

The Fischer-Tropsch synthesis : a mechanistic study using transient isotopic tracing

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The Fischer-Tropsch synthesis: A mechanistic study using transient isotopic tracing

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr. M. Rem, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op donderdag 22 maart 2001 om 16.00 uur

door

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Summary

It is expected that in the near future the feedstock for the chemical industry will shift from crude oil to natural gas due to the limited reserves of crude oil and the increasing environmental constraints. To enable its chemical conversion, natural gas is first transformed into synthesis gas, which is a mixture of carbon monoxide and hydrogen. This synthesis gas is the basis for a number of large-scale industrial processes. When maximizing the hydrogen content of the synthesis gas, it is mainly used as a feedstock for the production of ammonia. Moreover, the application of hydrogen for the production of electricity in fuel cells is of growing interest. In the gas-to-liquid technology, synthesis gas is converted into high-value liquids such as methanol, dimethylether (DME), and synthetic crude oil. The latter process is known as the Fischer-Tropsch synthesis process and is a promising route for the chemical liquefaction of natural gas. As such, it allows the economic exploitation of remote natural gas resources and constitutes an alternative route for the production of clean transportation fuels and petrochemical feedstock in relation to the classic refining of crude oil.

Aim of the study

Although the Fischer-Tropsch synthesis has a lively history of more than 70 years, the reaction mechanism is still not fully understood. The CO-insertion mechanism, the carbene mechanism, and the hydroxycarbene mechanism are proposed in literature, of which the carbene mechanism is most often referred to as the probable Fischer-Tropsch mechanism [Hinderman *et al.*, 1993]. In this mechanism, chain growth proceeds via the insertion of a $CH_{2,ads}$ species. This monomeric building block is formed via the hydrogenation of surface carbon following the dissociation of CO_{ads} . Within this mechanism there is no clear understanding of the quantity, reactivity, and chemical identity of the participating surface species. This thesis aims at a better understanding of the polymerization-like reaction mechanism of the Fischer-Tropsch synthesis by means of a transient kinetic investigation.

Understanding the reaction mechanism is essential for the design and optimization of industrial catalysts. The kinetic study has been performed on cobalt based catalysts using the **S**teady **S**tate Isotopic Transient Kinetic Analysis (SSITKA) technique. This technique is based on the abrupt replacement of one reactant by its isotopic labeled counterpart. The transient responses, representing the incorporation of this isotopic label into the reaction products in time, contain kinetic information. In comparison to steady state kinetic methods, transient techniques have a higher potential of revealing mechanistic aspects of complex reactions. In this respect, the SSITKA technique holds a special position among transient kinetic techniques, since it allows to study these mechanistic aspects at the most realistic working conditions of the catalyst, *i.e.* at steady state conditions.

Other research groups have already described the background and methodology of the SSITKA technique and of the product analyses methods that are also applied in this study [Happel, 1978; Bennett, 1982; Biloen *et al.*, 1983]. In relation to literature, however, the present study exploits the full potentials of the SSITKA technique. This is done in the first place by using a large variety of experimental conditions, *i.e.* comparing C-, O-, and H-labeling on different catalyst formulations. Secondly, a substantial part of the product spectrum is included in the isotopic transient analysis. Thirdly, following a preliminary qualitative interpretation of the experimental results, extensive mathematical modeling is applied for the identification and discrimination of the Fischer-Tropsch reaction mechanism.

The Fischer-Tropsch catalysts

The common Fischer-Tropsch catalysts are based on iron (Fe), ruthenium (Ru), or cobalt (Co) as the active metal. The costs for Fe-based catalysts are low, but these catalysts suffer from a low wax selectivity, deactivation, and inhibition of the productivity by water at large syngas conversions. Despite the high activity of Ru-based catalysts, their utilization is limited to scientific studies because of the high price of ruthenium. However, Co-based catalysts are stable and allow high syngas conversions, promoting the formation of heavy wax. In this study, a kinetic investigation of the Fischer-Tropsch reaction over a Co(12wt%)/Ru(0.18wt%)/TiO₂ catalyst, a Co(12wt%)/TiO₂ catalyst, and a full metal Co-sponge catalyst at 498 K and 1.2 bar is presented. The experiments are performed at intrinsic kinetic conditions in a fixed bed reactor, at differential synthesis gas conversions. The H₂/CO feed ratio is varied between 1 and 5. In all experiments the Fischer-Tropsch reaction is operated at dry conditions, where wax formation is suppressed. All products leave the reactor via the gas phase.

Low pressure versus high pressure operation

The steady state C_1 to C_9 product distribution at low pressure, as used in this study, is different from that at high pressure, as used at industrial conditions (25 bar). This results from the absence of a wax layer on the catalyst surface at low pressure. The most important secondary reaction is chain initiation by readsorbed 1-olefins. In literature it is suggested that other secondary reactions such as isomerization and double bond shift are sterically hindered In the presence of a wax layer [Schulz *et al.*, 1998]. However, in the absence of a wax layer these two reactions become important. The observed decreasing olefin to paraffin ratio with chain length indicates the carbon number dependence of the readsorption of the 1-olefins. It illustrates the presence of a physisorbed state of the hydrocarbon reaction products even at experimental conditions where the build-up of a wax layer on the catalyst surface is negligible.

The kinetic parameters obtained by regression analysis of the experimental results at 498 K and 1.2 bar are applied to simulate the product spectrum at industrial reaction conditions. At high pressure, wax formation occurs and the liquid hydrocarbon layer hinders chain branching and bond-shift reactions, thereby enhancing the formation of 1-olefins. This leads to an increased readsorption and subsequent chain initiation by 1-olefins, which results in the increased selectivity of heavy hydrocarbons at industrial conditions. These effects are successfully simulated assuming the parameters obtained at 1.2 bar to be chain-length independent starting at C_3 .

Kinetic modeling

Transients for the C_1 to C_5 hydrocarbons and the C_1 to C_3 alcohols are obtained by massspectrometry and gas-chromatography-mass-spectrometry following C-, H-, and O-labeling of the reactants CO and H₂. At first these results are interpreted qualitatively. Whereas qualitative interpretation of the experimental results is often limited to the identification of global mechanistic phenomena (*e.g.* surface heterogeneity for hydrocarbon formation), kinetic modeling is a more powerful tool for the identification of the chemical reaction network that can describe the experimental results. Because of the presence of reversible reactions for the reactants and products, the experimental results are modeled using a plug-flow reactor model. In the modeling, decoupling the methanation reaction and the formation of the higher hydrocarbons facilitates the model identification and discrimination.

Experimental observations and modeling results

CO adsorbs fast and reversible and its surface concentration does not change with H_2/CO feed ratio. The formation of methane is slow due to a hindered CO dissociation and a slow formation of chain initiators and monomeric building blocks. The dissociation of CO results in elementary carbon and its subsequent hydrogenation to methane probably proceeds via reversible steps. The catalyst surface is mainly covered by CO and methane intermediates, accounting for a global coverage of 90%. The catalyst surface is heterogeneous, caused by the presence of two distinct single-C species,

denoted $C_{\alpha,ads}$ and $C_{\beta,ads}$. Based on the methanation reaction alone, four indistinguishable models are presented. Although the inclusion of the formation of higher hydrocarbons results in an increase of the number of potential models, a model discrimination study indicates that only two indistinguishable models describe the experimental results. These two models share the common feature that both $C_{\alpha,ads}$ and $C_{\beta,ads}$ participate in the formation of methane and higher hydrocarbons. The number of active sites for the Fischer-Tropsch reaction increases upon Ru promotion, while the intrinsic activity of the sites is not influenced.

The formation of hydrocarbons proceeds via O-free surface species. Moreover, both single-C species, $C_{\alpha,ads}$ and $C_{\beta,ads}$, probably contain H. The surface heterogeneity, therefore, results from the presence of different surface sites for $C_{\alpha,ads}$ and $C_{\beta,ads}$ rather than from differences in chemical composition. Despite the slow formation of chain initiators and monomeric building blocks, the successive C-C coupling reaction is fast once a growing hydrocarbon chain is initiated on the catalyst surface. This results in a low surface concentration of growing hydrocarbon chains of typically 1.4%. The active surface site containing a growing hydrocarbon chain is believed to be a surface defect [Beitel *et al.*, 1997].



Schematic representation of the Fischer-Tropsch mechanism based on the transient isotopic tracing study presented in this study. The main features of the mechanism are:

- surface heterogeneity on the level of the single C-species;
- the presence of a physisorbed state;
- the possibility for 1-olefins to reenter the chain growth process by readsorption from the physisorbed state:
- alcohol formation via a CO-insertion termination reaction.

Readsorption of 1-olefins on the catalyst surface is evidenced, whereas the readsorption of internal- and iso-olefins is not significant. Although the concentrations of the C₁ to C₁₀ hydrocarbons in the physisorbed state are several orders of magnitude smaller than in the chemisorbed state, their influence on the chain length dependence of the readsorption process is marked. At higher operating pressure the capacity of the physisorbed state increases, making the SSITKA technique useless at industrial conditions. As expected, termination to paraffin proceeds via the hydrogenation of a growing hydrocarbon chain. The termination to olefin, however, proceeds via a desorption step rather than via a β -hydride elimination reaction. The chemical identity of the growing hydrocarbon chain is, therefore, associated with a C_xH_{2x,ads} species rather than a C_xH_{2x+1,ads} species. Going from C₃ to C₅, a shift in the preferential termination rate from olefin to paraffin is observed, which is not noted in literature during the operation of the Fischer-Tropsch reaction at higher pressure. This shift is caused by the occurrence of chain branching and bond-shift reactions of readsorbed 1-olefins.

Alcohol formation

The formation of alcohols is considered to be a termination step and proceeds via a COinsertion mechanism. The coupling of a growing hydrocarbon chain with CO_{ads} is two orders of magnitude slower than with a monomeric building block. Consequently, the surface concentrations of alcohol intermediates are very small. Spillover of alcohol intermediates from the Co-metal surface to the TiO₂ support gives rise to the formation of alcoxy species. The inverse spill over of alcoxy species from the TiO₂ support to the Co-metal and its subsequent decomposition into a hydrocarbon is of negligible importance.

Catalyst development

Both single-C species, $C_{\alpha,ads}$ and $C_{\beta,ads}$, contribute to methane formation and chain growth. The elimination of one intermediate by catalyst design will not lead to a more productive catalyst. This would be the case if one species would preferentially lead to methane formation. The active surface site containing a growing hydrocarbon chain is believed to be a surface defect. It is expected that the productivity of a Co-based Fischer-Tropsch catalyst will increase if the surface concentration of stable defects is increased. The bottleneck for catalyst development is thereby identified: despite the high surface concentration of monomeric building blocks and the high activity of the active site for C-C coupling, the catalyst productivity is limited by a low surface concentration of active sites for C-C coupling.

Samenvatting

In de nabije toekomst zal de grondstof voor de chemische industrie verschuiven van ruwe olie naar aardgas als gevolg van de beperkte reserves aan ruwe olie en de inperking van de belasting van het milieu. Om aardgas chemisch te converteren, wordt het eerst omgezet in synthesegas, wat een mengsel is van koolmonoxide en waterstof. Een groot aantal industriële processen is gebaseerd op dit synthesegas. Als de productie van waterstof wordt gemaximaliseerd, wordt het voornamelijk gebruikt voor de productie van ammonia. Daarnaast neemt de toepassing van waterstof voor de productie van elektriciteit in brandstofcellen toe. In de gas-naar-vloeistoftechnologie wordt synthesegas omgezet in hoogwaardige vloeistoffen zoals methanol, dimethylether (DME), of synthetische olie. Deze technologie staat beter bekend als het Fischer-Tropsch procedé, wat een belangrijk instrument vormt voor de chemische liquificatie van aardgas. Als zodanig laat het een economisch rendabele exploitatie van afgelegen aardgasreserves toe en vormt het een alternatieve route voor de productie van schone brandstoffen en grondstoffen voor de petrochemische industrie in vergelijking met de klassieke raffinage van ruwe olie.

Doelstelling van de studie

Hoewel de Fischer-Tropsch synthese een levendige geschiedenis kent van meer dan 70 jaar, wordt het reactiemechanisme nog steeds niet volledig begrepen. In de literatuur worden het COinsertiemechanisme, het carbeenmechanisme en het hydroxycarbeenmechanisme voorgesteld [Hinderman *et al.*, 1993]. Aan het carbeenmechanisme wordt voornamelijk gerefereerd als het meest waarschijnlijke Fischer-Tropsch mechanisme. In dit mechanisme verloopt de ketengroei via de insertie van een CH_{2,ads}-species. Dit monomeerblok wordt gevormd door de hydrogenering van oppervlaktekoolstof resulterend uit de dissociatie van CO_{ads}. Met betrekking tot dit mechanisme bestaat er geen consensus wat betreft de hoeveelheid, de reactiviteit en de chemische samenstelling van de deelnemende oppervlaktecomponenten. Dit proefschrift heeft als doelstelling het polymerisatieachtige reactiemechanisme van de Fischer-Tropsch synthese te verduidelijken door middel van een transiënte kinetische studie.

Het begrijpen van het reactiemechanisme is essentieel voor het ontwerpen en optimaliseren van industriële katalysatoren. De kinetische studie is uitgevoerd op katalysatoren die gebaseerd zijn op kobalt, waarbij gebruik gemaakt werd van de "Steady State Isotopic Transient Kinetic Analysis" (SSITKA) techniek. Deze techniek is gebaseerd op het abrupt vervangen van één van de reactanten door zijn isotoopgelabelde variant. De daaruitvolgende transiënten geven de incorporatie van dit isotoop label in de reactie producten als functie van de tijd weer en bevatten kinetische informatie. Vergeleken met stationaire methoden zijn transiënt kinetische technieken geschikter om mechanistische aspecten van complexe reacties te ontrafelen. In dit opzicht neemt de SSITKA-techniek een speciale positie in omdat de techniek het toestaat deze mechanistische aspecten te bestuderen onder stationaire reactiecondities. Met andere woorden, de katalytische eigenschappen zijn toegankelijk bij de meest realistische procescondities.

Andere onderzoeksgroepen hebben reeds de achtergrond en methodologie van de SSITKAtechniek alsmede de analyse van de reactieproducten beschreven, zoals die ook zijn gebruikt in deze studie [Happel, 1978; Bennett, 1982; Biloen *et al.*, 1983]. Vergeleken met de literaruur wordt de SSITKA-techniek in deze studie echter optimaal benut. Dit wordt in eerste instantie gerealiseerd door het toepassen van een breed scala aan experimentele condities, zoals C-, O-, en H-labelen bij verschillende katalysatorsamenstellingen. Ten tweede wordt een belangrijk deel van het productspectrum in de transiënt kinetische analyse betrokken. Ten derde wordt de kwalitatieve interpretatie van de experimentele resultaten gevolgd door een uitgebreide mathematische modellering ten behoeve van de identificatie en discriminatie van het Fischer-Tropsch reactiemechanisme.

De Fischer-Tropsch katalysatoren

De gangbare katalysatoren voor de Fischer-Tropsch synthese zijn gebaseerd op ijzer (Fe), ruthenium (Ru), of kobalt (Co) als actief metaal. De kosten van ijzerkatalysatoren zijn laag, maar ze vertonen een lage selectiviteit voor wasvorming, deactivering, en inhibitie van de productiviteit door water bij hoge synthesegasconversies. Ondanks de hoge activiteit van rutheniumkatalysatoren wordt de toepassing ervan beperkt tot wetenschappelijke studies vanwege de hoge rutheniumprijs. Kobaltkatalysatoren zijn echter stabiel en laten een hoge synthesegasconversie toe, waarbij de productie van was wordt bevorderd. In deze studie wordt een kinetische studie gepresenteerd van de Fischer-Tropsch reactie over een Co(12gew%)/Ru(0.18gew%)/TiO₂-katalysator, een Co(12gew%)/TiO₂-katalysator, en een volledig metallische kobaltspons-katalysator bij 498 K en 1.2 bar. De experimenten zijn uitgevoerd onder intrinsieke reactiecondities in een gepakt-bed-reactor bij differentiële synthesegasconversies. De H₂/CO-verhouding in de voeding varieert van 1 tot 5. Tijdens alle experimenten wordt de Fischer-Tropsch reactie uitgevoerd onder droge condities, waarbij de vorming van was wordt onderdrukt. Alle producten verlaten de reactor via de gasfase.

Lage druk versus hoge druk

De stationaire productverdeling voor de C₁-tot-C₉-koolwaterstoffen bij lage druk, zoals toegepast in deze studie, verschilt van die bij hoge druk, zoals bij de industriële toepassing (25 bar). Dit komt door de afwezigheid van een waslaag op het oppervlak van de katalysator bij lage druk. De belangrijkste secundaire reactie is keteninitiatie door geheradsorbeerde 1-olefinen. In de literatuur wordt gesuggereerd dat in aanwezigheid van een waslaag andere secundaire reacties, zoals isomerisatie en verschuiving van de onverzadigde binding, sterisch worden gehinderd [Schulz *et al.*, 1998]. Echter, in de afwezigheid van een waslaag worden deze twee reacties belangrijk. De afname van de olefine-paraffineverhouding met de ketenlengte illustreert de koolstofnummerafhankelijkheid van de heradsorptie van 1-olefinen. Dit toont de aanwezigheid van een gefysisorbeerde toestand van de koolwaterstoffen aan, zelfs bij reactiecondities waar de opeenhoping van was op het katalytische oppervlak te verwaarlozen is.

Met de kinetische parameters zoals verkregen uit de regressieanalyse van de experimentele resultaten bij 498 K en 1.2 bar, wordt de productverdeling onder industriële condities gesimuleerd. Bij hoge druk treedt er wasvorming op en de vloeibare laag koolwaterstoffen blokkeert isomerisatie- en bond-shiftreacties. Hierdoor wordt de vorming van 1-olefinen bevorderd. Dit leidt tot een toename van de heradsorptie en een daaropvolgende keteninitiatie door 1-olefinen, waarbij de selectiviteit van zware koolwaterstoffen toeneemt onder industriële condities. Als wordt aangenomen dat de parameters die zijn verkregen bij 1.2 bar vanaf C_3 ketenlengte onafhankelijk zijn, worden deze effecten succesvol gesimuleerd.

Kinetische modellering

Transiënten voor de C_1 -tot- C_5 -koolwaterstoffen en de C_1 -tot- C_3 -alcoholen worden verkregen door massaspectrometrie en gaschromatografie-massaspectrometrie toe te passen tijdens C-, H-, of O-labeling van de reactanten CO en H₂. De resultaten worden in eerste instantie op kwalitatieve basis geïnterpreteerd. Waar de kwalitatieve interpretatie van de experimentele resultaten vaak beperkt is tot de identificatie van globale mechanistische fenomenen (zoals oppervlakteheterogeniciteit voor de vorming van koolwaterstoffen), is de kinetische modellering een krachtiger instrument voor de identificatie van het chemische reactienetwerk dat de experimentele resultaten kan beschrijven. Vanwege de aanwezigheid van reversibele reacties van zowel de reactanten als de producten, wordt er een propstroomreactormodel gebruikt. Het ontkoppelen van de methanering en de vorming van de zwaardere koolwaterstoffen vergemakkelijkt de modelidentificatie en -discriminatie.

Experimentele waarnemingen en modellering van de resultaten

CO adsorbeert snel en reversibel en zijn oppervlakteconcentratie verandert niet met de H₂/CO-voedingsverhouding. De vorming van methaan is langzaam als gevolg van een gehinderde CO-dissociatie en een langzame vorming van keteninitatoren en monomeren. De dissociatie van CO leidt tot de vorming van elementair koolstof en de hydrogenatie ervan verloopt waarschijnlijk via reversibele stappen. Het katalysatoroppervlak wordt hoofdzakelijk bedekt door CO en intermediairen voor methaan, hetgeen zorgt voor een globale bedekking van 90%. Het katalysatoroppervlak is de aanwezigheid van heterogeen, wat wordt veroorzaakt door twee verschillende koolstofcomponenten, die worden weergegeven als $C_{\alpha,ads}$ en $C_{\beta,ads}$. Met de methaneringreactie als basis, worden vier ononderscheidbare modellen gepresenteerd. Hoewel het aantal mogelijke modellen toeneemt door de incorporatie van de vorming van zwaardere koolwaterstoffen, toont de modeldiscriminatie aan dat slechts twee ononderscheidbare modellen de experimentele resultaten beschrijven. Als gemeenschappelijk kenmerk hebben deze modellen dat zowel $C_{\alpha,ads}$ als $C_{\beta,ads}$ deelnemen in de vorming van methaan en hogere koolwaterstoffen. Het aantal actieve oppervlaktecentra voor de Fischer-Tropsch reactie wordt vergroot door de promotie van de katalysator met Ru, terwijl de intrinsieke activiteit van de centra niet verandert.

De vorming van koolwaterstoffen gebeurt via O-vrije oppervlaktecomponenten. Daarnaast bevatten zowel $C_{\alpha,ads}$ als $C_{\beta,ads}$ waarschijnlijk waterstof. De heterogeniteit van het oppervlak ontstaat waarschijnlijk eerder door verschillende oppervlaktecentra voor $C_{\alpha,ads}$ als $C_{\beta,ads}$ dan door verschillende chemische samenstellingen van $C_{\alpha,ads}$ en $C_{\beta,ads}$. Ondanks de langzame vorming van keteninitiatoren en monomeren is de daaropvolgende C-C-koppeling relatief snel. Dit heeft een lage oppervlakteconcentratie van groeiende koolwaterstofketens van 1.4% tot gevolg. Het wordt verondersteld dat het actieve centrum een oppervlaktedefect is [Beitel *et al.*, 1997].



Schematische weergave van het Fischer-Tropsch mechanisme gebaseerd op het ¹³CO-SSITKA-onderzoek. De belangrijkste kenmerken van het mechanisme zijn:

- de oppervlakteheterogeniciteit op het niveau van de species met een enkele C-atoom;
- de aanwezigheid van een gefysisorbeerde toestand;
- de mogelijkheid voor 1-olefinen om wederom te participeren in het ketengroeiproces via heradsorptie vanuit de gefysisorbeerde toestand; alcoholvorming via een CO-insertie-
- terminatiereactie.

De heradsorptie van 1-olefinen op het oppervlak wordt aangetoond, terwijl de heradsorptie van interne- en iso-olefinen minder evident is. Ondanks dat de concentraties van de C_1 -tot- C_{10} -koolwaterstoffen in de gefysisorbeerde toestand enkele ordes van grootte kleiner zijn dan die in de gechemisorbeerde toestand, is de invloed van de gefysisorbeerde toestand op de ketenlengteafhankelijkheid van het heradsorptieproces nadrukkelijk aanwezig. Bij hogere druk neemt

de capaciteit van de gefysisorbeerde toestand toe, hetgeen de SSITKA-techniek niet toepasbaar maakt onder industriële condities. Zoals verwacht verloopt de terminatie naar paraffine via de hydrogenering van een groeiende koolwaterstofketen. De terminatie naar olefine verloopt echter eerder via een desorptie reactie dan via een β -hydride-abstractiereactie. Daardoor wordt de chemische samenstelling van de groeiende koolwaterstofketen geassocieerd met een $C_xH_{2x,ads}$ -component en niet met een $C_xH_{2x+2,ads}$ -component. Gaande van C_3 naar C_5 verschuift de preferentiële terminatie van paraffine naar olefine, hetgeen niet in de literatuur wordt waargenomen onder hogere druk. De veschuiving wordt veroorzaakt door het optreden van isomerisatie en bondverschuivings reacties van geheradsorbeerde 1-olefinen.

De vorming van alcoholen

Er wordt aangenomen dat de vorming van alcoholen een terminatiereactie is en verloopt via een CO-insertiemechanisme. De koppeling van een groeiende koolwaterstofketen op het oppervlak met CO_{ads} is twee ordes van grootte langzamer dan met een monomeer. Daardoor zijn de oppervlakteconcentraties van de alcoholintermediairen erg laag. Op de TiO₂-drager worden alcoxycomponenten gevormd via de spillover van alcoholintermediairen van het kobaltmetaal naar de drager. De inverse 'spillover' van alcoxycomponenten van de TiO₂-drager naar het Co-metaal en de daaropvolgende ontleding tot een koolwaterstof is van ondergeschikt belang.

Katalysatorontwikkeling

Zowel $C_{\alpha,ads}$ als $C_{\beta,ads}$ nemen deel aan de vorming van methaan en aan ketengroei. De eliminatie van één van de twee intermediairen door middel van katalysatorontwerp, zal niet leiden tot een katalysator met een hogere productiviteit. Dit zou het geval zijn geweest wanneer slechts één intermediair preferentieel leidt tot de vorming van methaan. Het aktieve oppervlaktecentrum dat een groeiende koolwaterstofketen bevat, wordt beschouwd als een oppervlaktedefect. Het wordt verwacht dat de productiviteit van een op kobalt gebaseerde katalysator toeneemt als de concentratie van deze stabiele defecten wordt vergroot. Hiermee wordt het knelpunt voor de ontwikkeling van de katalysator geïdentificeerd: ondanks de hoge oppervlakteconcentratie van monomeren en de hoge activiteit van het actieve centrum voor de C-C-koppelingsreactie wordt de productiviteit van de katalysator beperkt door de lage oppervlakteconcentratie van actieve centra voor de C-C-koppelingsreactie.

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Introduction

1.1 Fischer-Tropsch synthesis in perspective

Fischer-Tropsch synthesis is the process that converts synthesis gas, *i.e.* a mixture of carbon monoxide and hydrogen, into a wide range of long chain hydrocarbons and oxygenates. As such, the Fischer-Tropsch synthesis constitutes a practical way for the chemical liquefaction of solid (coal) or gaseous (natural gas) carbon resources. In relation to the classic refining of crude oil, the liquefaction of these carbon sources via the Fischer-Tropsch synthesis provides alternative routes for the production of transportation fuels and petrochemical feedstock. While the commercial operation of Fischer-Tropsch plants is limited to two companies, *i.e.* Sasol in South Africa with a total capacity of 125,000 bbl·day⁻¹ and Shell in Malaysia with a capacity of 12,500 bbl·day⁻¹, the interest in the Fischer-Tropsch technology is increasing. The increasing importance of the Fischer-Tropsch synthesis for the near future is illustrated by four criteria:

- the world reserves of carbon-containing resources;
- the geographic location of these reserves;
- the demand for cleaner feedstock;
- the reduction of CO₂ emissions.

The worlds proven reserves of natural gas and especially coal are much larger than the proven reserves of crude oil. At the end of 1999, the worlds proven reserves of crude oil were $140 \cdot 10^9$ tons. The proven reserves of natural gas were $146 \cdot 10^{12}$ m³, which is $132 \cdot 10^9$ tons oil equivalent, and of coal $984 \cdot 10^9$ tons, which is $656 \cdot 10^9$ tons oil equivalent [BP Amoco, 2000]. The increase of the proven reserves of natural gas and oil from 1975 to 1999 is represented in figure 1.1. The proven reserves of natural gas rise, whereas the proven reserves of crude oil tend to stagnate. In the near future, the utilization of coal and especially natural gas opposed to crude oil will become increasingly important in the energy sector. The Fischer-Tropsch synthesis is one of the key processes to meet the future energy demand.

Natural gas reserves are usually located in remote areas or offshore, which are considered stranded. The former Soviet Union and the Middle East plus North Africa each possess about 40% of the world natural gas reserves. In figure 1.2 it is indicated that the geographic locations of reserves and consumption do not match: the consumptions in Europe and America are high, whereas the reserves are concentrated in the Middle East and the former Soviet Union. Although the reserves near the coast of North Africa and in Indonesia are easily exploited as LNG (Liquefied Natural Gas), the exploitation of the other reserves necessitates transport via pipelines. Transportation of natural gas via pipeline is more capital intensive than of crude oil because of the high costs of compression. It is only profitable for short distances. Transportation of natural gas over larger distances in the form of LNG is

realized by physical liquefaction of the natural gas via condensation at 110 K. This requires a capital intensive cryogenic chain: a liquefaction plant, cryogenic tankers, and a regasification plant at the receiving terminal. The chemical liquefaction of the natural gas via the Fischer-Tropsch synthesis at the source drastically reduces the transportation costs. The resulting synthetic crude oil can easily be transported with existing infrastructure for oil transportation and new infrastructure is less capital intensive than for natural gas. As an example, an economic study by the American Federal Energy Technology Center [Venkataraman *et al.*, 1999] indicates that the lifetime of the Trans Alaskan Pipeline System can be prolonged by 20 years if the decreasing crude oil production of the Prudhoe Bay field is compensated by a gas-to-liquid plant.



Figure 1.1: Proven reserves of oil and natural gas from 1974 to 1999 in 10⁹ tons oil equivalent [BP Amoco, 2000].

Figure 1.2: Geographic distribution of proven natural gas reserves compared to the natural gas consumption in 1999 [BP Amoco, 2000].

America Europe

Middle east

Asia/Pacific

Africa

Former Soviet Union

Natural gas is the cleaner feedstock of the three energy resources mentioned above. Starting from natural gas, the Fischer-Tropsch synthesis produces a clean hydrocarbon product. It is free of sulfur- (S) and nitrogen-containing (N) compounds, aromatics, and heavy metals. Crude oil and coal contain large quantities of S- and N-compounds and heavy metals, which are removed by processes such as hydro-desulfurisation and hydro-denitrification. The sulfur is recovered via the Claus process to meet environmental constraints on emissions. Due to tightening environmental legislation, these processes will become even more important in the near future. Moreover, to improve the production of transportation fuels, catalytic reforming of gasoline cuts and fluidized catalyst cracking (FCC) of heavier feeds are important processing steps in refineries. Both processes increase the level of aromatics in transportation fuel cuts. In addition, the catalytic reformer supplies the hydrogen necessary for hydro-desulfurisation and hydro-denitrification and the conversion of heavy feeds via hydrocracking. These processes are vital in the refining of heavy crude oils. The increasing constraints on the content of aromatics in fuels therefore pose a serious problem for refineries: more intensive conversions are necessary when using heavier crude oils, but the formation of aromatics must be limited.

Contaminants in natural gas resources mainly consist of H_2S and CO_2 , which are easily removed via scrubbing techniques. The purification of synthesis gas from coal, *i.e.* the removal of H_2S , NH₃, tars, and slag is also simple in comparison with the processes needed in refining crude oil. It is, therefore, suggested that small scale Fischer-Tropsch plants in refineries could provide high quality blends for the upgrading of lesser quality cuts [Wilson and Carr, 1999].

Until recently, associated gas (visualize, natural gas dissolved in crude oil, which is released during exploration) was considered as a useless byproduct of crude oil and was subsequently flared off or reinjected into the well. Energy saving policies and the awareness of the global warming due to

CO₂ emissions have led in some places to taxation of flaring. Nowadays, flaring and reinjection impose a negative value on associated gas.

1.2 Gas-to-liquid technology

In the gas-to-liquid technology, natural gas is converted into a liquid product containing hydrocarbons and oxygenates. Three basic technologies exist, *i.e.* the gas-to-methanol technology, the gas-to-dimethylether technology (DME), and the gas-to-hydrocarbons technology, better known as the Fischer-Tropsch process. The focus will be on the latter. The gas-to-hydrocarbons technology consists of the following process steps:

- synthesis gas manufacturing;
- Fischer-Tropsch synthesis;
- product upgrading.



Figure 1.3: Schematic representation of a Fischer-Tropsch plant [Dry, 1990; Tijm et al., 1995].

These three steps are schematically represented in the block diagram of figure 1.3. The synthesis gas manufacturing and the product upgrading rely on established technologies. Synthesis gas manufacturing is widely applied in the production of methanol and ammonia. Future developments are expected in the field of catalytic partial oxidation and in membrane techniques for oxygen purification [Venkatarama *et al.*, 2000]. Product upgrading processes directly originate from the refining industry and are highly optimized. Although Sasol and Shell practice their Fischer-Tropsch technologies on commercial scale for several years, the Fischer-Tropsch process is still subject to further development. EXXON has proven its technology in pilot plants and is ready to practice it on commercial scale [Eisenberg *et al.*, 1998]. Williams Energy, Syntroleum, Statoil, and Rentech claim to

have own technologies [Wilson and Carr, 1999; Benham and Bohn, 1999]. The Fischer-Tropsch synthesis still constitutes the major technology risk in the gas-to-liquid technology.

A capital cost breakdown for a coal fed Sasol Fischer-Tropsch plant by Dry [1990] indicates that 70% of the capital is used for the production of clean synthesis gas. More than 50% of the capital investments are ascribed to the syngas manufacturing for the Shell SMDS plant in Malaysia [Tijm et al., 1995]. Recent base-case economic evaluations of the gas-to-liquid technology by Amoco [Gradassi, 1999] and Arthur D. Little [Read et al., 1999] indicate that the current technology is viable at a crude oil price in excess of \$15 per barrel. This number is also cited for the Shell SMDS process [Tijm et al., 1995]. The gas-to-liquid manufacturing costs are equivalently divided between capital investment, the costs of natural gas, and operating expenses. These three cost factors define a minimum manufacturing cost of \$14 per barrel liquid Fischer-Tropsch products. In a recent review by Espinoza et al. [1999], a minimum manufacturing cost of \$10 per barrel is mentioned for the new Sasol slurry column process. Income taxes and an internal rate of return of 15% cause the manufacturing cost to rise from \$14 to \$26 per barrel [Gradassi, 1999], which corresponds to a crude oil price of \$18 per barrel. The manufacturing cost is most sensitive towards the natural gas price and the capital cost. Natural gas prices are generally low. Capital costs are strongly dependent on the location of the plant. Especially for the exploitation in remote areas, the lack of infrastructure increases the capital costs, which can be compensated by the economy of scale.

An overview of the oil price from 1946 to 2000 is given in figure 1.4. At this moment, the Fischer-Tropsch technology is feasible with a crude oil price in excess of \$18 per barrel. Because of the ongoing technological developments in the synthesis gas manufacturing and the Fischer-Tropsch process, the manufacturing costs for a gas-to-liquid plant will drop and a lively future for the gas-to-liquid technology is foreseen.

A brief discussion of each process, *i.e.* synthesis gas manufacturing, Fischer-Tropsch synthesis, and product upgrading, is given in the following sections.



Figure 1.4: Spot oil price in dollar per barrel for the West Texas Intermediate from 1946 to 2000 [BP Amoco, 2000].

1.2.1 Synthesis gas manufacturing

Synthesis gas is a mixture of carbon monoxide (CO) and hydrogen (H_2), which can be obtained from any carbon containing feedstock. Common feedstocks are natural gas (80%) on the one hand, and naphtha and coal (20%) on the other hand. Three basic methods of converting a feed stream into synthesis gas exist, *i.e.* reforming, partial oxidation, and catalytic partial oxidation. In all cases, a near-to-equilibrium synthesis gas mixture is obtained of which the H_2 /CO ratio can be adjusted via the water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$\Delta H = -42 \ kJ \cdot mole^{-1}$

• In reforming, the feed stream is passed over a Ni-based catalyst together with H₂O and/or CO₂ at high temperatures (1073-1173 K) and medium pressures (10-30 bar). Steam reforming and oxy-steam reforming (or so-called autothermal reforming) hold the leading positions among the commercial

processes of synthesis gas production in the synthesis of methanol and ammonia. Steam reforming of methane is highly endothermic:

 $CH_4 + H_2O \rightarrow CO + 3H_2$ Large furnaces are used, inflicting large capital investments. The endothermicity of the steam reforming process is compensated by the addition of oxygen in the autothermal reforming process. The synthesis gas from industrial steam reformers has a high H₂/CO ratio (H₂/CO=3-7 and CO/CO₂=0.3-1.5).

• In partial oxidation, the feed stream is mixed with oxygen and steam and fed to a high temperature flame (1573-1773 K). The feed is partially combusted followed by endothermic reforming steps and the water-gas shift reaction. This process is particularly suitable for heavy feeds, such as the residues from vacuum distillation and catalyst cracking (FCC). In the partial oxidation of coal, better known as gasification, an oxygen-water mixture is contacted with a fixed, entrained, or fluidized bed of fine coal particles. The synthesis gas from industrial partial oxidation has a low H₂/CO ratio (H₂/CO=0.5-2 and CO/CO₂=5-15).

• In the catalytic partial oxidation a catalyst takes over the function of the flame in the partial oxidation. The advantages of the catalytic partial oxidation of methane over steam reforming of methane are the low exothermicity of the process and the high reaction rates, leading to significant smaller reactors:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$

$\Delta H = -22 \ kJ \cdot mole^{-1}$

Although catalytic partial oxidation is a promising process for the production of H_2 -rich gas for small-scale fuel-cell applications, it still awaits a commercial breakthrough [de Smet, 2000].

1.2.2 Fischer-Tropsch synthesis

The Fischer-Tropsch reaction is the chemical heart in the gas-to-liquid technology. The highly exothermic Fischer-Tropsch reaction converts synthesis gas into a large range of linear hydrocarbons, schematically represented as:

 $nCO + 2nH_2 \rightarrow -(CH_2)_n - + nH_2O$ $\Delta H = -165 \ kJ \cdot mole^{-1}$

The industrial reaction conditions are 473-573 K and 25-40 bar.

The Fischer-Tropsch process has a lively history of more than 70 years [Anderson, 1984, Hindermann *et al.*, 1993, Van der Laan and Beenackers, 1999]. The CO hydrogenation capacity of nickel and cobalt was first reported by Sabatier and Senderens in 1902. However, it was only after the pioneering work of Franz Fischer and Hans Tropsch in the 1920's and 1930's that the commercial interest in the production of hydrocarbons and oxygenates started to grow.

Although all group VIII metals display some activity in the C-C coupling reaction during the hydrogenation of CO, the most active metals for the Fischer-Tropsch synthesis are ruthenium, iron, cobalt, and nickel [Anderson, 1984; Hindermann, 1993; Adesina, 1996; Schulz, 1999]. This is related to the capacity of the metals to dissociate CO. Going to the left and up in the group VIII metals, the CO dissociation intensifies and excessive carbonization of the metal is risked. Going to the right and down, CO dissociation becomes more difficult and the hydrogenation towards alcohols dominates. Iron, cobalt, nickel, and ruthenium display intermediate behavior and are excellent Fischer-Tropsch catalysts. The major disadvantage of nickel is that it readily forms volatile metal-carbonyls, limiting the reaction pressure and thus the Fischer-Tropsch productivity. At industrial conditions, nickel mainly produces methane.

Iron catalysts for the Fischer-Tropsch synthesis generally consist of precipitated iron, which is promoted with potassium and copper to obtain a high activity and selectivity, and with Al_2O_3 and SiO_2 added as structural stabilizers. Typically for these relatively cheap Fe-based catalysts is that the active phase for Fischer-Tropsch appears to be a Fe-carbide. Also, Fe-oxides are formed, which are active for the water-gas shift reaction. This high water-gas shift activity causes these catalysts to be flexible towards the H_2/CO feed ratio of the synthesis gas. This allows the utilization of a large variety of feedstocks, while every syngas manufacturing technology can be applied. Because coal results in a

syngas with a low H_2/CO ratio, this feedstock can only be used in combination with a Fe-based catalyst. However, the water-gas-shift activity of the catalyst also results in a low carbon efficiency of the gas-to-liquid process. At high temperature (613 K), Fe-based catalysts are selective for light olefins with a low selectivity towards methane. This only seems possible with Fe-based catalysts, making them unique in this respect. The application of Fe-based catalysts in the production of heavy wax is limited. This is mainly due to its tendency to form elemental carbon, causing deactivation of the catalyst. Moreover, water, which is produced in large quantities as side product, has an inhibiting effect on the activity, resulting in low conversions per pass. The latter effect results in large recycle streams after water removal.

Cobalt catalysts are usually supported on metal oxides due to the higher cobalt price and better catalyst stability. The active phase is metallic cobalt; the tendency of cobalt to form carbides at 473-573 K and 25-40 bar is low. The water-gas shift activity of Co-based catalysts is low and water is the main oxygen containing reaction product. The cobalt is generally poorly dispersed on metal oxide supports and Ru, Re, or Pt promoters are applied to prevent catalyst deactivation by carbon formation or oxidation. Compared to Fe-based catalysts, olefins tend to reenter the chain growth process by readsorption on Co-based catalysts, increasing the selectivity towards heavy hydrocarbons. Co-based catalysts are very suitable for wax formation in slurry bubble columns and can operate at high conversions per pass.

Ruthenium catalysts are the most active Fischer-Tropsch catalysts. A high molecular weight wax is obtained at reaction temperatures as low as 423 K. The catalyst is active in its metallic form and no promoters are required to stabilize its activity. However, the high price of ruthenium excludes its application on industrial scale and the use of Ru-based catalysts for the Fischer-Tropsch synthesis is limited to academic studies.

Fischer-Tropsch reactor:		CFBR=circulating fluidized bed reactor; FBR=fluidized bed reactor; TFBR=tubular fixed bed reactor; SBCR=slurry bubble column reactor			
Licencor	Status	Syngas production	F-T reactor	Catalyst	reference
Sasol	commercial	PO SR	CFBR FBR TFBR SBCR	Fe Fe Fe, Co	Dry [1996], Espinoza <i>et al.</i> [1999], Steynberg <i>et al.</i> [1999]
Shell	commercial	PO	TFBR	Со	Eilers <i>et al.</i> [1990], Geerlings <i>et al.</i> [1999]
Exxon	pilot plant	CPO	SBCR	Со	Eisenberg et al. [1998]
Syntroleum	laboratory	ATR	TFBR	?	reference in Van der Laan and Beenackers [1999]
Energy International	?	PO	SBCR	Со	Wilson and Carr [1999]
Rentech	pilot plant	PO, SR, ATR	SBCR	Fe	Benham and Bohn [1999]

Table 1.2: Overview of the current technologies used in the Fischer-Tropsch technology.

Syngas manufacturing: PO=partial oxidation, CPO=catalytic partial oxidation; SR=steam reforming, ATR=autothermal reforming

An overview of the existing Fischer-Tropsch technologies is given in table 1.2. With Sasol's fluidized bed processes (CFBR and FBR) as exceptions, all processes are aimed at high wax selectivities. For detailed descriptions of the individual processes the reader is referred to recent literature reviews by Van der Laan and Beenackers [1999] and Schulz [1999] and to the references given in table 1.2.

1.2.3 Product upgrading

The hydrocarbon product mixture leaving the Fischer-Tropsch reactor is frequently referred to as synthetic crude oil. This already illustrates that the standard product upgrading techniques that are used in refineries are also suitable for the upgrading of the Fischer-Tropsch wax. Fischer-Tropsch wax

consists mainly of linear hydrocarbon chains over a large boiling range and has a zero-level of S- or N-contaminants and aromatics. An overview of the Fischer-Tropsch wax based products is given below [Dry, 1990; Eilers *et al.*, 1990; Tijm *et al.*, 1995].

The Fischer-Tropsch process directly produces high quality waxes suitable for *e.g.* food applications and cosmetics & medicines. However, this is a limited market, which is easily saturated. The C₉-C₁₅ olefins are very suitable for the production of biodegradable detergents, whereas the paraffins are excellent lubricants. High selectivities towards fuels are obtained by hydrocracking the wax. Hydrocracking is a selective process, which converts heavy hydrocarbons into the C₄-C₁₂ range with low selectivities to C₁-C₃. This directly produces a high quality gasoil (high cetane index, low sulfur content, low aromatics) and kerosene (high paraffin content), which are very suitable as blending components to upgrade lower quality stock. The linearity of the Fischer-Tropsch naphtha is a drawback for gasoline production. The octane number of the hydrocracked wax is improved by processes such as isomerization, catalytic reforming, alkylation, and oligomerization. The naphtha is therefore better used as feedstock for the petrochemical industry. Its high paraffin content makes the naphtha an ideal cracker feedstock for ethylene and propylene production.

1.3 Aim, scope, and outline of this thesis

The work described in this thesis has been performed within the framework of the "Paraffin Selective Efficient Catalyst", or "ParSEC" JOULE project of the European Commission (no. JOF3-CT95-0016). The aim of the project was to develop new, more active Co-based catalysts for slurry phase operation of the Fischer-Tropsch synthesis in comparison to the Co/Ru/TiO₂ catalyst by Iglesia et al. [1993b]. Within this context, the present thesis aims at a better understanding of the Fischer-Tropsch synthesis reaction mechanism on Co-based catalysts by means of transient kinetic techniques. In literature, controversy still exists on the reactivity, the abundance, and the chemical identity of the surface species participating in the Fischer-Tropsch synthesis. In contrast to steady state kinetic techniques, transient kinetic techniques have a high potential to answer these questions. Of these transient techniques, the Steady State Isotopic Transient Kinetic Analysis technique (SSITKA) is most promising since the steady state is not disturbed and information is obtained at realistic reaction conditions. During a SSITKA experiment a reactant is abruptly replaced by its labeled counterpart and the evolution of the label in the reactant and the products is monitored in time. These transient responses contain information about the abundance, reactivity, chemical identity, and surface heterogeneity of the participating species, which renders the SSITKA technique powerful for mechanistic investigations of complex reactions.

In **chapter 2**, a literature review is presented on the mechanism of the Fischer-Tropsch synthesis. Because extensive literature reviews on the subject have appeared over the years [Anderson, 1984; Hindermann *et al.*, 1993; Dry, 1996; Van der Laan and Beenackers, 1999; complete volume of *Appl. Catal. A*, **186**, 1999], only the major aspects of the Fischer-Tropsch mechanism are discussed.

