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The effect of microwave treatment on potassium promoted iron Fischer-Tropsch catalysts

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Chapter 2

Literature review: Fischer-Tropsch synthesis

2.1 History and background information

Fischer-Tropsch synthesis (FTS) is an important gas-to-liquids (GTL) technology which converts syngas derived from coal, natural gas or biomass to transportation fuels and petrochemical substituents by the use of a catalyst.[1,2] This process is a promising option for environmentally sound production of chemicals and fuels from coal since the reserves of crude oil are being depleted and the price of crude oil continues to rise. The process was named after Franz Fischer and Hans Tropsch who discovered the process in 1923 by converting a mixture of carbon monoxide and hydrogen to hydrocarbons using an iron catalyst.

The early 20th century was a landmark period for industrial catalysis. It was an era of great discoveries.[3] The fact that a hydrocarbon (methane) could be catalytically produced from carbon monoxide and hydrogen over a nickel or cobalt catalyst at atmospheric pressure was first reported by Sabatier and Senderens in 1902.[4] In 1913 the Badische Anilin und Soda Fabrik (BASF) of Ludwigshafen, Germany, revealed that mixtures of higher hydrocarbons and oxygenated compounds could be catalytically produced from a similar mixture under high temperatures and pressures.[5] However, the greatest breakthrough in the conversion of carbon monoxide into liquid hydrocarbons was made by Franz Fischer and Hans Tropsch in 1923 at the Kaiser Wilhelm Institute for Coal Research (presently Max Plank Institute) in Mülheim, Germany. These scientists reported obtaining synthol, a mixture of hydrocarbons and oxygenated compounds, from the reaction of H_2 and CO over alkalized iron at 400-450 ^{o}C and 150 atmospheres pressure.[6] To test the usefulness of the products as transportation fuels, the oil layer was separated from the aqueous layer, de-acidified and fractionated by distillation and then subsequently road tested using a 1922 model NSU motorbike carrying two persons. The results were reported to be encouraging with the performance appearing to be similar to, or better than, a reference fuel. This, indeed, marked the beginning of an industry for the production of transportation fuels from synthesis gas.[3]

2.2 Industrialization of the Fischer-Tropsch process

The first Fischer-Tropsch plant was operated by Ruhrchemie AG in Oberhausen, Germany, in 1936 after acquiring exclusive patent rights to the FT process in 1934.[7] This small-scale plant had 52 reactors operated at atmospheric pressure, and it had a production capacity of 70 000 tonnes per annum. By 1938, nine plants with a combined production capacity of about 660 000 tonnes per annum were in operation.[8]

In South Africa, in 1955, the first large-scale plant was operated by the South African Coal, Oil and Gas Corporation's (SASOL) at Sasolburg. This plant, known as Sasol I, operated on fixed-bed Arge technology reactors, using a precipitated iron catalyst supported on silica and promoted by copper and an alkali.[9] Thereafter came two large-scale plants in 1980 and 1982 (Sasol II and Sasol III), promoted by the extremely cheap domestic coal and the particular state policies in South Africa. Sasol II and Sasol III initially operated using circulating fluidized-bed (CFB) reactors which were later improved to the Sasol Advanced Synthol (SAS) technology.

Later two FT plants operating on offshore methane were also built in South African and Malaysia. The first one, which was commissioned in 1992, was the Mossgas plant (now known as PetroSA), with a production capacity of 20 000 barrels per day. The second one was the Shell Bintuli plant (Malaysia) which produces 15 000 barrels per day. This plant was commissioned in 1993 and it utilizes the Shell middle distillate synthesis (SMDS) fixed-bed technology.[10]

In 2005 Oryx GTL, which is a joint venture between Sasol and Qatar Petroleum, commissioned another gas-to-liquid plant in Qatar in alliance with Chevron. The plant was strategically constructed at the Ras Laffan industrial city complex (Qatar) which is in close proximity to large natural gas reserves in the North of Qatar. The plant operates on Sasol's slurry phase technology, with a daily production capacity of 34 000 barrels per day. Since 2005 many FT plants have been planned or are being constructed by ExxonMobil, Syntroleum, BP, and Chinese companies. Not only gas-to-liquid (GTL) but also coal-to-liquid (CTL) and biomass-to-liquid (BTL) technologies have been developed with FTS as the key step.[11,12] A summary of other plants that have been or are yet to be commissioned are listed in Table 2.1.

Table 2.1 Currently operating and announced FT plants, together with the industrial companies and countries involved, the catalyst technology used, the expected production levels (barrels per day, bpd) and the expected year of start-up.[10]

Year	Company or companies	Technology	Production level (bpd)	Country
1955	Sasol	Sasol I	500	South Africa
1980	Sasol	Sasol II	11 000 (later 20 000)	South Africa
1982	Sasol	Sasol III	11 000 (later 20 000)	South Africa
1992	PetroSA	Sasol's slurry phase technology	20 000	South Africa
1993	Shell	Shell middle distillate synthesis (SMDS) fixed-bed technology	15 000	Malaysia
2005	Sasol and Qatar Petroleum, in alliance with Chevron	Sasol's slurry phase technology	34 000	Qatar
2007	Chevron Nigeria (Sasol/Chevron alliance) and Nigeria National Petroleum Company	Sasol's slurry phase technology	34 000	Nigeria
2009	Shell and Qatar Petroleum	Shell middle distillate synthesis (SMDS) fixed-bed technology	140 000	Qatar
2011	Exxon Mobile and Qatar Petroleum	Advanced gas conversion for the 21st century (AGC-21) technology	154 000	Qatar

2.3 The Fischer-Tropsch chemistry

2.3.1 Reactions

FTS is a polymerization reaction which produces various oligomers regularly distributed along the carbon number range.[13] The chemical reactions that take place in FTS can be sub-divided into [A] main reactions, [B] side reactions and [C] the reactions responsible for catalyst modification, as shown in equations 2.1 to 2.8.

