and Pettit, 1981; Brady III and Pettit, 1981b) or a reduction by surface hydride to yield alkanes (**figure 2.2**).

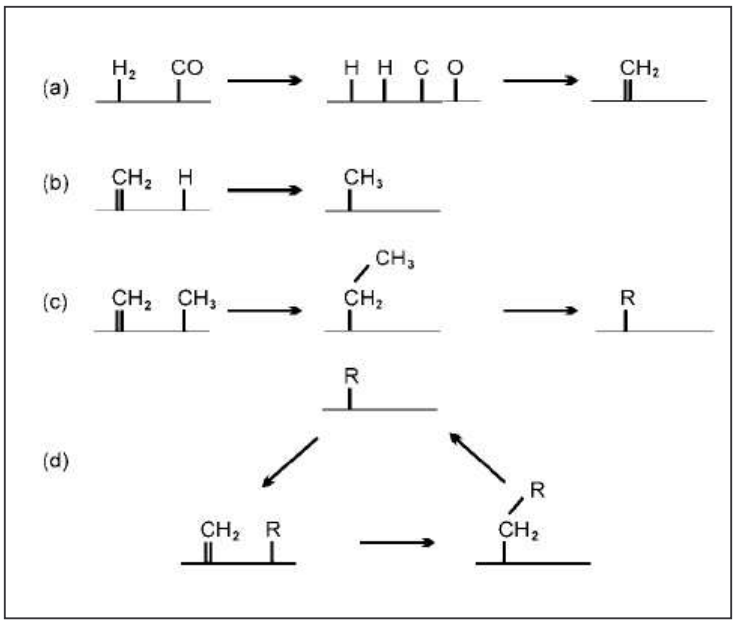


**Figure 2.2:** Alkyl mechanism for initiation and propagation of hydrocarbon chain: **(a)** methylene formation, **(b)** initiation of chains, **(c)** initiated chain growth, **(d)** propagation (Fernandes, 2005).

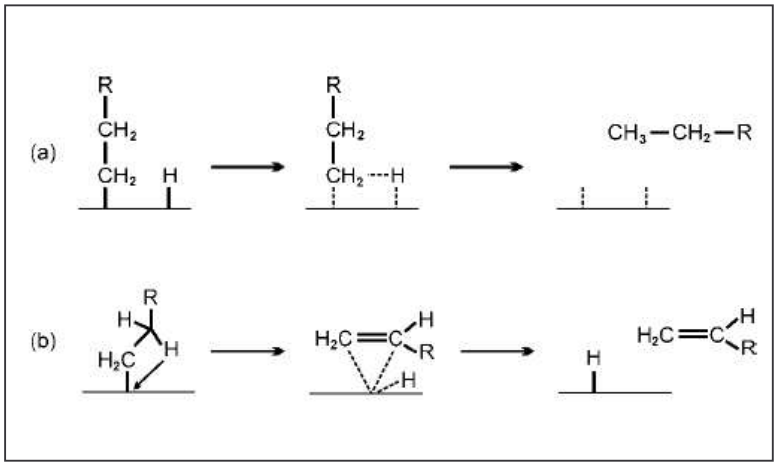


**Figure 2.3:** Alkyl mechanism for termination of hydrocarbon chains: (a) surface hydride termination giving alkanes, (b) β-elimination mechanism forming α-olefins (Fernandes, 2005).

Nevertheless, this theory (alkyl mechanism) has a number of limitations and it does not account for the formation of branched hydrocarbons. However Schulz reported that alkyl mechanism can be extended to account for the primary formation branched hydrocarbons (Schulz et al., 1990). The alkenyl mechanism which accounts for the formation of branched hydrocarbons was suggested by Maitlis and the co-workers (Maitlis et al., 1999).

### 2.2.3 ALKENYL MECHANISM

Maitlis et al. proposed the alkenyl mechanism which is initiated by the formation of the surface vinyl species ($-CH_2=CH_2$) formed through the coupling of surface methyne (CH) and a surface methylene ($CH_2$) (Maitlis et al., 1999; Long et al., 1997; McCandlish, 1983). The vinyl species is considered as the chain initiator and the methylene surface species is the chain propagation monomer. Chain growth is suggested to occur through the reaction of the vinyl species ($-CH_2=CH_2$) with a surface ($CH_2$) species to form an allyl species ($-CH_2CH=CH_2$) and proceeds by isomerization to a surface alkenyl species ($-CH=CHCH_3$), which is capable of reacting further. The alkenyl species then undergo hydrogenation by surface hydrogen to yield α-olefins (termination) (**figure 2.4**).

On the other hand, Claeys and van Steen postulated that though the alkenyl mechanism explains the formation of branched hydrocarbons by allyl isomerisation, it does not explain the formation of methane and oxygenated compounds (Claeys and van Steen, 2004).

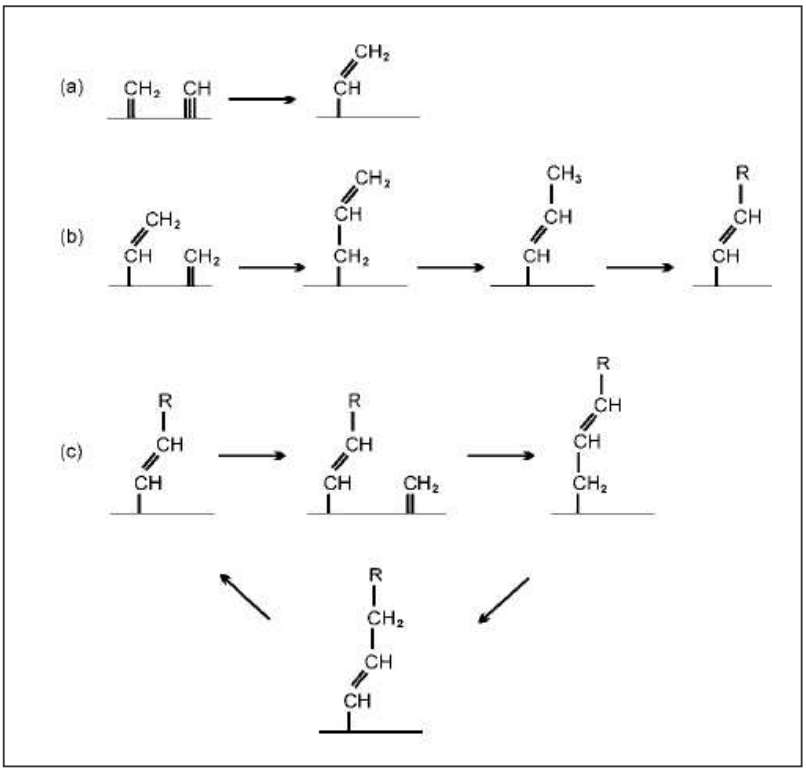


**Figure 2.4:** Alkenyl mechanism: **(a)** initiation of chain, **(b)** Chain growth including insertion of methylene and isomerization, **(c)** propagation of hydrocarbon chains (Fernandes, 2005).

## 2.2.4 OXYGENATE (ENOL) MECHANISM

In the 1950s, the enol mechanism achieved widespread acceptance (Evans, 1954; Storch et al., 1951). This mechanism involves the chemisorption of CO which reacts with adsorbed hydrogen to form enolic surface species (2) which serves as both the chain initiator and monomer (Storch et al., 1951). The enolic surface species (2) hydrogenates further resulting in the formation of the surface species (3) which converts to the methyl surface species (4). Two enol surface species can also undergo condensation and water elimination step resulting in chain growth (Dry, 1993). Chain termination forms α-olefins or alcohol (oxygenated compounds). N-Paraffins are formed from secondary reactions by hydrogenation of α-olefins. Storch et al. reported

also that in the enol mechanism, there is no experimental evidence for the existence of the enol surface species (Scorch et al., 1951).