The methodology of the SSITKA technique is discussed in **chapter 3**. It deals with the interpretation and modeling of isotopic transient kinetic measurements and highlights the strong and the weak points of the technique.

In **chapter 4**, the experimental set-up is discussed. It focuses on the analysis technique for the detection of the isotopic composition of the C_{2+} hydrocarbons and alcohols. The second part of **chapter 4** deals with the preparation and characterization of the Co(12wt%)/TiO₂ catalyst, the Co(12wt%)/Ru(0.18wt%)/TiO₂ catalyst, and the Co-sponge catalyst that are used in this work.

The steady state behavior of the catalysts at 498 K and 1.2 bar at varying H_2/CO feed ratio and residence time is discussed in **chapter 5**. It is observed that the absence of a wax layer on the catalyst surface has a clear influence on the occurrence of secondary reactions. Reactive olefins readily readsorb onto the catalyst surface. It is illustrated that, even in the absence of wax formation, the presence of a physisorbed state is essential to explain the experimental results. In **chapter 6** detailed mechanistic insight into the formation of hydrocarbons and oxygenates is presented by performing ¹³CO, C¹⁸O, and D₂-labeling experiments on the different Co-based catalysts. Moreover, the analysis of the isotope content of the reaction products is expanded from methane towards the C₂-C₅ hydrocarbons and C₁-C₃ alcohols. It focuses on mechanistic aspects such as the abundance and chemical identity of the surface species, the heterogeneity of the catalyst surface, and the occurrence of secondary reactions.

The steady state performance of the $Co/Ru/TiO_2$ catalyst and the transient experimental data as presented in **chapters 5** and **6**, respectively, are used in **chapters 7** and **8** to obtain a quantitative model for the Fischer-Tropsch synthesis. The emphasis in **chapter 7** is put on model identification, discrimination, and quantification for the methanation reaction, while the entire product spectrum of the Fischer-Tropsch reaction is accounted for. The rate coefficients of the methanation models in **chapter 7** are used for the quantification of the Fischer-Tropsch mechanism in **chapter 8**. The modeling further highlights characteristic mechanistic aspects of the Fischer-Tropsch synthesis on Co-based catalysts.

Finally, the main conclusions of this thesis are summarized in chapter 9.

2

The Fischer-Tropsch synthesis: A literature review

2.1 Introduction

In this chapter, a literature review is presented on the mechanism of the Fischer-Tropsch synthesis. Because extensive literature reviews on the subject have appeared over the years [Anderson, 1984; Hindermann *et al.*, 1993; Dry, 1996; Van der Laan and Beenackers, 1999], only the major aspects of the Fischer-Tropsch mechanism are discussed. The mechanistic aspects discussed in this chapter are used for the model formation of the methanation reaction in chapter 7 and the Fischer-Tropsch synthesis reaction in chapter 8.

After a description of the major features of the Fischer-Tropsch synthesis in section 2.2, the mechanisms presented in literature are discussed in section 2.3. The importance of secondary reactions on the Fischer-Tropsch product distribution is highlighted in section 2.4. The theory about the origin of the most important secondary reactions, *i.e.* the readsorption of reactive olefins, is discussed in section 2.5. Finally, an overview of the controversies about the Fischer-Tropsch mechanism is given, which the present work tries to answer.

2.2 The Fischer-Tropsch reaction: A polymerization process

The pioneering work by Fischer and Tropsch in the 1920's already led to the realization that hydrocarbon chain formation proceeds via the stepwise addition of one C-atom at the time. Detailed product analysis studies [*e.g.* Pinchler *et al.*, 1967] indicate that the reaction produces a vast array of hydrocarbons and oxygenates over a large boiling range. The major reaction products at high-pressure operation are linear paraffins, linear 1-olefins, and linear 1-alcohols. At lower pressures, the selectivity for mono-methyl branched hydrocarbons and internal-olefins increases. The formation of aromatics is only observed at higher temperatures on Fe-based catalysts and is not observed on Co-and Ru-based catalysts. Anderson [1984] shows that a polymerization-like process effectively describes the product distribution of the Fischer-Tropsch synthesis. This results in the so-called Anderson-Schulz-Flory (ASF) product distribution:

$$F_n = n \cdot (1 - \alpha)^2 \cdot \alpha^{n-1}$$

(2.1)

where F_n is the fraction of the C-atoms within a chain containing *n* C-atoms. Similar molecular weight distributions were already observed during polycondensation by Schulz and free-radical polymerization by Flory [Hinderman *et al.*, 1993].

The entire product spectrum is characterized by a single parameter, *i.e.* the chain growth probability α , defined as:

$$\alpha = \sum_{i=n+1}^{\infty} \phi_i \left/ \sum_{i=n}^{\infty} \phi_i \right. = \frac{r_p}{r_p + r_t}$$
(2.2)

where r_p and r_t are the rates of chain propagation and termination, respectively, and ϕ_i is the mole fraction of the product spectrum containing *i* carbon atoms. Often, the product distribution is described by the termination probability β instead of the chain growth probability. In 1946, Herington defined the termination probability β as:

$$\beta = \phi_i \Big/ \sum_{i=n+1}^{\infty} \phi_i = \frac{r_t}{r_p} = \frac{1-\alpha}{\alpha}$$
(2.3)

Equation (2.1) implies that the Fischer-Tropsch reaction is not selective towards a single reaction product or a specific carbon range, with methane as only exception. Methane can be produced with 100 % selectivity. This is schematically represented in figure 2.1, where the product selectivity is plotted against the chain growth probability α . The Fischer-Tropsch synthesis, however, can selectively produce one type of reaction product, *i.e.* the selectivity towards 1-olefins or paraffins can be optimized. The influence of the reaction conditions on the product distribution is indicated in table 2.1. Wax formation is favored at low temperature, high pressure, low H₂/CO feed ratios, and large residence times. Accordingly, Sasol's tubular fixed bed process, which aims at wax formation, is operated at 492-523 K and 25-40 bar [Espinoza *et al.*, 1999]. Sasol's circulating fluidized bed process, however, aims at gasoline and light olefins and is operated at 603-623 K and 25 bar [Steynberg *et al.*, 1999].

Table 2.1: Influence of the process conditions on the Fischer-Tropsch product distribution. O/P=olefin to paraffin ratio; S_{C_1} =methane selectivity; X_{syngas} =syngas conversion; +: increases with increasing parameter value; -: decreases with increasing parameter value; /: situation dependent.

	α	O/P	S _{C1}	X _{svnqas}	linearity
Temperature	-	+	+	+	-
Pressure	+	+	-	+	+
H ₂ /CO	-	-	+	+	/
Residence time	+	-	/	/	-

The restraints of the product distribution led to the development of low temperature operation of multi-tubular reactors and slurry column reactors, see table 2.1. At these conditions, chain growth probabilities in excess of 0.9 are obtained, at which the fuel-gas selectivity is low.

The Fischer-Tropsch reaction is not a polymerization reaction in the true meaning of the word. Firstly, the monomer has to be formed in-situ on the catalyst surface from the reactants CO and H₂. Secondly, the rates of surface reactions are chain length dependent for the formation of the C₁-C₄ hydrocarbons. Thirdly, primary products can undergo secondary reactions that influence the product distribution. These three deviations from ideal polymerization kinetics cause the Fischer-Tropsch product distribution to deviate from the ideal ASF distribution. As shown in figure 2.2, the observed differences between the experimental product distributions and the ideal ASF distribution are:

- a higher than expected C₁ selectivity;
- a lower than expected C₂ selectivity;
- a chain length dependent chain growth probability, leading to a curved distribution and a higher than expected selectivity of heavy hydrocarbons.

It should be noted that erroneous product analyses introduce systematic deviations in the product distribution, which are easily ascribed to mechanistic causes. A well-known problem is the condensation of hydrocarbons prior to product analysis. Because the condensation is chain length dependent, the resulting deviations in the product spectrum can easily be mistaken for mechanistic phenomena. Erroneous mechanistic explanations may also occur in short non-steady state operation of the reaction where stabilization of the product spectrum is not yet completed [Shi and Davis, 2000].



Figure 2.1: Theoretical product distribution as a function of the chain growth probability α according to the ASF distribution.



Figure 2.2: Experimental product distribution of a Co/TiO_2 catalyst at 473 K and 20 bar in comparison to the ASF distribution [Iglesia *et al.*, 1993a].

2.3 Identification of the reaction mechanism

Although the product distribution demonstrates the polymerization character of the Fischer-Tropsch synthesis, a great deal of controversy still exists on the chemical identity of the monomeric building block and, in relation to this, of the growing hydrocarbon chain. This results from the vast product spectrum of alkanes, alkenes, alcohols, and acids, observed during the Fischer-Tropsch synthesis. From literature, the three major reaction mechanisms for the Fischer-Tropsch synthesis are:

- 1. the carbene mechanism;
- 2. the hydroxy-carbene mechanism;
- 3. the CO-insertion mechanism.

For each mechanism, several variants are reported. Because extensive reviews can be found in literature [Anderson, 1984; Hindermann *et al.*, 1993; Dry, 1996], only the most important aspects of the reaction mechanisms are reported here.

2.3.1 Carbene mechanism

In the carbene mechanism, oxygen free $C_{1,ads}$ intermediates are formed from the hydrogenation of surface carbon following the dissociation of adsorbed CO. Chain growth proceeds via the insertion of a $CH_{x,ads}$ species into the metal-carbon bond of a $C_xH_{y,ads}$ species. The mechanism is represented in figure 2.3 in which the methylene species $CH_{2,ads}$ is the key intermediate. The mechanism was first proposed by Fischer and Tropsch in 1926 and in their proposal the synthesis proceeds via hydrogenation of surface carbides to methylene groups. These methylene groups polymerize to surface alkyl species that terminate to the reaction products.

There is a vast number of studies that support the carbene mechanism and it is often referred to as the most probable Fischer-Tropsch mechanism. These studies include the analysis of surface species [*e.g.* Winslow and Bell, 1984], C-tracer techniques [*e.g.* Zhou and Gulari, 1987], the addition of probe molecules [*e.g.* Van Barneveld and Ponec, 1984; Brady and Pettit, 1981], and olefin cofeeding studies [*e.g.* Iglesia *et al.*, 1991].

2.3.2 Hydroxycarbene mechanism

In the hydroxycarbene mechanism, chain growth proceeds via a condensation reaction of two hydroxycarbene species $CHOH_{ads}$ with the elimination of water. The mechanism is shown in figure 2.3 in which the hydroxycarbene species is the key intermediate. They are formed via the partial

hydrogenation of adsorbed CO_{ads}. The mechanism readily explains the formation of alcohols via hydrogenation, aldehydes via desorption, and hydrocarbons via the hydrogen assisted elimination of the -OH group.

The basis for the mechanism lies in the observation that cofeeding of alcohols during the Fischer-Tropsch reaction leads to the participation of these alcohols in chain growth. However, adsorption of cofed alcohols and the participation of the resulting intermediates in chain growth processes do not make evident that the growing chain on the catalyst surface is an O-containing species. Moreover, the C-C bond formation between two electrophilic hydroxycarbene species is not obvious.



Figure 2.3: Schematic representations of the three basic Fischer-Tropsch reaction mechanisms, *i.e.* the carbene mechanism, the hydroxycarbene mechanism, and the CO-insertion mechanism [Anderson, 1984].

2.3.3 CO-insertion mechanism

In the CO-insertion mechanism, chain growth proceeds via the insertion of a carbonyl intermediate (CO_{ads}) into the metal-alkyl bond. For the C-C coupling reaction to take place, the resulting species is first hydrogenated to an alkyl chain. This mechanism explains the formation of alcohols, aldehydes, and hydrocarbons. It is shown in figure 2.3 where the carbonyl species is the key intermediate. Pichler and Schulz first proposed the CO-insertion mechanism in 1970.

It is based on the work on organometallic complexes. Assuming that the active surface during heterogeneous catalysis should be considered to consist of individual active sites possessing a specific coordination, organometallic complexes represent chain growth sites during the Fischer-Tropsch synthesis. Indeed, CO-insertion into a metal-alkyl complex is frequently observed with Fe complexes [Brown and Davies, 1986] and Ru-complexes [Gafoor *et al.*, 1996]. However, methylene insertion according to the carbene mechanism, is also reported for organometallic systems [Zaera, 1994; references in Hindermann *et al.*, 1993].

There is still no exclusive experimental evidence for the CO-insertion as the key mechanism for the hydrocarbon formation during the Fischer-Tropsch synthesis.

2.3.4 Parallel mechanism

All three mechanisms mentioned above share one important common feature: the presence of a single key intermediate. None of the mechanisms is capable of predicting the whole product spectrum observed for the four Fischer-Tropsch metals of interest, *i.e.* iron, cobalt, ruthenium, and nickel. Moreover, the Fischer-Tropsch reaction over these catalysts produces comparable product spectra, while a carbidic surface is active for Fe-based catalysts and a metallic surface for Co- and Ru-based catalysts. In addition, the water-gas shift reaction on Fe-oxides is important on Fe-based catalysts, whereas this reaction is absent on Co- and Ru-based catalysts.

This has led researchers to assume that the Fischer-Tropsch mechanism likely involves more than only one key intermediate [Dry, 1990, 1996; Adesina, 1996]. In this respect, they proposed that a CO-insertion mechanism is responsible for the formation of oxygenates, while hydrocarbons are formed via the O-free carbene mechanism. Acids are formed via the insertion of CO_2 [Lox and Froment, 1993a, 1993b]. It is emphasized that a large variety of O-, H-, and C-containing species are present on the catalyst surface that all may be involved in the Fischer-Tropsch mechanism.

2.3.5 Surface structure sensitivity of the Fischer-Tropsch reaction

The adsorption of CO on group VIII metals is reported extensively in literature. At ultra-highvacuum conditions, different ordered surface structures are observed depending on the orientation of the single crystal, the temperature, and the surface coverage. The temperature of CO dissociation depends on the orientation of the single crystal. However, the relevance of conclusions drawn from UHV studies is unknown due to the pressure gap of 10 orders of magnitude between these UHV studies (10⁻⁶ mbar) and the industrial operation (25 bar) [Geerlings *et al.*, 1991; Beitel *et al.*, 1996].

At atmospheric pressure it is generally accepted that the CO hydrogenation reaction is structure insensitive. Johnson *et al.* [1991] show that submonolayer deposited Co/W catalysts display similar turn-over-frequencies and activation energies for CO consumption as Co/Al₂O₃ catalysts and polycrystalline Co. Similar results are observed for the methanation reaction on Ni-based catalysts and Ru-based catalysts. The chemical nature of the support appears to be the controlling factor in determining the activity and selectivity of supported Co-based catalysts. Iglesia *et al.* [1993b] report structure insensitivity for different low dispersed Co/TiO₂, Co/SiO₂, and Co/Al₂O₃ catalysts. Lathinen *et al.* [1993] report structure insensitivity for methanation on Co-based catalysts, but structure sensitivity of the formation of longer hydrocarbon chains. This is also reported by Geerlings *et al.* [1991a, 1991b]. However, activation energies for ethene, ethane, and propane formation do not depend on surface structure, indicating that the mechanism is structure insensitive.

Wilson and de Groot [1995] observe severe reconstruction of the surface of Co(0001) at high CO pressures leading to increased concentrations of edge sites. The formation of defect sites on Co(0001) in a CO atmosphere is also observed by Beitel *et al.* [1996]. Compared to annealed surfaces, sputtered surfaces are defect-rich and display a larger hydrocarbon build-up [Beitel *et al.*, 1997]. The defect sites are believed to be involved in hydrocarbon formation [Geerlings *et al.*, 1999].

2.4 Importance of secondary reactions

A polymerization reaction is characterized by the following reaction steps: i) chain initiation, ii) chain growth, and iii) chain termination. Besides these primary reactions, yielding primary products, mechanistic investigations indicate the presence of secondary reactions during the Fischer-Tropsch synthesis. Secondary reactions are defined as reactions following the readsorption of primary products on surface sites that do not display chain growth [Novac *et al.*, 1982]. They list the following secondary reactions for 1-olefins:

- isomerization to internal olefins;
- cracking and hydrogenolysis;

- hydrogenation to paraffin;
- insertion into a growing hydrocarbon chain;
- chain initiation.

In this respect there has been some debate about whether paraffins are primary products formed from the hydrogen-assisted termination of growing hydrocarbon chains or whether they are exclusively formed via the adsorption of olefins on secondary hydrogenation sites. It is, however, generally excepted that both paraffins and olefins are primary products. Additional to a primary hydrogenation reaction, Geerlings *et al.* [1999] include a secondary hydrogenation reaction step to explain their experimental results.

The definition that secondary reactions involve surface sites that do not display chain growth is unsatisfying. The readsorption of 1-olefins and the subsequent chain initiation clearly involves a chain growth site [Madon *et al.*, 1991]. Schulz and Claeys [1999] argue that the isomerization of 1-olefins to internal-olefins does not require a second type of surface sites and proceeds on chain growth sites. In their model Komaya and Bell [1994a] use a depolymerization reaction of $C_{2,ads}$ species that only involves surface sites participating in the primary reactions as defined above. Madon *et al.* [1991] also assume that isomerizations proceed on Fischer-Tropsch sites. It is not evident that the secondary reactions mentioned above proceed on surface sites that do not participate in chain growth.

Secondary reactions where the carbon number of the primary product is altered (cracking, hydrogenolysis, chain insertion, and chain initiation) obviously affect the product distribution. These reactions are partially responsible for the experimentally observed deviations from the ASF distribution. The probability of each secondary reaction to occur at Fischer-Tropsch reaction conditions will be discussed in the following paragraphs [Madon *et al.*, 1991; Iglesia *et al.*, 1993a; Schulz and Claeys, 1999; Van der Laan and Beenackers, 1999].

2.4.1 Inhibiting effect of H₂O and CO on secondary reactions

Iglesia *et al.* [1993a] mention that a large number of cofeeding studies have been performed at untypical Fischer-Tropsch conditions, *i.e.* low pressures and low CO conversions. They emphasize the role of CO and H_2O and argue that isomerization, hydrogenation, and depolymerization are strongly inhibited by large CO and H_2O partial pressures. Under these conditions, chain initiation by olefins is the most important secondary reaction. Studies indicating the inhibiting effect of the partial pressure of CO on the conversion of added olefins are reported by Schulz and Claeys [1999]. Apparently, a competitive adsorption between CO and olefins exists.

2.4.2 Isomerization

The isomerization model by Schulz and Claeys [1999] is schematically shown in figure 2.4. A 1-olefin can readsorb and form an alkyl chain bonded to the catalyst surface with the ultimate C-atom. This species is indistinguishable from a primary growing hydrocarbon chain. In addition, 1-olefins can form penultimate bonded alkyl species, which yield 2-olefins or paraffins. The hydrocarbon chain causes steric hindrance for chain growth at the penultimate C-atom and the formation of linear hydrocarbons is favored over the formation of methyl-branched hydrocarbons. The steric hindrance is less intensive in the absence of a wax layer on the catalyst surface, resulting in a larger chain branching probability at low reaction pressures [Schulz *et al.*, 1998]. They argue that this latter mechanism can proceed on chain growth sites and does not require a second type of site. A similar isomerization scheme is proposed by Jordan and Bell [1986].

Dry [1996] proposes a chain growth mechanism where the growing hydrocarbon chain is di- σ bonded to the surface. This species is a logic intermediate in the adsorption of 1-olefins on the catalyst surface. Olefin adsorption is assumed to primary result in a π -bounded intermediate, which converts into a 2- σ intermediate and a 1- σ intermediate, see figure 2.4. The hydrocarbon chain also causes steric hindrance for chain growth at the penultimate C-atom. The absence of steric hindrance causes



the low C₂ contribution. In an overview on secondary reactions, Madon *et al.* [1991] also refer to studies where cyclic intermediates are proposed for the π -bond shift and branching reactions.

Figure 2.4: Schematic representation of the mechanism for bond shift [Schulz and Claeys, 1999; Jordan and Bell, 1986] and the interaction of olefins with the catalyst surface [Madon *et al.*, 1991].

2.4.3 Cracking and hydrogenolysis

In a literature review, Schulz and Claeys [1999] illustrate that cofeeding of olefins generally results in an unchanged or decreased methane selectivity. The hydrogenolysis of growing hydrocarbon chains, leading to the formation of a $C_{1,ads}$ species, is generally negligible at Fischer-Tropsch reaction conditions. Akhter *et al.* [1988] demonstrate that the thermal stability of adsorbed C_2D_4 at UHV on Ni(100) and Ru(001) increases in the presence of co-adsorbed CO_{ads} . The site blocking effect of CO_{ads} hinders the thermal decomposition of the hydrocarbon fragments.

Tau *et al.* [1990] illustrate that the effects of cofeeding olefins on the steady state product spectrum are difficult to interpret. Labeling studies facilitate the identification of secondary reactions. They observe no depolymerization during a ¹⁴C tracer study of alkene incorporation on a Fe-based catalyst at 7 bar. Mims *et al.* [1990] report some extent of depolymerization during co-feeding of unlabeled 1-hexene and 1-octene to $H_2 l^{13}$ CO syngas at 1 bar, but the rate of polymerization is 5 times faster than the rate of depolymerization. They conclude that this does not differ significantly from irreversibility.

2.4.4 Insertion and oligomerization

Oligomerization of the added olefin leads to an oscillating product distribution. In case of cofeeding of ethene this is only observed at excessive high ethene/CO ratios [Jordan and Bell, 1986], illustrating that oligomerization is inhibited by CO_{ads} . The insertion of cofed olefins into hydrocarbon chains is easily mistaken with chain initiation by readsorbed olefins. Since insertion is a similar reaction as oligomerization, it is reasonable to assume that the importance of this reaction is negligible at Fischer-Tropsch reaction conditions.

Recently, a reconsideration of the experimental results of the group of Maitlis by Shi and Davis [2000] indicated that the labeling content per molecule for the C₂ to C₇ hydrocarbons is fairly constant during the addition of ${}^{13}C_{2}H_{4}$ to $H_{2}/{}^{12}CO$ syngas. This illustrates that ethene acts as chain initiator and not as chain propagator.

2.4.5 Chain initiation

Chain initiation of cofed olefins is widely observed in literature. The reversibility of the termination reaction to olefin was already proposed by Herington in 1946. This reaction is generally accepted as the most important secondary reaction of 1-olefins. As such, it reverses the termination probability to olefin, leading to a higher chain growth probability and a higher paraffin selectivity. Furthermore, the readsorption of olefins becomes more effective with increasing chain length. This results in a curved product distribution, in which the selectivity towards heavy products is higher than expected from the ASF distribution. The origin of the increased readsorption with increasing carbon number, which even leads to the absence of olefins at high carbon numbers [Madon *et al.*, 1991], will be discussed in the following section.

2.5 Chain length dependent readsorption of reactive olefins

2.5.1 Readsorption models

In slurry operation, the catalyst is suspended in the hydrocarbon slurry and its pores are filled with liquid. The enhanced readsorption of olefins with chain length is explained by the increased residence time of the olefins in the wax-filled catalyst pores with increasing carbon number. Three chain length dependent processes contribute to the increased residence time [Kuipers *et al.*, 1995]:

- diffusion through the wax;
- solubility in the wax;
- physisorption at the solid-wax interface.

Iglesia *et al.* [1991, 1993a] state that the enhanced residence time is caused by an increase of the diffusion time with chain length. They rejected the solubility argument by assuming that the chemical potentials in the gas phase and in the chemisorbed state are not influenced by the presence of a liquid phase. In that case the composition of the liquid phase has no influence on the occurrence of secondary reactions. This reasoning is only justified if the gas phase, the liquid phase, and the chemisorbed state are independent systems, *i.e.* non-interacting systems. However, this is not the case when it is assumed that the tail of the growing hydrocarbon chains resides in the liquid phase. Then the physisorbed layer and the chemisorbed state are interacting systems, and the assumption made by Iglesia *et al.* [1991, 1993a] is not valid.

Iglesia *et al.* [1991, 1993a] model the steady state product distribution by introducing an exponential decay of the diffusion coefficient with carbon number. This is, however, not confirmed by experimental data [*e.g.* Erkey *et al.*, 1990]. Moreover, polymer dynamics predict a proportional dependency of the diffusion coefficient on carbon number. Therefore, the enhanced residence time of the olefins with increasing chain length cannot stem from diffusion effects alone.

Using a cobalt-foil catalyst, Kuipers *et al.* [1995] illustrate that the exponential chain length dependency of the olefin to paraffin ratio is already observed at conditions where no significant wax layer is present and diffusion, therefore, does not play an important role. They conclude that the combined effect of solubility of the hydrocarbons in the wax-phase and preferential physisorption at the solid-wax interface is responsible for the observed chain length dependency of the readsorption of reactive olefins. Both solubility and physisorption display an exponential chain length dependency [references in Van der Laan and Beenackers, 1999]. The liquid-phase is in equilibrium with the gas phase, but not with the chemisorbed state. This equilibrium determines the composition at the solid-wax interface, where heavy products are preferentially present over light products. Transport limitations are important for low weight products at low conversions and large diffusion distances. In this case the chain length dependence of the readsorption is weaker because diffusion dominates over solubility. The diffusion limitation is always negligible for high weight olefins, since the increment

of the residence time with chain length due to solubility is stronger than due to diffusion limitation. Transport limitations therefore only dominate at special conditions.

According to this reasoning, the chain length dependence of the readsorption reaction is independent of the presence of a wax layer. However, the experimental observations prove the opposite. Geerlings *et al.* [1999] demonstrate that the chain length dependency of the readsorption is weaker in the presence of a wax layer than in the absence of a wax layer. The inability to predict this effect is a discrepancy in the model by Kuipers *et al.* [1995]. They, however, demonstrate that the exponential chain length dependency of the readsorption of olefins originates from solubility and preferential physisorption, rather than from diffusion limitations.

Geerlings *et al.* [1999] model the data obtained on the same system used by Kuipers *et al.* [1995] by assuming that the wax layer is homogeneous. The authors no longer differentiate between solubility and preferential physisorption and completely neglect diffusion limitations. They state that the wax layer behaves as a homogeneous boiling liquid and that the composition of the wax layer is in equilibrium with the gas-phase. They argue that a stronger exponential chain length dependency in the absence of a wax layer results from an increase of the effective heat of desorption. In the absence of a wax layer, the hydrocarbons desorb from a bare metal surface, whereas in the presence of a wax layer desorption takes place from a liquid. This will be discussed in section 2.5.2.

2.5.2 Dry operation versus wax formation

Caldwell and van Vuuren [1986] and Sie *et al.* [1988, 1999] define a critical chain growth probability; operating the Fischer-Tropsch synthesis with a chain growth probability in excess of the critical chain growth probability will inevitably lead to wax formation. The Fischer-Tropsch synthesis is operated at dry conditions if the chain growth probability does not exceed the critical value. Factors favoring dry operation of the Fischer-Tropsch reaction are low conversions, high temperatures, and low pressures [Sie *et al.*, 1999]. Roughly, dry operation is realized if the chain growth probability is smaller than the factor β with which the hydrocarbon vapor pressure decreases with carbon number:

$$P_i^{\sigma} = P_{i_{ref}}^{\sigma} \beta^{(i-i_{ref})}$$
(2.4)

This factor β is related to the incremental energy of vaporization per -CH₂- unit of the hydrocarbon chain. Using a large collection of experimental gas-liquid data, Caldwell and van Vuuren [1986] report an empiric relation for the vapor pressure as a function of temperature:

$$P_{i}^{\sigma} = P_{0} \beta^{i} \qquad \text{where} \qquad P_{0} = 1.78382 \cdot 10^{4} \, kPa$$
$$\beta = \exp\left(-427.218 \cdot \left(\frac{1}{T} - 1.029801 \cdot 10^{-3}\right)\right) \qquad (2.5)$$

In the present work, the vapor pressure according to equation (2.4) is rewritten as an exponential relation:

$$P_i^{\sigma} = P_0 \cdot e^{-\frac{E_{des}}{RT}i}$$
(2.6)

where E_{des}/R is the effective heat of desorption (or vaporization) per -CH₂- unit [Geerlings *et al.*, 1999]. The critical chain growth probability is then represented by:

$$\alpha_c = \beta = e^{-\frac{E_{des}}{RT}}$$
(2.7)

At 498 K, the critical chain growth probability is α_c =0.66.

Geerlings *et al.* [1999] argue that E_{des}/R depends on whether the reaction is operated at dry conditions or at wax formation conditions. If $\alpha > \alpha_c$, the wax behaves as a boiling liquid and the equilibrium is directly obtained from gas-liquid data. If $\alpha < \alpha_c$, the equilibrium is characterized by direct adsorption/desorption from the bare metal surface and the effective heat of desorption per -CH₂- unit increases. At a temperature of 493 K, the effective heat of desorption lies between 230 K for liquid behavior of the physisorbed state and 680 K for dry operation. For earlier results obtained on a Co-foil catalyst at 493 K by Kuipers *et al.* [1995], an effective heat of desorption of 410 K for the experiments

performed at 1 bar is obtained, and dry operation of the Fischer-Tropsch reaction is assumed. At 18 bar, however, an effective heat of desorption of 230 K is obtained, corresponding to the presence of a boiling wax layer.

Komaya and Bell [1994a] use a physisorbed state in their Fischer-Tropsch model on a Ru/TiO_2 catalyst at 1 bar and 523 K. At their experimental conditions, the reaction is essentially operated at dry conditions, and the maximum capacity of the physisorbed layer is assumed to be a monolayer on the available Ru metal surface. For the modeling, they assume an effective heat of desorption of 625 K. This is indeed a feasible value for the physisorption equilibrium at 523 K.

Schulz and Claeys [1999] use the solubility argument to explain their results during cofeeding of several 1-olefins in their slurry operation of the Fischer-Tropsch synthesis on a Co/Ru/ZrO₂/Aerosil catalyst at 443-483 K and 7.5-11 bar. They consider the wax phase to be a homogeneous boiling liquid in equilibrium with the gas-phase. In the calculation of the equilibrium coefficient, the non-ideality of the gas phase and the liquid phase is accounted for.

Van der Laan and Beenackers [1998] present a Fischer-Tropsch model on a precipitated Fecatalyst during slurry operation at 523 K and 15 bar that accounts for the readsorption of 1-olefins onto Fischer-Tropsch chain growth sites. They introduce an exponential dependency of the olefin concentration near the catalyst surface on the gas phase concentration:

$$\frac{C_{C_i H_{2i}}}{P_{C_i H_{2i}} / RT} \propto e^{c i}$$

$$(2.8)$$

The parameter c is determined by regression analysis and the model gives a good description of the experimental results for $c=0.29\pm0.07$. This corresponds to an effective heat of desorption of 152 ± 36 K, which is in close agreement with the effective heat of desorption of 197 K that is expected at a temperature of 523 K.

2.6 Relation to present study

From an engineering point of view, the mechanistic details of the Fischer-Tropsch mechanism are not important, since the general behavior of Fischer-Tropsch catalysts with varying process conditions is well known. Dry [1996] states that for the operation of pilot and commercial scale plants with a given catalyst, simple empirical rate equations suffice. However, these empirical rate equations do not give much insight into the surface chemistry of the reaction. The understanding of the surface chemistry of heterogeneous catalystic reactions is generally believed to be essential for catalyst design and optimization.

As illustrated in this chapter, controversies about the Fischer-Tropsch reaction still exist. Although the carbene mechanism receives most support as the Fischer-Tropsch mechanism, still no clear insight into the abundance, reactivity, and chemical identity of the participating surface intermediates is present. The **S**teady **S**tate Isotopic **T**ransient **K**inetic **A**nalysis technique (SSITKA) applied in this work is a suitable means to study these issues at steady state conditions.

A large variety of secondary reactions have been proposed to occur during the Fischer-Tropsch reaction. The extent and nature of the secondary reactions depends on the reaction conditions. At steady state operation at high pressure, chain initiation via the readsorption of reactive olefins onto the catalyst surface is believed to be the dominant secondary reaction. In this work, the Fischer-Tropsch reaction is studied at 498 K and 1.2 bar, leading to a low chain growth probability. It is indicated that at these reaction conditions chain initiation and isomerization are the two dominant secondary reactions of reactive olefins. This is closely related to the absence of a wax layer on the catalyst surface.

Moreover, it is evidenced that the presence of a physisorbed state is essential to explain the results even in the absence of wax formation. Modeling of the experimental results indicates that the chain length dependence of the physisorption equilibrium is responsible for the increasing readsorption of reactive olefins with increasing chain length.

3

Methodology of the Steady State Isotopic Transient Kinetic Analysis (SSITKA) technique

3.1 Introduction

For the kinetic investigation of the Fischer-Tropsch synthesis presented as in this thesis the **S**teady **S**tate Isotopic **T**ransient **K**inetic **A**nalysis (SSITKA) technique, initially developed by Happel, Bennett, and Biloen [Happel, 1978; Bennett, 1982; Biloen *et al.*, 1983], is applied. The technique is based on monitoring isotopic labels in reactants and products in time following an abrupt replacement of a reactant by its isotopic counterpart. The abrupt replacement is realized by a valve, switching between two feed streams that differ in the presence of a labeled reactant in the one feed and an inert tracer in the other. The response of the inert tracer represents the gas hold-up of the reactor system. As with all transient techniques, SSITKA allows the decoupling of rate coefficients and surface concentrations of the relevant species. However, with the SSITKA technique the reaction is operated at steady state conditions. The concentrations of the reaction intermediates present on the catalyst surface therefore do not change during the transient experiment. In contrast with other transient technique allows to study the steady state kinetic behavior of the reaction. The transient responses contain information about the chemical identity, reactivity, and abundance of surface species participating in the reaction.

In this chapter, the methodology of the SSITKA technique is discussed. It focuses on the interpretation and modeling of the experimental data and gives an overview of the strong and weak points of the technique. The SSITKA technique has proven itself in many heterogeneously catalyzed gas-phase reactions [Shannon and Goodwin, 1995], such as the oxidative coupling of methane [Nibbelke *et al.*, 1995], the partial oxidation of methane [Ekstrom and Lapszewich, 1989], the ammonia synthesis [Nwalor *et al.*, 1989], automotive exhaust catalysis [Oukaci *et al.*, 1992], and the methanation and Fischer-Tropsch synthesis [Zhang and Biloen, 1986; Komaya and Bell, 1994a].

3.2 Choice of reactor configuration

For the optimal interpretation of SSITKA data, the transient responses of the reactants and products measured at the reactor outlet must be fully determined by intrinsic kinetic processes. Therefore, knowledge of the transient of the isotope-substituted reactant at the inlet of the reactor is needed. This transient is defined as the forcing curve and is schematically represented in figure 3.1. In general, the isotope substituted reactant and the inert tracer have the same forcing curve, since one strives for inertness of the piping system. The forcing curve is determined by the flow characteristics of

the switching valve and the piping system to the reactor. The forcing curve is thus independent of the reactor configuration.

The transient responses at the outlet of the reactor are additionally determined by kinetics and by the flow characteristics of the reactor itself. The latter is identified by the inert tracer and is defined as the mixing curve. In figure 3.1, the mixing curves for a continuous stirred tank reactor (CSTR) and a plug flow reactor (PFR) are represented. The mixing curve depends on the reactor configuration. The shape of the mixing curve influences the response curves of the reactants and products, and puts an upper limit on the time scale of the processes that can be studied with a given system. The larger the time constant for the mixing curve, the more information about fast kinetic processes is overshadowed by the flow characteristics of the system [*e.g.* Oukaci *et al.*, 1992]. As long as the time constants of the kinetic processes are large compared to the time constant of the mixing curve, relevant kinetic information can be obtained.



Figure 3.1: Schematic representation of the forcing (F) and mixing curves for a PFR and a CSTR set-up (M_{PFR} and M_{CSTR}). The time constant of the forcing curve is 0.5 s and the residence time τ is 1.0 s for both reactor configurations. The time constant of the mixing curve of the PFR set-up remains 0.5 s, whereas the time constant of the mixing curve of the CSTR set-up rises to 1.5 s.

In a CSTR set-up the time constant of the mixing curve is always larger than the time constant of the forcing curve. The increase of the time constant is related to the average residence time in the reactor configuration, see figure 3.1. CSTR behavior of a packed bed configuration is created by:

- applying an external recycle over the packed bed;
- stimulating the back mixing in the packed bed itself.

The application of an external recycle involves the use of a large total volume of the reactor system compared to the volume of the catalyst bed, leading to an increased consumption of isotopes and to a decreased detectability of reaction products [Happel *et al.*, 1986; Koa *et al.*, 1992]. The back mixing in a catalyst bed is increased by using a shallow, wide catalyst bed and a special gas-inlet that mechanically enhances the formation of eddies [Stockwell *et al.*, 1988; Efstathiou and Bennett, 1989; Efstathiou, 1991; Efstathiou *et al.*, 1994].

Plug flow behavior of a gas-solid system is induced if the number of solid particles over the diameter of the reactor surpasses 10 and if the number of particles over the length of the reactor surpasses $20/Pe_{m,l}$, where $Pe_{m,l}$ is the Peclet number for axial mass transport [Froment and Bischoff, 1990]. For the PFR, the mixing curve represents the time delayed forcing curve, since axial gas mixing in the catalyst bed is absent. The mixing and the forcing curves therefore possess identical time constants, see figure 3.1. The time lag of the mixing curve with respect to the forcing curve is equal to the residence time. The configuration and the operation of a PFR are simple and the consumption of isotopic gases is low. It is therefore the most applied reactor configuration for SSITKA

experimentation. Now, only the time constant of the forcing curve determines the applicability of a given set-up. The time constant of the exponential decay of the forcing curve differs considerably between the experimental set-ups reported in literature. It ranges from 14 s for Biloen *et al.* [1983] and Brundage and Chuang [1996] to 2 s for Nibbelke *et al.* [1995]. The configuration in the present work has a time constant of 0.5 s, making it an excellent set-up to study fast kinetic processes.

3.3 Model formation

For an unambiguous interpretation of the transient responses obtained with SSITKA, the kinetic experiment has to obey several restrictions:

- absence of internal and external temperature and mass gradients on catalyst pellet scale;
- absence of kinetic isotope effects;
- isothermal and isobaric operation of the reactor;
- constant total molar flow rate;
- time constants of the kinetic processes sufficiently larger than those of the mixing curve.

A CSTR model is, obviously, justified in case of the operation of a CSTR. If in a PFR, however, the compositions of the gas-phase and of the catalytic surface are homogeneous throughout the catalyst bed, the reactor can be modeled with the assumption of CSTR behavior. Such a situation is generally referred to as differential operation.

A PFR model should be used if the reaction is operated at integral conditions or if reversible reactions are present leading to the occurrence of axial concentration profiles. Both models are discussed in the following sections.

3.4 CSTR model formation

In the CSTR approximation, the reactor model is reduced to a set of ordinary differential equations for the components that participate in the isotopic substitution. Time is the independent parameter. Biloen [1983] illustrates that analytical solutions are easily obtained for simple mechanisms, *i.e.* mechanisms with irreversible surface reactions and without any reversible adsorption of reactants and products. Shannon and Goodwin [1995] published analytical solutions for more complex mechanisms.



Figure 3.2: Simple illustrative reaction mechanisms.

When considering the simple mechanism A of figure 3.2 with only one surface intermediate and irreversible reactions, the mass balances for product *P* in the gas-phase and intermediate B_{ads} on the catalyst surface at steady state are:

$$\varepsilon_{b} V_{R} \frac{dC_{P}^{SS}}{dt} = -F_{V} C_{P}^{SS} + W_{cat} R_{w,P}^{SS} = -F_{V} C_{P}^{SS} + W_{cat} k_{2} L_{B}^{SS} = 0$$

$$dL_{B}^{SS} = -F_{V} C_{P}^{SS} + W_{cat} R_{w,P}^{SS} = -F_{V} C_{P}^{SS} + W_{cat} k_{2} L_{B}^{SS} = 0$$
(3.1)

 $\frac{dL_B}{dt} = k_1 C_R^{SS} - k_2 L_B^{SS} = 0$ (3.2) where C_P^{SS} is the steady state concentration of the gas-phase product *P* in mole m_{gas}^{-3} ; L_B^{SS} is the steady state surface concentration of intermediate B_{ads} in mole kg_{cat}^{-1} ; *t* the time in s; V_R is the volume

of the catalyst bed in the reactor in m_{bed}^{3} ; ε_b is the bed porosity in $m_{gas}^{3} \cdot m_{bed}^{-3}$; F_V is the total volumetric flow in $m_{gas}^{3} \cdot s^{-1}$; W_{cat} is the catalyst mass in kg_{cat}; k_i is the reaction rate coefficient for reaction i of
which the units are reaction dependent; $R_{W,P}^{SS}$ is the steady state production rate of product P in mole·kg_{cat}⁻¹·s⁻¹. In the SSITKA experiment, the reactant *R* is abruptly replaced throughout the whole reactor content by its isotopic substitute $R^{\#}$ at t=0, causing the formation of unlabeled *B* from *R* to drop to zero. The steady state rate of formation of the unlabeled product *P* is disturbed:

$$\frac{dC_P}{dt} = -\frac{1}{\tau}C_P + \frac{\rho_b}{\varepsilon_b}k_2 L_B$$
(3.3)

$$\frac{dL_B}{dt} = -k_2 L_B \tag{3.4}$$

where ρ_b is the bed density in kg_{cat}·m_{bed}⁻³, *i.e.* $\rho_b = W_{cat}/V_R$; and τ the residence time in s, *i.e.* $\tau = \varepsilon_b V_R/F_V$. The initial conditions for this system are:

Initial conditions: t = 0 $C_R = C_{P^{\#}} = L_{B^{\#}} = 0$; $C_{R^{\#}} = C_R^{SS}$ (3.5) Integration of the set of equations (3.3) to (3.5) leads to:

$$C_{P} = C_{P}^{SS} \exp(-t/\tau_{B}) = C_{P}^{SS} \exp(-k_{2} t)$$
(3.6)

$$L_B = L_B^{SS} \exp(-t/\tau_B) = L_B^{SS} \exp(-k_2 t)$$
(3.7)

The reaction rate coefficient k_2 is the reciprocal value of the mean surface residence time of the intermediate B_{ads} :

$$k_2 = \frac{1}{\tau_B} \tag{3.8}$$

Normalization of equations (3.6) and (3.7) leads to:

$$\gamma_{P} = \frac{C_{P}}{C_{P}^{SS}} = \exp(-k_{2} t) \qquad \text{and} \qquad \gamma_{P}^{\#} = 1 - \gamma_{P} = 1 - \exp(-k_{2} t)$$

$$\varphi_{B} = \frac{L_{B}}{L_{B}^{SS}} = \exp(-k_{2} t) \qquad \text{and} \qquad \varphi_{B}^{\#} = 1 - \varphi_{B} = 1 - \exp(-k_{2} t)$$
(3.9)
(3.9)
(3.10)

The transient of
$$P^{\#}$$
, according to equation (3.9), is represented by curve A in figure 3.5. This is a basic type mechanism having a unique response curve. A semi-logarithmic representation of the fraction unlabeled P in time yields the straight line A in figure 3.6, as expected for a pure exponential decay according to equation (3.9).

From the transient of $P^{\#}$ (or *P*), the reaction rate constant k_2 is directly obtained. From the steady state behavior of the reaction, the surface concentration of B_{ads} , L_B^{SS} , is obtained via rearrangement of the source term in equation (3.1):

$$L_B^{SS} = \frac{R_{w,P}^{SS}}{k_2} = R_{w,P}^{SS} \tau_B$$
(3.11)

where $R_{w,P}^{SS}$ is the steady state production rate of *P* in mole kg_{cat}⁻¹·s⁻¹.



As indicated by Shannon and Goodwin [1995], the mean surface residence time of the intermediate B_{ads} , τ_b , is represented by the surface areas between the mixing curve and the transient response for the gas-phase component $P^{\#}$, which is related to this intermediate. This is schematically

shown in figure 3.3. Via the steady state relation (3.11), the surface concentration of this species is obtained. It should be noted that this procedure is not related to any assumption concerning the reaction mechanism and that $\tau_{\rm b}$ is the main parameter that is directly obtained from SSITKA experiments.

The combination of the transient response with the steady state performance during the SSITKA measurement uncouples reaction rate coefficients and surface concentrations. A strong point of the technique is that values of these parameters are obtained at steady state operation of the reaction. However, the accessibility of concentrations of surface intermediates is related to the type of SSITKA experiment. As an example, consider mechanism B of figure 3.2 where an A-labeling experiment is performed via the following isotopic step change: A/B \rightarrow A[#]/B. The transient for A[#]-B is measured at the reactor outlet. Combining the transient with the steady state production rate of AB results in the surface concentration of A_{ads} and the lumped reaction rate coefficient k_3^* , where $k_3^* = k_3 L_B^{SS}$. The surface concentration of B_{ads} is not assessable and neither is the true reaction rate completely unravels the mechanism. Performing A-labeling experiments at different feed compositions reveals the dependency of the production rate of AB on the surface concentration of B, but does not give the absolute value for L_B^{SS} . Therefore, the optimal utilization of the SSITKA technique requires separate labeling of all atoms of all participating reactants.





Figure 3.4: Overview of basic reaction mechanisms, identifiable with the SSITKA technique.