[A.] Main reactions:

Paraffin formation:

$$n\mathrm{CO} + (2n + 1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O} \qquad (2.1)$$

Olefin formation:

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} \qquad (2.2)$$

Water-gas shift (WGS) reaction:

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad (2.3)$$

[B.] Side reactions:

Alcohol production:

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{H_2O} \qquad (2.4)$$

Boudouard reaction:

$$2\mathrm{CO} \rightarrow \mathrm{C} + \mathrm{CO_2} \qquad (2.5)$$

[C.] Catalyst modifications:

Catalyst oxidation/ reduction:

a. $\mathrm{M}_x\mathrm{O}_y + y\mathrm{H_2} \leftrightarrow y\mathrm{H_2O} + x\mathrm{M}$ (2.6)

b. $\mathrm{M}_x\mathrm{O}_y + y\mathrm{CO} \leftrightarrow y\mathrm{CO_2} + x\mathrm{M}$ (2.7)

Bulk carbide formation:

$$y\mathrm{C} + x\mathrm{M} \leftrightarrow \mathrm{M}_x\mathrm{C}_y \qquad (2.8)$$

where n is the carbon number. Depending on a number of factors, primarily the hydrogen to carbon monoxide ($\mathrm{H_2/CO}$) ratio in the syngas and the type of catalyst

employed, either paraffin formation (eqn. 2.1) or olefin formation (eqn. 2.2) predominates the synthesis.[14] Whereas the formation of paraffins is favoured by high H_2/CO ratios and catalysts with strong hydrogenating abilities, the formation of olefins is favoured in syngas with low H_2/CO ratios and a catalyst with less strong hydrogenating abilities. Apart from hydrocarbons, H_2O is also a primary product from FTS.[15] The presence of water is undesirable in FTS since it affects syngas conversion, hydrocarbon selectivity, FT product distribution and the catalyst longevity due to its influence on the degree of syngas adsorption on the catalyst, chain initiation, chain growth, methanation, hydrogenation to paraffins and dehydrogenation to olefins.[16] It is believed that a high H_2O concentration is one factor that leads to oxidation and deactivation of iron carbides,[17-20] and therefore understanding H_2O formation and desorption is important for enhancing FTS activity.

The water-gas-shift reaction (eqn. 2.3) consumes CO and water, formed in the FTS reaction, and converts the reactants to hydrogen and carbon dioxide. WGS activity is normally high over potassium-promoted iron catalysts and it is negligible over cobalt or ruthenium catalysts. This reaction helps to make up the deficit of H_2 in the syngas,[21,22] making iron based catalysts a better choice for coal-based FTS. Alcohols and oxygenates are also produced during FTS, in particular, for precipitated iron-based catalysts.[23-26] It has been reported[27] that oxygenate formation increases with potassium content, but there is an optimized potassium content for oxygenate yield over precipitated iron catalysts.[23,26] Dictor *et al.*[25] and Bukur *et al.*[28] have reported that potassium suppresses the formation of methanol and increases the formation of higher molecular weight alcohols.

Catalyst activation in FTS is done by reducing the catalysts with either H_2 (eqn. 2.6), CO (eqn. 2.7) or syngas. A cobalt catalyst is usually activated with H_2 and the metallic cobalt produced is believed to be the active phase for FTS in these catalysts.[29] However, it has been reported[18,30-34] that the reducing pre-treatments with H_2, CO or syngas often have significant effects on catalytic activity and selectivity for iron-based catalysts. For instance, for unsupported iron-based catalyst systems, H_2-reduced samples show lower activities for FTS than the CO- and syngas-reduced samples.[18] It has been reported that the reduction of iron-based samples with H_2 leads to a metallic state (α-Fe), and CO or syngas reduction leads to the metallic state and

small amounts of iron carbides. Dictor and Bell[25] have proposed that the active phase for FTS in iron catalysts is a mixture of χ- and γ-iron carbides.

2.3.2 Proposed mechanisms

The Fischer-Tropsch reaction mechanism has been, and still is, a topic of discussion ever since the first FTS mechanism was proposed in the original paper by Fischer and Tropsch.[35,36] One point of contention is whether the chemisorbed CO molecule participates as such in the chain growth or whether it first dissociates to C and O atoms. In the latter case, the C atom is hydrogenated to a CH_2-type species which participates as such in the chain growth.[37] In general, the FT reaction is widely recognised to follow the sequence: reactant adsorption - chain initiation - chain growth - product desorption – re-adsorption of reactive products and further reaction. Several reaction pathways have been proposed to explain the observed product distribution in the Fischer-Tropsch synthesis, including the surface carbide mechanism, the surface enol mechanism, the CO insertion mechanism and the alkenyl mechanism.

2.3.2.1 Surface carbide mechanism

The first, oldest and perhaps the most accepted mechanism[25,38] for FTS on iron is the surface carbide mechanism. The current view for this mechanism is illustrated in Scheme 2.1. Initially, Fischer and Tropsch suggested that the mechanism of the synthesis involved the formation and hydrogenation of metal carbides to give methylene groups on the surface of the metal, which then polymerized and reacted further to give the observed products.[39] Craxford and Rideal supported this idea through kinetic investigations and then proposed that CO is adsorbed on the surface of a metal and dissociates, in the presence of hydrogen, by forming water or CO_2, which rapidly desorbs and chemisorbed carbon is formed.[40] The chemisorbed carbon is subsequently hydrogenated to form chemisorbed CH_2 which oligomerizes to produce higher hydrocarbons. It was eventually recognized that this mechanism was inconsistent with thermodynamic data for the formation of hydrocarbons by hydrogenation of the carbide at the temperatures used for the synthesis reaction.[41] Another shortcoming of the initial carbide mechanism was that it did not explain the formation of oxygenated products.[42]