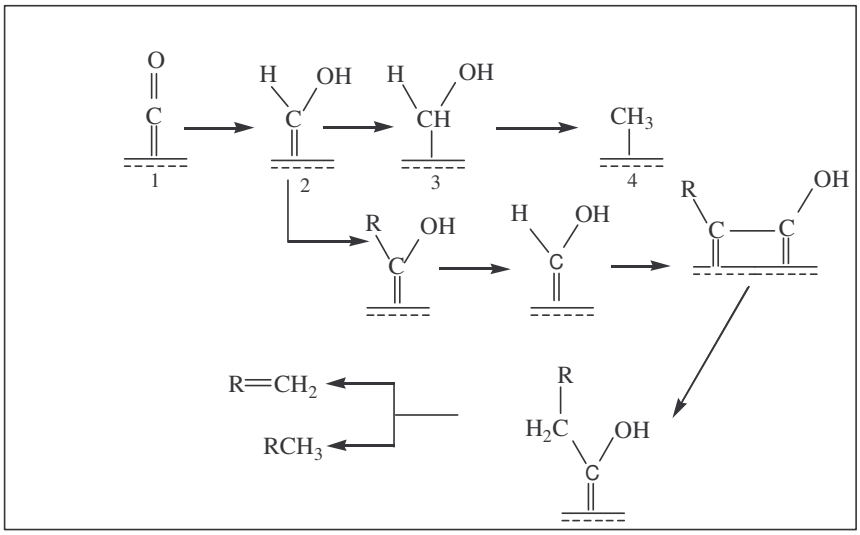


**Figure 2.5:** Enol mechanism (Storch et al., 1951).

## 2.2.5 CO INSERTION MECHANISM

Hindermann et al. and many others believed that CO insertion mechanism is the main reaction pathway which accounts for the formation of oxygenated compounds in FTS (Hindermann et al., 1993). The insertion mechanism involves the insertion of CO into a metal-alkyl (methyl or methylene) carbon bond which is then hydrogenated to produce an alcohol or alkene. Dry reported that the oxygenated compound can also eliminate oxygen to yield alkene (Dry, 1993).

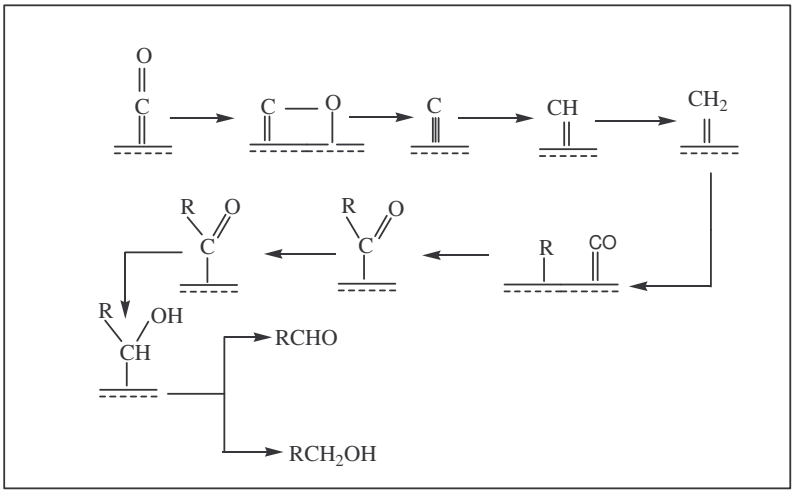


**Figure 2.6:** CO insertion mechanism (Hindermann et al., 1993).

## 2.2.6 FORMATION OF BRANCHED HYDROCARBONS

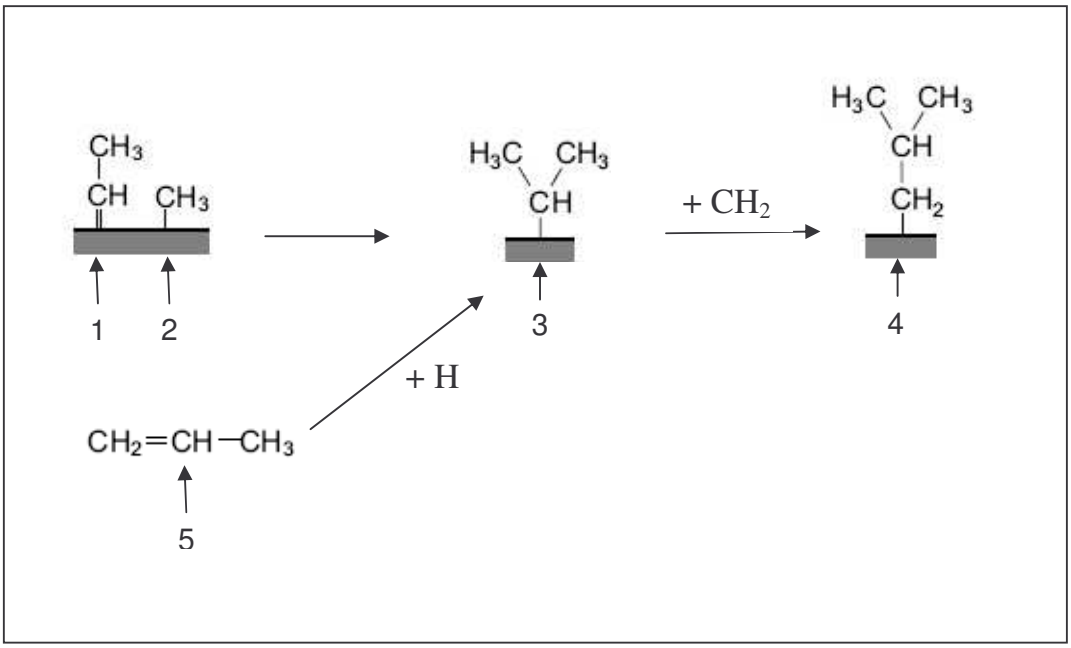


**Figure 2.7:** Formation of branched hydrocarbons (Schulz et al., 1970).

The FT CO hydrogenation produces linear chains of $CH_2$ groups. In addition to that, a variety of branched products, methyl and ethyl (although its amount is less than the amount of methyl branched compounds) can be found takes place. Any branching reaction was reported to be more demanding in space at the active sites than linear chain growth (Schulz, et al., 2002).

A reaction pathway which describes the formation of branched hydrocarbons was proposed by Pichler and the co-workers (Pichler et al., 1970). They discovered that branched hydrocarbons are formed from a reaction of alkylidene surface species (1) and a methyl surface species (2) to yield surface species (3). Branched hydrocarbons can also be formed by means of olefin (5) which readsorbs on the penultimate carbon atom (3) and then react with methylene to yield branched surface species (4). When the surface species (4) desorbs, it forms a methyl branched compound.

## 2.3 THE FISCHER-TROPSCH PRODUCT SPECTRUM

Since the discovery of FTS, researchers have been examining the different products obtained in this reaction. The FT reaction yields a variety of products including paraffins, olefins, oxygenates, alcohols and carboxylic acid (Anderson, 1984).

The product spectrum can be described by chain polymerisation kinetic model. Anderson, Schulz and Flory (ASF) proposed a kinetic model that is most frequently used to describe the product distribution obtained from FTS. The ASF kinetic model is shown in equation **2.4** below:

$$W_n/ N = (1-\alpha^2)* \alpha^{(n-1)} \qquad (2.4)$$

Where n is the carbon number, $W_n$ is the weight fraction of product containing n carbon atoms and $\alpha$ is the chain growth probability. The ASF kinetic model shown in equation 2.4 is a result of the ASF model assuming a constant chain growth

probability. It must be noted that deviations are typically described in terms of deviations from the ideal ASF model, i.e. with a constant chain growth probability.

Higher values of alpha correspond to higher molecular weight products whereas lower values correspond to the formation of gaseous products.