Besides the characteristic curves A in figures 3.5 and 3.6 for mechanism I in figure 3.4, two other basic type mechanisms are represented in figures 3.5 and 3.6 [Sadovskaya *et al.*, 1999]. Curve B is representative for a mechanism with two surface species in series, conform mechanism II in figure 3.4. In figure 3.6, curve B displays an upward convexity. Curve C is representative for a mechanism with either a parallel route or a buffer step, conform mechanisms III to VI in figure 3.4. In figure 3.6 curve C displays a downward convexity. Sadovskaya *et al.* [1999] only mention mechanisms III and IV as the latter basic type mechanism. However, in chapter 7 it is evidenced that mechanisms V and VI also belong to this group, *i.e.* mechanisms III to VI have identical characteristic transient responses.

The shape of the transient response for $P^{\#}$ of a single SSITKA experiment directly identifies which of these three basic type mechanisms is responsible for the formation of *P*. More complex reaction mechanisms, *e.g.* mechanism VII in figure 3.4, are combinations of these basic type mechanisms and can only be identified by multiple experiments at different gas-phase compositions.



Figure 3.5: Transient responses of the isotopic fraction of P. Curve A: τ =5 s; curve B: τ_1 =3 s, τ_2 =5 s; curve C: τ_1 =5 s, τ_2 =30 s;

The fact that mechanisms III to VI have identical characteristic curves in figures 3.5 and 3.6, is defined as model unidentifiability [Happel, 1986, Walter *et al.*, 1986; Soong *et al.*, 1986]. This implies that different mechanistic models give statistically identical descriptions of the experimental data. These unidentifiable models, however, result in different reaction rate parameters and surface concentrations for the intermediate species. Further discrimination between the unidentifiable models must be done in conjunction with information obtained from other sources, such as the use of surface sensitive techniques or theoretical calculations. Model unidentifiability is often neglected in kinetic studies but should be considered essential in mechanistic investigations. This aspect of kinetic modeling is discussed in detail for the Fischer-Tropsch synthesis in this study in chapter 7.

The application of analytical solutions of the ordinary differential equations to obtain quantitative information on the mechanism of methane formation during CO hydrogenation is frequently reported in literature. In most studies the experimental data are obtained in a PFR, while the analytical equations are based on CSTR behavior of the system. The simplest mechanism for methanation is represented by reaction (R-1), in which the CO adsorption is a reversible reaction:

$$CO_{g} \xleftarrow{k_{a}}{k_{d}} CO_{ads} \xrightarrow{k_{1}} C_{1,ads} \xrightarrow{k_{2}} CH_{4,g}$$
(R-1)

In a PFR this leads to the observation of a fast but delayed response for ¹³CO. This so-called chromatographic effect for CO is caused by a fast exchange between gaseous CO and adsorbed CO_{ads} . This reversibility induces an axial isotopic concentration gradient over the PFR, and all reaction steps involving CO_{ads} (CO adsorption, CO_{ads} desorption, and the formation of $C_{1,ads}$) cannot be modeled with the CSTR equations as presented above. It is, however, generally observed that the ¹³CH₄ transient is much slower than the ¹³CO transient. At differential conversions, the evolution of ¹³CH₄ from the $C_{1,ads}$ pool obeys CSTR behavior and the equations presented above can therefore still be applied to the hydrogenation of $C_{1,ads}$ to CH₄. Values for the reaction rate coefficient k_2 and the surface concentration for $C_{1,ads}$ are obtained from the ¹³CH₄ transient.

Shannon and Goodwin [1995] state that the chromatographic effect complicates the interpretation of SSITKA results and should be minimized by applying short residence times in a PFR. In relation to this, Zhang and Biloen [1986] consider the influence of the ¹³CO chromatographic effect on the ¹³CH₄ transient to be negligible if the area between the inert tracer and the ¹³CO transient is less than 20% of the area between the tracer and the ¹³CH₄ transient. This reasoning is not based on any mathematical consideration. We believe, however, that the occurrence of a chromatographic effect in itself reveals mechanistic aspects and does not form an obstacle for modeling. The advice by Shannon and Goodwin [1995] to use a CSTR to eliminate the isotopic concentration gradients and thus simplify the interpretation of transient responses is rejected because of the possible loss of information in CSTR operation of SSITKA experiments. Moreover, the decrease of the chromatographic effect can be used to study for example catalyst deactivation in time [Agnelli *et al.*, 1998]. If the experimental data are obtained in a CSTR reactor, both the ¹³CO and the ¹³CH₄ transients can be modeled and the mechanism of reaction (R-1) is completely quantified [Stockwell *et al.*, 1988].

3.5 PFR model formation

If the reaction mechanism contains reversible reaction steps of reactants or products, or if the experimental data are obtained in an integral operated PFR, the CSTR approach is no longer valid and a PFR model should be applied. The reactor model is represented by partial differential equations in time and in space for the components that participate in the isotopic substitution. The general equation for labeled gaseous component $X^{\#}$ is represented by equation (3.12), and for the labeled surface component $Y^{\#}_{ads}$ by equation (3.13) [Happel, 1986; Ottarod *et al.*, 1992; Nibbelke *et al.*, 1995]:

$$\frac{\partial C_{X^{\#}}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{X^{\#}}}{\partial x} = \frac{\rho_b}{\varepsilon_b} R_{w,X^{\#}}$$

$$\frac{\partial L_{Y^{\#}}}{\partial t} = R_{w,Y^{\#}}$$
(3.12)

The initial and boundary conditions for an isotope step from gas-phase reactant Z to $Z^{\#}$ are:

Initial conditions:	<i>t</i> = 0	$\forall x$	$C_{X^{\#}} = L_{Y^{\#}} = 0$	(3.14-a)
Boundary conditions:	<i>t</i> > 0	<i>x</i> = 0	$C_{Z^{\#}} = input function(t)$	(3.14-b)
	<i>t</i> > 0	<i>x</i> = 0	$C_{x^{\#}} = 0$ for $X^{\#} \neq Z^{\#}$	(3.14-c)

The continuity equations for the CSTR approximation are ordinary differential equations in time. The PFR approximation introduces an additional spatial-position variable, resulting in a set of partial differential equations in time and space. Analytical solutions can only be obtained for the simplest reaction mechanisms, and in general the set of continuity equations (3.12) and (3.13) with the initial and boundary conditions (3.14-a) to (3.14-c) has to be solved numerically.

3.5.1 Differential conditions

Differential operation of the reactor implies that all reaction rates are constant throughout the catalyst bed. In that case, the steady state composition of the gas-phase and catalyst surface is homogeneous within the catalyst bed. These conditions are normally obtained by operating the PFR at low conversions for every reactant. It implies that all product formation reactions are irreversible. The assumption of constant concentrations and constant reaction rates throughout the catalytic bed allows for:

1. The equations to be written in isotope fractions, which are defined as:

$$\gamma_X = \frac{C_{X^{\#}}}{C_X^{SS}}, \qquad \phi_Y = \frac{L_{Y^{\#}}}{L_Y^{SS}},$$
(3.15)

2. The incorporation of the steady state reaction rates into the equations.

$$R_{w,X}^{SS} = \frac{F_X X_X S_X}{W_{cat}} = \frac{\varepsilon_b}{\rho_b \tau} C_X^{SS}$$
(3.16)

This leads to a decreased number of parameters.

As an example, the C-tracing of the methanation reaction (R-1) is used. The continuity equations for CO and CH_4 in the gas-phase are represented by:

$$\frac{\partial C_{13}_{CO}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{13}_{CO}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left(-k_a C_{13}_{CO} + k_d L_{13}_{CO} \right)$$
(3.17)

$$\frac{\partial C_{13}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{13}}{\partial x} = \frac{\rho_b}{\varepsilon_b} k_2 L_{13} c_1$$
(3.18)

For CO_{ads} and $C_{1,ads}$ on the catalyst surface by:

$$\frac{\partial L_{13}}{\partial t} = k_a C_{13}_{CO} - k_d L_{13}_{CO} - k_1 L_{13}_{CO}$$
(3.19)

$$\frac{\partial L_{^{13}C_1}}{\partial t} = k_1 L_{^{13}CO} - k_2 L_{^{13}C_1}$$
(3.20)

At differential conditions the following steady state relations apply:

$$R_{w,CH_4}^{SS} = k_1 L_{CO}^{SS} = k_2 L_{C_1}^{SS} = \frac{\varepsilon_b}{\rho_b} \frac{C_{CH_4}^{SS}}{\tau}$$
(3.21)

$$k_a C_{CO}^{SS} = k_d L_{CO}^{SS} + k_1 L_{CO}^{SS}$$
(3.22)

where the rate of CO consumption is small compared to the rate of CO adsorption/desorption. The number of parameters in the set of partial differential equations (3.17) to (3.20) and the steady state relations (3.21) and (3.22) is eleven, *i.e.* k_a , k_d , k_1 , k_2 , C_{CO}^{SS} , $C_{CH_4}^{SS}$, L_{CO}^{SS} , $L_{C_1}^{SS}$, ε_b , ρ_b , and τ . Of these parameters ε_b and ρ_b are characteristics of the catalyst bed and C_{CO}^{SS} , $C_{CH_4}^{SS}$, and τ result from the steady state operation of the reaction. Incorporating the steady state relations (3.21) and (3.22) into the partial differential equations (3.17) to (3.20) and choosing k_a , L_{CO}^{SS} , and $L_{C_1}^{SS}$ as the model parameters, results in:

 $\frac{\partial \gamma_{co}}{\partial r} = \frac{1}{\partial \gamma_{co}} \frac{\partial \gamma_{co}}{\partial r}$

$$\frac{\partial \gamma_{CO}}{\partial t} + \frac{1}{\tau} \frac{\partial \gamma_{CO}}{\partial x} = \frac{\rho_b}{\varepsilon_b} k_a (\varphi_{CO} - \gamma_{CO})$$
(3.23)

$$\frac{\partial \gamma_{CH_4}}{\partial t} + \frac{1}{\tau} \frac{\partial \gamma_{CH_4}}{\partial x} = \frac{1}{\tau} \varphi_{C_1}$$
(3.24)

$$\frac{d\varphi_{CO}}{dt} = k_a \frac{C_{CO}^{SO}}{L_{CO}^{SO}} (\gamma_{CO} - \varphi_{CO})$$
(3.25)

$$\frac{d\varphi_{C_1}}{dt} = \frac{\varepsilon_b}{\rho_b \tau} \frac{C_{CH_4}^{SS}}{L_{C_1}^{SS}} \left(\varphi_{CO} - \varphi_{C_1} \right)$$
(3.26)

The advantage of the incorporation of the steady state equations (3.21) and (3.22) into the set of partial differential equations (3.17) to (3.20) is the reduction of the number of model parameters to three. The major drawback is the assumption that the steady state parameters C_{CO}^{SS} and $C_{CH_4}^{SS}$ are exact, *i.e.* without experimental error.

3.5.2 Integral conditions

The assumption of differential conditions is violated if the rate of at least one of the reaction steps varies throughout the catalyst bed. This can result from:

• Large conversion of at least one of the reactants, causing axial gradients for the concentrations in the gas-phase and on the surface. Nibbelke *et al.* [1995] correctly account for CH_4 conversions as high as 24 % and O_2 conversions as high as 85 % during a SSITKA study of the oxidative coupling of methane by considering axial concentration gradients.

• The readsorption of a reaction product, causing axial gradients for the concentration of at least the readsorbed reaction product in the gas-phase and on the surface. This is the case for the Fischer-Tropsch synthesis, where readsorption of reactive olefins occurs.

In this case, the reaction rates are a function of the axial position in the catalyst bed and the steady-state axial concentration profiles have to be accounted for. In the steady state the continuity equation for the sum of an unlabeled and labeled gas-phase component is written as:

$$\frac{dC_{X^{\#}+X}}{dx} = -\frac{\rho_b \tau}{\varepsilon_b} R_{w,X^{\#}+X}$$
(3.27)

At steady state, the continuity equation for the sum of an unlabeled and labeled surface intermediate reduces to the following algebraic equation:

$$R_{w,Y^{\#}+Y} = 0 \tag{3.28}$$

Integrating the continuity equations for the gas-phase components (3.17), and simultaneously solving the algebraic equations for the surface components (3.28) leads to the steady state axial concentration profiles.

3.6 Relation to present study

A modeling study by Wojciechowski [1988] illustrates that Fischer-Tropsch models based on completely different assumptions about the surface chemistry result in similar descriptions of the steady state product spectrum. This illustrates that steady state kinetic studies are not capable of proving a proposed reaction mechanism. Transient kinetic techniques are more promising in this respect, because they decouple reaction rate coefficients and surface concentrations. Hence, these techniques are very powerful to identify mechanisms in terms of abundance, reactivity, and chemical identity of the participating surface species. Imposing the transient by changing the feed composition, *i.e.* pulse experiments [Dautzenberg *et al.*, 1977], cyclic feed experiments [Adesina *et al.* 1995], and hydrogenation experiments [Winslow and Bell, 1984], mainly stimulates methane formation and the information obtained about higher hydrocarbon formation is limited. During SSITKA experiments, the steady state is not disturbed and the kinetics of higher hydrocarbon formation can be studied.

The larger part of the SSITKA studies in literature on the Fischer-Tropsch synthesis is limited to the methanation reaction [*e.g.* Schanke *et al.*, 1995]. Only a few studies focus on the C-C bond formation reaction [Zhang and Biloen, 1986; Mims and McCandlish, 1987; Komaya and Bell, 1994a]. Modeling of SSITKA experiments is mainly limited to the CSTR approach of tubular plug flow reactors, which is an unnecessary oversimplification [Bennett, 2000]. Only very few studies deal with plug-flow modeling [Nibbelke *et al.*, 1995; Walter *et al.*, 1995; Sadovskaya *et al.*, 2000].

In the present work, steady state and transient data for the C_1-C_5 hydrocarbon and C_1-C_3 alcohol are obtained using the SSITKA technique applying ¹³C-, ¹⁸O- and D-labeling. A qualitative interpretation of the transients in chapter 6 already highlights important mechanistic aspects. Whereas a qualitative interpretation of the experimental results is often limited to the identification of global mechanistic phenomena, modeling is a more powerful tool for model identification and discrimination. The occurrence of readsorption reactions of reaction products necessitates plug-flow reactor modeling in chapters 7 and 8.

4

SSITKA set-up and experimental procedures

4.1 Introduction

For the kinetic investigation of the Fischer-Tropsch synthesis presented in this thesis the **S**teady **S**tate Isotopic **T**ransient **K**inetic **A**nalysis (SSITKA) technique is applied. The principle of the technique is discussed in chapter 3. The technique is based on monitoring isotopic labels in reactants and products in time following an abrupt replacement of a reactant by its isotopic counterpart. The analysis of the isotope composition of the components in the effluent is generally done by mass spectrometry. However, overlap of the fragmentation patterns for the C₂₊ hydrocarbons during the Fischer-Tropsch synthesis limits the application of on-line mass spectrometry to the detection of methane only. Therefore, a gas chromatography mass spectrometry analysis (GCMS) is applied in this work to assess the isotopic composition of the C₂ to C₅ hydrocarbons and the C₁ to C₃ oxygenates. In this chapter, the preparation and characterization of the catalysts are also discussed.

4.2 The SSITKA set-up

The experimental SSITKA set-up consists of a feed, reactor, and analysis section. A schematic representation of the set-up is given in figure 4.1 and each section will be discussed in detail below. During the experiment, one reactant is abruptly replaced by its labeled counterpart, while an inert tracer is abruptly removed from the feed. The incorporation of the labeled atom into the reaction products is monitored in time and yields information about the underlying reaction mechanism and the chemical composition of the participating surface species.

For a ¹³C-labeling experiment, the isotopic step-change is represented by:

$He/Ne/CO/H_2 \rightarrow He/^{13}CO/H_2$

During the transient experiment, a fast isotopic step-change is required without pressure effects caused by the actual switching. Pressure effects will change the intensity of the signals measured at the outlet due to a changing total pressure in the analysis chamber of the mass spectrometer. Obviously, these responses are not related to changes in the composition of the gas phase and are therefore not desired. This is prevented if the following conditions are met:

- 1) equal total flows;
- 2) equal flow compositions;
- 3) equal pressure-drops towards vent and analysis section.

Restrictions 1) and 2) are met in the feed section, while restriction 3) is met in the reactor section.



Figure 4.1: Schematic representation of the SSITKA set-up. (FC=flow controller; FI=flow indicator; PI=pressure indicator; TC=temperature controller; TI=temperature indicator; TIC=temperature indicator controller; MS=mass spectrometer; GC=gas chromatograph; GCMS=gas chromatograph mass spectrometer; ----- indicates line heating)

4.2.1 Feed section

Mass flow controllers (Bronkhorst) for every component in the feed section provide two feed streams with identical composition and total flow. This satisfies the first two restrictions for the generation of an isotopic step-change without pressure effects. One feed stream contains a maximum of 5 vol% Ne as inert tracer to monitor both the quality of the isotopic step and the gas hold-up in the reactor system. In the other feed stream one reactant is replaced by its labeled counterpart, *i.e.* ¹³C¹⁶O or ¹²C¹⁸O instead of ¹²C¹⁶O, or D₂ instead of H₂. The synthesis gas is diluted with He in one feed stream or He plus Ne in the other feed stream. All except the isotopic gasses are cleaned for traces of oxygen and water by passing them over BTS and molesieve columns. Filters prevent small dust particles from reaching the mass flow controllers. Specifications of the gasses are given in table 4.1.

Gas	Purity	Supplier	Maximum flow
CO	99.997 %	Linde Gas UK	20 sccm
H ₂	99.999 %	Hoekloos	50 sccm
He	99.996 %	Hoekloos	50 sccm
Ne	99.99 %	Air Products	10 sccm
N ₂	99.9999 %	Hoekloos	50 sccm
¹³ CO	¹³ C 99%	Cambridge Isotope Laboratories	20 sccm
C ¹⁸ O	¹⁸ O >95%, ¹² C 99.9%	Isotec Inc.	20 sccm
D ₂	99.8%	Hoekloos	50 sccm

Table 4.1: S	pecifications of t	he gasses	used for the	SSITKA ex	perimentation

4.2.2 Reactor section

The reactor is a stainless steel tubular fixed bed reactor (I.D.=7.0 mm, bed length=40 mm), see figure 4.2. It consists of a main body and two nuts. The reactor is sealed by aluminum packing rings, placed on the inside of the reactor to eliminate dead volumes. The use of tapered reactor in- and outlets also eliminates axial gas mixing. The catalyst bed consists of typically 1 gram of catalyst, diluted with 1 gram of SiC, both with a particle size range from 0.212 to 0.250 mm. The catalyst bed is held in place by two metal gauzes. Two mass-spectrometral sample chambers are present, one upstream and one downstream the catalyst bed. Sampling from the chambers is performed using stainless steel capillaries (I.D.=0.13 mm, L=30 cm). For each sample chamber, two metal gauzes prevent particles from blocking the capillaries. With a 3-way valve (Valco N3WE) one of the two sample lines is linked to the mass-spectrometer. The sample is transferred to the mass-spectrometer via a silica capillary (I.D.=0.15 mm, L=1.0 m). To prevent condensation of water and hydrocarbons, the capillaries are heated to 388 K. The reactor is heated by an electric conductivity oven to a maximum temperature of 773 K.



Figure 4.2: Schematic representation of the SSITKA reactor.

The axial catalyst bed temperature is monitored with a movable thermocouple, placed in the thermocouple tube (I.D.=1.0 mm) in the center of the reactor. At the applied reaction conditions, the axial temperature profiles never exceeded 1 K. All product containing lines and valves are heated to 388 K.



Figure 4.3: Typical normalized Ne transient response of a He/Ne \rightarrow He step change with a total flow rate of 60 Nml·min⁻¹. The time constant for the exponential decay is 0.5 s.

A 4-way valve (Valco N4WE) with a small internal volume (100 μ I) realizes the fast switch between the two feed streams. It is electrically triggered and uses He at 5 bar for the pneumatic switch of the valve. Needle valves are installed in the lines upstream of this valve and in the lines downstream of the reactor and towards the vent. The function of these needle valves is twofold:

- by means of the needle valves downstream the reactor and in the vent the reaction pressure of 1.2 bar is fixed;
- by means of the needle valves upstream of the 4-way valve the pressure drops for both feed configurations are equalized:
 - 1. left through the reactor and right towards the vent
 - 2. right through the reactor and left towards the vent

In both feed lines a manometer is installed to monitor any pressure changes due to the switching of the 4-way valve. The reactor is connected to the 4-way valve via a SiC filled tube (I.D.=3.0 mm, L=60 mm). This tube is connected to the 4-way valve via a capillary (I.D.=0.40 mm, L=10 mm). This capillary is kept as short as possible to minimize axial gas mixing.

A characteristic step change He/Ne \rightarrow He is shown in figure 4.3, where the normalized Ne response goes from unity to zero in typically 2 s. Uniformity of the transient response upstream and downstream the catalyst bed confirms the plug-flow regime of the reactor. The exponential decay of the Ne transient has a time constant of 0.5 s.

Axial temperature gradients in excess of 1 K were not measured. Moreover, it was calculated that the pressure drop over the catalyst bed is negligible. It is verified that all criteria for intrinsic kinetics [Froment and Bischoff, 1990], are met for all applied experimental conditions. Intrinsic kinetic conditions imply the absence of concentration and temperature gradients:

- in the catalyst pellets;
- between the continuous gas phase and the pellet;
- in radial position in the catalyst bed.

4.2.3 Analysis section and data treatment

The steady state performance of the catalyst is monitored by on-line gas chromatography (GC), quantifying the C₁ to C₁₀ product spectrum. On-line quadrupole mass spectrometry (MS) with gas sampling via heated capillaries is used to monitor the transient responses of the reactants and products having characteristic m/e values. All products other than methane do not possess characteristic m/e values and therefore cannot be monitored by on-line MS. The transient responses of the C₂ to C₅ hydrocarbons and C₁ to C₃ oxygenates are therefore obtained on a gas chromatograph mass spectrometer (GCMS) equipped with a 12-loop sample valve. Each analysis is discussed in detail below.

On-line gas chromatography

The gas chromatograph uses two parallel lines:

- TCD detection of N₂, CO, CH₄, CO₂, C₂ to C₄ hydrocarbons, and C₁ to C₃ oxygenates;
- FID detection of C₄ to C₁₀ hydrocarbons and C₁ to C₄ oxygenates.

A schematic representation and the specifications of the analysis are given in appendix 1. Chromatograms for both lines and the corresponding peak identification are listed in appendix 2. The molar flows of the reactants and products in the first line are quantified using N₂ as internal standard. A mass flow controller feeds the N₂ between the outlet of the reactor and the inlet of the GC. In the second line the quantification of the molar flows is realized by coupling the sum of the C₄ components on both lines. The contribution of 1-butene in the total amount of C₄ on both lines is used as an extra check for a correct coupling of both lines.

The CO conversion is calculated according to the normalization method:

$$X_{CO} = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} = 1 - \frac{A_{CO}K_{CO}}{A_{CO}K_{CO} + \sum_{i=1}^{n} n_i A_{C_i}K_{C_i}}$$
(4.1)

The selectivities towards the individual components on carbon-basis are calculated according to the same principle:

$$S_{j} = \frac{n_{j}F_{j}}{F_{CO,in} - F_{CO,out}} = \frac{n_{j}A_{j}K_{j}}{\sum_{i=1}^{n} n_{i}A_{C_{i}}K_{C_{i}}}$$
(4.2)

Conversions and selectivities are calculated on a CO_2 free basis. This reaction product is not considered as a typical Fischer-Tropsch product for Co-based catalysts and its selectivity is generally low. Typical CO_2 selectivities of 3 mole C% are observed.

The product spectrum on the second line is identified by gas chromatography mass spectrometry using a Shimadzu QP 5000 GCMS. The product spectrum consists of n-paraffins, iso-paraffins, 1-olefins, internal-olefins, iso-olefins, 1-alcohols, and aldehydes. No aromatic products are identified. The iso-olefins and iso-paraffins are mainly methyl-components and the internal-olefins are mainly 2-olefins. The peak identification is in good agreement with peak identifications of naphtha [Shiomi *et al.*, 1991] and gasoline [White *et al.*, 1992]. Since water is not quantified, only the carbon mass balance is checked. All experiments have C-mass-balances with a maximum deviation of 5% from unity.

The calibration factors, K_{j} , in equations (4.1) and (4.2) are obtained from injection of gas and liquid mixtures of known compositions. The calibration factors for the FID detection of the D-labeled C₄ to C₁₀ hydrocarbons are assumed to be similar to the non-labeled hydrocarbons [Brundage and Chuang, 1996]. The calibration factors for the TCD detection of the D-labeled C₁ to C₄ hydrocarbons are corrected using the thermal conductivity factors for methane and ethene [Vargaftik *et al.*, 1996]. It is assumed that all C₂ to C₄ hydrocarbons display a similar increase in conductivity upon D-labeling as ethene does.

On-line mass spectrometry

The Balzers ThermoStar mass spectrometer is used for the detection of the Ne tracer, reactants, and light reaction products, as listed in table 4.2.

ne reactants, and light reaction products.						
Component	m/e value	Component	m/e value			
H ₂ - D ₂	2 - 4	Ne	20			
¹³ CH₄	17	CO, ¹³ CO	28, 29			
$CH_4 - CD_4$	15 - 20	CO_2 , ¹³ CO_2	44, 45			

Table 4.2: Overview of the m/e values for the on-line MS analysis of the Ne tracer, the reactants, and light reaction products.

The transient responses are normalized between the initial MS intensity before the isotopic step change and the final MS intensity at the moment in time when the unlabeled atom in all surface and gas phase species is replaced by its labeled counterpart.

The maximum sampling frequency of the mass-spectrometer is 50 Hz monitoring a single m/e value. To improve the signal to noise ratio, a frequency of 25 Hz is used. In section 6.2.1 the importance of a high signal to noise ratio will be emphasized. Monitoring a set of 7 m/e values results in a sampling frequency of 3 Hz.

The transient responses of methane in a D-labeling experiment cannot directly be obtained because of overlap of the fragmentation patterns going from CH_4 to CD_4 . Instead, the MS monitors all responses in the m/e region of 15-20, following the elimination of the disturbing signals for water (m/e region 16-20). The experimental procedure for the elimination of water is described in section 4.2.5. Baseline corrections are applied and a correction for the contribution of CO to the signal at m/e=16 is performed. The corrected m/e responses are then used to calculate the isotopic composition at every point in time using the same principles as with the GCMS analysis, which will be described in the next section. The major difference, however, is that the fragmentation patterns of the individual isotopic variants are not easily obtained from the non-labeled component due to the isotope effect on fragmentation, caused by replacing H by D [Derrick, 1983]. The fragmentation patterns of the isotopic variants are calculated according to the statistical model proposed by Lenz and Conner [1985], which accounts for the H/D isotope effect on fragmentation. Their model requires the fragmentation patterns for the perhydro- and the perdeutero-components and uses an isotope factor for the initial C-H bond rupture. This isotope factor reflects the preference of breaking a C-H bond over a C-D bond.

Furthermore, the decrease in the concentration of methane has to be taken into account. This change in steady state performance is due to the H/D isotope effect on reaction. This is discussed in detail in section 4.2.6.

The pump capacity of the mass-spectrometer is insufficient for the effective removal of H_2 from its analysis chamber. This results in the detection of H_2 molecules that dwell in the analysis chamber and causes the transients for H_2 to tail.

On-line Gas-Chromatography-Mass-Spectrometry

The specifications of the gas chromatography mass spectromety analysis are given in appendix 1. Chromatograms for the columns and the corresponding peak identification are listed in appendix 3. A 12-loop sampling valve (Valco E-3-CST-12P) is installed to collect samples during the transient experiment, which are sequentially analyzed by GCMS. This 12-loop valve is placed in a thermostat and the samples are kept at 373 K. Switching of both the 4-way valve before the reactor to initiate the transient experiment and the 12-loop valve is controlled by the HP-ChemStation software. This leads to well defined sample times.

The ¹³CO SSITKA experiment produces a hydrocarbon product mixture, containing not only different hydrocarbon types, but also the non-, partially, and fully labeled variants for each hydrocarbon type. The GCMS analysis of this mixture is represented in figure 4.4:

- 1. each sample is separated into the different reaction products;
- 2. the fragmentation pattern of each reaction product is recorded;
- the composition of the mixture of different isotopic variants of the particular reaction product is calculated from this fragmentation pattern.



Figure 4.4: Schematic representation of the GCMS analysis of the Fischer-Tropsch product spectrum:

1) separation of the Fischer-Tropsch product mixture into the different hydrocarbons by GC;

2) monitoring of the fragmentation pattern for every hydrocarbon;

3) calculation of contribution of every isotopic variant to the observed fragmentation pattern.

The observed fragmentation pattern is a linear combination of the individual fragmentation patterns of all isotopic variants of the reaction product. By minimizing the difference between the observed and the calculated values for every m/e position in the fragmentation pattern, the contribution of each isotopic variant can be quantified. The objective function is defined by:

$$S(\mathbf{x}) = \sum_{i=1}^{m} \left(\sum_{j=1}^{n} (x_{i,j} \cdot f_{i,j}^{ref}) - f_i^{obs} \right)^2 \xrightarrow{\mathbf{x}} minimum$$
(4.5)

where $S(\mathbf{x})$ is the objective function; *n* is the number of isotopic variants of a given reaction product; *m* is the number of m/e values of the fragmentation pattern of a given reaction product; f_i^{obs} is the observed intensity of the fragmentation pattern of the mixture at the ith m/e value; $f_{i,j}^{ref}$ is the intensity of

the fragmentation pattern of the jth isotopic variant at the ith m/e value; $x_{i,j}$ is the fractional contribution of the jth isotopic variant to the mixture at the ith m/e value.

This procedure requires the fragmentation patterns of each isotopic hydrocarbon in the product mixture to be known. These patterns are derived from the patterns of the non-labeled component, assuming that:

- peak intensities do not change when replacing ¹²C by ¹³C;
- secondary fragmentations can be neglected.

The quantification of the fragmentation patterns for every isotopic variant can, however, only be done for symmetrical hydrocarbons (n-paraffins, ethene, and 2-butenes) and for alcohols. For asymmetrical hydrocarbons (*e.g.* propene), the fragmentation patterns are too complex and only the overall fraction labeling can be obtained by using the m/e region corresponding to the non-fragmented molecule.

When applying the technique described above it is observed that the isotopic composition at the end of the SSITKA experiment does not reach a level of fully labeling, see figure 4.5. A typical isotopic composition at the end of the SSITKA experiment is $95\%^{13}C_x$ and $5\%^{12}C_{x-1}^{13}C_{x-1}$. This discrepancy is caused by:

- the negligence of the influence of ¹³C-labeling on the fragmentation pattern;
- the negligence of the natural ¹³C abundance in the non-labeled component from which all other fragmentation patterns are calculated;
- the negligence of the impurity of the ¹³CO gas.

These three effects cause the fragmentation pattern for e.g. ${}^{13}C_2H_6$ and ${}^{13}C_2H_4$ to deviate slightly from ${}^{12}C_2H_6$ and ${}^{12}C_2H_4$, as indicated in table 4.3. In this table all fragmentation patterns are calibrated with the pure components. The ${}^{13}C_2H_6$ and the ${}^{13}C_2H_4$ have an isotopic purity of 99% ${}^{13}C$. Both ${}^{12}C_2H_6$ and ${}^{12}C_2H_4$ have a natural abundance of ${}^{13}C$. If the fragmentation pattern for ${}^{12}C_2H_6$ is used to calculate the isotopic composition corresponding to the fragmentation pattern for ${}^{13}C_2H_6$ of table 4.3, the following composition is obtained: 0.4% ${}^{12}C_2H_6$, 1.6% ${}^{13}C^{12}CH_6$, and 98% ${}^{13}C_2H_6$. The same procedure for ethene results in 1.7% ${}^{12}C_2H_4$, 2.3% ${}^{13}C^{12}CH_4$, and 96% ${}^{13}C_2H_4$.

Iau	ie 4.3. Campialeu naginentation patterns ior.
1	$^{12}C_{2}H_{4}$ and $^{12}C_{2}H_{4}$ (^{13}C according to natural abundance)
~	1^{3} 1^{3} 1^{3} 1^{3} 1^{3} 1^{3} 1^{3}

2. C_2H_6 and	d ¹⁶ C ₂ H ₄ (99% ¹⁶	C)			
m/e	¹² C ₂ H ₆	¹³ C ₂ H ₆	m/e	¹² C ₂ H ₄	¹³ C ₂ H ₄
25	2		24	1	
26	17		25	7	
27	29	3	26	46	2
28	100	17	27	55	9
29	24	31	28	100	48
30	29	100	29		57
31		21	30		100
32		27			





Figure 4.5: Transient responses of the isotopic variants of ethane before correction.

 $1^{12}C_{2}H_{6}$; $\mathbf{I}^{12}C^{13}CH_{6}$; $\mathbf{A}^{13}C_{2}H_{6}$

Figure 4.6: Transient responses of the isotopic variants of ethane after correction for the final level of ¹³C-labeling. \blacklozenge ¹²C₂H₆; \blacksquare ¹²C¹³CH₆; \bigstar ¹³C₂H₆

For every SSITKA experiment a minimum of two samples are taken at the point in time that would correspond to a level of 100% labeling. This minimum of two sample points provides a reference for a correction for the deviation from 100% labeling. The resulting corrected transient responses of the isotopic variants for ethane are represented in figure 4.6. All characteristic features of the transient responses are maintained. This procedure is applied to all components that are monitored by GCMS.

Two other GCMS analysis techniques for the detection of the isotopic composition of Fischer-Tropsch product spectrum are reported in literature. Both techniques involve conversion of the hydrocarbons into C_1 species between the GC separation and the MS detection. The isotopic composition of the C_1 represents the overall isotopic composition of the corresponding hydrocarbon. The first technique involves combustion of the hydrocarbons to CO_2 [Matthews and Hayes, 1978], also known as isotope-ratio-monitoring-GCMS. A variant uses hydrocracking of the hydrocarbons to methane [Stockwell *et al.*, 1988]. The major disadvantage of both techniques is that the hydrocarbon skeleton is destroyed and only the overall fraction labeling is obtained.

4.2.4 Catalyst activation and conditioning

The activation and conditioning of the catalyst is performed as follows:

- 1. All catalysts are activated *in-situ* by reduction in diluted H₂ (60 Nml·min⁻¹, 20 vol% H₂ in He). A high gas flow and a low heating rate of 3 K·min⁻¹ is chosen to avoid catalyst destruction by the release of excess amounts of H₂O formed during the reduction. The final activation temperature is held for 16 hours and depends on the catalyst used, *i.e.* 673 K for the TiO₂ supported catalysts and 533 K for the sponge catalysts. The degree of reduction at these activation temperatures is verified by temperature programmed reduction experiments, which are discussed in section 4.5.2.
- 2. The catalyst is cooled to the reaction temperature in diluted H_2 (50 Nml·min⁻¹, 70 vol% H_2 in He).
- 3. The Fischer-Tropsch synthesis is started with diluted syngas (110 Nml·min⁻¹, 60 vol% He). The dilution is gradually decreased to the final reaction conditions (65 Nml·min⁻¹, 40 vol% He).
- 4. The catalyst is conditioned for at least 24 hours. The catalyst activity and some Fischer-Tropsch characteristics (chain growth probability, methane selectivity, and C₄ paraffin selectivity) for a typical experiment are illustrated in figures 4.7 and 4.8. During the conditioning, the CO conversion drops from initially 16% to a steady state level of 11%. The chain growth probability and the selectivity to methane are constant during the entire period, while the paraffin selectivity, plotted for the C₄ hydrocarbons in figure 4.8, decreases in the first 20 hours. From figures 4.7 and 4.8 it is concluded that the catalyst performance is stable after 20 hours of catalyst conditioning. The conditioning only causes the total number of active sites to decrease, because the product spectrum is hardly influenced and only the paraffin selectivity decreases. The increase in activity during the D₂ SSITKA experiment is due to the H/D kinetic isotope effect observed when replacing H₂ by D₂. This is discussed in detail in section 4.2.6.





Figure 4.7: CO conversion during catalyst conditioning and experimentation on the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H_2 /CO=2.

Figure 4.8: Methane selectivity (\bullet), paraffin selectivity for C₄ (\blacktriangle), and chain growth probability α (\Box) during catalyst conditioning and experimentation on the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H₂/CO=2.

4.2.5 Experimental procedures

Prior to the actual experiment, the isotopic step is optimized by eliminating any pressure effects during the step-change. Needle valves are used for the control, while pressure effects are monitored with manometers. Following the optimization of the step change, the relevant feed lines are flushed with the isotopic component. To minimize the loss of isotopes, the manometers are bypassed by means of 4-way valves. These 4-way valves have a low flow resistance. The HP-ChemStation software of the GCMS controls the time programming of the step-change, the filling of the sample-loops and the subsequent analysis of each loop. This assures a strict definition of the sample times.

When studying the incorporation of D_2 into methane with on-line MS during a D_2 SSITKA experiment, two adaptations to the experimental procedure are made:

- He is replaced by N₂ since He and D₂ both have a response at m/e=4. The isotopic step change is now represented by N₂/Ne/H₂/CO → N₂/D₂/CO.
- 2. The influence of D-labeled H₂O on the transient responses of D-labeled CH₄ has to be eliminated because CD_xH_{4-x}, where x=0-4, and D_xH_{2-x}O, where x=0-2, have overlapping fragmentation patterns.

For the latter, water is trapped by cooling the stainless steel sampling capillary downstream the reactor with cold-ice (water + acetone). In this way the transients due to D-labeled H_2O are eliminated. The capacity of the capillary is limited and the ice-cooling can only be applied for about 10 minutes before noticeable blocking occurs. However, this period is sufficiently long to perform the measurements. Subsequent heating easily cleans the capillaries.

The effectiveness of this method to eliminate the contributions of H₂O, HDO, and D₂O in the MS signals is illustrated in figures 4.9 and 4.10. In the figures, the transient responses in the m/e 15-20 range are shown following a N₂/Ne/CO/H₂ \rightarrow N₂/CO/D₂ step change. In figure 4.9 the results are shown when the capillary is heated to 383 K and in figure 4.10 when it is cooled to 263 K.



Figure 4.9: Transient responses of the m/e range from 15 to 20 when heating the capillary to 383 K.

Figure 4.10: Transient responses of the m/e range from 15 to 20 when cooling the capillary to 263 K.

In figure 4.9, all transients corresponding to H_2O , HDO, and D_2O , *i.e.* m/e values of 17-20, respond relatively slow. However, the transients not corresponding to water but to CH₄, *i.e.* m/e values of 15 and 16, are fast. If cooling is applied, the transient responses of figure 4.10 are obtained. Now, the intensities of m/e 18 and 20, corresponding to H_2O and D_2O respectively, are much lower, illustrative for the effectiveness of the cold trap. Besides that, the transient responses formerly corresponding to the isotopic variants of water are now as fast as the responses corresponding to CH₄. This also illustrates that the responses are dominated by the isotopic variants of methane. The contribution of water is not completely eliminated, as is illustrated by the slow decrease of the signal at m/e 18 and the small increase of the signal at m/e 20 at high times (>20 s), when the contribution of methane is already constant. Therefore, only the first 10-20 seconds of the transient responses after the step-change are used for mechanistic interpretations.

The detection of water by MS is problematic because of sorption in the capillaries and on the walls of the vacuum chamber of the MS. The elimination of the contributions of water is therefore an essential step in on-line MS analysis of methane during D_2 SSITKA experiments.

4.2.6 Kinetic isotope effects

The kinetic isotope effect is defined as the difference in reactivity of a labeled molecule or atom compared to its unlabeled counterpart. If severe kinetic isotope effects are observed experimentally, the interpretation of the results becomes more difficult and modeling becomes disputable if they are not accounted for. The identification of these effects is therefore important.

The kinetic isotope effect of ¹³CO and C¹⁸O is determined by comparing the steady state performance before, during, and after the isotopic replacement. No changes in CO conversion or in product selectivities are observed, indicating a negligible kinetic isotope effect for ¹³C- and ¹⁸O-labeling.

In contrast to ¹³C- and ¹⁸O-labeling, a clear isotope effect is observed when replacing H_2 with D_2 . The analysis of the activity in D_2 is executed one hour after the replacement of H_2 by D_2 . All other process conditions are kept constant.

i i i a coxponinioni					
H ₂ /CO	W _{cat} /F	$X_{CO}(D_2)/X_{CO}(H_2)$			
-	kg _{cat} ·s·mole⁻¹	-			
5	7.92	1.3			
5	13.7	1.3			
2	24.2	1.3			
2	36.6	1.4			
1	16.8	1.3			
1	44.8	1.3			

Table 4.4: Enhancement of CO conversion by replacing H_2 by D_2 during the D_2 SSITKA experiments at the various experimental conditions.

The replacement of H_2 by D_2 clearly enhances the CO conversion, and therefore the activity of the catalyst. This phenomenon is known as the H/D isotope effect on reaction [Kobori *et al.*, 1981], not to be confused with the H/D isotope effect in fragmentation [Derrick, 1983] as mentioned in section 4.2.3.2. The ratio of the CO conversion in the presence of D_2 to the CO conversion in the presence of H_2 is summarized in table 4.5. If this ratio is greater than unity, the isotope effect is called inverse, if the ratio is smaller than unity, the isotope effect is called normal. According to table 4.4, the inverse H/D isotopic effect on the overall activity of the catalyst amounts to 1.3 and is independent of the reaction conditions. An inverse H/D isotope effect is, for example, also observed by Kobori *et al.* [1981] and Agnelli *et al.* [1998] for the CO hydrogenation reaction. The first, however, mention that normal isotope effects and the absence of isotope effects have also been reported.

The replacement of H_2 by D_2 severely influences the Fischer-Tropsch product spectrum, see table 4.5. The chain growth probability increases, the selectivity to olefins increases (illustrated for C_5), and the methane selectivity decreases. The decreased methane selectivity is not solely the result of the increased selectivity for the heavier hydrocarbons, but also of the lower rate of methane formation.

 Table 4.5: Influence of the kinetic H/D-isotope effect on the Fischer-Tropsch product spectrum, illustrated for three experimental conditions.

			H ₂			D_2		
H ₂ /CO	W _{cat} /F	α_{3-9}	X _{co}	Solefin	α ₃₋₈	X _{co}	Solefin	C_{CH4}/C_{CD4}
-	kg _{cat} ·s·mole⁻¹	-	%	for C_5	-	%	for C_5	-
1	44.8	0.62	8.14	34.4	0.77	10.6	47.4	1.18
2	24.2	0.52	10.6	15.1	0.71	15.9	25.3	1.16
5	13.7	0.43	19.7	3.9	0.63	29.4	6.1	1.13

Brundage and Chuang [1996] observe a thermodynamic isotope effect for H_2/D_2 exchange during the ethylene hydroformylation reaction on a Rh/SiO₂ catalyst. They report a ratio of adsorption equilibrium constants for H_2 and D_2 larger than unity:

$$\frac{K_{H_2}}{K_{D_2}} = \frac{L_H^2}{L_D^2} > 1$$
(4.6)

The surface concentration of deuterium is therefore smaller than the surface concentration of hydrogen during the D₂ SSITKA experiment. Ozaki [1977] concludes that this is also true for the Fischer-Tropsch reaction on Ru and Ni supported catalysts. The same conclusion is obtained by analyzing the transient responses of ¹³C-labeling of methane published by Angelli *et al.* [1998] and Marquez-Alvarez *et al.* [1998]. Both articles report on SSITKA investigations of the methanation reaction under identical experimental conditions and on the same Ni/SiO₂ catalyst. Angelli *et al.* [1998] apply a ¹²CO/H₂ \rightarrow ¹³CO/H₂ isotopic step change and Marquez-Alvarez *et al.* [1998] a ¹²CO/D₂ \rightarrow ¹³CO/D₂ isotopic step change. The response time for methane is larger in the presence of D₂ than in the presence of H₂ at 523 K, atmospheric pressure, and H₂/CO=2. The mean surface residence time of the methane intermediate increases by a factor of 2. If it is assumed that the methanation reaction has a first order dependency on the surface concentration of H, we conclude that $\frac{12}{L_H} \leq L_D \leq L_H$ at their experimental conditions. The exact ratio depends on whether the isotope effect manifests itself in a change in surface concentration ($L_D = \frac{1}{2} L_H$) or in a change in hydrogenation activity ($L_D = L_H$).

The simultaneous increase in CO conversion, chain growth probability, and olefin selectivity in table 4.5 cannot be explained by a change in hydrogen surface concentration. Therefore, the inverse H/D isotope effect does not only result in a lower surface concentration of D_{ads} compared to H_{ads} , but also represents an increased reactivity of D_{ads} towards the formation of building blocks.

An elaborate investigation of the H/D kinetic isotope effects falls outside the scope of this thesis. Without the quantification of these effects, the results obtained by D_2 SSITKA are not suitable for modeling. However, a qualitative interpretation of the D-incorporation into methane, ethane, and ethene yields information about the chemical composition of surface species and the occurrence of surface reactions during the Fischer-Tropsch synthesis.

4.3 Catalyst preparation

For the experimental work on the SSITKA set-up, a $Co/Ru/TiO_2$ catalyst, a Co/TiO_2 catalyst, and a Co-sponge catalyst are used. The composition and the preparation of the $Co/Ru/TiO_2$ catalyst and the Co/TiO_2 catalyst are based on the work of Iglesia *et al.* [1993b].