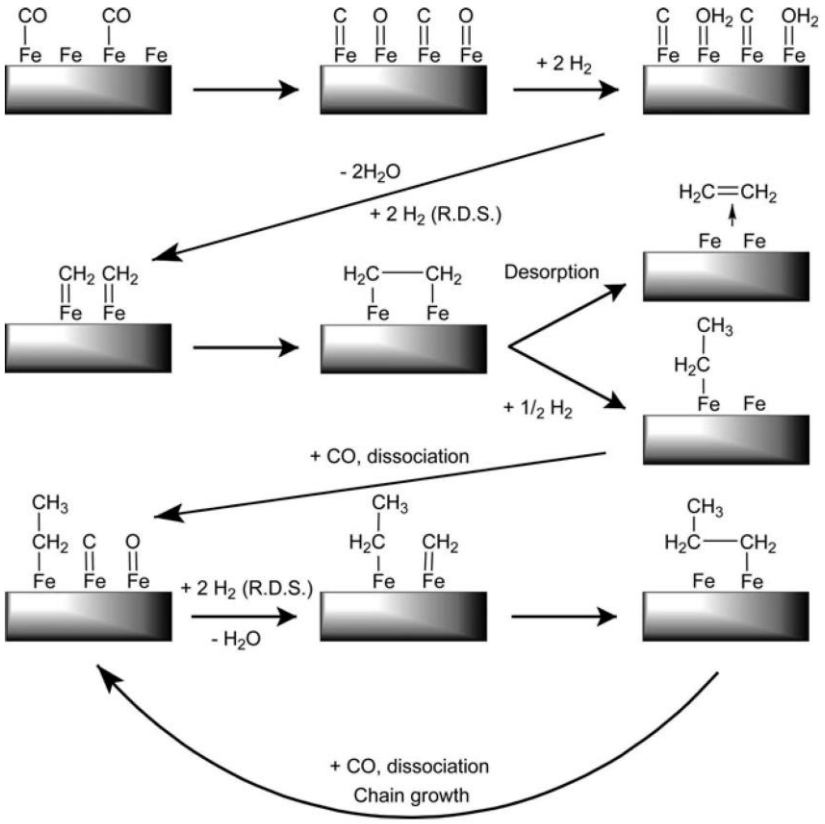
Variations to the carbide mechanism have been proposed to take into account some of the recent findings from surface science studies. With the advent of surface science instrumentation, it has been found that CO adsorbs on metal surfaces to produce a surface covered with carbon and little oxygen. This led to the conclusion that CO chemisorbs and then dissociates to adsorbed C and O on some metal surfaces; subsequently, under FT conditions, the rapid hydrogenation of adsorbed O to water occurs. The hydrogenation of adsorbed carbon to form CH_2 is much slower.[43] This led to the view that it was a surface, or near surface, metal carbide that was the initial surface species in the formation of carbenes.[44]

2.3.2.2 Surface enol mechanism

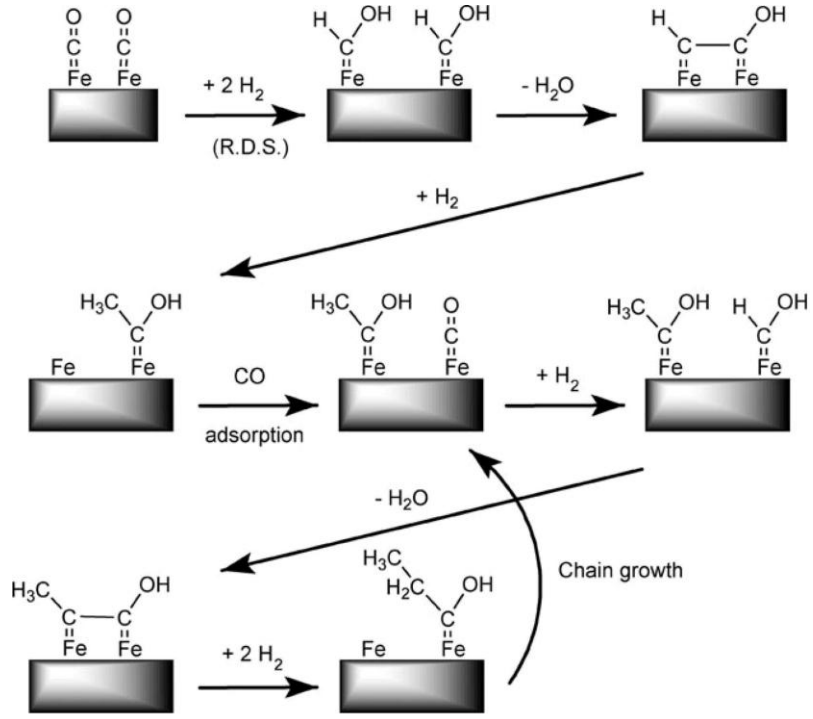
In the 1950s, the oxygenate (enol) mechanism gained widespread acceptance.[42,45] This mechanism proposes chain growth by the undissociative chemisorption of CO which reacts with adsorbed hydrogen to form enolic (HCOH) units (see Scheme 2.2). The product structure then grows by a combination of surface polymerization condensation and water elimination steps using adjacent groups.[46] Emmett *et al.*[47-50] used ^{14}C-tracer studies to support this mechanism. When performing these studies, a ^{14}C-labelled alcohol or alkene was added together with synthesis gas during FTS and the distribution of the isotopically labelled products was analysed. Their results showed that the added alkene or alcohol was able to initiate chain growth.