Conversely, most of FT product distributions do not obey the ASF kinetic model (Iglesia et al., 1993), that is they possess relatively high methane selectivity and low yield of ethene relative to the predicted ASF distribution, chain length dependent chain growth probability results in higher than expected selectivity towards heavy products.

Lower ethene yield occurs due to re-adsorption of reactive products or α-olefins into the chain growing chains (Schulz 1999).

## 2.4 THE EFFECT OF REACTION AND REACTOR VARIABLES ON THE PRODUCT SELECTIVITY

Factors, such as operating conditions i.e. synthesis gas ratio, temperature, total pressure, and reaction time on stream (TOS) can affect the FT product selectivity and composition. The product selectivity is influenced by the catalyst stability to promote chain propagation over chain termination.

### 2.4.1 CHOICE OF REACTOR

Many reactors such as the fixed-bed reactor, slurry-phase reactor and fluidised bed reactor can be used in FT processes. The choice of reactor represents a major challenge in FT product selectivity control.

The amount of the catalyst to be used in a reactor depends on a variety of factors:

1. How well small flows can be controlled.
2. How the ideal flow pattern within the reactor can be achieved
3. How good the association analytical system is.
4. How reproducible the catalyst preparation is.

A fixed bed reactor is mostly used as a FT reactor because it represents the simplest and cheapest technical solution to perform catalytic evaluations. Other reactors are also used in FTS for specific objectives like the continuous stirred tank reactor (CSTR). The slurry reactor has some advantages over a fixed bed reactor. The advantages are as follows: better control of temperature, possibility to extract the catalyst from the reactor without disturbing the reaction and better control of reaction hydrodynamics. The slurry reactor is quite expensive and requires large amounts of catalyst and the catalysts in slurry reactor can undergo attrition (Khodakov et al. 2007).

Oukaci et al. examined the behaviour of cobalt FT catalysts in fixed bed and slurry reactors and discovered that the most active catalyst in a slurry bubble column reactor at 3.2 bar was the least active one in a fixed bed reactor at atmospheric pressure (Oukaci et al., 1999).

## 2.4.2 OPERATING CONDITIONS

Product distribution depends on the process operating conditions: reaction temperature, total pressure, $H_2$:CO ratio, reaction time on stream (TOS) and the nature of the catalyst.

### 2.4.2.1 TOTAL PRESSURE

An increase in total pressure results in condensation of hydrocarbons which are in the gaseous phase at atmospheric pressure (Griboval-Constant et al., 2002). Griboval-Constant also reported that high pressures can result in high saturation of the catalyst pores by liquid reaction products. This then affects chemical reaction kinetics. In addition, Khodakov reported that the presence of liquid products on the catalyst surface results in very slow mass transfer (Khodakov et al., 2007). High reaction pressure can also result in restructuring of the catalytic surface which affects the number of active sites present in the catalyst. The rate of catalyst deactivation due to re-oxidization of the metallic FT catalyst particles is accelerated by water produced by high syngas conversions due to high total pressures. This occurs in the case of iron-based Fischer-Tropsch synthesis catalyst, although:

- The catalyst is not truly metallic (the carbide is thought to be the active phase).
- The oxidation of iron carbide yields magnetite, which catalyzes the water gas shift reaction thus limiting the extent to which the water partial pressure increases.

In the case of cobalt and ruthenium-based Fischer-Tropsch synthesis catalyst deactivation due to re-oxidation with the product water is unlikely to occur and is further thought to be independent of pressure (since it is thought to be a function of the ratio of the partial pressure of water to that of hydrogen, i.e. pressure neutral). Increase of total pressure also leads to higher chain growth probabilities.

### 2.4.2.2 REACTION TEMPERATURE

At present there are two FT operating modes, high temperature and low temperature FT processes (Dry, 2002). Both iron and cobalt can be used in the low temperature FT process (220-250 $^{o}$C) which employs fixed bed or slurry reactors for the synthesis

of long chain linear hydrocarbons such as waxes and paraffins (Jager, 1998). High molecular weight products such as high-quality sulfur-free diesel fuels are also produced in large quantities at low temperature Fischer-Tropsch synthesis.

### 2.4.2.3 $H_2$:CO RATIO

The $H_2$:CO ratio has a marked effect on the product composition and the length of chain in FTS. The new HTFT process has involved syngas with a high $H_2$:CO ratio, which is generated by partial oxidation using natural gas as a feed stock (Khodakov et al. 2007). High $H_2$:CO ratios lead to very low olefin content due to re-adsorption of primary olefins on the catalyst surface followed by hydrogenation to paraffins. The oxygenated compounds are also produced in minor quantities under hydrogen-rich conditions.

### 2.4.2.4 THE NATURE OF THE CATALYST

The nature of the catalyst and the number of active sites present are crucial for designing FT catalysts. It has been reported by many researchers that the unsupported metallic FT catalysts are active in FT reactions. The metallic phase was always detected in the active FT catalyst during and after the reaction (for cobalt, ruthenium and nickel catalyst). Fischer-Tropsch reaction occurs on the catalyst metal particles. However, iron carbide is thought to be the active phase in iron based Fischer-Tropsch synthesis.

To achieve a stable yield of long chain hydrocarbons, there is a serious need that the FT catalysts must have the best concentration of catalytic metal active sites. One must avoid loosing a lot of the active component in the support matrix for catalyst stability during FT reaction. This brings about a challenge in the preparation of FT catalysts, since one must prepare a catalyst which is enriched with a number of active sites. The number of active sites depends on the particle size of the active component

(metal catalyst) and its reducibility. The method of catalyst preparation used, catalyst activation process, good catalytic support and promotion with alkali metals or noble metals or metal oxide have to be considered to meet all these requirements needed to generate a better catalyst with a number of FT reaction active sites. Promoters play a crucial role in FT catalysts. The addition of a promoter on FT catalysts has a strong impact on the structure, dispersion, degree of reduction, product selectivity and FT reaction rates (Batley et al., 1975).

## 2.5 THE FISCHER-TROPSCH CATALYSTS

### 2.5.1 INTRODUCTION

Various types of catalysts can be used in FTS. In theory, all transition metals have the capacity to catalyze the FT process; however the most used ones are iron, cobalt, nickel and ruthenium. These metals can dissociatively adsorb CO and $H_2$. The most used metals are iron and cobalt; these metal are only practical catalysts used for industrial applications (Dry, 1981; Anderson, 1984). In the past, iron has been the catalyst of choice in industrial applications due to its low cost and availability (Dry, 1990).

### 2.5.2 IRON (Schulz, 1999)

Iron has a long history as a FT catalyst and was discovered by Fischer and Tropsch in their original research (Dry, 1981). Synthesis gas with lower $H_2$:CO ratios obtained from coal gasification can be used when iron catalysts are employed in FT process because iron is also active for WGS reaction.

Iron catalysts require alkali promotion to achieve high activity and stability e.g. $K_2CO_3$. The deposition of the iron metal on support ($SiO_2$, $TiO_2$, $Al_2O_3$, etc.) for structural promotion is applied on FT iron catalysts and the addition of a promoter (K,

Cu) for olefin selectivity. The main disadvantage of having to support the catalyst is the thermal instability of the supports. Other catalysts supports are thermal unstable e.g. $TiO_2$. The advantage of the support is that a high surface area of the catalyst is obtained (Dry, 1981).

The advantages of iron are as follows:

- Iron is by far cheapest metal to use.
- It has a higher selectivity for olefins (Dry 1993, Schulz 1999).
- It is an active water gas shift catalyst.

The disadvantage of iron catalyst is as follows:

- It deactivates quickly due to oxidation and coke deposition (Dry, 1990).

### 2.5.3 COBALT

Cobalt catalysts have been used extensively as FT catalysts. Activity and selectivity of cobalt catalyst has been investigated as a function of operating conditions by a number of researchers, cobalt catalysts form mainly straight-chain hydrocarbons. Water gas shift activity is low unlike with iron catalysts. The cobalt-based catalysts are in general more active than iron (Schulz, 1999). Because cobalt catalysts are inactive for water-gas shift reactions, a hydrogen-rich synthesis gas with $H_2$:CO ratios of ~2 is required.