The synthesis and characterization of the catalysts are discussed below. All catalysts are obtained as μ m-powder. To perform intrinsic kinetic measurements in packed bed reactors, particle sizes in the order of 0.20 mm are desirable. The catalysts are uniaxially pelletized at 10⁸ Pa during one minute. The resulting pellets are cleaned, crushed, and sieved into different particle size fractions. The particle size fractions of 0.150 mm to 0.212 mm and of 0.212 to 0.250 mm are used for the kinetic experiments.

Inert material

In particular cases the batches of catalyst in the SSITKA experiments are diluted with SiC. The SiC is obtained from Merck as particles at a sieve fraction of d_p <0.3 mm. The particles are cleaned by several cycles of boiling for 15 min in HNO₃ and for 30 min in demineralized water.

TiO₂ support pretreatment

 TiO_2 obtained from Degussa (P25, 16 % Rutile) is calcined at 923 K for 2 hours to increase the Rutile fraction to 76 %.

Co/TiO₂ synthesis

40 g of pretreated TiO₂ support is impregnated to incipient wetness with a solution of 34.8 g $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 35 ml water over a period of circa 1 hour. The wet solid is left overnight in a closed vessel to avoid evaporation, and then dried for 2 hours at 383 K. The calcination is performed in a closed vessel at 673 K during 4 hours following heating in two stages, *i.e.* 298 K to 573 K at 20 K min⁻¹, and 573 K to 673 K at 10 K·min⁻¹. The calcined Co/TiO₂ is transferred to a fixed bed reactor and reduced in a H₂ flow (2 NI·h⁻¹·g_{cat}⁻¹) at 673 K for 16 hours following heating at 10 K·min⁻¹. After cooling in a H₂ flow the catalyst is passivated with diluted O₂ (1 %) in N₂ for 2 hours (2 NI·h⁻¹·g_{cat}⁻¹).

Co/Ru/TiO₂ synthesis

The Co/TiO₂ catalyst is impregnated with an acetone solution of ruthenium nitrate of 10^{-3} M. The slurry is stirred for 2 hours and the solvent is slowly evaporated under vacuum. The solid is calcined at 573 K for 4 hours following a two step heating process from 298 K to 473 K at 20 K·min⁻¹ and from 473 K to 573 K at 10 K·min⁻¹. The subsequent elemental analysis determined the composition to be Co(12.04wt%)/Ru(0.18wt%)/TiO₂.

Co sponge catalyst

The cobalt sponge is prepared by pelletizing a Co powder, supplied by ALFA Johnson Matthey as a 1.6 μ m powder with a purity of 99.8 % on metal basis. The obtained Co-sponge catalyst had sufficient mechanical robustness and no additional H₂-sintering was necessary [Sakka, 1991].

4.4 Catalyst characterization

Inert material

The porosity of the SiC is analyzed via the N₂ BET method on the Micromeritics ASAP 2010 apparatus. The SiC is a non-porous material, having a specific gravity of 3220 kg \cdot m_p⁻³.

TiO₂ supported catalysts

The porosity and the surface area of the Co/Ru/TiO₂ catalyst are determined via the N₂ BET method performed on the Micromeritics ASAP 2010 apparatus. The surface area is 21 m²·g_{cat}⁻¹ and the porosity of the catalyst pellet is 0.37 m_g³·m_p⁻³. This leads to a specific density for the Co/Ru/TiO₂ catalyst of 2990 kg·m_p⁻³.

The Co-metal dispersion of the Co/Ru/TiO₂ catalyst is determined via different techniques within the ParSEC project. These include Temperature Programmed Reduction (TPR), O₂ pulse titration, CO pulse titration, and H₂ chemisorption. The results, together with the data from Iglesia *et al.* [1993], are listed in table 4.6. Apparently, the value for the Co-dispersion depends on the technique used. Schanke *et al.* [1995] indicate that the Co-dispersion of their Al₂O₃ and SiO₂ supported Co catalysts is different for CO and H₂ chemisorption. They report an H_{ads}/CO_{ads} ratio larger than unity, but they mention that H_{ads}/CO_{ads} ratios smaller than unity have also been reported. Based on the results in table 4.6, the Co-dispersion is taken to be 3.0 %. This results in a total number of active Co surface sites of 6.18 10^{-2} mole_{Co.surf} kg_{cat}⁻¹.

Technique	Partner	D /%
H ₂ chemisorption at 373 K	TUE	1.3
H ₂ chemisorption at 293 K	Sintef	3.4
CO-pulse	Bochum	1.7
TPR	Eniricerche	3.3
O ₂ pulse	Eniricerche	2.6
H ₂ chemisorption at 373 K	Iglesia <i>et al.</i> [1993a]	2.6

Table 4.6: Dispersion of the active metal of the Co/Ru/TiO₂ catalyst determined by different techniques.

The reducibility of the TiO₂ supported catalysts is studied by Temperature Programmed Reduction (TPR). The TPR is performed in a diluted H₂ flow (4 % H₂ in N₂) from ambient temperature to 1073 K with a heating rate of 3 K·min⁻¹. The TPR spectrum of the Co/TiO₂ catalyst is shown in figure 4.11, the one of the Co/Ru/TiO₂ catalyst in figure 4.12. For both catalysts two large peaks are observed, at 570 K and 471 K for the Co/Ru/TiO₂ catalyst and at 675 K and 615 K for the Co/TiO₂ catalyst. These two peaks are ascribed to the stepwise reduction of Co-oxide from Co₃O₄ via CoO to Co [Sexton *et al.*, 1986; Choi, 1995; Iglesia *et al.*, 1993]. The Ru-promotor is clearly responsible for the decrease in the reduction temperature by roughly 100 K.



Figure 4.11: TPR spectrum of the Co/TiO₂ catalyst. W_{cat} = 0.037 g, heating rate=3 K·min⁻¹.

Figure 4.12: TPR spectrum of the Co/Ru/TiO₂ catalyst. W_{cat} =0.029 g, heating rate=3 K·min⁻¹.

Co-sponge catalysts

Two Co-sponge catalyst samples are analyzed by X-ray defraction (XRD). A fresh Co-sponge catalyst consists of a mixture of hexagonal and cubic phases. No large contributions for Co-oxides are observed, indicating that the Co-sponge catalyst only contains a thin external oxide layer. A Co-sponge catalyst that is activated by reduction, used for Fischer-Tropsch synthesis, and cooled to room temperature under reductive conditions, is also analyzed. A catalyst subjected to such a procedure is referred to as "used". The used Co-sponge is mainly hexagonal and again no large Co-oxide phases are detected. The reduction procedure transforms the cubic phase into the thermodynamically more stable hexagonal phase with a site density of 11.2 atoms·nm⁻² [Reuel and Bartholomew, 1984].

Scanning electron microscopy (SEM) is applied to visualize the sponge structure of the Cosponge catalyst. In figures 4.13 and 4.14, SEM pictures of a used Co-sponge catalyst are presented. A characteristic pore diameter of 1 μ m is deduced from figure 4.19. In this figure the grain-size of 1.6 μ m of the original Co-powder is clearly observed. The structure of the used Co-sponge appears to be rougher than that of the fresh Co-sponge (SEM pictures not presented), but no other differences are observed.



Figure 4.13: SEM picture of the used Co-sponge catalyst at $100 \ \mu m$ as characteristic scale.



Figure 4.14: SEM picture of the used Co-sponge catalyst at 1 μ m as characteristic scale.

The porosity of the Co-sponge catalysts is analyzed by Kr BET and Hg-porosimetry. The Kr BET specific area of a fresh and a used Co-sponge sample is measured on a micromeretics ASAP 2010 apparatus, using the 0.30 to 0.25 mm particle size fraction. For the fresh sample, the specific surface area is $1.09 \text{ m}^2 \cdot \text{g}^{-1}$ and the porosity is $0.04 \text{ m}_g^3 \cdot \text{m}_p^{-3}$. The specific surface area for the used sample is $0.70 \text{ m}^2 \cdot \text{g}^{-1}$. It is assumed that this decrease is caused by sintering during the reduction procedure. The total number of active Co surface sites amounts to $1.31 \cdot 10^{-2} \text{ mole}_{\text{Co,surf}} \cdot \text{kg}_{cat}^{-1}$. The BET technique is specific for determining the porosimetry for micro-porous materials and the results indicate that the grains of the sponge are non-porous. The macro porosity cannot be assessed by the BET technique. For this, Hg-porosimetry is used instead. The fresh Co-sponge catalyst is a macro porous material with large pores in the order of $0.3-0.7 \,\mu\text{m}$ and has a porosity of $0.42 \,\text{m}_g^{-3} \cdot \text{m}_p^{-3}$.

The composition of the surface of the Co-sponge catalyst after activation by reduction is analyzed by X-Ray Photoelectron Spectroscopy (XPS). The samples are reduced ex-situ according to the standard activation procedure. When a fresh Co-sponge sample is compared with a used Co-sponge sample, no differences are seen. Neither of the samples contains Ni nor Fe.





The reducibility of the Co-sponge catalyst is determined by Temperature Programmed Reduction. The TPR is performed in a diluted H₂ flow (4 % H₂ in N₂) from ambient temperature to 1073 K with a heating rate of 3 K·min⁻¹. The TPR spectrum for the Co-sponge is represented in figure 4.15. Two responses of the H₂ uptake are observed at 433 K and at 503 K. This is representative for the stepwise reduction of Co-oxide from Co₃O₄ via CoO to Co [Sexton *et al.*, 1986; Choi, 1995]. The reduction of the metal-sponge catalysts proceeds at lower temperatures than the reduction of the TiO₂-supported catalysts. Apparently, the TiO₂ support stabilizes the Co-oxide phases.

5

The Fischer-Tropsch product spectrum on Co-based catalysts at 1 bar

5.1 Introduction

The Fischer-Tropsch synthesis is a polymerization reaction, in which the hydrocarbon reaction products are formed via the stepwise addition of a single carbon unit. Anderson [1984] shows that the product spectrum is described by a modified Flory-Schulz distribution, the ASF distribution. It is characterized by one kinetic parameter: the chain growth probability α . This parameter reflects the chance that a hydrocarbon chain on the catalyst surface undergoes chain growth rather than termination. As such, the reaction is non-selective for any reaction product other than methane.

The goal of this chapter is to obtain insight into the Fischer-Tropsch reaction mechanism by the quantification of the steady state product distribution. The steady state data are represented in three characteristic plots, *i.e.* the total yield plot (or ASF plot), the olefin and paraffin yield plot, and the olefin to paraffin ratio plot. Each of these three plots highlights characteristic features of the Fischer-Tropsch mechanism. Moreover, the quantification of the steady state product distribution is a vital step to reach the main goal of this work: the quantification of the kinetic parameters of a plausible Fischer-Tropsch reaction mechanism by modeling of SSITKA experiments.

Readsorption of olefins reverses the termination of growing hydrocarbon chains. Recent studies indicate that the readsorption of olefins is chain length dependent, resulting in a higher selectivity towards heavy hydrocarbon products than expected from the theoretical ASF-distribution. In this chapter it is indicated why the deviation from the ASF-distributions is not observed at the low-pressure operation of the reaction. Furthermore, it is evidenced that terminating chemisorbed hydrocarbon chains on the catalyst surface pass through a physisorbed state before reaching the gas-phase. The physisorbed state is in equilibrium with the gas-phase. It constitutes an essential part of the mechanism, even at reaction conditions where the surface coverage of physisorbed species is only a fraction of a monolayer coverage.

5.2 Differential syngas conversion and product-group identification

For every SSITKA experiment the steady state performance of the Co/Ru/TiO₂ catalyst, *i.e.* the CO conversion and product concentrations as well as the transient responses, are obtained at 498 K and 1.2 bar. An overview of the experimental data is presented in appendix 5. The steady state activity, expressed as CO conversion and H₂ conversion, is represented in figure 5.1. The O-atom from CO is preferentially eliminated as H₂O during the Fischer-Tropsch synthesis on Co-based

catalysts. However, due to the low reaction pressure, CO_2 is also observed with a typical selectivity of 3 C-mole% at the applied reaction conditions. The H₂O to CO_2 ratio represented in figure 5.2 increases with H₂/CO ratio.





Figure 5.1: Conversion of CO (solid lines) and H₂ (dashed lines) as a function of residence time, expressed as W_{cat}/F , and H₂/CO feed ratio for the Co/Ru/TiO₂ catalyst at 498 K and 1.2 bar.

H ₂ /CO=5	■:	X _{co} ;		X_{H2}	
H ₂ /CO=2	♦:	X _{co} ;	\diamond :	X_{H2}	
H ₂ /CO=1	▲ :	X _{co} ;	Δ :	X_{H2}	

Figure 5.2: H_2O to CO_2 ratio as a function of residence time, expressed as W_{cat}/F , and H_2/CO feed ratio for the Co/Ru/TiO₂ catalyst at 498 K and 1.2 bar.

:	H ₂ /CO=5
♦ : -	H ₂ /CO=2
A .	H ₂ /CO=1

The activity of the catalyst increases linearly with residence time up to CO conversions of about 20%. This indicates that the rate of syngas consumption is constant at these reaction conditions. Thus, the influence of the decreasing partial pressures for CO and H₂ throughout the reactor on the reaction rates is neglectible. The changes in surface concentrations of CO_{ads} and H_{ads} are therefore small and the plug flow reactor is differential with respect to these surface species.

The formulation of the Co/Ru/TiO₂ catalyst is based on the work by Iglesia *et al.* [1993b]. Comparing the activity of the catalyst used in this work with their catalyst is best done on the bases of turnover-frequencies (*TOF*). The turnover frequency represents the number of CO molecules that react per active site per second, according to:

$$TOF = \frac{R_{w,CO}}{a_s} = \frac{F_{CO} X_{CO}}{a_s W_{cat}} \qquad mole_{CO} \cdot mole_{Co,suff}^{-1} \cdot s^{-1}$$
(5.1)

In table 5.1, the activity of the $Co/Ru/TiO_2$ catalyst is compared to relevant studies in literature. The steady state activity reported in this work is in good agreement with the activities of the different Co-based catalysts at low pressure. The activity of the $Co/Ru/TiO_2$ catalyst increases with pressure, which is a well-known effect [Anderson, 1984].

catalyst	temperature	pressure	TOF	reference
	K	bar	s ⁻¹	
Co/Ru/TiO ₂	498	1.2	1.4·10 ⁻²	this work
Co/Zr/SiO ₂	493	1.3	0.8·10 ⁻² - 2.1·10 ⁻²	Ali <i>et al</i> ., 1995
Co/Ru/Al ₂ O ₃	493	1	1.5·10 ⁻² - 2.5·10 ⁻²	Kogelbauer <i>et al</i> ., 1996
Co-foil	493	1	1.5·10 ⁻²	Geerlings et al., 1999
Co/Ru/TiO ₂	473	20	5.6·10 ⁻²	Iglesia <i>et al</i> ., 1993b

Table 5.1: Comparison of activity of the Co/Ru/TiO₂ catalyst (in TOF) with relevant literature references at H₂/CO=2.

For the H₂/CO feed ratios of 1 and 2 the H₂ conversion is larger than the CO conversion, because the average H-atoms per C-atoms of the reaction products, the H/C ratio, for both conditions is larger than the H₂/CO feed ratio itself. This is not the case for H₂/CO=5. For the H₂/CO ratios of 1 and 2, the H/C ratio for the hydrocarbon reaction products amounts to 2.7 and 2.9, respectively, for H₂/CO=5 the H/C ratio is 5.3. The paraffin selectivity:

- increases strongly with increasing H₂/CO ratio;
- increases slightly with increasing residence time.

The product spectrum at a given set of experimental conditions is presented in three plots, each reflecting characteristic features of the Fischer-Tropsch mechanism:

- 1. the total yield plot, or ASF plot;
- 2. the individual yield plots for the paraffins and the olefins;
- 3. the olefin to paraffin ratio plot.

In the total yield plot no distinction between the different products of a given chain length is made. At the conditions applied in this study, considerable amounts of internal-olefins, iso-olefins, and iso-paraffins are produced beside 1-olefins and n-paraffins. A typical composition of the product gas, specified for all types of products as a function of carbon number, is given in figure 5.3. The n-paraffin and the 1-olefin, which are the major reaction products at high syngas pressure [Anderson, 1984], constitute about 30% of the C_{4+} product spectrum at the conditions applied in this study. This is mainly due to the low pressure and the dilution of the synthesis gas with 40% He.



In the individual yield plot and the olefin to paraffin ratio plot, the product spectrum is subdivided into two groups of reaction products, the olefins and the paraffins. Because readsorption of olefins reverses the termination reaction of growing hydrocarbon chains, the production of heavy products increases. In the next chapter it is demonstrated that the iso-olefins and internal-olefins readsorb much less than the 1-olefins. This is based on a comparison of the transient responses for the different reaction products and the conclusion is in close agreement with the observations made by Madon *et al.* [1991] and Iglesia *et al.* [1993a]. Since readsorption is the main secondary reaction, internal- and iso-olefins are seen as one group of reaction products together with n-paraffins and iso-paraffins. The 1-olefins demonstrate readsorption, and are considered as the second group of reaction products.

5.3 Chain length dependence of surface reactions

Typical plots for the total yield, individual yield and the olefin to paraffin ratio plots with the H_2/CO feed ratio as parameter are presented in figures 5.4 to 5.8 for the Co/Ru/TiO₂ catalyst. The experimental conditions are summarized in table 5.2.

	H ₂ /CO	W _{cat} /F	X _{CO}	α ₃₋₉
lace and $lace$	1	44.8	7.92	0.63
■ and □	2	24.2	10.4	0.55
\blacktriangle and \bigtriangleup	5	13.7	22.3	0.43

Table 5.2: Experimental conditions for the experiments representing the influence of the H_2/CO feed ratio at 498 K and 1.2 bar for the Co/Ru/TiO₂ catalyst.

In the total yield plot, figure 5.4, C_1 is slightly higher and C_2 is lower than expected from an Anderson-Schulz-Flory distribution. This is frequently observed in literature for Fe-based catalysts [Lox and Froment, 1993a], Co-based catalysts [Iglesia *et al.*, 1993a], and Ru-based catalysts [Everson and

Mulder, 1993]. For every H₂/CO feed ratio the plots show straight lines from C_3 onwards with slightly lower contributions for C_3 and C_4 than expected.

In literature, it is frequently concluded that the straight line in the initial part of the Anderson-Schulz-Flory distribution is representative for a constant chain growth probability. If the chain growth probability is carbon number independent, all surface reactions starting from C_3 proceed with chain length independent parameters. Then, the paraffin yield plot would be monotonically decreasing, and this is not observed in this study. For example, the paraffin yield plot in figure 5.6 shows a minimum for C_3 , rises again until C_5 , and then decreases monotonically.



Figure 5.4: Total yield plot for the hydrocarbons (closed markers) and the alcohols (open markers) on the Co/Ru/TiO₂ catalyst. \bullet and \bigcirc H₂/CO=1;

 \blacksquare and \square H₂/CO=2; \blacktriangle and \triangle H₂/CO=5



Figure 5.6: Olefin (\bigcirc) and paraffin (\bigcirc) yield plot for the Co/Ru/TiO₂ catalyst at H₂/CO=1.





Figure 5.5: Olefin to paraffin ratio plot for the Co/Ru/TiO₂ catalyst.

● H₂/CO=1; ■ H₂/CO=2; ▲ H₂/CO=5



Figure 5.7: Olefin (\Box) and paraffin (\blacksquare) yield plot for the Co/Ru/TiO₂ catalyst at H₂/CO=2.

Figure 5.8: Olefin (\triangle) and paraffin (\blacktriangle) yield plots for the Co/Ru/TiO₂ catalyst at H₂/CO=5

The chain growth probability for a growing hydrocarbon chain with i C-atoms on the catalyst surface is defined by:

$$\alpha_{i} = \frac{r_{p,i}}{r_{p,i} + r_{t,i}} = \frac{r_{p,i}}{r_{p,i} + r_{t,p,i}^{\text{eff}} + r_{t,o,i}^{\text{eff}}}$$
(5.2)

where $r_{t,o,i}^{eff}$ is the effective rate of termination towards olefin, *i.e.* the difference between the actual rate of termination of 1-olefin and the rate of its readsorption, and $r_{t,p,i}^{eff}$ the effective rate of termination

 $r_{t,o,i}^{\text{eff}} = r_{t,o,i} - r_{re,i} \quad \text{and} \quad r_{t,p,i}^{\text{eff}} = r_{t,n-paraffin,i} + r_{t,iso-paraffin,i} + r_{t,int\,ernal-olefin,i} + r_{t,iso-olefin,i}$ (5.3)

Going from C_3 to C_5 , the termination rate in the definition of α shifts from preferentially olefin to preferentially paraffin, whereas the sum of the two hardly changes. The lighter hydrocarbons, especially C_3 , prefer to terminate as olefin. This preference gradually changes towards paraffin and becomes constant starting from C_5 . This explains the S-shaped paraffin yield plot in combination with a relative constant value for the chain growth probability starting at C_3 . This characteristic shape is maintained at every H₂/CO ratio. Moreover, it is also observed for the Co/TiO₂ catalyst and for the Co-sponge catalyst (section 5.6).

Influence of wax layer on product distribution: change of surface chemistry

The present results illustrated that the S-shaped paraffin distribution is characteristic for the operation of the Fischer-Tropsch synthesis at dry conditions where no excessive wax formation occurs. From literature, this is also evidenced by comparing the steady state activities on Co-foil catalysts with and without the presence of a wax layer of at least one monolayer thickness [Kuipers *et al.*, 1995; Geerlings *et al.*, 1999]. In these studies, the total concentration plot as well as the olefin to paraffin ratio plot are published, of which the olefin and paraffin concentration plots are constructed here. The wax layer originates from:

- 1. variations in the pressure between 1 bar and 18 bar at 493 K [Geerlings *et al.*, 1999]. The total yield plots are shown in figure 5.9, the paraffin to olefin ratio plots in figure 5.10. The calculated olefin and paraffin yield plots are shown in figures 5.11 and 5.12 for 1 bar and 18 bar, respectively.
- manual addition of a wax layer on a clean Co-foil catalyst at 493 K and 1 bar [Kuipers *et al.*, 1995]. The total concentration plots are represented in figure 5.13 and the paraffin to olefin ratio plots in figure 5.14. The calculated olefin and paraffin concentration plots are shown in figures 5.15 and 5.16 for on the bear Co-foil the coated Co-foil, respectively.





Figure 5.9: Total yield plots for the hydrocarbons on a Cofoil at 493 K and H₂/CO=2 [Geerlings *et al.*, 1999].



Figure 5.11: Olefin (\bigcirc) and paraffin (\bigcirc) yield plots at 1 bar calculated according to the data of figures 5.9 and 5.10.

Figure 5.10: Paraffin to olefin ratio plot for a Co-foil at 493 K and H₂/CO=2 [Geerlings *et al.*, 1999].



Figure 5.12: Olefin (\triangle) and paraffin (\blacktriangle) yield plots at 18 bar calculated according to the data of figures 5.9 and 5.10.

At 493 K, the critical chain growth probability, α_c , below which the Fischer-Tropsch synthesis is operated at dry conditions and above which wax formation occurs, is α_c =0.63. At dry operation, the wax layer on the catalyst surface stays well below the monolayer coverage and all reaction products leave the reactor via the gas-phase. Both studies are performed at 493 K.

In the first study, the chain growth probability at 1 bar is α_{∞} =0.58 and the reaction is operated at dry conditions. At 18 bar, the chain growth probability is α_{∞} =0.93 and excessive wax formation via the Fischer-Tropsch reaction is observed. In the second study, the reaction is operated at intrinsic dry conditions, since the pressure is kept at 1 bar. The presence of the wax layer is mimicked by covering the Co-foil catalyst foil with a Santovac coating of 0.1 mm thickness. The Santovac coating is a hexaphenyl-dimethylether, which easily wets the Co-surface.

Although the origin of the wax layer in both studies is different, the results are comparable:

- In the absence of a wax layer the paraffin plot clearly displays a S-shape and the influence of the chain length of the growing hydrocarbon chain on the reaction rate coefficients is observed until C₅. The corresponding plots are represented in figures 5.11 and 5.15. Starting at C₅, the chain length independence ceases, resulting in constant slopes of the semi-logarithmic olefin and paraffin plots. These results are in good agreement with our experimental results.
- In the presence of a wax layer the S-shape of the paraffin plot disappears and the paraffin plot decreases monotonically. The corresponding plots are represented in figures 5.12 and 5.16. The influence of the chain length on the formation of paraffins and olefins is limited to C₃ at maximum. Starting at C₃, all surface reactions proceed with chain length independent rate coefficients.



Figure 5.13: Total concentration plots for a Co-foil catalyst with and without a Santovac coating at 493 K, 1 bar, $H_2/CO=2$ [Kuipers *et al.*, 1995].



Figure 5.15: Olefin (\bigcirc) and paraffin (O) concentration plots for the clean Co-foil catalyst, calculated from the plots in figures 5.13 and 5.14.



Figure 5.14: Paraffin to olefin ratio plots for a Co-foil catalyst with and without a Santovac coating at 493 K, 1 bar, $H_2/CO=2$ [Kuipers *et al.*, 1995].



Figure 5.16: Olefin (\triangle) and paraffin (\blacktriangle) concentration plots for the coated Co-foil catalyst, calculated from the plots in figures 5.13 and 5.14.

Moreover, in the presence of a wax layer on the catalyst surface, the slope of the semilogarithmic paraffin to olefin ratio curve becomes less steep. As explained in section 2.5.2, this illustrates a lowering of the value for the effective heat of desorption per $-CH_2$ - unit, expressed as E_{ads}/R in the captions of the figures. It indicates that the behavior of the physisorbed layer on the catalyst surface changes to that of a liquid. In the absence of a wax layer, the reaction products directly evaporate from metal surface, enhancing the effective heat of desorption per $-CH_2$ - unit.

These results are explained in relation to secondary reactions of readsorbed olefins. As explained in section 2.4.2, 1-olefins can readsorb and form a species that is bonded to the surface with either the ultimate C-atom, or the penultimate C-atom [Schulz and Claeys, 1999]. The first species is identical to a growing hydrocarbon chain and can undergo chain growth, termination to n-paraffin, and termination to 1-olefin. However, the second species is more likely to terminate as an internal-olefin or, if chain growth occurs, to terminate as an iso-paraffin, an iso-olefin, or an internal-olefin. The internal- and iso-olefins formed from the penultimate bonded species are unreactive towards readsorption, and the formation of these species by readsorption leads to an effective increase of the termination probability towards paraffin. Illustrative for such a mechanism is that the S-shaped paraffin plot starts at C₄, which is the first hydrocarbon from which the penultimate bonded species is sterically hindered in the presence of a wax layer, the formation of unreactive olefins is suppressed and the S-shape of the paraffin plot disappears. It is indeed observed that the selectivity towards iso-paraffins, iso-olefins and internal-olefins decreases with increasing reaction pressure [Anderson, 1984; Iglesia *et al.*, 1993a].

Chain length dependent readsorption of olefins

The constantly decreasing olefin to paraffin ratio with increasing carbon number in figure 5.5 illustrates a chain length dependent readsorption of reactive olefins. If the readsorption of reactive olefins is chain length independent, conform mechanism **A** in figure 5.17, the production rates for the paraffins and the olefins are defined as:

Paraffin:
$$R_{w,P_i}^{SS} = k_{t,p} L_{C_i}^{SS}$$
 Olefin: $R_{w,O_i}^{SS} = k_{t,o} L_{C_i}^{SS} - k_{re} C_{C_iH_{2i}}^{SS}$ (5.4)

where $L_{C_i}^{SS}$ is the steady state surface concentration of a growing chain of i C-atoms; $C_{C_iH_{2i}}^{SS}$ is the steady state gas-phase concentration of the olefin with i C-atoms; $k_{t,p}$ is the rate coefficient for termination to paraffin; $k_{t,o}$ is the rate coefficient for termination to olefin; k_{re} is the rate coefficient for readsorption from the gas-phase. In the figure 5.17, the effective termination towards olefins is carbon number independent starting at C₅. The plots for the paraffin yield and the olefin yield run parallel to each other and the olefin to paraffin ratio is constant. A constant olefin to paraffin ratio plot is also obtained if the readsorption of reactive olefins is absent. The results presented in figure 5.5 and from literature [*e.g.* Iglesia *et al.*, 1993; Kuipers *et al.*, 1995, Van der Laan and Beenackers, 1999] show that the olefin to paraffin ratio is not constant. The olefin yield always decreases faster than the corresponding paraffin yield and the olefin to paraffin ratio to paraffin ratio therefore decreases with carbon number.

A chain length dependency of the readsorption of reactive olefins is responsible for this phenomenon and the basis for this process is the increased residence time of the hydrocarbons at the catalyst surface with carbon number. As discussed in section 2.5.1, the enhanced surface residence time is most probably caused by the presence of a physisorbed hydrocarbon layer, from which readsorption of the reactive 1-olefin occurs. In case of physisorption equilibrium, schematically represented by mechanism **B** in figure 5.17, the production rates for the paraffins and the olefins are defined as:

Paraffin:
$$R_{w,P_i}^{SS} = k_{t,p} L_{C_i}^{SS}$$
 Olefin: $R_{w,O_i}^{SS} = k_{t,o} L_{C_i}^{SS} - \frac{\kappa_{re}}{\kappa_{C,H_{2i}}} C_{C_iH_{2i}}^{SS}$ (5.5)

where k_{re} is the rate coefficient for readsorption from the physisorbed layer; $K_{C_iH_{2i}}^{ph}$ is the physisorption equilibrium coefficient for an olefin with i C-atoms. The chain length dependency of the physisorption

equilibrium is exponential with carbon number, resulting in straight lines in the semi-logarithmic olefin to paraffin ratio plot, see mechanism **B** in figure 5.17.



Figure 5.17: Simulation of the total yield and the olefin to paraffin ratio plot for a chain length independent readsorption process (**A**) and a chain length dependent readsorption process (**B**).

In figure 5.5 it is observed that the slope of this semi-logarithmic olefin to paraffin ratio plot is independent of the H_2/CO feed ratio. This is also the case at every residence time (see section 5.4) and for the different types of Co-based Fischer-Tropsch catalysts (see section 5.7 for the Co-sponge catalyst). This illustrates that the composition of the physisorbed layer is comparable at all applied experimental conditions for every catalyst. It corresponds to a dry operation of the Fischer-Tropsch reaction, at which physisorbed layer does not exceed one monolayer. In chapter 8, modeling results indicate that this is indeed the case at the experimental conditions applied in this study.

5.4 Readsorption of olefins as function of residence time

The influence of the residence time, expressed as W_{cat}/F in kg_{cat}·s·mole⁻¹, on the steady state product spectrum of the Co/Ru/TiO₂ catalyst is illustrated in the figures 5.18 to 5.21. The corresponding experimental conditions and steady state characteristics are summarized in table 5.4.

ba	par, and H ₂ /CO=2.				
		W _{cat} /F	X _{co}	$lpha_{3-9}$	
		kg _{cat} ·s·mole⁻'	%	-	
Γ	ullet and $igcologies$	11.1	9.37	0.54	
	and	36.6	15 1	0.61	

Table 5.4: Experimental conditions for the experiments indicating the influence of the residence time at 498 K, 1.2 bar, and $H_2/CO=2$.

In figure 5.18 it is observed that an increase of the residence time causes a small increase of the chain growth probability. The major result of an increasing residence time is the increase in the paraffin selectivity, as can be seen from the downward shift of the olefin to paraffin ratio plot with increasing residence time in figure 5.19. The slope of the olefin to paraffin ratio in this semi-logarithmic plot does not change with changing residence time, as already mentioned in the former section. From figures 5.20 and 5.21 it is concluded that this increase in paraffinicity is caused by an upward shift of

the paraffin yield, whereas the olefin yield hardly changes. With increasing residence time not only the production, but also the consumption of olefins by readsorption and subsequent hydrogenation, chain-growth, chain-branching, and bond-shift increases.





Figure 5.19: Olefin to paraffin ratio plot for the Co/Ru/TiO2

Figure 5.18: Total yield plots for the Co/Ru/TiO₂ catalyst at $H_2/CO=2$.



catalyst at H₂/CO=2.

5.5 Ru-promotion: increased number of active sites

To illustrate the influence of the addition of 0.18 wt% Ru to the Co(12wt%)/TiO₂ catalyst on the steady state behavior, experiments at the same H_2 /CO ratio and residence time on the Co/TiO₂ catalyst and the Co/Ru/TiO₂ catalyst are compared. The reaction conditions and the steady state activity are summarized in table 5.5.

	••••		
		Co/Ru/TiO ₂	Co/TiO ₂
He dilution	mole%	66.7	66.7
W _{cat} /F	kg _{cat} ·s·mole⁻¹	38.0	36.1
X _{co}	mole%	14.4	7.37
$lpha_{4-6}$	-	0.41	0.37
S _{CH4}	mole-C%	60	64
Rwco	mole kg _{cat} -1.s ⁻¹	4.22·10 ⁻⁴	2.27·10 ⁻⁴

Table 5.5: Reaction conditions and steady state performance of the Co/TiO₂ catalyst and the Co/Ru/TiO₂ catalyst at 503 K, 1.2 bar, and H_2 /CO=2.

The activity of the Co/Ru/TiO₂ catalyst, calculated according to equation (5.6), is 1.9 times bigger than the activity of the unpromoted Co/TiO₂ catalyst. The increase in activity by Ru-promotion causes an increase of the chain growth probability from 0.37 to 0.41. Additional, the methane selectivity decreases slightly from 64 mole-C% to 60 mole-C% upon Ru-promotion and the olefin selectivity for the C₂ to C₄ products decreases.

$$R_{w,CO} = \frac{F_{CO} X_{CO}}{W_{cat}}$$
(5.6)

The doubling of the catalyst activity and the changes in the methane and olefin selectivities upon the addition of 0.2 wt% Ru to the Co(12wt%)/TiO₂ catalyst illustrate that the Ru-promotion leads to an increase of the total number of active sites. The activity increases and the higher degree of readsorption of reactive olefins leads to the observed changes in selectivities. By means of ¹³CO SSITKA experiments it is shown in section 6.2.5 that Ru-promotion does not change the intrinsic activity of the active Co site.

5.6 Co-sponge catalyst versus Co/Ru/TiO₂ catalyst

The steady state performance of the Co-sponge catalyst is only discussed briefly, because all the effects observed with the Co/Ru/TiO₂ catalyst are also observed with the Co-sponge catalyst. The Co-sponge catalyst is not studied as intensively as the Co/Ru/TiO₂ catalyst and only one set of experimental conditions will be discussed here. The total yield plot for the hydrocarbons and the alcohols are represented in figure 5.22, together with the reaction conditions in its caption. The olefin to paraffin ratio plot is represented in figure 5.23, and the olefin and paraffin yield plots are represented in figure 5.24.

Table 5.6: Reaction conditions and steady state performance of the Co-sponge catalyst and the Co/Ru/TiO₂ catalyst at 498 K and 1.2 bar .

		Co-sponge	Co/Ru/TiO ₂
H ₂ /CO	-	3	2
W _{cat}	kg _{cat}	4.91·10 ⁻³	8.22·10 ⁻⁴
F _{co}	mole⋅s⁻¹	5.69·10 ⁻⁶	6.80·10 ⁻⁶
X _{co}	mole%	5.57	10.4
α_{3-8}	-	0.57	0.55
S _{CH4}	mole-C%	25	42



Figure 5.22: Total yield plot for the hydrocarbons (\bullet) and the alcohols (\blacksquare) on the Co-sponge catalyst at 498 K, 1.2 bar, H₂/CO=3, and W_{cat}/F =130 kg_{cat} s mole⁻¹.





Figure 5.23: Olefin to paraffin ratio plot for the Co-sponge catalyst.

Figure 5.24: Olefin (\bigcirc) and paraffin (\bigcirc) yield plots for the Co-sponge catalyst.

As mentioned above, all characteristic features of the three plots for the Co/Ru/TiO₂ catalyst are also observed for the Co-sponge catalyst. The slope of the olefin to paraffin ratio in figure 5.28 is identical to the slopes observed for the Co/Ru/TiO₂ catalyst within the experimental accuracy. The activities of the Co-sponge catalyst and the Co/Ru/TiO₂ catalyst can only be compared if they are defined as turnover frequencies according to equation (5.1). The specific active surface area is $1.31 \cdot 10^{-2}$ mole_{Co,surf}·kg_{cat}⁻¹ for the Co-sponge catalyst and $6.18 \cdot 10^{-2}$ mole_{Co,surf}·kg_{cat}⁻¹ for the Co/Ru/TiO₂ catalyst. For the Co-sponge catalyst *TOF*=4.9·10⁻³ mole_{CO}·mole_{Co,surf}⁻¹·s⁻¹. This value is lower than for the Co/Ru/TiO₂ catalyst at H₂/CO=2, where *TOF*=1.4·10⁻² mole_{Co}·mole_{Co,surf}⁻¹·s⁻¹.

The chain growth probability is slightly higher for the unsupported Co-sponge catalyst, *i.e.* α =0.57 at H₂/CO=3, than for the Co/Ru/TiO₂ catalyst, *i.e.* α =0.55 at H₂/CO=2 and α =0.46 at H₂/CO=5. The methane selectivity of the Co-sponge catalyst is also lower than for the TiO₂ supported catalyst. Under the reaction conditions of this study, the Co-sponge catalyst has better Fischer-Tropsch characteristics (lower methane selectivity and higher chain growth probability) than the Co/Ru/TiO₂ catalyst.

5.7 Conclusions

In this chapter, the influence of the H_2/CO feed ratio, the residence time, and the catalyst composition on the steady state performance of the Fischer-Tropsch reaction (activity and selectivities) are presented. The results presented in this chapter lead to the qualitative conclusions summarized below. These conclusions are confirmed by modeling in chapters 7 and 8.

- Readsorption of 1-olefins occurs and the continuous decreasing olefin to paraffin ratio illustrates the presence of a physisorbed hydrocarbon layer on the catalyst surface from where the olefins readsorb into a chemisorbed state. The characteristics of this layer are independent of the reaction conditions and catalyst composition. This indicates that the experiments are performed at dry conditions, *i.e.* all reaction products leave the reactor in the gas-phase. The surface coverage of the physisorbed layer is expected to stay below a monolayer coverage.
- In the absence of a substantial wax layer, an S-shaped paraffin yield plot is observed. This is caused by the occurrence of secondary reactions such as isomerization and double-bond shifts at dry operation. Via these reactions, reactive 1-olefins are transformed into unreactive olefins. In the presence of a wax layer, isomerization and double-bond shifts become less important than chain growth of readsorbed 1-olefins due to steric hindering. In this case the S-shape of the paraffin yield plot vanishes.
- Promotion of the Co(12wt%)/TiO₂ catalyst with 0.18wt% Ru appears to increase the total number of active sites for the Fischer-Tropsch process, while the intrinsic activity of the sites does not change. This is confirmed by ¹³CO SSITKA experiments in section 6.2.5.
- The activity of the Co-sponge catalyst is three times smaller than that of the Co/Ru/TiO₂ catalyst based on the *TOF* numbers indicating that the reducibility of the Co-sponge catalyst is lower than of the Co/Ru/TiO₂ catalyst. At the applied reaction conditions, the Co-sponge catalyst has a lower methane selectivity and a higher chain growth probability.
- The steady state data of the Co/Ru/TiO₂ catalyst are suitable for modeling purposes:
 - 1. the reaction is operated at differential conditions for the consumption of CO and H₂;
 - 2. the reaction is operated at dry conditions;
 - 3. the composition of the physisorbed layer is independent of reaction conditions.

6

SSITKA investigation of the Fischer-Tropsch synthesis mechanism on Co-based catalysts

6.1 Introduction

In this chapter a transient kinetic investigation of the Fischer-Tropsch synthesis reaction is presented using the SSITKA technique. In the analysis, the kinetic processes are studied at steady state reaction conditions. The chemical composition of the catalyst surface does not change during the transient experiment, providing the most realistic environment at which the catalytic processes are identified and quantified.

The goal of this chapter is to obtain detailed insight into the reactivity, abundance, and chemical identity of the surface intermediates participating in the Fischer-Tropsch reaction via a qualitative interpretation of the experimental SSITKA results. The experiments are characterized by:

- The execution of ¹³C-labeling, ¹⁸O-labeling, and D-labeling experiments. The major reaction products of the Fischer-Tropsch synthesis are hydrocarbons, causing ¹³CO SSITKA experiments to be the most applied tracer technique in literature. But focussing on ¹³C-labeling alone would neglect the participation of H- and O-atoms in the reaction mechanism. Combining ¹³C-labeling SSITKA experiments with ¹⁸O- and D-labeling experiments results in a more detailed characterization of the individual reaction rates and the associated surface concentrations.
- The expansion of the traditional mass spectrometric analysis of ¹³CO and ¹³CH₄ with a gas chromatographic mass spectrometric analysis of the C₂-C₅ hydrocarbons and C₁-C₃ alcohols. In addition to the methanation reaction, this allows the assessment of the characteristic C-C coupling reaction.
- The use of a Co/Ru/TiO₂ catalyst, a Co/TiO₂ catalyst, and a fully metallic Co-sponge model catalyst. This allows the identification of the different catalytic properties of the individual components of the industrial interesting Co/Ru/TiO₂ catalyst.

In section 6.2, TiO_2 supported catalysts are used for the identification of surface heterogeneity for the formation of hydrocarbons, the identification of the chemical composition of the participating surface species, the influence of Ru on the activity of the catalyst, and the role of TiO_2 during alcohol formation. In section 6.3, the alcohol formation mechanism on the Co-metal is studied in more detail. The experimental results are mainly discussed in a qualitative basis, resulting in a global mechanism for the Fischer-Tropsch synthesis. These mechanistic conclusions are confirmed and studied in more detail by reactor modeling in chapters 7 and 8.

6.2 Steady state isotopic transient kinetic analysis of TiO₂ supported catalysts

In this section the steady state isotopic transient kinetic analysis of the mechanism of the Fischer-Tropsch synthesis on the Co/Ru/TiO₂ and the Co/TiO₂ catalysts is discussed. The emphasis is put on the Co/Ru/TiO₂ catalyst, while the unpromoted Co/TiO₂ catalyst is used to assess the role of the Ru-promotor. To obtain a detailed insight into the kinetic mechanism, different types of isotopic step changes are applied:

- 1. He/Ne/¹²CO/H₂ \rightarrow He/¹³CO/H₂
- 2. $N_2/Ne/CO/H_2 \rightarrow N_2/CO/D_2$

The isotopic composition of a wide range of reaction products is analyzed under different experimental conditions. In section 6.2.1 the methanation reaction is studied by means of ¹³CO SSITKA experiments, while in section 6.2.2 the incorporation of ¹³C into the C₂-C₅ hydrocarbons is discussed. The ¹³C incorporation into methanol and ethanol is discussed in section 6.2.3. The role of the Ru-promotor is highlighted by comparing the ¹³C incorporation into the C₁-C₅ hydrocarbons on both the Co/Ru/TiO₂ and the Co/TiO₂ catalysts under comparable reaction conditions.

6.2.1 ¹³C-labeling of CO and CH₄

Experimental observations: varying the H₂/CO feed ratio

The influence of the H₂/CO feed ratio on the transients of Ne, ¹³CO, and ¹³CH₄ following a He/Ne/¹²CO/H₂ \rightarrow He/¹³CO/H₂ isotopic step change are given in figures 6.1 to 6.4. All experiments are obtained at 498 K and 1.2 bar. The specific experimental conditions are included in the captions of the figures.



Figure 6.1: Normalized responses of Ne, ¹³CO, and ¹³CH₄ on the Co/Ru/TiO₂ catalyst at H₂/CO=1 and W_{cat}/F =44.8 kg_{cat}'s-mole⁻¹.



Figure 6.3: Normalized responses of Ne, ¹³CO, and ¹³CH₄ on the Co/Ru/TiO₂ catalyst at H₂/CO=5 and W_{cat}/F =13.7 kg_{cat}'s mole⁻¹.



Figure 6.2: Normalized responses of Ne, ¹³CO, and ¹³CH₄ on the Co/Ru/TiO₂ catalyst at H₂/CO=2 and W_{cat}/F =24.2 kg_{cat}·s·mole⁻¹.



Figure 6.4: Representation of the first 50 s of the transients represented in figure 6.2.

The following observations are made:

• The Ne transient decreases from unity to zero in about 2 seconds. The Ne response at the inlet of the reactor is identical to the response at the outlet of the reactor, indicating that the reactor is operated at plug-flow conditions.

• At all conditions, the normalized ¹³CO response is fast. It is delayed in time with respect to the Ne transient. This implies the presence of a time period in which no breakthrough of ¹³CO is observed. Moreover, the ¹²CO transient is the inverse of the ¹³CO response, as observed in figure 6.4. The ¹²CO and the ¹³CO responses cross at 50 % labeling.

• In all the figures 6.1 to 6.4, the ${}^{13}CH_4$ response already starts before breakthrough of ${}^{13}CO$ is observed. This is emphasized in figure 6.4, where only the first 50 s of the transients of figure 6.2 are represented.

• The ${}^{13}CH_4$ transient is slower than the ${}^{13}CO$ transient, and the H₂/CO feed ratio influences the time scale of the transient of ${}^{13}CH_4$. It becomes faster with increasing H₂/CO feed ratio. The spikes in the transients, especially at low residence times as observed in figure 6.3, result from the switching of the 12-loop valve of the GCMS set-up. During the switch, the outlet flow is temporarily blocked and the subsequent pressure build up is responsible for the spikes in the responses.