2.3.2.3 CO insertion mechanism

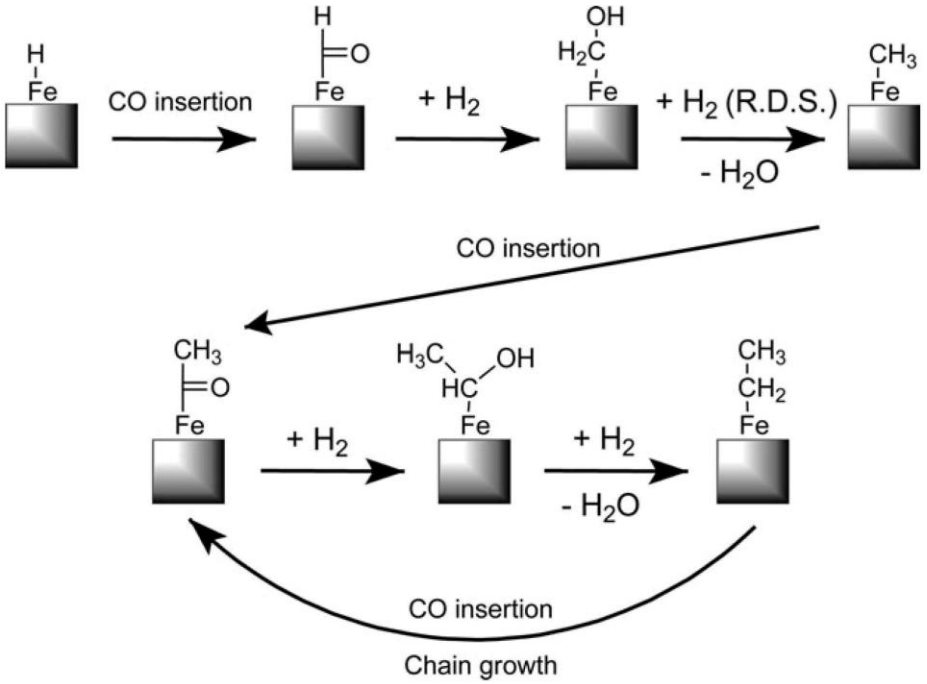
This mechanism involves the insertion of CO into a metal-methyl or metal-methylene carbon bond which is then hydrogenated to produce an alcohol or alkene. The alcohol or alcohol precursor can also eliminate oxygen to produce an alkene. As illustrated in Scheme 2.3 the initiation step involves the insertion of a CO molecule into a metal-H bond, the resulting aldehyde is then hydrogenated to CH_3 in a rate determining step. At this point CO insertion then occurs as shown in the scheme. This mechanism was first proposed in 1958.[51] It was modernized years later by Pichler and Schulz,[52] and further modified by Henrici-Olivé and Olivé,[53] and Masters.[54]



Scheme 2.1 Representation of the surface carbide mechanism. The rate determining steps (RDS) are indicated in the scheme.[55]



Scheme 2.2 Representation of the surface enol mechanism. The rate determining steps (RDS) are indicated in the scheme.[55]

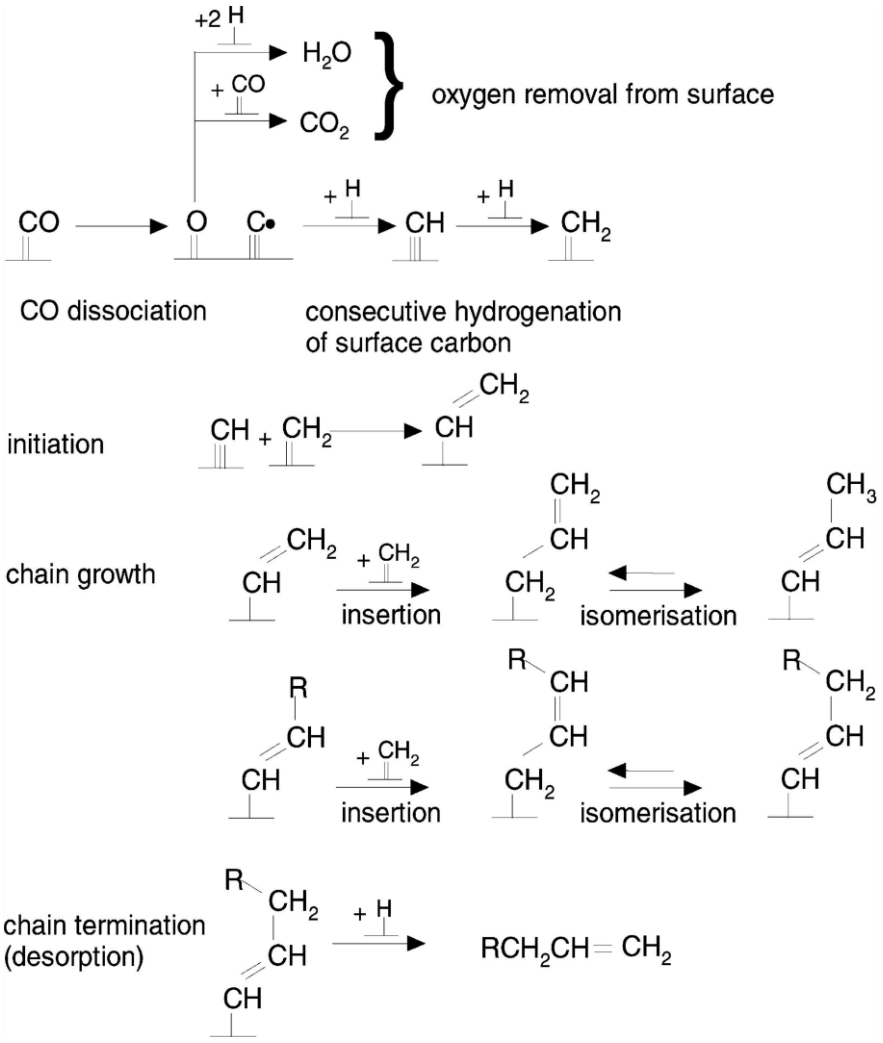


Scheme 2.3 Representation of the CO insertion mechanism. The rate determining steps (RDS) are indicated in the scheme.[55]

2.3.2.4 Alkenyl mechanism

The alkenyl mechanism proposed by Maitlis and co-workers[56] is illustrated in Scheme 2.4. The mechanism suggests that polymer chain carriers are surface alkenyl rather than alkyl species. The CH_2 surface species is regarded as the chain propagation monomer. As shown in the scheme the surface vinyl species ($–CH=CH_2$), which is the chain starter, is formed by the reaction of a surface methyne (≡CH) and surface methylene ($=CH_2$) species. Chain growth occurs by the coupling of a sp^2 (alkenyl) carbon with a sp^3 (methylene) carbon to form an allyl species ($–CH_2CH=CH_2$). It has been shown in the literature[57] that the coupling of sp^2 with sp^3 carbons in metal complexes is a lower energy process than a $Csp^3 + Csp^3$ coupling reaction. The surface allyl species then isomerises to the more reactive propenyl species ($–CH=CHCH_3$). Termination occurs by the reaction between surface hydrogen and the surface alkenyl species yielding predominantly α-olefins.