### 2.5.4 RUTHENIUM (Schulz, 1999)

Ruthenium was first investigated by Fischer in 1925. Ruthenium catalysts are the most active FT catalysts (Vannice, 1975) and can be used at low reaction

temperatures. It produces high molecular weight wax. It operates as a pure metal without any promoter added to stabilize its activity.

The availability of ruthenium is very limited as the results its price is relatively high. The high price of ruthenium and the limited world resource exclude it from being used at an industrial scale. The main disadvantage of using ruthenium in FT reaction is the use of metal.

### 2.5.5 NICKEL

Nickel was the first FT catalyst to be implemented for commercial production. Nickel-based catalysts are capable of producing high molecular hydrocarbons. On the other hand, nickel-based catalysts tend to produce methane at industrial conditions. In general, nickel is more active in hydrogenation reactions than cobalt which again is more active than iron. Nickel has been reported to be very active when supported on $TiO_2$ (Ho et al. 1992); $SiO_2$ or $Al_2O_3$ (Huang et al. 1987).

### 2.5.6 OTHER FISCHER-TROPSCH CATALYSTS

Most metals of the group 8-10 can be used as catalysts for the FT reaction since these metals can dissociatively adsorb CO and $H_2$. Vannice (1975) established the detailed activity of most group 8-10 metals. These metals were ranked in the order: Ru> Fe>Ni>Co>Rh>Pd>Pt. The most vital metals are iron and cobalt. The relative price of active FT metal catalysts was reported by Dry in 2004 (Dry, 2004).

**Table 2.1:** Approximate relative price of metals for FTS in 2004 (Dry, 2004).

| Metal | Price |
|---|---|
| Fe | 1 |
| Co | 1000 |
| Ni | 250 |
| Ru | 48000 |
| Rh | 700 000 |

It is relatively easy to obtain iron, hence this work involves iron-based catalysts for FT reactions. However, industrial catalysts are made up of three components, the metal, the support and the promoters.

## 2.5.7 PROMOTERS

A promoter is described as a constituent of the catalyst that does not play a part in the catalytic reaction but improves the catalytic properties or structural integrity of the catalyst. Promoters play a crucial role in FT catalysts.

The FT reaction is well-known to give a wide product distribution (Bartholomew, 1991). It is possible to modify this distribution to favour olefins over paraffins due to the use of promoters. The uses of promoters in FT catalysts include:

- Improving the structural features of the catalyst by enhancing the catalyst surface area while maintaining its stability in a catalytic reaction (Forzatti et al., 1984). This kind of promotion is referred to as structural promoter.
- Increasing the catalyst reduction levels, for example when Fe is promoted with Cu which decreases the reduction temperature of iron catalyst (Richardson, 1989). This kind of promotion is referred to as reduction promoter.

Promoters can be divided into three types: chemical, reduction and structural promoters.

### 2.5.7.1 CHEMICAL PROMOTERS

In order to obtain excellent performance of iron FT catalysts, a lot of attempts have focused on the addition of chemical promoters such as $K_2O$ and CuO. Chemical promoters have been always thought to facilitate the reduction of the catalyst as well as the adsorption of and dissociation of CO (Wan et al., 2006). The way in which

promoters affect the catalyst is electronic in nature. This occurs due to changes in the electronic environment of the catalyst surface.

#### 2.5.7.1.1 POTASSIUM

Potassium has long been used as a chemical promoter for iron catalysts. It provides effective changes in catalyst activity and product selectivity (Anderson et al., 1952, Dry, 1981). Potassium has been reported to increase FTS rates on precipitated iron FTS precursors (Anderson et al., 1956, Anderson, 1984). Earlier studies suggested that potassium promotes CO chemisorption, facilitates CO dissociation while inhibiting hydrogen chemisorption (Bell et al., 1986) thus resulting in an increase of CO conversion via water gas shift reaction, formation of carbides and free surface carbon (Dry, 1981). This also results in higher product molecular weight and greater olefin content (Anderson et al., 1951). Potassium titrates the acid sites present in the catalyst and creates some basic sites for the FT reaction. The basicity of potassium has a significant effect on both FT catalyst activity and product selectivity.

The presence of potassium in iron oxide precursors lowers $CH_4$ selectivity and increases $C_5^+$ selectivity (Li et al., 2001). This was found to be due to the limited availability of $H_2$ atoms required for termination of growing chains via hydrogen addition reactions to form paraffins as the adsorption/desorption mobility of hydrogen on promoted FT catalyst is restricted. Potassium is also reported to inhibit secondary reactions of α-olefins, such as isomerization to branched olefins and hydrogenation to n-paraffins (Li et al., 2001).

Although, potassium is known to improve the FTS activity and heavy product fraction, high potassium loading covers the surface of the iron catalyst, resulting in limited promotion effect and a decrease in FTS conversions (Davis et al., 2003). It has been reported that potassium facilitates the desorption of CO and strengthens the Fe-C bond (Wang, 1990). Therefore, potassium enhances the selectivity of long chain products resulting in high-alpha product distribution. The effect of potassium on the behaviour of iron catalysts involves higher chain growth probabilities which result in a higher average molecular weight of the products. Potassium promotion of cobalt catalysts results in a decrease in activity (Liu, 1992), however, effect on selectivity

similar to those on iron catalysts are observed. It is still unclear how $K_2O$ or $K_2CO_3$ interacts with $FeC_x$ species to produce the atomic contact needed for the proposed electronic effect (Liu, 1992).

### 2.5.7.1.2 EFFECT OF OVER-PROMOTING IRON CATALYST WITH POTASSIUM

It is well known that the stronger bases of group 1A metals, especially potassium, are essential promoters in iron Fischer-Tropsch synthesis. They have a marked effect on both activity and selectivity of iron catalyst. Potassium has been shown to increase catalytic activity (Anderson et al., 1952, Dry 1981, Bukur et al., 1990), decrease activity (Dry 1981), and in some cases the activity has been shown to reach a maximum with further addition of potassium (Anderson et al., 1952, Dry 1981). Three levels of potassium were loaded on iron catalysts and the results obtained are shown in **figure 2.8**. At low synthesis gas conversion levels, or low space velocity, the catalyst with the lowest potassium promotion displayed the highest synthesis gas conversion. However, at intermediate conversion levels, the catalyst with intermediate potassium loading exhibited the highest synthesis gas conversion. **Figure 2.8** shows that at the highest conversion levels, the synthesis gas conversion displayed by all three of the catalysts closely approached one another. In addition, the results also showed that the trend in synthesis gas conversion with potassium loading is dependent on the space velocity employed (Davis et al., 1998).

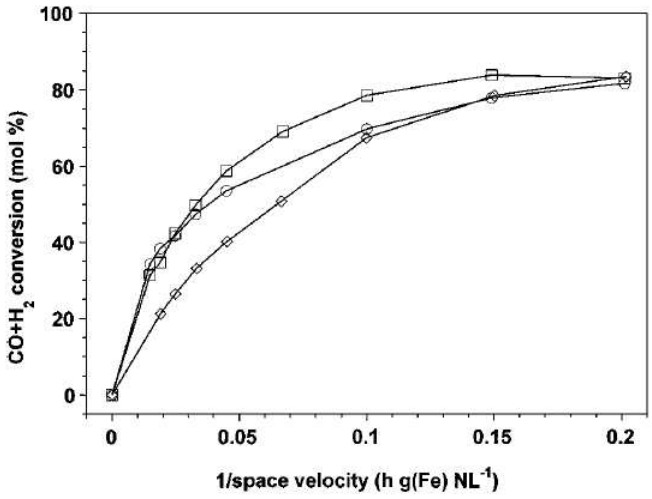


**Figure 2.8:** Synthesis gas conversion as a function of reciprocal flow rate. ○, 0.36 K; □, 1.4 K; ◊, 2.2 K, (Davis et al., 1998).

