

Mechanistic pathways of the high temperature Fischer-**Tropsch** synthesis

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Mechanistic Pathways of the High

Temperature Fischer-Tropsch Synthesis

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. F.P.T. Baaijens, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op maandag 5 oktober 2015 om 16.00 uur

door

Jack Vincent Fletcher

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Summary

Mechanistic Pathways of the High Temperature Fischer-Tropsch Synthesis

To date, the mechanism of the Fischer-Tropsch synthesis (FTS) is not well understood and remains a highly controversial topic in heterogeneous catalysis. One of the difficulties which arises in determining the mechanism is that the intermediates occur as chemisorbed species on the catalyst surface and are therefore not reachable for kinetic measurement via the gas phase. Steady State Isotopic Transient Kinetic Analysis (SSITKA) allows for the measurement of surface concentrations and identification of active intermediates without disturbance to the reaction system and is ideal for the study of mechanisms in heterogeneous catalysis. As such, SSITKA and other isotopic techniques are applied in this thesis for the study of the high temperature Fischer-Tropsch synthesis over an iron catalyst at an $H_2 / CO = 10, 330$ °C, 6 bar and GHSV = 3600 ml(n).gcat⁻¹.hr⁻¹.

SSITKA, using both ¹³C and ¹⁸O labelled CO indicated that CO oxidation to some extent occurs via a Mars and van Krevelen mechanism. Modelling the oxygen pathway for reversible addition of lattice oxygen to adsorbed CO in **Chapter 3** resulted in a good fit to the experimental data for CO₂ formation and a precise model estimation of the oxygen diffusion coefficient D.

The results of further steady state ¹³C and ¹⁸O labelled CO isotopic switching experiments in conjunction with oxygenate co-feeding are presented in **Chapter 4**. The difference between the formation of a primary 1-alcohol vs. that of an aldehyde is thought to be due to the type of oxygen surface species which adds to the carbon chain. Furthermore, the presence of both ¹⁶O and ¹⁸O labelled species,

after all C¹⁶O has eluted from the reactor, suggests that lattice oxygen may also contribute to oxygenate formation.

The SSITKA data of this thesis were measured at significantly higher pressures than previous isotopic studies for the HTFT synthesis and re-evaluation of the earlier mechanistic models with the high pressure data resulted in a newly proposed hydrocarbon formation pathway. This pathway is presented in **Chapter 5** and accounts for the formation of ethene via the reaction of an adsorbed CO and C₁ species while ethane is formed via the addition of two dissimilar C₁ species, neither of which contain oxygen. Further chain growth of the C₃₊ alkenes and alkanes occur via a stepwise addition of the same C₁ monomer species.

Finally in **Chapter 6** the effect of sulphur promotor addition to iron catalysts was investigated. The results of 13 CO and D₂ isotopic switches point toward a decrease in the coverage of adsorbed carbon species and the rate of chain growth upon sulphur addition to the catalyst.

Chapter 1

Introduction

1.1 The Fischer-Tropsch synthesis

The Fischer-Tropsch Synthesis (FTS) discovered in 1923 by Fischer and Tropsch^[1], can briefly be defined as the means used to convert synthesis gas containing hydrogen and carbon monoxide over a group VIII metal catalyst to produce mainly hydrocarbon products and water^[2] (Eq 1.1). Of the group VIII metals iron, cobalt, nickel and ruthenium are the most active catalysts for the FTS. Over these metals synthesis gas is converted to aliphatic (long chain) hydrocarbons via a mechanism where reaction intermediates do not desorb from the catalyst surface^[3]. Only iron and cobalt are utilized commercially as FT catalysts. Nickel is too hydrogenating and results in high methane yields while the scarcity coupled to the high cost of ruthenium eliminates its application for industrial use as a catalyst in the FTS^[2].

The most common feeds used to prepare synthesis gas for FTS are coal and natural gas. Other feedstock examples are coal bed methane, heavy oils, bitumen, and petroleum coke. In general the feedstock will become more desirable as the hydrogen content increases, since this will increase the efficiency with which it can be converted to hydrocarbon products ^[2,4].

In commercial practice FT can be classified according to the temperature range in which the synthesis is performed. This results in two modes of FT operation. The low temperature (200-250 °C) Fischer-Tropsch process (LTFT) with either iron or cobalt catalysts is utilized for high molecular mass linear wax production. Both catalyst variations of the LTFT process (iron and cobalt) result in a three phase system (gas, solid and liquid) ^[5] and are operated commercially using either multi-

¹ Fischer F., Tropsch H., Brennstoff-Chem., Vol. 7. (1926), 97

² Steynberg A. P., Dry M.E. (Eds.), Stud. Surf. Sci. Catal, Vol. 152, Elsevier, Amsterdam, (2004)

³ Schulz H., Appl. Cat., Vol. 186, (1999) 3

⁴ Aasberg-Peterson K., Christensen I., Dybkjaer I., Sehested M., Ostberg M., Coertzen R., Keyser M.J., Steynberg A.P., *Stud. Surf. Sci. Catal.*, **Vol. 152**, (2004) 258

⁵ Espinoza R.L., Steynberg A.P., Jager B., Vosloo A.C., Appl. Cat. A, Vol 186, (1999), 41

tubular packed bed reactors or slurry phase reactors ^[2]. The high temperature Fischer-Tropsch (HTFT) (300-350 °C) process utilises iron-based catalysts for the direct production of gasoline and linear low molecular mass alkenes ^[6,7]. Other than temperature, a key distinguishing factor between the HTFT and LTFT synthesis is that there is no liquid phase present outside the catalyst particles during HTFT making this two-phase process well suited for application in commercial fluidised bed reactors ^[2].

The major fraction of oxygen produced from CO dissociation results in water. The water produced in the Fischer-Tropsch reaction can be consumed in the successive water-gas shift (WGS) reaction (Eq 1.2) yielding carbon dioxide and hydrogen. For cobalt-based LTFT catalysts the extent of the water gas shift (WGS) reaction is negligible and can be treated as an irreversible reaction producing a trivial amount of carbon dioxide ^[8]. For the HTFT process the WGS reaction is rapid and goes to equilibrium allowing carbon dioxide to be converted to FT products via the reverse WGS reaction ^[2].

FT:
$$nCO+2nH_2 \rightarrow -(CH_2)_n - +nH_2O$$
 1.1

Where ΔH^{R} (250 °C) = -158 kJ.mole⁻¹ for n = 1

WGS:
$$CO+H_2O \rightleftharpoons CO_2 + H_2$$
 1.2
Where ΔH^R (250 °C) = -39.5 kJ.mole⁻¹

The bulk of the FT product is composed of linear hydrocarbons (alkenes and alkanes) with lesser amounts of oxygenates (alcohols, carboxylic acids and

⁶ Dry M.E., *Catal. Today*, **Vol 71**, (2002), 227

⁷ Dry M.E., Appl. Catal. A, Vol 189, (1999), 185

⁸ Van der Laan G.P., Beenackers A.A.C.M., *Catal. Rev. – Sci. Eng.*, Vol. 41, (1999), 255

carbonyls), cyclic's and aromatics ^[9]. These products are formed by a type of polymerization reaction with in-situ establishment of the chain initiator from CO and H_2 . Chain growth occurs via stepwise addition of a C_1 species and finally desorption of the product into the gas phase ^[2]. The resulting product distribution with regard to carbon chain length is dependent on the probability for product desorption versus further chain growth. Assuming the chain growth (hence product desorption) probability is carbon number independent, a chain growth probability between 0 and 1 will result in a distribution of products with varying carbon numbers as illustrated in Figure 1. Commercial FT synthesis is typically operated at a chain growth probability of 0.7 to 0.95 depending on the products required i.e. gas (C_1 to C_4), liquid fuels (C_5 to C_{20}), lubricant oils and speciality waxes (C_{20+}) . To further increase selectivity towards valuable products, process parameters such as temperature, pressure and reactant feed ratios can be optimised since they have an effect on the chain growth probability and product type. A summary of the effect of varying process parameters on the FT selectivity is given in Table 1 below.

⁹ Dry M.E., *Catalysis Vol. IV*, Reinhold Publishing Corp., New York, (1981)



Figure 1 Calculated product composition (wt. %) as a function of chain growth probability assuming a maximum carbon number of 100, chain growth is carbon number independent, no formation of branched products and the formation of only one type of product (Ideal ASF kinetics)

Another competing reaction that may occur during the FTS is the Boudouard reaction (Eq 1.3). Disproportionation of CO can lead to the formation of unreactive surface carbon blocking active sites and hence catalyst deactivation ^[2]. The carbon formed may also be incorporated into the catalyst itself forming metal carbides (Eq. 1.4). For iron catalysts, the iron carbide phase is believed to be the active catalytic phase during FTS ^[9].

Boudouard reaction:	$2CO \rightarrow C + CO_2$	1.3
Carbide formation:	$M + C_{surface} \rightarrow MC$	1.4

[10,11]
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Table 1

Increasing parameter	Chain	CH₄	Alkene	Oxygenate	Alkene to	Chain
	length	selectivity	selectivity	selectivity	Alkane ratio	branching
Temperature	I	+	*	I	+	+
Pressure (Total)	÷	ı	*	+	+	ı
H ₂ /CO (feed)	ı	+	ı	ı	ı	*+
P _{Hydrogen} (reactor)	ı	÷	ı			*
Pcarbon monoxide (reactor)	+	1	+			*
Residence time	*+	*+	ı		I	*+
Space velocity	*	ı	+	ı		*
K (Fe catalyst)	+	ı	÷	+		ı
			•		4 • •	

Note: Increases with increasing parameter +; decreases with increasing parameter -; complex relation *; discrepancies in literature +*.

¹⁰ Claeys M., PhD Thesis, (1997), University of Karlsruhe, Karlsruhe, Germany

¹¹ Van Dijk, H.A.J., PhD Thesis, (2001), Technische Universiteit Eindhoven, Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/200111083.pdf

1.2 Mechanisms of the Fischer-Tropsch Synthesis

The mechanism of the Fischer-Tropsch synthesis (FTS) still remains a highly controversial topic in heterogeneous catalysis. While several mechanisms have been proposed to account for the diversity of products, the reaction pathway is still not well understood ^[12]. One of the complications which arises, is that most of these reaction steps occur in an adsorbed state of chemisorbed intermediates on the catalyst surface and as such are not reachable for kinetic measurement via the gas phase ^[13]. The key to understanding the FT mechanism is thus the in-situ measurement of surface concentrations and identification of active intermediates at the relevant FT operating conditions.

A suitable FT mechanistic model must account for all the unique aspects of the FT product ^[14], these include:

- Formation of hydrocarbons and oxygenates
- Products are primarily linear carbon chains but aromatics are observed at higher temperatures
- The fraction of alkenes to alkanes of the same carbon number is higher than predicted by thermodynamics
- Branching, typically as methyl groups on the penultimate carbon, i.e. formation of methyl ketones

Of the many reaction pathways proposed for the FT synthesis in the open literature, only a few account for hydrocarbons and oxygenates as primary Fischer-Tropsch products. Since one of the aims of this thesis is to investigate oxygenate formation and reaction pathways, three of the most popular steady state macro kinetic mechanisms, which include oxygenate formation, are discussed below. They are

¹² Schulz H., *Topics in Catal.*, Vol. 26., (2003), 73

¹³ Schulz H., Beck K., Erich E., Fuel Proc. Tech., Vol. 18., (1988), 293

¹⁴ Dry M.E., Appl. Catal. A., Vol. 138., (1996), 319

the CO insertion mechanism, the Enol or Oxygenate mechanism and the Alkyl mechanism with addition of an OH group. In the following chapters micro kinetic mechanisms based on steady state kinetic isotope analysis are presented (SSITKA).

1.2.1 CO insertion mechanism

In this mechanism, depicted in Figure 2 and originally proposed by Sternberg and Wender ^[15], chain initiation occurs by insertion of chemisorbed CO (<u>1</u>) into a surface methyl, CH₃ (<u>2</u>) bond forming a surface acyl species (<u>3</u>). Surface species (<u>4</u>) can desorb as a primary aldehyde or alcohol or form a surface alkyl species (<u>5</u>). The surface alkyl species can continue to propagate following further CO insertion / oxygen elimination steps or desorb as a primary alkene or alkane.



Figure 2 CO-insertion mechanism

¹⁵ Sternberg A., Wender J., Proc. Intern. Conf. Coordination Chem, The Chemical Society, London., (1959), 53

1.2.2 Enol (oxygenate) mechanism

The mechanism proposed by Storch *et al.* ^[16] was originally based on results from ¹⁴C experiments carried out at the Mellon Institute, together with the work at the US Bureau of Mines^[17]. The results showed that the dominant source of hydrocarbons was not from the direct hydrogenation of bulk iron carbide (see section 1.2.3) but rather the reaction of CO with H₂, probably involving the formation and condensation of groups containing oxygen ^[16, 17]. In this mechanism presented in Figure 3 chemisorbed CO (<u>1</u>) is hydrogenated to an enol (<u>6</u>) surface species. Chain growth then occurs via a condensation reaction between two enol surface species resulting in species (<u>8</u>) via elimination of water. Hydrogenation of surface species (<u>8</u>) leads to surface species (<u>9</u>) which can desorb as an aldehyde or hydrogenate further and desorb as an alcohol and finally an alkene. Although this mechanism can account for the primary formation of 1-alkenes, 1-alcohols and aldehydes, the authors themselves acknowledge that these are merely hypothetical reactions and that some of the details of the mechanism may be incorrect.



Figure 3 Enol mechanism with chain growth at the end carbon [16]

¹⁶ Storch H. H., Golumbic N., Anderson R. B., John Wiley & Sons, Inc., New York, (1951)

¹⁷ Davis B. H., Catal. Today., Vol. 141., (2009), 25

1.2.3 Alkyl mechanism with formation of surface oxygenates

The Alkyl mechanism originally proposed by Fischer and Tropsch ^[1] is also known as the carbide or carbene mechanism and takes place via the dissociative chemisorption of CO (<u>1</u>), followed by successive hydrogenation of surface carbon (<u>10</u>) to species CH, CH₂ and CH₃ (<u>11</u>, <u>12</u> and <u>13</u> respectively) as indicated in Figure 4. Chain growth is initiated by insertion of the methylene species CH₂ (<u>12</u>) into the metal-methyl (<u>13</u>) bond to yield a surface alkyl species (<u>5</u>). Further chain growth occurs via successive incorporation of the methylene species. Finally, product desorption takes place through hydrogen addition or β -hydrogen elimination yielding primary n-alkanes or 1-alkenes, respectively.



Figure 4 Classical alkyl mechanism

More recently, there is increasing evidence to indicate that the chain growth initiator and monomer may preferentially be chemisorbed carbon (<u>10</u>) or methylidyne (<u>11</u>) rather than the methylene (<u>12</u>) surface species. CO hydrogenation experiments with H_2/D_2 exchange over Ni-based catalysts ^[18,19] at 210 to 250°C showed that chemisorbed methylidyne (<u>11</u>) and carbon (<u>10</u>) were the most abundant C₁ surface species. Further H_2/D_2 isotopic experiments by Govender

¹⁸ Marquez-Alvarez C., Martin G.A. and Mirodatos C., Stud. Surf. SCi. Catal., Vol. 119, (1998), 155

¹⁹ Happel J., Cheh H.Y., Otarod M., Ozawa S., Severida A.J., Yoshida T. and Fthenakis V., *J. Catal.*, Vol. 75 (1982), 156

^[20] over a Fe based catalyst at 330 °C and 1.2 bar also indicated that the methylidyne species is the precursor for ethene and ethane formation. Here D-transients for ethene and ethane resulted in only one intermediate, a C_2H_1D species, indicating a CCH surface species is formed by the reaction of a methylidyne species with a reactive carbon species. Further hydrogenation of this species leads to a range of different C_2 intermediates such as CCH₃.

Importantly, the formation of primary oxygenates from the alkyl mechanism does not include oxygen in the chain growth monomer. Addition of oxygen to the growing chain intermediate would in all likelihood require diffusion of the alkyl species over the catalyst surface, the result halting further chain growth. Johnston and Joyner ^[21] propose an ethylidene (CCH₃, CHCH₃) type of species as a common intermediate in the formation of both hydrocarbons and oxygenates. In this mechanism the ethylidene species (<u>14</u>) is attacked by an adsorbed OH (<u>15</u>) species, forming an adsorbed oxygenate intermediate (16) (see Figure 5).



Figure 5 Formation of surface oxygenates ^[21]

²⁰ Govender N.S., PhD Thesis., Technische Universiteit Eindhoven (2010), Eindhoven., The Netherlands, http://alexandria.tue.nl/extra2/689931.pdf

²¹ Johston P., Joyner R. W., Stud. Surf. Sci. Catal., Vol.75 (1993), 165

1.3 Steady State Isotopic Transient Kinetic Analysis (SSITKA) based on the Fischer-Tropsch Synthesis

As mentioned above, the in-situ measurement of surface concentrations and identification of active intermediates is crucial to fully understanding the FT mechanism.

The Steady State Isotopic Transient Kinetic Analysis (SSITKA) is a method in which at least one reactant species is abruptly substituted with its isotopically labelled counterpart during an appropriate kinetic experiment at steady-state conditions and in the absence of kinetic isotope effects ^[22,23,24]. The quantifiable isotopic transients allow fitting of the relevant reaction rate constants for the elementary reaction steps and calculation of surface species concentrations based on a proposed reaction mechanism without the assumption of a rate limiting step ^[11]. Fitting of the transient data to proposed mechanistic models allows for discrimination between them and as such is the perfect method to provide detailed kinetic analysis and information on the nature of the active intermediates for the FT mechanism ^[11, 20].

Van Dijk ^[11] used both ¹³CO and C¹⁸O labelled CO SSITKA to explain methane, hydrocarbon and alcohol formation for the Co catalysed FT synthesis at 210 to 240 °C and 1.2 bar. Based on his results, van Dijk proposed that methane is formed from at least two C₁ surface species, these species being comparable in chemical composition but dissimilar with regard to position on the surface. Furthermore, he considered a single CH₂ surface monomer species to be responsible for hydrocarbon chain growth where C-C coupling is fast compared to the formation

²² Bennett C.O in: Understanding Heterogeneous Catalysis Through the Transient Method, Bell A. T,. Hegedus L.L., (Eds.), Am. Chem. Soc. Symp., (1982), 1

²³ Biloen P., *Mol. Catal.*, Vol. 21, (1983), 17

²⁴ Happel J., Chem. Eng. Sci., Vol. 33, (1978), 1567

of the monomer and chain initiation species. He also showed a pathway for alcohol formation via CO insertion into growing hydrocarbon chains, where the adsorbed oxygenated intermediates desorbs from the partially oxidised catalyst support as alcohols following spillover from the Co-metal. Interestingly, inverse spillover of alcohol intermediates to form hydrocarbons was not observed.

Govender ^[20] followed a similar approach to that of van Dijk, where he used ¹³CO SSITKA to determine the reaction pathways for methane as well as C₂₊ hydrocarbon formation in the iron catalysed FT synthesis at 330 °C and 1.2 bar. His results also indicated the presence of at least two carbon containing surface intermediates for methane formation. In addition he showed that two C₂ surface intermediates are required to describe the C₂₊ hydrocarbon transients. Ethene re-adsorption back to the ethane precursor was also found to be preferred over re-adsorption back to the ethene precursor. Further co-feeding and deuterium tracing experiments indicated that an adsorbed CH monomer is favoured for the iron catalysed FT synthesis as compared to the CH₂ monomer proposed by van Dijk for the Co catalysed system.

Some questions which remain for the iron catalysed HTFT synthesis include; i) whether the hydrocarbon reaction pathways developed by Govender at 1.2 bar, also hold at higher pressures ii) if the monomers identified by Govender for C₂ formation are common to higher hydrocarbon product formation, iii) what is the pathway of the WGS reaction and how does this relate to the FT mechanism and iv) how oxygenate formation fits into the overall FT reaction mechanism i.e. are oxygenate surface intermediates shared with other FT products.

1.4 Aim and scope of this thesis

The aim of this thesis is to investigate the elementary reaction steps of the HTFT synthesis which occur in-situ during well defined, steady state and commercially

relevant operating conditions. The mechanism of the HTFT synthesis is highly complex with the likely existence of more than one rate limiting step, the parallel occurrence of the reverse WGS reaction and the presence of multiple dynamic iron phases (carbide and oxide) complicating data interpretation and hence mechanistic understanding. Since most of the FT reaction steps occur through reaction intermediates on the catalyst surface, an isotopic tracer technique such as SSITKA is well suited to provide detailed information with regard to the elementary reaction steps. As indicated in section 1.3, the use of SSITKA to provide mechanistic information for the FTS over both Co and Fe based catalysts has already been shown to be successful. The current study is intended to be an extension of the HTFT SSITKA work by Govender ^[20] and will be conducted at higher reaction pressures and include both carbon and oxygen labelling experiments. Furthermore, as with the previous studies of van Dijk and Govender, detailed MS and GCMS product analysis will be carried out on the resulting isotopically labelled products.

1.5 Thesis outline

Chapter 2 provides a detailed explanation of the experimental setup and the reactor design for isotopic experiments at elevated pressures. The methodology of isotopic experiments and the various analysis techniques are described in detail. Lastly, modeling of SSITKA transients which result from an integral plug flow reactor are described.

Chapter 3 investigates the elementary reaction pathways of oxygen, via carbon and oxygen isotope switches.

Chapter 4 deals with oxygenate formation and reaction pathways during HTFT synthesis. SSITKA together with co-feeding of various oxygenates are used to

further elucidate and in some cases confirm the reactions and interactions of the oxygenates present during the HTFT synthesis.

Chapter 5 is an extension of the mechanistic pathway for hydrocarbon chain growth over a Fe catalyst at HTFT reaction conditions ^[20]. In this chapter, the model proposed by Govender is evaluated and extended to C_{3+} hydrocarbons taking into account the formation of CO_2 via the reversible WGS reaction.

Chapter 6 makes use of isotopic techniques to provide fundamental insight into the effect of sulphur promotion of precipitated Fe catalysts with regard to increasing the light alkene selectivity.

Chapter 7 is a general summary of the main conclusions from this thesis.

Chapter 2

Experimental Procedures and Model Formation

In this chapter, a description of the setup used and the procedures for the isotopic experiments are given. The reactor was purpose built for isotopic experiments and the absence of internal or external temperature and mass gradients were confirmed. The analysis of component concentrations and isotopic compositions were achieved by on-line gas chromatography, mass spectrometry and gas chromatography mass spectrometry. An integral plug flow reactor (PFR) model accounted for axial concentration gradients resulting from high conversions and reversible reactions.

2.1 The SSITKA set-up

Steady State Isotopic Kinetic Analysis (SSITKA) is a method in which at least one reactant species is abruptly substituted with its isotopically labeled counterpart during an appropriate kinetic experiment while maintaining steady state conditions ^[1], for a switch in the feed from ¹²CO/H₂ to¹³CO/H₂. The incorporation of the labelled atom into the reaction products is monitored in time and provides information on the reaction mechanism and the coverages of surface intermediates ^[2,3]. The transients for the labeled and non-labeled species are collected by means of online MS and GCMS. The GCMS is equipped with 16 heated sample loops prior to the injector which allow for the fast collection and storage of samples during the transient period. The stored samples are then analyzed sequentially allowing for sufficient separation in the GC column.

In order to maintain steady state reaction conditions, the total flows of each stream, the composition of these streams and the pressure drop towards the vent and analysis section must be equal. These conditions are met by means of a purpose built experimental setup allowing for SSITKA and other isotopic experiments to be carried out at elevated pressures (0 to 10 bar). The setup consists of a feed section, a reactor section and an analysis section. A schematic representation is given in Figure 1. Each section is discussed in detail below.

¹ Van Dijk, H.A.J., PhD Thesis, (2001), Technische Universiteit Eindhoven, Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/200111083.pdf

² Bal'zhinimaev B.S., Sadovskaya E. M., Suknev A. P., Chem. Eng. J., Vol. 154, (2009), 2

³ Shannon S.L., Goodwin J., Chem. Rev., Vol. 95, (1995), 677-695



Figure 1 Schematic representation of the experimental set-up. (FIC = flow indicator controller; PIC = pressure indicator controller; TIC = temperature indicator controller; TI = temperature indicator; PI = pressure indicator; MS = mass spectrometer; GC = gas chromatograph; GCMS = gas chromatograph mass spectrometer; dashed lines show heated sections; A = saturator; B = fast switching 4-way valve; C = reactor with heating mantle; D and E = hot and cold knock out pots, respectively

2.1.1 Feed section

Bronkhorst mass flow controllers are used to control the gas flow rates of each feed species. As depicted in Figure 1, the non-labelled feed enters from the left via two separate lines (i and ii) and the isotopically labelled feed enters from the right via line iii. The non-labelled species which are not substituted by their isotopic counterparts are fed through line ii. The "lower" feed stream (ii), can also be diverted through the saturator (A) if additional species are to be co-fed to the reactor (further information on the saturator is given in the following section). Before stream ii enters the reactor it is combined with the "upper" feed stream (i) which exits the 4-way valve (B), together they make up the total feed to the reactor. Depending on the position of the 4-way valve, the total feed stream contains either the non-labelled species with 5 ml(n)/min Ar (stream ii) or the isotopically labelled species with 5 ml(n)/min Ne (or Kr) (stream iii). The gas stream which does not join with stream ii leaves through and electronic back pressure controller to the vent.

Importantly, streams i and iii entering the 4-way valve must be equal in total flow and composition and must have equal pressure drops towards the vent and analysis section. The use of carefully calibrated mass flow controllers satisfies the flow and composition requirements while the electronic back pressure controller on the vent and a split back pressure controller (pressure indicator upstream of the reactor with controller downstream of the reactor) are both set for the same total pressure and fine-tuned by two needle valves to ensure equal pressure drop during the SSITKA experiments. Table 1 gives an overview of the gasses used and their purities while Figure 6 shows an example of an isotopic switch at steady sate reaction conditions.

Gas	Purity
Ar	99.999%
Ne	99.999%
Kr	99.995%
H ₂	99.999%
D ₂	99.9%
СО	99.997%
C ¹⁸ O	95% ¹⁸ 0
¹³ CO	99% ¹³ C, <2% ¹⁸ O
¹³ CO ₂	99% ¹³ C

Table 1 Gasses used for experiments and their purities

2.1.1.1 Saturator design and operation

The introduction of oxygenate components to the reactor for the experiments of Chapter 4 was accomplished by using a stainless steel jacketed tubular saturator (vessel A of Figure 1) with dimensions of 6 cm internal diameter and liquid height between 22 and 30 cm (see Figure 2). The configuration of the setup allowed for the standard gaseous feed to bypass the saturator until steady state operation was achieved. Once steady state operation was confirmed, feed stream ii was diverted through the saturator. The saturator was designed and constructed so as to completely saturate a gaseous feed stream with the desired oxygenate component. The calculation of saturator temperature for the required flow rate of co-fed components and the design of the saturator for complete saturation are as follows: The saturator temperature (T), was calculated according to the Antoine equation ^[4], equation 2.1, for each component:

$$T = \frac{B}{A - \log P_v} - C$$
 2.1

where P_{ν} is the vapour pressure of a component in Pa; and *A*, *B* and *C* are component specific coefficients for the Antoine equation ^[4]

In addition to using a sintered metal filter ^[5] to create small gas bubbles (ca. 0.002m in diameter), the saturator height was optimised, using equation 2.2, in order to fully saturate the feed stream with the component being co-fed.

$$\frac{dc_{G}}{dz} = \left(\frac{k_{g} \cdot a \cdot \left(\left(\frac{P_{v(T)}}{R \cdot T}\right) - C_{G}\right)}{u_{G}}\right)$$
2.2

Where k_g , is the gas phase mass transfer resistance in m.s⁻¹; a is the specific interfacial area in m⁻¹; R is the universal gas constant in Pa.m³.mole⁻¹.K⁻¹; T is the saturator temperature in K; c_G is the gas concentration in moles.m⁻³ and u_G is the gas velocity m.s⁻¹.

The saturator internal diameter was set to 0.06m and the liquid height (Z) was varied from 0 to 1 m. Taking into account the various oxygenates that were to be co-fed and the gas flow rate through the saturator. The optimised liquid height was calculated to be 0.2 m. For additional assurance and to allow for the decrease in the liquid level during an experiment, the maximum liquid height was set at 0.3 m.

⁴ NIST Chemistry WebBook, from http://webbook.nist.gov/chemistry/

⁵ *Mott Corporation.*, from http://www.mottcorp.com/

The fraction of the co-fed component in the gaseous feed was controlled by adjusting the temperature of a water bath which supplied a water/antifreeze solution at a specific temperature to the saturator jacket, the saturator temperature was checked by means of a thermocouple inserted into the saturator (Table 2). In order to prevent condensation of the co-fed component in the line leading to the reactor inlet, the temperature of the saturated vapour leaving the saturator was monitored with an inline thermocouple and controlled at 120 °C which was significantly above that of the saturator. To ensure that the gaseous feed stream was fully saturated with the component being co-fed, a sintered metal filter ^[5] was used to create small gas bubbles at the base of the saturator and hence a large mass transfer area. Furthermore, the dimensions of the saturator were optimised to ensure complete saturation of the feed gas at the set temperatures. Finally, the saturator was filled with excess liquid before the start of a run to ensure that the liquid level never dropped below the minimum required during the run confirming complete saturation of the gaseous feed. The stream exiting the 4-way valve was combined with the saturated feed stream just before the reactor inlet.



Figure 2 Saturator used to co-feed oxygenates

The flow rate of the co-fed component was $0.1 \text{ ml}_{(n)}$.min⁻¹ with the exception of 2butanone which was fed at $0.2 \text{ml}_{(n)}$.min⁻¹. The reason for the increased flow rate of 2-butanone is due to its high vapour pressure and the minimum temperature of the saturator.

Table 2 Desired flow rates of components to be co-fed and the corresponding saturator temperatures required for complete saturation of the H_2/Ar stream

Component	Desired volumetric	H_2/Ar flow rate	Saturator
to be co-fed	flow rate of component	into saturator	temperature
	ml _(n) .min⁻¹	ml _(n) .min⁻¹	°C
Ethanol	0.1	42	-12.2
1-Propanol	0.1	42	+12.3
2-Propanol	0.1	42	+2.7
2-Butanone	0.2	42	-7.2

2.1.2 Reactor section

The stainless steel, fixed bed reactor depicted in Figure 3 and Figure 1 (as unit C) has a reaction zone of 5 mm I.D. x 80 mm length. The reactor is sealed by flanges containing a re-usable silver gasket (top and bottom) to ensure that no leaks occur during high pressure operation (up to 10 bar). At the top of the reactor, a T union is used to connect the feed line and to allow the MS capillary to enter the reactor away from the heated zone; the same methodology is applied at the bottom of the reactor. The stainless steel capillaries extended up to the frits directly above and below the reaction zone and transport a small fraction of the gas stream to the MS. The source of the sample, which is analysed by MS, depends on the position of the 3-way valve depicted in Figure 1. The valve is typically set to sample from the capillary at the bottom of the reaction zone during a SSITKA experiment. To prevent condensation in the capillaries and the 3-way valve these sections are heated to 120 °C. At the exit of the reactor, the

remaining reaction products, unreacted feed components and inert gasses exit via the main line before entering the hot knockout pot set at 120 °C (see Figure 1, D). This knockout pot removes a small fraction of heavy wax and tar products which would otherwise accumulate in the exit lines over time. The line exiting the hot knockout pot is heated to 120 °C to prevent condensation of water and light hydrocarbon products still remaining. The line splits, with the smaller stream passing to the analysis section and the larger stream connects to a second knockout pot at ambient temperature. This removes water before the dry gas stream passes through an electronic back pressure regulator and exits via the vent.

The reactor is heated by an external electric heating mantle. A thermocouple placed inside the reactor wall and halfway down the catalyst bed controls the temperature of the reactor. The catalyst bed was loaded in such a way so that it was in the middle of the heating zone (about 28 cm from the top), to ensure an isothermal reaction zone. The reactor temperature was 420 °C during catalyst activation and 330 °C during FT synthesis.

This reactor was designed and manufactured so as to eliminate dead volume as well as axial gas mixing i.e. with SSITKA experiments in mind. Figure 4 (left) shows the forcing and mixing curves measured over the catalyst bed during a typical SSITKA experiment at 6 bar. The time constant for both curves are identical as shown in Figure 4 (right) and indicates no axial gas mixing. The residence time is represented by the time lag of the mixing curve with respect to the forcing curve and is 5.8 seconds under the reaction conditions described for Figure 4.

For explicit interpretation of the SSITKA data, the absence of internal or external temperature and mass gradients for this system were confirmed in a prior document ^[13].



Figure 3 Schematic of SSITKA reactor used



Figure 4 (*left*) Ne transients measured by mass spectrometry above (forcing curve) and below (mixing curve) the reaction zone; (*right*) Ne transients for the forcing and mixing curves superimposed to show the near ideal plug flow characteristics of this reactor. The data were obtained at inlet $H_2/CO = 10$, 330°C, 6 bar and GHSV = 3600 ml_(n).g_{cat}-1.h⁻¹

2.1.3.1 Gas Chromatography

Performance of the catalyst was monitored by an online Varian CP-3800 Gas Chromatograph (GC) equipped with two detectors:

- Thermal conductivity detector (TCD), for analysis of the permanent gasses
 N₂, CO, CO₂, H₂, H₂O and CH₄.
- Flame ionisation detector (FID), for analysis of C₁ to C₅ organic compounds.