This mechanism was tested by adding ethene-$^{13}C_2$ probes during FTS. NMR spectra of the 1-alkene products showed that two ^{13}C atoms were incorporated and were generally adjacent at the alkyl ends ($^{13}CH_3{}^{13}CH_2(CH_2)_nCH{=}CH_2$). Advantages of this mechanism include explaining; the formation of branched products (for example by allyl isomerization), the low amount of C_2 products, and the release of 1-alkenes as primary products (by a favourable hydrogenation reaction).[58] However this mechanism is inadequate when explaining the formation of n-paraffins and the formation of oxygenates. The key step in the mechanism proposed by Maitlis *et al.* is the allyl–vinyl isomerisation, yet no experimental evidence for such a facile isomerization has been given.



Scheme 2.4 The alkenyl chain growth mechanism in the Fischer–Tropsch synthesis as summarised by van Steen and co-workers.[59]

2.3.3 Product selectivity

FTS has been recognized as a polymerization reaction.[60] The reactants, CO and H_2, adsorb and dissociate on the surface of the catalyst and react to form a chain initiator (CH_3), and methylene monomer (CH_2) and H_2O. FTS is kinetically controlled and the intrinsic kinetics is step-wise chain growth, in effect the polymerization of -CH_2- groups on a catalyst surface. FTS is therefore characterized by non-selectivity towards products. A typical product spectrum consists of a complex multicomponent mixture of linear and branched hydrocarbons and oxygenated products. The polymerization rates, and therefore the kinetics, are independent of the products formed. The probability of chain growth and chain termination are also independent of chain length.

Selectivity for longer chain products is governed by the ability of a catalyst to preferentially enhance the rate of chain propagation above that of chain termination. Anderson, Schultz and Flory (ASF) proposed a kinetic model that is frequently used to describe the product distribution obtained from FTS. In this model, the FTS reaction is assumed to be an ideal polymerization reaction in which there is one single growth probability factor, α, which determines the hydrocarbon chain length distribution. The ASF kinetic model is shown as equation 2.9:

$$m_n = (1 - \alpha)^2 \alpha^{n-1} \qquad (2.9)$$

where m_n is the mole fraction of a hydrocarbon with chain length n and the growth probability factor α is independent of n. The growth probability factor (α) is given by equation (2.10) where r_p and r_t represent the rate of chain propagation and the rate of chain termination, respectively:

$$\alpha = \frac{r_p}{r_t + r_p} \qquad (2.10)$$

A graphical representation of the product distributions as predicted by the model is illustrated in Figure 2.1.

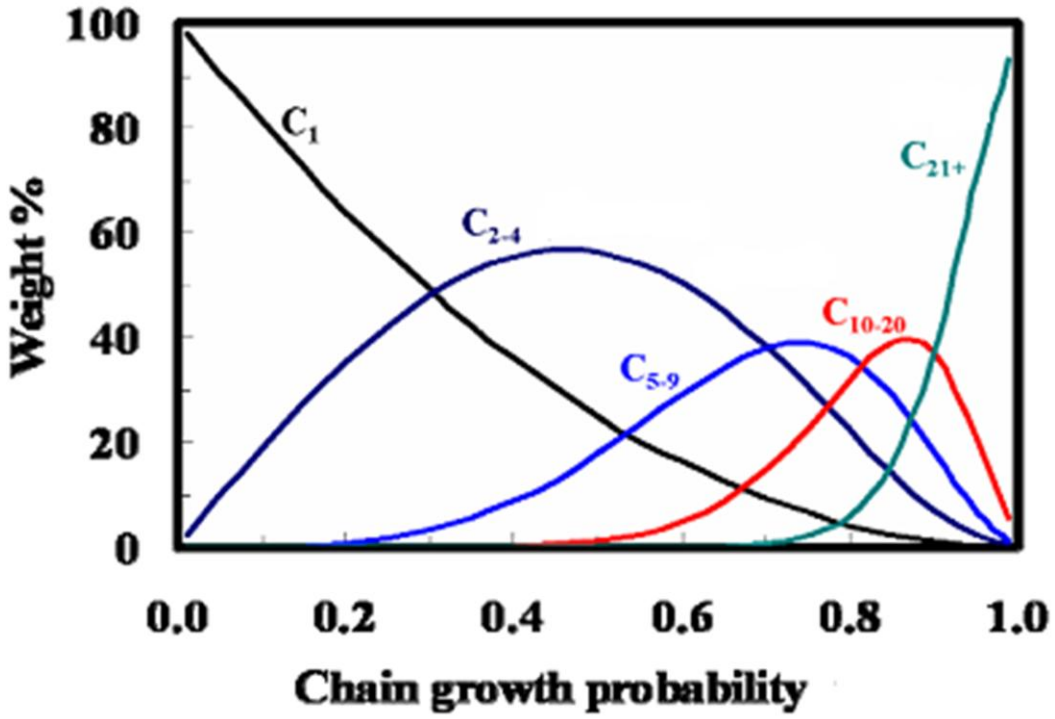


Figure 2.1 FTS product distribution as predicted by the ASF kinetic model.[61]

Unpromoted and unsupported iron catalysts are normally associated with low α-values indicating a propensity towards gaseous products. The activities of catalysts can be improved by many methods such as modifying the support, the feedstock ratio, reaction temperature, increasing the dispersion, promoting catalyst by adding a noble metal, and improving the preparation method. The ASF pattern always leads to a gradual decrease in selectivity with an increase in carbon number (n), which limits the formation of desired middle distillates and heavy hydrocarbons (wax).[53]

However, studies show that the measured product distribution from the FTS reactions seldom obeys the predictions from the ASF model. Common deviations of the distribution are a relatively high yield of methane[62,63] especially over Co and Ru catalysts, and a relatively low yield of ethene[64] in comparison to the ASF distribution. Higher surface mobility or reactivity of C_1 and C_2 precursors and rapid re-adsorption of ethene give the most reasonable explanation for the deviations of the short-chain hydrocarbons from the ASF distribution.[65] Also, the change in chain growth parameter α and the exponential decrease of the olefin-to-paraffin ratio with increasing carbon number also results in deviations from the ASF model. These

deviations are predominantly caused by secondary reactions of α-olefins, which may be due to re-adsorbed olefins on growth sites of the catalyst which are incorporated into existing hydrocarbons.