Experimental observations: varying the residence time

The influence of the residence time on the transients of Ne, ¹³CO, and ¹³CH₄ following a $He/Ne/^{12}CO/H_2 \rightarrow He/^{13}CO/H_2$ isotopic step change is given in figures 6.5 to 6.7. All experiments are obtained at 498 K and 1.2 bar. The following observations are made:

• The delay in time of the CO response with respect to the Ne response increases with increasing residence time.

• The ¹³CH₄ transient, however, is hardly influenced by the residence time.



Figure 6.5: Normalized responses of Ne, ¹³CO, and ¹³CH₄ on the Co/Ru/TiO₂ catalyst at H₂/CO=2 and W_{cat}/F =11.1 kg_{cat}'s mole⁻¹.





Figure 6.6: Normalized responses of Ne, ¹³CO, and ¹³CH₄ on the Co/Ru/TiO₂ catalyst at H₂/CO=2 and W_{cat}/F =24.2 kg_{cat}'s mole⁻¹.

Figure 6.7: Normalized responses of Ne, ¹³CO, and ¹³CH₄ on the Co/Ru/TiO₂ catalyst at H₂/CO=2 and W_{cal}/F =36.6 kg_{cat} s mole⁻¹.

Characteristics of the step change

A fast isotopic step change in a plug-flow reactor provides the optimal experimental condition for SSITKA studies [Happel, 1986; Bennett, 2000]. In the plug-flow regime, all changes relative to the inlet signal are ascribed to kinetics. This is not the case for SSITKA experimentation in a continuous stirred tank reactor with a relatively large residence time of the gases in the reactor. In that case, the
mixing curve of the CSTR can obscure the changes of the signal due to kinetics. The faster the step change, the better the monitoring of fast kinetic processes. The normalized response of the inert tracer applied in this work corresponds to an exponential decay with a time scale of 0.5 s. As mentioned in section 3.3.2, time scales ranging from 2 s to 14 s are normally reported in literature. The current set-up is therefore very suitable for the detection of fast reaction steps.

Chromatographic effect for CO

The delay in time of the normalized ¹³CO response with respect to the normalized Ne response is caused by the adsorption and desorption of CO on the catalyst surface. This is also known as the chromatographic effect [Happel, 1986; Shannon and Goodwin, 1995], characteristic for the group VIII metals on which CO is able to adsorb non-dissociative. Due to the chromatographic effect ¹³CO moves as a front through the plug flow reactor. Because the responses of ¹²CO and ¹³CO are each other's inverse, CO exchanges on a one-to-one basis and does not involve an isotope effect.

Surface concentrations based on mean surface residence times

The chromatographic effect of CO increases with residence time. An increased residence time caused by an increase of the amount of catalyst results in an increase of the total number of adsorption sites in the reactor, reflecting a larger delay of the CO response. An increased residence time caused by a decrease of the total gas flow results in an increase of the number of actual adsorption/desorption steps per CO molecule, also reflecting a larger delay of the CO response.

The absolute values for the surface concentrations of CO_{ads} and the intermediate $C_{1,ads}$ towards the hydrocarbon reaction products are directly accessible via the transients of Ne, ¹³CO, and ¹³CH₄. As mentioned in chapter 3, the area between the transient of a component that is participating in the reaction and the transient of the inert tracer, represents the mean surface residence time of the surface species related to the transient. Combining this mean surface time with the steady state activity of the catalyst results in estimates of the surface concentrations of the intermediates. It must be stressed that:

- these estimates are not related to any assumptions about the reaction mechanism;
- it is the most general quantitative number which can be obtained by SSITKA experiments. The surface concentration of CO_{ads} is calculated according to:

$$L_{CO} = \frac{\tau_{CO} F_{CO}}{W_{cat}} = \frac{F_{CO}}{W_{cat}} \int_{t=0}^{\infty} [E_{12}CO}(t) - E_{Ne}(t)] dt$$
(6.1)

where L_{CO} is the surface concentration of CO_{ads} in mole·kg_{cat}⁻¹; F_{CO} is the molar feed rate of CO in mole·s⁻¹; τ_{CO} is the mean surface residence time of CO_{ads} in s; E_{12}_{CO} is the normalized transient of ¹²CO (note that $E_{12}_{CO} = 1 - E_{13}_{CO}$); E_{Ne} is the normalized transient of Ne, representing the gas-phase holdup in the reactor.

Under the assumption that the methane intermediates are the most abundant growing hydrocarbon chains on the catalyst surface, its surface concentration is represented by:

$$L_{C_{1}} \approx \frac{\tau_{C_{1}} F_{CO} X_{CO}}{W_{cat}} = \frac{F_{CO} X_{CO}}{W_{cat}} \left(\int_{t=0}^{\infty} [E_{12_{CH_{4}}}(t) - E_{Ne}(t)] dt - \frac{1}{2} \int_{t=0}^{\infty} [E_{12_{CO}}(t) - E_{Ne}(t)] dt \right)$$
(6.2)

where X_{CO} is the conversion of CO. In this equation, a correction for the chromatographic effect is introduced. Since CO moves as a front through the reactor, the mean surface residence time for the C_{1,ads} pool is lowered by half the means surface residence time for CO_{ads}.

Table 6.1 and figure 6.8 represent the surface concentrations calculated with equations (6.1) and (6.2). The CO surface concentration is constant at the applied reaction conditions. Moreover, the surface concentration of $C_{1,ads}$ is two times smaller than the surface concentration of $C_{0,ads}$ and decreases slightly with H₂/CO feed ratio. The total number of surface sites is $6.2 \cdot 10^{-2}$ mole·kg_{cat}⁻¹, leading to an average surface coverage with CO_{ads} and $C_{1,ads}$ of 91%. The reactor is operated differentially with respect to CO, *i.e.* the change in CO surface concentration due to reaction is

negligible. These results are in line with the steady state data on the CO conversion as a function of residence time, presented in figure 5.1 of the previous chapter.

Table 6.1: Surface concentration	ons of CO _{ads} and C	1,ads based on the	integration of the transients.

H ₂ /CO	W _{cat} /F	L _{co}	L_{C_1}	$ heta_{CO}$	θ_{C_1}
	kg _{cat} ·s·mole ⁻¹	mole ⋅ kg _{cat} -1	mole ⋅ kg _{cat} -1	%	%
1	16.8	$3.5 \cdot 10^{-2}$	1.9·10 ⁻²	57	31
1	44.8	4.0·10 ⁻²	1.9·10 ⁻²	65	31
2	11.1	3.9·10 ⁻²	1.7·10 ⁻²	63	28
2	24.2	3.9·10 ⁻²	1.5·10 ⁻²	63	24
2	36.6	4.0·10 ⁻²	1.7·10 ⁻²	65	28
5	7.94	3.8·10 ⁻²	1.2·10 ⁻²	61	19
5	13.7	4.0·10 ⁻²	1.2·10 ⁻²	65	19



Figure 6.8: Surface concentrations of CO_{ads} (\bullet) and $C_{1,ads}$ (\triangle) as a function of H₂/CO feed ratio for the Co/Ru/TiO₂ catalyst.

Interaction of CH₄ with the catalyst

The detection of ${}^{13}CH_4$ at the outlet of the reactor before ${}^{13}CO$ breaks through indicates the absence of any significant interaction of methane with any of the components of the Co/Ru/TiO₂ catalyst. From literature it is known that the dissociative adsorption of methane on cobalt to form carbides, *i.e.* thermal activation of methane, only proceeds at temperatures in excess of 623 K [Koerts, 1992; Guczi *et al.*, 1997]. A temperature gap between the thermal activation of methane and the hydrogenation of surface carbides to methane exists. Based on thermodynamics, both reactions cannot occur simultaneously.

Methanation during the Fischer-Tropsch synthesis

The difference in time scales of the methane transient compared to the CO transient implies that CO hydrogenation to methane proceeds with at least one slow irreversible reaction step via a surface intermediate. It is generally accepted that CO hydrogenation towards methane proceeds via CO dissociation and subsequent hydrogenation of surface carbon, *i.e.* via the carbene mechanism. Further evidence for this is presented in chapter 7. The CO dissociation cannot be the sole rate-determining step in the mechanism since this would imply that the methane intermediate pool is small and that its isotopic composition closely follows that of the CO pool. The methane transient would then have a time scale comparable with the time scale of the CO transient. This is not observed, the methane transient is much slower than the CO transient. The rate of CO dissociation, however, is limited, because a large reservoir of non-dissociated CO is present on the surface. The slow response of the intermediate is relatively slow. Which of the additions of H to the intermediate to produce methane is the slowest cannot be assessed on the basis of these ¹³CO SSITKA experiments. Further elaboration on this issue will be presented in the sections 6.2.4 and 6.3.4.

The H_2/CO feed ratio has a clear influence on the rate of the methanation response. As described in chapter 3, the reciprocal value of the mean residence time of the methane intermediate,

 τ_{C_1} , equals the first order rate constant k_2 in the single route methanation mechanism of figure 6.9 A).

This leads to equation (6.3). The true rate constant k_2^* is represented by equation (6.4) if a first order dependency of the reaction rate on the surface concentration of H_{ads} is assumed. The surface concentration of H_{ads} needs to be lumped in the rate parameter obtained from the mean residence time resulting from ¹³CO SSITKA experiments.

$$k_{2} = \frac{1}{\tau_{C_{1}}}$$

$$k_{2} = k_{2}^{*} \theta_{H}$$
(6.3)
(6.4)

0

Figure 6.9: Different fundamental mechanisms for the methanation reaction (see also section 3.4)



A decreasing mean residence time for the methane intermediate with increasing H_2/CO feed ratio reflects an increasing surface concentration of H_{ads} . The ¹³CH₄ transient is not influenced by changes in the residence time, as expected since the reaction is performed under differential conditions regarding the methanation reaction. In section 5.2 it was evidenced that the consumption of the reactants CO and H_2 proceeds at differential reaction conditions.

Surface heterogeneity on C_{1,ads} scale

In figure 6.10, the semi-logarithmic decay of the ¹²C content of methane, corresponding to figures 6.1 to 6.3, is depicted. The H₂/CO feed ratio is the parameter. In this figure the curves are shifted in time in order to prevent overlap. As mentioned in section 3.5.3, the shape of this decay curve bears information about the mechanism that is responsible for the formation of the product. A curve with a downward convexity is characteristic for a mechanism with either a parallel path (figure 6.9 B)) or a buffer step (figure 6.9 C)) [de Pontes *et al.*, 1987; Sadovskaya *et al.*, 1999]. In both mechanisms, two reactive species, represented as $C_{\alpha,ads}$ and $C_{\beta,ads}$, are distinguished.

Modeling in chapter 7 evidences the presence of two reactive intermediates for all three H_2/CO feed ratios. Two remarks should be made:

- The decay curves in figure 6.10 do not display a discontinuous derivative at the start of the experiment, but start with a zero-slope. This is caused by the occurrence of the chromatographic effect for CO, leading to a mixed ¹³CO_{ads}/¹²CO_{ads} pool on the surface from which methane is formed. This zero-slope is not representative for a methanation mechanism with pools-in-series.
- 2. As mentioned by de Pontes *et al.* [1987], the noise-level of the data seriously influences the conclusions that can be drawn from the data. If the change in slope in the plot has not occurred before the overall fraction labeling reaches the value of the natural logarithm of the standard deviation of the noise, *i.e.* $\ln(\sigma_{noise})$, the change in slope is not significant. For the experimental

conditions reported here, the standard deviation of the noise is typically 0.004 to 0.008. A change in slope is therefore significant if it occurs at $\ln(1-E_{ov})<-4.5$. The intensity of the noise level mainly depends on the concentration of the reaction product. The higher the production of methane, the lower the noise level on the signal, the more accurate the observed transient.

Because the changes in the shapes of the curves in figure 6.10 occur before $ln(1-E_{ov})=-4.5$, the conclusion of the presence of two reactive intermediates is justified.

In literature, surface heterogeneity has frequently been observed for CO hydrogenation catalysts. Several reactive intermediate C-species have been identified by different techniques, such as SSITKA, H-titration, and isotopic tracer techniques. However, as was discussed in chapter 2, there is still no consensus about the chemical identity of these reactive intermediate species. The most frequently mentioned surface species are elementary carbon, short alkyl chains and graphite [Bell, 1989; Yokomizo and Bell, 1989].

It should be stressed that the present results are obtained by ¹³CO labeling experiments, meaning that only information is obtained about reactions in which ¹³C participates. Therefore, the Hand O-content of the two reactive intermediate species cannot be assessed on the basis of these experiments alone [Hoost and Goodwin, 1992]. However, the D-labeling experiments on methane, ethane, and ethene formation, the ¹³C- and ¹⁸O-labeling experiments on C₁ to C₃ alcohol formation on the Co/Ru/TiO₂ catalyst and the Co-sponge catalyst shed more light upon these questions.

6.2.2 ¹³CO SSITKA on higher hydrocarbon formation

Experimental observations

Typical transients of all isotopic variants of ethane and ethene following a He/Ne/¹²CO/H₂ \rightarrow He/¹³CO/H₂ isotopic step change are presented in figures 6.11 and 6.12. These transients are obtained at different residence times, while all other reaction conditions are kept constant. The transients of n-butane, 1-butene, and t-2-butene are represented in figures 6.13 and 6.14. The following observations are made:

• In the figures, all responses of the intermediate isotopic variants show a maximum, since the experiment starts with zero labeling and ends at full labeling. These maxima shift in time with increasing isotope content of the intermediate isotopic variant for the C_{3+} hydrocarbons, *e.g.* for ${}^{12}C_{3}{}^{13}CH_{10}$, ${}^{12}C_{2}{}^{13}C_{2}H_{10}$, and ${}^{12}C_{3}{}^{13}C_{3}H_{10}$ in figure 6.13.

• Comparison of the transients of the isotopic variants for ethane in figure 6.11 with the transient of methane in figure 6.1 indicates that the transient for ${}^{13}C_2H_6$ displays similar tailing as ${}^{13}CH_4$. With increasing H_2/CO ratio the responses of the C_2 to C_5 hydrocarbons become faster in a similar way as the ${}^{13}CH_4$ transient does.

• In figure 6.11 it is clear that all transients of ethene are similar in shape as the corresponding transients for ethane, only delayed in time. The delay in time is observed at every H_2/CO ratio and increases with residence time. This is apparent from the smaller delay observed at $W_{cat}/F=16.8$ kg_{cat}·s·mole⁻¹ in figure 6.12 compared to the delay at $W_{cat}/F=44.8$ kg_{cat}·s·mole⁻¹ in figure 6.11. In general, the transients of the isotopic variants of the C_{2+} paraffins are hardly influenced by changes in the residence time, similar to the behavior of the transients of methane with increasing residence time (section 6.2.1). Only the olefin responses shift in time with increasing residence time.

• The same effect is also observed for propane/propene and for butane/1-butene, of which the latter is represented in figure 6.13. In this figure the responses corresponding to non-labeled n-butane and 1-butene are not shown for clarity reasons. For the C₄ hydrocarbons, considerable amounts of t-2-butene and c-2-butene are detected. The responses of t-2-butene are similar to those of n-butane in figure 6.14. It appears that this internal olefin, in contrast to 1-butene, displays almost no delay in time with respect to the n-butane. This absence of a delay in time is also observed for c-2-butene.



Figure 6.11: Normalized ¹³C-labeling responses of ethane (closed markers) and ethene (open markers) at H₂/CO=1 and $W_{cat}/F=44.8 \text{ kg}_{cat} \cdot \text{s} \cdot \text{mole}^{-12} \text{C}_2 H_6;$



1.0 normalized response /-____ ____ 0.8 0.6 0.4 0.2 0.0 0 50 100 150 200 time /s

Figure 6.12: Normalized ¹³C-labeling responses of ethane (closed markers) and ethene (open markers) at H₂/CO=1 and $W_{cat}/F=16.8 \text{ kg}_{cat} \cdot \text{s} \cdot \text{mole}^{-12}$ $A \xrightarrow{12} C_2 H_6; \quad A \xrightarrow{12} C_2 H_6;$ ¹²C¹³CH₆;

¹³C₂H₆;



Figure 6.13: Normalized ¹³C-labeling responses of n-butane (closed markers) and 1-butene (open markers) at H₂/CO=1



Figure 6.14: Normalized ¹³C-labeling responses of n-butane (closed markers) and t-2-butene (open markers) at H₂/CO=1



Readsorption of ethene

In accordance with the reasoning about the delayed CO response with respect to the Ne response, the delay of the ethene responses is due to the ability of ethene to readsorb on the catalyst surface. Ethane does not have this ability: once it is formed, it stays in the gas phase and is transported through the reactor. The readsorption of reactive olefins is a very important feature in the Fischer-Tropsch synthesis, as has already been noticed by Pichler et al. [1967]. The readsorption is responsible for the non-Anderson-Schulz-Flory behavior at higher carbon numbers, *i.e.* the increased yield of heavy products. It reverses the overall termination and therefore increases the chain growth probability. A chain length dependence of this readsorption process explains the deviations from the ASF distribution at higher carbon numbers [Iglesia et al., 1993; Kuipers et al., 1995].

Readsorption of 1-olefins versus internal- and iso-olefins

The readsorption behavior is not observed for the internal- and iso-olefins of the C₄ hydrocarbons, since they are hardly delayed compared to the n-butane. It is therefore concluded that the 1-olefins are the major candidates for readsorption. Internal and iso-olefins may also readsorb, but to a much lesser extent than the 1-olefin. An increase in residence time increases the probability for readsorption of the reactive olefins, which results in a larger time delay compared to the paraffin.

C-C coupling versus hydrogenation for $C_{\alpha,ads}$ and $C_{\beta,ads}$

In figure 6.15, the decay of ¹²C in propane is compared to the decay of ¹²C in methane at $H_2/CO=2$. The overall fraction ¹³C in propane (*i.e.* n=3) is calculated according to :

$$E_{ov} = \frac{1}{n} \sum_{i=1}^{n} i \cdot E_{{}^{12}C_{n-i}{}^{13}C_i}$$
(6.5)

The curve for methane is obtained by on-line MS analysis and for propane by GCMS analysis, leading

to a lower number of actual data points. Both curves are similar in shape, having the same downward convexity. Moreover, the curve for propane closely follows the curve for methane. These results indicate that:

- 1. the two reactive intermediate species leading towards methane, C_{α} and C_{β} , both participate in the chain growth process. The similarity in shape between the decay plot for methane and propane indicates that the surface heterogeneity observed for methanation reflects itself on higher hydrocarbon formation. For methanation, two reactive intermediates are present. If one intermediate would only lead to methane formation while the other also would result in hydrocarbon formation, methane formation would be characterized by a two pool mechanism, while hydrocarbon formation would be characterized by a single pool mechanism. In that case the decay curves for methane and the higher hydrocarbons would no longer be similar in shape. Therefore, it is concluded that the two pools of reactive intermediates not only lead to methane formation.
- 2. the formation of the C_{2+} hydrocarbon reaction products involves fast reactions compared to the formation of monomeric and chain initiation species. The decay of the ¹²C content in propane closely follows that of methane. If the chain growth process is considered to be irreversible, this implies low surface concentrations of the growing hydrocarbon chains on the catalyst surface compared to the surface concentrations of the reactive intermediates towards methane, $C_{\alpha,ads}$ and $C_{\beta,ads}$. In this case the isotopic composition of the small surface pools of growing hydrocarbon chains closely follows that of the reactive intermediates. Low surface concentrations of the growing hydrocarbon chains only result if the C-C coupling reaction and the termination reactions are fast compared to the formation of monomeric and chain initiator species.

These two conclusions are both supported and contradicted in literature. In a ¹³CO SSITKA study on the Fischer-Tropsch synthesis over an unsupported Co catalyst, Zhang and Biloen [1986] obtain transients of the C₁ to C₃ hydrocarbons by on-line mass spectrometry. They model these results using a mechanism with one C-intermediate, which is represented by the lines in figure 6.16. It is clear that the tailing of both the C₁ and the C₃ transients is not properly described. The authors state that the tailing of the transients is indicative for surface heterogeneity, but they do not take this aspect into account in their model. Since both C₁ and C₃ transients show similar tailing, we conclude that their results are in agreement with the first points presented above: two reactive intermediates, C_α and C_β, are present, which lead to methane and participate in hydrocarbon chain growth. Their modeling results are in contradiction with our second conclusion. They calculate a rate constant for C-C coupling ≤0.1 s⁻¹ for the unsupported Co catalyst, which is not particular fast as is indicated in chapter 7. However, since they neglect the surface heterogeneity in their model, the resulting rate constants may be distorted.

Both conclusions are supported by the results of Stockwell *et al.* [1988] on a Fe/Al₂O₃ catalyst. The overall ¹³C content of the C₁-C₅ synthesis products is determined by GCMS at 533 K and H₂/CO=2.5. Following the GC separation the hydrocarbons are hydrocracked to methane, of which the isotopic content is measured by MS. The transients of the C₂ to C₅ hydrocarbons in figure 6.17 follow each other closely and are similar in shape as the one for methane.

Mims and McCandlish [1987] present transients of all isotopic variants of 1-butene, obtained from ¹³CO SSITKA experiments over a Co/SiO₂ catalyst via GCMS detection. In their comparison of the overall fractions labeling of 1-butene and methane, see figure 6.18, it is observed that the fraction ¹²C in 1-butene decreases faster in time than for methane. Moreover, the curve for the overall fraction labeling for methane shows a clear change in slope at around 50% labeling, whereas this change in slope for 1-butene is not as pronounced. This means that methane is formed from several intermediate species, of which at least one does not participate in the formation of 1-butene. The observed shapes of the curves for the overall fraction labeling can, however, also result from incorrect normalization procedures for either one of the responses, although the differences between the two curves are substantial. These results are in contradiction with our first conclusion presented above. By using NMR analysis in combination with ¹³CO SSITKA experiments, Mims and McCandlish [1987] are able to determine the distribution of ¹³C over the different positions in the 1-olefinic reaction products. They conclude from the uniform distribution of ¹³C over all positions in the 1-olefins of the C₂ to C₆ hydrocarbons that the chain growth process is fast compared to the isotopic exchange of the monomeric pool. In that case, the isotopic composition of the reaction product at a certain time during the SSITKA experiment reflects the average isotopic composition of the monomeric pool. Their conclusion is based on a different experimental technique and is in good agreement with our second conclusion presented above.



Figure 6.15: The semi-logarithmic decay of the ¹²C content for methane (dashed line), and higher hydrocarbons, represented by propane (^{-D-}).



Figure 6.17: Fractional ${}^{13}C$ content for C₁ to C₅ hydrocarbons on a Fe/Al₂O₃ catalyst at 533 K, 1 bar, and H₂/CO=2.5 [Stockwell *et al.*, 1988].



Figure 6.16: Transients of C_1 and C_3 hydrocarbons on a Cometal catalyst at 483 K, 1 bar, and $D_2/CO=3$. Lines: model calculations, symbols: data points [Zhang and Biloen, 1986].



Figure 6.18: The semi-logarithmic decay of the ${}^{12}C$ content for methane (+) and 1-butene (\bigcirc) on a Co/SiO₂ catalyst at 475 K, 1.2 bar, and H₂/CO=2 [Mims and McCandlish, 1987].

Komaya and Bell [1994a] study the higher hydrocarbon formation of the Fischer-Tropsch synthesis over a Ru/TiO₂ catalyst at 523 K via ¹³CO SSITKA experiments using isotope-ratio-monitoring-GCMS analysis of the C₂ to C₈ hydrocarbons. Their responses of the overall labeling of the C₂ to C₆ hydrocarbons follow each other closely, in agreement with our second conclusion of a fast chain initiation and chain growth process. However, their transients do not indicate heterogeneity of the pool of methane intermediates.

Surface heterogeneity by species on the TiO₂ support

Lapidus *et al.* [1992] suggest that the active centers for methanation and those for hydrocarbon chain growth are different in nature. They state that an important methanation route involves the presence of CH_xO complexes on the support. These are formed by spillover of hydrogen and CO onto the support, which diffuse over the support and are decomposed to methane when they again reach metal crystallites. Our results are not in line with this suggestion. Komaya *et al.* [1994a] indicate that if such a spillover on the TiO₂ support takes place, the contribution to methane formation is negligible for their experiments on Ru/TiO₂ and Ru/SiO₂/TiO₂ catalysts under Fischer-Tropsch conditions. A more detailed elaboration on the presence of CH_xO complexes on the TiO₂ support and the role of this species in the Fischer-Tropsch reaction is continued in sections 6.2.3 and 6.3.1.

6.2.3 ¹³CO SSITKA on alcohol formation

Experimental observations

The responses corresponding to alcohol formation on the Co/Ru/TiO₂ catalyst show some remarkable features. In figure 6.19 the transients of ethane and ethanol are shown following a He/Ne/¹²CO/H₂ \rightarrow He/¹³CO/H₂ isotopic step change. The response of the non-labeled isotopic variant of ethane is excluded from the figure for clarity reasons. The following observations are made:

Ethanol reaches full labeling at a larger time scale than ethane does.

• The two intermediate labeled variants of ethanol, *i.e.* ${}^{12}CH_{3}{}^{13}CH_{2}OH$ and ${}^{13}CH_{2}OH$, both have small responses. The maximum response of ${}^{12}CH_{3}{}^{13}CH_{2}OH$ is only 6% and for ${}^{13}CH_{3}{}^{12}CH_{2}OH$ only 4%, whereas the maximum response of ${}^{12}C{}^{13}CH_{6}$ amounts to 50%. The isotopic composition of ethanol therefore mainly consists of the non- and fully labeled variants.

• Methanol shows the same features as ethanol, as shown in figure 6.20. The responses of methanol and ethanol have similar time scales.



Figure 6.19: Normalized responses of ethane (closed markers) and ethanol (open markers) for the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H₂/CO=2, and W_{cat}/F =28.2 kg_{cat}·s-mole⁻¹.



500

time /s

750

1000



Figure 6.20: Normalized responses of methanol (closed markers) and ethanol (open markers) for the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H₂/CO=2, and W_{cat}/F =28.2 kg_{cat}·s·mole⁻¹.





Alcohol evolution via single pool mechanism

250

-6+ 0

The decay of the ¹²C content in ethane, ethanol, and methanol is shown in figure 6.21. The straight lines in these plots for methanol and ethanol are representative for a single pool process as the prevailing mechanism for the evolution of the alcohols on the Co/Ru/TiO₂ catalyst. The curve for ethane is much faster, and, moreover, has a clear change in slope, as is to be expected for the hydrocarbon formation as indicated in the previous section.

The actual rates of formation of the alcohols and hydrocarbons on the active Co-surface are likely to be similar. If the formation kinetics determine the transients, the reactivity distribution plots for the alcohols will be similar to the plots for the hydrocarbons. This is clearly not the case. If the alcohols can reside on the partially reduced TiO_2 support and if the surface concentration of adsorbed species on the TiO_2 surface is larger than on the active Co-metal, it represents a single pool process. In this

situation, the interaction of the alcohols with the TiO_2 support governs the shapes of the responses and straight lines for the alcohols in figure 6.21 are indeed expected.

Formation of alcoxy species on TiO₂

Adsorption on a partially reduced TiO_2 surface can be more readily expected for alcohols than for hydrocarbons, since the surface of the TiO_2 support itself contains -OH groups and oxygen vacant sites. Adsorption of alcohols can occur from the gas phase and/or via spillover from the Co-metal to the support and will most likely result in the formation of alcoxy species over formate species [Taylor and Griffin, 1988; Robbins and Marucchi-Soos, 1989].

The slow responses of the alcohols are explained as follows. Before the isotopic step change is made, the alcohol-pool on the TiO_2 surface completely exists of the non-labeled components. When the experiment is executed, ¹³C is incorporated into the alcohols during the formation process on the active Co-surface. The oxygenate products formed on the Co are immediately transferred to the TiO_2 support and the non-labeled alcohol-pool on the TiO_2 support is gradually exchanged by labeled alcohols. The intermediate labeled variants are formed for a short period of time on the Co-metal surface, comparable to the formation of $^{12}C^{13}CH_6$ in figure 6.20. On the TiO_2 support they are mixed with a large quantity of non-labeled and fully labeled variants. The latter is constantly produced after the step change. The observed responses of the intermediate labeled variants are therefore small and the transients are completely determined by the sorption process on the TiO_2 support.

The presence of methoxy species, represented as CH₃O_{ads}, on the support of Ni-based catalysts is frequently observed in literature with TPR studies. Sen and Falconer [1990] observe two distinct methane formation peaks during TPR experiments of preadsorbed CO on a Ni/TiO₂ catalyst. Lee and Bartholomew [1989] obtain similar results on Co/Al₂O₃ catalysts. The first peak is ascribed to CO chemisorbed on the metal surface. The second peak is ascribed to the presence of a CH₃O_{ads} species on the support that spills over to the metal and hydrogenates towards methane at higher temperatures. Isotopic labeling of CO indicated that the two species are physically distinct and that the two species do not intermix significantly. These results are supported by the occurrence of peaks during the TPD of coadsorbed CO and H₂ that are not present when CO and H₂ are adsorbed alone. Sen and Falconer [1990] mention that on partially reduced TiO₂ supports, the Ti³⁺ sites are responsible for the formation of CH₃O_{ads}. Taylor and Griffin [1988] have identified the CH₃O species on TiO₂ powder via IR. They show that methanol displays molecular adsorption resulting in CH₃OH_{ads}, or dissociative adsorption resulting in CH₃O_{ads}. During TPD the molecular adsorbed species converts to the dissociated species at 473 K and the latter species is stable until 723 K. The onset of the decomposition of CH₃O_{ads} on the TiO₂ to CH₄, H₂, and CO₂ occurs at 623 K. Robbins and Marucchi-Soos [1989] indicate that the O atom of the CH₃O_{ads} species originates from CO and not from the oxide support.

Suitability for TiO₂ supported catalysts to study alcohol formation

It is concluded that the mechanism for the formation of alcohols cannot be studied in the presence of the TiO_2 support. $C^{18}O$ labeling experiments are therefore not useful to obtain insight into the formation mechanism of alcohols on the Co/Ru/TiO₂ catalyst. Comparison of ¹³CO with $C^{18}O$ experiments may give information about the species that results from adsorption of alcohols on the TiO_2 support. If the CH₃O_{ads} species does not exchange with O from the oxide support, ¹³CO and $C^{18}O$ SSITKA experiments would result in identical responses of the alcohols.

However, these issues are beyond the scope of this thesis. Information about the alcohol formation kinetics is obtained by eliminating the TiO_2 support by using a full metal Co-sponge catalyst. In sections 6.3.2 and 6.3.3 the formation of alcohols is studied by ¹⁸O- and ¹³C-labeling experiments on this catalyst.

Experimental observations: H₂, HD, and D₂ transients

• Typical transients of Ne, H₂, D₂, and HD are represented in figures 6.22 and 6.23 following a N₂/Ne/CO/H₂ \rightarrow N₂/CO/D₂ step change. The responses in figure 6.22 are determined upstream the catalyst bed, in figure 6.23 downstream the catalyst bed.



Figure 6.22: Normalized responses of Ne, H₂, D₂, and HD at the entrance of the Co/Ru/TiO₂ catalyst bed at 498 K, 1.2 bar, H₂/CO=1, and W_{cat}/F =16.8 kg_{cat}·s·mole⁻¹.





Figure 6.23: Normalized responses of Ne, H₂, D₂, and HD behind the Co/Ru/TiO₂ catalyst bed at 498 K, 1.2 bar, H₂/CO=1, and W_{cal}/F =16.8 kg_{cat}'s·mole⁻¹.



The following observations are made:

• In figure 6.22, the initial response of H_2 is as fast as the response of Ne, but tails significantly afterwards. Tailing of D_2 is also observed, but less than with H_2 . Moreover, HD is also observed

• The tailing of D_2 is small during sampling upstream the catalyst bed. However, the tailing of the H_2 and D_2 responses increases considerably during sampling downstream the catalyst bed. For HD, not only the maximal response, but also the tailing becomes more pronounced.

Compared to CO, the adsorption/desorption rate for H_2 is slower, see figure 6.24. D_2 breaks through immediately, whereas CO does not. In other words, the frequency with which H_2 adsorbs/desorbs on the Co-surface is lower than for CO. The dissociative character of the sorption of H_2 is indicated by the enhanced formation of HD measured after the catalyst bed. It is checked by blank experiments that the reactor wall, the steel capillaries, and the SiC dilution of the catalyst bed do not display significant H_2 sorption effects.

Experimental observations: isotopic variants of methane

As indicated in section 4.3.5, the transients of CD_xH_{4-x} , where x=0-4, are calculated at every point in time from the MS intensities in the m/e range 15-20. For these calculations, the isotopic effect during fragmentation leads to uncertainties in the fragmentation patterns for CD_xH_{4-x} , where x=0-4, and to a lower accuracy of the obtained transients. Moreover, a kinetic H/D isotope effect exists, leading to changes in the product spectrum due to the replacement of H₂ by D₂, as observed in section 4.3.6. The transients of D-methane are shown in figure 6.26. The markers in the figure are actual MS data points, representing a sample frequency of 1.6 Hz. The following observations are made:

• The experimental and calculated MS intensities in the m/e range 15-20 are depicted in figure 6.25. The inverse kinetic H/D isotope effect is introduced in the calculations, leading to a decrease of

the methane concentration by a factor of 0.58 upon the replacement of H_2 by D_2 . Based on the steady state GC analysis, an inverse kinetic H/D isotope effect of 0.85 is observed in section 3.3.6. Although in both cases an inverse kinetic H/D isotope effect is observed, the discrepancy between the values is not clear.

• In figure 6.26, the transients of D-methane are normalized to 100% labeling at roughly t=15 s according to the procedure outlined in section 4.3.3. The reason for this is that the small changes of the MS intensities past this point are caused by the influence of D-labeled H_2O . The experimental procedure outlined in section 4.3.5 does not provide a total elimination of water.

• From figure 6.23, however, it appears that at t=15 s the exchange of H_2 in the gas phase by D_2 is not yet complete. The overall D-content of hydrogen in the gas phase amounts to roughly 90%, as is illustrated in figure 6.27. Normalization of the D-methane transient to fully labeling at this moment after the step change is therefore not justified. However, the major contributions of both the D_2 and the D-methane transients occur in the first few seconds of the experiment and are representative for the fast D-exchange on the Co-surface. In figure 6.27 it is clearly observed that:

- 1. D-labeling of methane starts immediately when the step-change is initiated;
- the D-content in methane reaches a constant level at the same moment that the tailing of the D₂ signal starts.



Figure 6.25: Fits for the MS intensities in the m/e range 15 to 20: x 15 : + 16 : \triangle 17 : \Box 18 : \bigcirc 19 : \bigcirc 20





Figure 6.26: Normalized D-labeling responses of CH_xD_{4x} for the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H₂/CO=1, and W_{cat}/F =16.8 kg_{cat}·s·mole⁻¹.

Õ	Ne	•	CH₄		CH₃D
	CH_2D_2	•	CHD₃	*	CD_4

Figure 6.27: Normalized responses of Ne (\square), overall D-labeling content of H₂, HD and D₂ (\bigcirc), and the overall D-labeling content in methane (\triangle) at H₂/CO=1.

Intrinsic kinetics versus hydrodynamics

Tailing of H_2 is the result from the lack of sufficient pump capacity of the Balzers mass spectrometer. The low pump capacity for H_2 leads to backscattering of H_2 in the MS ionization chamber and to tailing of the signal. This is a well-known effect in mass spectrometry and is only relevant in case of light molecules [Zou *et al.*, 1994]. The HD in figure 6.22 results from the reaction between H• and D• radicals produced at the MS filament in the simultaneous presence of D_2 and H_2 due to backscattering. In the absence of backscattering, HD would be absent. The increased tailing in figure 6.23 is attributed to the interaction of H_2 and D_2 with the Co/Ru/TiO₂ catalyst. The initial responses of H_2 and D_2 are fast, representing the adsorption and desorption on the active metal. The increased tailing of the responses behind the catalyst bed is ascribed to the exchange with the partially reduced TiO₂ support. This probably proceeds via spillover of atomic hydrogen and deuterium from the metal to the support. Analog, the activation of H_2 by dissociative adsorption on metal surfaces and the subsequent spillover to the oxidic support is generally accepted to explain the enhanced reduction of the support in the presence of metal particles [Komaya *et al.,* 1994b]. The complete exchange of H by D present on the TiO₂ support is much slower than on the Co-metal, due to the lower diffusion rates of hydrogen on oxide supports and due the large surface area of TiO₂ resulting in large diffusion distances. The tailing in figure 6.23 is caused by the slow exchange on the TiO₂ support and the support therefore influences the transients considerably.

Identification of rate determining step during C_{1,ads} hydrogenation

The D-incorporation into methane is a fast process and that the overall fraction D-labeling in methane closely follows the average isotopic content of the H-pool on the metal surface. Two models are tested:

- 1. under the assumption of irreversible surface hydrogenation of C_{ads} to CH₄;
- 2. under the assumption of reversible surface hydrogenation of C_{ads} to CH₄.

Table 6.2: Kinetic scheme for methanation according to the carbene mechanism.

General reaction steps			
$CO_g + * \leftrightarrow CO_{ads}$			(R6.1)
$H_{2,g} + 2* \leftrightarrow 2H_{ads}$			(R6.2)
$CO_{ads} + * \rightarrow C_{ads} + O_{ads}$			(R6.3)
A: Irreversible hydrogenation		B: Reversible hydrogenation	
$C_{ads} + H_{ads} \rightarrow CH_{ads} + *$	(R6.4a)	$C_{ads} + H_{ads} \leftrightarrow CH_{ads} + *$	(R6.4b)
$CH_{ads} + H_{ads} \rightarrow CH_{2,ads} + *$	(R6.5a)	$CH_{ads} + H_{ads} \leftrightarrow CH_{2,ads} + *$	(R6.5b)
$CH_{2,ads} + H_{ads} \rightarrow CH_{3,ads} + *$	(R6.6a)	$CH_{2,ads} + H_{ads} \leftrightarrow CH_{3,ads} + *$	(R6.6b)
$CH_{3,ads} + H_{ads} \rightarrow CH_{4,g} + 2*$	(R6.7a)	$CH_{3,ads} + H_{ads} \rightarrow CH_{4,g} + 2*$	(R6.7b)

In the case of **irreversibility**, the hydrogenation of surface carbon, arising from CO_{ads} dissociation, to methane proceeds via the unidirectional stepwise addition of atomic hydrogen, as represented by mechanism **A** in table 6.2. The transients in figure 6.25 indicate low surface concentrations of $CH_{x,ads}$ species, where x=1-3. A low surface concentration of CH_x species, where x=1-3, implies that the first hydrogenation step, *i.e.* reaction (R6.4), is the rate limiting step and all other additions of H_{ads} are relatively fast.

In the case of **reversibility**, the $CH_{x,ads}$ species undergo hydrogenation and dehydrogenation reactions according to mechanism **B** in table 6.2. Note that the hydrogenation of $CH_{3,ads}$ is irreversible, as explained in section 6.2.1. The experimental results indicate that the hydrogenation and dehydrogenation steps are relatively fast compared to the net production of methane. Now, the surface concentrations of these species are not assessable with the SSITKA technique.

On the basis of this qualitative interpretation of the SSITKA experiments, no exclusion on the H-content of C_{α} and C_{β} can be given. However, the viability of both the irreversible and the reversible mechanism is probed by simulations in chapter 7.

In literature, controversy still exists on this subject. A short overview of different published results is presented below.

In the group of Mirodatos and co-workers, similar transients as presented in this work are obtained for D₂ and ¹³CO-SSITKA experiments on the methanation reaction over a Ni/SiO₂ catalyst. Agnelli *et al.* [1998] perform ¹³CO/H₂ \rightarrow ¹²CO/H₂/He step changes and Marquez-Alvarez *et al.* [1998] perform CO/H₂ \rightarrow CO/D₂/He step changes. The resulting transients are shown in figure 6.28 and 6.29, respectively. Based on the delay of the overall D-labeling of methane with respect to the overall D-

labeling of the hydrogen transient, the H-content of the $CH_{x,ads}$ intermediate corresponds to 0.5 < x < 0.8. According to the authors, CH_{ads} is the most abundant methane intermediate and the hydrogenation of CH_{ads} to $CH_{2,ads}$, *i.e.* reaction (R6.5a) in table 6.2, is the rate limiting step in the methanation over Ni/SiO₂. However, the shapes of the transients of the isotopic variants for D-methane do not correspond to the situation where CH_{ads} is the most abundant surface species in the irreversible mechanism **B** in table 6.2. Since the exchange of H_{ads} by D_{ads} is fast, the evolution of the isotopic variants for D-methane results from a surface titration of the $CH_{x,ads}$ species. If CH_{ads} is the most abundant species, CHD_3 is expected to have a much larger contribution than observed experimentally. Additional, the CD_4 response would show considerable tailing, which is also not observed experimentally. The conclusions by Marquez-Alvarez *et al.* [1998] are therefore not consistent with their experimental observations. This is confirmed by simulations in section 7.4.



Figure 6.28: Normalized responses of He, ¹²CO, ¹³CO, ¹²CH₄, and ¹³CH₄ following the switch ¹³CO/H₂ \rightarrow ¹²CO/H₂ for a Ni/SiO₂ catalyst at 503 K, 1 bar, and H₂/CO=2 [Agnelli *et al.*, 1998].

Figure 6.29: Normalized responses of, CH₄, CH₃D, CH₂D₂, CHD₃, and CD₄ following the switch CO/H₂ \rightarrow CO/D₂ for a Ni/SiO₂ catalyst at 523 K, 1 bar, and H₂/CO=2 [Marquez-Alvarez *et al.*, 1998].

An indication of the irreversibility of the hydrogenation reactions (R6.4) to (R6.7) is supplied by cofeed studies [van Barneveld and Ponec, 1984]. In this study, different C₁ precursors were added to the syngas mixture. Van Barneveld and Ponec [1984] add CHCl₃, CH₂Cl₂, or CH₃Cl to a syngas mixture with H₂/CO=1.75 at 483 K and 1.1 bar over Ni and Co metal catalysts. All three probes give rise to different effects on the selectivity of the Fischer-Tropsch synthesis. The addition of CH₃Cl does not result in an increased C₂₊ selectivity, whereas the C₂₊ selectivity increases by adding CH₂Cl₂ and CHCl₃. The increase in C₂₊ selectivity is most pronounced by adding CHCl₃ on both catalysts. These results are indicative for the irreversible nature of reactions (R6.4) to (R6.6), since all probes would evoke similar effects on the selectivity if they were exchangeable via fast reversible H-exchange reactions.

Happel [1986] models D-tracer experiments of the methanation reaction on a Ni-catalyst. He performs D_2 SSITKA experiments in a gradientless external recycle reactor. The surface concentrations of the intermediates towards methane, CH_{ads} , $CH_{2,ads}$, and $CH_{3,ads}$, are calculated to be 4.44 Nml·g_{cat}⁻¹, 0.54 Nml·g_{cat}⁻¹, and 0.21 Nml·g_{cat}⁻¹. During a subsequent deuterium titration of the catalyst after steady state operation, the amount of CD_4 is assumed representative for the surface concentration of non-hydrogenated carbidic carbon. Its concentration amounts to 2.41 Nml·g_{cat}⁻¹. All methane intermediates, C_{ads} , $CH_{2,ads}$, and $CH_{3,ads}$, are present on the catalyst surface in measurable quantities. The author concludes that the hydrogenation of CH_{ads} (R-6.5a) is the rate-controlling step during methane formation.

A theoretical study by Bell and Shustorovich [1990] suggests that the hydrogenation of surface C_{ads} is the rate-limiting step in the hydrogenation of CO. By means of the Bond-Order Conservation Morse-Potential (BOC-MP) method, the authors study the CO hydrogenation pathways on the (111) surfaces of Ni and Pd. On the basis of energetic considerations they demonstrate that the hydrogenation of C_{ads} to CH_{ads} , conform reaction (R6.4a), is rate-determining on Ni. Since Ru and Co

display similar behavior as Ni in the CO hydrogenation, it may be expected that reaction (R6.4a) is also the rate-determining step on these metals.

By performing ¹³C and D-labeling SSITKA experiments Stockwell *et al.* [1988] concluded that the most probable number of H-atoms for the $CH_{x,ads}$ species on their Ni/Al₂O₃ catalyst is zero. In accordance with our experimental results, they observe that the CD₄ transient is much faster than the ¹³CH₄ transient during methanation at 493 K, 1 bar, and H₂/CO=1-9. Moreover, no C-H contributions in the IR analysis are detected at the reaction conditions. These observations imply that reaction (R6.4a) is rate determining.

In several other studies, remarks on the rate-determining step in the methanation reaction are given. By varying the CO partial pressure, Zhou and Gulari [1987] observe that the surface concentration of carbidic carbon does not change, whereas the total reaction rate decreases. From this they conclude that the overall reaction rate is not controlled by CO dissociation, *i.e.* reaction (R6.3), but by one of the hydrogenation reactions. The results of the TPR experiments performed by Lee and Bartholomew [1989] also suggest that the rate-determining step in the CO hydrogenation involves the hydrogenation of carbidic carbon resulting from CO dissociation. Yates *et al.* [1985] report that the hydrogenation of CH_{3,ads} to methane ((R6.7a) and (R6.7b)) is six orders of magnitude faster than the rate of methane formation from CO. Geerlings *et al.* [1991a, 1991b], however, mark the final hydrogenation step ((R6.7a) and (R6.7b)) as the slowest reaction step.