The molar flows of the permanent gasses are quantified by addition of a known amount of N_2 as an internal standard to the gas stream just before the GC (TCD). The C_1 to C_5 organic compounds are quantified by calibration of the FID with external standards from calibration gas mixtures of known concentration. The results of GC analysis indicated when steady state operation was achieved and also allowed for the quantification of the kinetic isotope effect (KIE) as discussed in Chapter 6. The TCD and FID specifications including the GC oven program are given in Appendix 1.

Since the water-gas shift reaction is reversible at high temperature Fischer-Tropsch conditions, CO_2 can be both a reactant and a product. As such, the conversion of carbon (from CO or CO_2) to Fischer-Tropsch products is calculated as:

$$X_{CO+CO_{2}} = \frac{\left(F_{CO,in} - F_{CO,out}\right) + \left(F_{CO_{2},in} - F_{CO_{2},out}\right)}{F_{CO,in} + F_{CO_{2},in}}$$
2.3

where X is the conversion and F_i is the molar flow rate for species i
2.1.3.2 Mass Spectrometry

An online Balzers Thermostar mass spectrometer (MS) was used to detect the inert tracer species (Ne, Ar, Kr), reactants (H₂, CO) and light reaction products (CH₄, CO₂ etc.). The MS was connected to either of two sample points via a 1 metre heated capillary and a heated 3-way valve which could be set to sample from directly above or below the reaction zone. During a SSITKA switch, the MS collected data for m/e values of the various species as indicated in Table 3. The transient responses for these species are normalised between the MS intensity before the SSITKA switch and the stabilised MS intensity following the SSITKA switch to the isotopically labelled species, see equation 2.4.

$$E_{i,norm} = \frac{E_{i,t} - E_{i,min}}{E_{i,max} - E_{i,min}}$$
2.4

where $E_{i,norm}$ is the normalised transient of species i, $E_{i,t}$ is the MS intensity of species i, $E_{i,min}$ is the minimum intensity of species i and $E_{i,max}$ is the maximum intensity of species i.

Generally, a stable MS signal indicates that the unlabelled atom in all surface and gas phase species has been replaced by its labelled counterpart. It should however be noted that if a large pool of very slow reacting unlabelled atoms already exist on or near the catalyst surface, the MS signal may appear to stabilise while in fact not all the unlabelled atoms have been replaced. See Chapter 3 for further discussion of this concept.

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	Species Measured on MS						
SSITKA Switch	Ar,	¹² C ¹⁶ O,	¹² C ¹⁶ O ₂ ,	¹² CH ₄ ,	¹² C ¹⁶ O,	¹² C ¹⁶ O ₂ ,	H ₂ ¹⁶ O,
(syngas + labelled	Ne, Kr	¹³ C ¹⁶ O	¹³ C ¹⁶ O ₂	¹³ CH ₄	¹² C ¹⁸ O	¹² C ¹⁸ O ₂ ,	H ₂ ¹⁸ O
species)						¹² C ¹⁶ O ¹⁸ O	
¹² C ¹⁶ O to ¹³ C ¹⁶ O							
and	•	•	•	•			
¹² C ¹⁶ O ₂ to ¹³ C ¹⁶ O ₂							
¹² C ¹⁶ O to ¹² C ¹⁸ O	•				•	•	•

Table 3 Species measured on MS

2.1.3.3 Gas Chromatography Mass Spectrometry

Due to the variation and complexity of the FT product, the analysis of the isotopically labelled C₂ to C₄ hydrocarbons and oxygenates via characteristic m/e values by on-line MS is not possible. The transient responses of these products are obtained from their fragmentation patterns resulting from on-line gas chromatographic mass spectrometry (GCMS) analysis. The GCMS is equipped with 16 heated sample loops (120 °C) prior to the injector, which allow for the fast collection and storage of samples. The stored samples are then analyzed sequentially to allow for sufficient separation and analysis between injections. The timing for the collection of samples in the sample loops can be varied in order to ensure samples are collected over the entire transient period.

Following analyses of all 16 sample loops by GCMS, the resulting fragmentation patterns for each component are compiled and the isotopic composition of each component is calculated and plotted as a function of time (the time of the SSITKA switch is defined as time 0). For further details on the method of calculating the isotopic composition see van Dijk ^[1]. Following an isotope switch it is expected that the normalised transient responses for the isotopically labelled species will

increase from zero to unity as all the non-labelled species leave the system. Typically however, the normalised transient response for the labelled species level off at values slightly less than unity. This is due to the slight differences that different isotopes have on the GC-MS fragmentation pattern and the purity of the isotopic gases used. Importantly, when the transient responses are stable and do not increase further with time, it indicates that the majority of reactive nonlabelled species have left the system.

For Chapter 4 the isotopic compositions of the components presented in the bar graphs are taken from averages of the data during the stable period following a SSITKA switch (see Appendix 3). The GCMS was not calibrated to quantify each component; as such the effect of co-feeding various components in Chapter 4 were qualified by comparison of the species area counts from before and during the component addition. In order to eliminate the effect of variations in the sample volume injected, the species area counts were compared with respect to the area counts of propene for each injection. As an additional provision, propene was specifically chosen as the reference species since the alkene formation rate is thought to be unaffected by primary alcohol addition as indicated in Figure 5. This is in accordance with the findings of Tau *et al.*^[6] which indicated that added 1-propanol was directly hydrogenated to the corresponding alkane and not via a stepwise hydrogenation first to the alkene.

An example of the formation rate for propene is given for the ethanol co-feeding experiment in Figure 5 and indicates that the propene selectivity does not vary as a result of ethanol co-feeding. The observed decrease in propene selectivity with time-on-line is due to slight catalyst deactivation. The specifications of the GCMS are given in Appendix 1.

⁶ Tau L., Dabbagh H. A., Halasz J., Davis B. H., *J. Mol. Cat.*, Vol. 71, (1992) 37



Figure 5 Example of component whose formation rate does not vary due to co-feeding. This component is used as a reference component in Chapter 4 to account for the differences in sample volume injected on the GCMS allowing for a direct comparison of species area counts.

In Chapter 5 sufficient transient data were required for parameter estimation. As such, six SSITKA switches were made where the sample intervals of the 16-loop sample valve were varied for each switch. The six SSITKA switches took place over three separate experiments at the same reaction conditions to ensure that the effect of time on-line (TOL) with regard to activity and selectivity was minimised.

2.2 Fischer-Tropsch catalyst used in the experiments

The catalyst used in Chapters 3, 4 and 5 was supplied by Sasol Technology Research and Development and the preparation process for this "bulk" fused iron catalyst is described in considerable detail by Dry ^[7] and only a summary is given here; The catalyst is prepared via the fusion of iron oxide with chemical and

⁷ Steynberg A. P., Dry M.E. (Eds.), Stud. Surf. Sci. Catal, Vol. 152, Elsevier, Amsterdam, (2004)

structural promoters such as K₂O and MgO or Al₂O₃. Once the iron oxide and promoters have been added to an arc furnace and smelted, the mixture is poured into casting trays and cooled. The solid ingots are then crushed and milled; the milled catalyst is sieved in the laboratory to attain the desired particle size distribution before being loaded into the reactor. The iron oxide catalyst consists predominantly of the magnetite (Fe₃O₄) phase and is reduced in-situ to Fe metal prior to the start of FT synthesis ^[7]. Typical surface areas for this catalyst in its reduced form are in the range of 5 to 15 m² per gram of unreduced sample depending on the type and level of promoters used ^[7]. All fused catalysts used for the experiments of this thesis originated from the same catalyst batch.

The work of Chapter 6 used two different precipitated iron catalysts. Both catalysts having the same composition in terms of Fe mass % and grams Na₂O/100 g Fe, only one catalyst comprising additional sulphur as a promoter, see Table 4. The catalysts were supplied by Sasol Technology Research and Development and the method of preparation was via co-precipitation ^[8]. The exact method of preparation and the final catalyst composition are not provided here due to confidentiality.

Catalyst		Elemental Analysis	S
	Element	Unit	Measured
Standard Precipitated	S	/100 g Fe	0
Sulphur promoted	S	/100 g Fe	0.03 - 0.2 ^[9]

Table 4 Sulphu	[•] composition [•]	for the two	catalysts	used in	Chapter	6
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⁸ R.L. Espinoza, T.C. Bromfield, F.G. Botes, J.L. Visagie, K.H. Lawson and P. Gibson, Sasol Technology. US Patent, US 6844370, (2005)

⁹ T.C. Bromfield, R. Crous, EP Patent No. 2193841, assigned to Sasol Technology PTY. Ltd. Filed Dec. 4, (2009)

2.3 Start-up procedures

Typically, 1 gram of catalyst (particle diameter 40 to 100 μ m) was mixed with silica carbide (SiC, particle diameter 100 to 150 μ m) and loaded into the reactor. Additional SiC was used to position the catalyst bed in the middle of the reaction zone and fill the remaining dead volume between the frits. The larger particle size of the SiC reduces the pressure drop over the catalyst bed while still maintaining a homogeneous mixture with the catalyst. The dilution ratio (SiC to catalyst) is also considered in order to prevent gas bypassing effects ^[10, 11].

The catalyst was then reduced in a (3:1) H₂/Ar mixture with total gas hourly space velocity (GHSV) of 5000 ml_(n).g-cat⁻¹.h⁻¹, for 16 hours at 420 °C and atmospheric pressure. This was done to ensure low water partial pressures and allow for efficient catalyst reduction. After reduction, the reactor is cooled to 330 °C in flowing Ar. Synthesis is started by introducing a (1:10:9) CO/H₂/Ar feed mixture at GHSV of 3600 ml_(n).g-cat⁻¹s⁻¹ and increasing the total pressure to 6 bar. Online TCD and FID analysis indicated when steady state conversion and selectivity were reached. Steady state operation is related to the catalyst phase composition since the "working" FT catalyst consists of a mixture of mainly iron carbides and oxides which under the applied reaction conditions evolve over the first ca. 24 hours TOL ^[12].

Once steady state operation was achieved, steady state isotopic transient kinetic analyses (SSITKA) experiments were carried out. Figure 6 indicates the standard procedure followed for a SSITKA experiment i.e. *i*) development of steady state operation with the "standard" non-labelled species, *ii*) followed by the fast replacement of a feed species with its isotopically labelled counterpart (isotope

¹⁰ Berger R. J., Perez-Ramirez J., Kapteijn F., Moulijn J. A., Chem. Eng. Journal. Vol 90, (2002), 173

¹¹ Van den Bleek C.M., van der Wiele K. and van den Berg P.J., Chem.Eng.Sci. 24 1969: 681-694.

¹² Schulz H., SchaubG., Claeys M., Riedel T., Appl. Catal. A: Gen., Vol 186, (1999), 215

switch) while maintaining the steady state condition *iii*) and finally confirmation of the steady state after re-introduction of the "standard" non-labelled species. Steps *ii* and *iii* can be repeated as required with the same or different isotopically labelled components given that steady state operation is maintained. In the case of H_2/D_2 switches, steady state is no longer assumed due to the kinetic isotope (KIE) effect discussed further in Chapter 6.



Figure 6 CO + CO₂ conversion (conversion of CO to FT products) indicating the development of steady state operation and isotopic switches under typical experimental conditions. Inlet $H_2/CO = 10, 330$ °C, 6 bar and GHSV = 3600 ml_(n).g_{cat}⁻¹.h⁻¹

2.4 Estimating the CO and C₁ surface concentrations from transient responses

In the absence of the water gas shift reaction (WGS) and assuming that the intermediates leading to methane are the most abundant hydrocarbon species on the surface, the surface species concentrations which lead to CO and CH_4 respectively can be calculated from normalised transient responses according to ^[1]:

$$L_{co} = \frac{F_{co}}{W_{cat}} \int_{t=0}^{\infty} [E_{12}_{co}(t) - E_{inert}(t)] dt$$
 2.5

$$L_{c1} = \frac{F_{c0}X_{c0}}{W_{cat}} \left(\int_{t=0}^{\infty} [E_{12}_{CH_4}(t) - E_{inert}(t)] dt - \frac{1}{2} \int_{t=0}^{\infty} [E_{12}_{C0}(t) - E_{inert}(t)] dt \right)$$
 2.6

Where L_{CO} is the sum of the surface species concentrations which lead to gas phase CO; L_{C1} is the sum of surface species concentrations which lead to methane in mole.kg_{cat}⁻¹; F_{CO} is the molar feed flow rate of CO in moles.s⁻¹; X_{CO} is the conversion of CO [%]; $E_{_{12}CO}$ is the normalized transient for ¹²CO; E_{inert} is the normalized transient for the inert gas (in this case Ne) and $E_{_{12}CH_4}$ is the normalized transient for ¹²CH₄.

The surface species surface concentrations can be represented as a fractional coverage based on the method given in Appendix 2.

2.5 Reactor modelling

A detailed description of the model formation for SSITKA experiments in both CSTR and PFR reactors is given by Van Dijk^[1]. As such, only brief description of the relevant material is given here.

The experiments were carried out at integral conditions where alkene readsorption and reversible WGS was taken into account. The resulting axial concentration profiles require a plug flow reactor (PFR) model. The following assumptions were made with regard to the model equations:

- The absence of axial dispersion (i)
- The absence of radial concentration profiles (ii)
- The absence of mass transfer limitations (iii)
- Isothermal operation (iv)
- A constant volumetric flow rate (v)

The above assumptions (i to v) are verified in a separate report by Masthoff ^[13]. Van Dijk ^[1] showed no change in conversion and selectivity for the FT synthesis over a Co based catalyst, when switching the inlet flow from ¹²CO to ¹³CO and C¹⁶O to C¹⁸O. This is a good indication for the absence of kinetic isotope effects in the FT synthesis and was assumed to also be the case for this work.

The continuity equations describing the labelled gas phase component x' and labelled surface species y' under integral PFR conditions can be written as:

Gas phase:

$$\frac{\partial C_{x'}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{x'}}{z} = \frac{\rho_{b}}{\varepsilon_{b}} R_{w,x'}$$
2.7

Surface:

 $[\]frac{\partial L_{v'}}{\partial t} = R_{v'}$ 2.8

¹³ Masthoff L.P.J, Graduation Report, Technische Universiteit Eindhoven, (2012),

http://alexandria.tue.nl/extra1/afstversl/st/Masthof_2012.pdf

The initial and boundary conditions for equations 2.7 and 2.8 given an isotope step from gas-phase reactant i to i' are:

at t = 0,
$$z \ge 0$$
, $C_{x'} = L_{y'} = 0$ 2.9(a)

$$t > 0, z=0, C_{t'} = input function f(t)$$
 2.9(b)

$$t > 0, z=0, C_{x'}=0 \text{ for } x' \neq z'$$
 2.9(c)

where C_{x^i} is the labelled concentration of component x in the gas phase [mole.mg⁻³]; L_{y^i} is the surface concentration of species y [mole.kg_{cat}⁻¹]; τ is the residence time [s]; t is the time [s]; ρ_b is the catalyst bed density [kg_{cat}.mb⁻³]; ε_b is the catalyst bed porosity [mg³.mb⁻³]; R_{w,i^i} is the production rate of species i [mole.kg_{cat}⁻¹.s⁻¹] and z is the dimensionless axial position in the catalyst bed.

The input function f(t) describes the transient of the inert tracer species. An empirical function is used to fit the inert transient as indicated in Figure 7.



Figure 7 Input function f(t) fitted to inert tracer data for a ¹²CO to ¹³CO SSITKA switch. *The* data points were measured with online MS at $H_2/CO = 10$, 330 °C, 6 bar and GHSV = 3600 $ml(n).g_{cat}$ ⁻¹.hr⁻¹; a₁ = 24.16, a₂ = 2.12 and a₃ = 15, t in f(t) in s.

Fitting of experimental data to the model predictions is accomplished with the gPROMS software package ^[14]. The maximum likelihood formulation (Equation 2.10) is used which provides simultaneous estimation of parameters in both the physical model and the variance model.

$$\Phi = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min_{\theta} \left\{ \sum_{i=1}^{NE} \sum_{j=1}^{NV_i} \sum_{k=1}^{NM_{ij}} \left[\ln(\sigma_{ijk}^2) + \frac{(\tilde{z}_{ijk} - z_{ijk})^2}{\sigma_{ijk}^2} \right] \right\}$$
 2.10

where Φ is the objective function; N is the total number of measurements taken for all experiments; θ is the set of parameters to be estimated; NE is the number of experiments; NV_i is the number of variables measured in the *i*th experiment; NM_{ij} is the number of measurements of the *j*th variable in the *i*th experiment; σ_{ijk}^2 is the variance of the *k*th measurement of variable *j* in experiment *i*; \tilde{z}_{ijk} is the *k*th measured value of variable *j* in experiment *i* and $z_{ijk} k^{th}$ (model-)predicted value of variable *j* in experiment *i*.

Once the objective function is satisfied, the results are subjected to statistical analysis such as calculation of the confidence interval and the correlation of parameters to each other. Lastly the model is compared to the experimental data using a "lack of fit test", if the weighted residual is less than the χ^2 value the model is determined to be a good fit.

¹⁴ GPROMS version 3.4.0, 2011, computer software, Process Systems Enterprise Ltd., Hammersmith, London

2.6 Appendices

2.6.1 Appendix 1

Analytical specifications for GC and GCMS

	GC	GCMS
Column	TCD: CP-PoraBOND Q (I.D.=0.53	PoraBOND Q (I.D.=0.32 mm,
	mm, L=10m),	L=50 m)
	CP-PoraBOND Q (I.D.=0.53 mm,	
	L=25m),	
	CP-Molsieve 5a (I.D.=0.53 mm,	
	L=25m)	
	FID: PoraBOND Q (I.D.=0.25 mm,	
	L=25m)	
Carrier gas	Argon	Helium
Temperature	For TCD and FID (same oven)	5 min at -50 °C
program	4 min at 40 °C	Ramp 10 °C min ⁻¹ to 130 °C
	Ramp 10 °C min ⁻¹ to 85 °C (hold 5	(hold 5 min)
	min)	Ramp 15 °C min ⁻¹ to 240 °C
	Ramp 2 °C min ⁻¹ to 110 °C	(hold 10 min)
	Ramp 15 °C min ⁻¹ to 240 °C (hold	
	20 min)	
Column flow	Line 1 (TCD): 2.0 ml min ⁻¹	2.06 ml min ⁻¹
	Line 2 (FID1): 1.8 ml min ⁻¹	
MS Method		Scanning range: mass 12 to 150
		Scan Speed: 416 scan min ⁻¹
		Ion Source (EI),T: 230 °C
		Interface T: 250 °C

2.6.2 Appendix 2

Calculating the fractional surface coverage

In Chapter 3 and Chapter 6 the fractional surface coverages are calculated and compared to one another and to those measured previously by Govender^[15]. The following method is used:

$$Fe_{moles surf} = \frac{\frac{SA_{cat}}{SA_{Fe atom}}}{N_{A}}$$
2.11
Species $i_{cov} = \frac{Species i_{moles ads}}{Fe_{moles surf}}$
2.12

where $Fe_{moles surf}$ is the moles of iron at the catalyst surface in moles.g_{cat}⁻¹; SA_{Fe tom} is the surface area of an iron atom in nm² (based on diameter of 0.074 nm); SA_{cat} is the surface area of the catalyst in nm².g⁻¹; N_A is the Avogadro constant of 6.022E²³ mole⁻¹; Species_{icov} is the fractional coverage of species i and Species Species i_{moles ads} is the number moles of species i adsorbed on the catalyst surface in mole.kg_{cat}⁻¹.

¹⁵ Govender N.S., PhD Thesis., Technische Universiteit Eindhoven (2010)., Eindhoven., The Netherlands, http://alexandria.tue.nl/extra2/689931.pdf

2.6.3 Appendix 3

Example for construction of bar chart figures from Chapter 4 showing stable isotope compositions following isotope switches

In order to establish the reaction pathways of the co-fed species presented in Chapter 4, the stable isotopic compositions of the products as indicated in Figure 8 (following replacement of reactive ¹²C or ¹⁶O with their isotopic counterparts) are averaged (Table 5) and plotted as a bar graph, Figure 9. The stable isotopic compositions for all the products of interest can then be combined in one figure for comparison of carbon isotope composition.



Figure 8 Propene transient resulting from ¹²CO/H₂/Ar to ¹³CO/H₂/Ne isotope switch

Table 5 Stable	e isotopic	composition	of	propene	following a	¹² CO/H ₂ /Ar	to	¹³ CO/H ₂ /Ne
isotope switch	i							

Isotopic fraction	Average of stable (last 3) data points [%]
¹² C- ¹² C- ¹² C	3
¹² C- ¹² C- ¹³ C	3
¹² C- ¹³ C- ¹³ C	6
¹³ C- ¹³ C- ¹³ C	88



Figure 9 Stable propene isotope content following $^{12}\text{CO}/\text{H}_2/\text{Ar}$ to $^{13}\text{CO}/\text{H}_2/\text{Ne}$ isotope switch

Chapter 3

Role of Lattice Oxygen in CO Hydrogenation over a Bulk Fe Catalyst

In this chapter the Steady State Isotopic Kinetic Analysis (SSITKA) technique is utilized in order to investigate the elementary mechanistic pathways of oxygen species over a fused iron catalyst during the high temperature Fischer-Tropsch (HTFT) synthesis ($H_2/CO = 10, 330$ °C, 6 bar and GHSV = 3600 ml(n).g_{cat}⁻¹.hr⁻¹). The results of ¹³CO and C¹⁸O isotope switches with and without hydrogen in the feed indicate that CO oxidation to some extent occurs via a Mars and van Krevelen type of mechanism. Additional modelling of the reaction pathways including reversible diffusion of oxygen from the catalyst surface to the bulk, verifies the existence of reactive lattice oxygen. The simulations for the oxygen diffusion coefficient, D resulted in values of (6.84 ± 0.04) 10^{-14} and (8.64 ± 0.56) 10^{-14} m².s⁻¹ for reactions with and without hydrogen respectively.

3.1 Introduction

During preliminary C¹⁶O/H₂/Ar to C¹⁸O/H₂/Ne SSITKA experiments at high temperature Fischer-Tropsch (HTFT) reaction conditions, it was noted that the partially labelled transient of CO₂ (C¹⁸O¹⁶O) continues to elute long after the switch to C¹⁸O was made. After reaching a maximum, this transient remained relatively stable and did not decrease back to zero in the time scale expected if all the surface ¹⁶O had been replaced by ¹⁸O from C¹⁸O in the feed. This was shown to be a genuine catalytic effect since the SSITKA switch from C¹⁸O/H₂/Ne back to C¹⁶O/H₂/Ar, resulted in the C¹⁸O¹⁶O transient following an inverse trajectory, returning back to its starting value i.e. zero C¹⁸O¹⁶O as indicated in Figure 1.



Figure 1 Ion current measured on mass spectrometer for partially labelled CO_2 m/z = 46 ($C^{18}O^{16}O$) during a forward and back SSITKA switch, the blue line indicates the switch from $C^{16}O$ to $C^{18}O$ while the red line indicates the switch from $C^{18}O$ back to $C^{16}O$

This failure of the partially labelled species to return back to zero has previously been reported by Peil *et al.* ^[1] and Nibbelke *et al.* ^[2] for the oxidative coupling of

¹ Peil P. K., Goodwin J_R J. G., Marcelin G., *J. Catal.*, Vol 131, (1991), 143

methane over MgO-based catalysts up to temperatures of 645 °C and 750 °C respectively. In both cases, O_2 and methane reactants were fed to the reactor along with Ar as inert tracer and He as a diluent. Once steady-state conditions were achieved, ¹⁶O₂/CH₄ to ¹⁸O₂/CH₄ SSITKA switches were carried out. Other than the fully labelled ¹⁶O₂ and ¹⁸O₂ transients, the results from both studies showed the formation of the ¹⁶O¹⁸O transient, which after reaching a maximum failed to decrease back to zero. This was shown to be due to the existence of an additional oxygen source which is available for exchange, i.e. other than the oxygen from the feed. This extra oxygen source was thought to originate from lattice oxygen in the bulk of the oxide catalyst. Peil *et al.*^[1] found that the surface coverage of oxygen increased with increasing temperature, the coverage exceeding a monolayer by as much as an order of magnitude at temperatures above 600°C. To explain this result, it was suggested that there is an additional "surface" oxygen species distinct from the bulk oxygen which resides in a subsurface region. This oxygen species is readily available for exchange at the surface as indicated in Figure 2.



Figure 2 Scheme representing oxygen exchange between the gas phase and the bulk, adapted from ^[3]

² Nibbelke R.H., Scheerova J., de Croon M. H. J. M., Marin G. B., J. Catal., Vol 156, (1995), 106

³ Karasuda T., Aika K., J. Catal., Vol 171, (1997), 439

Although oxygen exchange between gas phase and the catalyst bulk have not been reported for the FT synthesis, various oxide phases are known to occur for Fe based FT catalysts. Dry ^[4] showed that for the HTFT synthesis the "working" catalyst is typically comprised of various iron carbide and iron oxide phases which evolve during synthesis according to the relative rates of the carbiding and reducing reactions. Experimental data of Davis ^[5] further suggested that the iron catalyst particle at low temperature FT conditions consists of an iron oxide core surrounded by an iron carbide shell. Figure 3 shows a scanning electron microscope (SEM) image of a spent fused iron catalyst taken after a HTFT experiment ^[6]. Combined with energy-dispersive X-ray spectroscopy (EDX) line scans to determine the elemental composition at different areas of the catalyst, the results further indicate that the "shell" correlates to an iron carbide phase and the "core" to iron oxide phase.



Figure 3 SEM image of polished, spent fused iron catalyst (approximately 40 μ m diameter) from a lab scale CSTR reactor following HTFT synthesis. This image indicates a particle with an iron carbide "shell" and iron oxide "core".

⁴ Steynberg A. P., Dry M.E. (Eds.), Stud. Surf. Sci. Catal, Vol. 152, Elsevier, Amsterdam, (2004)

⁵ Davis B. H., *Catal. Today*, **Vol 141**, (2009), 25

⁶ Ter Stege G., Moodley P., (2011), personal communication, 19 September, ghislaine.terstege@sasol.com

Assuming that oxygen diffusion to and from the catalyst bulk may take place during the HTFT synthesis, the aim of this chapter is to further investigate the nature of interaction of oxygen with the catalyst, quantify the oxygen surface coverages and determine the oxygen diffusion coefficient in the iron based catalyst particle.

Transient data gathered via SSITKA experiments will be used to quantitatively fit a mechanistic model describing the reaction steps of the various oxygen species including oxygen diffusion to and from the bulk. Finding a realistic value for the oxygen diffusion coefficient, ca. 1×10^{-15} m.s⁻¹^[7] will strongly support the notion that the formation of CO₂, H₂O and possibly the oxygenates occur to some extent via a Mars and van Krevelen (MvK) type of mechanism ^[8, 9] during the HTFT synthesis. An example of the MvK mechanism for CO oxidation is given in Figure 4. This mechanism differs from a Langmuir Hinshelwood mechanism in the respect that some products leave the catalyst surface containing a component of the catalyst lattice ^[9]; initially (part a), the activated oxygen lattice is created from reactive oxygen originating from gas phase or bulk, which fill a vacancy at the catalyst surface. CO oxidation (part b) then occurs via reaction of the lattice oxygen with adsorbed CO to form CO₂ and create a new oxygen vacancy which can be filled again.

⁷ Castle J.E., Surman P.L., J. Phys. Chem., Vol. 71 – 13, (1967), 4255

⁸ Zhu J., van Ommen J. G., Bouwmeester H. J. M., Lefferts L., *J. Catal.*, Vol 233, (2005), 434

⁹ Doornkamp C., Ponec V., J. Molec. Catal. A: Chem. Vol 162, (2000), 19



Figure 4 Mars and van Krevelen mechanism for CO oxidation

3.2 Experimental results

Two conditions were distinguished for the SSITKA experiments, i) non FT reaction conditions and ii) FT reaction conditions.

3.2.1 ¹²C¹⁶O to ¹³C¹⁶O and ¹²C¹⁶O to ¹²C¹⁸O SSITKA with <u>no</u> HTFT synthesis (CO /Ar)

For these experiments, the standard start-up procedure was followed and synthesis was initiated as per normal, i.e. with synthesis gas (CO and H₂). Once steady-state operation was achieved and the various catalyst phases had evolved, the synthesis gas was stopped and the system was flushed with argon (60 ml_(n).min⁻¹) for 1 hour to remove all reactive gas phase species. Thereafter, CO together with additional argon (to replace the hydrogen) was fed to the reactor. Since CO is the reactant and CO₂ the product of this reaction, there may be a net loss of oxygen from the catalyst for the case where the additional oxygen atom originates from the catalyst bulk and not directly from the dissociation of adsorbed CO. The removal of bulk oxygen as CO₂ during the time of the SSITKA

experiment is however considered to be insignificant compared to the large amount of bulk oxygen available for reaction (the total oxygen removed as CO₂ was calculated to be approximately 4% of total bulk oxygen available assuming the catalyst is made up of iron oxide). The results of this experiment are therefore assumed to be representative of a system at steady state conditions. After an initial period of stabilization (approximately 2 hours), ¹²C¹⁶O to ¹³C¹⁶O and ¹²C¹⁶O to ¹²C¹⁸O SSITKA switches were carried out in the absence of Fischer-Tropsch reaction so as to study the "simplified" interaction of oxygen and carbon with the catalyst i.e. without water, hydrocarbon or oxygenate formation.

The <u>CO</u> transients resulting from two separate SSITKA switches (¹³C and ¹⁸O labelled CO) are given in Figure 5 (left). For clarity, the ¹²CO and C¹⁶O responses are not shown but are easily calculated; by definition, the sums of the carbon or oxygen fractions equal one. The following observations are made:

- The normalized transient responses for ¹³CO and C¹⁸O are not the same. The ¹³CO transient elutes at almost the same time as the inert gas (all ¹²C species leading to CO have been replaced by ¹³C) while the C¹⁸O transient does not attain full labelling even 20 minutes after the SSITKA switch.
- The difference in the transient responses of ¹³CO vs. C¹⁸O, is expected for the case of reversible dissociation of adsorbed CO (reaction step *ii* of Table 1) where the adsorbed C and O have different surface coverages. If irreversible CO dissociation (reaction step *iii* of Table 1) took place, then the transient responses for ¹³CO and C¹⁸O would be identical ^[10].
- At 20 minutes time on-line (TOL), the C¹⁸O transient is relatively stable at ca.
 0.9 and seems to have reached a pseudo steady state. This indicates that some reactive ¹⁶O is still present in the "system", most likely the catalyst bulk

¹⁰ Van Dijk, H.A.J., PhD Thesis, (2001), Technische Universiteit Eindhoven, Eindhoven, the Netherlands.http://alexandria.tue.nl/extra2/200111083.pdf

^[2]. The difference between the complete replacement of the $C^{16}O$ with $C^{18}O$ and the pseudo steady state of $C^{16}O$ is known as the offset and indicates the contribution of the bulk/lattice oxygen to the overall oxygen exchange ^[1].

Table 1 Elementary reaction steps for formation of CO2 via reversible and irreversible COdissociation including oxygen diffusion to and from the catalyst bulk

i)	$CO_{(g)} \rightleftharpoons CO_{(ads)}$
ii)	$CO_{(ads)} \rightleftharpoons C_{(ads)} + O_{(ads)}$
iii)	$CO_{(ads)} \rightarrow C_{(ads)} + O_{(ads)}$
iv)	$CO_{2(ads)} \rightleftharpoons CO_{(ads)} + O_{(ads)}$
v)	$O_{(ads)} \rightleftharpoons O_{(bulk)}$

The <u>CO₂</u> transients resulting from two separate SSITKA switches (13 C and 18 O labelled CO) are given in Figure 5 (right). The following observations are made:

- The transient for ¹³CO₂ elutes fully, approximately 7 minutes after the SSITKA switch and then remains constant, indicating that all ¹²C surface species leading to CO₂ have been replaced by ¹³C.
- The transient response for C¹⁸O₂ does not follow the expected trend for the full replacement of ¹⁶O with ¹⁸O intermediates. The transient for C¹⁸O₂ only increases to approximately 73% ¹⁸O labelling following the SSITKA switch and then remains relatively constant with TOL.
- The transient for $C^{16}O_2$ decreases to zero and thus indicates that the predominant pathway for CO_2 formation is via the oxidation of molecular CO i.e. CO + O (reaction step *iv* of Table 1). If CO_2 was formed via the stepwise reaction of C + O + O, the transient of $C^{16}O_2$ would not decrease to zero since there would always be the possibility of two bulk ¹⁶O atoms combining with the same carbon to form $C^{16}O_2$.

For the transient containing both oxygen isotopes (C¹⁸O¹⁶O), full replacement of ¹⁶O would result in an initial increase to a maximum and then decreases back to zero as ¹⁶O was replaced by ¹⁸O. The C¹⁸O¹⁶O transient of Figure 5 (right) does not decrease back to zero and levels off at an offset value of approximately 0.29. This indicates that some ¹⁶O still reacts with C¹⁸O long after all the ¹⁶O directly available at the surface was replaced by ¹⁸O.



Figure 5 (left) Transients for ¹³C and ¹⁶O labeled CO species. (right), Transients for ¹³C and oxygen labeled CO₂ species. The data points were measured under <u>non-FT</u> reaction conditions (CO and Ar) with online MS at 330 °C, 6 bar and GHSV = $3600 \text{ ml}_{(n)} \cdot g_{cat}^{-1} \cdot hr^{-1}$

3.2.2 ¹²C¹⁶O to ¹³C¹⁶O vs. ¹²C¹⁶O to ¹²C¹⁸O SSITKA during Fischer-Tropsch reaction (CO/H₂/Ar)

For this work, the standard start-up procedure was followed and synthesis was initiated as per normal, i.e. with synthesis gas (CO and H₂). Once steady-state operation was achieved $^{12}C^{16}O$ to $^{13}C^{16}O$ and $^{12}C^{16}O$ to $^{12}C^{18}O$ SSITKA switches were carried out during Fischer-Tropsch reaction conditions. The results of these experiments are then compared to those for no FT synthesis.