Currently there are two FT operating regimes.[21,66] FTS can either be a low temperature FT (LTFT) process or a high temperature FT (HTFT) process depending on the products required. HTFT utilizes iron-based catalysts at temperatures varying from 300 ^{o}C to 350 ^{o}C for the production of gasoline and linear hydrocarbons. LTFT operates on both cobalt- and iron-based catalysts for the production of waxy materials.[67] The main advantage of HTFT over LTFT is that there is no liquid phase around the catalyst particles in the HTFT process. The typical product distributions for the LTFT and HTFT processes are shown in table 2.2.

Table 2.2 Typical product selectivities from two Sasol processes.[68]

Products (wt. %)	**LTFT**	**HTFT**
CH_4	4	7
C_2 to C_4 olefins	4	24
C_2 to C_4 paraffins	4	6
Gasoline	18	36
Middle distillate	19	12
Heavy oils/waxes	48	9
Oxygenates	3	6

2.4 FT reactor technologies

Reactor type and operation are governing factors in the control of product distribution during FTS.[27] The challenge in FTS reactor design is the efficient and rapid removal of the large heat of reaction ($-\Delta H$ = 165-204 kJ mol^{-1}) accompanying the process. High temperatures in the reactor lead to excessive methane yields, carbon deposition and catalyst loss due to particle fragmentation. Three main catalytic reactor configurations (Figure 2.2) have been designed and used commercially: fixed bed, fluid bed and slurry bubble columns.

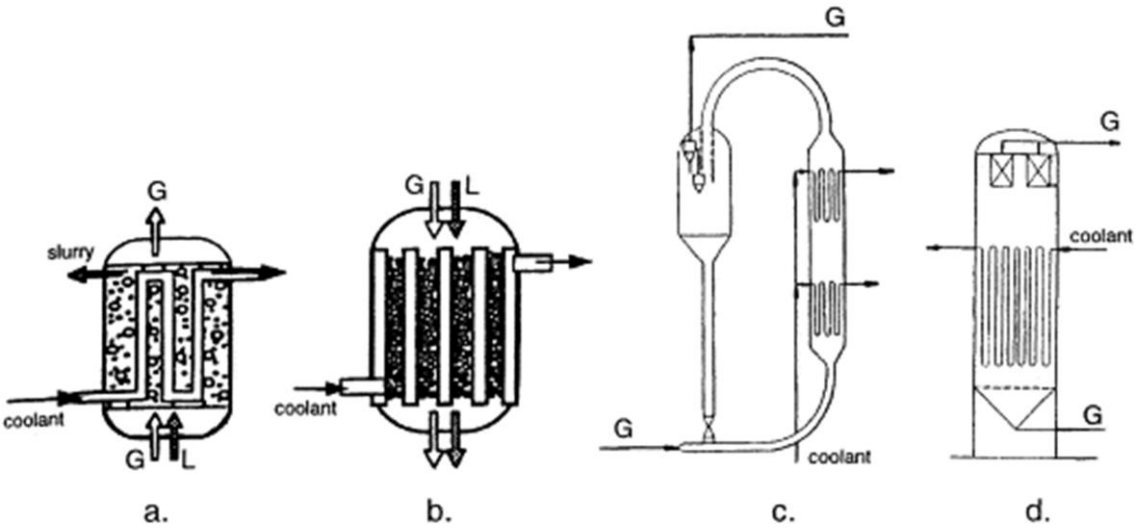


Figure 2.2 Possible reactors for FTS: (a) slurry bubble column reactor; (b) multi-tubular trickle bed reactor; (c) circulating; (d) fluidized-bed reactor [G: gas, L: liquid].[69]

2.4.1 Fixed bed tubular reactor

The fixed-bed tubular reactor (also known as the ARGE reactor) is one of the most competitive reactor technologies and it occupies a special position in FTS industrial practices, as exemplified by the large-scale commercial operations of Sasol[70] and Shell.[71] ARGE reactors were first commissioned at Sasol I in 1955. The original reactors consist of a shell containing 2050 tubes, 12 m long, 5 cm in diameter, packed with an iron based catalyst. Sasol also designed a 5 000 tube fixed-bed reactor that was not eventually used following the development of a more efficient slurry bed reactor. Fixed bed reactors (see Figure 2.2b) operate at a temperature of about 220°C and reactor pressures in the range 25-45 bar. Heat removal from the FT process is achieved by utilizing steam that is generated on the shell side of the reactor. However, this mechanism is not very effective as it results in axial and radial temperature profiles in the tubes.

Typical industrial FTS processes with fixed-bed reactors normally produce complex mixtures consisting of hydrocarbons ranging from methane to wax. For the reasons of reducing pressure drop and facilitating heat removal, catalyst particles of a few millimeters in size are generally needed to be used in fixed-bed reactors, contributing to the existence of intra-particle pore-diffusion limitations.[71] As a result of diffusion

limitations and capillary condensation, the catalyst pores are often filled with a stagnant phase formed by the heavy waxy products.[72-74] The major problems associated with fixed bed reactors are that they are expensive to assemble and they do not readily permit on-line catalyst changing which may be necessitated by catalyst poisoning. The latter results in long down-times thus compromising the overall efficiency of the plant.

2.4.2 Fluidized reactor

Fluidized reactors consist of two phases (gas and solid) and they can either have a fixed or a circulating bed. The distinguishing feature between the two types of reactors is that in the fixed fluidised bed reactor (FFD) the catalyst bed remains stationary and the gases pass upward through the bed (see Figure 2.2d) while in the circulating fluidised bed reactor (CFB) the catalyst is entrained in the fast moving gas stream (see Figure 2.2c).