At low potassium concentration, Bukur reported that potassium promotion enhances Fischer-Tropsch activity (Bukur et al., 1990). In addition, it was reported that the promotion with potassium in the range of 0.2 to 1 wt% increases the activity of the Fischer-Tropsch synthesis and the water gas shift reactions together with the average molecular weight of hydrocarbon and other organic products.

In their findings, they postulated that potassium promotion inhibits iron reduction, and as a result, the potassium-promoted catalyst requires a longer time to achieve the steady-state activity.

Davis and the co-workers reported that potassium also improves the FTS activity and heavy product fraction but high potassium loading covers the surface of the iron catalyst, resulting in limited promotion effect and a decrease in FTS conversions (Davis et al., 2003).

Yang et al. (2004) investigated changes taking place on the surface areas of the Fe-Mn catalysts promoted with different potassium loading. Potassium was found to influence the BET surface area, pore volume, and pore size distribution as illustrated in **Table 2.2**

**Table 2.2:** Effect of potassium promotion on the BET surface area, pore volume and average pore diameter of the potassium promoted Fe/Mn catalysts as prepared (Yang et al., 2004).

| The content of K (wt.%) | 0 | 0.2 | 0.7 | 1.5 | 3.0 |
|---|---|---|---|---|---|
| Specific area ($m^2/g$) | 52 | 30 | 26 | 19 | 17 |
| Volume of pore ($cm^3/g$) | 0.27 | 0.23 | 0.23 | 0.18 | 0.16 |
| Average pore diameter (nm) | 20.57 | 30.85 | 35.75 | 34.61 | 35.86 |
| Fe/Mn atomic ratio | | | | | |
| Bulk | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 |
| Surface | 3.4 | 2.3 | 2.4 | 2.0 | 2.1 |
| K/Fe ($\times 10^2$ atomic ratio) | | | | | |
| Bulk | 0 | 0.5 | 1.6 | 3.4 | 6.9 |
| Surface | 0 | 0.7 | 2.5 | 4.7 | 8.7 |

The results showed that at high potassium loading, the catalyst has lower specific surface area and pore volume (Yang et al., 2004, Dry 1968). The decrease in specific surface area was found to be attributed to the fact that potassium could improve the agglomeration of the FeOOH precursor and could further enlarge the crystallite size of $\alpha$-$Fe_2O_3$ after being calcined at 773K for 5 h which would induce the surface area. Li et al. has discovered opposite results from these ones (Li et al., 2001). The discrepancy in this case was found to be due to different methods of catalyst preparation (Yang et al., 2004). In addition, the pore diameter of the catalyst increases with increasing potassium content. They concluded that the loss of surface area is due to crystallite growth. XPS analysts revealed that K/Fe atomic ratio on the surface is larger than in the bulk which suggests that potassium is concentrated on the surface of the catalyst. In addition, Fe was also found to be concentrated on the catalyst surface. Moreover, XRD results investigated that after potassium promotion, the peak intensity of $\alpha$-$Fe_2O_3$ increases. This suggests that the addition of potassium on iron-manganese catalyst promotes the aggregation of $\alpha$-$Fe_2O_3$ crystallite, therefore the peak intensity of $\alpha$-$Fe_2O_3$ increases with the addition of potassium (Yang et al., 2004).

#### 2.5.7.1.3 EFFECT OF PROMOTING IRON CATALYST WITH POTASSIUM ON THE WATER GAS-SHIFT REACTION

The water gas shift reaction is a side reaction which is catalyzed by iron catalysts. This reaction makes the iron catalysts flexible towards the $H_2$:CO feed ratio of the synthesis gas. For synthesis gas with low $H_2$:CO feed ratio, the extent of the water gas shift reaction is very important in achieving a high conversion of carbon monoxide. The degree of the water gas shift reaction increases with potassium loading which implies that the overall Fischer-Tropsch synthesis activity should be the highest for the iron catalyst with the highest potassium promotion (Davis et al., 1998).

### 2.5.7.2 REDUCTION PROMOTERS

Generally, FT catalysts with high degrees of reduction are more active. Iron oxide precursors are synthesized as hematite ($\alpha$-$Fe_2O_3$) and must be subjected to activation treatment before they become active for FTS. However, ferrihydrite as a precursor can also be present which results in an active catalyst. During catalytic activation or reduction, a number of phases are known to be present and these include the metallic iron, iron oxides and iron carbides. At high temperatures, iron catalysts lose surface area due to increase in crystallite size (sintering). Copper is frequently used in iron FT catalysts for reduction promotion. Noble metals such as Pt, Pd and Ru are generally used in cobalt-based FT catalysts. Many researchers have reported that copper, when present, increases the reduction level which results in activity enhancement without any changes in selectivity (Davis et al., 1997, Li, 2002).

#### 2.5.7.2.1 COPPER

Copper is generally used as a promoter for iron FT catalysts. It is added to the catalyst as a promoter to increase the rate of $Fe_2O_3$ reduction to $Fe_3O_4$ in hydrogen. This is most likely to be due to a hydrogen spill-over process from the reduction

promoter to the metal oxide (Haggin, 1991). Copper provides a better dispersion of the active phase ($Fe_3O_4$ or $Fe_xC_y$) and greater availability of active sites.

It was reported that the presence of copper on iron FT catalysts predominantly influences the intrinsic oxygen removal selectivity by promoting the removal of oxygen using CO (Li et al., 2001). Copper also introduces some active sites with low chain growth probability and high olefin hydrogenation activity. Copper can also minimize the sintering of iron catalysts by lowering the reduction temperature (Dry et al., 1981). Dry reported that the role of copper is also to allow lower reduction temperatures and yield catalysts with a higher activity than monometallic iron catalysts. The presence of copper on iron FT catalysts lowers the rate of carbon formation on the surface of the catalyst (Anderson, 1956; US Patent, 1975). In addition, many patents published have reported that copper improves the selectivity for oxygenated compounds (Deutsches Patentschrift, 1955; Deutsches Patentschrift, 1956).

### 2.5.7.3 STRUCTURAL PROMOTERS OR SUPPORTS

In order to obtain excellent performance of FT iron-based catalysts, structural promoters ($SiO_2$, $Al_2O_3$, ZnO, $TiO_2$ and MgO) are incorporated into them. Silica was found to be the most preferable one in terms of both activity and selectivity (Yang et al. 2005, Dlamini et al., 2002). Structural promoters serve the purpose of improving the attrition resistance and stability (Vannice et al., 1980; Jung et al., 1982; Pham et al., 2000; Zhao et al., 2001). It has been generally observed that the nature of the support greatly affects catalytic performance. Both the structure and the performance of FT catalysts depend on the catalyst support. The selection of a suitable support is regarded as one of the key aspects for designing a stable catalyst for FT reaction. The choice of support has a significant effect on the activity and selectivity of the catalysts due to metal-support interactions (Vannice, 1992). Supported nickel catalysts have shown an enhancement in activity and have long life without obvious deactivation through the selection of a suitable support.

Supports are usually metal oxides which have a high surface area, porosity, good mechanical properties and relative inertness. The support is used to maximise the dispersion of the active phase (metal). The interaction between the metal and support hinders the reducibility of the catalyst precursor (Tauster, 1978). Supported catalysts with very strong metal-support interaction tend to be reduced at temperatures higher than expected.

Different kinds of supports have been employed in FT processes, these include alumina, silica, titania, zirconia and magnesia (Sewell et al., 1996). It was shown that impregnated zirconia improves activity of $Co/SiO_2$ for FTS by creating a protecting layer preventing major interactions or reaction between silica and cobalt with formation of cobalt silicate, which can be reduced only at elevated temperature (above 800K) (Oukaci et al., 1999).