Figure 6 (left) shows the elution of labelled <u>CO</u> from two separate SSITKA switches under FT reaction conditions (¹³C and ¹⁸O labelled CO). The following observations are made:

- Similar to the experiments with no FT reaction, the normalized transient responses during FT reaction for ¹³CO and C¹⁸O differ from one another. The difference between the transients is however smaller and is thought to indicate a decrease in reversible CO dissociation due to the presence of hydrogen.
- The ¹³CO transient for FT reaction conditions is similar to the ¹³CO transient for non FT conditions, eluting at almost the same time as the inert gas.
- Under FT reaction conditions, the C¹⁸O transient elutes fully within 15 minutes of the SSITKA switch. This is different to the result obtained for the transient under non FT conditions. This difference is thought to result from the preferred reactions of surface carbon and oxygen with hydrogen to form hydrocarbons and water as opposed to the reaction of carbon with oxygen for reversible CO dissociation.

The results of two separate SSITKA switches (¹³C and ¹⁸O labelled CO) for the formation of <u>CO₂</u> from CO under FT reaction conditions are given in Figure 6 (right). The trends for the CO₂ transients are similar to those for the non FT reaction conditions, the following observations are made:

- The transient for ¹³CO₂ elutes fully at approximately the same time as that for non FT conditions after the SSITKA switch, indicating that all ¹²C surface species leading to CO₂ have been replaced by ¹³C.
- The transient response for C¹⁸O₂ does not follow the expected trend for the full replacement of ¹⁶O with ¹⁸O intermediates. The transient for C¹⁸O₂ increases to approximately 70% ¹⁸O labelling following the SSITKA switch and

then remains relatively constant during the remaining time of the SSITKA experiment.

- The transient for C¹⁶O₂ decreases to zero indicating that the predominant pathway for CO₂ formation is via the oxidation of molecular CO i.e. CO+O.
- The C¹⁸O¹⁶O transient does not decrease back to zero and levels off at an offset value of approximately 0.28 indicating a fraction of bulk ¹⁶O contributes to the overall oxygen exchange. Given that iron oxide phases are present in the fused iron catalyst during steady state synthesis and the failure of the C¹⁸O¹⁶O transient to decrease back to zero long after all the "surface" ¹⁶O has been replaced by ¹⁸O, strongly indicates that at least part of the CO₂ formed in the FT synthesis occurs via a Mars and van Krevelen mechanism.
- The transient for H₂¹⁸O was measured by GCMS and as such only limited data points are available. As for CO₂, this transient does not reach full labelling in the time of the SSITKA experiment indicating that a fraction of ¹⁶O from the bulk is hydrogenated to water.



Figure 6 (left) Transients for ¹³C and ¹⁶O labeled CO and H₂O species. (right), Transients for ¹³C and oxygen labeled CO₂ species. *The data points were measured under <u>FT</u> reaction conditions with online MS and GCMS (water) at H₂ / CO = 10, 330 °C, 6 bar and GHSV = 3600 ml_(n).g_{cat}⁻¹.hr⁻¹*

3.2.3 Calculation of surface coverages

Since the inert feed component does not interact with the catalyst surface, the transient response for the inert exiting the catalyst bed represents the gas phase holdup. The area between the transient of a reactive species and the transient of the inert therefore gives the mean surface residence time of the surface species related to that transient. By combining the mean surface residence time with the steady state activity of the catalyst, estimates for the sum of intermediate surface species concentrations which lead to that species can be made ^[10]. For the reaction under no FT conditions, the carbon present in CO and CO₂ could have been present on the catalyst surface as CO_{ads}, C_{ads} and CO_{2,ads}. It is therefore not possible to determine the surface coverages L_{CO}, L_C and L_{CO2} separately, but only the sum of the three:

$$L_{c,tot} = L_{co} + L_{co_2} + L_c = \frac{F_{co}}{W_{cat}} \int_{t=0}^{\infty} \left[E_{12}_{co}(t) - E_{inert}(t) \right] dt + \frac{F_{co2,out}}{W_{cat}} \left(\int_{t=0}^{\infty} \left[E_{12}_{co_2}(t) - E_{inert}(t) \right] dt - 0.5 \int_{t=0}^{\infty} \left[E_{12}_{co}(t) - E_{inert}(t) \right] dt \right)$$
3.1

This also applies to L_{CO} , L_{C} and L_{CO2} for the reaction under FT conditions. Here, carbon also leaves the reactor as hydrocarbons. Assuming that the C₁ precursors leading to CH₄ are by far the most predominant hydrocarbon precursor, the CH₄ transient depicted in Figure 7 is used to determine the average surface coverages of the carbon containing surface species leading to all hydrocarbon products.



Figure 7 Transient for ¹³CH₄ measured under <u>FT</u> reaction conditions with online MS at $H_2/CO = 10, 330$ °C, 6 bar and GHSV = 3600 ml_(n).g_{cat}⁻¹.hr⁻¹

Therefore the surface coverage of carbon containing surface species for the reaction under FT reaction conditions can be estimated by:

$$L_{c,tot} = L_{c0} + L_{c0_2} + L_c = \frac{F_{c0}}{W_{cat}} \int_{t=0}^{\infty} \left[E_{12}_{c0}(t) - E_{inert}(t) \right] dt + \frac{F_{c02,out}}{W_{cat}} \left(\int_{t=0}^{\infty} \left[E_{12}_{c0_2}(t) - E_{inert}(t) \right] dt - 0.5 \int_{t=0}^{\infty} \left[E_{12}_{c0}(t) - E_{inert}(t) \right] dt \right) + \frac{F_{cH4,out}}{W_{cat}} \left(\int_{t=0}^{\infty} \left[E_{12}_{cH_4}(t) - E_{inert}(t) \right] dt - 0.5 \int_{t=0}^{\infty} \left[E_{12}_{c0}(t) - E_{inert}(t) \right] dt \right) \right)$$
3.2

where $L_{c,tot}$ is the sum of carbon surface species concentrations mole.kg_{cat}⁻¹ leading to ¹²C species in the gas phase; L_i is the surface species concentration of species *i* in mole.kg_{cat}⁻¹; F_i is the molar feed flow rate of species *i* in mole.s⁻¹; E_i is the normalized transient response for species *i* and W_{cot} is the catalyst mass in kg

The offset for both the C¹⁶O and C¹⁸O¹⁶O transients (*left and right*) of Figure 5 and the C¹⁸O¹⁶O transients (*right*) of Figure 6 indicate the contribution of the bulk to the overall oxygen exchange. For non FT conditions the offset at approximately 10

minutes TOL for the C¹⁶O transient is 0.1 and for the C¹⁸O¹⁶O transient is 0.29. For FT reaction conditions the offset at approximately 10 minutes TOL for the C¹⁸O¹⁶O transient is 0.28 and for the H₂¹⁶O transient approximately 0.3. In order to calculate the surface coverage of oxygen containing intermediates, a correction for the bulk phase contribution must be made. The method developed by Peil *et al.* ^[1] is used. The results are given in Figure 8.

$$E_{\text{corr,}^{16}O,CO_{2}}(t) = \frac{2E_{C^{16}O_{2}}(t) + E_{C^{16}O^{18}O}(t) - E_{b,CO_{2}}(t)}{2}$$
3.3

$$E_{corr, {}^{16}O, CO}(t) = E_{C^{16}O}(t) - E_{b, CO}(t)$$
3.4

$$E_{b,x}(t) = \left(offset\right)_{x} \left(1 - exp\left(\frac{t}{t - t_{ss}}\right)\right)$$
3.5

where $E_{corr, {}^{16}O, x}(t)$ is the corrected fraction of ${}^{16}O$ on the surface leaving the reactor as species x [-]; $E_y(t)$ is the fraction of species y leaving the reactor [-]; t_{ss} is the time when the transient reaches steady state (pseudo steady state) i.e. time the offset value is reached [min]; (offset)_x is the fraction of bulk oxygen which contributes to the overall exchange [-]; $E_{b,x}(t)$ is the correction for the bulk phase contribution [-].



Figure 8 (left) CO and CO₂ transients under non FT reaction conditions, corrected for bulk diffusion, (right) CO₂ and water transients under FT reaction conditions, corrected for bulk diffusion.

Figure 8 (left) gives the CO and CO₂ transients corrected for the bulk phase, oxygen contribution during experiments with no FT reaction. Assuming that CO₂ is the major oxygen containing product, the total coverage of oxygen surface species leading to gas phase CO and CO₂, ($L_{oxy,tot}$) can be calculated by:

$$L_{Oxy,tot} = L_{CO} + L_{CO_2} = \frac{F_{CO}}{W_{cat}} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{F_{CO}X_{CO}}{W_{cat}} \left(\int_{t=0}^{\infty} \left[E_{C^{16}O_2}(t) - E_{inert}(t) \right] dt - 0.5 \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt \right)$$
3.6

Under the assumption that the oxygen concentration in the oxygenate fraction is negligible compared to the oxygen concentration of the CO, CO₂ and water fractions and CO₂ and water are the major oxygen containing products resulting from the conversion of CO. The total oxygen surface coverage $L_{oxy,tot}$ for the experiment under FT synthesis is calculated from the inverse of the C¹⁸O transient of Figure 6 and the CO₂ and water transients of Figure 8 (left):

$$L_{Oxy,tot} = L_{co} + L_{co_2} + L_{H_2O} = \frac{F_{co}}{W_{cat}} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{F_{co}X_{co}}{W_{cat}} \left[\left(\int_{t=0}^{\infty} \left[E_{C^{16}O_2}(t) - E_{inert}(t) \right] dt \right] + \int_{t=0}^{\infty} \left[E_{H_2^{16}O}(t) - E_{inert}(t) \right] dt - \frac{1}{2} \right] dt - \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt - \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt - \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt + \frac{1}{2} \int_{t=0}^{\infty} \left[E_{C^{16}O}(t) - E_{inert}(t) \right] dt$$

where $L_{O_{species}}$ is the sum of oxygen surface species concentrations mole.kg_{cat}⁻¹ leading to ¹⁶O species in the gas phase; F_{co} is the molar feed flow rate of CO in mole.s⁻¹; W_{cat} is the catalyst mass in kg; E_i is the normalized transient response for species *i* and X_{co} is the conversion of gas phase CO (in this case to CO₂).

The results for the carbon and corrected oxygen surface coverages calculated from equations 3.1, 3.2 and 3.6, 3.7 are given in Table 2. In addition to the surface species concentrations, the fractional surface coverages are also calculated according to the method described in Chapter 2, Appendix 2. The following observations are made:

- The total active carbon surface coverage for the experiment under non FT reaction conditions is approximately twice that of the system under FT reaction conditions. Given that the reaction conditions as well as the partial pressure of CO was kept constant for both experiments, the difference in active carbon surface coverages is believed to be due to the formation of hydrocarbon products under FT reaction conditions rather than an increased rate of active carbon formation via the Boudouard reaction under non FT reaction conditions.
- If the calculated oxygen surface coverages for either or both experiments significantly exceeded a monolayer this would indicate the presence of near or sub surface oxygen for that experimental condition as indicated by Peil *et al.*^[1] where oxygen coverages exceeded a monolayer by as much as an order

of magnitude above 600°C. For this work the oxygen surface coverages for both non FT and FT reaction conditions are well below a monolayer at 0.091 and 0.081 at 330°C respectively. As such, the presence of near / sub surface oxygen as depicted in Figure 2 cannot be confirmed for this catalyst.

- Although no direct evidence for near / sub surface oxygen is provided here and the limited magnification of the SEM image presented in Figure 3 only points to a particle with an iron carbide shell and iron oxide core. An alternative representation of the "working catalyst" may be one similar to that depicted in Figure 9. Here the source of reactive "bulk" oxygen may reside in smaller iron oxide islands within the iron carbide shell. The advantage of this interpretation allows for oxygen vacancy diffusion at or close to the catalyst surface and thus an MvK mechanism for CO oxidation.
- At this stage, the exact origin of the oxide core indicated in Figure 3 is not clear. It may be residual oxygen from the original magnetite particle which was not fully reduced (mostly "inert" oxygen) or it may have formed from a fully reduced iron particle during the initial stages of the FT reaction (reactive oxygen). An experiment where C¹⁸O syngas is used from the start of synthesis and then switched to C¹⁶O after steady state is reached would provide further insight into the origin of the reactive "bulk" oxygen.

Parameter	Units	No FT reaction	FT reaction (with	Change
		(without H ₂)	H ₂)	[%]
L _{C, tot}	[mole.k _{gcat} -1]	2.10×10^{-02}	1.00×10^{-02}	
θ _{C, tot}	[-]	0.014	0.0065	-53.6
L _{oxy, tot}	[mole.k _{gcat} ⁻¹]	8.75 × 10 ⁻⁰²	7.85×10^{-02}	
θ _{oxy, tot}	[-]	0.091	0.081	-11.0

Table 2: Surface coverages calculated from experimental data



Figure 9 Proposed representation of an iron oxide "core" surrounded by an iron carbide "shell" containing oxide islands

3.3 Model formulation for oxygen pathways including bulk oxygen diffusion

3.3.1 Reaction mechanisms to describe isotopic labelling experiments including bulk oxygen diffusion

The mechanism described in Table 3 takes reversible CO dissociation (*i*, *ii*), diffusion of oxygen to and from the catalyst bulk (*iii*), formation of H_2O (*iv*), CO_2 formation via oxidation of CO (*v*, *vi*) and the formation of hydrocarbons (*vii*) into account. It should be noted that in an attemp to keep this mechanism basic, CO adsorption, CO dissociation and CO oxidation are modeled as sharing the same surface species (CO_{ads}). Furthermore, the formation of water is assumed to occur in a single step via the direct hydrogenation of surface oxygen. Oxygenate formation is neglected since the fraction of oxygen contained in the oygenates is negligable as compared to that contained in CO, CO_2 and H_2O .

i)	$CO_{(g)} \rightleftharpoons CO_{(ads)}$
ii)	$CO_{(ads)} \rightleftharpoons C_{(ads)} + O_{(ads)}$
<i>iii)</i>	$O_{(ads)} \rightleftharpoons O_{(\mathit{bulk})}$
iv)	$O_{(ads)}$ +2 $H_{(ads)}$ \rightleftharpoons $H_2O_{(g)}$
v)	$O_{(ads)}+CO_{(ads)} \rightleftharpoons CO_{2(ads)}$
vi)	$CO_{2(ads)} \rightleftharpoons CO_{2(g)}$
vii)	$xC_{(ads)} + yH_{(ads)} \rightarrow C_{x}H_{y(g)}$

Table 3 Reaction mechanism used to describe SSITKA experiments

The schematics depicted in Figure 10 and Figure 11 are used to model the oxygen pathways for non FT and FT reaction conditions including the formation of CO₂ via a type of Mars van Krevelen mechanism. These models (S-1 and S-2) are based on the reaction steps given in Table 3. In addition to the approximation of the kinetic parameters, the oxygen diffusion coefficient, D is also estimated. It should be noted that the exact structure of the surface species is not known, as such they may differ from the structures presented in the figures.



Figure 10 Schematic representation of oxygen pathway for CO oxidation under non Fischer-Tropsch reaction conditions



Figure 11 Schematic representation of oxygen pathway for CO oxidation under Fischer-Tropsch reaction conditions

3.3.2 Reactor model

As described in Chapter 2, the reactions are carried out in an isothermal plug-flow reactor (PFR) containing fused iron catalyst diluted with SiC under integral reaction conditions. In order to determine the kinetic parameters from the SSITKA data, the experiments must be carried out under conditions absent from (i) axial dispersion (ii), radial concentration profiles (iii), mass transfer limitations and (iv) kinetic isotope effects. These conditions are verified in Chapter 2 and in a report by Masthoff ^[11].

The continuity equations describing the labelled gas phase component x' and labelled surface species y' under integral PFR conditions are given in Chapter 2. Taking into account the oxygen diffusion to and from the catalyst bulk for the oxygen lableled isotope experiments, the oxygen flux at the surface of the catalyst is calculated via Fick's first law of diffusion,

¹¹ Masthoff L.P.J, Graduation Report, Technische Universiteit Eindhoven, (2012), http://alexandria.tue.nl/extra1/afstversl/st/Masthof_2012.pdf

$$J_{0} = -D \frac{\partial S_{0}}{\partial r} \bigg|_{r=R_{\text{particle}}}$$
3.8

The flux of oxygen atoms towards the bulk of the catalyst is calculated from Fick's second law of diffusion,

$$\frac{\partial S_{0}}{\partial t} = D \frac{\partial^{2} S_{0}}{\partial r^{2}}$$
3.9

Where J_0 is the oxygen flux [mole.m_{cat}⁻².S⁻¹], D is the oxygen diffusion coefficient [m_{cat}².s⁻¹], S₀ the oxygen concentration in the in the catalyst bulk [mole.m_{cat}⁻³] and r the particle radius [m_{cat}].

The concentration of oxygen in the catalyst bulk at point $r=R_{particle}$ is related to the surface concentration of oxygen via,

$$S_0\Big|_{r=R_{\text{narrive}}} = \rho_{\text{cat}} \cdot L_0$$
3.10

Where ρ_{cat} is the catalyst density $[kg_{cat}.m_{cat}^{-3}]$ and L_0 is the oxygen surface concentration [moles.kg_{cat}^{-1}].



Figure 12 Diffusion of oxygen to and from the catalyst particle bulk

Appendi gives an example of the model equations used to describe Model S-2. The partial differential equations which describe the gas phase components and
the algebraic equations for the surface species must be solved simultaneously. Parameter estimation is accomplished with the gPROMS software package ^[12] as described in Chapter 2.

3.4 Parameter estimation results

To simplify the estimation of the kinetic parameters, a similar procedure to that of Govender ^[13] was used to fix the rate constants for k_{ads} and k_{des} . By assuming that the adsorption/desorption of CO for the FT reaction is a fast reaction and in equilibrium, it was found that the consumption to products relative to desorption of CO_{ads} was insignificant for values of k_{ads} greater than 0.116 m³g.kg_{cat}-1.s⁻¹. Given the assumption above, initial values for k_{des} can be calculated and fixed in the parameter estimation process. Since it is plausible that more than one surface species may lead to the formation of CO, for example via reverse WGS, the value of CO_{ads} is only an approximation and the value of k_{des} is optimised in the final step of the parameter estimation process. Finally, the resulting values for the reaction rate constants and surface coverages are given in Table 5 and assessment of experimental vs. model flow rates and conversions are presented in Table 4.

¹² GPROMS version 3.4.0, 2011, computer software, Process Systems Enterprise Ltd., Hammersmith, London

¹³ Govender N.S., PhD Thesis., Technische Universiteit Eindhoven (2010), Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/689931.pdf

		No FT reaction		FT reaction	
Parameter	Units	Experimental	Model	Experimental	Model
		values	prediction	values	prediction
C _{CO} , out	[mole.s ⁻¹]	2.09 × 10 ⁻⁰⁶	2.14 × 10 ⁻⁰⁶	1.67 × 10 ⁻⁰⁶	1.77 × 10 ⁻⁰⁶
C _{CO2} , out	[mole.s ⁻¹]	1.50 × 10 ⁻⁰⁷	5.00×10^{-08}	1.80×10^{-07}	2.10 × 10 ⁻⁰⁷
C _{H2O, out}	[mole.s ⁻¹]	—	_	5.20 × 10 ⁻⁰⁷	3.00×10^{-08}
X _{co}	[%]	6	4	25	21
X _{CO + CO2}	[%]	_	_	17	11

Table 4 Comparison of	steady state	molar flow r	rates and	conversion
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The predictions for the CO and CO₂ transients using the optimised parameters of Table 5 for Model S-1 and S-2 are presented in Figure 13 and Figure 14, respectively. Both models result in the correct predictions of the trends observed for the experimental results. Model S-1 provides an accurate description of the transient data for the non FT reaction and can be considered a good fit given a constant variance in the experimental data of less than 5%, additionally none of the parameters where correlated to one another. Model S-2 describes the transient data for FT reaction conditions less accurately and only gives a good fit when the variance in the experimental data was set above 5%. Both models do however predict the diffusion coefficient, D equally well with no correlation to any other parameters and with reasonable standard deviations (a 95% t-value smaller than the reference t-value) indicating that the diffusion coefficient is estimated precisely. The value of D is similar for both non FT and FT reaction conditions indicating that diffusion of oxygen to and from the catalyst bulk is not influenced by the presence of hydrogen.

The lack of Model S-2 to describe the FT reaction transient data given a variance of less than 5% could indicate that either i) there is insufficient experimental data or ii) Model S-2 is fundamentally incorrect and further parallel or buffer steps may be required to describe the measured transients . The water transient resulting from the FT reaction conditions were also fitted to model S-2 and are given in Figure 15. The results of Figure 15 clearly indicate that additional steps for the hydrogenation of surface oxygen to water and additional experimental data must be included for a more realistic representation. An example of an extended model is simulated in Section 3.5 below.

Comparison of the optimised parameter estimates from Table 5 for Model S-1 and S-2 indicate that addition of hydrogen leads to:

- A decrease in the reaction rate for reversibility of CO dissociation.
- A slight decrease in the total oxygen surface coverage. Interestingly the surface coverage of O_{ads} remains relatively constant upon hydrogen addition and it is the COO_{ads} coverage which decreases most significantly.



Figure 13 Model results for the CO and CO₂ transients under non FT reaction conditions using Model S-1, dashed lines indicate model prediction, the experimental data was obtained from MS analysis



Figure 14 Model results for the CO and CO₂ transients under FT reaction conditions using Model S-2, dashed lines indicate model prediction, the experimental data was obtained from MS analysis



Figure 15 Model results for the H₂O transient obtained under FT reaction conditions using Model S-2, dashed line indicates model prediction, the experimental data for H₂O were obtained from GCMS analysis

Table 5 Optimized parameter estimates for the oxygen pathways according to Models S-1 and S-2

		Model S-1 (no	FT reaction)	Model S-2 (wi	th FT reaction)
Parameter	Units	Estimated value	Standard deviation	Estimated value	Standard deviation
۵	[m ² .s ⁻¹]	8.637×10^{-14}	5.547×10^{-15}	6.839×10^{-14}	3.904×10^{-16}
kads	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	1.160×10^{-01}	I	1.160×10^{-01}	I
k _{des}	[S ⁻¹]	$1.133 \times 10^{+02}$	$1.069 \times 10^{+01}$	$2.154 \times 10^{+01}$	3.178×10^{-01}
kco, dis	[S ⁻¹]	3.188×10^{-02}	8.840×10^{-03}	2.299×10^{-02}	9.589×10^{-04}
kco, ass	[S ⁻¹]	2.545×10^{-02}	2.211×10^{-02}	1.272×10^{-07}	5.900×10^{-03}
kco2, dis	[S ⁻¹]	8.196×10^{-02}	1.693×10^{-03}	$1.580 \times 10^{+01}$	$2.869 \times 10^{+00}$
kco2, ass	[kg _{cat} .mole ⁻¹ .s ⁻¹]	$7.493 \times 10^{+02}$	$7.914 \times 10^{+01}$	$1.977 \times 10^{+02}$	$4.693 \times 10^{+00}$
kco2, des	[S ⁻¹]	2.438×10^{-03}	3.096×10^{-04}	$2.183 \times 10^{+01}$	5.744×10^{-01}
kco2, ads	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	5.000×10^{-08}	1.947×10^{-04}	1.336×10^{-02}	2.835×10^{-03}
KH2O, des	[S ⁻¹]	I	I	$9.639 \times 10^{+00}$	$4.081 \times 10^{+00}$
KH2O, ads	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	I	I	4.838×10^{-01}	2.641×10^{-02}
Lco, ads	[mole.kg _{cat} -1]	2.187×10^{-03}		9.528×10^{-03}	
Lcoo, ads	[mole.kg _{cat} -1]	1.860×10^{-02}		1.635×10^{-04}	
Lo, ads	[mole.kg _{cat} -1]	9.582×10^{-04}		1.520×10^{-03}	
Loxy, tot	[mole.kg _{cat} -1]	2.175×10^{-02}		1.21×10^{-02}	
O _{oxy} , tot	[-]	2.300×10^{-02}		1.300×10^{-02}	

3.5 Extended oxygen pathway for Fischer-Tropsch reaction conditions

Based on the parameter estimation results above, Model S-2 was extended to Model S-2.1 as indicated in Figure 16. Three additional surface species OH_{ads} , H_2O_{ads} and $CO_{\beta, ads}$ are included in Model S-2.1. OH_{ads} and H_2O_{ads} are added to account for the stepwise hydrogenation of oxygen to water. $CO_{\beta,ads}$ introduces a second adsorbed CO species, this species is comparable to $CO_{\alpha,ads}$ in chemical composition but differs with regard to the presence of different surface sites. In Model S-2.1 CO dissociation and CO oxidation occur as different oxygen species, $CO_{\alpha,ads}$ dissociates to form O_{ads} while $CO_{\beta,ads}$ reacts with O_{ads} to form COO_{ads} .

Based on the limited data set and an increased number of parameters of Model S-2.1, parameter estimation resulted in rate constants that were highly correlated and had a high standard deviation. A simulation of the best case is shown in Figure 17 for CO and CO₂ and Figure 18 for H₂O, these results indicate the potential of the extended Model S-2.1 to predict the trends of the experimental data but more data are required to optimise the reaction rate constants and as such, they are not reported here.





Figure 16 Schematic representation of extended oxygen pathway based on Model S-2



Figure 17 Simulation results for the CO and CO₂ transients under FT reaction conditions using Model S-2.1, dashed lines indicate model prediction



Figure 18 Simulation results for the H₂O transient under FT reaction conditions based on Model S-2.1, dashed lines indicate model prediction

3.6 Discussion

For the HTFT synthesis at steady state reaction conditions, the presence of ¹⁶O in the product CO_2 (for FT and non FT reaction conditions) as evidenced by the stable C¹⁸O¹⁶O transient long after a SSITKA switch from C¹⁶O to C¹⁸O was made, indicates the existence of an additional reactive oxygen source besides the oxygen which originates from the gas phase. This additional oxygen source originates from lattice oxygen in the bulk where it diffuses to and from the surface of the catalyst. The formation of CO_2 seems in part at least to follow a Mars and van Krevelen (MvK) mechanism. Modelling the reversible addition of lattice oxygen to adsorbed CO to describe the oxygen pathway for CO_2 formation (an MvK type mechanism) resulted in a good fit to experimental data and the precise model estimation of the oxygen diffusion coefficient D. The qualitative and quantitative results of the SSITKA experiments at HTFT reaction conditions therefore reveal that CO oxidation over bulk iron catalysts may to some extent take place via an MvK mechanism. Although not conclusively presented in this work, the transient for water (Figure 15) also indicates that it could in part be formed via an MvK type of mechanism since the H₂¹⁶O transient does not decrease to zero in the time period of the SSITKA experiment indicating an alternative source of ¹⁶O.

The ¹³CO and C¹⁸O transients for non FT and FT reaction conditions illustrated in Figure 5 (left) and Figure 6 (left) do not elute simultaneously. This difference in residence time indicates that reversible CO dissociation takes place and the carbon and oxygen surface coverages which lead to adsorbed CO are not the same. The presence of hydrogen significantly decreases the rate of reverse CO dissociation as indicated by the partial convergence of the ¹³CO and C¹⁸O transients under FT reaction conditions. The rate of forward CO dissociation however remains relatively constant i.e. 3.19 10⁻⁰² [s⁻¹] with no hydrogen and 2.30 10⁻⁰² [s⁻¹] with hydrogen. This suggests that hydrogen assisted CO dissociation, resulting in surface oxygen does not occur to any significant extent. The presence of hydrogen is thought to mainly increase the rate of removal of adsorbed carbon, most likely as hydrocarbon products.

3.7 Conclusions and recommendations

Steady state isotopic transient kinetic analysis using ¹³C and ¹⁸O labelled CO, have provided a qualitative and quantitative description of the oxygen reaction pathways over bulk iron catalysts operating at high temperature Fischer-Tropsch reaction conditions. Both in the absence and presence of hydrogen, oxygen resulting from unassisted CO dissociation adsorbs and exchanges with oxygen on the catalyst surface and lattice oxygen in the bulk of the catalyst. In the absence of hydrogen, reversible CO dissociation takes place readily; the presence of hydrogen, however, significantly decreases the reverse rate. The formation of CO₂ and most likely H₂O, occur to some extent via a Mars and van Krevelen (MvK) type of mechanism where CO₂ is formed via the oxidation of CO and not via the stepwise addition of oxygen to carbon.

Values for reaction rate constants, surface coverages and oxygen diffusion coefficient in the "working" iron HTFT catalyst where obtained via the simultaneous solution of the mixed system of algebraic, ordinary differential and partial differential equations using the parameter estimation procedures and objective function in gPROMS^[12]. The diffusion coefficient together the concept of an MvK mechanism and irreversible CO dissociation at FT reaction conditions can now be included in future modelling of HTFT reaction mechanisms, hopefully leading to a better mechanistic understanding for the formation of oxygenate compounds and hence better catalyst design for tailored selectivity and activity.

A SSITKA experiment where a bulk iron catalyst is reduced as per usual but synthesis is started with syngas containing $C^{18}O$ instead of $C^{16}O$ would clarify whether or not incomplete reduction of the catalyst is a possible source of the iron oxide core.

3.8 Appendices

3.8.1 Appendix 1

Model equations describing the oxygenate pathway given in Figure 11 (Model S-2) for the formation of CO_2 and H_2O as well as bulk diffusion of oxygen to and from the catalyst surface

Model Equations 1: Steady state species

The subscript ss denotes steady state operation.