6.2.5 Increase of number of active sites upon Ru-promotion

The influence of the Ru-promotor on the catalytic performance of the Co/Ru/TiO₂ catalyst is studied by comparing the transients of CO, methane, propane, and propene following a He/Ne/¹²CO/H₂ \rightarrow He/¹³CO/H₂ isotopic step change over a Co/TiO₂ catalyst with those over a Co/Ru/TiO₂ catalyst at identical reaction conditions. The transients of Ne, ¹³CO, and ¹³CH₄ for both catalysts are shown in figure 6.30. The transients of all but the non-labeled isotopic variants for propane and propene are shown in figure 6.31 for the promoted Co/Ru/TiO₂ catalyst and in figure 6.32 for the unpromoted Co/TiO₂ catalyst.



 $\begin{array}{c} \text{markers) and propene (open markers) for the Co/Ru/TiO_2} \\ \text{catalyst at 503 K, 1.2 bar, H_2/CO=2, 67% He dilution.} \\ & & {}^{12}C_2{}^{13}CH_8; \quad \blacksquare \quad {}^{12}C_1{}^{13}C_2H_6; \quad \triangleq \quad {}^{13}C_3H_6; \\ & & {}^{12}C_2{}^{13}CH_6; \quad \square \quad {}^{12}C_1{}^{13}C_2H_6; \quad \triangle \quad {}^{13}C_3H_6 \\ \end{array}$

The following observations are made:

- The chromatographic effect for CO on the unpromoted catalyst is smaller than on the Co/Ru/TiO₂ catalyst at comparable residence times.
- The transients of methane on the two catalysts are more or less the same.
- When comparing figure 6.31 with 6.32, it is obvious that propene has a bigger time lag with respect to propane on the promoted catalyst than on the unpromoted catalyst.

• As for the methane transients, the propane transients for both catalysts are more or less the same.

• The increase in time lag between the transients of the 1-olefin and the paraffin with Ru-promotion is observed for all the C_2 to C_5 hydrocarbons (not shown).

Ru related increase of active surface sites

In section 3.6 it was observed that the addition of 0.2wt% Ru to the 12wt% Co/TiO₂ catalyst results in an almost doubling of the CO conversion. This increase in activity led to a small increase of the chain growth probability and a decrease in the methane selectivity. Since the transients of all paraffinic reaction products are identical on both catalysts, it appears that the increased activity is not caused by a change of the reaction rates of the various steps in the mechanism, but rather results from a simple increase in the number of active sites on the catalyst surface.

The increase in the number of active sites is illustrated by the doubling of the time delay of the CO transient (chromatographic effect) due to Ru-promotion. Moreover, the time lag of the propene transients increases due to the increase of the number of active sites per surface area when the catalyst is promoted. However, the transients of the paraffins, which do not interact with the catalyst surface after formation, are similar on the Co/Ru/TiO₂ and the Co/TiO₂ catalysts. This illustrates the absence of changes in the reaction mechanism due to R-promotion.

The results are in good agreement with the effect observed by Iglesia *et al.* [1993b] for their $Co(12wt\%)/Ru(0.14wt\%)/TiO_2$ and $Co(23wt\%)/Ru(0.26wt\%)/SiO_2$ promoted and unpromoted catalysts. The activity per total metal surface area increased upon promotion by a factor of 3.3 for the Co/TiO_2 catalyst and a factor of 1.7 for the Co/SiO_2 catalyst at 473 K and 20 bar. At the reaction conditions applied in their study, the methane selectivity decreased and the C_{5+} selectivity increased due to Ru promotion. They claim that Ru promotion increases the reducibility of the catalyst and inhibits the build-up of carbonaceous deposits and oxygen species during reaction, both effects leading to a higher number of active sites per metal surface area. For both the promoted and unpromoted catalysts similar activation energies and pressure dependencies of the CO conversion are observed, indicating that the intrinsic activity of the active site has not changed. The increase in surface concentration of active site leads to a higher degree of readsorption of reactive olefins and thus to a higher paraffin selectivity and a higher chain growth probability. The Ru promotion is only effective if an intimate contact between Co and Ru is established by a calcination treatment at 573 K. Without this calcination step the activity only increases slightly. The added Ru facilitates the reduction of Co-oxides and prevents catalyst deactivation during reaction.

Bruce *et al.* [1993] report a threefold increase of the Fischer-Tropsch activity during doping of a $Co(11wt\%)/CeO_2$ catalyst with 0.3wt% Ru, without a significant change of selectivity. They tested the catalysts at 485 K and 1 bar.

Similar results for Ru promotion of Co/Al₂O₃ catalysts are observed by Kogelbauer *et al.* [1996]. The Fischer-Tropsch activity increased by a factor of 2 to 3 upon Ru addition at 493 K, 1.8 bar, and $H_2/CO=10$, while the product distribution was hardly influenced. By studying the methane formation using ¹³CO SSITKA, they concluded that the intrinsic rate parameters did not change. The increase in activity was rather caused by the increase of the number of active Co-sites. The authors claim that the increase stems from an increased reducibility and dispersion of the Co-particles on the Al₂O₃ support. In a similar study on Pt-promotion of Co-based catalysts on SiO₂ and Al₂O₃ supports, Schanke *et al.* [1995] report a 3 to 5 fold increase in methanation activity at 483 K, 1 bar, and $H_2/CO=7$. The reported absence of any change in the chain growth probability or olefin selectivity results from the low reaction pressure and the high H_2/CO ratio, both favoring methane formation.

Belambe *et al.* [1997] used ¹³CO SSITKA to indicate that severe calcination of Ru-promoted Co/Al_2O_3 catalysts results in a decrease of the total number of active sites, whereas the intrinsic activity of the sites does not change. They report the absence of a change of the chain growth probability, but they do not specifically report olefin and paraffin selectivities.

6.3 Steady state isotopic transient kinetic analysis on Co-sponge catalyst

In this section the transient kinetic analysis of the Fischer-Tropsch synthesis on the Cosponge catalyst is discussed. This model catalyst allows assessing the kinetics on the Co-metal itself, without the interference of the TiO₂ support. From the previous section it appears that the TiO₂ support influences the evolution of ¹³C-labeled alcohols on the one hand and the H₂/D₂ exchange during D₂ SSITKA experiments on the other hand. The first effect completely obscures the actual formation kinetics of alcohols, while the latter effect disturbs the measurements leading to a troublesome interpretation of the experimental results. The Co-sponge catalyst is not studied to the same extent as the Co/Ru/TiO₂ catalyst since the goal is to obtain a qualitative comparison between the supported and unsupported catalysts.

Both types of experiments are repeated on the Co-sponge catalyst. In section 6.3.1 the ¹³Clabeling of the C₁ to C₅ hydrocarbons is discussed. The alcohol formation is studied by means of ¹³CO SSITKA in section 6.3.2 and by means of C¹⁸O SSITKA in section 6.3.3. The D-labeling of methane, ethane, and ethene is discussed in section 6.3.4.

6.3.1 ¹³CO SSITKA on methanation and higher hydrocarbon formation

The normalized transients of Ne, ¹³CO, and ¹³CH₄ for the Co-sponge catalyst following a He/Ne/¹²CO/H₂ \rightarrow He/¹³CO/H₂ isotopic step change are shown in figure 6.33. The transients for ethane are represented in figure 6.34. The reaction conditions are 498 K, 1.2 bar, H₂/CO=3, and W_{cat}/F =130 kg_{cat}·s·mole⁻¹. The following observations are made:

• Compared to the Co/Ru/TiO₂ catalyst, the residence time expressed as W_{cal}/F is large for the Cosponge catalyst, because the sponge catalyst is fully metallic and has a relatively low surface area.

• The shape of the transients, as well as their time scales, are comparable to the transients obtained on the Co/Ru/TiO₂ catalyst. All the expected features are present, *i.e.* the chromatographic effect for CO, the immediate breakthrough of ¹³CH₄ before ¹³CO, and the delay of the 1-olefin compared to the paraffin.



Figure 6.33: Normalized ¹³C-labeling responses of Ne, ¹³CO, and ¹³CH₄ for the Co-sponge catalyst at 498 K, 1.2 bar, H₂/CO=3, and W_{cal}/F =130 kg_{cal}·s·mole⁻¹.



Figure 6.34: Normalized ¹³C-labeling responses of ethane for the Co-sponge catalyst at 498 K, 1.2 bar, H₂/CO=3, and $W_{cal}/F=130 \text{ kg}_{cat} \text{ s mole}^{-1}$. \blacktriangle ¹²C₂H₆ \clubsuit ¹²C₁³CH₆ \blacksquare ¹³C₂H₆

Similarity between Co/Ru/TiO₂ catalyst and Co-sponge catalyst

The behavior of the Co-sponge catalyst for the methanation reaction and the higher hydrocarbon formation during ¹³CO SSITKA experiments is similar to that of the Co/Ru/TiO₂ catalyst.

In figure 6.35, plots for the decay of the ¹²C content in methane and ethane are represented. As with the Co/Ru/TiO₂ catalyst, the plots for methane and the C₂₊ hydrocarbons (represented by ethane) are quite similar, both showing a downward convexity and following each other closely. As for the Co/Ru/TiO₂ catalyst, the surface heterogeneity is present on the Co-sponge catalyst and the C-C coupling reaction is relatively fast. Comparing the decay of the ¹²C content in methane for the Co/Ru/TiO₂ catalyst and the Co-sponge catalyst, figures 6.15 and 6.35 respectively, reveals that the change in slope is more pronounced with the Co-sponge catalyst than with Co/Ru/TiO₂ catalyst. This illustrates the difference in rate constants for the formation and consumption of both C_{α,ads} and C_{β,ads}. This likely results from a different surface structure of the sponge catalyst due to the absence of the TiO₂ support. This leads to different surface concentrations for H_{ads} and empty surface sites. The presence of two reactive intermediates towards methane for unsupported Co-metal catalysts is also reported by Siddall *et al.* [1989] at H₂/CO=3, 1bar, and 518-533 K. This is concluded from modeling of the ¹³CH₄ transients from block-forcing ¹³CO SSITKA experiments on an unsupported Co catalyst.



Figure 6.35: Decay of the ¹²C content in methane (dashed line), monitored by MS, and ethane ($^{-}$), monitored by GCMS at 498 K, 1.2 bar, H₂/CO=3, and W_{cal}/F =130 kg_{cat}'s-mole⁻¹.

Influence of TiO₂ support

The experimental results prove that the TiO_2 support does not seriously influence the mechanism of the formation of the hydrocarbon reaction products. All possible influences of TiO_2 on the formation of methane or higher hydrocarbons seem to be of minor importance. The methane formation route via CH_xO_{ads} species on the support, of which several researchers emphasize the importance during the Fischer-Tropsch synthesis [Sen and Falconer, 1990; Lapidus *et al.*, 1992; Lee and Bartholomew, 1989], has an inappreciable contribution under the reaction conditions applied in this study. If spillover of oxygenate intermediates from the Co-metal surface to the TiO_2 support occurs, as was suggested in section 6.2.3, the inverse spillover is absent. Komaya *et al.* [1994a] also mention that this route is negligible in their study on the influence of metal-metal oxide interactions on the Fischer-Tropsch synthesis on Ru/TiO₂ and TiO₂-promoted Ru/SiO₂ catalysts.

However, effects caused by the TiO_2 support that do not influence the mechanism of hydrocarbon product formation, but lead to a shift in reaction rates within the mechanism, can still be present. Examples of those effects are:

- The migration of TiO_x fragments onto Ru during reduction of a Ru/TiO₂ catalyst has been frequently identified in literature [Komaya *et al.*, 1994a, 1994b].
- H-spillover from the metal to the support.
- Increase in CO conversion and chain growth probability caused by an enhancement of the CO dissociation by TiO₂ [Komaya *et al.*, 1994]. Chen and Goodwin [1995] report an increased rate of CO dissociation resulting from Zr promotion of Co/SiO₂ catalysts and Borer *et al.* [1994] for the Zr promotion of Rh/SiO₂ catalysts. Boffa *et al.* [1994] report that only the metal oxides that show partial reduction enhance the methanation rate for CO on decorated Rh-foils.

6.3.2 ¹³CO SSITKA on alcohol formation

The kinetics for the alcohol formation are studied on the Co-sponge catalyst by $He/Ne/^{12}CO/H_2 \rightarrow He/^{13}CO/H_2$ isotopic step change experiments. The normalized transients of Ne, CO, and methanol are displayed in figure 6.36 and of methanol and ethanol in figure 6.37. The transient for non-labeled ethanol is not included for clarity reasons. The reaction conditions are summarized in the caption of figure 6.36. The following observations are made:

• Since the effect of sorption of alcohols on the TiO₂ support is eliminated, the observed transients are fully determined by kinetic phenomena on the active Co-metal.

• The transient of methanol (figure 6.36) is faster than of methane (figure 6.33). It starts immediately when the step change is initiated, before breakthrough of ¹³CO is observed. The response for ¹³C-labeled methanol reaches full labeling at the same moment ¹³CO reaches full labeling.

• Where the transient of methanol is similar in shape to the one for CO, the transients of ethanol (figure 6.37) are similar to those for ethane on the Co-sponge catalyst (figure 6.34).

• The response of the methyl labeled variant, *i.e.* ${}^{13}CH_3{}^{12}CH_2OH$, is small, while the response of the alcohol labeled variant, *i.e.* ${}^{12}CH_3{}^{13}CH_2OH$, is large.





Figure 6.36: Normalized ¹³C-labeling responses of Ne (solid line), ¹³CO (dashed line), and methanol (\triangle) for the Cosponge catalyst at 498 K, 1.2 bar, H₂/CO=4, and W_{cat}/F=135 kg_{cat}·s·mole⁻¹.





Methanol formation: O-content of methane intermediates

Because the transient of ¹³C-labeled methanol is much faster than the transient for ¹³C-labeled methane, methanol is formed via the hydrogenation of adsorbed CO. The intermediate species are represented by CH_yO_{ads} , where y=1-3. The following mechanistic aspects on the methanol formation are deducted from the transients of figure 6.36:

- Once methanol is formed, it does not have any significant interaction with the Co-sponge catalyst. This is illustrated by the immediate breakthrough of ¹³CH₃OH.
- Under the assumption of irreversible reactions during the formation of methanol, the surface concentration of CH_yO_{ads} is small. As CO moves as a front through the reactor, the pool of adsorbed ¹²CO on the Co-surface is gradually replaced by ¹³CO while mixing in the axial direction is negligible. The average isotopic composition of the CO-pool is proportional to time during the ¹³CO transient. Since the transient for methanol starts at the moment that the isotopic step change is initiated and reaches unity at the same moment as the transient for CO does, the isotopic content of methanol represents the average isotopic composition of the adsorbed CO pool. If it is assumed that methanol is formed via unidirectional mechanistic steps, it implies that the surface concentration for CH_yO is small and the isotopic exchange of ¹²CH_yO by ¹³CH_yO is rapid. This means that the surface concentration of methanol intermediates is much smaller than the surface concentration of methane intermediates, from which it is concluded that the pool of methane intermediates, *i.e.* C_{α,ads} + C_{β,ads}, consists of O-free species.

Ethanol formation: CO- or CH_vO-insertion

Due to the symmetry of the ethane and ethene molecule, only one intermediate labeled species exists. Ethanol, however, is asymmetric and two intermediate labeled species are distinguished, yielding extra mechanistic information. In figure 6.37 the isotopic variant with a labeled alcohol function, *i.e.* ¹²CH₃¹³CH₂OH, is more abundant than the variant with a labeled methyl function, *i.e.* ¹³CH₃¹²CH₂OH. The hydroxy-carbene mechanism, in which C-C coupling occurs by combination of two hydroxy-carbene species under the elimination of water, would give rise to equal amounts of the two intermediate labeled ethanol species. This mechanism is clearly not valid as the prevailing C-C coupling reaction. The CO-insertion mechanism, where C-C coupling occurs via the combination of a CH_x species with CO, can explain the observed low contribution of the methyl labeled intermediate of ethanol. According to the carbene mechanism methane is a direct result of the complete hydrogenation of a CH_x species. The transient of methane represents the isotopic composition of the pool of CH_{x,ads} species. In a short period of time ¹²CO_{ads} is completely exchanged by ¹³CO_{ads}, while the $CH_{x,ads}$ -pool still consists of ¹²CH_{x,ads} and ¹³CH_{x,ads}. The formation of a methyl labeled ethanol intermediate from ¹³CH_{x,ads} and ¹²CO_{ads} is therefore no longer possible, and only the alcohol labeled ethanol intermediate is formed as long as ${}^{12}CH_{x,ads}$ is present on the surface. The response of the methyl labeled intermediate, however, does not need to be zero. During the time scale of the CO chromatographic effect, both unlabeled and labeled CO_{ads} and CH_{x.ads} species are present on the surface and both intermediate labeled variants are formed.

However, the same reasoning holds for a CH_yO -insertion mechanism for alcohol formation under the restriction that the surface concentration of the CH_yO species is small. Earlier in this paragraph, it was concluded from the methanol transient that the surface concentration of the CH_yO species is small. In this case, the isotopic composition of the CH_yO pool resembles the isotopic composition of the CO pool, and no methyl labeled ethanol intermediate is formed after CO has reached full labeling. On the basis of qualitative reasoning, no distinction can be made between the CO-insertion and the CH_yO -insertion mechanism. A modeling approach, however, gives more insight into the differences between the two mechanisms, which is discussed in section 8.7.

6.3.3 C¹⁸O SSITKA on alcohol formation

The alcohol formation kinetics are also studied by $He/Ne/C^{16}O/H_2 \rightarrow He/C^{18}O/H_2$ isotopic step change experiments. In the ¹⁸O-labeling experiments, only transients for O-containing species are obtained. The transients of Ne, CO, and methanol are displayed in figure 6.38 and of methanol, ethanol, and propanol in figure 6.39. The experimental conditions are identical to the alcohol ¹³C-labeling experiments of figures 6.36 and 6.37.



Figure 6.38: Normalized ¹⁸O-labeling responses of Ne (solid line), C¹⁸O (dashed line), and methanol (\triangle) for the Cosponge catalyst at 498 K, 1.2 bar, H₂/CO=4, and W_{cat}/F =135 kg_{cat}'s-mole⁻¹.

Figure 6.39: Normalized ¹⁸O-labeling responses of methanol (\triangle), ethanol (\Box), and propanol (\bigcirc) for the Co-sponge catalyst at 498 K, 1.2 bar, H₂/CO=4, and W_{cat}/F=135 kg_{cat}·s·mole⁻¹.

In figure 6.38, all the transients are identical to the ones observed in figure 6.36 for the ¹³Clabeling experiment under the same experimental conditions. The time lags for ¹³CO and C¹⁸O are identical, which is expected for an irreversible dissociation of CO_{ads} to C_{ads} and O_{ads} . In case of a reversible dissociation, different surface capacities for C_{ads} and O_{ads} will result in different transients of $C^{18}O$ and ^{13}CO .

The methanol transient in figure 6.38 is identical to the transient for ¹³C-labeled methanol in figure 6.36. This is expected if methanol is produced via the direct hydrogenation of CO_{ads} . The transients of ethanol and propanol have become as fast as the transient for methanol. This, again, is indicative for a CO-insertion or a CH_vO-insertion mechanism for the formation of alcohols.

6.3.4 D₂ SSITKA on methanation and higher hydrocarbon formation

Experimental observations

The transients of Ne, H₂, and D₂ are presented in figure 6.40 as measured upstream the catalyst bed and in figure 6.41 as measured downstream the catalyst bed. In contrast to the similar experiments performed on the Co/Ru/TiO₂ catalyst, tailing of H₂ and D₂ is observed in both situations. This is caused by a low pump capacity of the MS due to fouling of the membrane pump. The intensity of the tailing for H₂ and D₂ is, however, similar in both situations. This was not the case for the Co/Ru/TiO₂ catalyst, where the TiO₂ support provided an extra adsorption capacity responsible for the tailing observed behind the catalyst bed.

In figure 6.42 the transients of Ne, D_2 , and the overall fraction D-labeling in methane are represented. The procedure for obtaining the response for the overall fraction D-labeling in methane is identical to that applied with the Co/Ru/TiO₂ catalyst in paragraph 6.2.4. As for the Co/Ru/TiO₂ catalyst, it is observed that the transient for the overall fraction D-labeling of methane is as fast as the D_2 transient.



Figure 6.40: Normalized responses of Ne, H₂, and D₂ upstream the Co-sponge catalyst bed at 498 K, 1.2 bar, H₂/CO=5, and W_{cal}/F =90.7 kg_{cat} s mole⁻¹.





Figure 6.41: Normalized responses of Ne, H₂, and D₂ downstream the Co-sponge catalyst bed at 498 K, 1.2 bar, H₂/CO=5, and W_{cal}/F =90.7 kg_{cat}·s·mole⁻¹.

Figure 6.42: Normalized responses of Ne (\square), D₂ (\bigcirc), and the overall D-labeling content in methane (\triangle) for the Co-sponge catalyst at 498 K, 1.2 bar, H₂/CO=5, and *W*_{cal}/*F*=90.7 kg_{cat}·s·mole⁻¹.

Now that the adsorption capacity of the TiO_2 support is eliminated, it is meaningful to study the incorporation of deuterium in ethene and ethane. For this purpose, the GCMS set-up is used because of the heavy overlap of fragmentation patterns. Compared with the sampling via MS, the number of sampling points per unit time is drastically reduced. The resulting transients of the isotopic variants for ethene are presented in figure 6.43 and for ethane in figure 6.44.



Figure 6.43: Normalized responses of ethene for the Cosponge catalyst at 498 K, 1.2 bar, H₂/CO=3, and W_{cat}/F =129 kg_{cat}'s·mole⁻¹. \blacklozenge C₂H₃D; \blacksquare C₂H₂D₂; \blacktriangle C₂HD₃; \bigcirc C₂D₄ Figure 6.44: Normalized responses of ethane for the Cosponge catalyst at 498 K, 1.2 bar, H₂/CO=3, and W_{cat}/F =129 kg_{cat}'s·mole⁻¹. \blacklozenge C₂H₅D; \blacksquare C₂H₄D₂; \blacklozenge C₂H₃D₃; \bigcirc C₂D₄

The transients of D-ethene and D-ethane are both fast. The maximum responses of the intermediates C_2H_3D and $C_2H_2D_2$ in figure 6.43 amount to 19% and 17% respectively and both are only observed in one GCMS sample. Only C_2HD_3 has contributions larger than zero for several GCMS samples and its maximum response is 14%. For ethane, a similar behavior is observed. The maximum responses of intermediates C_2H_5D , $C_2H_4D_2$, $C_2H_3D_3$, and $C_2H_2D_4$ are 13%, 3%, 22%, and 4% respectively. Only C_2HD_5 has contributions larger than zero for several GCMS samples and its maximum response is 13%.

Discussion

The intensity of the tailing of H_2 and D_2 observed with the Co-sponge catalyst does not change when the transients measured up- and downstream of the catalyst bed are compared. A drastic increase of intensity of the tailing was observed on the TiO₂ supported catalyst in section 6.2.4. It was concluded that the H₂-adsorption capacity of the partially reduced TiO₂ support is responsible for the observed tailing. The results on the Co-sponge catalyst are in agreement with this.

As with the Co/Ru/TiO₂ catalyst, the D-labeling of methane is as fast as the D_2 transient. This supports the conclusions drawn in section 6.2.4 for the Co/Ru/TiO₂ catalyst:

- if the hydrogenation of CH_{x,ads} is irreversible, C_{ads} is the most abundant intermediate;
- if the hydrogenation of CH_{x,ads} is reversible, the hydrogenation and dehydrogenation are fast compared to the net rate of methane formation.

Although the H_2/CO feed ratio is lower, it is observed that the D-incorporation into ethane and ethene proceeds on a similar time scale as for methane. This is illustrative for a low capacity of the catalyst surface for H-containing growing hydrocarbon chains. This result is in good agreement with the conclusions drawn from the ¹³C-incorporation into the C₂-C₅ hydrocarbons presented in section 6.2.2 for the Co/Ru/TiO₂ catalyst and in section 6.3.1 for the Co-sponge catalyst. In these sections it is indicated that the average isotopic composition of the C₂₊ hydrocarbon reaction products closely follows that of methane, indicating that the surface concentration of growing hydrocarbon chains is some orders of magnitude smaller than that of the C₁ intermediates. Modeling in chapter 8 validates this conclusion.

6.4 Conclusions

The SSITKA technique is a powerful tool to perform mechanistic investigations of heterogeneous catalyzed reactions. The kinetic information includes the identification of surface species, the determination of surface coverages of these species, and the identification of surface reactions. It is demonstrated in this chapter that the power of the technique to identify mechanistic aspects and the chemical composition of reaction intermediates is optimized when the labeling of all participating reactants is applied at similar experimental conditions. The present SSITKA investigation of the Fischer-Tropsch reaction results in a detailed insight into the reaction mechanism. This results from an extensive kinetic investigation, comprising:

- 1. ¹³C-, ¹⁸O-, and D-labeling experiments under comparable experimental conditions
- 2. analysis of 13 C-incorporation into C₁ to C₅ hydrocarbons and C₁ to C₃ alcohols
- 3. analysis of ¹⁸O-incorporation into C_1 to C_3 alcohols
- 4. analysis of D-incorporation into C_1 and C_2 hydrocarbons
- 5. use of a Co/Ru/TiO₂ catalyst, a Co/TiO₂ catalyst, and a Co-sponge catalyst at comparable experimental conditions

The qualitative interpretation of the transients lead to the following conclusions:

- The molecular sorption of CO is fast and reversible.
- The reversible dissociative sorption of H_2 is slower than the molecular sorption of CO.
- The spillover of H_{ads} between the Co-surface and the TiO₂ support occurs on the Co/Ru/TiO₂ catalyst, while it is not observed for CO_{ads}.
- The catalyst surface is heterogeneous with respect to the methane intermediate. Two intermediates are defined, $C_{\alpha,ads}$ and $C_{\beta,ads}$.
- Both methane intermediates participate in chain initiation and chain growth. The results do not support a model where one intermediate preferential leads to methane formation, while the other is responsible for chain growth. This excludes the role of the TiO₂ support as a buffer for methane intermediates.
- The surface concentrations of CO, C_{α,ads}, and C_{β,ads} are large, resulting in a total fractional surface coverage of 0.91. The surface concentrations of growing hydrocarbon chains are small.
- The methane intermediates $C_{\alpha,ads}$ and $C_{\beta,ads}$ are O-free surface species.
- Chain initiation and chain propagation are fast surface reactions compared to the CO_{ads} dissociation and C_{1,ads} hydrogenation.
- The readsorption of 1-olefins is an important feature in the mechanism. Internal- and iso-olefins readsorb much less than 1-olefins.
- The formation of alcohols is a termination reaction via a CO-insertion or a COH-insertion mechanism.
- Alcoxy species are formed on the partially reduced TiO₂ support of the Co/Ru/TiO₂ catalyst. They
 result from the adsorption/desorption of alcohols and/or the spillover of alcohol intermediates from
 the Co-metal to the TiO₂ support.
- The Ru-promotor increases the number of active sites, whereas the intrinsic activity of the sites is unchanged.
- The D-methane transients are interpreted using two models, differing in the assumption of the reversibility of the stepwise hydrogenation of surface carbon to methane:
 - In case of irreversibility, C_{ads} is the most abundant surface intermediate and $C_{\alpha,ads}$ and $C_{\beta,ads}$ are H-free species.
 - In case of reversibility, the hydrogenation and dehydrogenation steps are relatively fast compared to the overall production of methane while the surface concentrations of CH_{x,ads}, where x=0-3, are unknown.

Because the experiments are conducted at well-defined experimental conditions in a welldefined reactor environment, the ¹³C- and ¹⁸O-labeling results are suitable for modeling purposes. The mechanistic aspects highlighted in this chapter are combined with the findings based on the steady state behavior of the catalysts and the aspects from the literature review in chapter 2 to yield a mechanistic model for the Fischer-Tropsch reaction. The kinetic parameters of this mechanistic model are quantified by modeling in chapters 7 and 8.

7

Intrinsic kinetics of the methanation reaction

7.1 Introduction

In literature, modeling of experimental results obtained with ¹³CO-SSITKA investigations on the CO hydrogenation and the Fischer-Tropsch reaction is generally limited to the application of oversimplified CSTR reactor models [Schanke *et al.*, 1995a; Komaya and Bell, 1994a]. Such reactor models are not capable of describing the reversibility of the adsorption and desorption of CO and the readsorption of reactive olefins during Fischer-Tropsch reactions. The goal of this chapter is the identification and quantification of feasible mechanisms for the methanation reaction at Fischer-Tropsch reaction conditions on the Co/Ru/TiO₂ catalyst and the Co-sponge catalyst by modeling the experimental results from chapters 5 and 6 using a plug-flow reactor model. Modeling is a tool to study the reaction mechanism in terms of:

- identification and quantification of the reaction network;
- identification and quantification of the chemical composition of surface species.

In this chapter, only the methanation reaction is considered and the results are used to model the Fischer-Tropsch reaction in chapter 8. The reasons to model the methanation reaction apart from the Fischer-Tropsch reaction are threefold:

- The surface heterogeneity observed in chapter 6 induces several a number of interactions between the various surface species and gas phase components, leading to numerous potential models. To minimize the time required for model discrimination, the methanation reaction is considered in section 7.3.1, which is extended in section 7.3.2 with the chain initiation reaction by introducing the formation of ethane. This procedure effectively identifies two Fischer-Tropsch mechanisms out of a dozen potential models.
- The transient data for the methanation reaction are more accurate than those for the C₂-C₅ hydrocarbons. By decoupling the methanation reaction from the Fischer-Tropsch reaction, rate coefficients for the initial part of the mechanism are fixed by means of the methane transient only.
- To account correctly for the readsorption of reactive olefins, a plug-flow reactor model is used. A large set of partial differential equations needs to be solved numerically in chapter 8. The computation time decreases if the number of variables is reduced by fixing the rate coefficients for the methanation reaction in this chapter.

Because the experimental data are obtained at differential reactant conversions, the methanation reaction and the formation of the C_{2+} hydrocarbons are decoupled by representing the C_{2+} hydrocarbon formation in section 7.3.3 by a net consumption term of methane intermediates. Finally, simulations of D-labeling SSITKA experiments on the methanation reaction identify the mechanism of the hydrogenation of surface carbon in section 7.4

7.2 Model formation for the Fischer-Tropsch synthesis

7.2.1 Mechanistic considerations

Definitions concerning the pool of methane intermediates are given for clarity reasons. This pool contains single C-species represented by $C_{1,ads}$. The previous chapter indicated the heterogeneity of this pool, dividing it into two pools of $C_{\alpha,ads}$ and $C_{\beta,ads}$. Since methane formation is the stepwise hydrogenation of surface carbon, the pool of $C_{1,ads}$ is made up by the H-containing intermediates C_{ads} , CH_{ads} , $CH_{2,ads}$, and $CH_{3,ads}$. In mathematical terms:

 $L_{C_1} = L_{C_{\alpha}} + L_{C_{\beta}} = L_C + L_{CH} + L_{CH_2} + L_{CH_3}$ (7.1)

The model for the Fischer-Tropsch synthesis is presented in figure 7.1. It is based on the carbene chain growth mechanism and results from a number of considerations, which result from the literature review in chapter 2, the qualitative interpretation of the steady state results in chapter 5, and the transient SSITKA results in chapter 6.

• Reversible molecular sorption of CO on the catalyst surface, evidenced by the observation of a chromatographic effect for CO during ¹³CO SSITKA experiments in chapter 6.

• The catalyst surface is heterogeneous. The presence of two reactive intermediates towards both methane formation and higher hydrocarbon is illustrated by means of ¹³CO SSITKA on the Co/Ru/TiO₂ catalyst (section 6.2.2), on the Co/TiO₂ catalyst (section 6.2.5), and on the Co-sponge catalyst (section 6.3.1). These two reactive intermediates are denoted $C_{\alpha,ads}$ and $C_{\beta,ads}$.

• Both intermediates $C_{\alpha,ads}$ and $C_{\beta,ads}$ are O-free. This implies that the formation of the chain initiator and the monomeric building block in the carbene mechanism proceeds via the stepwise hydrogenation of C_{ads} following CO_{ads} dissociation. A H-assisted CO_{ads} dissociation via enolic surface intermediates is highly improbable.

• The D₂-SSITKA experiments (sections 6.2.4 and 6.3.4) imply either (i) low H-contents of $C_{\alpha,ads}$ and $C_{\beta,ads}$ and C_{ads} as the most abundant surface species compared to CH_{ads} , $CH_{2,ads}$, and $CH_{3,ads}$, or (ii) a reversible stepwise hydrogenation of C_{ads} to $CH_{3,ads}$. In the latter case, the surface concentrations of $CH_{x,ads}$, where x=0 to 3, are not accessible with this technique. Further elaboration on the reversibility of these hydrogenation reactions is presented in section 7.4.

• Since both intermediates $C_{\alpha,ads}$ and $C_{\beta,ads}$ have similar chemical identities, the difference between the two surface species is assumed to result from distinct surface sites [Chen and Goodwin, 1996].

Chain initiation occurs via the combination of two intermediates from the C_{1,ads} pool.

• Chain growth proceeds via the stepwise addition of CH_{2,ads}, characteristic for the carbene Fischer-Tropsch mechanism.

• Chain initiation and chain growth are assumed to occur via irreversible reactions, *i.e.* hydrogenolysis of surface chains is insignificant.

• A growing surface chain can terminate as paraffin or as olefin. Both are considered to be primary reaction products.

• Reactive olefins, *i.e.* 1-olefins, can readsorb onto the catalyst surface in the chemisorbed state, resulting in a species identical to the growing surface chain. Other olefins, *i.e.* internal- and iso-olefins, readsorb much less, as evidenced by ¹³CO SSITKA experiments (section 6.2.2). Their behavior in the mechanism is identical to the paraffins.

• A physisorbed state for the hydrocarbon reaction products is present, as illustrated by the steady state results in section 5.3. As discussed in section 2.4, it is assumed that this physisorbed layer is in equilibrium with the gas phase. The capacity of the physisorbed layer equals the total Co-metal surface.



Figure 7.1: Schematic representation of the Fischer-Tropsch mechanism studied by ¹³CO SSITKA, featuring:

- i) two intermediates towards methane and hydrocarbons,
- ii) readsorption of reactive olefins,
- iii) the presence of a physisorbed layer.

7.2.2 Model considerations

SSITKA.

Based on the reaction mechanism in figure 7.1, the following model considerations are made: **1.** The experimental data are obtained at isothermal and intrinsic reaction conditions (chapter 5). Neither heat-balances nor terms for mass transfer are taken into account.

2. The conversions of CO and H_2 are low and the experimental PFR is operated at differential conditions for these reactants. This is evidenced by the linear dependency of the conversions of CO and H_2 on the residence time (section 5.2). Since the axial concentration gradients for CO and H_2 in the gas phase are small, it is assumed that the surface concentrations of H_{ads} and CO_{ads} are constant throughout the catalyst bed.

3. The interaction of CO with the catalyst surface proceeds via a reversible process. To model the adsorption and desorption of CO, a plug flow reactor model is used.

4. The readsorption of reactive olefins severely influences their gas phase concentrations and the surface concentrations of growing hydrocarbon chains. To model the formation of C_{2+} hydrocarbon reaction products correctly, the steady state axial concentration gradients are taken into account.

5. All surface concentrations of non C-containing surface intermediates are lumped with the reaction rate coefficient for the reaction of interest. The most important non C-containing surface intermediates are H_{ads} and vacant surface sites. For example:

- The steady state rate for ethane formation is written as:

$$r_{t,C_2}^{SS} = k_{t,2}^* L_H^{SS} L_{C_2}^{SS} = k_{t,2} L_{C_2}^{SS}$$
(7.2)

where $k_{t,2}$ is the true reaction rate coefficient for this termination reaction. The surface concentration of H_{ads} is lumped into $k_{t,2}$ and modeling of ¹³CO SSITKA experiments gives access to this lumped reaction rate coefficient in stead of the true reaction rate coefficient.

- The steady state rate for CO adsorption is written as:

$$r_{ads}^{SS} = k_{ads}^* L_{vacant}^{SS} C_{CO}^{SS} = k_{ads} C_{CO}^{SS}$$
 (7.3)
Similarly, the surface concentration of vacant sites is lumped with the true reaction rate coefficient k_{ads}^* to obtain the lumped reaction rate coefficient k_{ads} that is accessible with ¹³CO

6. The steady state concentration of a component at a certain axial position in the catalyst bed is the sum of the different ¹³C-labeled isotopic variants of the component at that specific axial position:

$$C_{C_{i}H_{2i(+2)}}^{SS}(x) = \sum_{j=0}^{i} C_{j}C_{j}C_{i-j}H_{2i(+2)}(x) \quad \text{and} \quad L_{C_{i}}^{SS}(x) = \sum_{j=0}^{i} L_{j}C_{j}C_{i-j}(x) \quad (7.4)$$

7. The gas phase and the physisorbed layer are in equilibrium, the model equations for the physisorbed state, therefore, need not be considered. The concentrations of the reactive olefins in the physisorbed state from where they can readsorb into the chemisorbed state, are directly coupled to the gas phase concentrations via the physisorption equilibrium constant.

7.2.3 Transient continuity equations

The mechanism for the Fischer-Tropsch synthesis represented in figure 7.1 is used for the formulation of the model equations for the ¹³C-labeling experiments. The set of partial differential equations for the PFR model is represented by equations (7.5) to (7.10) for the components in the gas phase and by equations (7.11) to (7.15) for the components in the chemisorbed state. The equations are specified for the product spectrum until C_2 .

In the equations a ¹³C-labeled atom is represented as ^{*i*}C. The subscript 'tot' refers to the sum of the concentrations of the labeled and unlabeled variants. The gas phase concentrations are expressed as C_{C_i} in mole·m_g⁻³ and the surface concentrations as L_{C_i} in mole·kg_{cat}⁻¹.

For the gas phase components the following set of equations is obtained:

$$\frac{\partial C_{CO}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{CO}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left(-k_{ads} C_{CO} + k_{des} L_{CO} \right)$$
(7.5)

$$\left(1 + \frac{\rho_b}{\varepsilon_b \cdot K_1^{ph}}\right) \frac{\partial C_{'CH_4}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{'CH_4}}{\partial x} = \frac{\rho_b}{\varepsilon_b} k_{t,1} L_{'C_\beta}$$
(7.6)

$$\left(1+\frac{\rho_b}{\varepsilon_b\cdot K_2^{ph}}\right)\frac{\partial C_{C_2H_6}}{\partial t} + \frac{1}{\tau}\frac{\partial C_{C_2H_6}}{\partial x} = \frac{\rho_b}{\varepsilon_b}K_{t,p,2}L_{C_2}$$
(7.7)

$$\left(1+\frac{\rho_b}{\varepsilon_b\cdot K_2^{ph}}\right)\frac{\partial C_{"C_2H_6}}{\partial t} + \frac{1}{\tau}\frac{\partial C_{"C_2H_6}}{\partial x} = \frac{\rho_b}{\varepsilon_b}K_{t,p,2}L_{"C_2}$$
(7.8)

$$\left(1+\frac{\rho_{b}}{\varepsilon_{b}\cdot K_{2}^{ph}}\right)\frac{\partial C_{C_{2}H_{4}}}{\partial t}+\frac{1}{\tau}\frac{\partial C_{C_{2}H_{4}}}{\partial x}=\frac{\rho_{b}}{\varepsilon_{b}}\left(k_{t,o,2}L_{C_{2}}-k_{re,2}\frac{C_{C_{2}H_{4}}}{K_{2}^{ph}}\right)$$
(7.9)

$$\left(1+\frac{\rho_b}{\varepsilon_b\cdot K_2^{ph}}\right)\frac{\partial C_{''C_2H_4}}{\partial t} + \frac{1}{\tau}\frac{\partial C_{''C_2H_4}}{\partial x} = \frac{\rho_b}{\varepsilon_b}\left(k_{t,o,2}L_{''C_2} - k_{re,2}\frac{C_{''C_2H_4}}{K_2^{ph}}\right)$$
(7.10)

For the chemisorbed surface components the following set of equations is obtained:

$$\frac{\partial L_{CO}}{\partial t} = k_{ads} C_{CO} - k_{des} L_{CO}$$
(7.11)

$$\frac{\partial L_{C_{\alpha}}}{\partial t} = k_{m,2} L_{CO} - k_{m,3} L_{C_{\alpha}}$$
(7.12)

$$\frac{\partial L_{C_{\beta}}}{\partial t} = k_{m,1} L_{C_{0}} + k_{m,3} L_{C_{\alpha}} - k_{t,1} L_{C_{\beta}} - k_{ini} \left(L_{C_{\beta}} L_{C_{\beta}} + 2L_{C_{\beta}}^{2} \right) - \sum_{i=2}^{\infty} k_{p,i} L_{C_{\beta}} L_{C_{i},tot}$$
(7.13)

$$\frac{\partial L_{C_2}}{\partial t} = 2k_{ini} L_{C_\beta} L_{C_\beta} - k_{t,p,2} L_{C_2} - k_{t,o,2} L_{C_2} + k_{re,2} \frac{C_{C_2H_4}}{K_2^{ph}} - k_{p,2} L_{C_\beta, tot} L_{C_2}$$
(7.14)

$$\frac{\partial L_{''C_2}}{\partial t} = k_{ini} L_{'C_{\beta}}^{2} - k_{t,p,2} L_{''C_2} - k_{t,o,2} L_{''C_2} + k_{re,2} \frac{C_{''C_2H_4}}{K_2^{ph}} - k_{p,2} L_{C_{\beta},tot} L_{''C_2}$$
(7.15)

Expressions for the partial differential equations for the C_{3+} hydrocarbon reaction products in the gas phase and on the catalyst surface are listed in appendix 7. They are similar to the equations for the C_2 components.

2

For the isotopic step change where CO is replaced by ¹³CO, the following set of initial and boundary equations applies.

Initial conditions:

$$C_{CO} = C_{C_j C_{j-j}} = L_{C_j C_{j-j}} = 0$$
 (7.16)

Boundary conditions: t > 0 x = 0, $\forall 0 \le j \le i$

t = 0

 $\forall x, i, 0 \leq j \leq i$

$$C_{I_{CO}} = f(t), C_{I_{C_i}C_{i-i}} = 0$$
(7.17)

The input function f(t) is represented by the transient of the Ne tracer. An empirical function is used to fit the Ne transient, which is, together with the optimal fit, shown in figure 7.2.



The set of steady state equations are obtained from the set of partial differential equations presented above by eliminating the time dependent term and applying model consideration number 6 (section 7.2.2). For the resulting combined set of ordinary differential equations for the components in the gas phase and of algebraic equations for the components in the chemisorbed state, the following initial condition applies:

Initial condition: $x = 0, \forall i$ $C_{CO} = C_{CO}^0, C_{C_i} = 0$ (7.18)

7.2.4 Physisorption equilibrium

As illustrated in section 5.3, $\alpha < \alpha_c=0.66$ at all reaction conditions. Therefore, all experiments are performed at dry conditions and the physisorption layer is expected to cover only a small fraction of the catalyst surface. The physisorption equilibrium coefficient is defined as:

$$K_{i}^{ph} = \frac{C_{C_{i}H_{2i}}}{L_{C_{i}H_{2i}}^{ph}} = \frac{C_{C_{i}H_{2i+2}}}{L_{C_{i}H_{2i+2}}^{ph}} = K^{0} \cdot e^{-\frac{E_{des} \cdot i}{RT}}$$
(7.19)

For a given carbon number, no distinction is made between the different groups of reaction products, *i.e.* 1-olefin, internal-olefin, iso-olefin, n-paraffin, and iso-paraffin. For the C₂ to C₄ hydrocarbons the physisorption equilibrium constants for the 1-olefin, the iso-olefin, and the iso-paraffin are about 15% higher than for the n-paraffin, while the deviations for the internal-olefin are smaller. These differences are small compared to the decrease of the physisorption constant with increasing C-number by a factor of 0.47 at 498 K (see equation (2.5)). On the dry Fischer-Tropsch catalyst, the effective heat of desorption, E_{des}/R , is obtained from the slope of the olefin to paraffin ratio plot and amounts to 374 K. The pre-exponential term, K^0 , is correlated to the pure vapor liquid equilibrium at a temperature of 498 K via the Henry coefficient:

$$H_i = \frac{y_i}{x_i} = \frac{P_i^{\sigma}}{P} = H^0 \cdot e^{-\frac{E_{des}^{G/L} \cdot i}{RT}}$$
(7.20)

where y_i is the mole fraction of component i in the gas phase and x_i is the mole fraction of component i in the liquid phase. The capacity of the physisorption layer is related to the total number of exposed Co-metal surface atoms of the catalyst, L_{tot}^{ph} .

The pre-exponential term, K^{0} , is then represented by:

$$K^{0} = H^{0} \frac{P}{RT L_{tot}^{ph}}$$
(7.21)

An overview of the values of the parameters in this equation are presented in table 7.1. The fit for the Henry coefficient for the pure C_2 to C_{25} n-paraffins at a temperature of 498 K is shown in figure 7.3. The physisorption equilibrium coefficient is given in figure 7.4.





Figure 7.3: Henry coefficient for the pure C_2 to C_{25} n-paraffins at 498 K and 1.2 bar.