Moradi and co-workers conducted a study of a promotion of $Co/SiO_2$ FT catalysts with zirconium (Moradi et al., 2003). They found that zirconium as a promoter has an effect on the product distribution. The $C_5^+$ selectivity and $C_{10}^+$ fraction increased with the addition of Zr. This was found to be due to the higher amount of the surface cobalt metal present at the steady-state and to the larger cobalt particle size. The increase in particle size of cobalt was attributed to the presence of Co-Zr interactions instead of $Co\text{-}SiO_2$ interactions which resulted in increase in degree of reduction of cobalt (Moradi et al., 2003). Silica was reported as the best support for iron-based catalysts in terms of activity and wax production (Eilers et al., 1997). This study focuses mainly on silica and it is the only support used.

Eilers and the co-workers discovered that silica is the best support for iron-based FT catalyst (Eilers et al., 1997), the reason being that it maintains the surface area and can modify the texture of the catalyst (Dry, 1983; Bartholomew et al., 1986). Silica maintains high metal dispersion thereby increasing the concentration of active metal sites. It also improves the ageing characteristics of the catalysts.

Kresge and the co-workers also performed a study to determine the effects of silica as a binder and process conditions on the activity, stability and selectivity of precipitated

iron catalyst. They discovered that the addition of silica to the precipitated unsupported iron catalyst resulted in decreased activity with increasing support content and that the catalyst was more stable with the addition of silica. They reported that total olefin content decreased but the fraction of the internal olefin increased with an increase in silica content respectively (Kresge et al., 1992).

#### 2.5.7.3.1 SILICA ($SiO_2$)

Silica is a group IV metal oxide, which has good electrical insulation and high thermal stability. It is one of the common chemical compounds. It exits in three polymorphic forms, silica sand, sandstone and quartzite, the most common of which is quartz. It is insoluble in all acids with the exception of hydrogen fluoride (HF). It is used as supports for metal catalysts. In this research silica is used as a support for iron FT catalysts.

$SiO_2$ has been extensively investigated as a structural promoter by many researchers (Cagnoli et al., 1990). It was found to the most preferable structural promoter (Dlamini et al., 2002). In recent years, $SiO_2$ was chosen as a principal structural promoter for the preparation of iron FT catalysts with high attrition resistance using co-precipitation method of catalyst preparation. The impact of $SiO_2$ content on the reduction and catalytic performances over precipitated Fe-Mn catalyst was investigated by Yang and the co-workers (Yang et al., 2005). The results investigated that a small amount of $SiO_2$ incorporated into Fe-Mn catalyst decreases the catalyst crystalline size, favors the reduction of $Fe_2O_3 \rightarrow FeO$, enhances the selectivity to heavy hydrocarbons and improves the catalyst stability.

$SiO_2$ was chosen as a support, because of its high surface area, good mechanical properties and relative thermal stability. It has also been extensively employed as a support for Co FT catalysts by many workers (Moradi et al., 2003).

# 2.6 CHANGES WITHIN THE CATALYST DURING FT SYNTHESIS

## 2.6.1 PHASE CHANGE

In recent years, there have been several studies attempting to characterize iron FT catalysts with a view to understanding the phase transformation in the catalyst as a result of exposure to various activation and reaction treatments and to identify the active catalytic phase. During synthesis conditions iron FT catalysts are vulnerable to phase changes. This might affect the characteristics of the catalyst. Under normal synthesis conditions to a lesser extent Co and Ni are also exposed to such phase changes. Ru is the least prone to changes (Dry, 1981).

## 2.6.2 IRON PHASE

FT iron catalysts are synthesised as hematite ($\alpha$-$Fe_2O_3$) or ferrihydrite. Iron oxide catalyst precursors undergo a series of phase changes during activation and use in FTS. The hematite phase must be reduced to the metallic phase before FT reaction. During catalyst reduction, most of the iron is converted to the metallic phase. When the FTS begins, the reduced iron transforms into the carbide or the magnetite phases. Which one of the two is active phase during FT reaction remains a question. Many researchers have reported that magnetite is the predominant iron phase in a sample of mature catalyst. The relative amount of each phase depends on the degree of reduction (Espinoza et al., 1999). Espinoza reported that a degree of reduction of at least 70% is necessary to achieve the maximum in catalyst stability (Espinoza et al., 1999).

## 2.6.3 CATALYST DEACTIVATION

### 2.6.3.1 INTRODUCTION

Catalyst deactivation is the loss of catalytic activity or selectivity over time. It is a phenomenon in which the structure and state of the catalyst change, resulting in loss of active sites on the catalyst surface. It is attributed to interactions (physical or chemical) between the catalyst and the impurities present in the feed. Catalyst deactivation is a result of a number of unwanted chemical or physical changes. In most cases, deactivation leads to the replacement of an aged catalyst to a new one, and the shortened catalyst lifetime. The causes of catalyst deactivation are divided into five basic kinds: chemical deactivation through reversible and irreversible poisoning, physical deactivation through fouling, thermal deactivation through sintering, loss of active material by vaporization and mechanical deactivation through attrition (Bartholomew, 2001).

During FTS, catalysts may undergo certain changes in structure and lose in activity due to poison by contaminants such as sulphur in the feed (Bromfield, Coville, 1999; Bartholomew, 1987). The surface of the catalyst may be contaminated by means of carbon produced by cracking reactions of hydrocarbon reactants or products (Trimm, 1983). When iron FT catalysts are exposed to high temperatures during the activation process, crystalline growth or sintering occurs; this gives rise to a loss in surface area and may deactivate the catalyst (Bartholomew, 2001). The formation of $CO_2$ (due to water-gas shift reaction) and $H_2O$ (from FT reaction) can cause a transformation in the oxidation state of catalytically active phase (Dry, 1981; Jager, Espinoza, 1995). Therefore catalyst deactivation with time on stream is brought about by three factors: poisoning, fouling, thermal degradation (sintering/oxidation/evaporation).

Deactivation mechanisms i.e. coke formation, poisoning, sintering of the active metal particles, sintering and solid-solid phase transitions of the washcoat and encapsulation of active metal particles are summarized in **figure 2.9** (Suhonen, 2002).

### 2.6.3.2 POISONING

Poisoning is defined as a loss of catalytic activity due to the chemisorption of impurities on the active sites of the catalyst. The most common poisons for FT catalysts are: $H_2S$, COS, arsenic, $NH_3$ and metal carbonyls (Bartholomew, 1991). Fe, Co and Ru are very sensitive to poisoning by sulphur-containing compounds such as $H_2S$. The origin of these sulphur-containing compounds is coal that is used to produce the synthesis gas. A few parts per million of sulphur containing compounds in the feed can deactivate iron FT catalysts (Dry, 1981; Bromfield, Coville, 1999). For that reason, one has to devise with ways of removing sulphur-containing compounds from the feed (synthesis gas). For example at Sasol, the sulphur containing gases are removed in the "Rectisol" process (cold methanol scrubbing) which lowers the sulphur content very well (Dry, 1990).

Chlorine was also discovered as a strong poison for iron FT catalysts (Dry, 1999). The acidic compounds present in the feed (synthesis gas) or catalyst can drastically reduce catalyst activity and the life of the catalyst.

Espinoza et al. speculated that if a low rate of sulphur poisoning takes place while there is still a reduced iron core in the middle of the catalyst, the sulphur may poison some crystallites already separated from the core, but that new area is subsequently exposed for reaction (Espinoza et al., 1999). He claims that in this case a very low level of sulphur poison would reduce the catalytic activity, but some recovery should take place as the new area is exposed. According to this assumption, the degree of recovery is a function of the age of the catalyst. No recovery would occur on a completely mature catalyst. Therefore, though sulphur is generally considered as a poison for FT catalysts, there are still some disagreements in the literature. These involve the amount of sulphur required to deactivate the catalyst, the rate at which it acts as a poison for the catalyst and the catalyst tolerance.