Gas phase

$$\frac{1}{\tau} \frac{\partial C_{\text{co,ss}}}{\partial z} = \frac{\rho_{\text{b}}}{\varepsilon_{\text{b}}} \left(k_{\text{co,des}} L_{\text{co,ss}} - k_{\text{co,ads}} C_{\text{co,ss}} \right)$$
B.1

$$\frac{1}{\tau} \frac{\partial C_{CO_2, ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{CO_2, des} L_{COO_2, ss} - k_{CO_2, ads} C_{CO_2, ss} \right)$$
B.2

$$\frac{1}{\tau} \frac{\partial C_{H_2O,ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{H_2O,ass} L_{O,ss} - k_{H_2O,dis} C_{H_2O,ss} \right)$$
B.3

Surface

$$\frac{\partial L_{co,ss}}{\partial t} = 0 = k_{ads}C_{co,ss} - k_{des}L_{co,ss} - k_{co,diss}L_{o,ss} + k_{co,ass}L_{co,ss} +$$

$$\frac{\partial L_{co_2,ss}}{\partial t} = 0 = k_{co_2,diss} C_{co_2,ss} - k_{co_2,des} L_{coo,ss} + k_{co_2,ass} L_{co,ss} L_{o,ss} - k_{co_2,dis} L_{coo,ss}$$
B.5

$$\frac{\partial L_{O,ss}}{\partial t} = 0 = k_{CO,dis} L_{CO,SS} - k_{CO,ass} L_{O,ss} + k_{CO_2,dis} L_{COO,ads} - k_{CO_2,ass} L_{O,ss} L_{O,ss}$$

$$-k_{H_2O,des} L_{O,ss} + k_{H_2O,ads} C_{H_2O,ss} - \left(D \frac{\partial S_{O,ss}}{\partial r} \bigg|_{r=Rparticle} As \right)$$
B.6

Model Equations 2: Labelled species

Gas phase

$$\frac{\partial C_{c^{18}O}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{c^{18}O}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{co,des} L_{c^{18}O} - k_{co,ads} C_{c^{18}O} \right)$$
B.7

$$\frac{\partial C_{c^{18}O^{18}O}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{c^{18}O^{18}O}}{\partial z} = \frac{\rho_{b}}{\varepsilon_{b}} \left(k_{CO_{2},des} L_{C^{18}O^{18}O} - k_{CO_{2},ads} C_{C^{18}O^{18}O} \right)$$
B.8

$$\frac{\partial C_{c^{18}O^{16}O}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{c^{18}O^{16}O}}{\partial z} = \frac{\rho_{b}}{\varepsilon_{b}} \left(k_{CO_{2},des} L_{c^{18}O^{16}O} - k_{CO_{2},ads} C_{c^{18}O^{16}O} \right)$$
B.9

$$\frac{\partial_{H_{2}^{18}O}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{H_{2}^{18}O}}{\partial z} = \frac{\rho_{b}}{\varepsilon_{b}} \Big(k_{H_{2}O,ass} L_{18}O - k_{H_{2}O,dis} C_{H_{2}^{18}O,ss} \Big)$$
B.10

Surface

$$\frac{\partial L_{c^{18}0}}{\partial t} = k_{ads} C_{c^{18}0} - k_{des} L_{c^{18}0} + k_{c0,ass} L_{18}_{0} - k_{c0,dis} L_{c^{18}0} + k_{c0,ass} L_{18}_{0} - k_{c0,dis} L_{c^{18}0} + k_{c0,ass} L_{c^{18}0} + k_{c0,ass} L_{c^{18}0} \left(L_{c^{18}0} + L_{c0} \right)$$
B.11

$$\frac{\partial L_{C^{18}O^{18}O}}{\partial t} = k_{CO_2,ads} C_{C^{18}O_2} - k_{CO_2,des} L_{C^{18}O^{18}O} - k_{CO_2,diss} L_{C^{18}O^{18}O} + k_{CO_2,ass} L_{C^{18}O} L_{18}O$$
B.12

$$\frac{\partial L_{c^{18}0^{16}0}}{\partial t} = k_{c0_{2},ads} C_{c^{18}0^{16}0} - k_{c0_{2},des} L_{c^{18}0^{16}0} - k_{c0_{2},dis} L_{c^{18}0^{16}0}$$

$$+ k_{c0_{2},ass} \left(L_{c^{18}0} L_{16}0 + L_{c^{16}0} L_{18}0 \right)$$
B.13

$$\frac{\partial L_{_{^{18}O}}}{\partial t} = k_{_{CO,dis}}L_{_{C^{^{18}O}}} - k_{_{CO,ass}}L_{_{^{18}O}} + k_{_{H_2O,ads}}C_{_{H_2}^{^{18}O}} - k_{_{H_2O,des}}L_{_{^{18}O}}$$
$$+ k_{_{CO_2,dis}}\left(L_{_{C^{^{18}O}}^{^{18}O}} + \frac{1}{2}L_{_{C^{^{18}O}}^{^{16}O}}\right) - k_{_{CO_2,ass}}L_{_{^{18}O}}\left(L_{_{C^{^{18}O}}} + L_{_{C^{^{16}O}}}\right) - \left(D\frac{\partial S_{_{^{18}O}}}{\partial r}\right|_{r=Rparticle} As\right) \qquad B.14$$

$$\frac{\partial S_{18_0}}{\partial t} = D \frac{\partial^2 S_{18_0}}{\partial r^2}$$
B.15

The boundary conditions are:

At z = 0

$$C_{CO,ss} = C_{CO,in}$$
 B.16

$$C_{c^{16}O} = C_{CO,in}(1-f(t))$$
 B.17

$$C_{C^{18}O} = C_{CO,in}f(t)$$
B.18

$$C_{CO_2,ss} = C_{H_2O,ss} = L_{CO_2,ss} = L_{O,ss} = 0$$
 B.19

$$C_{C^{18}O_2} = C_{C^{18}O^{16}O} = C_{H_2^{18}O} = L_{C^{18}O} = L_{C^{18}O_2} = L_{C^{18}O^{16}O} = L_{18}O = 0$$
B.20

At
$$z = 0$$
 and for \forall r; $S_{18_0} = 0$ B.21

For z > 0 and r=0;
$$\frac{\partial S_{180}}{\partial r} = 0$$
 B.22

For z > 0 and r =
$$R_{particle}$$
; $S_{18_0} = \rho_{cat} L_{18_0}$ B.23

Starting values:

At t = 0 and for z > 0

Mechanistic Pathways of the High Temperature Fischer-Tropsch Synthesis	77
$L_{c^{16}O}(z) = L_{CO,ss}(z)$	B.24
$L_{C^{16}O_2}(z) = L_{CO_2,ss}(z)$	B.25
$L_{16_{O}}(z) = L_{O,ss}(z)$	B.26
$C_{C^{16}O}(z) = C_{CO,ss}(z)$	B.27
$C_{C_{16}O_{2}}(z) = C_{CO_{2},ss}(z)$	B.28
$C_{H_2^{16}O}(z) = C_{H_2O,ss}(z)$	B.29
$C_{C^{18}O}(z) = C_{C^{18}O_2}(z) = C_{I^{6}O^{18}O}(z) = C_{H_2^{18}O}(z) = L_{C^{18}O}(z)$	B.30
$= L_{C^{18}O_2}(z) = L_{C^{16}O^{18}O}(z) = L_{18}O(z) = 0$	
At t = 0, for $z > 0$ and $0 > r > R_{particle}$	
$S_{_{16}O}(z) = \rho_{cat}L_{O,ss}(z)$	B.31
$S_{18_0}(z) = 0$	B.32

Gas phase concentrations, C [mole.mg⁻³], and surface concentrations, L [mole.kg_{cat}⁻¹], and bulk concentration S [mole.m_{cat}⁻³] are a function of the dimensionless reactor length (z) while $\rho_{\rm b}$ denotes the bed density [kg_{cat}.m_r⁻³], $\varepsilon_{\rm b}$ the catalyst bed porosity [mg³.m_r⁻³], D the oxygen diffusion [m_{cat}².s⁻¹] and As the surface area of the catalyst [m_{cat}².kg_{cat}⁻¹]. The different k's express the reaction rate constants. The reaction rate constants k_{ads}, k_{co2,ads} and k_{H20,ads} are expressed in [mg³.s⁻¹.kg_{cat}⁻¹]; k_{des}, k_{co2,des}, k_{H20,des}, k_{co,dis}, k_{co2,dis} and k_{co2,ass} in [s⁻¹], and k_{co2,ass} in [kg_{cat}.mole⁻¹.s⁻¹].

 $\frac{1}{\tau} = \frac{F_{\nu}}{V_r \varepsilon_b}$ where F_{ν} is the volumetric flow $[m_{g3}.s^{-1}]$ and V_r is the reactor volume $[m_r^3]$.

Chapter 4

Oxygenate Reaction Pathways

In this chapter, the oxygenate reaction pathways of the high temperature Fischer-Tropsch synthesis are investigated using ¹³CO and C¹⁸O isotopic switches in conjunction with ¹²C, ¹⁶O oxygenate co-feeding under steady state reaction conditions at 6 bar, 330 °C, H₂/CO ratio of 10:1 and GHSV = 3600 ml_(n).g_{cat}⁻¹.hr⁻¹. The results show that the difference between the formation of a primary 1-alcohol vs. that of an aldehyde is due to the type of oxygen surface species which add to the carbon chain. Furthermore, the presence of both ¹⁶O and ¹⁸O labelled species, after all C¹⁶O has eluted from the reactor, suggests that lattice oxygen may contribute to oxygenate formation.

4.1 Introduction

Together with hydrocarbons, oxygenates are also produced in the FT synthesis. At commercial Fischer-Tropsch (FT) conditions over iron catalysts, the oxygenate fraction may account for 6 to 12 wt. % of the total product ^[1]. The bulk of the oxygenate fraction consists of n-alcohols (primary) and n-aldehydes while methyl-ketones, n-alcohols (secondary), branched alcohols, carboxylic acids and esters occur to a lesser extent ^[2,3,4].

The selectivity towards oxygenates in the FT synthesis can be maximised by operating the process with catalysts having high alkali content, at low temperature, with short residence time, high pressure (CO + H₂) and carbon monoxide rich synthesis gas ^[2,3,5]. The most abundant oxygenates, n-alcohols (primary) and n-aldehydes are generally considered together with 1-alkenes to be primary products of the FT synthesis ^[2]. Thermodynamic evaluation by Weitkamp ^[6] of the equilibrium compositions at 327 °C for various reactions indicated that both alcohols and aldehydes may be primary products. Schulz ^[7], further noted that molar logarithmic distributions of his data for linear alcohols and aldehydes resulted in parallel lines indicating their primary nature, since secondary reactions would have yielded different distributions. Finally, the decreased selectivity of n-alcohols (primary) and n-aldehydes with increasing residence time ^[2] implies that these products can re-adsorb and take part in secondary reactions.

¹ Jager B., Stud. Surf. Sci. Catal., Vol. 107, (1997), 219

² Steynberg A. P., Dry M.E. (Eds.), Stud. Surf. Sci. Catal, Vol. 152, Elsevier, Amsterdam, (2004)

³ Cairns P., PhD Thesis, University of Cape Town, (2008), Cape Town, South Africa

⁴ Fletcher J. V., MSc. Thesis., University of Cape Town (2009), Cape Town, South Africa

⁵ Storch H. H., Golumbic N., Anderson R. B., John Wiley & Sons, Inc., New York, (1951)

⁶ Weitkamp A. W., Frye C. G., Ind. Eng. Chem., Vol. 45, No. 2, (1953), 363

⁷ Schulz H., Erich E., Gorre H., van Steen E., *Catal. Letters.*, **Vol. 7** (1990), 157

4.1.1 Reactions of oxygenates in the FT synthesis

The determination of the primary and secondary oxygenates as well as the secondary reactions which the primary oxygenates undergo is an important feature in determining the reaction mechanism (or mechanisms) for the FT synthesis ^[6]. The main obstacle to the initial work on oxygenate formation was the rudimentary analytical technology available at that time. However, in 1953 a significant effort was made to comprehensively identify the oxygenate products in the water and oil fractions ^[8,9]. The results of this work were examined in detail ^[6] and indicated that 1-olefins, 1-alcohols, aldehydes and carboxylic acids may be primary products of the FT synthesis and those of the same carbon number are in equilibrium with each other. Furthermore, the degree of branching for the primary alcohols vs. carboxylic acids indicated that it was unlikely that 1-alcohols were formed from the corresponding acid. In addition to these oxygenates, ketones and secondary alcohols were also observed as products (see Figure 1). Although not close to equilibrium, the ketones were thought to be formed via the ketonic decarboxylation reaction depicted in Figure 2, while the secondary alcohols were assumed to be formed in a subsequent hydrogenation of the ketones. Dry [2] showed that acetic acid co-feeding over an iron catalyst at 340 °C increased the yield of acetone thus supporting the conclusions of Weitkamp for the formation of the ketones via ketonic decarboxylation.

⁸ Steitz A. and Barnes D. K., Ind. Eng. Chem., Vol. 45, No. 2, (1953), 353

⁹ Weitkamp A.W. and Bowman N. J., *Ind. Eng. Chem.*, Vol. 45, No. 2, (1953), 359



Figure 1 Summary of proposed oxygenate reaction pathways by Weitkamp^[6]

$$2\begin{pmatrix} OH \\ I \\ R-C=O \end{pmatrix} \longleftrightarrow \begin{matrix} O \\ R-C \\ R-C \end{matrix} + CO_2 + H_2O$$

Figure 2 Ketonic decarboxylation reaction ^[2]

Based on the results of C₈ oxygenate co-feeding with synthesis gas over a precipitated iron catalyst at 300 °C and 21 bar, Cairns ^[3] proposed an extended version of the oxygenate interactions originally proposed by Weitkamp, see Figure 3. The advantage of this study was the extensive analysis of the reaction products by gas chromatography mass spectroscopy (GC-MS) which allowed for further insight into the mechanistic steps of oxygenate formation. The data of Cairns showed that when one of the C₈ oxygenates (1-alcohol, aldehyde or carboxylic acid) is added to the feed the other two are formed at an increased rate. Furthermore, the C_9 methyl-ketone was also formed in excess, when co-feeding any of the three C_8 oxygenates mentioned above. However, when the methyl-ketone was added to the synthesis gas the formation rate of the 1-alcohol, aldehyde and carboxylic acid did not change and only the secondary alcohol was observed to have an increased yield. Based on this data, Cairns proposed that the primary alcohol, aldehyde and carboxylic acid readily interact and these reactions are reversible, most likely occurring through an acyl intermediate indicated by species (3) of Figure 3^[3]. The formation of methyl-ketones were thought to take place via the irreversible addition of a surface methyl species to the acyl intermediate, and the secondary alcohol being formed from reversible hydrogenation of the methyl-ketone. The addition of a methyl group to an adsorbed oxygenate species was also suggested by Hanlon and Satterfield ^[10] who noted an increase in the acetone yield when ethanol was added to the syngas. Interestingly, propanone and not 1-propanol was formed from the added ethanol; indicating that re-adsorbed ethanol bonds to the catalyst surface at the oxygenated carbon.



Figure 3 Kinetic scheme of oxygenate interactions for the HTFT reaction as proposed by Cairns ^[3]

Emmett and co-workers ^[11,12,13,14] showed that addition of radioactive (¹⁴C) labelled alcohols to the synthesis gas at atmospheric pressure, 235 °C and H₂/CO ratio of 1:1 resulted in a hydrocarbon product with an approximate constant radioactivity per mole. This indicated that the co-fed alcohols acted as chain initiators but did not take part in chain propagation. Radioactive methanol and formaldehyde were

¹⁰ Hanlon R. T., Satterfield C. N., *Energy & Fuels.*, Vol. 2, (1988), 196

¹¹ Kummer J. T., Emmett P. H., FT Synth. Mech. Stud., Vol. 75, (1953), 5177

¹² Hall, K. W., Kokes R. J., Emmett P. H., J. Am. Chem. Soc., Vol. 79, No. 12, (1957), 2983

¹³ Kokes R. J., Hall K. W., Emmett P. H., *Symposium of Nuclear Technology in the Petroleum and Chemical Industries.*, (1957), 127

¹⁴ Hall K. W., Kokes R. J., Emmett P. H., J. Am. Chem. Soc., Vol. 85, No. 5, (1960), 1027

also added to the synthesis gas but only served to initiate hydrocarbon chain growth further indicating that the C₁ intermediate responsible for chain growth does not closely resemble that of an adsorbed alcohol. In experiments where the pressure was increased and a doubly promoted iron catalyst (MgO and K₂O) was used ^[10] the ethanol incorporation decreased from 18% at 1 bar to 2.2% at 21 bar. This is consistent with the work of Cairns ^[3] whose data for a doubly promoted, precipitated iron catalyst at 21 bar showed no direct evidence for the hydrogenation or incorporation of oxygenates to the corresponding hydrocarbon.

Experiments conducted by Tau *et al.* ^[15,16] at atmospheric pressure using ¹⁴C labelled alcohols indicated that, although not a significant pathway for the formation of alkanes, they may be formed by a type of decarboxylation of the adsorbed alcohol producing an alkane with one less carbon and CO₂, the source of the additional oxygen is however not known. The pathway proposed by Davis for the decarboxylation reaction is given in Figure 4 ^[17].

¹⁵ Tau L., Dabbagh H. A., Davis B. H., Energy & Fuels., Vol. 5, (1991), 174

¹⁶ Tau L., Dabbagh H. A., Halasz J., Davis B. H., J. Mol. Cat., Vol. 71, (1992) 37

¹⁷ Davis B. H., Fuel Proc. Tech., Vol. 71, (2001) 157



Figure 4 Conversion of alcohol to hydrocarbon with one fewer carbon atoms and CO₂

Furthermore, but to an even smaller extent, Tau showed that alkanes were formed via direct hydrogenolysis of the alcohol and not via stepwise hydrogenation to an alkene and then to an alkane. By comparison of the radioactivity of the alcohols and hydrocarbons, the alkenes were shown to not be formed from the added alcohols and as such, alcohols were not regarded as intermediates in alkene formation. Furthermore, labelled n-alcohols added to the synthesis gas formed labelled n-alkanes and labelled methyl-alcohols formed labelled iso-alkanes. These results show that intermediates resulting from the adsorption of primary and secondary alcohols differ from one another and do not interconvert. To explain these results, it was postulated that oxygen stays attached to the adsorbed species until an irreversible step is reached.

In summary of the literature above, primary alcohols, aldehydes and carboxylic acids of the same carbon number appear to share a common oxygenate intermediate and are in equilibrium. Methyl ketones have been proposed to form via either a ketonic decarboxylation reaction or the irreversible addition of a surface methyl species to the shared oxygenate intermediate, both pathways resulting in a methyl ketone with an additional carbon atom than the oxygenated precursor. At low pressures, alcohols were observed to act as chain initiators for hydrocarbon chain growth or take part in further secondary reactions such as direct hydrogenolysis to the corresponding alkane or decarboxylation to an alkane with one fewer carbon atoms and CO₂. At high pressure FT reaction conditions over doubly promoted Fe catalysts, incorporation of primary alcohols into hydrocarbon chains was shown to be minor and in most cases no reactions of oxygenates to hydrocarbons was reported.

This chapter is aimed at expanding the current understanding regarding the formation and reaction of oxygenates in the high temperature Fischer-Tropsch synthesis. This will be achieved via the interpretation of the isotopic compositions of the FT synthesis products following ¹³CO and C¹⁸O switches in the feed together with co-feeding of various (¹²C, ¹⁶O) oxygenates. In this work, three techniques (isotopic labelling, co-feeding and GCMS) are combined for the first time to elucidate the carbon and oxygen pathways which result in the Fischer-Tropsch products.

4.2 Oxygenate results and Discussion

4.2.1 Baseline isotopic experiments with no co-feeding:

Once an isotopic substitution has been made and the isotopic compositions of the products no longer vary with time (as described in Chapter 2, Appendix 3), comparisons of their isotopic make-up provide information on the type/source and reactivity of the intermediate species from which the various products are formed.

Part A: Isotopic switches of CO with labelled carbon

Assuming that gas phase CO is the only source of reactive carbon for the FT synthesis and the exchange of gas phase ¹²CO with ¹³CO takes place completely following a SSITKA switch (i.e. exit composition is stable at 100% ¹³CO), it would be a reasonable assumption that the isotopic composition of the C₁ surface species following total replacement of CO would consist entirely of ¹³C and as such, so would all the carbon of the products formed from these species.

This is, however, not the case as the isotopic transients for ethene from Figure 5 and the pseudo stable isotopic compositions from Figure 6 following a $^{12}CO/H_2/Ar$ to $^{13}CO/H_2/Ne$ SSITKA switch indicate. Apart from the results for CO₂ (as shown in Chapter 3, formation from the reaction of CO and O and not C + O + O) all isotopic compositions for the C₁ to C₄ products include a fraction of ^{12}C to a varying degree. Even after correcting for the purity of the ^{13}CO feed (99% ^{13}C) the products still contain ^{12}C which does not directly originate from the isotopically labelled feed (^{13}CO and H₂). These results therefore indicate that another source of reactive ^{12}C is present in the reactor and remains long after a SSITKA switch from ^{12}CO to ^{13}CO has been made. Since the isotopic compositions of the products are observed to stabilise over time, the reactive ^{12}C is thought to originate from a very large carbon pool where diffusion to and from the active site / surface of the catalyst is slow thereby limiting its replacement by ^{13}C resulting in a "pseudo stable" state is presented in Figure 5.



Figure 5 Ethene transient from baseline isotopic experiment with no co-feeding

Given that methane is formed from the hydrogenation of active C_1 surface species and assuming that carbon chain growth occurs by the stepwise addition of these same C₁ surface species at a rate independent of the carbon number, it follows that the carbon isotopic compositions of all other hydrocarbons may be predicted based on the isotopic composition of methane (C_1 surface species which lead to methane). Based on the assumptions above and given the measured isotopic composition of methane from Figure 6, the predicted composition of the C2 hydrocarbons would be 83% ¹³C-¹³C, 16% ¹³C-¹²C and 1% ¹²C-¹²C. Again this is not the case for ethene and ethane, here the partially labelled fraction is over predicted and the fully as well as the non-labelled fractions are under predicted. The differences in isotopic composition for the C_2 hydrocarbons (predicted vs. measured) when based on the methane composition could be due to: i) the C_{2+} hydrocarbons not being formed from the same C_1 surface species (not having the same isotopic composition) as those which result in methane or ii) variation of the reaction rate for carbon-carbon coupling according to the type / source of the C_1 species, the coverage of these species and the carbon chain length to which this species bonds.

In order to ascertain if any of these explanations are likely, two calculations were made to check if the experimental composition of ethene and ethane could be predicted. Firstly, the values for the isotopic composition of the "two" C₁ species (¹³C and ¹²C) were varied. Secondly, the isotopic composition of methane (C₁ species) was kept constant but the reactivity for the formation of each type of carbon-carbon bond i.e. ¹³C + ¹³C, ¹³C + ¹²C and ¹²C + ¹²C was varied. The calculation of the compositions for the C₂ species follows from:

Fraction
$${}^{12}C^{12}C = N_{config} \bullet rel, r_{{}^{12}C+{}^{12}C} \bullet {}^{12}C_{1, frac} \bullet N_{{}^{12}C, atoms}$$
 4.1

Fraction
$${}^{12}C{}^{13}C = N_{\text{config}} \bullet \text{rel}, r_{{}^{12}C+{}^{13}C} \bullet {}^{12}C_{1,\text{frac}} \bullet N_{{}^{12}C,\text{atoms}} \bullet {}^{13}C_{1,\text{frac}} \bullet N_{{}^{13}C,\text{atoms}}$$
 4.2

Fraction
$${}^{13}C^{13}C = N_{config} \bullet rel, r_{{}^{13}C^{+}{}^{13}C} \bullet {}^{13}C_{1, frac} \bullet N_{{}^{13}C, atoms}$$
 4.3

where N_{config} is the number of configurations which may occur for a particular fraction [-]; rel, $r_{12/13}_{C_{+}^{12/13}C}$ is the relative reactivity of carbon-carbon bond formation [-]; $^{12/13}C_{1,frac}$ are the isotopic fractions for C₁ [-]; $N_{12/13}_{C,atoms}$ is the number of carbon atoms with a specific isotopic label in the fraction of interest [-].

In the case of the C₂ products, the number of configurations which occur is 1 for ${}^{12}C^{12}C$ and ${}^{13}C^{13}C$ and 2 for ${}^{12}C^{13}C$ as indicated in Figure 8. The results of the calculations are given in Figure 7 and clearly show that variation of the C₁ isotopic composition does not predict the experimental C₂ composition but variation of the reactivity for carbon-carbon bond formation for the various C₁ species for chain growth does. Since the kinetic isotope effect between ${}^{13}C$ and ${}^{12}C$ is considered to be trivial, this result shows that by variation of the rate of carbon-carbon bond formation, CH₄ and the C₂ products can be formed from the same C₁ species. The carbon isotopic compositions of the C₃ and C₄ hydrocarbons as well as the

oxygenates could also be fitted by variation of the reactivity of the C₁ species for carbon-carbon bond formation, the rate of carbon bond formation is therefore thought to vary with respect to the overall chain length and the carbon species taking part in the bond formation.

The data in Figure 6 shows ethene and ethane have the same isotopic content but propene and propane as well as 1-butene and n-butane do not. The difference between the alkene and alkane isotopic compositions of the C_3 and C_4 hydrocarbons may be explained by secondary reactions such as ethene incorporation into growing chains or reversible chain growth, however no direct evidence for either is given here.

The stable carbon isotopic composition of ethanol and ethanal from Figure 6 are similar, indicating that it may be the step following chain growth ending, which determines the type of oxygenate that is formed. Additionally, the isotopic compositions of the C₂ hydrocarbons and C₂ oxygenates differ from one another, indicating that hydrocarbon and oxygenate chain growth may occur at different positions/sites on the catalyst surface i.e. where the concentration of carbon species leading to chain growth differ from one another. This result is supported by the work of Miller and Moskovits ^[18] who co-fed deuterated ethene with syngas having a H₂/CO ratio of approximately 2:1 over an iron catalyst at 330°C and 6.8 bar. The results indicated that deuterated ethene was incorporated almost entirely into the hydrocarbons as CD₂ units but no deuterium incorporation was found for the oxygenates. Based on these findings they concluded that oxygenates and hydrocarbons are synthesized on different portions of the catalyst surface.

¹⁸ Miller D., Moskovits M., J. Am. Chem. Soc., Vol. 111, (1989), 9250



Figure 6 Pseudo stable isotopic carbon composition of C1 to C4 products with no co-feeding following a SSTIKA switch from ¹²CO/H2/Ar to ¹³CO/H₂/Ne



Figure 7 Predicted isotopic composition of ethene based on C1 surface species composition

Figure 8 shows the potential pathways for the formation of C₂ products from carbon-carbon coupling of C₁ intermediates to account for the isotopic carbon distributions of ethene, ethane, ethanol and ethanal presented in Figure 6. Given that the isotopic transients no longer vary with time and assuming that replacement of the remaining ¹²C by ¹³C takes place very slowly. The ¹²C and ¹³C fractions immediately following stabilization of the isotopic transients represent different carbon pools. These carbon pools are indicated in Figure 8 as C_α and C_β for ¹²C and ¹³C respectively. The findings of van Dijk ^[19] over Co based FT catalysts at 225°C and 1.2 bar as well as those of Govender ^[20] over an Fe based FT catalyst at 330°C and 1.2 bar support the concept of two carbon pools as both authors required at least two distinct C_{1, ads} pools to successfully model the CH₄ and C₂ hydrocarbon formation pathways. Van Dijk further noted that these two carbon pools can be represented as distinct surface sites and do not merely differ in in the number of hydrogen atoms i.e. C_{ads} vs. CH_{ads}. Further work by Govender using

¹⁹ Van Dijk, H.A.J., PhD Thesis, (2001), Technische Universiteit Eindhoven, Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/200111083.pdf

²⁰ Govender N.S., PhD Thesis, Technische Universiteit Eindhoven (2010)., Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/689931.pdf

 H_2/CO to D_2/CO ITKA (isotopic transient kinetic analysis) resulted in $C_2H_1D_5$ and $C_2H_1D_3$ transients for ethane and ethene respectively, indicating that C_2 hydrocarbon formation occurs predominantly via the addition of a CH surface species to a C surface species.



Figure 8 Surface configurations to account for C₂ product isotopic composition

Part B: Isotopic switches of CO with labelled oxygen

Following a SSITKA switch from C¹⁶O/H₂/Ar to C¹⁸O/H₂/Ne and (as for the carbon labelling experiments) allowing the C¹⁸O to replace the C¹⁶O, resulted in the stable oxygen isotopic compositions shown in Figure 9. The data shows two distinct oxygen configurations; methanol, ethanol and acetone are predominantly made up of ¹⁸O (73, 74 and 68% respectively) while ethanal, propanal and water predominantly contain ¹⁶O (87, 81 and 91% respectively). As with the carbon labelling experiments, the stable oxygenate compositions contain both isotopes indicating that there must be at least another source of active oxygen, distinct from that originating directly from the gas phase CO. As described above for the carbon labelling experiments and from the earlier work discussed in Chapter 3, the remaining ¹⁶O is thought to originate from a large but much less reactive pool of oxygen from which the oxygen diffuses to and from the active surface sites. This

pool is not quickly replaced by ¹⁸O from the feed C¹⁸O and ¹⁶O continues to be incorporated in the FT products long after the SSITKA switch from C¹⁶O to C¹⁸O has taken place.

Interestingly, it seems that the type of oxygenate is related to a specific source of oxygen. If the partial oxidation of an alcohol to an aldehyde or vice versa (reduction) only included the loss or gain of hydrogen atoms, the resulting oxygen isotopic content would be the same for alcohols and aldehydes of the same carbon number. This is not the case for the data presented in Figure 9 where the oxygen compositions of ethanol and ethanal are vastly different to one another, ethanol contains 74% ¹⁸O and 26% ¹⁶O vs. 13% ¹⁸O and 87% ¹⁶O for ethanal. This effect was eluded to in the work of Orita et al.^[21] over Rh/SiO₂ catalysts where the ¹⁸O in ethanol was consistently higher than that in the ethanal indicating that ethanol could not be derived from the mere hydrogenation of the ethanal primary product alone. As such, the inter conversion of alcohols and aldehydes of the same carbon number must in addition to loss or gain of hydrogen atoms include C-O bond cleavage i.e. exchange of the oxygen atom during oxidation or reduction reactions. Oxygen exchange during alcohol oxidation has not been reported for the FT synthesis but work from Yan et al. ^[22] for partial oxidation of 2-butanol to 2butanone over oxygen pre-covered Au(111) showed similar results. In this work ¹⁶O, 2-butanol was dosed onto Au(111) pre-covered with ¹⁸O, the 2-butanone which formed contained both ¹⁶O and ¹⁸O.

In Figure 6 the carbon isotope compositions for ethanol and ethanal are similar but in Figure 9 their oxygen isotope compositions vary. This indicates that the carbon skeleton of both ethanol and ethanal are formed via the same chain growth route while oxygen addition differs. Additionally, oxygenate formation via CO insertion

²¹ Orita H., Naito S., Tamaru K., J. Catal., Vol. 90 Issue 2 (1984), 183

²² Yan T., Gong., Mullins C.B., J. Am. Chem. Soc., Vol. 131 (2009), 16189

does not seem to be a probable route since it would most likely result in alcohols and aldehydes having similar oxygen isotopic compositions (high in ¹⁸O).

A possible mechanism to describe the isotopic results for the C₂ oxygenates could be one where a growing carbon chain on the catalyst surface reacts with adsorbed oxygen species, thereby forming adsorbed "alkoxide like" or "carboxylate like" (RO⁻ or RCOO⁻) surface intermediates. These intermediates form adsorbed alcohols or aldehydes which may interact reversibly with each other, the nature of the adsorbed species seemingly dependent on the "type" of surface oxygen species the hydrocarbon chain adds to. Importantly, in this mechanism the oxygen and not the carbon is bonded to the catalyst surface thereby halting further chain growth. A large fraction of oxygen which comprises the aldehyde does not originate from the gas phase C¹⁸O and is thought to originate from a pool of less reactive, predominantly ¹⁶O oxygen which remains on or near to the catalyst surface long after the SSITKA switch from C¹⁶O to C¹⁸O has been made. The origin of oxygen for the alcohols and aldehydes is therefore assumed to be from two different oxygen pools. The 1st oxygen pool is more likely to end up in alcohols and CO₂, while the 2nd pool is more likely to end up as aldehydes and H₂O.





Figure 9 Pseudo stable isotopic oxygen composition of oxygenate products with no cofeeding following a SSTIKA switch from $C^{16}O/H_2/Ar$ to $C^{18}O/H_2/Ar$

Figure 10 depicts the mechanism proposed above for alcohol / aldehyde formation; the exact nature of species (14) is unknown and x may vary from 0 to 3. Although the surface alkyl species (x=2) has previously been observed under Fischer-Tropsch conditions ^[23] theoretical studies over Fe(100) surfaces indicate that reactions between C and R (R = $CH/CH_2/CH_3$) to form a surface alkylidyne species (x=0) are kinetically more feasible than CH+R or CH₂+R $^{[24]}$. Surface species (15) and (16) represent two distinct adsorbed oxygen pools (O_{α} and O_{β}) which may react reversibly with one another. Species/pool (15) is assumed to originate from dissociation of chemisorbed CO originating directly from the feed where the chemisorbed oxygen species resides on the catalyst surface. Species/pool (16) is thought to initially form in the early stages of the FT reaction i.e. during the catalyst phase changes from the reduced Fe metal to the working FT catalyst (iron carbides and iron oxides) as described in Chapter 3 and diffuses to and from the active surface sites, possibly exchanging with species (15). Although likely, it is not clear from the results whether or not any of the oxygen species contain hydrogen i.e. hydroxyl groups (OH) as suggested by Johnston and Joyner^[25]. Surface species (17) and (20) represent an adsorbed primary alcohol and an adsorbed η^1 – aldehyde respectively. While surface species (17) is generally considered to occur via donation of a lone pair of electrons from the oxygen to the surface, species (20) may occur in both the η^1 (O) and η^2 (C, O) – aldehyde configurations over group VIII transition metals ^[26]. The η^1 (O) adsorption geometry has, however, been shown to be the preferred species over oxygen-pre-covered surfaces of these metals ^[26] and is depicted in Figure 10. Species (18) represents an adsorbed "alkoxide like" species, while species (19) represents an adsorbed "carboxylate like" species.

²³ Wang C.J. and Ekerdt J., J. Catal., Vol. 84 (1984), 382

²⁴ Lo J.M.H. and Ziegler T., J. Phys. Chem., Vol. 111 (2007) 13149

²⁵ Johston P., Joyner R. W., Stud. Surf. Sci. Catal., Vol.75 (1993), 165

²⁶ Mavrikakis M. and M. A. Barteau., J. Mol. Catal. A: Chem. Vol. 131 (1998) 135



Figure 10 Proposed reaction pathway to describe the stable oxygen compositions of the alcohols and aldehydes following a $C^{16}O/H_2/Ar$ to $C^{18}O/H_2/Ar$ SSITKA switch

4.2.2 The effect of Ethanol and 1-Propanol co-feeding following ¹³CO and C¹⁸O SSITKA

It was envisaged that the comparison of ethanol and 1-propanol co-feeding results would provide further mechanistic information regarding the formation and interaction of 1-alcohols such as chain growth and secondary reactions to aldehydes and ketones. Once the FT reaction reached steady state, depending on the experiment, 0.1 ml_(n)/min of ethanol or 1-propanol was added to the total reactor feed using a saturator as described in Chapter 2. To monitor the effect of co-feeding on steady-state behaviour the conversions as well as the major product formation rates were closely monitored by GC (TCD and FID) before and during co-feeding. Extraction of the ion chromatograms from the GC-MS analysis further allowed for identification and qualification of the components and for the calculation of all component isotopic compositions following ¹³CO and C¹⁸O SSITKA switches.

4.2.2.1 Conversion and selectivity results for Ethanol and 1-Propoanol co-feeding Table 1 gives the FT conversion before and during co-feeding as well as the conversion of the co-fed ethanol and 1-propanol. The $CO + CO_2$ conversion was not affected by ethanol or 1-propanol co-feeding and indicates that the added 1alcohols did not affect steady state operation. The majority of added 1-alcohols passed through the reactor, only 9% of the added ethanol and 2% of the added 1propanol being converted.

Conversion [%]	Before co-feeding	During co-feeding
CO + CO ₂ (ethanol co-feed)	11	10
CO + CO ₂ (1-propanol co-feed)	13	11
Ethanol *	-	9
1-Propanol*	_	2

Table 1 Conversion before and during 1-alcohol co-feeding

*Conversion based on a set co-feeding flow rate of 0.1 ml_(n).min⁻¹)

As discussed in section 4.1.1, primary 1-alcohols may take part in various reactions during Fischer-Tropsch synthesis, the resulting reaction products may be hydrocarbons and oxygenates of the same but also varying carbon number. During 1-alcohol co-feeding, significantly more alcohol is converted than hydrocarbons or oxygenates are formed (on a molar basis 2.5 times ethanol than C₂ and 40 more times ethanol than C₄). It is therefore anticipated that any noteworthy reactions of the co-fee alcohols will be apparent by comparison of selectivity data from before and during co-feeding.