Figure 7.4: The physisorption equilibrium coefficient as a function of carbon number at 498 K and 1.2 bar according to equation (7.19).

By quantifying the physisorption parameters, the total number of model parameters diminishes by two, *i.e.* K^0 and E_{des}/R . The exponential relationship of the physisorption equilibrium is fixed, which implies a considerable speeding up of the convergence of the regression analysis. Preliminary modeling, where the physisorption parameters K^0 and E_{des}/R were model parameters, led to estimates close to the values which are obtained with the procedure outlined above. This indicates that the approach as indicated above is realistic.

Henry relation at 498 K, equation (7.20)			Physisorption equilibrium, equations (7.19) and (7.21)		
H ⁰	-	346	L ^{ph} _{tot}	mole·kg _{cat} -1	6.1·10 ⁻²
E ^{G/L} /R	к	228	K ⁰	kg _{cat} ⋅m _g ⁻³	1.4·10 ⁵
			E _{des} / R	К	374

Table 7.1: Overview of the parameters for equations (7.19), (7.20), and (7.21).

7.2.5 Numerical methods

The set of partial differential equations for the components in the gas phase and on the catalyst surface (equations (7.5) to (7.15)) describes the transients for the C-containing components. This set of equations is solved with the standard integration routine D02NCF from the Numerical Algorithm Group [NAG, 1991] for integrating an initial value problem for a stiff system of explicit ordinary differential equations. The routine performs the integration in time, while the axial position in the catalyst bed is discretized by using a uniform grid.

The set of ordinary differential equations for the gas phase components together with the set of algebraic equations for the surface components describe the steady state concentration profiles in the axial direction of the reactor for the C-containing components. These sets of equations are solved with the standard routine D02NHF for integrating an initial value problem for a stiff system of implicit ordinary differential equations coupled with a set of algebraic equations. Initial estimates for the surface concentrations are obtained using the routine C05NBF. This routine finds a solution for a system of nonlinear algebraic equations via a modification of the Powell hydrid method.

Estimations of the kinetic parameters are obtained by nonlinear multi response regression analysis. The method is based on the least squares method and minimizes the objective function:

$$S(\mathbf{b}) = \sum_{i=1}^{n} [\mathbf{f}_{i}(\mathbf{x}_{i}, \mathbf{b}) - \mathbf{y}_{i}]^{T} \omega_{\varepsilon_{i}} [\mathbf{f}_{i}(\mathbf{x}_{i}, \mathbf{b}) - \mathbf{y}_{i}] \xrightarrow{\mathbf{b}} \text{minimum}$$
(7.22)

where $S(\mathbf{b})$ is the objective function; *n* is the number of experiments; \mathbf{y}_i is the vector of j responses for the ith experiment, which contains either isotope fractions, gas phase concentrations, or ratios of gas phase concentrations; \mathbf{x}_i is the vector of explanatory variables of the ith experiment; $\mathbf{f}_i(\mathbf{x}_i, \mathbf{b})$ is the vector of j response values for the ith experiment calculated with the reactor model; ω_{ε_i} is the vector of

weight factors for the errors of the j responses for the ith experiment; **b** is the parameter vector.

The objective function is based on the assumption that the responses contain experimental errors that have a standard normal distribution with a zero mean. The minimization of the objective function is achieved with the ODRPACK software package for weighted orthogonal distance regression [Boggs *et al.*, 1992]. The package uses the Levenberg-Marquard procedure.

Depending on the complexity of the reaction mechanism under study, the response values consist of:

- 1. isotopic fractions for the labeled variants of the C₂ to C₅ olefins and paraffins;
- 2. steady state gas phase concentrations of the C₂ to C₉ olefins and paraffins;
- 3. ratios of the steady state gas phase concentrations of the C₂ to C₉ olefins and paraffins;

The parameter estimates are tested for their statistical significance on the basis of their individual *t*-values. With transient data, the individual responses are not independent and the absolute values of the *t*-test for the parameter estimates are insignificant. However, the relative value of this parameter indicates the significance within a given model; the parameter with the lowest *t*-value is the least significant and in this study a parameter is considered insignificant if its *t*-value is more than three orders of magnitude lower than the *t*-values of the so-called *F*-test. The *F*-test accounts for the number of responses and the number of parameters, resulting in a tool for the comparison of the goodness of fit between models. The *F*-test is used to discriminate between rival models if this is not possible by direct observation or by physicochemical considerations.

In the regression analysis, weight factors for the different responses are introduced. The reason for this is that not all responses are of identical importance. Moreover, not every group of responses has an equal number of experimental data points and the values of the responses have different orders of magnitude. The statistically correct introduction of the weight factors is not straightforward [Boggs *et al.*, 1992] and the following global guidelines are applied:

- 1. Within a group, the weight factors are inversely proportional to the absolute value of the response.
- 2. Between the groups, the weight factors are proportional to the number of responses per group, assuming all groups are equally important.

The weight factors between groups are adjusted via trial and error, where the goodness of fit is judged by a graphical comparison of the fits.

7.3 Modeling the methanation reaction

In this section, a model discrimination and quantification study of the methanation reaction during the Fischer-Tropsch synthesis is presented. In section 7.3.1 it is shown that four out of five models for the methanation reaction result in identical fits of the experimental data. These four models are indistinguishable. In section 7.3.2, the model discrimination is extended by including chain initiation in the form of ethane formation into the four methanation models. The two best models are again indistinguishable. In these two models the catalyst surface is heterogeneous on the $C_{1,ads}$ level, and both resulting species contribute to methanation and chain growth. In section 7.3.3, a net consumption term for the $C_{1,ads}$ species that represents C_{2+} hydrocarbon formation, is introduced. This allows the quantification of the reaction rate coefficients for the methanation reaction at Fischer-

Tropsch reaction conditions for the two models of section 7.3.2. The parameter estimates are used for the quantification of the Fischer-Tropsch reaction in chapter 8.

For the experiments on the $Co/Ru/TiO_2$ catalyst, an overview of the characteristics of the catalyst bed as well as the steady state behavior at the different sets of experimental conditions is given in appendix 5.

7.3.1 Model identification of the methanation reaction

The presence of two reactive intermediates towards methane, $C_{\alpha,ads}$ and $C_{\beta,ads}$, has been observed during the SSITKA experiments in chapter 6. Based on two gas phase components (CO and CH₄) and three surface components (CO_{ads}, $C_{\alpha,ads}$ and $C_{\beta,ads}$) several models are defined, as already mentioned by Happel [1986] and Soong *et al.* [1986]. The most basic models, *i.e.* the models with the minimum number of reaction steps, are represented as models 2 to 6 in figure 7.5. Additionally, the model with only one intermediate towards methane, model 1, is also included. In figure 7.5 the two surface intermediates are directly formed from CO in models 3 and 4. In models 2, 5, and 6 only one surface intermediate is formed from CO while a conversion between the surface intermediates is present. Both surface intermediates directly form methane in models 3 and 5, while this reaction is related to only one surface intermediate in models 2, 4, and 6. Models 2 and 6 both possess a buffer step: model 2 represents a sequential buffer while model 6 represents a parallel buffer.

Happel [1986] reports on modeling results obtained with two mechanisms for the methanation reaction corresponding to model 5 and model 6 in figure 7.5. Soong *et al.* [1986] use models 2, 3, and 6 in their study on the methanation reaction.

In the models presented in figure 7.5 the formation of higher hydrocarbons is neglected. By neglecting a part of the product spectrum, the surface concentrations of $C_{\alpha,ads}$ and $C_{\beta,ads}$ are underestimated. Since the goal of the regressions is to study the capability of the models to describe the experimental results at one set of reaction conditions, the negligence of the C_{2+} hydrocarbon formation is acceptable.



Figure 7.5: Overview of the potential methanation reaction mechanisms with one or two surface intermediates towards methane.

The experimental data on the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H₂/CO=2 and $W_{cat}/F=24.2$ kg_{cat}·s·mole⁻¹ are used to study the six models in figure 7.5. It is verified that the results presented below are valid for every set of experimental data.

Estimates for the kinetic rate coefficients for models 1 to 6 are given in table 7.2 together with the values of the *F*-tests. The corresponding values of the surface concentrations of CO_{ads} , $C_{\alpha,ads}$, and

 $C_{\beta,ads}$ in mole kg_{cat}^{-1} are given in table 7.3. The calculated transients for ¹³CO and ¹³CH₄ are compared to the experimental data in figures 7.6 and 7.7.

Table 7.2: Parameter estimates for the methanation reaction according to the models in figure 7.5. Experimental conditions: 498 K, 1.2 bar, $H_2/CO=2$, $W_{cat}/F=24.2$ kg_{cat} s·mole⁻¹ Italic values: Insignificant parameter estimates

	model 1	model 2	model 3	model 4	model 5	model 6
k_{ads} m _g ³ ·kg _{cat} ⁻¹ ·s ⁻¹	5.9·10 ⁻²					
k_{des} s ⁻¹	9.0·10 ⁺⁰					
<i>k</i> ₁ s ⁻¹	9.6·10 ⁻³	9.6·10 ⁻³	3.9·10 ⁻³	6.3·10 ⁻³	9.3·10 ⁻³	9.3·10 ⁻³
k_2 s ⁻¹	-	4.7·10 ⁻²	5.4·10 ⁻³	3.0·10 ⁻³	4.3·10 ⁻²	2.8·10 ⁻²
<i>k</i> ₃ s ⁻¹	-	2.1·10 ⁺¹	1.3·10 ⁻¹	3.2·10 ⁻²	3.2·10 ⁻²	$4.7 \cdot 10^{-2}$
<i>k</i> ₄ s ⁻¹	6.4·10 ⁻²	6.4·10 ⁻²	3.2·10 ⁻²	1.3·10 ⁻¹	9.1·10 ⁻²	9.1·10 ⁻²
<i>F</i> -value	1.1·10 ⁶	7.0·10 ⁵	3.8·10 ⁶	3.8·10 ⁶	3.8·10 ⁶	3.8·10 ⁶

Table 7.3: Calculated surface concentrations of CO_{ads} , $C_{\alpha,ads}$, and $C_{\beta,ads}$ in and gas phase concentration of CH₄ in corresponding to the parameter estimates in table 7.2. Italic values: Insignificant parameter estimates

	model 1	model 2	model 3	model 4	model 5	model 6
L _{CO} mole·kg _{cat} ⁻¹	3.8·10 ⁻²	3.8·10 ⁻²	3.8·10 ⁻²	3.8·10 ⁻²	3.8·10 ⁻²	3.8·10 ⁻²
$L_{C_{\alpha}}$ mole·kg _{cat} ⁻¹	5.7·10 ⁻³	3.0 [.] 10 ⁻⁵	1.5·10 ⁻³	3.6·10 ⁻³	3.6·10 ⁻³	2.3·10 ⁻³
$L_{C_{\beta}}$ mole·kg _{cat} ⁻¹	· · ·	5.7·10 ⁻³	4.7·10 ⁻³	2.7·10 ⁻³	2.7·10 ⁻³	3.9·10 ⁻³
$L_{C_1,tot}$ mole·kg _{cat} ⁻¹	5.7·10 ⁻³	5.7·10 ⁻³	6.3·10 ⁻³	6.3·10 ⁻³	6.3·10 ⁻³	6.2·10 ⁻³
$L_{C_{\alpha}} / (L_{C_{\alpha}} + L_{C_{\beta}})$	· · ·	-	25 %	58 %	58 %	37 %
C_{CH_4} mole·m _g ⁻³						
data	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹
model	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹	2.53·10 ⁻¹





Figure 7.6: Regression results according to models 1 and 2 from figure 7.5.

Figure 7.7: Regression results according to models 3, 4, 5, and 6 from figure 7.5.

In figure 7.8, the calculated forcing curve, the mixing curve, and the transients of ¹³CO and ¹³CH₄ corresponding to figure 7.7 are represented on a time scale of 20 s. The mixing curve is identical to the time shifted forcing curve. This shift in time equals the residence time of 0.56 s. The characteristic breakthrough of ¹³CH₄ before ¹³CO is correctly described by the PFR model.

The model description of the ¹³CO transient is identical for all models, see figure 7.6 for models 1 and 2 and figure 7.7 for models 3 to 6. Models 1 and 2 give identical fits for the ¹³CH₄ transient, illustrated in figure 7.6. The model calculations result in a single exponential increase of the ¹³C content of CH₄. This is indicated by the straight line in the semi-logarithmic plot of the decay of the ¹²C content in methane with time, represented by curve A in figure 7.9. Since the estimates for k_2 and k_4 in model 2 are not significant, $C_{\alpha,ads}$ is eliminated from the model. Model 2 then equals model 1 and the estimates for the significant parameters for both models are identical.





Figure 7.8: Calculated responses of the forcing curve (F), the mixing curve (M), ^{13}CO , and $^{13}CH_4$ according to the models 3 to 6.

Figure 7.9: Calculated decay of the ¹²C content in methane in comparison to the experimental data.

Models 3 to 6 give identical fits for the ¹³CH₄ transient, as observed in figure 7.7. Curve B in figure 7.9 represents the calculated decay of the ¹²C content in CH₄ with time. As illustrated in chapter 3, the observed downward convexity is illustrative for the basic type of mechanism with either two parallel paths or a buffer step. The fit of the experimental data is better on statistical basis, evidenced by the four times larger *F*-value of models 3 to 6 compared to models 1 and 2. Models 3 to 6 are indistinguishable on the basis of these experiments. All four models result in the same value of the sum of the surface concentrations of $C_{\alpha,ads}$, and $C_{\beta,ads}$, but the contribution of both species differs between the models. In model 3, $C_{\alpha,ads}$ is the most abundant of the two. In models 4 and 5, both species have almost equal contributions, and in model 6 $C_{\beta,ads}$ is most abundant. If the ratio between the two intermediates is assessable via surface sensitive techniques, this would render a possibility for model discrimination.

Due to the negligence of the C₂₊ formation, the sum of the calculated surface concentrations of C_{α ,ads} and C_{β ,ads} in table 7.3 is lower than the value of $1.5 \cdot 10^{-2}$ based on the mean surface residence time, reported in table 6.1 in section 6.2.1.

7.3.2 Model identification for the Fischer-Tropsch reaction

As discussed in the previous section, methanation models 3 to 6 are suitable candidates for the formation of the Fischer-Tropsch reaction model. Since chain-initiation and chain-growth, which are the characteristic reactions for the Fischer-Tropsch synthesis, can proceed from both surface intermediates, $C_{\alpha,ads}$ and $C_{\beta,ads}$, the number of potential models increases drastically.

To study the potential models, three simplifications in the reaction mechanism are applied, resulting in unrealistic parameter estimations. The absolute parameter values, however, are not of vital importance since the goal at this stage is merely to screen models. The simplifications are:

- Expansion of the product spectrum from the methanation reaction to the formation of ethane. The formation of ethene and the C₃₊ hydrocarbons, *i.e.* the remaining part of the Fischer-Tropsch product spectrum, is neglected.
- The negligence of the physisorbed state. When paraffins are the only reaction products at this stage, the readsorption of reactive olefins is absent. In this case, the physisorbed state represents a small additional capacity compared to the capacity of the intermediates to methane and ethane in the chemisorbed state.
- 3. The rate constants for adsorption and desorption of CO are fixed. The values are taken identical to the values obtained in the previous section for models 3 to 6.

These simplifications will lead to an underestimation of the surface concentration of $C_{\alpha,ads}$, $C_{\beta,ads}$, and $C_{2,ads}$. The models are subdivided into three groups (A, B, and C) with increasing complexity, which is reflected in the number of reaction steps required.

A. Chain depolymerization

In the simplest model, the surface pool of growing hydrocarbon chains makes up the buffer capacity of the $C_{\alpha,ads}$ pool of methanation model 6, see model 1.2 in figure 6.10. Chain initiation towards C2,ads occurs, while depolymerization of this species again results in C1,ads species, i.e. the C-C coupling reaction is reversible. Only one C_{1,ads} species exists in this model and the catalyst surface is homogeneous. Compared to the methanation models, one extra reaction step is introduced, i.e. the termination of $C_{2,ads}$ to ethane.

B. Surface heterogeneity on C_{1,ads} scale

The two reactive intermediates, $C_{\alpha,ads}$ and $C_{\beta,ads}$, represent single-C containing species and the catalyst surface is heterogeneous. The addition of ethane formation introduces a minimum of two additional reaction steps, i.e. the coupling of two carbon species towards C2,ads and the termination of this species towards ethane. The methanation models 3 to 6 in figure 7.5 are expanded with these two reaction steps. This results in three variants for every methanation model, except for the symmetric methanation model 3, which has two variants.





Figure 7.10: Mechanisms for methane and ethane formation based on models 1 and 3 in figure 7.5.









Chain initiation can proceed via the combination of:

- two $C_{\alpha,ads}$ species, ethane production rate: $R_{w,C_2H_6} = k_5 L_{C_{\alpha}}^2$;
- a $C_{\alpha,ads}$ and a $C_{\beta,ads}$ species, ethane production rate: $R_{w,C_2H_6} = k_5 L_{C_{\alpha}} L_{C_{\beta}}$;
- two $C_{\beta,ads}$ species, ethane production rate: $R_{w,C_2H_s} = k_5 L_{C_s}^2$.

Based on the four methanation models 3 to 6 in figure 7.5, a total number of eleven potential mechanisms for the Fischer-Tropsch synthesis arise. These are represented in figures 7.11 to 7.15. The chemical feasibility of the models is not considered at this stage. For the verification of these models one set of data is used (identical to section 7.4.1); it is verified that the conclusions based on these calculations are valid for every set of reaction conditions.

Of all models in figures 7.10 to 7.13, models 4.1 and 6.1 give the best descriptions of the experimental data. These two models are again indistinguishable on the basis of the goodness of fit, evidenced by their identical *F*-values in table 7.4. The modeling results for the transients of ¹³CH₄, ¹³C¹²CH₆, and ¹³C₂H₆ are represented in figure 7.15. The estimates of the model parameters and the calculated values of the surface and gas phase concentrations are listed in table 7.4. All parameter estimates of these two models in table 7.4 are statistically significant. The models correctly describe the change in slopes in the ¹²C-decay plots in figure 7.16.

Table 7.4: Parameter estimates and calculated surface and gas-phase concentrations of models 4.1, and 6.1. Experimental conditions: 498 K, 1.2 bar, H₂/CO=2, *W*_{cat}/*F*=24.2 kg_{cat}·s·mole⁻¹. Fixed values: *k*_{ads} and *k*_{des}.

		a., 11 <u>2</u>	model 4.1	model 6.1		model 4.1	model 6.1
<i>k_{ads}</i>	m _g ³ ·kg _{cat} ⁻¹ ·s ⁻¹	fixed	5.9·10 ⁻²	5.9·10 ⁻²	L _{CO} mole·kg _{cat} ⁻¹	3.8·10 ⁻²	3.8·10 ⁻²
k _{des}	s ⁻¹	fixed	9.0·10 ⁺⁰	9.0·10 ⁺⁰	$L_{C_{\alpha}}$ mole·kg _{cat} -1	4.0·10 ⁻³	2.6·10 ⁻³
<i>k</i> ₁	s ⁻¹		7.2·10 ⁻³	1.1·10 ⁻²	$L_{C_{\beta}}$ mole·kg _{cat} ⁻¹	2.8·10 ⁻³	4.2·10 ⁻³
<i>k</i> ₂	s ⁻¹		3.4·10 ⁻³	3.0·10 ⁻³	$L_{C_1,tot}$ mole·kg _{cat} ⁻¹	6.8·10 ⁻³	6.8·10 ⁻³
k 3	S ⁻¹		3.3·10 ⁻²	4.9·10 ⁻²	$L_{C_{\alpha}} / (L_{C_{\alpha}} + L_{C_{\beta}})$	58 %	38 %
<i>k</i> 4	s ⁻¹		1.3·10 ⁻¹	8.7·10 ⁻²	L _{C2} mole·kg _{cat} -1	5.1·10 ⁻⁵	5.1·10 ⁻⁵
<i>k</i> 5	kg _{cat} ·mole ⁻¹ ·s ⁻¹		2.8·10 ⁺⁰	1.3·10 ⁺⁰	C_{CH_4} mole·m _g ⁻³		
k_6	S ⁻¹		4.4·10 ⁻¹	4.4·10 ⁻¹	data	2.53·10 ⁻¹	2.53·10 ⁻¹
<i>F</i> -va	lue		7.2·10 ⁴	7.2·10 ⁴	model	2.53·10 ⁻¹	2.53·10 ⁻¹
					$C_{C_2H_6}$ mole·m _g - ³		
					data	1.53·10 ⁻²	1.53·10 ⁻²
					model	1.53·10 ⁻²	1.53·10 ⁻²

All the other models, *i.e.* models 1.1, 3.1, 3.2, 4.2, 4.3, 5.1, 5.2, 5.3, 6.2, and 6.3, are not capable of describing the transients of methane and ethane. The fits of the methane and ethane transients for these models are similar and shown in figure 7.14. The corresponding semi-logarithmic plots for the decay of the ¹²C content in methane and ethane are represented by curve B in figures 7.16. The *F*-values of these models are at least a factor 3.5 lower than for models 4.1 and 6.1.

These modeling results show that the introduction of a part of the Fischer-Tropsch product spectrum into the modeling reduces the number of acceptable models to two. The common feature of the models 4.1 and 6.1 is that the two pools of surface intermediates towards methane, $C_{\alpha,ads}$ and $C_{\beta,ads}$, both contribute to chain initiation and chain growth. Methane formation, chain initiation, and chain growth start from the $C_{\beta,ads}$ pool, while the $C_{\alpha,ads}$ pool indirectly participates in these reactions, *i.e.* $C_{\alpha,ads}$ first needs to be converted to $C_{\beta,ads}$. The $C_{\alpha,ads}$ species constitutes either a parallel route for the formation of $C_{\beta,ads}$ (model 4.1) or a buffer capacity of $C_{\beta,ads}$ (model 6.1).





Figure 7.14: Regression results for methane and ethane according to models 1.1, 3.1, 3.2, 4.2, 4.3, 5.1, 5.2, 5.3, 6.2, and 6.3.

Figure 7.15: Regression results for methane and ethane according to models 4.1 and 6.1.



 Image: Content in methane
 A
 models 4.1 and 6.1

 Ata for methane
 A
 models 1.1, 3.1, 3.2, 4.2, 4.3, 5.2, 5.3, 6.2, and 6.3

 B
 models 1.1, 3.1, 3.2, 4.2, 4.3, 5.2, 5.3, 6.2, and 6.3

Models 4.1 and 6.1 are similar to the methanation models of the previous section 7.4.1 with respect to:

- the value of the sum of the surface concentrations of C_{α,ads} and C_{β,ads};
- the ratio of the two surface concentrations of C_{α,ads} and C_{β,ads};
- the parameter estimates.

Because ethane is included in the models 4.1 and 6.1, the surface concentrations of $C_{\alpha,ads}$ and $C_{\beta,ads}$ are slightly higher than for the methanation models. Models 4.1 and 6.1 yield identical surface concentrations of $C_{2,ads}$. The differences between the two models, therefore, do not affect the C_{2+} formation and only influences the methanation part of the Fischer-Tropsch mechanism. The surface concentrations of $C_{2,ads}$ is two orders of magnitude lower than the sum of the surface concentrations of $C_{\alpha,ads}$ and $C_{\beta,ads}$. Only a small fraction of the catalyst surface is active for chain initiation and chain growth. However, by neglecting ethene and the C_{3+} hydrocarbons, the surface concentrations of $C_{2,ads}$ is underestimated. This becomes apparent in section 8.3.1, where surface concentrations are presented in case the entire product spectrum is accounted for. The true reaction rate coefficient of chain initiation is two orders of magnitude larger than the lumped rate coefficients corresponding to the formation of $C_{\alpha,ads}$ and $C_{\beta,ads}$.

In model 1.2, the introduction of the depolymerization reaction transforms the pool of growing surface chains into a buffer for the methane intermediate. This is in accordance with the model proposed by Zhou and Gulari [1987]. However, the results in this section indicate that the sole incorporation of the depolymerization reaction of growing hydrocarbon chains into the methanation model does not explain the observed transients of methane and ethane. The depolymerization of
growing hydrocarbon chains observed by Zhou and Gulari [1987] at severe hydrogenation conditions does not appear to be a necessary reaction to explain the experimental results at Fischer-Tropsch reaction conditions.

C. Complete surface heterogeneity

The models in groups A and B are characterized by a single chain initiation reaction with the participation of $C_{\beta,ads}$. In group C, models are presented in which chain initiation starts from both $C_{\alpha,ads}$ and $C_{\beta,ads}$, as illustrated by models 3.3 and 5.4 in figure 7.17. These models are extensions of model 3.1 and model 5.1, respectively, via the introduction of one extra chain initiation step, *i.e.* reaction step 7. The resulting pool of growing hydrocarbon chains is considered to be homogeneous.

The description of the tailing of the transients of both methane and ethane by models 3.3 and 5.4 are comparable to that of models 4.1 and 6.1. However, the goodness of fit of models 3.3 (*F*-value= $4.4 \cdot 10^4$) and 5.4 (*F*-value= $1.8 \cdot 10^4$) is significantly lower than that of models 4.1 and 6.1 (*F*-value= $7.2 \cdot 10^4$). Models 5.4 and 3.3, therefore, are not adequate and models 4.1 and 6.1 still give the best descriptions of the experimental data.



Figure 7.17: Mechanisms for methane and ethane formation based on methanation models 3 and 5 in figure 7.5.

Based on model 3.3, model 3.4 in figure 7.17 represents the situation where the surface heterogeneity is not limited to the $C_{1,ads}$ pool but also involves the pool of growing hydrocarbon chains. In this model the heterogeneous character of the surface is represented by two distinct sites, each forming a separate route for the Fischer-Tropsch reaction. This leads to a model that can represent:

- the presence of a "low α" site and a "high α" site for the Fischer-Tropsch synthesis, also known as the "dual sites" model as proposed by Donnelly and Satterfield [1989];
- the presence of different surface sites for the different reaction products, also known as the "distributed sites model" as proposed by Wojchiechowski [1988] and Adesina [1996].

This extension again increases the number of reaction steps by one, *i.e.* reaction step 8. Model 3.4 describes the experimental data in a similar way as model 3.3, since they only differ slightly (they are identical if $k_6 = k_8$). The goodness of fit of model 3.4 (*F*-value=3.7·10⁴) is slightly lower than of model 3.3 (*F*-value=4.4·10⁴). These results suggest that the surface heterogeneity is limited to the pool of methane intermediates; the pool of growing hydrocarbon chains is homogeneous.

7.3.3 Parameter quantification of the methanation reaction

Models 4.1 and 6.1 in section 7.3.2 give the best description of the experimentally observed responses of methane and ethane. These models are used to quantify the reaction rate parameters of the methanation reaction while accounting for the complete Fischer-Tropsch product spectrum.

For the model discrimination, data at one set of reaction conditions are used. However, for the parameter quantification the total set of experimental conditions is used. A complete overview of the data sets is given in appendix 5. The different H_2/CO feed ratios give rise to different surface concentrations of H_{ads} and vacant sites, which are lumped into the reaction rate constants. Therefore, parameter estimations are performed at each H_2/CO feed ratio with variable residence time.

At this stage of modeling, the formation of the C₂₊ hydrocarbons from C_{α ,ads} and C_{β ,ads} is lumped into one term representing the net consumption rate of these surface species. The net consumption rate, expressed in mole kg_{cat}⁻¹·s⁻¹, is related to the C₂₊ formation via the chain growth probability α according to the following equations:

net consumption of methane intermediates

$$= \frac{F_{V}}{W_{cat}} \sum_{i=2}^{\infty} i \left(C_{C_{i}H_{2i}}^{SS} + C_{C_{i}H_{2i+2}}^{SS} \right)$$
(7.23)

$$=\frac{F_{V}}{W_{cat}}\left(2\left(C_{C_{2}H_{4}}^{SS}+C_{C_{2}H_{6}}^{SS}\right)+\left(C_{C_{3}H_{6}}^{SS}+C_{C_{3}H_{8}}^{SS}\right)\sum_{i=1}^{\infty}(i+2)\alpha^{i-1}\right)$$
(7.24)

where F_V is the total volume flow in $m_g^{3} \cdot s^{-1}$; W_{cat} is the loading of the catalyst bed in kg_{cat}; $C_{C_iH_{2i(+2)}}^{SS}$ is the steady state gas phase concentration of a hydrocarbon with i C-atoms in mole m_g^{-3} . As indicated in section 5.3, the chain growth probability α is constant starting from C₃ and increases only moderately with residence time. For every H₂/CO feed ratio a constant value of α and thus for the net consumption rate is assumed, which is in analogy with the differential operation of the reactor for CO and H₂. The reason to define a net consumption rate for the sum of C_{α .ads} and C_{β ,ads} is threefold:

- 1. The entire product spectrum can be accounted for via the chain growth probability α .
- 2. The transient continuity equation for single labeled $C_{\beta,ads}$ on the catalyst surface, L_{C_a} , is

represented by equation (7.13) in section 7.2.2. The transformation of $C_{\beta,ads}$ into the C_{2+} reaction products in these equations is represented by:

- 1. chain initiation, *i.e.* $k_{ini} \left(L_{C_{\beta}} L_{C_{\beta}} + 2L_{C_{\beta}}^{2} \right)$
- 2. chain growth, *i.e.* $\sum_{i=2}^{\infty} k_{p,i} L_{C_{\beta}} L_{C_{i},tot}$

The chain growth term comprises the surface concentrations of the growing hydrocarbon chains. By replacing these two terms by the net consumption term of equation (7.24), the entire Fischer-Tropsch product spectrum is accounted for while no knowledge is required on the values of the surface concentrations of the growing hydrocarbon chains. In other words, the methane formation and the C₂₊ hydrocarbon formation are uncoupled. Both parts of the Fischer-Tropsch mechanism can now be modeled separately, resulting in a simplified data treatment. The transient continuity equation (7.13) for L_{C_2} becomes:

$$\frac{\partial L_{C_{\beta}}}{\partial t} = k_{m,2} L_{CO} + k_{m,3} L_{C_{\alpha}} - k_{t,1} L_{C_{\beta}} - \text{net consumption}$$
(7.13b)

3. The transient of methane obtained with on-line MS is believed to be more accurate than the transients of the C₂ to C₅ hydrocarbons obtained with GCMS. By using the net consumption rate, the most realistic values of the surface concentrations of $C_{\alpha,ads}$ and $C_{\beta,ads}$ are fixed by the methane transient and not influenced by the transients of the C₂ to C₅ hydrocarbons.

A schematic representation of the application of the net consumption term in models 4.1 and 6.1 is given in figure 7.18. The two resulting models are denoted as **model A** and **model B**. Model A is based on model 4.1, model B is based on model 6.1.



Figure 7.18: Models A and B for the incorporation of the net consumption of $C_{\alpha,ads}$ and $C_{\beta,ads}$ towards the C_{2+} hydrocarbon products based on models 4.1 and 6.1, respectively. With these models, the methanation reaction is quantified, while the entire Fischer-Tropsch product spectrum is accounted for.

Chain initiation and chain growth are assumed to be irreversible, *i.e.* the hydrogenolysis of growing surface chains is absent. The isotopic composition of $C_{\alpha,ads}$ and $C_{\beta,ads}$ are therefore independent of the formation of the C₂₊ hydrocarbons. This is a necessary assumption to apply the net consumption term.

Three sets of parameter estimates per model are obtained for the three different H₂/CO feed ratios. An overview of the parameter estimates is presented in table 7.5. The calculated values of the surface concentrations of CO_{ads}, C_{α ,ads}, and C_{β ,ads} are listed in table 7.5, together with the experimental and calculated values of the steady state concentrations of methane at the different H₂/CO feed ratios.

 Table 7.5: Parameter estimates of models A and B of figure 7.18 concerning methanation in combination with a net consumption rate.

	model A			model B			
	H ₂ /CO=1	H ₂ /CO=2	H ₂ /CO=5	H ₂ /CO=1	H ₂ /CO=2	H ₂ /CO=5	
k_{ads} mg ³ ·kg _{cat} ⁻¹ ·s ⁻¹	3.9·10 ⁻²	6.2·10 ⁻²	1.4·10 ⁻¹	3.9·10 ⁻²	6.2·10 ⁻²	1.4·10 ⁻¹	
k _{des} s⁻¹	8.9·10 ⁺⁰	9.1·10 ⁺⁰	1.1·10 ⁺¹	8.9·10 ⁺⁰	9.1·10 ⁺⁰	1.1·10 ⁺¹	
<i>k_{m,1}</i> s ⁻¹	7.3·10 ⁻³	$1.7 \cdot 10^{-2}$	3.1·10 ⁻²	$1.4 \cdot 10^{-2}$	2.3·10 ⁻²	3.9·10 ⁻²	
<i>k</i> _{m,2} s ⁻¹	6.8·10 ⁻³	6.6·10 ⁻³	7.4·10 ⁻³	$3.2 \cdot 10^{-2}$	$2.5 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	
<i>k_{m,3}</i> s ⁻¹	2.0·10 ⁻²	3.0·10 ⁻²	5.7·10 ⁻²	3.9·10 ⁻²	4.2·10 ⁻²	7.2·10 ⁻²	
$k_{t,1}$ s ⁻¹	3.4·10 ⁻²	5.2·10 ⁻²	1.4·10 ⁻¹	1.8·10 ⁻²	3.7·10 ⁻²	1.1·10 ⁻¹	
<i>F</i> -value	2.7·10 ⁶	1.4·10 ⁶	3.9·10 ^⁵	2.7·10 ⁶	1.4·10 ⁶	3.9·10 ^⁵	

Table 7.6: Calculated surface concentrations and steady state gas phase concentration of models A and B of figure 7.19 concerning methanation in combination with a net consumption rate. Surface concentrations in mole kg_{cat}^{-1} , gas phase concentrations in mole m_{q}^{-3} , W_{cat}/F in kg_{cat} 's mole⁻¹.

	model A			model B			
	H ₂ /CO=1	H ₂ /CO=2	H ₂ /CO=5	H ₂ /CO=1	H ₂ /CO=2	H ₂ /CO=5	
L _{CO}	3.9·10 ⁻²	4.0·10 ⁻²	3.8·10 ⁻²	3.9·10 ⁻²	4.0·10 ⁻²	3.8·10 ⁻²	
$L_{C_{\alpha}}$	1.3·10 ⁻²	8.6·10 ⁻³	4.9·10 ⁻³	8.3·10 ⁻³	5.9·10 ⁻³	3.4·10 ⁻³	
$L_{C_{\beta}}$	5.3·10 ⁻³	7.1·10 ⁻³	6.5·10 ⁻³	1.0·10 ⁻²	9.8·10 ⁻³	8.0·10 ⁻³	
L _{C1,tot}	1.8·10 ⁻²	1.6·10 ⁻²	1.1·10 ⁻²	1.8·10 ⁻²	1.6·10 ⁻²	1.1·10 ⁻²	
$L_{C_\alpha} \ / (L_{C_\alpha} + L_{C_\beta})$	72 %	55 %	43 %	45 %	38 %	30 %	
W _{cat} /F	16.8	11.1	7.9	16.8	11.1	7.9	
C_{CH_4} data	8.87·10 ⁻²	1.48·10 ⁻¹	2.20·10 ⁻¹	8.87·10 ⁻²	1.48·10 ⁻¹	2.20·10 ⁻¹	
C_{CH_4} model	8.90·10 ⁻²	1.18·10 ⁻¹	2.05·10 ⁻¹	8.90·10 ⁻²	1.18·10 ⁻¹	2.05·10 ⁻¹	
_{cat} /F	44.8	24.2	13.7	44.8	24.2	13.7	
C_{CH_4} data	2.38·10 ⁻¹	2.53·10 ⁻¹	3.46·10 ⁻¹	2.38·10 ⁻¹	2.53·10 ⁻¹	3.46·10 ⁻¹	
C_{CH_4} model	2.38·10 ⁻¹	2.58·10 ⁻¹	3.54·10 ⁻¹	2.38·10 ⁻¹	2.58·10 ⁻¹	3.54·10 ⁻¹	
W _{cat} /F	-	36.6	-	-	36.6	-	
C_{CH_4} data	-	3.85·10 ⁻¹	-	-	3.85·10 ⁻¹	-	
C_{CH_4} model	-	3.91·10 ⁻¹	-	-	3.91·10 ⁻¹	-	

The steady state concentration of methane is predicted with a maximum error of 20% and an average error of 3%. The models give identical fits for the transients. They are shown in figure 7.19 for H₂/CO=2 and the three residence times. The fits of the transients at H₂/CO=1 and H₂/CO=5 are presented in appendix 6. The dependency of the surface concentrations of CO_{ads}, C_{α ,ads}, and C_{β ,ads} with the H₂/CO feed ratio are represented in figure 7.20 for models A and B. Finally, the relation of the estimates of the reaction rate constants with the H₂/CO feed ratio are represented in figure 7.21 for models A and B.

Chromatographic effect for CO

The models correctly describe the chromatographic effect for CO at the different residence times, see figure 7.19 for H₂/CO=2. From table 7.5 and figure 7.20 it is obvious that the surface concentration of CO_{ads} is independent of the H₂/CO ratio and amounts to $3.9 \cdot 10^{-2}$ mole·kg_{cat}⁻¹. Because the CO adsorption and desorption mechanism is identical for model A and model B, the estimated rate coefficients and CO_{ads} surface concentrations are identical. The lumped rate constant for CO adsorption depends on the H₂/CO ratio, whereas the true rate constant for desorption does not, as illustrated in figure 7.20. This is in good agreement with a reversible CO adsorption process represented by reaction (R-1):

$CO_q + * \longleftrightarrow CO_{ads}$

The increase of this lumped rate coefficient for adsorption reflects an increase in the concentration of vacant surface sites with increasing H_2/CO feed ratio. The desorption does not require any accompanying species and is independent of the H_2/CO ratio.





Figure 7.19: Modeling results for the responses of Ne, ¹³CO, and ¹³CH₄ at 498 K, 1.2 bar, H₂/CO=2, and different residence times for the methanation part of the Fischer-Tropsch mechanism. Model A and model B in figure 7.18 give identical fits for the responses and for the steady state activity.

(R-1)

Model indistinguishability

The models A and B are indistinguishable on a statistical basis and result in identical descriptions of the transients and the steady state performance with respect to methanation. The values of the *F*-tests, listed in table 7.5, are identical for models A and B at the different H_2/CO ratios.

Quantification of surface concentrations

The negligence of the C₂₊ hydrocarbon products during the model discrimination in sections 7.3.1 and 7.3.2 lead to the underestimation of the surface concentrations of C_{$\alpha,ads}$ and C_{$\beta,ads}$ by a factor 2.5. An increase with approximately 6% was already observed when ethane was added to the methanation model in section 7.4.2. As already suggested in the previous section, CO and the two reactive intermediates are the most abundant surface species, having a total surface concentration of $5.5 \cdot 10^{-2}$ mole·kg_{cat}⁻¹. About 28% of these three surface species is made up by the two reactive intermediates C_{$\alpha,ads}$ </sub> and C_{$\beta,ads}$ </sub> and 72% by CO_{ads}. The total number of Co surface atoms is $6.2 \cdot 10^{-2}$ mole·Co_{surf}·kg_{cat}⁻¹ (see section 4.5.2) and the degree of surface coverage with CO_{ads}, C_{$\alpha,ads}$ </sub>, and C_{$\beta,ads}$ </sub> amounts to 89%. The surface is thus largely covered by C_{$\alpha,ads}$ </sub>, C_{$\beta,ads}$ </sub>, and CO_{ads}, of which the latter is the most abundant.</sub></sub>



Figure 7.20: Surface concentrations of CO (\bigcirc), $C_{\alpha,ads}$ (\triangle), $C_{\beta,ads}$ (\blacktriangle), $C_{\alpha,ads} + C_{\beta,ads}$ (\blacksquare) as a function of the H₂/CO feed ratio for the methanation models A and B of figure 7.19 at 498 K and 1.2 bar.

The values of these calculated surface concentrations are in good agreement with data reported in literature. For their Ru/TiO₂ catalyst, Komaya and Bell [1994a] observe a surface coverage for the methane intermediate of 20% to 30%, with CO as the major complementary species. A surface coverage for the methane intermediate of 18% is observed by Belambe *et al.* [1997] for their Co/Ru/Al₂O₃ catalyst. Agnelli *et al.* [1998] observe surface coverages for the methane intermediate as a function of temperature ranging from 8% at 503 K to 32% at 623 K on their Ni/SiO₂ catalyst. Rothmaemel *et al.* [1997] obtain a surface coverage of 30% for their Co/Re/Al₂O₃ catalysts and Mims and McCandlish [1987] a surface coverage of 24% on their Co/SiO₂ catalyst.

The sum of the surface concentrations of the methane intermediates $C_{\alpha,ads}$ and $C_{\beta,ads}$ decreases slightly with increasing H₂/CO feed ratio for both models, as illustrated in figure 7.20. It changes from 32% at H₂/CO=1, to 28% at H₂/CO=2, and to 23% at H₂/CO=5. In contrast to these results, Bajusz and Goodwin [1997] report an increase in the surface concentration of methane intermediates for a H₂/CO=3.9 - 20. Chen and Goodwin [1996] report a constant surface concentration of methane intermediates for H₂/CO=5 - 15.

The calculated surface concentrations of CO_{ads} and $C_{\alpha,ads} + C_{\beta,ads}$ are in good agreement with the values directly obtained from the transients, which are presented in table 6.1 and figure 6.8 in section 6.2.1. The values reported in table 6.1 are not related to any assumptions concerning the reaction mechanism since they are solely based on the surface areas of the transients. In contrast to that procedure, the model is capable to differentiate quantitatively between $C_{\alpha,ads}$ and $C_{\beta,ads}$ in figure

7.21. For model A, the surface concentration of $C_{\alpha,ads}$ decreases with increasing H₂/CO feed ratio, while the surface concentration of $C_{\beta,ads}$ increases. The most abundant surface intermediate shifts from $C_{\alpha,ads}$ at the low H₂/CO ratio to $C_{\beta,ads}$ at the high H₂/CO ratio. For model B both surface concentrations decrease with increasing H₂/CO feed ratio, that of $C_{\alpha,ads}$ faster than of $C_{\beta,ads}$. In model B, $C_{\beta,ads}$ is always the most abundant surface intermediate.

Besides CO_{ads} , $C_{\alpha,ads}$, and $C_{\beta,ads}$, other surface species present on the catalyst surface are growing hydrocarbon chains, H_{ads} , vacant sites, O_{ads} and OH_{ads} , and Co-oxides. The likely presence of Co-oxides is caused by an incomplete reduction of the Co-surface [Khodakov *et al.*, 1997] and/or by the partial reoxidation of the Co-surface at reaction conditions [Schanke *et al.*, 1995]. The hydrogenation of O_{ads} via OH_{ads} to water is believed to be fast, resulting in low surface concentrations of these species. The modeling in the next section indicates that the total surface coverage of growing hydrocarbon chains amounts to roughly 1%. The surface coverages of H_{ads} and vacant sites are believed to constitute a substantial part of the remaining Co-surface sites, however, quantification is not possible.

Quantification of reaction rate coefficients

The estimates of the reaction rate coefficients as a function of H_2/CO ratio are shown in figure 7.21 for both models. The following observations are made:

- For model A, two out of six rate coefficients are independent of the H₂/CO ratio, *i.e.*:
 - the rate coefficient for desorption of CO, k_{des} ;
 - the rate coefficient for formation of $C_{\alpha,ads}$ from CO_{ads}, $k_{m,2}$.
- For model B, three out of six rate coefficients are independent of the H₂/CO ratio, *i.e*:
 - the rate coefficient for desorption of CO, *k*_{des};
 - the rate coefficient for the transformation of $C_{\beta,ads}$ into $C_{\alpha,ads}$, $k_{m,2}$;
 - the rate coefficient for the transformation of C_{α,ads} into C_{β,ads}, k_{m,3}.
- For both models the other rate coefficients display a similar increase with increasing H₂/CO ratio.



 Figure 7.21: Parameter estimates for the methanation reaction of models A and B as a function of the H₂/CO feed ratio at 498 K and 1.2 bar.

 \bigstar k_{ads} \bigstar $k_{m,1}$ \diamondsuit $k_{m,2}$ \bigtriangleup $k_{m,3}$ \square $k_{t,1}$

The surface concentration of H_{ads} is lumped into the rate constant for termination to methane, since this reaction step represents the hydrogenation of a $C_{\beta,ads}$ species. The increase of the rate coefficient for termination, $k_{t,1}$, with increasing H_2 /CO ratio therefore reflects the increase of the surface concentration of H_{ads} . This is in good agreement with the results presented by Bajusz and Goodwin [1997], who observe a twofold increase of the relative surface concentration of H_{ads} with a threefold increase of the hydrogen partial pressure at a constant CO partial pressure. Chen and Goodwin [1996] report a similar dependency of the relative surface concentration of H_{ads} with the hydrogen partial pressure. It is, however, emphasized that our results suggest that both surface concentrations of H_{ads}

and of vacant sites display a similar increase with H_2/CO ratio. The slopes for $k_{t,1}$ and k_{ads} are similar. The first is associated with the surface concentration of H_{ads} , the latter with the surface concentration of vacant sites.