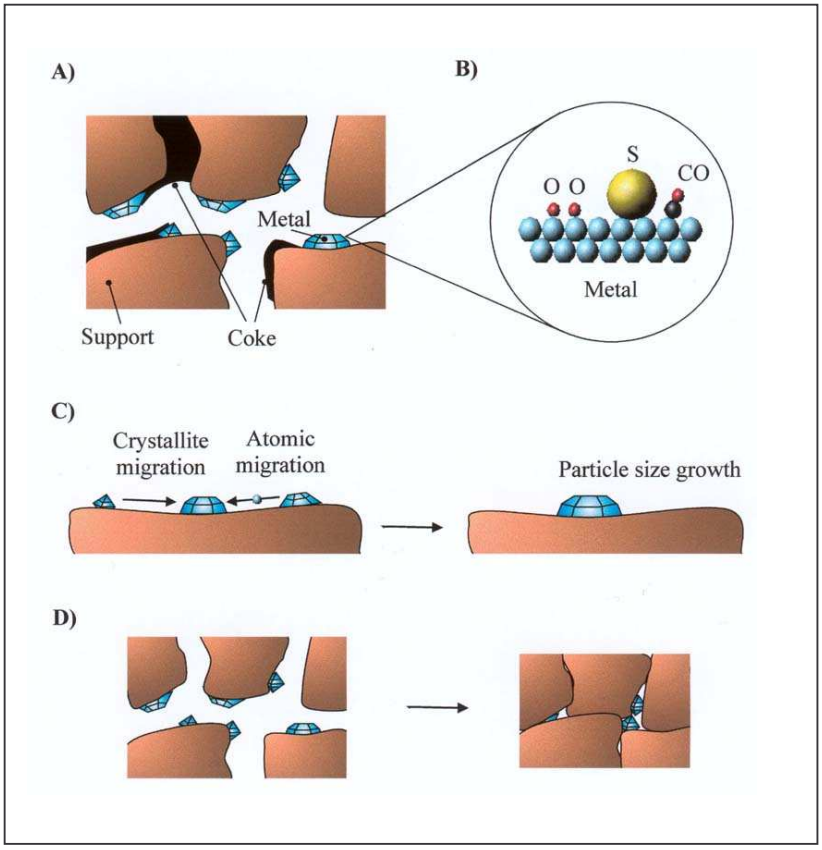


**Figure 2.9:** Deactivation mechanisms A) Coke formation, B) Poisoning, C) Sintering of the active metal particles and D) Sintering and solid-solid phase transitions of the washcoat and encapsulation of active metal particles (Suhonen, 2002).

### 2.6.3.3 FOULING

Fouling is the accumulation and deposition of living organisms or non-living materials on a hard surface i.e. deposition of anything on the catalytically active surface. It was discovered that carbon deposition on the surface of the FT catalysts result in lower activity (Dry, 1990). Carbon formation during FT process causes the structure of the catalysts to change from the freshly reduced catalyst to the fully mature catalyst. This occurs via the Boudouard reaction (equation 2.3).

Disproportionation of CO leads to the formation of carbon which causes catalyst deactivation. As the amount of carbon increases, the small reactive iron particles

separate within the main catalyst particles. As the catalyst ages, it swells due to the increasing carbon content and the iron core shrinks. As a result, the morphology of iron catalyst changes during the FT process.

When iron is used in the FT process, the rate of carbon deposition was found to be extremely high that after a few months, the amount of carbon deposited on the surface will be equal to the amount of iron present in the catalyst but the catalyst does not lose its activity (Dry, 1990).

Carbon deposition in fluidised beds is reported as the main problem in FT processes because the bed expands and the reactor loses the fine catalyst. When carbon-rich aromatics deposit on the catalyst surface, the catalyst loses its activity.

### 2.6.3.4 SINTERING

Temperature has become increasingly recognized as an important factor for the deactivation of FT catalysts. During catalytic activation (thermal treatment), the catalyst loses surface area due to crystallite growth (sintering) of the catalytically active phase (Wanke, Flynn, 1975; Bartholomew, 2001). Sintering is probably the main cause for the deactivation of FT catalysts. It is a physical process leading to a catalyst deactivation at high temperatures because of the loss of catalytic surface area due to crystal growth of the catalytic phase. In the case of supported metal catalysts, the loss of surface area occurs via agglomeration of small metals into larger ones (Gunter et al., 1997). Two different representations have been suggested for sintering: the atomic migration and the crystallite migration representations. Sintering occurs either due to metal atoms migrating from one crystallite to another via the surface or via the gas phase by diminishing small crystallites in size and increasing the larger ones (atomic migration model) (Bartholomew, 2001). **Figure 2.9 c** shows a schematic representation of atomic migration and crystallite migration models.

Sintering processes are directly linked to the melting temperature as defined by two semi-empirical relations, involving the so-called Huttig (2.5) and Tamman (2.6)

temperatures. Sintering is strongly dependent on temperature (Forzatti, Lietti, 1999). At the Huttig temperature, surface recrystallization occurs and bulk recrystallization occurs at the Tamman temperature.

Moulijn reported that the temperature at which the solid phase becomes mobile depends on texture, size, and morphology (Moulijn et al. 2001). When temperature increases the mobility of atoms increases as well (Moulijn et al., 2001). He also recommended that the two semi-empirical relations for Hüttig and Tamman temperatures may be used (with T measured in K):

$$T_{Hüttig} = 0.3T_{melting} \quad (2.5)$$

$$T_{Tamman} = 0.5T_{melting} \quad (2.6)$$

In most cases, supported metal catalysts are used for FT processes and experimental observations show that supported metal catalysts sinter quickly under oxidizing atmospheres (Wanke, Flynn, 1975). Sintering is a common problem in FT processes and can result in catalytic deactivation. Therefore ways of avoiding it should be pursued, and employed to avoid such deactivation.

## 2.7 EFFECT OF TEMPERATURE PRE-TREATMENT (CALCINATION) OF THE CATALYST ON THE PERFORMANCE OF THE CATALYST

There is a strong advantage with respect to reducibility by decreasing the number of calcinations steps used to prepare the catalyst. For example, figure 2.9 shows profiles for two different series of rhenium promoted 15 % $Co/Al_2O_3$ catalysts. The difference between the two series of catalysts is the method of catalyst preparation. The dark line spectra correspond to catalysts prepared by loading the Co by three successive incipient wetness impregnation (IWI) steps followed by loading of the promoter, in this case the catalyst was dried between the each impregnation step. Only one

calcination step was used after loading the promoter. The other series of the catalyst was prepared in the same approach, except that the catalyst was calcined after each impregnation and drying step for four times. The TPR traces investigate the effect of calcination on the reducibility of Co catalyst. The dark line spectra correspond to catalyst prepared with one calcination step after the loading of the promoter. The results showed that calcining the catalyst result to a retard in its reduction temperature. Jacobs et al. suggested that excessive calcination increases the formation of Co surface support species, which are more difficult to reduce (Jacobs et al., 2002). The results are displayed in **figure 2.10** below.

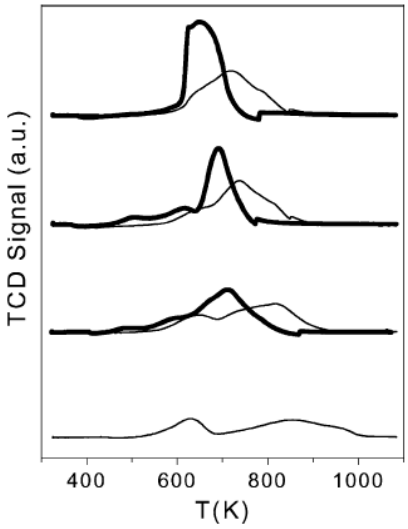


**Figure 2.10:** TPR spectra of the unpromoted and promoted $Co/Al_2O_3$ catalysts with different loading of rhenium with (light) and without interval calcination (dark).