The results of Figure 11 show no discernible change in the C_2 to C_4 hydrocarbon formation rates upon ethanol or 1-propanol addition and suggest that 1-alcohol hydrogenation (increase in corresponding hydrocarbons) or incorporation (increase in n + 1 hydrocarbons) does not take place to a significant degree. Furthermore, the constant alkene content of the total hydrocarbon fraction given in Table 2, indicates that 1-alcohol co-feeding did not inhibit ethene hydrogenation ^[27] or lead to a considerable degree of direct hydrogenolysis to the corresponding alkane ^[15,16].

These results are in line with that of Cairns ^[3] who noted that hydrocarbon formation rates remained largely unaffected upon 1-octanol co-feeding. This selectivity behaviour may be due to the reaction conditions used since both this work and that of Cairns was carried out at conditions above atmospheric pressure and high temperature i.e. 6 bar, 330 °C and 25 bar and 300 °C respectively.



Figure 11 Distribution for the linear hydrocarbons vs. carbon number before and during ethanol and 1-propanol co-feeding

 Table 2 Linear alkene content in the fraction of linear hydrocarbons (alkenes/ alkenes + alkanes) before and during 1-alcohol co-feeding

	Ethanol		1-Propanol		
Carbon number	Before	During	Before	During	
	co-feeding	co-feeding	co-feeding	co-feeding	
2	0.56	0.52	0.59	0.55	
3	0.84	0.83	0.84	0.82	

²⁷ Xu. L., Bao S., Tau L. M., Chawla B., Dabbagh H., Davis B.H., 11th Int. Pittsburgh Coal Conf. Proc.., (1994), 88
4	0.87	0.85	0.87	0.87

Given the reaction schemes in Figure 1 and Figure 3, the addition of 1-alcohols to the FT reaction would be expected to result in an increase of the corresponding aldehyde, carboxylic acid, n+1 methyl-ketone and the n+1 methyl-alcohol. To evaluate these effects, the peak area ratios from GCMS analysis with no co-feeding are compared to those of 1-alcohol co-feeding in Table 3. The ratios of the peak area counts are compared in an additional column to give the relative change in product selectivity brought about by 1-alcohol co-feeding.

It is clearly evident from Table 3 that the added ethanol undergoes a reaction to form ethanal and to a lesser extent acetone, but no acetic acid or 2-propanol is observed. Similarly, the major product formed from co-feeding 1-propanol was propanal with considerably less 2-butanone formed. Interestingly, it seems that there was a slight increase in the formation of ethanol upon 1-propanol addition to the feed. No propionic acid or 2-butanol is observed. Based on the increase in ethanol (following 1-propanol addition), additional acetone may have been formed but the acetone peak could not be integrated since it eluted beneath the large propanal peak.

The secondary formation of aldehydes from alcohols is proposed to take place via the partial hydrogenation of the alcohol together with oxygen exchange as indicated in Figure 10. The formation of methyl-ketones in the Fischer-Tropsch synthesis have been proposed to occur via two routes. The work of Cairns as well as that of Hanlon and Satterfield ^[3,10] indicate that the methyl-ketones may be formed by addition of a methyl group to an adsorbed oxygenate species, while the work of Dry and Weitkamp ^[2, 9] suggest that methyl-ketones are the result of ketonic decarboxylation (Figure 2). Both routes for the formation of methyl-ketones [D] and

[E] of Appendix 1 and cannot be discounted. As such, both routes are evaluated further in the following section by the use of isotopic labelling. If the formation of acetone via ketonic decarboxylation of acetic acid is at or close to thermodynamic equilibrium almost all of the acetic acid would be consumed, explaining why none was measured during this work. Moreover, no methyl-alcohol was observed, this is thought to be due a combination of the low methyl-ketone selectivity and the inability of the analytical techniques to detect the methyl-alcohols at such low concentrations.

It is important to note that during the 1-alcohol co-feeding experiments; the n+1 methyl-ketone is formed instead of the methyl-alcohol. This indicates that 1-alcohols re-adsorb with the oxygen bonded to the surface preventing further chain growth as indicated by the reaction pathway presented in Figure 10.

The data of Table 3 again show the hydrocarbon formation to remain relatively unchanged upon 1-alcohol addition. For the reaction conditions applied in this work the product formation data indicate that there is no significant reaction of 1-alcohols to hydrocarbons. Isotopic tracer experiments with labelled carbon are, however, more sensitive and have previously shown that ethanol and 1-propanol can act as chain starters for hydrocarbons ^[11,13,15,28]. To conclusively show whether or not 1-alcohols react to hydrocarbons at the reaction conditions of this work, the results of ¹³CO SSITKA experiments during fully ¹²C labelled ethanol and 1-propanol co-feeding are evaluated in the rest of this section.

²⁸ Davis B.H., Catal. Today., Vol. 141., (2009), 25

refer to the co-fi	ed species, red num	bers refer to a significant	increase and black numbers	s indicate no change	
Species, <i>i</i>	no-co-feeding	Ethanol co-feeding	Ethanol rel. difference	1-Propanol co –feeding	1-Propanol rel. difference
	Area Species i	Area Species i	Ratio with co-feeding	Area Species i	Ratio with co-feeding
	Area propene	Area propene	Ratio no co-feeding	Area propene	Ratio no co–feeding
CH₄	11.55	12.31	1.1	18.06	1.6
CO2	11.39	7.73	0.7	11.32	1
Methanol	0.01	n/a*	n/a*	n/a*	n/a*
Ethene	0.96	0.65	0.7	0.58	0.6
Ethane	0.41	0.56	1.4	0.22	0.5
Ethanal	0.07	0:00	12.1	0.12	1.6
Ethanol	0.02	7.26	Co-fed	0.06	2.4
Propene**	1	1	-1	1	1
Propane	0.26	0.18	0.7	0.31	1.2
Propanal	0.01	0.01	-1	2.69	289.6
Acetone	0.01	0.03	2.1	Peak overlap	I
1-Propanol	0	0	0	21.37	Co-fed
1-Butene	0.45	0.45	-1	0.37	0.8
n-Butane	0.11	0.07	0.64	0.11	0.9
2-Butanone	0	0	0	0.22	undefined
*Peak area too si	mall to quantify, **B	ase component			

Table 3 Area count ratios and relative difference in product formation before and during ethanol and 1-propanol co-feeding, blue numbers

Chapter 4: Oxygenate Reaction Pathways

4.2.2.2 Isotopic labelling results for Ethanol and 1-Propanol co-feeding

The pseudo stable isotopic compositions of the reaction products during ethanol and 1-propanol co-feeding following a SSITKA switch from ¹²CO to ¹³CO SSITKA are given in Figure 12 and Figure 14. If a fraction of the co-fed ethanol or 1-propanol was hydrogenated to a C₂ or C₃ hydrocarbon respectively, the ¹²C-¹²C fraction of the C₂ and the ¹²C-¹²C-¹²C fraction of the C₃ hydrocarbons would be expected to increase. Similarly, if ethanol or 1-propanol acted as chain initiators, an increase in the ¹²C-¹²C-¹³C and ¹²C-¹²C-¹³C isotopic fractions of the respective C₃ and C₄ hydrocarbons would be expected.

Compared to the ¹³CO SSITKA experiment with no co-feeding, the isotopic composition of the hydrocarbon products during ethanol co-feeding show very little ¹²C-¹²C in the hydrocarbons (less than 4% of the 1-propene was made up of ¹²C-¹²C-¹³C). This fraction of ¹²C in 1-propene is, however, similar to that for the experiments of ¹³CO SSITKA with no ethanol co-feeding (see Figure 23, Appendix 3). Remarkably, the area counts for methane in Figure 12 remain constant but the isotopic composition clearly shifts to include more ¹²C compared to before ethanol co-feeding (from 9 to 36% ¹²C, Figure 6 vs. Figure 12). The reason for this change in isotopic composition of methane is thought to be due to a secondary pathway described by Tau *et al.* ^[15] for the decarboxylation of adsorbed 1-alcohols to alkanes. The decarboxylation of adsorbed alcohols is thought to be a likely route since a corresponding increase in the ¹⁶O content of CO₂ from Figure 16 was observed, the ¹⁶O originates from ethanol, possibly leading to an increased C¹⁸O¹⁶O fraction in CO₂.

Compared to the ¹³CO SSITKA experiment with no co-feeding, the hydrocarbon isotope compositions for the C_1 to C_3 products show no noteworthy increase in the ¹²C content during 1-propanol co-feeding (see Appendix 3). The ¹²C content of 1-butene and n-butane do, however, seem to have increased slightly for the ¹²C-¹²C-

 $^{12}C^{-13}C$ fraction during 1-propanol co-feeding. Although no increase in the steady state formation rates or olefinicity of the C₄ hydrocarbons was observed, the isotopic data do suggest that a small fraction of the converted 1-propanol may have initiated chain growth leading to C₄ hydrocarbons.

The results of the area count ratios and the isotopic labelling, therefore, show that under the reaction conditions of these experiments, 1-alcohols are not partially hydrogenated to their corresponding hydrocarbons. Some of the added ethanol did, however, result in an increase in the ¹²C composition of methane while 1-propanol was incorporated to a very small degree in the C₄ hydrocarbon fraction.

In addition to the formation of hydrocarbons, the effect of co-feeding ¹⁶O labelled ethanol and 1-propanol on oxygenate formation following ¹²CO to ¹³CO and C¹⁶O to C¹⁸O SSITKA switches are presented in Figure 13 and Figure 15. The effect of co-feeding ¹²C, ¹⁶O ethanol is clearly visible as the isotopic composition leaving the reactor goes from 17% ¹²C-¹²C and 26% ¹⁶O during normal FT synthesis to 98% ¹²C-¹²C and 95% ¹⁶O during ethanol co-feeding. Similarly the ¹²C, ¹⁶O fraction of 1-propanol leaving the reactor is 93% ¹²C-¹²C ¹²C while the oxygen fraction is 94% ¹⁶O. If the co-fed 1-alcohols now partake in further reactions, the ¹²C and ¹⁶O fractions of the resulting products are expected to increase as compared to their stable isotopic compositions following the ¹³CO and C¹⁸O SSITKA experiment with no co-feeding.

The most significant isotopic effect on isotopic fractions following ¹³CO SSITKA with ethanol co-feeding is observed for ethanal, where the ¹²C-¹²C content goes from 22% to 90%. This result together with the increase in the ethanal yield upon ethanol co-feeding proves that ethanol can react to form ethanal with the original carbon skeleton of ethanol retained in the ethanal. The ¹⁶O isotopic composition of ethanal (42%) does not, however, correlate to that of the co-fed ethanol (95%) but can be explained by the mechanism indicated in Figure 10. Here the pathway of ethanol re-adsorption and reaction to ethanal is proposed to proceed via a pathway capable of oxygen exchange.

In addition to the increase in the 12 C composition of ethanal, comparison of the acetone isotopic composition from before and during ethanol co-feeding also shows an increase with regard to the ¹²C. The ¹²C-¹²C fraction of acetone increased from 28% to 37% while the ¹²C-¹²C-¹³C fraction increased from 18% to 32% (see Figure 6 and Figure 12). Overall the ¹²C composition of acetone increased from 45% to 63% (see Appendix 3). If acetone is formed entirely via the decarboxylation of acetic acid and assuming that most of the acetic acid is formed from co-fed ethanol ^[2, 3, 6] i.e. ¹²C-¹²C acetic acid, the resulting acetone isotopic composition would contain predominantly the ¹²C-¹²C-¹²C fraction. On the other hand, if acetone is formed entirely via addition of a methyl species to a C2 oxygenate such as ethanol or ethanal, the resulting acetone isotopic composition would consist predominantly of the ¹²C-¹²C-¹³C fraction with some ¹²C-¹²C-¹²C, since the reactive methyl species on the catalyst surface would have an isotopic composition similar to that of methane. The results for the acetone isotopic composition therefore indicate that both decarboxylation and methyl addition to a C_2 oxygenate species may take place at the reaction conditions of this work. Based on the relative increase in isotopic labels for the various acetone fractions, methyl addition to a C₂ oxygenate species does however seem to be the major route.

The stable isotopic data for 1-propanol co-feeding following a ¹²CO to ¹³CO SSITKA switch given in Figure 14 and Appendix 3, clearly show an increase in the ¹²C fraction for propanal, ethanol and ethanal. The fraction of ¹²C in propanal increased from ca. 29% to 95%, all of the ¹²C appearing in the ¹²C-¹²C-¹²C fraction of propanal. This result together with the large increase in propanal formation during 1-propanol co-feeding (Table 5) indicates that 1-propanol can react to propanal with the original carbon skeleton of the alcohol retained in the aldehyde. The ¹²C

content of ethanol increased from 24% to 80% while that of ethanal increased from 29% to 41%. Although the change in acetone peak area is not known due to peak overlap by propanal, some increase in the ¹²C-¹²C-¹²C fraction was observed. The large increase in the ¹²C composition of ethanol was unexpected but may be explained by reversible chain growth of the co-fed 1-propanol ^[29]. The subsequent increase in ¹²C composition for the ethanal and acetone then follows according to the mechanisms proposed in Figure 3. Furthermore, 2-butanone was not observed in the experiment with no co-feeding, therefore the change in isotopic composition brought about by 1-propanol co-feeding could not be quantified. The isotopic content of 2-butanone given in Figure 14 is, however, mainly composed of the ¹²C-¹²C-¹²C-¹³C fraction (55%), indicating that a significant intermediate for 2-butanone formation is a ¹²C-¹²C-¹²C species which may react with a surface methyl species forming the methyl-ketone.

The stable isotopic data for 1-propanol co-feeding following a C¹⁶O to C¹⁸O SSITKA switch are given in Figure 15. Even though 1-propanol addition led to an increase in the formation of propanal, 2-butanone, ethanol, ethanal and most likely acetone it is not reflected in the ¹⁶O composition of these products. Instead the large ¹⁶O content of 1-propanol does not seem to affect the trend of oxygen compositions observed for the earlier experiments with and without co-feeding. The trend observed follows according to a similar mainly ¹⁸O content for the 1-alcohols and ketones and a similar but mostly ¹⁶O content for the aldehydes and water. This result strongly suggests that 1-propanol re-adsorption takes place according to a mechanism such as the one described in Figure 10 where C-O bond cleavage can take place.

²⁹ Mims C. A., Krajewski J. J., Rose K. D., Melchior M. T., Catal. Letters., Vol 7., (1990) 119







Figure 13 Pseudo stable isotopic oxygen composition of oxygenate products during ethanol co-feeding following a SSTIKA switch from $C^{16}O/H_2/Ar$ to $C^{18}O/H_2/Ar$





 12 CO/H₂/Ar to 13 CO/H₂/Ne



Figure 15 Pseudo stable isotopic oxygen composition of oxygenate products during 1propanol co-feeding following a SSITKA switch from C¹⁶O/H₂/Ar to C¹⁸O/H₂/Ne



Figure 16 Pseudo stable isotopic oxygen composition of CO₂ during ethanol and 1-propanol co-feeding following SSITKA switches from C¹⁶O/H₂/Ar to C¹⁸O/H₂/Ne

4.2.3 The effect of 2-Propanol and 2-Butanone co-feeding following ¹³CO and C¹⁸O SSITKA

In addition to the 1-alcohols, 2-propanol and 2-butanone were also co-fed to the reactor following a ¹³CO and C¹⁸O SSITKA switch. It was envisaged that the co-feeding of 2-propanol and 2-butanone would provide further insight into the understanding of oxygenate interactions during the high temperature Fischer-

Tropsch synthesis and confirm the kinetic scheme presented in Figure 3. In this figure, Cairns ^[3] proposed that the hydrogenation of the methyl-ketone to the corresponding methyl-alcohol (2-alcohol) is reversible.

4.2.3.1 Conversion and selectivity results for 2-Propanol and 2-Butanone cofeeding

Table 4 gives the Fischer-Tropsch conversion (CO + CO₂) before and during 2propanol and 2-butanone co-feeding. The decreased Fischer-Tropsch conversion measured during co-feeding for both the 2-propanol and 2-butanone experiments does not occur suddenly, but rather takes place over the length of the experiment. As such, the change in Fischer-Tropsch conversion is believed to be due to slight catalyst deactivation with time on-line and not a result of the oxygenate co-feeding.

The results of Table 5 show that the conversion of 2-propanol is much higher than that obtained for the 1-alcohols, ca. 41%, and that the converted 2-propanol forms acetone almost exclusively. The conversion of 2-butanone is not given here since the desired flow rate of $0.2 \text{ml}_{(n)}$.min⁻¹ was not achieved, the actual flow rate was calculated to have been less than $0.2 \text{ ml}_{(n)}$.min⁻¹ but was not measured. The results of Table 5 indicate that the products formed from 2-butanone co-feeding include 2-butanol, propanal, acetone, ethanal, n-butane, ethane and ethanol.

Conversion [%]	Before co-feeding	During co-feeding
CO + CO ₂ (2-Propanol co-feed)	17	12
CO + CO ₂ (2-Butanone co-feed)	15	12
2-Propanol	—	41
2-Butanone	—	—

Table 4 Conversion before and during 2-propanor and 2-butanone co-recurs
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The significant increase in acetone formation with 2-propanol co-feeding and 2butanol formation upon 2-butanone co-feeding indicate that the reaction of methyl-alcohols to the corresponding methyl-ketones is reversible. Furthermore, the formation of propanal from 2-butanone also indicates that the reaction of alcohols or aldehydes to n+1 methyl-ketones is to some extent reversible. The mechanism for the formation of ethanal and ethanol is not clear and is discussed in further detail with regard to their isotopic compositions in the following section.

Based on the data presented in Appendix 2, co-feeding of 2-propanol did not lead to a measurable change in the formation rates of the linear C_1 to C_4 hydrocarbons (alkene + alkane). Furthermore, the alkene content of the total linear hydrocarbon fraction remained constant upon 2-propanol addition to the reactor. As such, the results indicate that hydrogenation, incorporation, decarboxylation or direct hydrogenolysis of 2-propanol does not take place to a significant extent. Co-feeding of 2-butanone was not observed to result in an increase of the hydrocarbon formation rate of the linear C_1 to C_4 hydrocarbons. The olefinicity (alkene content of the linear hydrocarbons) of the C_2 and C_4 hydrocarbon fractions did however decrease slightly upon 2-butanone addition and was a result of an increased nbutane and ethane formation.

numbers refer to	the co-fed species	, red numbers refer to a sig	gnificant increase and black	k numbers indicate no chang	Ø
Species, <i>i</i>	No co - feeding	2-Propanol co - feeding	2-Propanol rel. difference	2-Butanone co – feeding	2-Butanone rel. difference
	Area Species i	Area Species i	Ratio with co-feeding	Area Species i	Ratio with co-feeding
	Area propene	Area propene	Ratio no co– feeding	Area propene	Ratio no co–feeding
CH4 CH4	11.55	14.65	1.3	15.21	1.3
CO ₂	11.39	9.08	0.8	10.09	0.9
Methanol	0.01	n/a*	n/a*	n/a*	n/a*
Ethene	0.96	0.57	0.6	0.67	0.7
Ethane	0.41	0.66	1.6	0.84	2
Ethanal	0.07	0.07	1	0.19	2.6
Ethanol	0.02	0.03	1.4	0.04	1.6
Propene**	1	1	1	-1	Ţ
Propane	0.26	0.36	1.4	0.2	0.8
Propanal	0.01	Peak overlap	I	0.05	5.2
Acetone	0.01	4.14	314.8	0.04	3.1
1-Propanol	0	0	0	0	0
2-propanol	0	16.07	Co-fed	0	0
1-Butene	0.45	0.3	0.7	0.58	1.3
n-Butane	0.11	0.09	0.8	0.27	2.4
2-Butanone	0	0	0	45.19	Co-fed
2-Butanol	0	0	0	1.74	Undefined
*Peak area too s	mall to quantify, **	Base component			

Table 5 Area count ratios and relative differences in product formation before and during 2-propanol and 2-butanone co-feeding, blue

4.2.3.2 Isotopic labelling results for 2-Propanol and 2-Butanone co-feeding

The stable ¹²C isotopic compositions of the reaction products during 2-propanol and 2-butanone co-feeding following a SSITKA switch from ¹²CO to ¹³CO are given in Figure 17 and Figure 19.

Compared to the ¹³CO SSITKA experiment with no co-feeding, the hydrocarbon isotope compositions for the C₁ to C₃ 1-alkenes and n-alkanes show no noteworthy increase in the ¹²C content during 2-propanol co-feeding. For 2-butanone co-feeding, the ¹²C content for the C₂ and C₃ hydrocarbons remained relatively constant but the 1-butene and n-butane compositions increased significantly. The ¹²C content of 1-Butene increased from 10% to 37% while that of n-butane increased from 14% to 64% upon 2-butanone addition (see Appendix 3). The C₄ hydrocarbon data of Figure 19 indicates that the majority of the additional ¹²C occurred in ¹²C-¹²C-¹²C fraction, signifying the added 2-butanone (¹²C-¹²C-¹²C) as the source.

In addition to the formation of hydrocarbons from oxygenates, the effect of cofeeding ¹⁶O labelled 2-propanol and 2-butanone following ¹²CO to ¹³CO and C¹⁶O to $C^{18}O$ SSITKA switches on oxygenate formation is presented in Figure 18 and Figure 20.

The stable isotopic data collected during 2-propanol co-feeding following a ¹²CO to ¹³CO SSITKA switch is given in Figure 17 and clearly shows an increase in the ¹²C content of acetone. The ¹²C-¹²C-¹²C fraction in acetone increased from ca. 28% to 94%, exactly matching that of the co-fed 2-propanol. This result together with the large increase in acetone formation during 2-propanol co-feeding (Table 5) clearly indicates that 2-propanol can react to form acetone with the original carbon skeleton of the methyl-alcohol retained in the methyl-ketone. No other products were observed to increase with regard to their ¹²C compositions upon 2-propanol co-feeding.

The stable isotopic data for 2-propanol co-feeding following a C¹⁶O to C¹⁸O SSITKA switch are given in Figure 18. The co-fed 2-propanol leaving the reactor consists of 99% ¹⁶O but the main product formed from the 2-propanol, acetone, contains 24% ¹⁶O. This result is consistent with the notion that oxygenate re-adsorption and further reaction includes carbon oxygen bond cleavage together with addition or elimination of hydrogen atoms.

The stable isotopic data, collected for the oxygenate species during 2-butanone cofeeding following a ¹²CO to ¹³CO SSITKA switch, are given in Figure 17. The formation of 2-butanol with the same isotopic composition as the co-fed 2butanone (ca. 95%, ¹²C-¹²C-¹²C) is clearly evident. This result together with the large increase in 2-butanol formation during 2-butanone co-feeding and the results from 2-propanol addition clearly indicate that a methyl-alcohol can react reversibly to form a methyl-ketone with the original carbon skeleton of the methyl-alcohol retained in the methyl-ketone. The ¹²C composition as well as the formation of propanal was also observed to increase during 2-butanone co-feeding following a ¹²CO to ¹³CO SSITKA switch. The isotopic composition of propanal, given in Figure 19 shows an increase in ¹²C mainly for the ¹²C-¹²C-¹²C fraction suggesting that the formation of methyl-ketones by methyl addition to an adsorbed oxygenate species is reversible. Finally, the ¹²C composition of ethanal and ethanol also increased upon 2-butanone co-feeding. Since the ¹²C content of ethanal and ethanol are lower than that of the 2-butanone, 2-butanol and propanal it is not clear from which component the additional carbon in the C₂ oxygenates originated. The ¹²C content of ethanal is, however, higher than that of the ethanol indicating that the ethanol was formed from ethanal, providing further evidence to support the reversibility of the 1-alcohol - aldehyde interaction.

The stable isotopic data for 2-butanol co-feeding following a C¹⁶O to C¹⁸O SSITKA switch is given in Figure 20. The trend for the oxygen labelling follows that of the

previous results, the 1-alcohols and methyl-ketones contain a higher fraction ¹⁸O while the aldehydes, methyl-alcohols and water contain a higher fraction of ¹⁶O.







Figure 18 Pseudo stable isotopic oxygen composition of oxygenate products during 2propanol co-feeding following a SSITKA switch from $C^{16}O/H_2/Ar$ to $C^{18}O/H_2/Ne$







Figure 20 Pseudo stable isotopic oxygen composition of oxygenate products during 2-butanone co-feeding following a SSITKA switch from $C^{16}O/H_2/Ar$ to $C^{18}O/H_2/Ne$

4.3 Conclusions

In this chapter the oxygenate reaction pathways which occur during the high temperature Fischer-Tropsch synthesis over an iron catalyst at steady state are studied by means of ¹²CO to ¹³CO and C¹⁶O to C¹⁸O isotopic switches in conjunction with alcohol (ethanol, 1-propanol and 2-propanol) and methyl-ketone (2-butanone) co-feeding. The combination of these techniques together with GCMS analysis of the isotopically labelled products resulted in significantly improved detail and clarity with regard to the reactions and interactions of the oxygenates.

The steady state activity and selectivity results showed no discernable change in the hydrocarbon formation rate upon 1-alcohol addition to the feed and therefore agree with the findings of Carins ^[3] for FT at elevated pressures. On the other hand, the results of the more sensitive isotopic tracer experiments indicated that co-fed ethanol, 1-propanol and 2-butanone may to some extent take part in secondary reactions such as hydrogenolysis or decarboxylation to form hydrocarbons, particularly n-alkanes as previously indicated from the work of Hall *et al.* ^[12] and Tau *et al.* ^[15] at atmospheric pressure. Importantly, the extent of oxygenate secondary reactions to form hydrocarbons seem to be highly dependent on the total pressure, this effect decreasing significantly at elevated pressures. The secondary formation of hydrocarbons from oxygenates are thus proposed to be insignificant at commercially relevant operating conditions.

Isotopic tracer experiments with ¹³CO and C¹⁸O revealed that at least two different reactive C₁ intermediate species (C_{α} and C_{β}) are present on the catalyst surface. Assuming that these same species form the carbon chains which leading to the primary organic Fischer-Tropsch products, the rate of carbon-carbon bond formation for chain growth must vary with regard to the type of C₁ species involved in the bond formation, the concentration of these species and the length of the carbon chain to which this species bonds.

The observation that the carbon isotopic compositions of ethanol and ethanal are similar but their oxygen isotopic compositions are considerably different leads to the conclusion that the carbon skeleton which comprises both species, forms prior to the addition of oxygen. Furthermore, under the reaction conditions of this work oxygen addition via CO insertion is considered to be unlikely since it would result in both oxygenates having a similar isotopic oxygen composition. Based on the results from this chapter, the formation of an oxygenate species can be visualised to take place via a mechanism where the growing hydrocarbon chain reacts with an adsorbed oxygen species to form "alkoxide like" or "carboxylate like" surface intermediates halting further chain growth. These intermediates may react reversibly with each other or ultimately desorb as primary alcohols and aldehydes. The type of oxygenate which forms seems to be dependent on the type of oxygenate species to which the carbon chain bonds. The difference between the formation of a primary 1-alcohol or aldehyde is thought to be due to the type of oxygen species which adds to the carbon chain (of which at least two have been identified i.e. O_{α} and O_{β}). As such, interconversion of alcohols and aldehydes of the same carbon number may, in addition to loss or gain of hydrogen atoms, include C-O bond cleavage.

¹³CO and C¹⁸O isotopic switches in conjunction with co-feeding conclusively showed that secondary reactions of 1-alcohols result in the formation of the corresponding aldehydes and (n+1) methyl ketones. Interestingly, the preferential formation of the methyl ketone vs. the methyl alcohol during 1-alcohol co-feeding indicates readsorption of the alcohol via the oxygen atom attached to the surface. Furthermore, the reaction of 1-alcohols to the corresponding aldehyde is reversible and 1-propanol added to the feed resulted in a slight increase in the C₂ oxygenates, possibly indicating reversible chain growth. Given that there are common intermediates involved in the formation of 1-alcohols, aldehydes and (n+1) methylketones, these products can be formed via primary or secondary reactions. The major route for the formation of methyl-ketones is believed to proceed via addition of a surface C_1H_x species (where x = 0 to 3) to an adsorbed oxygenate species. While the formation of propanal following 2-butanone co-feeding suggests that this reaction may be reversible. It was also conclusively shown that methyl-alcohols react reversibly via C-O bond cleavage with the corresponding methyl-ketones.

4.4 Appendices

4.4.1 Appendix 1

Thermodynamic equilibrium predictions of selected C_2 oxygenate reactions at $330^{\circ}C$

	Reaction and product ratio	Equilibrium Constant	Ratio at equilibrium*
		К	
[A]	$Ethanol \rightleftharpoons Ethanal + H_2$	1.48	
	Ethanal / Ethanol		0.3
[B]	$Ethanol + H_2O \rightleftharpoons Acetic acid + 2H_2$	1.99	
	Acetic acid/Ethanol		0.04
[C]	$Ethanal + H_2O \rightleftharpoons Acetic acid + H_2$	1.34	
	Acetic acid/Ethanal		0.015
[D]	2(Acetic acid) \rightleftharpoons Acetone + CO ₂ + H ₂ O	612078	
	Acetone/Acetic acid ²		3 x 10 ⁺¹¹
[E]	$Ethanol + CO + H_2 \rightleftharpoons Acetone + H_2O$	30731	
	Acetone / Ethanol		24280

* At the average partial pressures over the reactor

** Calculations made in Aspen^[30] using an equilibrium reactor model and PSRK thermodynamic model

³⁰ Aspen Plus V7.3, (2012), computer software, Aspen Technology, Inc. Bedford, Massachusetts

4.4.2 Appendix 2



Additional data for 2-propanol and 2-butanone co-feeding experiments

Figure 21 Distribution for the linear hydrocarbons vs. carbon number before and during 2propanol and 2-butanone co-feeding

 Table 6 Linear alkene content in the fraction of linear hydrocarbons (alkenes/alkenes + alkanes) before and during 2-propanol and 2-butanone co-feeding

	2-Propanol		2-Butanone	
Carbon number	Before	During	Before	During
	co-feeding	co-feeding	co-feeding	co-feeding
2	0.48	0.49	0.57	0.44
3	0.76	0.77	0.83	0.80
4	0.84	0.84	0.86	0.76



Figure 22 Pseudo stable isotopic oxygen composition of CO_2 during 2-propanol and 2butanone co-feeding following SSITKA switches from $C^{16}O/H_2/Ar$ to $C^{18}O/H_2/Ne$



4.4.3 Appendix 3



Chapter 5

Pathways for Hydrocarbon Formation

In this chapter, ¹³CO SSITKA and other isotopic gradient experiments are used to determine the carbon pathways for hydrocarbon formation at $H_2/CO = 10, 330 \,^{\circ}C$, 6 bar and GHSV of 3600 $ml_{(n)}.g_{cat}$ ⁻¹.hr⁻¹. In order to correctly account for hydrocarbon chain growth four main reaction steps were taken into account; i) formation of the C₁ monomer species, ii) initiation of chain growth via coupling of two C₁ species, iii) stepwise addition of a C₁ species to a growing chain and iv) the desorption of the surface species. The final mechanistic model accounts for the formation of ethene via the reaction of an adsorbed CO and C₁ species while ethane forms via the addition of two dissimilar C₁ species. Further chain growth of the C₃₊ alkenes and alkanes occurs via the stepwise addition of the same C₁ monomer species.

5.1 Introduction

The determination of the active chemisorbed intermediates which lead to the Fischer-Tropsch (FT) reaction products and measurement of their respective surface concentrations is a highly complex task. This complexity has resulted in the FT mechanism, especially over Fe catalysts, not being well understood and remains a controversial topic in the field of heterogeneous catalysis ^[1]. The steady state isotopic transient kinetic analysis (SSITKA) technique allows for the determination of the concentration of chemisorbed intermediates. In conjunction with MS and GCMS product analysis, SSITKA has been successfully applied by both van Dijk ^[2] and Govender ^[3] to model the FT mechanism and kinetics over Co and Fe catalysts, respectively.

The SSITKA technique using both C and O labelled CO (¹³CO and C¹⁸O) in conjunction with detailed MS and GCMS product analysis to determine the mechanism for methanation, hydrocarbon and alcohol formation was applied by van Dijk ^[2]. For this work he used a Co based catalyst at 210 to 240°C and 1.2 bar. The chain growth model developed was based on the alkyl mechanism originally proposed by Fischer and Tropsch ^[4] (see Chapter 1). For the model, presented in Figure 1, he assumes surface heterogeneity for the formation of methane and higher hydrocarbons, i.e. formation from at least two surface species comparable in chemical composition but which differ due to the presence of different surface sites. Furthermore, van Dijk considered a single chain growth species from which the chemisorbed alkene and alkane may desorb initially via a physisorbed state and then to the gas phase, or grow by the stepwise addition of an adsorbed CH₂ monomer species. C-C coupling was fast compared to the formation of the

¹ Schulz H., *Topics in Catal.*, Vol. 26., (2003), 73

² Van Dijk, H.A.J., PhD Thesis, (2001), Technische Universiteit Eindhoven, Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/200111083.pdf

³ Govender N.S., J. Catal., Vol. 312., (2014), 98

⁴ Fischer F., Tropsch H., Brennstoff-Chem., Vol. 7. (1926), 97

monomer building blocks and the chain initiators from adsorbed CO. He also showed that alcohols were formed via CO insertion into growing hydrocarbon chains on the catalyst surface, spillover of these alcohol intermediates from the Co-metal to the partially oxidised support resulted in the formation of alcoxy species, which could desorb as alcohols. The inverse, spillover of alcohol intermediates to form hydrocarbons was not observed. Important model considerations were: 1-alkenes may readsorb onto the catalyst surface via the physisorbed phase to result in a species identical to that of the chain growth species, the reaction rate coefficient for chain growth and alkene re-adsorption where considered to be constant from C_3 onwards i.e. chain length independent, while the termination to an alkene was considered to take place via a desorption process rather than via β -hydrogen elimination.