A commercial plant utilizing FFD reactor technology was erected in Brownsville, Texas, by Carthage Hydrocol in the 1950's. This reactor was 18 m high and 4 m in diameter with a nominal capacity of 180 000 tonnes per year.[75] In this type of reactor the reaction heat is removed by vertical bundles of cooling tubes submersed in the bed. However this plant was shut down in 1956 due to technical and economic reasons. In a CFB system a fine catalyst bed (between 40 and 150 mm diameter) is entrained by a high velocity (1–2 m/s) gas stream through a riser reactor. The catalyst is separated from the effluent by cyclones and is then returned to the reactor inlet. Two cooling zones in the riser are used for removing the reaction heat. The improved version of this CFB reactor was named a Synthol reactor at Sasol. The main disadvantage of the two fluidised bed reactors is that should any poison enter the reactor the entire catalyst bed is poisoned whereas in the fixed bed tubular reactor, the poison is adsorbed on the top layer of the catalyst leaving the rest of the bed intact.

2.4.3 Slurry bubble column reactor

The idea of a slurry bed reactor (see Figure 2.2a) was first tried out during the Second World War and up to the late 1970's by Kölbel and co-workers.[76] Sasol's involvement in the development of slurry reactors dates back to the early 1980's, even though it

was on a small scale. A commercial-scale slurry reactor (5 m diameter, 22 m high) was commission in May 1993 at Sasol and this reactor has been operated successfully since that time. In these three-phase reactors syngas is distributed from the bottom and it rises through the slurry that consists of a high thermal capacity liquid (predominantly the FT wax product), with the catalyst particles suspended in it. As FTS proceeds in the reactor, the heavy hydrocarbon products form part of the slurry phase while the lighter gaseous products and water diffuse through the gas bubbles and then to the gas outlet.

Unlike tubular fixed bed reactors which have a tendency of developing hot-spots in the catalyst bed, hot-spots are non-existent in slurry systems because of the churning nature of the slurry and controlled slurry mixing. As a consequence, the slurry phase is sufficiently well mixed to give isothermal operation, giving a different perspective to temperature control in the highly exothermic FT system.[77] It has been calculated that the heat transfer coefficient for the cooling surfaces in a slurry phase reactor are five times higher than those for fixed bed reactors.[78-80] Furthermore, the average synthesis temperature can be higher than that used in a tubular reactor without the risk of catalyst degradation. Higher reactor temperatures lead to higher CO conversions to products.

2.5 FTS catalysts

2.5.1 Active metals in FTS

The choice of catalyst is critical in FTS because the product distribution is dependent on the properties of the catalyst being used. The three key properties of an FT catalyst are catalytic activity, lifetime and product selectivity.[81,82] When the FTS process was discovered by Franz Fisher and Hans Tropsch in 1923 an iron catalyst was used to facilitate the conversion of syngas ($CO + H_2$) to liquid fuels. Other catalysts such as cobalt, nickel and ruthenium have also been shown to be catalytically active in FTS. Comparisons of the different characteristics for these metals are shown in Table 2.3. Nickel displays undesirably high methane selectivity and during the reaction Ni carbonyls (highly toxic) are formed, which result in loss of activity. Ruthenium is the most active FT element working at the lowest reaction temperature, e.g., very high molecular weight products have been isolated even at 150 ^{o}C.[10] However, Ru is too

expensive and its worldwide reserves are insufficient for large-scale industrial use, therefore both Ni and Ru are not commonly used as FT catalysts. Iron- and cobalt-based catalysts are the only catalysts presently used industrially, hence they have been reviewed in detail in the following sub-sections.

Table 2.3 Overview of characteristics of Ni-, Fe-, Co- and Ru-based FT catalysts.[10]

Active metal	*Price*	*FT activity*	*WGS activity*	*Hydrogenation activity*
Ni	++++	+	+/-	+++++
Fe	+	+	+++	+
Co	+++	+++	+/-	+++
Ru	+++++	+++++	+/-	+++

2.5.1.1 Iron

Iron is the catalyst of choice for many industrial applications because not only are they relatively inexpensive to prepare, but they also tolerate flexible operation conditions, and they give a good turnover with a broad product spectrum.[83-85] Iron-based catalysts are usually promoted with an alkali such as potassium or sodium to increase the average molecular weight and the olefinity of the hydrocarbons produced, as well as promote the water-gas-shift reaction.[28] A typical catalyst also contains copper to enhance catalyst reducibility, along with some silica or zinc oxide to improve the amount of iron atoms interacting with the synthesis gas (i.e. catalyst dispersion). When iron is used as the active metal it promotes the occurrence of the water-gas-shift (WGS) reaction (equation 2.3). This reaction consumes CO and water formed by the FTS reaction to produce additional hydrogen as well as carbon dioxide.[29] The WGS activity favours the use of synthesis gas that has a low H_2/CO ratio.

Iron phases that co-exist during and after activation include metallic iron, carbidic iron and iron oxides. Surface carbidic iron species are believed to be the active species in FTS[29] however this remains controversial. Schulz *et al.*[86] studied the behaviour of a Fe-Al-Cu/K_2O catalyst and concluded that the FT activity was related to the formation of Hägg carbides (Fe_5C_2). The authors also reported that metallic iron

was less active. Metallic iron is reported to rapidly transform to these carbides (Fe_5C_2) upon introducing syngas[27] if activation is performed using hydrogen. The major problems associated with iron-based catalysts are the high deactivation rates and the relatively short catalyst life-time.

2.5.1.2 Cobalt

Cobalt-based catalysts are much more expensive than iron-based ones hence they are only used industrially as supported catalysts. Commonly used supports include SiO_2,[87] TiO_2[88] and Al_2O_3.[89] Co-based catalysts have a higher hydrogenation activity, hence they tend to produce higher yields of high molecular weight paraffins and much less oxygenates when compared to iron catalysts. Generally Co catalysts are about 3 times more reactive than Fe catalysts in FTS, yet they are about 250 times more expensive. Nonetheless, Co catalysts have a longer lifetime, usually over five years time on stream. This is because they are not susceptible to deactivation by carbide or oxide formation as found for Fe catalysts. Co catalysts show little water-gas-shift activity and thus only small amounts of CO_2 can be found in the reactor at any given time.