In addition, work done by Zhao et al. showed that with increasing calcination temperature, the surface area of zirconia support decreased while the average pore diameter was increasing (Zhao et al., 2003). In addition, upon loading cobalt on the support, the catalysts showed a drastic change in the surface area (smaller than the counterparts support). This is due to the fact that cobalt crystallites blocked the pores of the support material. **Table 2.3** shows that at low calcination temperature, the cobalt crystallites blocked the smaller pores of the support thereby increasing the pore

diameter of the support material. The supports (Zr120 and Zr400) displayed lower pore diameter than their counterparts CoZr120 and CoZr400 and this suggests that when these samples were calcined at 120 and 400 $^{o}$C, the cobalt crystallites blocked the pores of the supports thereby increasing the pore size of the support.

However, Zr600 and Zr400 showed larger pore size as compared with their counterparts CoZr600 and CoZr800. This means that at high calcination temperatures (600 and 800 $^{o}$C) the pores of the support material increases in such a way that the cobalt fits and gets adsorbed on the inner wall and therefore the average pore diameter of CoZr600 and CoZr800 decreased (Zhao et al., 2003).

**Table 2.3:** Textural properties of samples (Zhao et al. 2003).

| Samples | BET/$m^2 \cdot g^{-1}$ | Pore diameter/nm |
|---|---|---|
| Zr120 | 349 | 3.1 |
| Zr400 | 101 | 6.6 |
| Zr600 | 32 | 17.6 |
| Zr800 | 15 | 25.5 |
| CoZr120 | 133 | 4.8 |
| CoZr400 | 68 | 6.7 |
| CoZr600 | 26 | 14.7 |
| CoZr800 | 13 | 22.5 |

Moreover, XRD results showed that the particle size of cobalt increases with calcination temperature. This is investigated by the increase in the intensity of the diffraction peaks pertaining to $CoO_3$ phase present. The results are displayed in **figure 2.11** respectively as discovered by Zhao et al., 2003.

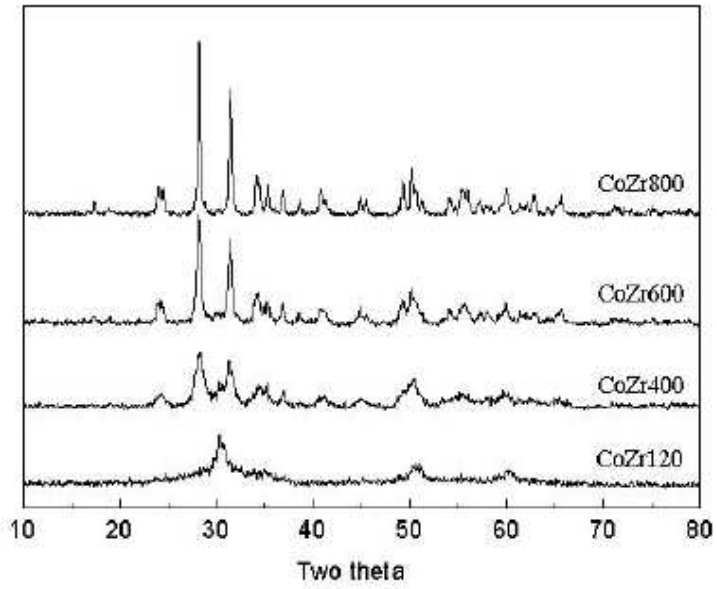


**Figure 2.11:** XRD profiles of $CoZrO_2$ catalysts (Zhao et al., 2003).

# 2.8 METHODS OF CATALYST PREPARATION

## 2.8.1 INTRODUCTION

The catalytic properties of heterogeneous catalysts are strongly affected by each and every step of preparation. The choice of a method of catalyst preparation depends on the physical and chemical characteristics desired in the final composition. Even though catalyst procedures differ significantly from one catalyst to another, three broad categories can be introduced to classify the catalysts with respect to the preparation method: bulk catalysts and supports and impregnated catalysts.

Bulk catalysts such as silica-alumina for hydrocarbon cracking, Zn-Cr oxide catalyst for conversion of $CO$-$H_2$ mixtures to methanol and iron-molybdate for methanol oxidation are mainly comprised of active substances (Perego et al., 1997). Impregnated catalysts are typically obtained from preformed supports by impregnation with the active phase (Kolthoff et al., 1973).

Main unit operations for bulk catalysts and support preparation are: precipitation (Kolthoff et al., 1973), gelation and flocculation, hydrothermal transformation, decantation, filtration, centrifugating and, drying, calcination, forming operations and forming grains.

The catalyst performance of FT catalysts strongly depends on the method of catalysts preparation. Catalyst preparation can be divided into chemical synthesis steps, the calcination step and the activation step (reduction).

## 2.8.2 SUPPORTED CATALYSTS

Supported catalysts are preferred catalysts because they provide a high dispersion of the active phase on the support and a high degree of thermostability of the catalytic component (Che et al., 1997). The most common preparation methods for supported catalysts are: precipitation and impregnation methods.

Ion-exchange and deposition of organometallic compounds on the support material, eggshell catalyst, sol-gel method, plasma method and chemical vapour deposition are the other methods of catalyst preparation but are used less frequently.

It is very important to select a good support for chemical catalysts. A good support is required to have the following characteristics: inertness, resistance towards attrition, hardness, compressive strength, stability under reaction and regeneration conditions, high surface area, porosity and low expense.

There is quite a diversity of supports which can be used, but only a few possess these characteristics: alumina, silica and activated carbon (Che et al., 1997). Alumina and silica are most widely used ones.

Both supported and unsupported catalysts can be used in FT processes.

### 2.8.2.1 PREPARATION OF SUPPORTED FT CATALYSTS

Unsupported FT catalysts are normally prepared by precipitation methods whereas supported catalysts are normally prepared by precipitation or impregnation methods.

#### 2.8.2.1.1 PRECIPITATION METHOD

Precipitation involves two steps: precipitation of solution in bulk and pore fluid and interaction with the support surface (Perego et al., 1997).

Precipitation has been commonly used for the preparation of iron and cobalt FT catalysts. In the precipitation method, the precursor of the active metals, are dissolved in water to form a homogeneous solution. A homogeneous solution is allowed to stir at room temperature while adding a precipitating agent ($NH_4$ solution) dropwise to precipitate the metal ions. The pH is adjusted to force the metal ions to precipitate. The pH adjustment can be done in the presence of a support material or the support material can be formed via co-precipitation (Dry, 1981). In general, co-precipitation yields much smaller metal crystallites on the support (Bartholomew, 1984) compared with impregnation techniques. The precipitation method is preferred to the deposition route for loadings higher than 10-20%. Below this value, impregnation is usually applied.

#### 2.8.2.1.2 IMPREGNATION METHOD

The impregnation method involves three steps: contacting the support with impregnating solution for a certain period of time, drying of the support to remove excess liquid and activating the catalysts (calcination and/or reduction).

Incipient wetness impregnation is the most common method used to prepare iron/cobalt-supported FT catalysts. In the incipient wetness method, a solution of

iron/cobalt nitrate salt is contacted with a dry porous support. The incipient wetness takes place when all pores of the support are filled with the liquid and there is no excess liquid required the fill the pores (Khodakov, 2007). The amount of water to be used depends on the pore volume of the support material. Immediately after impregnation, the interaction between the metal precursor and the support is relatively weak, this allows redistribution of the active phase over the support during drying and calcination (Khodakov, 2007). Liquid is then removed by drying, this step is followed by calcination (further heat treatment beyond drying) resulting to a catalyst precursor. The impregnation method was discovered to be the fast method of catalyst preparation (Huang and Schwarz, 1987).

However, in most cases it is not easy to prepare catalysts with high metal loadings and to obtain good dispersion of the metal on the support by means of impregnation method (Dry, 1981).