Figure 1 Representation of the Fischer-Tropsch mechanism based on ¹³CO SSITKA from the thesis of van Dijk ^[2]. The data were collected over a Co catalyst at $H_2/CO = 1$, 225 °C, 1.2 bar and a range of GHSV's

To determine the mechanistic pathway for methanation and C₂₊ hydrocarbon formation over a co-precipitated Fe/K catalyst at 330°C and 1.2 bar, Govender ^[6] followed a similar approach to that of van Dijk i.e. SSITKA in conjunction with MS and GCMS analysis. Parameter estimation of various methanation models indicated that at least two carbon containing surface intermediates are required to explain his experimental results. Two reaction mechanisms for methanation were found to give a statistically good fit to the experimental data but could not be distinguished from one another (see Figure 2). Based on the results of alkene co-feeding and deuterium tracing experiments, Govender proposed further pathways for higher hydrocarbon formation during the HTFT synthesis. The chain growth model proposed by Govender, presented in Figure 3, is also based on an alkyl-like mechanism where the monomer is an adsorbed CH surface species rather than CH₂.

The model proposed by van Dijk over Co-based catalysts was not able to predict the C₂ transients measured by Govender over an iron-based catalyst. Therefore, Govender included an additional C₂ surface intermediate to account for a delayed ethane transient as compared to the transient for ethene. Modelling the readsorption of ethene directly towards the alkane surface intermediate gave the best fit, while setting the rate of chain growth equal for all chain growth steps made no difference to the model fit, indicating chain length independent growth.



Figure 2 Statistically indistinguishable methanation models 3.2 (left) and 5.2 (right) from thesis of Govender ^[6]. The data were collected over a Fe catalyst at $H_2/CO = 15$, 330 °C, 1.2 bar and GHSV = 7412 ml.gcat⁻¹.hr⁻¹

It should be noted that limited transient data for the partially labeled C_3 's made it difficult to optimize their rate coefficients and a good fit was not obtained for the C_3 's. Govender did however conclude that for a co-precipitated Fe/K catalyst at 330 °C and 1.2 bar, the model could be extended to account for higher hydrocarbon formation.



Figure 3 Representation of the Fischer-Tropsch mechanism based on ¹³CO SSITKA from the thesis of Govender ^[6]. The data were collected over a Fe catalyst at $H_2/CO = 15$, 330 °C, 1.2 bar and GHSV = 7412 ml.gcat⁻¹.hr⁻¹

The aim of this chapter is to determine if the hydrocarbon pathway developed by Govender ^[6] for the HTFT synthesis at 1.2 bar and indicated in Figure 3 holds true at elevated pressure or if another pathway is favoured as a result of the increased pressure. Furthermore, it is intended that a better fit for the C₃ hydrocarbons is obtained. This information will assist in an improved understanding of the intermediates which lead to hydrocarbons and the mechanism/s responsible for chain growth at commercially relevant reaction conditions. To achieve this, the SSITKA data measured at 6 bar will be fitted to the carbon pathway proposed by Govender and also newly proposed pathways based on the qualitative results in the following sections.

Since the FT synthesis is a type of polymerisation reaction with in-situ monomer formation, all proposed reaction mechanisms must account for; i) formation of the C₁ monomers / chain initiator species, ii) the initiation of chain growth via coupling of two C₁ species to form a C₂ species), iii) further chain growth via the stepwise addition of a C₁ species to form the C₃₊ species and iv) termination of chain growth and formation of the gas phase species. It is therefore necessary that a complete mechanistic model for chain growth includes at least a description for the formation of methane as well as the C₂ and C₃ hydrocarbons, while accounting for the formation and possible reaction of CO_2 in cases where the WGS or reversible WGS reaction is active.

5.2 Experimental

In order to collect sufficient transient data for the species used in parameter estimation, six SSITKA switches ($^{12}CO/H_2/Ar$ to $^{13}CO/H_2/Ne$) were made where the sample intervals of the 16-loop sample valve were varied for each switch. The six SSITKA switches took place over three separate experiments at the same reaction conditions to ensure that the effect of time on-line (TOL) with regard to activity and selectivity was minimised. The transient data were obtained over a fused iron catalyst at inlet H₂/CO = 10, 330 °C, 6 bar and GHSV = 3600 ml_(n).g_{cat}⁻¹.h⁻¹.

At the reaction conditions of this work a significant amount of CO₂ is formed and this must be accounted for in the overall mechanistic pathway. The water gas shift (WGS) reaction is, however, reversible at high temperature FT reaction conditions. This further complicates the overall mechanism for hydrocarbon formation since it is no longer clear from which carbon source (CO, CO₂ or both) the hydrocarbons are formed. Previous work showed isotopic switches of the feed from $H_2/^{12}CO_2$ to $H_2/^{13}CO_2$ result in ¹³CO and ¹³CO₂ transients which elute at the same time, becoming kinetically indistinguishable from each other ^[5, 6]. As a result, relatively standard isotopic labelling experiments cannot be used to directly determine the carbon source of organic products (CO or CO₂) in the HTFT synthesis.

To address this issue an experiment was designed so as to create an isotopic gradient through the catalyst bed. For this type of experiment, described in Figure 4, H_2 , CO and CO₂ are fed to the reactor; once steady state is achieved an isotopic

⁵ Krishnamoorthy S., Li A., Iglesia E., Catal. Letters., Vol. 80, No. 1-2., (2002), 77
switch from $H_2/^{12}CO/^{12}CO_2$ to $H_2/^{12}CO/^{13}CO_2$ is made. Since the reaction is carried out in an integral fixed bed reactor and the WGS reaction is close to equilibrium, ¹³C exchanges from CO₂ to CO and ¹²C exchanges from CO to CO₂.

As indicated in the example given in Figure 4, the ¹³C composition over the length of the catalyst bed increases for CO and decreases for CO₂. It therefore follows that if a hydrocarbon was formed from CO alone, its carbon isotopic composition could not contain more ¹³C (equal to or less) than the ¹³C content of CO. Alternatively, if a hydrocarbon was formed from CO₂ only, its carbon isotopic composition could not contain less ¹³C (equal to or more) than the ¹³C content of CO₂. Finally, if a hydrocarbon product is in part made up of ¹³C from both CO and CO₂ the isotopic composition of the hydrocarbon would be between that of the ¹³CO and ¹³CO₂ isotopic compositions. For the case where the hydrocarbon species are formed from CO and CO₂ and the isotopic transients of ¹³CO and ¹³CO₂ intersect along the bed length, the isotopic compositions for the hydrocarbons will be equal to that of CO and CO₂ at the juncture point and then return to a composition between that of ¹³CO and ¹³CO₂ further along the bed length.

It is important that these experiments are completed at different residence times (short and long) to ensure that hydrocarbons are not fully or in part formed from CO₂ at very short residence times and CO at long residence times or vice versa. Furthermore, it is assumed that there is no kinetic isotope effect for CO, CO₂, or the hydrocarbons.



Figure 4 Representation of the isotopic composition CO and CO₂ through the catalyst bed with $H_2/^{12}CO/^{13}CO_2$ feed composition. It should be noted that the reaction is at steady state and the total rate of formation of the products is constant

5.3 Experimental results and discussion

5.3.1 ¹³CO SSITKA for CO, CO₂ and CH₄

In Figure 5 (left) the typical ¹³CO, ¹³CO₂ and ¹³CH₄ transient responses, measured with MS for a ¹²CO/H₂/Ar to ¹³CO/H₂/Ne SSITKA experiment over a fused iron catalyst, are given. In Figure 5 (right) the decay curves for CO, CO₂ and CH₄ are given. The reaction conditions are kept constant at an inlet H₂/CO ratio of 10, 330°C, 6 bar and GHSV of 3600 ml_{(n).gcat}⁻¹.h⁻¹. The following observations are made:

- The normalised ¹³CO transient is only marginally delayed with regard to the inert transient, both transients eluting at almost identical times. This indicates a low coverage of surface species which result in gas phase CO.
- No chromatographic effect was observed for the normalised ¹³CO response, i.e. a delay in the normalised ¹³CO response with regard to the normalised inert response. This result is in line with those in literature over Fe catalysts at HTFT ^[6] and LTFT ^[7] conditions and indicates very low CO surface coverages.
- The normalised ¹³CO₂ transient is delayed with regard to ¹³CO. The full replacement of ¹²CO₂ by ¹³CO₂ takes approximately 5 minutes.
- The shape of the decay plot for ¹³CO₂ in Figure 5 (right) indicates that CO₂ is formed via a "complex" mechanism, as described by Bal'zhinamaev *et al.* ^[8], and may include a parallel route or buffer step.
- The normalised ¹³CH₄ transient only reaches full labelling approximately 15 to 20 minutes after the SSITKA switch from ¹²CO to ¹³CO is made. This is faster than the ¹³CH₄ transient observed in the work of Govender which was also at HTFT reaction conditions ^[6] where full elution of ¹³CH₄ took up to 40 minutes. The difference in CH₄ elution time is most likely due to the much higher hydrogen partial pressure (and thus H_{,ads} concentration) of this work vs. that of Govender as indicated in Table 1. Van Dijk showed this effect on the methane transient, where an increase in the H₂/CO ratio (increased H_{,ads} concentration) resulted in a decrease of the mean residence time for the intermediates leading to CH₄ ^[2].
- The shape of the decay plot for ¹³CH₄ is similar to that observed by van Dijk and Govender over Co and Fe catalysts respectively. The modelling results of both authors clearly indicated that methane formation occurs via a

⁶ Govender N.S., PhD Thesis., Technische Universiteit Eindhoven (2010)., Eindhoven., The Netherlands, http://alexandria.tue.nl/extra2/689931.pdf

⁷ Mims C. A., McCandlish L. E., J. Phy. Chem., Vol. 91, (1987), 929

⁸ Bal'zhinimaev B.S., Sadovskaya E. M., Suknev A. P., Chem. Eng. J., Vol. 154, (2009), 2

mechanism originating from at least two kinetically distinct carbon pools, operating in parallel (see Figure 2).



Figure 5 (left), Normalized transient responses for inert, ¹³CO, ¹³CO₂ and ¹³CH₄. (right), semi-logarithmic decay of ¹²C content in CO, CO₂ and CH₄. The data were obtained from MS analysis.

5.3.2 ¹³CO SSITKA for hydrocarbons

The normalised hydrocarbon transients presented in Figure 6 for the C_2 's (ethene, ethane) and Figure 7 for the C_3 's (propene, propane) show the results of several ¹²CO/H₂/Ar to ¹³CO/H₂/Ne SSITKA experiments. The reaction conditions for these experiments are kept constant at an inlet H₂/CO ratio of 10, 330 °C, 6 bar and GHSV of 3600 ml_{(n).gcat}⁻¹.h⁻¹, all isotopic hydrocarbon analyses were carried out using GCMS. The normalised transients for the C₄ hydrocarbons are given in Appendix 1 and show similar trends to those of the C₂ and C₃ hydrocarbons. The following observations are made:

 The fully labelled ¹³C, C₂ to C₄ alkene transients elute before the respective alkane transients. For the reaction conditions of this work, the alkenes all reach full labelling approximately 4 minutes following the SSITKA switch, while the alkanes all fully elute at approximately 20 minutes.

- The partially labelled alkene intermediate species also reach a peak maximum prior to the respective alkane intermediates i.e. ${}^{12}C{}^{13}C_2$ (alkene) elutes at 0.2 minutes where the ${}^{12}C{}^{13}C_2$ (alkane) elutes at 0.3 minutes.
- The peak maximum of the propane intermediate is higher than that for the corresponding propene intermediate; furthermore, the peak maximum for both alkanes and alkenes increases as the ¹³C content of the intermediate increases.
- Tailing of the partially labelled species is more significant for the alkanes than for the alkenes and also increases with increasing ¹³C content; i.e. for the C₃ hydrocarbons tailing increases from ¹²C₂¹³C₁ (alkene) < ¹²C₂¹³C₁ (alkane) < ¹²C₁¹³C₂ (alkene) < ¹²C₁¹³C₂ (alkane).
- There is no observable shift in peak maxima of the partially labelled C₃ and C₄ intermediates as the ¹³C content increases; this indicates very fast chain growth as compared to the rate of isotope displacement in the precursors to chain growth.



Figure 6 Normalized transient responses for (left) ethene and (right) ethane. The figures are made up of the combined GCMS data from several SSITKA experiments



Figure 7 Normalized transient responses for (left) propene and (right) propane. The figures are made up of the combined GCMS data from several SSITKA experiments

In Figure 8 (left) the normalized fully labelled curve 13 CO transients of the C₂ to C₄ hydrocarbons are given, while the decay plots of these products including those for methane and CO₂ are given in Figure 8 (right). The following observations are made:

- As indicated above and clearly presented in Figure 8 (left), the fully labelled ¹³C, C₂ to C₄ alkene transients elute before the respective alkane transients. This result is consistent with the work of Govender over a Fe catalyst at HTFT reaction conditions ^[6]. Govender showed that a mechanism with at least two surface intermediates leading to the C₂₊ hydrocarbons is required to describe the delay in alkenes with respect to the alkanes.
- The decay plots of methane and the C₂ to C₄ alkanes are similar in shape and follow each other closely. This indicates that the reactive intermediate species, which lead to methane formation, also participate in the chain growth mechanism for higher alkane formation.
- The trajectory and shape of the decay plots for the C₂ to C₄ alkenes differ from that of methane and the alkanes. This result indicates that the formation

alkanes and alkenes take place via several intermediate species of which at least one being unrelated.

 Increased tailing of the intermediates suggests that the monomer species may partly originate from an unreactive carbon source ^[2].



Figure 8 (left) Combined, fully labelled transients for the C_2 to C_4 hydrocarbons, (right) semi-logarithmic decay of ¹²C content in CH₄, CO₂ and the C₂ to C₄ hydrocarbons. The CH₄ and CO₂ data were obtained from MS and the C₂ to C₄ from GCMS analysis

Rapid chain growth for hydrocarbons compared to the formation of chain initiation species is evidenced by the isotropic incorporation of the labelled monomer for the intermediate C₃ and C₄ hydrocarbon species in Figure 7 and Figure 22 (see Appendix 1). This result agrees with that of Mims and McCandlish ^[9, 7] over Fe and Co catalysts and of van Dijk ^[2] over Co catalysts. Mims and McCandlish further note that when chain growth is fast compared to the residence time of the chain growth precursor for irreversible chain growth, the surface coverage of growing chains will be very small compared to that of the C₁ precursor for chain growth. For the case where chain growth is reversible, the surface coverage of growing chains may be much higher but this will be determined by the relative rates of polymerization and de-polymerization. Work

⁹ Mims C. A., McCandlish L. E., J. Am. Chem. Soc., Vol. 107, (1985), 696

by Mims et al. ^[10] over a Ru/Al catalyst at one atmosphere and 182 °C showed some reversibility of chain growth. Preliminary simulations of these results indicated that the overall chain growth rate did not differ significantly and the surface coverage of chain growth precursors would still be significantly higher than that of the growing carbon chains. In the following sections, modeling of the transients will allow for a comparison of the C₁ and hydrocarbon surface coverage.

Van Dijk ^[2] showed the semi-logarithmic decay of the ¹²C content in propane to follow that of methane. As a result, he concluded that the reactive intermediate species leading to methane formation also participate in the hydrocarbon chain growth process. This conclusion is seemingly at odds with the data of Mims and MacCandlish ^[7], who showed the semi-logarithmic decay of the ¹²C content in 1-butene to deviate from that of methane, indicating that at least one intermediate species for the formation of methane differs to that for the hydrocarbon chain growth process. The data of Figure 8 (right) shows the semi-logarithmic decay of both the C₂ to C₄ alkanes and alkenes; here the trends for the alkanes follow methane while the trends for the alkenes do not. Therefore, the data from both van Dijk and Mims are shown to be correct. The data of Figure 8 indicate that the same C₁ intermediate species, which lead to methane formation, also lead to higher alkane formation. The difference between the trends of the alkanes and alkenes however indicate that their formation takes place via several intermediate species of which at least one being unrelated.

¹⁰ Mims C. A., Krajewski J. J., Rose K. D., Melchior M. T., Catal. Letters., Vol. 7, (1990), 119

5.3.3 Increase of pressure

Table 1 gives a comparison of the inlet partial pressures of this work vs. those of Govender. This table clearly illustrates the significant increase in the inlet partial pressures of H₂ and CO for this work. The higher reactant partial pressures are closer to commercial operating conditions and are expected to result in an increased FT rate (hydrogenation and chain growth) and reaction steps, previously undetected at low pressure conditions (such as CO insertion) may now become apparent. The relatively high flow rate of Ar was used to maintain a constant total molar flow rate throughout the catalyst bed.

Partial pressure [bar]	Work of Govender	This work	Factor increase
H ₂	0.988	3.00	3.04
СО	0.066	0.30	4.55
Ar	0.146	2.70	18.49
Total Pressure	1.2	6	5.00

Table 1 Comparison of feed partial pressures to those used by Govender [6]

A comparison on the SSITKA data measured by Govender at 1.2 bar and this work at 6 bar is given in Figure 9. The increase in the total pressure and hence the partial pressures of CO and H₂ result in two main changes with regard to the SSITKA transients. Firstly, the increased hydrogen partial pressure is thought to decrease the mean residence time for the methane intermediates, due to an increasing surface concentration of H_{ads} ^[2]. This effect is observed by the decreased residence time of the methane and alkane intermediates at the higher H₂ partial pressure. Importantly, the shape of the transient curves for methane and the alkanes remain the same indicating that the carbon pathways for their formation are largely unaffected by the increased CO partial pressure. Secondly, a combination of the increase in partial pressures of CO and H₂ seems to lead to a decreased mean residence time as well as a change in the carbon pathway for alkene formation. It is not clear from this data to what degree each of the reactants affects the mean residence time or the carbon pathway and exactly how the alkene pathway changes at high pressures. Fitting of the SSITKA data to carbon pathways must be completed for further information in this regard.



Figure 9 (left) Normalised transient responses of methane, this study (solid line) and the study of Govender ^[6] (open markers with line). (right) Normalised transient responses of ethane and ethene this study (*closed markers*) and the study of Govender ^[6] (open markers with line)

5.3.4 Role of CO₂ in hydrocarbon intiation and chain growth

At HTFT reaction conditions of this work (330 °C), the water gas shift (WGS) reaction is reversible and the CO₂ formed from CO may act as a reactant, which can be hydrogenated via the reverse WGS reaction. For the purposes of this chapter, i.e. to determine the mechanistic pathway for hydrocarbon formation, it is important to determine if CO₂ can be directly hydrogenated to hydrocarbons or if CO₂ first reacts to CO in the gas phase before reabsorbing on FT sites for hydrocarbon formation.

Previously, Xu and co-workers $^{[11]}$ co-fed 14 CO₂ with synthesis gas (12 CO and H₂) to a CSTR reactor containing fused iron catalyst at 270 °C and 8 bar total pressure. Their results showed the hydrocarbon products to have a higher radioactivity than could have resulted from hydrocarbon formation from CO only. Following detailed analysis of the radioactivity per mole for each of the hydrocarbons they concluded that an intermediate of the WGS reaction also acts as an initiator for chain growth in the FT synthesis. More recently Krishnamoorthy et al. [5] questioned this finding based on the significant interconversion between CO and CO₂ brought about by the reversibility of the WGS reaction at the reaction conditions used by Xu et al.. To re-evaluate the role of CO₂ in hydrocarbon formation, Krishnamoorthy carried out an experiment over a co-precipitated Fe/Zn/Cu/K catalyst in a PFR at 235°C and 8 bar where ¹³CO₂ was added to the synthesis gas (12 CO and H₂). The difference between this work and that of Xu *et al.* is that these experiments were conducted at conditions far removed from WGS equilibrium conditions; this significantly reduced the possibility for exchange of ¹³C from CO₂ to CO and allowed the ¹²CO exiting the reactor to retain its ¹²C isotopic purity. The resulting hydrocarbons had a much lower ¹³C fraction than CO₂, and in most cases it was below the detection limit of the analytical methods used. This result indicated that CO₂ was much less reactive than CO towards chain initiation or chain growth and did not appear to compete with CO for the direct formation of hydrocarbons.

Although the work of Krishnamoorthy was done in a much more controlled manner, the view from literature is not consistent and further insight is provided in this section to determine the carbon pathway for CO_2 hydrogenation during HTFT synthesis. The results of the method described in Section 5.3 where H₂, ¹²CO and ¹³CO₂ are fed to the reactor to create an isotopic gradient in CO and CO₂

¹¹ Xu L.,Bao S., Tau L.M., Chawla B., Dabbagh H., Davis H. H., 11th Annual Int. Pittsburgh Coal Conf. Proc., (1994), 88

through the catalyst bed length are given in Figure 10 for different residence times / reactor lengths. Following a SSITKA switch i.e. once the ${}^{12}CO_2$ has been fully replaced by ${}^{13}CO_2$ and the isotopic transients are constant with time on-line the following observations are made for methane:

- A significant fraction of both reactions (methanation and WGS) occurs in the first 20 percent of the catalyst bed.
- The ¹³C composition of CH₄, is less than that of CO at both residence times indicating that: i) CH₄ is formed entirely from CO over the full length of the catalyst bed and ii) the rate of CH₄ formation is faster than the WGS reaction.



Figure 10 Stable isotopic compositions of CO₂, CO and CH₄ at the reactor outlet for two different residence times

A similar method as that used to calculate the source of carbon in methane is used for the C_{2+} hydrocarbons. For the C_2 hydrocarbons there are four possible

isotopic combinations which must be taken into account; these are indicated in Figure 11.



Figure 11 Different isotopically labelled C2 carbon chains forming on the catalyst surface

Although the partially labeled gas phase species for ethene and ethane ($^{12}C^{13}C$ and $^{13}C^{12}C$) are not chemically different from one other, the probability for their formation must be known. Assuming that hydrocarbons are formed from CO only and given that the isotopic composition of CO is known at a specific point on the reactor axis, the resulting ^{13}C fraction for each of the possible carbon-carbon bond combinations can be calculated at this point. Similarly, assuming that hydrocarbons are formed directly from CO₂, the ^{13}C fraction for each isotopic can also be calculated. Comparison of the measured isotopic fractions to those calculated for various residence times provide information on the carbon source since the ^{13}C fraction of CO increases with residence time and that of CO₂ decreases.

Assuming that the C₂ hydrocarbons are formed from CO only and based on the experimental data for the isotopic composition of CO at the full residence time, the <u>maximum</u> ¹³C composition of ¹²C¹²C, ¹²C¹³C and ¹³C¹³C at the full residence time are calculated as follows:

 $(0.49^{12}CO \bullet 0.49^{12}CO) \bullet 1 = 0.24^{12}C^{12}C$

$$(0.51^{13}CO \bullet 0.51^{13}CO) \bullet 1 = 0.26^{13}C^{13}C$$
$$(0.49^{12}CO \bullet 0.51^{13}CO) \bullet 2 = 0.5^{13}C^{12}C$$

Assuming that the C₂ hydrocarbons are formed from CO₂ only and based on the experimental data for the isotopic composition of CO₂ at the full residence time, the <u>minimum</u> ¹³C composition of ¹²C¹²C, ¹²C¹³C and ¹³C¹³C at the full residence time would be:

$$(0.47^{12}CO_2 \bullet 0.47^{12}CO_2) \bullet 1 = 0.22^{12}C^{12}C (0.53^{13}CO_2 \bullet 0.53^{13}CO_2) \bullet 1 = 0.28^{13}C^{13}C (0.47^{12}CO_2 \bullet 0.53^{13}CO_2) \bullet 2 = 0.5^{13}C^{12}C$$

The values of the maximum and minimum fractions for the C_2 hydrocarbons are compared to those measured for two residence times are presented in Figure 12. The following observations are made:

- The 13 C composition (partially and fully labelled) of ethene and ethane, is less than that of CO at both residence times indicating that the C₂ hydrocarbons are formed entirely from CO over the full length of the catalyst bed.
- Following from the previous point, for both residence times and ¹³C compositions respectively, the ethane product contains more ¹³C than the ethene. This indicates that the rate of ethane formation is slower than ethene. A large fraction of the ethane is therefore formed at longer residence times when the CO is richer in ¹³C.

An important implication of ethene and ethane having different isotopic compositions and hence different rates of formation is that it must be the formation of at least one monomer species or the actual C-C coupling reaction which differs between them. Furthermore, if a major route of alkene formation was via beta-hydrogen elimination from a common adsorbed C₂ surface intermediate, the alkene and alkane would have the same or very similar isotopic compositions and this is not the case.



Figure 12 Stable isotopic composition of C₂ hydrocarbons at two different reactor residence times (0.2 and 1). The data is obtained from GCMS analysis

For these experiments, the labelled alkenes and alkanes show a decreasing trend of ¹³C labelling with every additional carbon number. This can be understood from the decreasing probability of two, three, four etc. ¹³C carbon-carbon bonds being formed from CO which enters the reactor having 100% ¹²C and exits having a mixture of ¹³C and ¹²C. The results of this work, therefore, give no indication of CO₂ as a direct chain initiator in the formation of hydrocarbons and will be assumed to first react to gas phase CO before taking part in FT. The decreasing ¹³C isotopic composition is therefore just a result of the decreasing probability for multiple ¹³C bonds to be formed.

5.4 Mechanistic implications from qualitative results

Based on the qualitative observations from the ¹³CO SSITKA and isotopic gradient experiments at 6 bar, it is necessary that the existing models of Govender ^[3] be reassessed so as to incorporate the observations described in section 5.3. Below, each section of the mechanistic model is discussed separately and finally combined into a complete description for the formation of CH₄ and the C₂ to C₃ hydrocarbons while taking into account the formation and reaction of CO₂.

Formation of chain monomers, CO, CO₂ and CH₄:

Given that the methanation models of Govender for CO and CH₄ are consistent with the SSITKA data obtained in this work i.e. account for a fast breakthrough of ¹³CO, as well as the complex formation of CH₄ via a mechanism having at least a buffer or parallel step. No further adjustments to the existing methanation model of Govender are anticipated.

In order to extend the methanation model of Govender to account for CO₂ formation. The SSITKA data indicate that CO₂ is formed from a mechanism consisting of a buffer or parallel step and not a linear mechanism as reported by Botes ^[12]. In order to simplify the model as much as possible a basic two pool mechanism is proposed where the adsorbed CO species may react with lattice oxygen to form adsorbed CO₂ and an oxygen vacancy consistent with the Mars and van Krevelen (MvK) type of mechanism as discussed in Chapter 3. Furthermore, the mechanism given in Figure 13 includes a buffer step describing the formation of the formate (COOH_s) intermediate.

¹² Botes F.G., Appl. Catal. A:, Vol 328., (2007), 237



Figure 13 Basic two carbon pool Mars – van Krevelen type of mechanism with buffer step to describe the formation of CO_2

Finally, results of the isotopic gradient experiments above indicate that direct CO₂ hydrogenation directly to CH₄ or hydrocarbons does not take place and CO₂ must first react via the reverse WGS reaction to gas phase CO. The gas phase CO can then readsorb onto FT sites for further reaction to CH₄ and hydrocarbons. The proposed carbon pathway to account for the ¹³CO, ¹³CO₂ and ¹³CH₄ transients is therefore expected to follow that presented in Figure 14 and accounts for the C₁ product formation of Model C fitted in section 5.6



Figure 14 Methanation model 3.2 of Govender ^[6] developed for an iron catalyst at HTFT reaction conditions. Additional steps to describe the CO₂ transient added.

Formation of C₂ hydrocarbons:

Consistent with the results of Govender for the C₂ hydrocarbons at HTFT reaction condition over a Fe catalyst ^[3], the alkene transients of this work eluted prior to

those of the corresponding alkane. Govender showed that a mechanistic pathway with two, C_2 surface intermediates is required to predict this behaviour. This pathway is presented in Figure 15 and is considered in further model proposals. A further similarity between the results of Govender and this work is that the decay

plots for CH₄ and the C₂₊ alkanes presented in Figure 8 follow each other closely, indicating that the reactive intermediates leading to CH₄ also participate in C₂₊ alkane formation. The shape of the C₂₊ alkene decay plots do however not follow the CH₄ and alkanes. This suggests that an additional intermediate will be required to describe alkene formation correctly.

Chain growth of C₃₊ hydrocarbons:

Once the C₂ surface species has formed, this species may desorb to the gas phase or continue to grow via the stepwise addition of a C₁ monomer species. Since more than one type of monomer species may exist on the catalyst surface, i.e. CO_{ads} or CH_{2,ads}, it is important to fit the C₃ transient data to mechanistic models, so that the chain growth monomer/monomers can be identified.

Chain termination to gas phase products:

Based on the results of isotopic gradient experiments from section 5.3.4 for the C₂ hydrocarbons it seems unlikely that β -hydride elimination is a major route for the formation alkenes. Furthermore, Govender ^[6] and van Dijk ^[2] both found β -hydride elimination to be an unlikely route for alkene formation. For the C₂ models of Govender, the formation of both the alkene and alkane occur via hydrogenation of the respective adsorbed C₂ species while van Dijk described alkene formation via desorption and alkane formation for this work does not take β -hydride elimination into account and the formation of hydrocarbons via desorption / hydrogenation is preferred.

5.5 Model selection

In all cases, the methanation and CO₂ formation pathways are taken from that proposed in Figure 14. Readsorption of an alkene to an alkane surface species and hydrogenation of an alkene precursor to an alkane precursor are also common attributes of all three models. The naming of the models below continues from those of Govender ^[6] where the final model was named Model C.

5.5.1 Present description of chain growth in the HTFT synthesis

Model C with CO₂ formation pathway:

Model C of Govender ^[6] contains two C₂ surface intermediates in series (C_{2α} and C_{2β}). The formation of the C_{2α} intermediate occurs via the reaction of a C_α with a C_β surface species; this species may i) desorb as gas phase ethene, ii) be hydrogenated to the C_{2β} species or iii) continue to grow to a C_{3α} species by the addition of a C_β surface species. The formation of the C_{2β} species primarily occurs via the hydrogenation of the C_{2α} surface species but may also form from ethene readsorption. The C_{2β} species may react further by i) hydrogenation to gas phase ethane or ii) dehydrogenation back to the C_{2α} surface species. This reversible hydrogenation accounts for further chain growth as a result of alkene readsorption. In this model, the formation of higher hydrocarbons (C₃₊) occurs via the same mechanistic pathways as the C₂'s.

5.5.2 Extended carbon pathways to include the role of adsorbed CO in higher hydrocarbon formation

The qualitative results of section 5.3 for the SSITKA and isotopic gradient experiments strongly indicate that an additional surface species (other than $C_{\alpha,ads}$ and $C_{\beta,ads}$) are required to correctly predict the alkene transient at elevated CO

and H₂ partial pressures. Given that increasing H₂ partial pressure leads to shorter residence times of the adsorbed intermediates but not to changes in the carbon pathways for CH₄ and hydrocarbon formation, the origin of the additional C₁ surface species to correctly account for alkene formation must relate to the increase in CO partial pressure. In the following two cases, the direct role of adsorbed CO in C₂₊ hydrocarbon formation is investigated further; these two cases deal with i) CO insertion to the alkane precursor to form an n+1 alkene, Model D, Figure 16 and ii) CO insertion as chain initiator for the alkene precursor, Model E, Figure 17.

In addition to the differences with regard to the monomer species, the reverse hydrogenation of the alkane precursor, $C_{n\beta}$ to $C_{n\alpha}$ has been omitted, given that Models D and E accommodate for chain growth of reabsorbed alkenes directly from the alkane precursor. The models below deal with either one chain growth monomer and two growing chains or two chain growth monomers and two growing chains.

Model D:

Model D, illustrated in Figure 16, differs from those described previously. The first difference being the formation of the C_2 and C_3 surface species while the second being the pathway for further chain growth. The formation of the alkene precursor ($C_{2\alpha,ads}$) occurs via the combination of adsorbed CO (CO_{ads}) and C_1 species ($C_{\beta,ads}$), importantly the $C_{2\alpha,ads}$ species does not directly take part in further chain growth and must first be hydrogenated to the corresponding alkane precursor before further chain growth can take place. The formation of the alkane precursor ($C_{2\beta,ads}$) is similar to that of previous models in the respect that this species may form from the hydrogenation of the $C_{2\alpha,ads}$ species or from readsorption of ethane. In addition this model also allows for the direct formation of $C_{2\beta,ads}$ from the combination of the two methane precursors, $C_{\alpha,ads}$ and $C_{\beta,ads}$.

Model E:

For Model E, illustrated in Figure 17, the formation of the alkene precursor $(C_{2\alpha,ads})$ occurs via the combination of the adsorbed CO (CO_{ads}) and C₁ species $(C_{\beta,ads})$ while the alkane precursor $(C_{2\beta,ads})$ forms via the combination of the C_{$\alpha,ads}$ and C_{β,ads} species. Chain propagation takes place via the stepwise addition of only the C_{β,ads} species to both the C_{2 $\alpha,ads} and C_{2<math>\beta,ads}$ species, respectively.</sub></sub></sub>

This model differs from Model D since CO serves to initiate ethene formation while further chain growth takes place via the addition of the $C_{\beta,ads}$ species to both the C_{2+} alkene and alkane precursors, albeit at potentially different rates.