For cobalt it is generally accepted that metallic nanoparticles are the active phases in FTS.[90,91] Metallic cobalt can exist in different crystalline forms, including α-Co (hcp) and β-Co (fcc). The former form is more stable at low temperatures for bulk cobalt. However, cobalt crystallites with a particle size less than 20 nm are more stable as the pure fcc phase.[92]

2.5.2 The use of promoters

The catalyst surface often contains substances called promoters that are added deliberately to modify the turnover rate for a given catalytic reaction. A promoter is considered to be a component of the catalyst that does not take part in the catalytic reaction but it alters the activity, selectivity or stability of a catalyst.

Promoters can perform one or more of the following;[93]

(a) Supply a catalytic effect that is not possessed by the catalytic metal alone
(b) Facilitate catalyst preparation, conditioning or regeneration

(c) Inhibit catalyst poisoning
(d) Improve the physical nature of the support

There are two types of promoters, namely chemical and structural promoters. Structural promoters are known to improve the catalyst's structural features such as its surface area and its stability. Chemical promoters on the other hand are known to alter the electronic environment on the surface on the catalyst.

2.5.2.1 Structural promoters

The choice of a structural promoter can have profound effects on the activity and the selectivity of the catalyst. Advantages of using structural promoters/supports include;

(a) They enhance the surface area of the catalyst and hence the dispersion of the metal
(b) They improve the stability of the catalyst during the FT reaction
(c) They inhibit sintering of the metal crystallites

Structural promoters also enhance reproducibility and attrition resistance of the active phase of the metal within the catalyst. In principle they do not influence the product selectivity since they only increase the number of active sites in a catalyst. Typical materials used as structural promoters in FTS include SiO_2, TiO_2, Al_2O_3, MgO, MnO, Cr_2O_3, zeolites, activated carbon and more recently carbon nanotubes.[93] In this work SiO_2 was used as a support since it has been shown to be superior for Fe-based FT catalysts. SiO_2 has also been found to reduce the basicity caused by chemical promoters, especially when alkali promoters have been used.

2.5.2.2 Chemical promoters

Typical chemical promoters used in FTS are copper (Cu), manganese (Mn) and potassium (K). These are known to alter the electronic environment on the surface of the metal, hence the activity and the product selectivity of the catalyst are improved. The main function of Cu in FTS, particularly when bubble column slurry reactors are employed, is to decrease the temperature required to reduce iron oxides.[76] Mn has also been widely used as a promoter for FT catalysts, and it shows complex electronic and structural effects on iron catalysts. It has been reported to promote the production of

$C_2 – C_4$ olefins[94-97] and also increase the sulfur-tolerance property of iron catalysts.[98] In this work, the effect of potassium as a promoter was investigated on microwave-modified FTS catalysts. Thus an in-depth survey of reported effects of potassium is summarized below.

2.5.2.2.1 The effects of potassium in FTS

Numerous studies have shown that the addition of small amounts of potassium to iron catalysts used for Fischer-Tropsch synthesis affects the performance of such catalysts in a variety of ways.[72,99] Studies done by Dry and co-workers[100] with alkali-promoted magnetite found that the addition of alkali caused a decrease in the surface area, which led them to postulate that the promotional effect of potassium was chemical in nature. Some effects of potassium in iron catalysts for FTS include increasing the average molecular weight of the products, the olefin to paraffin ratio, and the content of oxygenated products. The addition of potassium also increased carbon deposition and hence the catalyst deactivation rate. Other reports suggest that potassium causes a decrease in the H_2 to CO usage ratio due to an increased water-gas-shift (WGS) activity.

The increase in the average molecular weight of the products is due to the increase in CO surface coverage compared to H_2 surface coverage in the presence of potassium. The potassium ion is an electron donor and can thus enhance the chemisorption of electron acceptor species such as CO and O_2, and suppress the chemisorption of electron donors such as hydrogen and olefins. As a consequence of the increased electron density, the metal is available for back-bonding to the 2p* orbitals of the CO and other diatomic electron acceptor species, enhancing their dissociation capacity.[101] Contrary to this, hydrogen donates electrons to iron and its bond to iron is weakened by the presence of potassium. The net result is that potassium strengthens the Fe—C bond and weakens the Fe—H and the C—O bonds. The preferential chemisorption of CO in the presence of potassium favours chain propagation over chain termination, since chain termination results from the hydrogenation of the Fe—C bond.

The increase of the olefin content, which is usually listed as the olefin (alkenes) to paraffin (alkanes) ratio, is due to the decrease in secondary hydrogenation of olefins

after the addition of potassium. This is explained by the strengths of CO and H_2 chemisorption caused by potassium as described earlier. The addition of potassium increases the chemisorption of CO while simultaneously weakening the chemisorption of H_2, and this results in a low hydrogenation activity. Herzog and Gaube[102] also suggested that this could be because the olefin hydrogenation reaction is first order with respect to both 1-alkene and hydrogen, yet with respect to CO the reaction order is between -1 and -2. Using the competitive adsorption model, this means that increasing CO adsorption promotes the desorption of 1-alkenes thereby reducing the rate of olefin hydrogenation.

Potassium has also been shown by Dry and co-workers[103] to lower the surface area of the catalyst. This has been attributed to the fact that potassium could improve agglomeration of the FeOOH precursor and could further increase the crystallite size of α-Fe_2O_3, which would lower the surface area. These observations dispel suggestions that the loss in surface area could be due to pore blocking after potassium addition. Yang *et al.*[23] have also shown using thermal gravimetric analysis (TGA) that potassium inhibits the reduction of iron. They found that the net weight that is lost at the same temperature point decreases with the increase of potassium content. The results were explained to be due to the strong interaction between potassium oxide and iron oxide. The strong interaction of these oxides could suppress the adsorption of hydrogen on the catalyst surface thus restraining the reduction of iron. The loss in surface area with increasing crystallite size decreases the surface area that can be in contact with the H_2 reductant, thus inhibiting the reducibility of iron.

2.6 References

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