Figure 15 Model C of Govender with methanation model 3.2 including the proposed carbon pathway for CO₂ formation from Figure 14



Figure 16 Model D, chain growth from alkane precursor only and alkene formed by addition of CO to the alkane precursor (closed circles indicate carbon-carbon bond formation)



Figure 17 Model E, chain initiation step includes CO insertion for alkene but chain growth by $C_{\beta,ads}$ only (closed circles indicate carbon-

carbon bond formation)

5.6 Model discrimination

By comparison of the model predictions given in Figure 18 (A) and (B) it appears that all three carbon pathway models (C, D and E) are capable of describing the experimental data for ¹³CO, ¹³CO₂ and ¹³CH₄ measured at 6 bar. As such, all three models (C, D and E) are used in fitting of the C₂ transient data. The respective rate coefficients estimated for methanation and CO₂ formation are fixed for each model and used in the further estimation of the C₂'s.

From the parameter estimation results presented in Figure 19 (A and B) it is apparent that Model C does not predict the fully labelled ethane transient (A) or the partially labelled ethene and ethane transients (B) as well as the other two models. The reason Model C does not fit the data is because there is no additional monomer / chain initiation species to account for the difference in carbon pathways between the alkene and alkane brought about by the increase in CO partial pressure. Models D and E which contain an additional C₁ surface species fit the experimental data much better. The addition of a third surface species is therefore shown to be necessary to describe C₂ hydrocarbon formation at reaction conditions where CO or a similar C₁ surface species may insert into carbon chains forming alkene precursors (Model D), or at least initiate alkene chain growth (Model E).



Figure 18 (A) model predictions of ¹³CO and Ne and (B) ¹³CO₂ and ¹³CH₄ for models C, D and E illustrated in Figure 15, Figure 16 and Figure 17. The symbols are the experimental data points



Figure 19 (A) model predictions of ¹³C₂H₄ and ¹³C₂H₆ and (B) ¹³C¹²CH₄ and ¹³C¹²CH₆ for models C, D and E illustrated in Figure 15, Figure 16 and Figure 17. The symbols are the experimental data points

The model predictions of the C₃ transients are given in Figure 20 (A, B and C). For the fully labelled, single labelled and double labelled transients Model E predicts the experimental data with greater accuracy than Model D. Model D is based on the assumption that the C₃ alkene is formed from CO insertion to the C₂ alkane precursor (C_{2β,ads}) to form the C₃ alkene precursor (C_{3α,ads}). The delay of the C₂ alkane vs. the C₂ alkene is then transferred to both the C₃ alkene and alkane in the next chain growth step. This result is in line with very fast chain growth compared to the formation of the C_1 monomer species.



Figure 20 (A) model predictions of ${}^{13}C_3H_6$ and ${}^{13}C_3H_8$, (B) ${}^{13}C^{12}C_2H_6$ and ${}^{13}C^{12}C_2H_8$, (C) ${}^{13}C_2{}^{12}CH_6$ and ${}^{13}C_2{}^{12}CH_8$ for models D and E illustrated in Figure 16 and Figure 17. The symbols are the experimental data points

Of the three models fitted to the SSITKA data measured at 330 °C, 6 bar, $H_2/CO=10$ and GHSV = 3600 ml_(n).g_{cat}⁻¹.h⁻¹, Model E was able to describe the formation of CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ best. Figure 21 indicates the preferred mechanism based on the carbon pathways from Model E. In this mechanism the alkene chain is initiated by the reaction of adsorbed CO and CH₂ to form an adsorbed CHCH₂ intermediate which may be hydrogenated to primary ethene. The alkane is initiated from the reaction of an adsorbed CH₂ and CH₃ species to form an adsorbed CH₂CH₃ intermediate, consistent with the Alkyl mechanism, where the alkane is formed from the hydrogenation of this species. Further chain growth of both the alkene and alkane precursors occur via stepwise CH₂ insertion. The alkene follows the chain growth mechanism similar to that proposed by Maitlis ^[13] while the alkane continues along the chain growth steps of the alkyl mechanism.

¹³ Maitlis P.M., Quyoum R., Long H.C., Turner M.L., Appl. Catal. A., Vol 186., (1999) 363

Monomer formation:



Figure 21 Reaction steps of the preferred mechanism for the Fischer-Tropsch synthesis describing primary hydrocarbon formation according to Model E over iron based catalysts at HTFT reaction conditions

It should be noted that the data of this chapter were measured at HTFT reaction conditions over an iron catalyst and an alternative carbon pathway to the one represented by Model E may provide a better fit for FT data measured at different reaction conditions and over different catalysts.

5.7 Parameter estimation

The rate constants for each of the models above (C, D and E) were estimated in a stepwise manner. In the first step, the models were limited to describe the formation of CO, CO₂ and CH₄ with the remaining carbon accounted for in a net consumption term, $C_{2, NET}$ (an example is given for Model C in Figure 14). Once the parameters describing the formation of CO, CO₂ and CH₄ were estimated, they were fixed and the model was extended in the second step to account for the formation of ethene and ethane with a net consumption term in the second step accounting for the formation of the C_{3, NET} species. Finally, once the parameters describing the formation of ethene and ethane have been estimated and fixed, the model is once again extended to account for the formation of propene and propane with a net consumption term, C_{4, NET} accounting for the remaining carbon species.

During parameter estimation, the values of $C_{2, NET}$, $C_{3, NET and} C_{4, NET}$ were allowed to vary marginally due to the experimental / analytical errors associated in their measurement. The result is that the carbon balances estimated from the model results do not always add up to 100% as indicated from the molar flow rates given in Table 4.

The results of fitting Model E, Figure 17 are given in Table 2, Table 3 and Table 4 below. Although Model E accounts for the experimental observations, a statistically good fit (weighted residual smaller than the χ^2 value) was not achieved and some of the reaction rate constants from Table 2 could not be estimated precisely. For a statistically good fit of Model E and the precise estimation of reaction rate constants, further SSITKA data for the C₂ and C₃ hydrocarbon transients is required. An analysis / measurement error of 5% was assumed for the experimental measurements.

Table 2: Parameter estimates of reaction rate constants from Model E, for formation of CO, CO₂, CH₄ as well as C₂ and C₃ hydrocarbons at 330 °C, 6 bar, H₂/CO ratio = 10 and GHSV = $3600 \text{ ml}(n).g_{cat}^{-1}.hr^{-1}$

Parameter	Dimentions	Estimated value
k _{ads}	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	2.81 × 10 ⁻⁰¹
k _{des}	[S ⁻¹]	$2.28 \times 10^{+04}$
k _{fwgs,1}	[S ⁻¹]	2.65×10^{-04}
k _{fwgs,2}	[S ⁻¹]	$3.54 \times 10^{+00}$
k _{fwgs,3}	[S ⁻¹]	3.41×10^{-01}
k _{rWGS,1}	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	$3.73 \times 10^{+00}$
k _{rWGS,2}	[S ⁻¹]	7.25 × 10 ⁻⁰²
k _{rWGS,3}	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	1.71 × 10 ⁻⁰³
k _{bf}	[S ⁻¹]	1.69×10^{-02}
k _{br}	[S ⁻¹]	8.15 × 10 ⁻⁰²
k _{CO1}	[S ⁻¹]	$9.69 \times 10^{+00}$
k _{CO2}	[S ⁻¹]	$5.68 \times 10^{+00}$
k _{tp}	[S ⁻¹]	3.85 × 10 ⁻⁰³
k _{tp1}	[S ⁻¹]	9.49×10^{-02}
k _{inio}	[kg _{cat} .mole ⁻¹ .s ⁻¹]	8.32 × 10 ⁺⁰²
k _{inip}	[kg _{cat} .mole ⁻¹ .s ⁻¹]	5.57 × 10 ⁻⁰²
k _{to2}	[S ⁻¹]	2.29 × 10 ⁻⁰²
k _{tp2}	[S ⁻¹]	$9.09 \times 10^{+02}$
k _{re2}	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	1.06 × 10 ⁻⁰³
k _{hf2}	[S ⁻¹]	3.25 × 10 ⁻⁰⁴
k _{o3}	[kg _{cat} .mole ⁻¹ .s ⁻¹]	$2.06 \times 10^{+01}$
k _{p3}	[kg _{cat} .mole ⁻¹ .s ⁻¹]	$1.00 \times 10^{+04}$
k _{to3}	[S ⁻¹]	$1.55 \times 10^{+01}$
k _{tp3}	[S ⁻¹]	3.12 × 10 ⁻⁰²
k _{re3}	$[m_g^3.s^{-1}.kg_{cat}^{-1}]$	1.43×10^{-06}
k _{hf3}	[S ⁻¹]	1.63 × 10 ⁻⁰³
k _{o4}	[kg _{cat} .mole ⁻¹ .s ⁻¹]	5.02 × 10 ⁺⁰³
k _{p4}	[kg _{cat} .mole ⁻¹ .s ⁻¹]	1.00×10^{-06}

In Table 3, the surface coverages of growing hydrocarbon chains are much lower than that of the C_1 precursors for chain growth. This indicates that reversible chain growth needs not be taken into account.

Table 3: Estimated surface covera	ges from Model E,	, for formation of C	CO, CO ₂ , CH	as well
as C ₂ and C ₃ hydrocarbons at 330 °	C, 6 bar, H₂/CO rat	tio = 10 and GHSV=	3600 ml _(n) .	g _{cat} -1.hr-1

Species	Dimensions	Estimated value
CO _{ads}	[mole.kg _{cat} ⁻¹]	1.99 × 10 ⁻⁰⁵
$C_{\alpha,ads}$	[mole.kg _{cat} ⁻¹]	2.87×10^{-02}
$C_{\beta,ads}$	[mole.kg _{cat} -1]	1.44×10^{-03}
C _{2α,ads}	[mole.kg _{cat} -1]	4.49×10^{-04}
C _{2β,ads}	[mole.kg _{cat} ⁻¹]	1.42×10^{-08}
C _{3α,ads}	[mole.kg _{cat} -1]	5.84×10^{-07}
C _{3β,ads}	[mole.kg _{cat} ⁻¹]	2.54 × 10 ⁻⁰⁹
CO _{WGS}	[mole.kg _{cat} -1]	7.35×10^{-05}
COO, _{ads}	[mole.kg _{cat} -1]	1.45×10^{-03}
COO,buff	[mole.kg _{cat} -1]	7.01×10^{-03}

The molar flows predicted by Model E and presented in Table 4 are quite close to those measured experimentally. The carbon balance based on the model data is 98.3% vs. the 101.0% based on experimental data. As indicated above, the reason for the carbon balance of the model not adding up to 100% is due to experimental errors in the values for the total molar flow rates. The molar flow rate of propane is considerably underestimated by the model but the molar flow rate of this stream is small and does not contribute much to the overall carbon balance, only 0.3%.

Table 4: Steady state molar flow rates from experimental data and Model E, for formation of CO, CO₂, CH₄ as well as C₂ and C₃ hydrocarbons at 330 °C, 6 bar, H₂/CO ratio = 10 and GHSV = $3600 \text{ ml}(n).g_{cat}$ ⁻¹.hr⁻¹

Component	Experimental value	Model prediction
	[moles.s ⁻¹]	[moles.s ⁻¹]
CO _{in}	3.35E-06	-
CO _{out}	2.50E-06	2.46×10^{-06}
CO2	3.12E-07	3.04×10^{-07}
CH4	4.92E-07	4.25×10^{-07}
C ₂ H ₄	1.13E-08	1.14×10^{-08}
C ₂ H ₆	8.35E-09	1.26×10^{-08}
C ₃ H ₆	1.25E-08	1.82×10^{-08}
C ₃ H ₈	1.70E-09	6.58×10^{-14}

In this chapter, the results of ¹³CO SSITKA as well as isotopic gradient experiments were used to qualitatively and quantitatively evaluate the carbon formation pathways for CH₄, C₂ and C₃ hydrocarbons at 330 °C, 6 bar, H₂/CO=10 and GHSV = 3600 ml_(n).g_{cat}⁻¹.h⁻¹. The mechanistic pathway (Model C) proposed by Govender as well as two new pathways (Model D and E) were evaluated against the high pressure SSITKA data of this thesis. In addition, CO₂ formation was incorporated into all three models to account for the reverse WGS reaction, which was active at these conditions.

Interpretation of the qualitative results of this work indicated that alkane and alkene formation occurs in part via separate mechanistic pathways. The formation of CH₄ and the higher alkanes follow from the same C₁ surface intermediates, while at least one of the intermediate species leading to alkene formation is different. Furthermore, chain growth was found to be very rapid compared to the formation of the chain initiation species and chain termination via β -hydride elimination was not found to be a major route for alkene formation. With regard to the reversible WGS reaction, no evidence for direct CO₂ hydrogenation could be found and it is proposed that carbon from CO₂ must first react to gas phase CO before it can be incorporated into CH₄ or any other hydrocarbon products of the FT synthesis.

Model discrimination and parameter estimation results validate the findings of the data interpretation and the mechanistic model which fit the data best was Model E. This model accounts for primary alkene formation via the combination of and adsorbed CO species and C₁ surface species (C_{β,ads}) while CH₄ as well as the primary alkanes are formed from the C_{α,ads} and C_{β,ads} surface species. In this model, further chain growth to C₃₊ hydrocarbons takes place via the addition of the C_{β,ads} species to both the C₂₊ alkene and alkane precursors while chain termination occurs via hydrogenation of the respective surface species. Note should be taken, that although the experimental and model results support the formation of a C_2 alkene precursor via a CO insertion step, the actual identity of this species was not confirmed and further experimental evidence is required to verify this species to be CO_{ads} .

Although Model E could account for all the experimental observations a statistically good fit where the weighted residual is smaller than the χ^2 value was not achieved. Although an effort was made to collect sufficient data for accurate estimation of the model parameters, some of the reaction rate constants from Table 2 could not be estimated precisely and resulted in large standard deviations for these parameters. For a statistically good fit of Model E and the precise estimation of reaction rate constants, further SSITKA data for the C₂ and C₃ hydrocarbons are required.

5.9 Appendices

5.9.1 Appendix 1

C₂ to C₄ data from GCMS

The fully ¹²C labelled C₄ transient is omitted from Figure 22 for clarity.



Figure 22 Normalized transient responses for (left) 1-butene and (right) n-butane. The figures are made up of the combined GCMS data from several SSITKA experiments
5.9.2 Appendix 2

Model equations for Model E, Figure 17

The subscript ss denotes steady state operation.

Gas phase

$$\frac{1}{\tau} \frac{\partial C_{\text{CO,ss}}}{\partial z} = \frac{\rho_{\text{b}}}{\varepsilon_{\text{b}}} \left(k_{\text{CO,des}} L_{\text{CO,ss}} - k_{\text{CO,ads}} C_{\text{CO,ss}} + k_{\text{rWGS1}} L_{\text{CO,WGS,ss}} - k_{\text{fWGS1}} C_{\text{CO,ss}} \right)$$
A.1

$$\frac{1}{\tau} \frac{\partial C_{co_2,ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{fwgs3} L_{coo,ss} - k_{rwgs3} C_{co_2,ss} \right)$$
A.2

$$\frac{1}{\tau} \frac{\partial C_{CH_4,ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp} L_{C\alpha,ss} + k_{tp1} L_{C\beta,ss} \right)$$
A.3

$$\frac{1}{\tau} \frac{\partial C_{c_2 H_4, ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{to2} L_{c_2 \alpha, ss} - k_{re2} C_{c_2 H_4, ss} \right)$$
A.4

$$\frac{1}{\tau} \frac{\partial C_{c_2 H_6, ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp2} L_{c_2 \beta, ss} \right)$$
A.5

$$\frac{1}{\tau} \frac{\partial C_{c_3 H_6, ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{to3} L_{c_3 \alpha, ss} - k_{re3} C_{c_3 H_6, ss} \right)$$
A.6

$$\frac{1}{\tau} \frac{\partial C_{C_3 H_8, ss}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp3} L_{C_3 \beta, ss} \right)$$
A.7

Surface

$$\frac{\partial L_{co,ss}}{\partial t} = 0 = k_{ads}C_{co,ss} - k_{des}L_{co,ss} - k_{co2}L_{co,ss} - k_{co1}L_{co,ss} - k_{inio}L_{co,ss}L_{c\beta,ss}$$
A.8

$$\frac{\partial L_{co_{wgs},ss}}{\partial t} = 0 = k_{rwgs1}C_{co,ss} - k_{fwgs1}L_{co_{wgs},ss} + k_{rwgs2}L_{coo,ss} - k_{fwgs2}L_{co_{wgs},ss}$$
A.9

$$\frac{\partial L_{coo,ss}}{\partial t} = 0 = k_{fWGS2} L_{co_{WGS},ss} - k_{rWGS2} L_{coo,ss} + k_{br} L_{coo_{buff},ss} - k_{bf} L_{coo,ss}$$

$$+ k_{rWGS3} C_{co_2,ss} - k_{fWGS3} L_{coo,ss}$$
A.10

$$\frac{\partial L_{coo_{buff},ss}}{\partial t} = 0 = k_{bf} L_{coo_{buff},ss} - k_{br} L_{coo_{buff},ss}$$
A.11

$$\frac{\partial L_{c\alpha,ss}}{\partial t} = 0 = k_{co2} L_{co,ss} - k_{tp} L_{c\alpha,ss} - k_{inip} L_{c\alpha,ss} L_{c\beta,ss}$$
A.12

$$\frac{\partial L_{c\beta,ss}}{\partial t} = 0 = k_{c01}L_{c0,ss} - k_{tp1}L_{c\beta,ss} - k_{inip}L_{c\beta,ss}L_{c\alpha,ss} - k_{inio}L_{c\beta,ss}L_{c0,ss} - k_{p3}L_{c\beta,ss}L_{c_{2}\beta,ss} - k_{o4}L_{c\beta,ss}L_{c_{3}\alpha,ss} - k_{c\beta,ss}L_{c\beta,ss}L_{c3}L_{c\beta,ss}L_{c3}L_{$$

$$\frac{\partial L_{c_{2}\alpha,ss}}{\partial t} = 0 = k_{inio}L_{CO,ss}L_{C\beta,ss} - k_{to2}L_{c_{2}\alpha,ss} - k_{hf2}L_{c_{2}\alpha,ss} - k_{o3}L_{C\beta,ss}L_{c_{2}\alpha,ss}$$
A.14

$$\frac{\partial L_{C_2\beta,ss}}{\partial t} = 0 = k_{inip}L_{C\alpha,ss}L_{C\beta,ss} + k_{hf2}L_{C_2\alpha} + k_{re2}C_{C_2H_4,ss} - k_{tp2}L_{C_2\beta,ss} - k_{p3}L_{C_2\beta,ss}L_{C\beta,ss}$$
A.15

$$\frac{\partial L_{C_{3}\alpha,ss}}{\partial t} = 0 = k_{o3}L_{c\beta,ss}L_{c_{2}\alpha,ss} - k_{to3}L_{C_{3}\alpha,ss} - k_{hf3}L_{C_{3}\alpha,ss} - k_{o4}L_{C_{3}\alpha,ss}L_{c\beta,ss}$$
A.16

$$\frac{\partial L_{C_{3}\beta,ss}}{\partial t} = 0 = k_{p3}L_{C\beta,ss}L_{C_{2}\beta,ss} + k_{hf3}L_{C_{3}\alpha} + k_{re3}C_{C_{3}H_{6},ss} - k_{tp3}L_{C_{3}\beta,ss} - k_{p4}L_{C_{3}\beta,ss}L_{C\beta,ss}$$
A.17

Model Equations for species containing ¹³C

The concentration of the fully ¹²C labelled species is calculated from the steady state concentration minus the sum of the labelled species concentrations. For surface species i, $L_i = \text{zero } {}^{13}\text{C}$, $L'_i = \text{one } {}^{13}\text{C}$, $L''_i = \text{two } {}^{13}\text{C}$ and $L'''_i = \text{three } {}^{13}\text{C}$ atoms respectively.

Gas phase

$$\frac{1}{\tau} \frac{\partial C_{\text{'CO}}}{\partial z} = \frac{\rho_{\text{b}}}{\varepsilon_{\text{b}}} \left(k_{\text{co,des}} L_{\text{'CO}} - k_{\text{co,ads}} C_{\text{'CO}} + k_{\text{rWGS1}} L_{\text{'CO,WGS}} - k_{\text{fWGS1}} C_{\text{'CO}} \right)$$
A.18

$$\frac{1}{\tau} \frac{\partial C_{,co_2}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{fwgs3} L_{,coo} - k_{rwgs3} C_{,co_2} \right)$$
A.19

$$\frac{1}{\tau} \frac{\partial C_{CH_4}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp} L_{C\alpha} + k_{tp1} L_{C\beta} \right)$$
A.20

$$\frac{1}{\tau} \frac{\partial C_{C_{2H_4}}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{to2} L_{C_2 \alpha} - k_{re2} C_{C_2 H_4} \right)$$
A.21

$$\frac{1}{\tau} \frac{\partial C_{c_2 H_6}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp2} L_{c_2 \beta} \right)$$
A.22

$$\frac{1}{\tau} \frac{\partial C_{C_{3}H_{6}}}{\partial z} = \frac{\rho_{b}}{\varepsilon_{b}} \left(k_{to3}L_{C_{3}\alpha} - k_{re3}C_{C_{3}H_{6}} \right)$$
A.23

$$\frac{1}{\tau} \frac{\partial C_{c_3 H_8}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp3} L_{c_3 \beta} \right)$$
A.24

$$\frac{1}{\tau} \frac{\partial C_{{}^{n}C_{2}H_{4}}}{\partial z} = \frac{\rho_{b}}{\varepsilon_{b}} \left(k_{to2} L_{{}^{n}C_{2}\alpha} - k_{re2} C_{{}^{n}C_{2}H_{4}} \right)$$
A.25

$$\frac{1}{\tau} \frac{\partial C_{c_2 H_6}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp2} L_{c_2 \beta} \right)$$
A.26

$$\frac{1}{\tau} \frac{\partial C_{{}^{"}C_{3}H_{6}}}{\partial z} = \frac{\rho_{b}}{\varepsilon_{b}} \left(k_{to3}L_{{}^{"}C_{3}\alpha} - k_{re3}C_{{}^{"}C_{3}H_{6}} \right)$$
A.27

$$\frac{1}{\tau} \frac{\partial C_{"c_3H_8}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{tp3} L_{"c_3\beta} \right)$$
A.28

$$\frac{1}{\tau} \frac{\partial C_{\text{```}_{C_3}H_6}}{\partial z} = \frac{\rho_b}{\varepsilon_b} \left(k_{\text{to}3} L_{\text{'``}_{C_3}\alpha} - k_{\text{re}3} C_{\text{'``}_{C_3}H_6} \right)$$
A.29

$$\frac{1}{\tau} \frac{\partial C_{\text{m}_{C_3H_8}}}{\partial z} = \frac{\rho_{\text{b}}}{\varepsilon_{\text{b}}} \left(k_{\text{tp3}} L_{\text{m}_{C_3\beta}} \right)$$
A.30

Surface

$$\frac{\partial L_{co}}{\partial t} = 0 = k_{ads}C_{co} - k_{des}L_{co} - k_{co2}L_{co} - k_{co1}L_{co} - k_{inio}L_{co}L_{c\beta,ss}$$
A.31

$$\frac{\partial L_{co_{wes}}}{\partial t} = 0 = k_{rwgs1}C_{co} - k_{fwgs1}L_{co_{wgs}} + k_{rwgs2}L_{coo} - k_{fwgs2}L_{co_{wgs}}$$
A.32

$$\frac{\partial L_{coo}}{\partial t} = 0 = k_{fwgs2}L_{cowgs} - k_{rwgs2}L_{coo} + k_{br}L_{coobuff} - k_{bf}L_{coo} + k_{rwgs3}C_{coo} - k_{fwgs3}L_{coo}$$
A.33

$$\frac{\partial L_{coo_{buff}}}{\partial t} = 0 = k_{bf} L_{coo} - k_{br} L_{coo_{buff}}$$
A.34

$$\frac{\partial L_{c\alpha}}{\partial t} = 0 = k_{c02}L_{c0} - k_{tp}L_{c\alpha} - k_{inip}L_{c\alpha}L_{c\beta,ss}$$
A.35

$$\frac{\partial L_{c\beta}}{\partial t} = 0 = k_{c01}L_{c0} - k_{tp1}L_{c\beta} - k_{inip}L_{c\beta}L_{c\alpha,ss} - k_{inio}L_{c\beta}L_{c0,ss} - k_{p3}L_{c\beta}L_{c_{2}\beta,ss}$$
A.36

$$-\mathsf{K}_{o_3}\mathsf{L}_{c_\beta}\mathsf{L}_{c_2\alpha,ss} - \mathsf{K}_{p_4}\mathsf{L}_{c_\beta}\mathsf{L}_{c_3\beta,ss}\mathsf{K}_{o_4}\mathsf{L}_{c_\beta}\mathsf{L}_{c_3\alpha,ss} - \mathsf{L}_{c_\beta} / \mathsf{L}_{c_{\beta,ss}}\mathsf{C}_{_{4}\,\mathsf{net}}$$

$$\frac{\partial L_{c_2\alpha}}{\partial t} = 0 = k_{inio}L_{co}L_{c\beta} + k_{inio}L_{co}L_{c\beta} - k_{to2}L_{c_2\alpha} - k_{hf2}L_{c_2} - k_{o3}L_{c_2\alpha}L_{c\beta,ss}$$

$$\frac{\partial L_{c_2\beta}}{\partial t} = 0 = k_{inip}L_{c\alpha}L_{c\beta} + k_{inip}L_{c\alpha}L_{c\beta} + k_{hf2}L_{c_2\alpha} + k_{re2}C_{c_2H_4} - k_{tp2}L_{c_2\beta}$$

$$-k_{p3}L_{c_2\beta}L_{c\beta,ss}$$
A.38

$$\frac{\partial L_{C_{3}\alpha}}{\partial t} = 0 = k_{03}L_{C_{\beta}}L_{C_{2}\alpha} + k_{03}L_{C_{\beta}}L_{C_{2}\alpha} - k_{t03}L_{C_{3}\alpha} - k_{hf3}L_{C_{3}\alpha} - k_{04}L_{C_{3}\alpha}L_{C_{\beta},ss}$$
A.39

$$\frac{\partial L_{c_{3}\beta}}{\partial t} = 0 = k_{p3}L_{c_{\beta}}L_{c_{2}\beta} + k_{p3}L_{c_{\beta}}L_{c_{2}\beta} + k_{hf3}L_{c_{3}\alpha} + k_{re3}C_{c_{3}H_{6}} - k_{tp3}L_{c_{3}\beta} - k_{tp3}L_{c_{3}\beta}$$

$$-k_{p4}L_{c_{3}\beta}L_{c_{\beta},ss}$$
A.40

$$\frac{\partial L_{"C_{2}\alpha}}{\partial t} = 0 = k_{inio}L_{'CO}L_{'C\beta} - k_{to2}L_{"C_{2}\alpha} - k_{hf2}L_{"C_{2}\alpha} - k_{o3}L_{"C_{2}\alpha}L_{C\beta,ss}$$
A.41

$$\frac{\partial L_{"C_{2}\beta}}{\partial t} = 0 = k_{inip}L_{'C_{\alpha}}L_{'C_{\beta}} + k_{hf_{2}}L_{"C_{2}\alpha} + k_{re2}C_{"C_{2}H_{4}} - k_{tp2}L_{"C_{2}\beta} - k_{p3}L_{"C_{2}\beta}L_{C_{\beta},ss}$$
A.42

$$\frac{\partial L_{"C_{3}\alpha}}{\partial t} = 0 = k_{o3}L_{'C\beta}L_{'C_{2}\alpha} + k_{o3}L_{C\beta}L_{"C_{2}\alpha} - k_{to3}L_{"C_{3}\alpha} - k_{hf3}L_{"C_{3}\alpha} - k_{o4}L_{"C_{3}\alpha}L_{C\beta,ss}$$
A.43

$$\frac{\partial L_{"C_{3}\beta}}{\partial t} = 0 = k_{p3}L_{'C_{2}\beta}L_{'C_{2}\beta} + k_{p3}L_{C\beta}L_{"C_{2}\beta} + k_{hf3}L_{"C_{3}\alpha} + k_{re3}C_{"C_{3}H_{5}} - k_{tp3}L_{"C_{3}\beta} - k_{tp3}L_{"C_{3}\beta}$$

$$-k_{p4}L_{"C_{3}\beta}L_{C\beta,ss}$$

$$\frac{\partial L_{\text{III}}_{C_{3}\alpha}}{\partial t} = 0 = k_{o3}L_{c\beta}L_{\text{II}}_{C_{2}\alpha} - k_{to3}L_{\text{III}}_{C_{3}\alpha} - k_{hf3}L_{\text{III}}_{C_{3}\alpha} - k_{o4}L_{\text{III}}_{C_{3}\alpha}L_{c\beta,ss}$$
A.45

$$\frac{\partial L_{\text{III}}_{C_{3}\beta}}{\partial t} = 0 = k_{p3}L_{C_{\beta}}L_{C_{2}\beta} + k_{hf3}L_{C_{3}\alpha} + k_{re3}C_{C_{3}H_{6}} - k_{tp3}L_{C_{3}\beta} - k_{p4}L_{C_{3}\beta}L_{C_{\beta},ss}$$
A.46

Chapter 6

Isotopic Experiments to Understand the Effect of Sulphur Promotion on Iron Fischer-Tropsch Catalysts

In this chapter steady state isotopic transient kinetic analysis (SSITKA) and isotopic kinetic analysis (ITKA) are carried out to investigate the promoter effect of sulphur when added to iron catalysts under high temperature Fischer-Tropsch conditions $(H_2/CO = 10, 330 \ ^{\circ}C, 6$ bar and GHSV = 3600 ml_(n).g_{cat}⁻¹.hr⁻¹). Steady State results indicate improved steady state C₂ to C₄ selectivity while maintaining low methane yields. The results of $^{12}CO/H_2$ to $^{13}CO/H_2$ and CO/H_2 to CO/D_2 switches point toward a decrease in the coverage of adsorbed carbon species and rate of chain growth upon sulphur addition to the catalyst.

6.1 Introduction

For large scale Fischer-Tropsch (FT) projects, such as the Secunda plant in South Africa, it is commercially viable to extract and separate out valuable products such as the C₂ to C₄ alkenes, which can be utilised in the chemical industry as building blocks for polymers, solvents, cosmetics and detergents ^[1]. To further increase selectivity towards valuable products, process parameters such as temperature, pressure and reactant feed ratios can be optimised since they have an effect on the carbon chain length and product type, see Chapter 1. In addition to changing process parameters, catalysts can be developed which are more selective toward the desired products.

For the high temperature Fischer-Tropsch (HTFT) process, sulphur is conventionally known to be a catalyst poison ^[2,3]. Recently however, at high temperature FT conditions, addition of low levels of sulphur has shown promising selectivity results towards the production of light hydrocarbons (C_2 to C_4) especially alkenes ^[4,5]. An interesting consequence of the shift towards the lighter product slate is that it occurs without the expected increase in methane selectivity. Based on the stepwise chain growth mechanism of the FTS, an increase in the light product selectivity corresponds to decrease in the chain growth probability; therefore methane selectivity is expected to increase but for the case of sulphur addition does not.

¹ Torres Galvis H.M., de Jong K.P., ACS Catal., Vol. 3 (9), (2013), 2130

² Steynberg A. P., Dry M.E., Eds., Stud. Surf. Sci. Catal. Vol. 152, Elsevier, Amsterdam, (2004)

³ Kritzinger J.A., Catalysis Today 71 (2002), 307

⁴ T.C. Bromfield, R. Crous, EP Patent No. 2193841, assigned to Sasol Technology PTY. Ltd. Filed Dec. 4, (2009)

⁵ Torres Galvis, H.M., Bitter, J.H., Khare, C.B., Ruitenbeek, M., Dugulan, A.L., de Jong, K.P., *Science*. **335** (2012), 835

The work of Govender^[6] over precipitated iron catalysts at HTFT conditions showed that the formation of methane and further chain growth can occur from two different carbon containing surface species or " carbon pools". The promoter effect resulting from sulphur addition could therefore be due to a blockage/modification of one of these sites. If this theory holds and the addition of "specific" promoters (promoters which poison specific catalyst sites) can be carefully controlled, a commercial iron based FT catalyst could be designed which is highly selective to short chain alkenes. To investigate this theory at a more fundamental level, steady state isotopic transient kinetic analysis (SSITKA) with ¹³CO and isotopic kinetic analysis (ITKA) with D₂ were carried out over two precipitated iron catalysts. The two catalysts differing in the respect that one was promoted with sulphur.

6.2 Comparison of Steady State Selectivity

Selectivity data were collected during steady state operation for both catalysts and compared at similar activity and time on line (TOL). Figure 1 shows the C₁ to C₅ hydrocarbon selectivity as a function of carbon number for the "standard" catalyst and the sulphur promoted catalyst. From these data, it is clear that sulphur promotion leads to a significant change in selectivity. The main effect of sulphur addition is an overall decrease in the chain growth probability (increase in the C₂ to C₄ fraction) and a lower than expected methane selectivity compared to that of the standard precipitated iron catalyst at the same reaction conditions.

Given ideal ASF kinetics ^[2] over typical iron FT catalysts, the measured methane selectivity is higher than expected while the C_2 content is lower than expected;

⁶ Govender N.S., PhD Thesis., Eindhoven University of Technology, (2010). Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/689931.pdf

these effects are clearly indicated in Figure 1 for the standard catalyst. Upon sulphur promotion, however, the methane selectivity drops to that predicted by the ideal ASF distribution with the C_2 content remaining lower than predicted. Another difference between the two catalysts is the amount of free carbon deposited, this was merely a visual observation but a clear difference in the spent catalysts is apparent. At the operating conditions required for high C₂ to C₄ olefin selectivity (high temperatures), there is typically a large amount of visible free carbon on the standard spent catalyst i.e. carbon deposition via the Boudouard reaction^[2].

For bulk iron catalysts such as the precipitated iron catalyst, the build-up of free carbon can lead to rupture of the particle and in severe cases widespread particle disintegration ^[5]. Another concern for both, supported and bulk iron catalysts at HTFT conditions when used in fluidised bed reactors is decreasing catalyst bed density coupled with bed expansion as a result of free carbon formation^[7]. The decrease in bed density leads to catalyst entrainment and bed expansion past the cooling coils makes it difficult to remove reaction heat. In the case of the sulphur promoted spent catalyst run at the same reaction conditions, there was no visible free carbon formation and the spent catalyst was pyrophoric when unloaded from the reactor. Sulphur promotion of iron catalysts for HTFT synthesis may therefore be beneficial for both high C_2 to C_4 selectivity and significantly decreased rate of free carbon formation.

Torres Galvis et al.^[5] measured similar selectivity shifts in methane and C₂ to C₄ hydrocarbons for a supported sulphur promoted iron catalyst and rationalised the effect by assuming the simplified "surface carbide" mechanism^[5]. In this case the promoter effect of sulphur is assumed to limit hydrogenation reactions so as to favour chain growth and termination steps via β -hydride abstraction.

⁷ Dry M.E., *Catalysis Letters* **7**, (1990), 241

Alternatively, the results could be explained by a mechanism where there is more than one site responsible for CH₄ formation ^[6, 8]. In this case, sulphur addition may modify or block a methanation site, limiting the methane formation to methane formed from FT sites, with a proportional and concurrent increase in the termination probability of the growing carbon chains due to increased hydrogen available on the catalyst surface.



Figure 1 Steady state, C_1 to C_5 hydrocarbon carbon atom selectivity [%] as a function of carbon number. The data was obtained at, inlet $H_2/CO = 10$, 330 °C, 6 bar and GHSV = 3600 $ml_{(n)}.g_{cat}^{-1}.h^{-1}$, $X_{CO+CO2} = 15\%$ and 22 % for the standard and sulphur promoted catalysts respectively

⁸ Schulz H., van Steen E., Claeys M., Stud. Surf. Sci. Catal. 81., (1994), 455

6.3 ¹³CO SSITKA

6.3.1 Experimental observations

The data presented in Figure 2 and Figure 3 show the transient data of Ne, 13 CO and 13 CH₄ following a 12 CO/H₂/Ar to 13 CO/H₂/Ne SSITKA switch. For clarity, the inverse 12 C labelled transients are omitted from the figures.

The following observations are made:

- The ¹³CO transients for both catalysts are delayed only slightly with respect to the Ne transient. This indicates a low surface coverage of adsorbed CO and is consistent with the results of Govender^[6] over precipitated iron catalysts under HTFT reaction conditions.
- The ¹³CO transient for the sulphur promoted catalyst elutes only marginally before that of the standard catalyst, suggesting that sulphur promotion leads to a negligible decrease in the already low coverage of adsorbed CO.
- The complete replacement of ¹²CH₄ by ¹³CH₄ occurs significantly faster for the sulphur promoted catalyst than for the standard precipitated catalyst (ca. 10 vs. 18 minutes). Given that the reaction conditions for both experiments were the same, it indicates that total surface coverage of C₁ species leading to methane formation is lower for the sulphur promoted catalyst as compared to the standard catalyst.
- The decay plots in Figure 3, show an upward convexity to both trends and confirm a complex mechanism for methane formation such as those proposed by van Dijk ^[9] and Govender ^[6] over cobalt and precipitated iron catalysts, respectively, with at least two carbon pools in parallel.

⁹ Van Dijk, H.A.J., PhD Thesis, (2001), Technische Universiteit Eindhoven, Eindhoven, The Netherlands, http://alexandria.tue.nl/extra2/200111083.pdf

Based on the observations for the ¹³CO SSITKA experiments, the decrease in the surface coverage of adsorbed CO and C_1 species following sulphur promotion of the catalyst are most likely due to an increased hydrogenation rate, particularly for the C_1 surface species leading to methane, as is shown in Figure 2 by the large decrease in the mean residence time for methane formation. A decrease in mean residence time is directly evident from the figure since the reaction conditions and CO conversion were similar for both experiments.

The hypothesis that sulphur promotion leads to an increased hydrogenation rate is further supported by the results of van Dijk ^[9], where an increasing H₂/CO feed ratio (increasing hydrogenation rate) led to a decreasing mean residence time for the C₁ species leading to methane. It must, however, be noted that even though the methane formation rate increases upon sulphur promotion, the total methane yield decreases. This is most likely due to the existence of more than one distinct methane precursor (as revealed by the shape of the decay plots) and the relative interaction of sulphur with these precursor sites.



Figure 2 (left) Normalised responses for Ne and ¹³CO over the standard and sulphur promoted catalyst, (right) Normalised response for ¹³CH₄ over the standard and sulphur promoted catalyst



Figure 3 Decay curves of the ¹²C content of CH₄ for the standard and sulphur promoted catalyst

In section 6.4.2, the results for the ¹³CO SSITKA experiments are fitted to methanation model 3.2 of Govender ^[6]. The resulting catalyst surface coverages and reaction rate constants are then compared to determine which elementary reaction steps are influenced by sulphur promotion.

6.4 Modelling the CO and CH₄ transients following a ¹³CO SSITKA switch

6.4.1 Model considerations

The methanation model 3.2 from the thesis of Govender was selected as the basis for the comparison of catalyst surface coverages and reaction rate constants for the sulphur promoted vs. the standard precipitated Fe catalysts. This was done in order to account for the formation of CO_2 but still limit the number of parameters that require fitting while at the same time, more accurately calculate the surface concentration of CO_{ads} . The formation of CO_2 was accounted for by lumping the elementary reaction steps for WGS into two reaction rate constants, $k_{f,WGS}$ and $k_{r,WGS}$ to represent the forward and reverse WGS reaction pathways respectively (see Figure 4). Furthermore, it was assumed that CO adsorption for the formation of CO₂ occurs on a different site as that for CO hydrogenation and that the adsorbed species from each site must first desorb to CO in the gas phase before it can re-adsorb on the opposing site. This follows from the results of Chapter 3 where the reversibility of CO dissociation becomes negligible in the presence of hydrogen i.e. during FT reaction conditions. The resulting model is therefore a simplification with respect to the formation of CO₂ and the isotopic transients for CO₂ are not fitted together with those for CO and CH₄.

To simplify the estimation of the reaction rate coefficients indicated in Figure 4, initial values for k_{ads} and k_{des} are calculated as described in Chapter 3. These values are based on the total surface concentration of carbon from Equation 3.2, Chapter 3. For both catalysts it was found that the consumption of CO to products relative to desorption of CO_{ads} was insignificant for values of k_{ads} greater than 0.15 $m_{g}^{3}.kg_{cat}^{-1}.s^{-1}$; therefore k_{ads} was fixed at this number. It must, however, be noted that the value for total carbon coverage is an estimate of the adsorbed CO, and as such the values for k_{des} were optimised in the final step of the parameter estimation process. The resulting values for reaction rate coefficients are given in Table 1.



Model 3.2.1

Figure 4 Schematic representation of the extended Model 3.2 of Govender ^[6] to account for the net formation of CO₂ via the WGS reaction

6.4.2 Modelling results

The parameter estimation was carried out using the constant variance model with a variance (experimental error) of 3% or less, depending on the experimental data set. The resulting values for the weighted residual were less than the χ^2 -value for both the standard and sulphur promoted catalysts, indicating a good fit of model 3.2.1 to the experimental data. The model predictions for ¹³CH₄ are given in Figure 5 and are based on the optimised parameters resulting from the parameter estimation method described above (see Table 1 and 2).

The following observations are made with regard to the modelling results given below:

Model 3.2.1 presented in Figure 4 and originally proposed by Govender ^[6] as a potential mechanistic pathway for methane formation over iron based catalysts, adequately describes the CH₄ transients for both catalysts in this study. This allows for a micro kinetic comparison to be made between the two catalysts.

- As previously indicated ^[6], at HTFT reaction conditions with iron catalysts, the surface concentration of CO_{ads} is less than the concentration of $C_{1, tot}$ ($C_{\alpha} + C_{\beta}$). This effect is clearly evident for the standard catalyst (CO_{ads} 10% of $C_{1, tot}$), but is not as significant for the sulphur promoted catalyst (CO_{ads} 62% of $C_{1, tot}$) Overall, the adsorbed CO and C_1 species only cover a minute fraction of the total Fe surface.
- Sulphur addition preferentially affects the surface concentration of the $C_{\alpha,ads}$ species decreasing it by approximately 8 times. The $C_{\beta,ads}$ species also decreases but only by ca. 3 times while the concentration of the CO_{ads} species remains relatively constant.
- Based on the parameter estimation results, the selectivity differences observed between the two catalysts appear to stem from i) a slightly slower rate for methane formation ca. 2 times slower (from both the $C_{\alpha,ads}$ and $C_{\beta,ads}$ species) and ii) an even slower rate of chain growth, from 6 to 40 times depending on the C₁ species involved ($C_{\alpha,ads}$ vs. $C_{\beta,ads}$). This allows for desorption of the surface species before addition of the next carbon species and hence a decrease in the chain growth probability.



Figure 5 Model results for the ¹³CH₄ transients of the standard and sulphur promoted precipitated Fe catalysts given model 3.2.1.

Table 1 Parameter estimates for the standard and sulphur promoted precipitated Fecatalysts given the methanation reaction according to model 3.2.1 in Figure 4

	Standard catalyst		sulphur promoted catalyst	
Rate coefficient	Parameter	standard	Parameter	standard
	estimate	deviation	estimate	deviation
\mathbf{k}_{ads} [m ³ g.kg _{cat} ⁻¹ .s ⁻¹]	1.50 × 10 ⁻⁰¹	_	1.50 × 10 ⁻⁰¹	_
k _{des} [S ⁻¹]	$6.40 \times 10^{+01}$	$1.41 \times 10^{+00}$	$7.75 \times 10^{+01}$	$1.21 \times 10^{+01}$
k co1 [S ⁻¹]	1.02 × 10 ⁻⁰¹	2.24 × 10 ⁻⁰³	1.64 × 10 ⁻⁰¹	1.21 × 10E ⁻⁰²
k _{CO2} [S ⁻¹]	4.36×10^{-02}	1.03×10^{-03}	2.51 × 10 ⁻⁰²	2.29×10^{-03}
k _{tp} [S ⁻¹]	5.02 × 10 ⁻⁰³	6.98 × 10 ⁻⁰⁵	1.76 × 10 ⁻⁰²	1.07×10^{-03}
k tp1 [S ⁻¹]	2.25 × 10 ⁻⁰¹	1.35 × 10 ⁻⁰²	3.44 × 10 ⁻⁰¹	5.05 × 10 ⁻⁰²
$\mathbf{k}_{f,wgs} \ [m^3g.kg_{cat}^{-1}.s^{-1}]$	$1.38 \times 10^{+00}$	5.40×10^{-04}	$1.38 \times 10^{+00}$	1.98×10^{-02}
$\mathbf{k}_{r,wgs} \ [m^{3}g.kg_{cat}^{-1}.s^{-1}]$	$7.57 \times 10^{+00}$	2.36 × 10 ⁻⁰²	$6.18 \times 10^{+00}$	8.68×10^{-02}
\mathbf{k}_{ini} [kg _{cat} ⁻¹ ·mole ⁻¹ .s ⁻¹]	3.03 × 10 ⁻⁰³	3.78 × 10 ⁻⁰³	4.81 × 10 ⁻⁰³	4.78×10^{-01}

Table 2: Surface coverage's calculated for the standard and sulphur promoted precipitatedFe catalysts given the methanation mechanism of Figure 4 and corresponding parameterestimates in Table 1

Species		Standard	Sulphur Promoted
		Catalyst	Catalyst
CO _{ads}	[mole.kg _{cat} -1]	3.31×10^{-03}	2.61×10^{-03}
$C_{\alpha,ads}$	[mole.kg _{cat} -1]	3.05E × 10 ⁻⁰²	3.73×10^{-03}
$C_{\beta,ads}$	[mole.kg _{cat} -1]	8.96 × 10 ⁻⁰⁴	2.71×10^{-04}
$C_{1, tot} (C_{\alpha, ads} + C_{\beta, ads})$	[mole.kg _{cat} -1]	3.14×10^{-02}	4.00×10^{-03}



Figure 6 (left) Standard catalyst and (right) sulphur promoted catalyst, surface coverage's (moles adsorbed species per gram catalyst) based on 1.54 moles of surface Fe per kg catalyst

6.5 H₂ / D₂ ITKA

To gain further insight into the selectivity changes resulting from sulphur promoter addition to the standard precipitated catalyst. Isotopic kinetic analysis (ITKA) was carried out, and the kinetic isotope effect (KIE) of hydrogen vs. deuterium was measured for CO and $C_{1,ads}$ hydrogenation over the standard and sulphur promoted catalysts at HTFT reaction conditions.

The KIE is defined as the ratio of the reaction rates when a molecule is replaced by its isotopic counterpart in a chemical reaction. The isotopic substitution can lead to a change in the reaction rate if the isotopic replacement occurs in a rate limiting step. KIEs are grouped into two types: primary isotope effects where the isotope replacement occurs in a chemical bond being formed or broken and secondary isotope effects where isotope replacement occurs at a site other than the site of the bond being formed or broken. Although there is no clear cut-off point between the primary and secondary KIEs, for the case of hydrogen, deuterium substitutions the primary KIE (for C-H bonds) can be quite large ($k_{\rm H}/k_{\rm D}$ > 2) whereas the secondary KIE is smaller, typically in the range of $k_{\rm H}/k_{\rm D} = 0.7 - 1.5$ ^[10]. Secondary KIE's result from the tightening or loosening of a C-H bond, the effect is typically due to a change in orbital hybridisation for example, a change from a sp^3 to a sp^2 carbon (resulting in a normal KIE, $k_H/k_D > 1$) or sp^2 to a sp^3 carbon(resulting in an inverse KIE, $k_{\rm H}/k_{\rm D}$ < 1) ^[10]. The magnitude of the KIE resulting from hydrogen deuterium isotope switches can therefore be used to reveal details of the reaction mechanism.

With previous studies using Fe and Co catalysts in the FT synthesis, it has been shown that the observed KIE could result from a combination of kinetic and

¹⁰ Carey A. C., Sundberg R. J., Adv. Org. Chem., Fifth Ed., Springer Science and Business media, LLC, 2007, Part A

thermodynamic effects ^[11,12,13]. For example, assuming that the stepwise hydrogenation of C_{ads} to CH_{ads}, CH_{2,ads} and CH_{3,ads} are kinetically relevant steps in the FTS and that the adsorption of H₂, (D₂) and CO are in equilibrium. The rate of hydrogenation (r_H) will depend on the rate constant for hydrogenation (k_H) and the surface coverage's of hydrogen and CO (θ_{H} , θ_{CO}) where the surface coverages are a function of their adsorption equilibrium constants K_{H2} and K_{CO}. For the case where the formation of the CH_{x,ads} species from CH_{x-1,ads} (x = 1, 2 or 3) is the kinetically relevant step, and assuming that the coverage of intermediates is small with hydrogen less than that of the carbon containing intermediates, the overall KIE is represented by:

$$\frac{\mathbf{r}_{\mathrm{H}}}{\mathbf{r}_{\mathrm{D}}} = \frac{\mathbf{k}_{\mathrm{H}}}{\mathbf{k}_{\mathrm{D}}} \mathbf{\bullet} \left[\frac{\mathbf{K}_{\mathrm{H2}}}{\mathbf{K}_{\mathrm{D2}}} \right]^{\mathrm{V}} \tag{6.1}$$

Where y = 0.5, 1 and 1.5 for CH_{x-1,ads} to CH_{x,ads} when x = 1, 2 and 3 respectively.

6.5.1 Role of H₂ in CO consumption

Kinetic isotope effects have proved a useful tool in determining whether or not hydrogen plays a role in CO dissociation pathways for FT synthesis ^[11]. Figure 7 shows the KIE as a function of CO hydrogenation rate (moles CO converted to FT products) and the CO₂ formation rate. The following observations are made:

• CO hydrogenation rates were higher with D₂/CO than with H₂/CO. An I(inverse) KIE ($r_H/r_D < 1$) is observed for hydrocarbon formation from CO and the KIE is greater for the sulphur promoted catalyst compared to the standard catalyst.

¹¹ Ojeda M., Li A., Nabar R., Nilekar A.U., Mavrikakis M., Iglesia E., J. Phys. Chem. C, 114, 2010, 19761

¹² Wilson T.P., J. Catal. 60 (1979), 167

¹³ Raje A., Davis B. H., in Spivey J. J., Ed., Catal. Vol. 12., Royal Soc. of Chemistry, Cambridge, (1996), Chapter 3

The CO₂ formation rate was lower with D₂/CO than with H₂/CO. A KIE ((r_H/r_D > 1) is observed for CO₂ formation and the KIE is greater for the standard catalyst compared to the sulphur promoted catalyst.

The IKIE observed for CO hydrogenation over both catalysts indicates that the overall KIE may be dominated by thermodynamic effects leading to preferential chemisorption of D₂ and a higher surface coverage of adsorbed D vs. H. The IKIE observed for CO hydrogenation is therefore thought to arise from a dominant thermodynamic isotope effect, opposite in magnitude to the kinetic isotope effect. Following from this, the lower CO₂ formation rate (r_H/r_D) would be expected for HTFT reaction conditions where the parallel water-gas shift reaction also operates and H₂ and CO₂ are products.



Figure 7 Kinetic isotope effect for CO hydrogenation and CO₂ formation over the standard and sulphur promoted catalysts.

6.5.2 H₂/D₂ effects on product formation rates

Figure 8 shows the ratio of hydrocarbon product formation rates as a function of carbon number when hydrogen vs. deuterium is used as feed to the reactor. The following observations can be made:

- An IKIE (r_H/r_D < 1) is measured for the formation of hydrocarbon products over both catalysts. Only ethane formation over the sulphur promoted catalyst resulted in a KIE of approximately 1. These results are most likely due a combination of secondary KIEs and equilibrium effects.
- For the standard catalyst the IKIE increases with increasing carbon number and is larger for the paraffin vs. the olefin of the same carbon number.
- For the sulphur promoted catalyst the IKIE increases with increasing carbon number for the alkanes and alkenes respectively, but the IKIE for paraffin formation is smaller than that for olefin formation of the same carbon number (opposite to that observed for the standard catalyst).
- For the same species, the IKIE is greater over the standard catalyst compared to the sulphur promoted catalyst.

Although it is challenging to elucidate mechanistic information for the individual components based on their IKIEs, i.e. due to the combination of kinetic and equilibrium effects taking place, the difference of IKIE between the alkenes and alkanes of the same carbon number over the same catalyst could indicate differences in chain initiation, chain desorption or both. Assuming that the IKIE leads to a higher surface coverage of adsorbed D vs. H the rate of chain initiation may differ as a result of additional hydrogenation steps of the surface carbon species i.e. CH_{2,ads} to a CH_{3,ads} before carbon-carbon coupling takes place. For chain desorption the IKIE could be due to an increase in hydrogen addition to form alkanes or a decrease in the probability of hydrogen elimination to form alkenes.

Furthermore, the systematic variation with carbon number of the IKIE for the alkenes and alkanes, respectively; indicates that chain propagation involves a variation in C-H bond strength resulting from orbital hybridisation of the monomer during its addition to a growing carbon chain on the catalyst surface.

The decrease in the IKIE for the paraffin vs. olefin formation over the sulphur promoted catalyst and the overall decrease in the IKIE for the hydrocarbon species over the sulphur promoted catalyst compared to the standard catalyst may be due to a decrease in the contribution of the equilibrium effect to the overall observed KIE. This result may be rationalised from an decrease in the adsorption constant for hydrogen over the sulphur promoted catalyst and may not necessarily indicate differences in the reaction mechanisms resulting from sulphur promoter addition.



Figure 8 Kinetic isotope effect as a function of carbon number and product type for the standard and sulphur promoted catalysts.

6.6 Conclusions

Sulphur promotion of precipitated iron catalysts in the HTFT synthesis leads to improved steady state C_2 to C_4 selectivity while maintaining low methane yields and an observed decrease in free carbon formation. The results of ¹³CO SSITKA and H_2/D_2 KIE experiments provided further fundamental insight and indicate that sulphur promotion preferentially decreases the coverage of the adsorbed C_{α} species and the rate of chain growth.

The transient and decay plots for the ¹³CO SSITKA experiments together with the good fit of the ¹³CO transient data to the methanation model of Govender ^[6], indicates that more than one carbon pool is responsible for methane formation and that sulphur promoter addition does not necessarily lead to variations of the reaction mechanism.

The application of specifically formulated sulphur promoted precipitated iron catalysts for the HTFT synthesis is a commercially viable option for selective production of C_2 to C_4 hydrocarbons while maintaining a low methane selectivity and a low free carbon formation rate in both, commercial fixed bed and fluidised bed reactors^[4,5].

Chapter 7

Conclusions and Outlook

7.1 Conclusions

The high temperature (300-350 °C) Fischer-Tropsch (HTFT) synthesis utilises ironbased catalysts for the direct production of gasoline and light (low molecular mass) alkenes from synthesis gas. The mechanism of the HTFT synthesis is highly complex with the likely existence of more than one rate limiting step. The occurrence of the reverse WGS reaction in parallel to that of the FT reaction and the presence of multiple dynamic catalyst phases (iron carbide and iron oxide) during synthesis, complicate the data interpretation and hamper efforts for detailed mechanistic understanding. Since most of the FT reaction steps occur via a series of reaction intermediates on the catalyst surface, an isotopic tracer technique such as SSITKA is well suited to provide information regarding the elementary reaction steps.

In this thesis, isotopic tracer studies such as SSITKA were extensively applied to investigate the elementary reaction steps of the HTFT synthesis occurring in-situ under well defined, steady state and commercially relevant operating conditions (H_2 / CO = 10, 330 °C, 6 bar and GHSV = 3600 ml_(n).g_{cat}⁻¹.hr⁻¹). To achieve this, a setup

capable of isotopic experiments at elevated pressures was designed and purpose built. Furthermore, the absence of internal or external temperature and mass gradients were confirmed for this system.

Role of lattice oxygen

In Chapter 3, the role of oxygen surface species was investigated by SSITKA, using both ¹³C and ¹⁸O labelled CO. The results showed that under commercial reaction conditions i.e. with hydrogen present, the reverse rate of CO dissociation is negligible. In addition, the formation of CO₂ and, most likely, H₂O occur to some extent via a Mars - van Krevelen (MvK) type of mechanism where CO₂ is formed via the oxidation of CO and not via the stepwise addition of oxygen to carbon (see Figure 1). Modelling the addition of lattice oxygen to adsorbed CO to describing the oxygen pathway for CO₂ formation (an MvK type mechanism) resulted in a good fit to experimental data and the precise estimation of the lattice oxygen diffusion coefficient, D = (8.64 ± 0.56) 10⁻¹⁴ m².s⁻¹.



Figure 1 Mars - van Krevelen Mechanism for CO₂ formation via CO oxidation with lattice oxygen during high temperature Fischer-Tropsch synthesis

Oxygenate reaction pathways

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In Chapter 4, the results of ¹³CO and C¹⁸O isotopic switches in conjunction with ¹²C, ¹⁶O oxygenate co-feeding allowed for a detailed investigation of the oxygenate reaction pathways. The results indicated that the carbon skeleton of both alcohols and aldehydes of the same carbon number are formed via the same chain growth route. Oxygen addition to these species, however, differs and it is the step following the termination of chain growth which determines the type of oxygenate species that is formed. Following from this, the interconversion of alcohols and aldehydes of the same carbon number were shown to occur readily and in addition to loss or gain of hydrogen atoms C-O bond cleavage was observed to occur i.e. exchange of the oxygen atom during oxidation or reduction reactions. Figure 2 illustrates the proposed reaction pathway describing the interaction of alcohols and aldehydes via adsorbed alkoxide (18) and carboxylate (19) species. Based on the findings from Chapter 3 and the contrasting isotopic oxygen compositions of the alcohols and aldehydes of the same carbon number. The results further suggest the oxygen exchange between the alcohol and aldehyde occur largely via a Mars - van Krevelen type of mechanism where O_{α} and O_{β} of Figure 2 represent surface oxygen and lattice oxygen respectively.





oxygen exchange via a Mars - van Krevelen type of mechanism

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The use of isotopic tracing together with the oxygenate co-feeding experiments in this thesis allowed for validation of some of the oxygenate interactions proposed in literature ^[1,2]; the results are illustrated in Figure 3. The interaction of 1-alcohols and aldehydes of the same carbon number was confirmed and a novel set of intermediate steps where the oxygenate species is attached to the surface by an oxygen is proposed (Figure 2) in place of the acyl intermediate suggested by Cairns ^[2]. Both Weitkamp and Cairns observed the interaction of carboxylic acid with the alcohol and aldehyde of the same carbon number. This was not observed in this work and may have been due to decarboxylation of the acid to methyl ketones at the reaction conditions used. The formation of n+1 methyl-ketones from aldehydes / 1-alcohols and the interaction of the methyl-ketone with a 2-alcohol of the same carbon number was confirmed by isotopic labelling.



Figure 3 Summary of oxygenate interactions

Based on the work of Cairns ^[2], together with the reaction conditions and the type of catalyst used for this work, the formation of hydrocarbons from co-fed oxygenates was not expected. The results of the more sensitive isotopic tracer experiments did however indicate that co-fed ethanol, 1-propanol and 2-butanone did to some extent take part in secondary reactions such as hydrogenolysis or decarboxylation forming minor fractions of hydrocarbons, particularly n-alkanes as

¹ Weitkamp A.W. and Bowman N. J., Ind. Eng. Chem., Vol. 45, No. 2, (1953), 359

² Cairns P., PhD Thesis., University of Cape Town, (2008), Cape Town, South Africa

previously indicated from the work at atmospheric pressure. Importantly, the extent of oxygenate secondary reactions which form hydrocarbons seem to be highly dependent on the total pressure, this effect decreasing significantly at elevated pressures. The secondary formation of hydrocarbons from oxygenates are thus proposed to be insignificant at commercially relevant operating conditions.

Hydrocarbon formation pathways

The results of Chapter 5 indicate that at commercially relevant reaction conditions, alkane and alkene formation occur in part via separate mechanistic pathways. The formation of CH_4 and the higher alkanes follow from the same C_1 surface intermediates, while at least one of the intermediate species leading to alkene formation is different. Figure 4, represents the proposed mechanism based on the carbon pathways of Model E (see Figure 17 of Chapter 5). In this mechanism, alkene formation is initiated by the reaction of adsorbed CO and CH₂ species to form an adsorbed CHCH₂ intermediate which may be hydrogenated to primary ethene or continue to take part in chain growth. Chain growth takes place via stepwise addition of CH₂ surface species followed by double bond isomerisation similar to that proposed by Maitlis ^[3] for the alkenyl mechanism. The adsorbed alkene precursor may also be hydrogenated to the alkane precursor, CH_2CH_3 . Alkane formation is initiated from the reaction of an adsorbed CH₂ and CH₃ species forming an adsorbed CH_2CH_3 intermediate, ethane is formed from via hydrogenation of this species which is consistent with the alkyl mechanism ^[4]. Further chain growth of the alkane precursor occurs via stepwise CH₂ insertion. The findings from Chapter 5 demonstrate the importance including the C_3 hydrocarbons in the reaction pathway to fully understand chain growth.

³ Maitlis P.M., Quyoum R., Long H.C., Turner M.L., Appl. Catal. A., Vol 186., (1999) 363

⁴ Fischer F., Tropsch H., Brennstoff-Chem., Vol. 7. (1926), 97

With regard to the reversible WGS reaction, no evidence for direct CO_2 hydrogenation could be found and it is proposed that carbon from CO_2 must first react to gas phase CO before it can be incorporated into CH_4 or any other hydrocarbon products of the FT synthesis.

Monomer formation:



C₂ hydrocarbon formation (C-C coupling):



C₃ hydrocarbon formation (chain growth):



Figure 4 Proposed reaction mechanism for hydrocarbon formation in the High Temperature Fischer-Tropsch synthesis

Influence of promoter addition

In chapter 6, the use of isotopic techniques such as ¹³CO SSITKA and H_2/D_2 ITKA are shown valuable tools in understanding promoter effects. For the case of sulphur promotion it was shown that sulphur addition preferentially decreases the coverage of the adsorbed C_{α} species and hence the rate of chain growth. The qualitative and quantitative results indicate that more than one carbon pool is responsible for methane formation and that sulphur promoter addition does not necessarily lead to variations of the reaction mechanism.

7.2 Outlook

This thesis covers a broad spectrum of the reaction pathways which occur in the HTFT synthesis. Qualitative results of the isotopic experiments at elevated pressures provided valuable new insights for various reaction pathways while quantitative analysis of the SSITKA transients allowed for discrimination between these pathways.

For the HTFT synthesis, the occurrence of a Mars – van Krevelen type of mechanism using lattice oxygen and the interconversion of alcohols and aldehydes of the same carbon number via exchange of the oxygen atom are novel. Further experiments at different reaction conditions (reducing vs. oxidising) and over different FT catalysts such as Co which do not consist of a significant fraction of oxides will assist in further understanding of this phenomenon. Importantly this work should be carried out at elevated pressures so as to account for increased surface coverages of monomer species.

The quantitative investigation of the oxygen reaction pathways in the HTFT synthesis is a highly complex task and would merit a separate study. As such, the kinetic analysis of these pathways was not attempted in this thesis. Detailed modelling of the combined oxygenate, hydrocarbon and WGS pathways would, however, assist in understanding the relationship between the intermediates of these species and how they interact.

The extension of hydrocarbon chain growth models to include the C₄+ products may provide further information on the formation of branched products, dienes etc. This will however require considerably detailed workup for the isotopic compositions of the products following SSITKA together with a significant modelling effort and, again, merit a separate study.

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List of Publications

Oral presentations

- J.V. Fletcher, R van der Westhuizen, M.J. van Vuuren, and E. van Steen. (November 2006). *Effect of Temperature on Fischer-Tropsch Selectivity*. Oral presented at the annual meeting of the Catalysis Society of South Africa (CATSA). Mossel Bay.
- J.V. Fletcher, N.S. Govender, M.H.J.M de Croon and J.C. Schouten. (March 2012). *Reactivity of CO₂ in the High Temperature Fischer-Tropsch synthesis*. Oral presented at the Netherlands Catalysis and Chemistry Conference (N3C). Noordwijkerhout, the Netherlands.
- N.S. Govender, J.V. Fletcher, M.H.J.M de Croon and J.C. Schouten. (November 2012). *Modelling the C2+ hydrocarbons during the Fischer-Tropsch synthesis using transient kinetics*. Oral presented at the annual meeting of the Catalysis Society of South Africa (CATSA). Langebaan, South Africa.
- J.V. Fletcher, L.J.P. Masthoff, N.S. Govender, M.H.J.M de Croon, J.C. Schouten. (June 2012). *Reactivity of surface and bulk oxygen originating from CO dissociation in the Fe catalysed high temperature Fischer-Tropsch synthesis.* Oral presented at the SynFuel Symposium. Munich, Germany.
- J.V. Fletcher, N.S. Govender, M.H.J.M de Croon and J.C. Schouten. (June 2012). Mechanistic study of hydrocarbon chain growth in the Fe-catalysed Fischer-Tropsch synthesis. Oral presented at the International Congress on Catalysis (ICC). Munich, Germany.
- J.V. Fletcher, N.S. Govender, M.H.J.M de Croon and J.C. Schouten. (June 2013). Isotopic labelling experiments to understand the promoter effects upon sulphur addition to iron catalysts in the high temperature Fischer-Tropsch synthesis. Oral presented at the North American Catalaysis Society Meeting. Louisville, Kentucky.
Poster presentations

 J.V. Fletcher, J. Riegman, N.S. Govender, M.H.J.M de Croon and J.C. Schouten. (October 2010). H₂/CO₂ as Synthesis Gas in the High Temperature Fischer-Tropsch Synthesis. Poster presented at the Netherlands Process Technology Symposium (NPS), Veldhoven, the Netherlands

About the author

Jack Vincent Fletcher was born in Pretoria, South Africa on 2 May 1980 and graduated from Lyttelton Manor High School in Centurion, Gauteng in 1998. In January 1999 he registered for a course in Chemical Engineering Technology at the Tshwane University of Technology. He completed the bachelor's degree at the end of 2002 with full bursary from Sasol Technology R&D for his final year of study. During this period he also worked at the University of Cape Town (UCT), Department of Chemical Engineering, Catalysis Group from January 2001 to December 2001.

In January 2003 he Joined Sasol Technology R&D working full time in the Fischer-Tropsch Catalyst Development group. In 2004 while still working full time at Sasol he registered for a bridging course (additional undergraduate course-work) and taught master's program in Chemical Engineering and Catalysis at the University of Cape Town. In December 2007 Jack was seconded by Sasol to join the process development team in Enschede, the Netherlands. During this time he obtained his MSc degree in applied science from the Department of Chemical Engineering, UCT under the supervision of Professor Eric van Steen with a thesis entitled "Effect of reaction temperature on the formation of olefins in the Fischer-Tropsch synthesis". After approximately one and a half years in Enschede, Jack moved to 's-Hertogenbosch and started his PhD project in April 2009 in the group of Professor Jaap Schouten at the Eindhoven University of Technology (TU/e). After three years at TU/e Jack returned to Sasol Technology R&D in Sasolburg, South Africa where he continued the writeup of this thesis, the results of which are presented here.

Since February 2015, Jack is working as a Postdoctoral Research Fellow at Hydrogen South Africa (HySA)/Catalysis, co-hosted by the University of Cape Town where he is directly involved in the development of hydrogen fuel processor systems.