The rate coefficient for the formation of $C_{\beta,ads}$ from CO_{ads} , $k_{m,1}$, increases with H₂/CO ratio. As with the rate coefficient of adsorption of CO, this reflects the increase of the rate by an increase of the number of vacant sites:

$$CO_{ads} + * \longrightarrow C_{\beta,ads} + O_{ads}$$
 (R-2)

The surface concentration of vacant sites is lumped into $k_{m,1}$.

For both models it is observed that the rate coefficient for the formation of $C_{\alpha,ads}$, $k_{m,2}$, is independent of the H₂/CO ratio. In model A, $C_{\alpha,ads}$ is formed via the dissociation of CO_{ads}. The chemical compositions of the two intermediates towards methane, $C_{\alpha,ads}$ and $C_{\beta,ads}$, are similar and the difference between the two species reflects the presence of two distinct surface sites. It is plausible that the two rates of formation of $C_{\alpha,ads}$ and $C_{\beta,ads}$ then display different dependencies on the surface concentrations of H_{ads} and vacant sites.

In model B, $C_{\alpha,ads}$ is formed via the transformation of $C_{\beta,ads}$. This reaction is independent of the surface concentrations of H_{ads} and vacant sites:

$$C_{\alpha,ads} \longrightarrow C_{\beta,ads}$$
 (R-3)

For model A, the rate coefficient for the transformation of $C_{\alpha,ads}$ to $C_{\beta,ads}$, $k_{m,3}$, increases with H₂/CO feed ratio. It can not be identified if this reflects a dependency on the surface concentration of H_{ads} or on the surface concentration of vacant sites. For model B, the rate coefficient for the transformation of $C_{\alpha,ads}$ to $C_{\beta,ads}$, $k_{m,3}$, is fairly independent of the H₂/CO feed ratio. This indicates that in this model the backward reaction of (R-3) does not involve H_{ads} or vacant sites. Constant rate coefficients for the inter-exchange between $C_{\alpha,ads}$ and $C_{\beta,ads}$ for model B, $k_{m,2}$ and $k_{m,3}$, imply a constant ratio between these two surface species. The modeling results do not correspond to this, as is observed in table 7.9. However, the variance of the contribution of $C_{\alpha,ads}$ to these two surface species is less pronounced for model B, *i.e.* $L_{C_{\alpha}}/(L_{C_{\alpha}} + L_{C_{\beta}})=30-45\%$, than for model A, *i.e.* $L_{C_{\alpha}}/(L_{C_{\alpha}} + L_{C_{\beta}})=43-72\%$.

7.4 Simulating the D-labeling of methane

As indicated in section 6.2.6, the D_2 SSITKA experimental data are not suitable for modeling. To study the hydrogenation mechanism of surface C_{ads} to CH_4 , simulations of the transients of the Dmethane variants are presented in this section.

The calculated transients of the isotopic variants of D-methane for different kinetic regimes are compared to the transients of ${}^{13}CH_4$. The latter is a reference for the D-labeling simulations with respect to the total surface concentration of methane intermediates. The simulation of ${}^{13}C$ -labeling of methane formation is discussed first.

Simulation of ¹³C-labeling of the methanation reaction

For the simulation, the simplest mechanism for ¹³C-incorporation is used:

$$CO_{g} \xrightarrow[k_{a}]{k_{a}} CO_{ads} \xrightarrow{k_{1}} C_{1,ads} \xrightarrow{k_{2}} CH_{4,g}$$
(R-4)

The simulations are performed using a plug-flow reactor model. The set of continuity equations for the ¹³C-labeling of the methanation reaction was presented in section 3.5.1. The model parameters are $L_{C_1}^{SS}$, k_a , and L_{CO}^{SS} , while all other variables in these equations are fixed and listed in table 7.7. The simulated transients of the Ne tracer, ¹³CO, and ¹³CH₄ are shown in figure 7.22. All characteristics are present in the responses, *i.e.* the chromatographic effect of ¹³CO, the evolution of

¹³CH₄ before ¹³CO breakthrough, and the slow response of ¹³CH₄. The surface concentration of the methane intermediate, $L_{C_1}^{SS}$, is used as reference value for the sum of the methane intermediates during the D-labeling of the methanation reaction, *i.e.* C_{ads}, CH_{ads}, CH_{2,ads}, and CH_{3,ads}.



Figure 7.22: Simulated responses of Ne, ¹³CO, and ¹³CH₄. Values for parameters are listed in table 7.7.



Figure 7.24: Responses of the isotopic variants for methane when the rate-determining step is: $CH_{3,ads} + H_{ads} \xrightarrow{k_4} OH_{4,g} + 2*$



Figure 7.26: Responses of the isotopic variants for methane when the rate-determining step is:

$$CH_{ads} + H_{ads} \xrightarrow{\kappa_2} CH_{2,ads} +$$



Figure 7.23: Simulated responses of Ne, H_2 , HD, and D_2 for all situations. Values for parameters are listed in table 7.7.



Figure 7.25: Responses of the isotopic variants for methane when the rate-determining step is:



Figure 7.27: Responses of the isotopic variants for methane when the rate-determining step is:

100

Time /s

150

200

50

$$C_{ads} + H_{ads} \xrightarrow{\kappa_1} CH_{ads} + *$$

0.0

0

Table 7.7: Values for the characteristics of the catalyst bed, the steady state performance, and the model parameters used in the simulations of the ¹³C-labeling of methane.

catalyst bed			ed	steady state			model parameters		
	$ ho_{b}$	$kg_{cat} \cdot m_{R}^{-3}$	500	$C_{CO}^{SS} = C_{H_2}^{SS}$	mole ·mg ⁻³	1·10 ⁺⁰	$L_{C_1}^{SS}$	mole·kg _{cat} -1	2·10 ⁻³
	ε_{b}	m _g ³ ·m _R ⁻³	0.5	$C_{CH_4}^{SS}$	mole ·m _g -3	2·10 ⁻²	k _a	mole·kg _{cat} -1	1·10 ⁻¹
	τ	S	0.5				L_{CO}^{SS}	mole·kg _{cat} ⁻¹	5·10 ⁻²

Simulation of D-labeling of the methanation reaction

In the methanation reaction, C_{ads} , resulting from CO_{ads} dissociation, is stepwise hydrogenated to CH₄. Four intermediates are identified, *i.e.* C_{ads} , CH_{ads}, CH_{2,ads}, and CH_{3,ads}, of which the sum equals the surface concentration of the methane intermediate during ¹³C-labeling:

 $L_{C}^{SS} + L_{CH}^{SS} + L_{CH_{2}}^{SS} + L_{CH_{3}}^{SS} = L_{C_{1}}^{SS}$ (7.25)

The set of continuity equations is represented in appendix 10. The stepwise hydrogenation is considered to be either irreversible or reversible, both of which are discussed below.

Irreversible hydrogenation

Irreversibility of the hydrogenation reaction implies the absence of H-exchange between the $CH_{x,ads}$ species on the catalyst surface. The simulation parameters are L_{CH}^{SS} , $L_{CH_2}^{SS}$, $L_{CH_3}^{SS}$, k_a , and L_{H}^{SS} , while all other variables are fixed and similar to the ¹³C-incorporation case, see table 7.7. Four situations are distinguished, differing in the definition of the rate-determining step. The first situation is discussed in detail, while the reasoning for the other three situations is similar.

1. The final hydrogenation of CH_{3,ads} to CH₄ is the rate-determining step. The steady state formation rate of CH₄ is represented by:

$$R_{w,CH_4}^{SS} = k_1 L_H^{SS} = k_2 L_{CH}^{SS} L_H^{SS} = k_3 L_{CH_2}^{SS} L_H^{SS} = k_4 L_{CH_3}^{SS} L_H^{SS} = \frac{\varepsilon_b}{\rho_b \tau} C_{CH_4}^{SS}$$
(7.26)

The assumption that $k_4 < k_3 = k_2 = k_1$ implies that $L_{CH_3}^{SS} > L_{CH_2}^{SS} = L_{CH}^{SS} = L_C^{SS}$. In table 7.8 the values of the simulation parameters are listed and in figure 7.23 the simulated transients of Ne, H₂, HD, and D₂ are shown. Again, the characteristics of the responses are conform the experimental observations. The transients of the D-labeled variants of methane are shown in figure 7.24. It appears that CH₃D is the most abundant labeled variant of methane and that the time scale of the CD₄ response equals the time scale of the ¹³CH₄ response in figure 7.22.

- 2. If the hydrogenation of $CH_{2,ads}$ to $CH_{3,ads}$ is the rate-determining step, the most abundant intermediate is $CH_{2,ads}$. The calculated transients are shown in figure 7.25.
- 3. If the hydrogenation of CH_{ads} to $CH_{2,ads}$ is the rate-determining step, the most abundant intermediate is CH_{ads} . The calculated transients are shown in figure 7.26.
- 4. If the first hydrogenation of C_{ads} to CH_{ads} is the rate-determining step, the most abundant methane intermediate is C_{ads}. The calculated transients are shown in figure 7.27.

Logically, the responses of Ne, H₂, HD, and D₂ are independent of the rate determining step. Going from the final hydrogenation to the first hydrogenation as rate determining step, the most abundant methane intermediate shifts from $CH_{3,ads}$ to C_{ads} . Simultaneously, the most abundant isotopic variant of methane in the figures 7.24 to 7.26 shifts from CH_3D to CHD_3 while the transient of CD_4 is as slow as the transient of ¹³CH4. The last situation is an exception; the transients for all the isotopic variants for methane in figure 7.27 become fast. This situation is in good agreement with the experimental observations in section 6.2.4.

 Table 7.8: Overview of the simulation parameters of the D-tracing of the methanation reaction for the different rate determining steps.

	L_{H}^{SS} =5.0·10 ⁻² mole·kg _{cat} ⁻¹			$k_a = 5.0 \cdot 10^{-3} \text{ m}_{g}^{3} \cdot \text{kg}_{cat}^{-1} \cdot \text{s}^{-1}$		
rate determining step	L_C^{SS}	L_{CH}^{SS}	$L_{CH_2}^{SS}$	$L_{CH_3}^{SS}$	Sum:	
$C_{ads} + H_{ads} \xrightarrow{k_1} CH_{ads} + *$	1.7·10 ⁻³	1.0·10 ⁻⁴	1.0·10 ⁻⁴	1.0·10 ⁻⁴	2.0·10 ⁻³	
$CH_{ads} + H_{ads} \xrightarrow{k_2} CH_{2,ads} + *$	1.0·10 ⁻⁴	1.7·10 ⁻³	1.0·10 ⁻⁴	1.0·10 ⁻⁴	2.0·10 ⁻³	
$CH_{2,ads} + H_{ads} \xrightarrow{k_3} CH_{3,ads} + *$	1.0·10 ⁻⁴	1.0·10 ⁻⁴	1.7·10 ⁻³	1.0·10 ⁻⁴	2.0·10 ⁻³	
$CH_{3,ads} + H_{ads} \xrightarrow{k_4} CH_{4,g} + 2*$	1.0·10 ⁻⁴	1.0·10 ⁻⁴	1.0·10 ⁻⁴	1.7·10 ⁻³	2.0·10 ⁻³	

Reversible hydrogenation

If the stepwise hydrogenation is assumed to be reversible, the rate coefficients for the dehydrogenation reactions, *i.e.* k_{-1} to k_{-3} in the continuity equations in appendix 10, are non-zero. The following assumptions are made:

- equal surface concentrations of the methane intermediates, *i.e.* $L_{CH_3}^{SS} = L_{CH_2}^{SS} = L_{CH}^{SS}$;
- equal rate coefficients for the three dehydrogenation reactions, *i.e.* $k_{-1}=k_{-2}=k_{-3}$.

The net production rate of CH₄ is defined as:

 $R_{w,CH_4}^{SS} = k_4 L_{CH_3}^{SS} L_H^{SS} = k_i L_{CH_{i-1}}^{SS} L_H^{SS} - k_{-i} L_{CH_i}^{SS} = R_{w,i,f}^{SS} - R_{w,i,b}^{SS}$ with $1 \le i \le 3$ (7.27) where $R_{w,i,f}^{SS}$ is the hydrogenation rate in mole $kg_{cat}^{-1} \cdot s^{-1}$ and $R_{w,i,b}^{SS}$ is the dehydrogenation rate in mole $kg_{cat}^{-1} \cdot s^{-1}$ for $1 \le i \le 3$. The net methanation rate is the difference between the forward reaction rate and the backward reaction rate. Two situations are considered in table 7.9;

- 1. at $k_{-1}=k_{-2}=k_{-3}=1.0 \text{ s}^{-1}$, the backward reaction is faster than the net production;
- 2. at $k_{-1}=k_{-2}=k_{-3}=1.0\cdot 10^{-2} \text{ s}^{-1}$, the backward reaction is slower than the net production.

For both situations, the net methanation rate is constant; $R_{w,CH_4}^{SS} = 4.0 \cdot 10^{-5}$ mole·kg_{cat}⁻¹·s⁻¹. In figure 7.28, the simulated transients of the CH_xD_{4-x}, where x=0-4, are shown for situation 1 and in figure 7.29 for situation 2. For situation 1 the backward reaction is 12.5 times faster than the net rate of methanation and the simulated transients are in good agreement with the experimental observations in section 6.2.4.



Figure 7.28: Transient of D-labeled methane with reversible hydrogenation steps and $k_{.7}=k_{.2}=k_{.3}=1.0 \text{ s}^{-1}$.

Figure 7.29: Transients of D-labeled methane with reversible hydrogenation steps and $k_{.7}=k_{.2}=k_{.3}=1.0\cdot10^{-2}$ s⁻¹.

 Table 7.9: Overview of the simulation parameters of the D-tracing of the methanation reaction.

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$C_{ads} + H_{ads} \xleftarrow{k_1 k_{-1}} CH_{ads} + *$	$L_H^{SS} = 5.0$	10 ⁻² mole	kg _{cat} ⁻¹	<i>k_a</i> =5.0·10⁻³ m	ng ³ ·kg _{cat} ⁻¹ ·s ⁻¹		
$CH_{ads} + H_{ads} \xleftarrow{k_2 k_{-2}} CH_{2,ads} + *$	$L_{CH_3}^{SS} = L_C^S$	$C_{H_2}^S = L_{CH}^{SS} =$	$=L_C^{SS}=5.0$	10 ⁻⁴ mole kg _{cat} ⁻¹			
$CH_{2,ads} + H_{ads} \xleftarrow{k_3 k_{-3}} CH_{3,ads} + *$	k ₋₁ /s ⁻¹	k ₋₂ /s ⁻¹	k ₋₃ /s ⁻¹	$R_{w,i,f}^{SS}$	$R_{w,i,b}^{SS}$		
$CH_{3,ads} + H_{ads} \xrightarrow{k_4} CH_{4,a} + 2*$	1.0·10 ⁰	1.0·10 [°]	1.0·10 [°]	5.4·10 ⁻⁴	5.0·10 ⁻⁴		
- 3,aus aus - 4,y	1.0·10⁻²	1.0·10 ⁻²	1.0·10⁻²	4.5·10 ⁻³	5.0·10 ^{-°}		

Irreversible versus reversible hydrogenation

When comparing the simulations with the experimental transients of CH_xD_{4-x} in section 6.2.4 two situations emerge:

- <u>irreversible hydrogenation</u>: the hydrogenation of C_{ads} is the rate determining step and the pool of C_{α,ads} and C_{β,ads} consist of H-free surface species;
- reversible hydrogenation: the H-exchange between the CH_{x,ads} species, where x=0-3, is fast compared to the net rate of methane formation and the surface concentration for these species are not accessible with the SSITKA technique.

The experimental results published by Marquez-Alvarez *et al.* [1998] and Angelli *et al.* [1998] are similar. Marquez-Alvarez *et al.* [1998] publish transients of the isotopic variants of CH_xD_{4-x}

following a $CO/H_2 \rightarrow CO/D_2$ isotopic step change for the methanation reaction on a Ni/SiO₂ catalyst. These transients are reproduced in figure 7.31. Angelli *et al.* [1998] publish transients of ¹³CH₄ following a ¹³CO/H₂ \rightarrow CO/H₂ isotopic step change at a slightly lower temperature, but on the same catalyst. These transients are reproduced in figure 7.30. The transient of ¹³CH₄ in figure 7.30 is slow and full ¹³C-labeling is achieved in about 100 s. The transients of the isotopic variants for CH_xD_{4-x}, however, are much faster. Fully D-labeling is reached within 25 s, which is comparable with the time scale of the He tracer. This situation is comparable with our experimental results presented in chapter 6. Marquez-Alvarez *et al.* [1998] conclude that CH_{ads} is the most abundant methane intermediate and that the hydrogenation of this species is the rate-determining step.

On the basis of the simulations presented above, we conclude that the shapes of the transients in figures 7.30 and 7.31 do not support the hydrogenation of CH_{ads} being the rate-determining step. These experimental results indicate that either the hydrogenation of C_{ads} is the rate-determining step, or that the hydrogenation reactions are reversible. An average calculated CH_x composition of 0.5<x<0.8 supports the latter situation [Marquez-Alvarez *et al.*, 1998].



1.0 CD Normalized response CH4 0.8 0.6 CH_D 0.4 CHE CHD 0.2 0.0 10 20 30 Time /s

Figure 7.30: Normalized responses of He, ¹²CO, ¹³CO, ¹²CH₄, and ¹³CH₄ following the switch ¹³CO/H₂ \rightarrow ¹²CO/H₂ for a Ni/SiO₂ catalyst at 503 K, 1 bar, and H₂/CO=2 [Agnelli *et al.*, 1998].

Figure 7.31: Normalized responses of, CH₄, CH₃D, CH₂D₂, CHD₃, and CD₄ following the switch CO/H₂ \rightarrow CO/D₂ for a Ni/SiO₂ catalyst at 523 K, 1 bar, and H₂/CO=2 [Marquez-Alvarez *et al.*, 1998].

7.5 Conclusions

In this chapter, the methanation reaction during the Fischer-Tropsch synthesis is studied. Decoupling of the methanation reaction and the formation of the C_{2+} product spectrum efficiently decreases the computational time for the model identification study on the methanation reaction (section 7.3.1) and the model discrimination study on the Fischer-Tropsch reaction (section 7.3.2). Moreover, it allows the quantification of the methanation mechanism while the entire Fischer-Tropsch product spectrum is accounted for (section 7.3.3). The conclusions from the model identification (section 7.3.1) are:

- The pool of methane intermediates is heterogeneous and the definition of two surface species, $C_{\alpha,ads}$ and $C_{\beta,ads}$, is sufficient to describe the experimental results.
- Four out of the five mechanisms for the methanation reaction give identical modeling results and are therefore indistinguishable.
- Of the four models, three models result in different ratios of the surface concentrations of the two methane intermediates. Surface sensitive techniques or theoretical calculations are necessary tools for model discrimination.

The conclusions from the model discrimination (section 7.3.2) are:

 Although the number of potential models increases going from the methanation reaction alone to the incorporation of chain initiation, the number of acceptable models decreases. This indicates the potential of the GCMS analysis of the C₂-C₅ hydrocarbons in combination with the SSITKA technique.

- The catalyst surface is heterogeneous on the level of the C_{1,ads} species and homogeneous towards chain initiation and chain growth. The modeling rejects the "dual sites" model proposed by Donnelly and Satterfield [1989] and the "distributed sites model" proposed by Wojchiechowski [1988] and Adesina [1996].
- The two reactive intermediates C_{α,ads} and C_{β,ads} both contain only one C-atom and both participate in methane formation and chain growth. The participation of C_{β,ads} in C-C bond formation is direct and the participation of C_{α,ads} is indirect, *i.e.* it first needs transformation into C_{β,ads}.
- The depolymerisation of growing hydrocarbon chains is not a necessary step to describe the experimental results.
- The two best methanation models (models 4.1 and 6.1 in section 7.3.2) are indistinguishable.
- The surface concentration of C_{2,ads} and the reaction rate coefficient for termination to ethane do not depend on the choice of the methanation mechanism. This implies that the rate coefficients for the C₂₊ formation do not depend on which of the methanation models is used as basis for the mechanism of the Fischer-Tropsch reaction.

The conclusions from the model quantification in section 7.3.3 are:

- The methanation reaction and the formation of the C₂₊ hydrocarbons are uncoupled and modeled separately. The formation of the C₂₊ hydrocarbons is accounted for via a net consumption term.
- The dependencies of the rate coefficients on the H₂/CO feed ratio implies that both the surface concentrations of H_{ads} and vacant surface sites increase with increasing H₂/CO feed ratio.
- CO_{ads} , $C_{\alpha,ads}$, and $C_{\beta,ads}$ are the most abundant surface species. Coverages of CO_{ads} and $C_{\alpha,ads}$ + $C_{\beta,ads}$ amount to 65% and 35% respectively and are in good agreement with values reported in literature.
- The surface concentration of CO_{ads} is independent of the H₂/CO feed ratio, while the sum of the surface concentrations of C_{α,ads} + C_{β,ads} decreases with increasing H₂/CO feed ratio.

Besides the modeling of the ¹³C-labeling of the methanation reaction, simulations are performed on the D-labeling of this reaction to assess the hydrogenation mechanism of C_{ads} to CH₄. Comparison of the simulations with the experimental observed transients of CH_xD_{4-x}, where x=0-4, leads to the following conclusions:

- If the stepwise hydrogenation of C_{ads} to CH_{3,ads} is assumed to be irreversible, the hydrogenation of C_{ads} is the rate determining step. This leads to low surface concentrations of CH_{ads}, CH_{2,ads}, and CH_{3,ads}. In this case C_{α,ads} and C_{β,ads} are H-free surface species.
- If the stepwise hydrogenation of C_{ads} to CH_{3,ads} is assumed to be reversible, the hydrogenation and the dehydrogenation are faster than the net rate of formation of CH₄ by one order of magnitude. The surface concentrations of CH_{x,ads}, where x=0-3, cannot be assessed via the D₂-SSITKA technique and the H-content of C_{α,ads} and C_{β,ads} is unknown.

8

Intrinsic kinetics of the Fischer-Tropsch reaction

8.1 Introduction

Modeling of the intrinsic kinetics of the Fischer-Tropsch reaction in literature is mainly limited to steady state studies. The kinetic parameters obtained in these studies consist of reaction rate coefficients and surface concentrations, which are not quantified separately. Transient kinetic methods, especially SSITKA, are effective in decoupling rate coefficients and surface concentrations. The majority of the SSITKA investigations on the CO hydrogenation reaction, however, is limited to the methanation reaction. Only a few published transient kinetic investigations address the characteristic C-C coupling reaction and list values for the reaction rate coefficients and surface concentrations of the participating species [Biloen, 1983; Zhang and Biloen, 1986; Mims and McCandlish, 1987; Komaya and Bell, 1994a].

The goal of this chapter is to obtain an in-depth understanding of the mechanism of the Fischer-Tropsch reaction via modeling of ¹³C incorporation into the C_2 to C_5 reaction products in which the C-C bond formation is an essential step. For the modeling a plug flow reactor model is used to correctly account for the readsorption of reactive olefins.

In the chapter 7, the methanation part of the Fischer-Tropsch reaction was quantified by treating the C_{2+} formation as a net consumption term for the methane surface intermediates. Estimates for the reaction rate coefficients of the two best models were obtained. In this chapter, methanation model A is used for the quantification of the kinetic parameters associated with the C_{2+} hydrocarbon formation of the Fischer-Tropsch reaction. The parameters representing the methanation part of the Fischer-Tropsch synthesis are fixed. In section 8.3, the modeling results at H₂/CO=2 indicate that the C-C coupling reaction is fast and that the surface concentrations of growing hydrocarbon chains are small. The dependency of the reaction rate coefficients on the H₂/CO feed ratio is discussed in section 8.4. The chemical composition of the growing hydrocarbon chain corresponds to a $C_iH_{2i,ads}$ species. In section 8.5 a comparison of the parameter estimates with studies presented in literature is made. In section 8.6 it is shown that the mechanism for the formation of oxygenates on Co-metal proceeds via a CO-insertion mechanism, while large amounts of alcoxy species on the TiO₂ support are formed via the spillover of the alcohol intermediates from the Co-metal to the TiO₂ support. Conclusions on the characteristic C-C bond formation reactions are summarized in section 8.7.

8.2 Modeling considerations

In section 7.2.1, an overview was presented of mechanistic aspects of the methanation reaction. For the C_{2+} hydrocarbon formation, additional modeling considerations are given in this section:

8. As illustrated in chapter 5, secondary reactions, *i.e.* chain branching and bond-shift, cause a shift in preferential termination from olefin to paraffin going from C_3 to C_5 at the applied experimental conditions. This is modeled by assuming the termination rate coefficients to be a function of the chain length until C_5 . Starting at $C_{5,ads}$, all surface reactions proceed with chain-length independent reaction rate coefficients. Preliminary modeling of the data at H₂/CO=1 indeed indicates that the rate coefficient for chain growth, k_p , and the rate coefficient for readsorption, k_{re} , are constant from $C_{3,ads}$ onwards.

9. In contrast to the continuity equation (6.13) for the surface concentration of $C_{\beta,ads}$, the chain initiation and chain growth in the continuity equations for the growing hydrocarbon chains can now be written in terms of intrinsic kinetics. The surface concentration of $C_{\beta,ads}$ is known at this stage of the modeling.

10. The transients for olefins and paraffins are very similar. Hence, it is assumed that they are identical, halving the number of continuity equations for the isotopic components in the gas-phase. For example, for single labeled ethane and ethene this assumption implies that:

$$\frac{C_{C_2H_4}}{C_{C_2H_4}^{SS}}\Big|_{x,t} = \frac{C_{C_2H_6}}{C_{C_2H_6}^{SS}}\Big|_{x,t}$$
(8.1)

Subsequent incorporation into the continuity equation (6.14) for single labeled C_{2,ads} results in:

$$\frac{\partial L_{C_2}}{\partial t} = 2k_{ini} L_{C_\beta} L_{C_\beta} - k_{t,p,2} L_{C_2} - k_{t,o,2} L_{C_2} + k_{re,2} \frac{C_{C_2H_6}}{K_2^{ph}} \frac{C_{C_2H_6}^{SS}}{C_{C_2H_6}^{SS}} - k_p L_{C_\beta, tot} L_{C_2}$$
(8.2)

11. The sets of data obtained at different H_2/CO feed ratios are regressed separately because of the different values for the surface concentrations of H_{ads} and empty sites, while the residence time is variable. Since the modeling considers intrinsic data, the different residence times represent different axial positions within the catalyst bed.

8.3 Kinetic model parameters for H₂/CO=2

In this section, the modeling results at $H_2/CO=2$ are discussed. The conclusions based on the other H_2/CO feed ratios, *i.e.* $H_2/CO=1$ and $H_2/CO=5$, are similar and are not discussed separately. First the model description of the steady state performance is discussed, followed by the model description of the transients for the C_2 to C_5 paraffins. Finally, a critical evaluation of the parameter estimates is given.

8.3.1 Steady state performance

The steady state concentrations of the C_1 to C_9 hydrocarbon reaction products at $H_2/CO=2$ are shown in figures 8.1 to 8.3 for the different residence times. The steady state performance of the catalyst is quantified in three graphs as a function of carbon number: the olefin and paraffin gas-phase concentrations (graph A), the total gas-phase concentration plot (graph B), and the olefin to paraffin ratio plot (graph C). The Fischer-Tropsch mechanism of table 7.1 is capable to describe all experimental observations in a qualitative and quantitative way:

- The characteristic S-shape of the paraffin concentration with increasing carbon number as observed in graph A of figures 8.1 to 8.3.
- The low value for the ethene concentration as observed in graph A of figures 8.1 to 8.3.
- The typical ASF plot with the lower than expected contribution for C₂ and the higher than expected contribution for C₁ in graph B of figures 8.1 to 8.3.

- The small increase of the olefin concentration with increasing residence time in contrast to the large increase of the paraffin concentration for every carbon number.
- The slight increase of the chain growth probability with increasing residence time.
- The parallel downward shift of the olefin to paraffin ratio plot with increasing residence time. The slope starting at C₅ is dictated by the value for the effective heat of desorption per CH₂ unit in the physisorption equilibrium, which is a constant at the present experimental conditions.





For the shortest residence time, the difference between the calculated gas-phase concentrations and the experimental values is largest. For every carbon number in figure 8.1A) the calculated values are lower than the experimental values. In section 5.2 it was already observed that this experiment displayed a higher than expected activity in terms of CO conversion, see figure 5.1. These observations indicate that during this experiment the catalyst displays a slightly increased activity.

The application of a plug flow reactor model allows assessing the steady state concentration profiles of the reaction products as a function of the reactor axis. This is discussed below for the components in the gas-phase, the components in the chemisorbed state, and the components in the physisorbed state.

Gas-phase

In figure 8.4, the concentration profiles of the C₁ to C₄ hydrocarbons in the gas-phase are shown. In this figure, the concentrations at the end of the reactor (axial position=1) correspond to the maximum residence time, *i.e.* $W_{cat}/F=36.6$ kg_{cat}·s·mole⁻¹.



Figure 8.4: Calculated concentrations of the C_1 to C_4 hydrocarbons in the gas-phase as a function of the axial position in the reactor at $H_2/CO=2$. Gas-phase concentrations in mole·m_g⁻³. Solid lines: Paraffins Dashed lines: Olefins The concentration profiles for ethene, propene, and 1-butene display a strong upward convexity, while the concentration profiles for ethane, propane, and butane display a weak downward convexity. The upward convexity for the olefins is caused by the increasing consumption of reactive olefins via readsorption with increasing residence time. Their steady state concentrations only increase moderately with the axial position in the bed. The weak downward convexity for the paraffins results from the partial hydrogenation of the readsorbed olefins. The steady state concentrations of the paraffins increase stronger than for the olefins. From the figure it is clear that the olefin to paraffin ratio decreases with the axial bed position. The concentrations at every axial reactor position obey to the ASF distribution, *i.e.* low contributions for ethane + ethene and high for propane + propene.

Chemisorbed state

In figure 8.5, the steady state concentration profiles of the $C_{2,ads}$ to $C_{9,ads}$ growing hydrocarbon chains on the catalyst surface are represented. Although the surface concentrations of CO_{ads} , $C_{\alpha,ads}$, and $C_{\beta,ads}$ are constant throughout the reactor, the readsorption of the reactive olefins causes the surface concentrations of the growing hydrocarbon chains to increase with the axial position in the reactor. The surface concentrations at a certain axial position, however, monotonically decrease with increasing carbon number. In contrast to the low gas-phase concentration of ethane + ethene, no minimum in the surface concentrations for $C_{2,ads}$ is observed. The surface concentration of $C_{2,ads}$ is 50 times smaller than the surface concentration of the methane intermediates. The total surface coverage of the growing hydrocarbon chains on the catalyst surface is 1.4% at $W_{cat}/F=36.6$ kg_{cat}·s·mole⁻¹. This number is in good agreement with the surface coverage of maximal 1% for a Co/SiO₂ catalyst reported by Mims and McCandlish [1987], and of 3.7 % for a Ru/TiO₂ catalyst reported by Komaya and Bell [1994a].



Figure 8.5: Calculated concentrations of the $C_{2,ads}$ to $C_{9,ads}$ growing hydrocarbon chains on the catalyst surface as a function of the axial position in the reactor at H₂/CO=2. Surface concentrations in mole kg_{cat}⁻¹.

This illustrates that only a small fraction of the total available Co surface consists of surface sites capable to contain a growing hydrocarbon chain. It is believed that these sites have a distinct geometry. Several researchers suggest that the active sites for C-C coupling consist of surface defects [Geerlings *et al.*, 1999; Beitel *et al.*, 1996, 1997]. Beitel *et al.* [1996] indicate that initially smooth surfaces undergo roughening by the formation of defect sites in a high-pressure/high-temperature CO treatment. In a succeeding paper Beitel *et al.* [1997] indicate that a Co-surface which is rich of defects is more active in the Fischer-Tropsch synthesis than a smooth annealed surface. Their study reveals a striking similarity between a surface where defects are introduced via an Ar bombardment, via a CO treatment, or via a Fischer-Tropsch treatment. The roughening of a smooth Co(0001) surface after 1 hour of syngas at 4 bar and 523 K is also observed by Wilson *et al.* [1995].

Physisorbed state

In figure 8.6, the steady state concentration profiles of the C₂ to C₉ hydrocarbons in the physisorbed state are shown. As expected, the surface concentrations of the physisorbed hydrocarbons increase with carbon number due to the decreasing physisorption equilibrium constant. In contrast to the chemisorbed state, the concentrations of the physisorbed hydrocarbons are zero at zero residence time because of the absence of hydrocarbon reaction products at the inlet of the reactor. Starting at C₅ the concentrations in the physisorbed layer increase strongly along the axial position, whereas this increase is moderate for C_2 to C_4 . For C_2 , the surface concentration in the physisorbed layer is 250 times smaller than in the chemisorbed state. For C5 this ratio is only 10 and it decreases further with increasing chain length. In figure 8.7, the calculated values for the surface concentrations of the growing hydrocarbon chains and the physisorbed hydrocarbons are represented for the C_1 to C_{20} reaction products for three different axial reactor positions (0.2, 0.6, and 1.0). The surface concentration of growing hydrocarbon chains decreases with increasing chain length, whereas the concentration of physisorbed reaction products increases. With increasing residence time, the increase of the capacity of the physisorbed state is more pronounced than that of the chemisorbed state. The surface concentrations in the physisorbed layer are 4 orders of magnitude lower than the total number of active surface sites, indicating that at the present experimental conditions no noticeable wax formation occurs. The reaction is run at dry conditions, *i.e.* all reaction products leave the reactor via the gas-phase. Although the surface coverage of the physisorbed layer for C_2 to C_{20} only amounts to 0.3 %, the incorporation of a physisorbed state for the hydrocarbon reaction products in the kinetic model is essential to explain the steady state behavior of the catalyst.



8.3.2 Transients of the C₂ to C₅ paraffins

The transients for ethane, propane, butane, and pentane at $H_2/CO=2$ are displayed in figures 8.8 to 8.10 for the different residence times. It is observed that the Fischer-Tropsch model based on methanation model A from section 7.3.3 is capable to describe the transients for all isotopic variants for the C₂-C₅ hydrocarbons. This was already observed during the modeling in section 7.3.2 where the methanation model A was expanded towards ethane. Additionally, it is shown here that the descriptions of the transients of the C₃-C₅ hydrocarbons are also satisfying. The model correctly describes the transients of each fully labeled variant as well as the maximum responses of the partially labeled isotopic variants. The goodness of fit decreases going from ethane to pentane:

- the calculated responses are slower than the experimental responses;
- the difference between the calculated and experimental response values at the maxima of the partially labeled isotopic variants increases.

This decreasing goodness of fit is believed to result from the increased inaccuracy of the experimental transients. With increasing number of C-atoms in the molecule, the number of isotopic variants increases drastically and, moreover, the differences between the fragmentation patterns of the different isotopic variants become smaller. Therefore, the accuracy of the calculation of the isotopic composition of a product sample (section 4.2.3) decreases.

In figure 7.13 of section 7.3.3, the calculated methane transient at the lowest residence time $(W_{cat}/F=11.1 \text{ kg}_{cat} \cdot \text{s} \cdot \text{mole}^{-1})$ was slightly slower than the experimental transient. This trend is continued in the description of the transients for the C₂-C₅ hydrocarbons, as is observed in figure 8.8.



Figure 8.8: Normalized responses for ethane, propane, butane and pentane at $H_2/CO=2$ and $W_{cat}/F=11.1$ kg_{cat}·s·mole⁻¹. Dashed lines and open symbols: data; solid line and closed symbols: model calculations.



Figure 8.9: Normalized responses for ethane, propane, butane and pentane at $H_2/CO=2$ and $W_{cat}/F=24.2$ kg_{cat} s mole⁻¹. Dashed lines and open symbols: data; solid line and closed symbols: model calculations.



Figure 8.10: Normalized responses for ethane, propane, butane and pentane at $H_2/CO=2$ and $W_{cat}/F=36.6$ kg_{cat} s mole⁻¹. Dashed lines and open symbols: data; solid line and closed symbols: model calculations.

The shapes of the transients of the C_1 - C_5 hydrocarbons are dictated by the capacity of the chemisorbed state and contain information about the surface kinetics. For these responses the capacity of the physisorbed state is small. However, as illustrated in figure 8.7, the capacities of the chemisorbed state and the physisorbed state are equally large at about C_8 for x=1. From this carbon number onwards, the influence of the capacity of the physisorbed state on the transients becomes dominant. This is illustrated in figure 8.11, where the simulated transients of the overall fraction ¹³C in some reaction products are presented. The transients are similar in shape as long as the concentration in the physisorbed state is small. The transients deform at the moment the

concentration of a reaction product in the physisorbed state approaches that of the chemisorbed state. For C_{14} , the concentration in the physisorbed state is 50 times larger than in the chemisorbed state. Its transient is completely governed by the physisorption equilibrium and does no longer bear information about the surface reactions responsible for its formation. This illustrates that the SSITKA technique can only be applied to the Fischer-Tropsch synthesis in the absence of a significant wax layer on the catalyst surface. A SSITKA investigation of the Fischer-Tropsch reaction at high pressure does therefore not provide any mechanistic information.



Komaya and Bell [1994a] publish transients of the overall fraction ¹³C in the C₂-C₈ reaction products during the Fischer-Tropsch synthesis on a Ru/TiO₂ catalyst at 523 K and 1 bar. They report that the increase in response times for the hydrocarbons with increasing residence time is larger than expected. We conclude that this is the result from excessive wax formation. The critical chain growth probability at 523 K is 0.69 (see section 2.4.2). At their conditions α varies between 0.65-0.78. Therefore, an enhanced capacity for physisorption due to wax formation at higher residence times may cause the increase in response time with increasing residence time. In their study, the deformation of the transient of C₇ is similar to the deformation of the transient for C₁₀ of figure 8.11 at our experimental conditions. This illustrates the higher degree of wax formation during their experiments. The same influence is reported by Biloen *et al.* [1983] at 488 K and 3 bar. They mention the deviation of the transients at α >0.5. Indeed, the critical chain growth probability for wax formation at their experimental conditions is α_c =0.56.

8.3.3 Parameter estimates

Estimates of the reaction rate coefficients for C_{2+} hydrocarbon formation are listed in table 8.1. The parameter estimates for the methanation reaction were already discussed in section 7.4.3 and are not repeated here. As indicated in section 8.2, the rate coefficients for chain growth, k_p , and for readsorption of reactive olefins, k_{re} , are constant starting from C_3 . The rate coefficients for termination towards paraffin, $k_{t,p}$, and olefin, $k_{t,o}$, are constant starting from C_5 . The parameters are presented in figures 8.12 and 8.13. The main observations regarding C-C coupling, termination, and readsorption are discussed below.

Table 8.1 : Estimates of the reaction rate coefficients for C_{2+} formation at 498 K, 1.2 bar, and $H_2/CO=2$.							
carbon	k_{ini}, k_p	$k_{t.p,i}$	<i>k_{t.o.i}</i>	k _{re.i}			
number	Kg _{cat} ·mole ·s	S	S	S			
2	2.7·10 ⁺⁰	1.2·10 ⁻¹	1.6·10 ⁻¹	2.9·10 ⁺²			
3	8.6·10 ⁺¹	9.3·10 ⁻²	7.9·10 ⁻¹	4.1·10 ⁺¹			
4		2.9·10 ⁻¹	8.0·10 ⁻¹				
5		5.5·10 ⁻¹	4.1·10 ⁻¹				



Figure 8.12: Parameter estimates for k_{ini} , k_p , (\blacksquare) and k_{re} **Figure 8.13**: Parameter estimates for $k_{t,o}$ (\blacklozenge) and $k_{t,p}$ (\boxdot) at $H_2/CO=2$, 498 K, and 1.2 bar.

C-C coupling

The rate coefficient for chain initiation (*i.e.* $2 C_{\beta,ads} \rightarrow C_{2,ads}$) is one order of magnitude smaller than the rate coefficient for chain propagation (*i.e.* $C_{\beta,ads} + C_{2,ads} \rightarrow C_{3,ads}$), see figure 8.12. Once a hydrocarbon chain is formed by the first C-C coupling reaction, the subsequent growth of the chain via the addition of a next CH_{2,ads} species is fast. However, the definitions of both reaction rates involve the surface concentration of $C_{\beta,ads}$:

- chain initiation is second order in the surface concentration of $C_{\beta,ads}$, *i.e.* $R_{ini} = k_{ini} L_{C_a}^2$;
- chain growth is first order in the surface concentration of $C_{\beta,ads}$, *i.e.* $R_p = k_p L_{C_s} L_{C_s}$.

Because chain initiation and chain growth are based on the surface concentration of $C_{\beta,ads}$ and not of $CH_{2,ads}$, the estimates represent the lower limits for the true reaction rate coefficients, while the difference between the two true rate coefficients is smaller than the factor 30 in figure 8.12. For example, chain growth is written as:

$$R_{p} = k_{p} L_{C_{\beta}} L_{C_{i}} = k_{p}^{*} L_{CH_{2}} L_{C_{i}} \qquad \text{where} \qquad L_{CH_{2}} < L_{C_{\beta}} \qquad \text{and} \qquad k_{p}^{*} > k_{p} \qquad (8.3)$$

where k_p is the rate coefficient for chain growth based on $C_{\beta,ads}$ and k_p^* is the true rate coefficient for chain growth based on $C_{H_{2,ads}}$.

If it is assumed that the true rate coefficients for chain initiation and chain growth are equal, in other words if the C-C coupling reaction is chain length independent, approximately 3% of the $C_{\beta,ads}$ pool consists of $CH_{2,ads}$ species. The rate coefficient for chain initiation and chain growth then amounts to $2.8 \cdot 10^{+3}$ mole·kg_{cat}⁻¹·s⁻¹, or $1.7 \cdot 10^{+2}$ s⁻¹ based on turn-over-frequency. This value is more than one order of magnitude higher than values reported in literature, see section 8.5.

Termination

The chain growth probability of a growing hydrocarbon chain is defined as:

$$\alpha_{i} = \frac{r_{p,i}}{r_{p,i} + r_{t,i}} = \frac{r_{p,i}}{r_{p,i} + r_{t,p,i} + r_{t,o,i} - r_{re,i}}$$
(8.4)

In figure 8.13, the total termination rate (= $k_{t,p,i} + k_{t,o,i}$) increases going from C₂ to C₃, whereas it is more or less constant for C₃-C₅. This indicates that the chain growth probability for C₂ is drastically larger than for C₃, but only changes moderately from this point onwards. This is illustrated in figure 8.14, where the calculated chain growth probability as a function of carbon number is given.



Although the total termination rate is constant going from C_3 to C_5 , a shift is observed from a preferential termination to olefin for C_3 ($k_{t,o,3} / k_{t,p,3} = 8.4$) to a preferential termination to paraffin for C_{5+} ($k_{t,o,5} / k_{t,p,5} = 0.75$). This shift in termination rates while its sum is constant is responsible for the experimentally observed S-shaped paraffin distribution with chain length. In section 5.2, it was explained that this is caused by the occurrence of chain-branching and bond-shift reactions. These secondary reactions of adsorbed of 1-olefins, characteristic for low-pressure operation of the Fischer-Tropsch reaction, cause the net termination to paraffin to increase and the net termination to olefin to decrease starting at C_4 . The net termination to paraffin is defined as the sum of termination to n-paraffin, iso-paraffin, and internal-olefin. The net termination to olefin is defined as the difference between termination to 1-olefin and readsorption of 1-olefin (see section 5.3).

Readsorption

The rate coefficient for ethene readsorption is one order of magnitude larger than the rate coefficient for the readsorption of the C_{3+} 1-olefins, see figure 8.12. This preferential readsorption for ethene is only partially responsible for the low concentration of C_2 in the ASF product distribution. As is observed in figure 8.13, the low termination rate to ethene is the other main cause.

8.4 Kinetic model parameters for all H₂/CO ratios

In this section, the dependency of the rate coefficients on the H_2/CO feed ratio is discussed. The modeling results of the methanation reaction in section 7.3.3 suggested that both the surface concentrations of H_{ads} and of vacant surface sites increase with increasing H_2/CO feed ratio. The model predictions of the experimental data at $H_2/CO=1$ and $H_2/CO=5$ are represented in appendix 9 for the steady state performance and in appendix 10 for the transients.

In figure 8.15 the rate coefficients for chain initiation, k_{ini} , chain growth, k_p , and readsorption of reactive olefins, k_{re} , are shown. Figure 8.16 presents the rate coefficients for termination to paraffin, $k_{t,p}$, of the C₂-C₅ growing hydrocarbon chains. The rate coefficients for the termination to olefin, $k_{t,o}$, of the C₁-C₅ growing hydrocarbon chains are shown in figure 8.17.



C-C coupling

The rate coefficients for C-C coupling, *i.e.* chain initiation and chain growth, are fairly independent of the H₂/CO feed ratio. Both reactions only involve C-containing species, the rate coefficients are not lumped with unknown surface concentrations of H_{ads} or vacant sites. The decreasing surface concentration of $C_{\beta,ads}$ with increasing H₂/CO ratio is accounted for by the model.

The independence of the rate coefficient for initiation and propagation on the surface concentration of H_{ads} does not support CO-insertion as the mechanism for hydrocarbon formation. In this mechanism the insertion of CO_{ads} into a growing hydrocarbon chain is followed by the removal of the O-atom via a hydrogenation step (see figure 2.3 in section 2.3.3). This would render the rate coefficients for C-C bond formation dependent on the surface concentration of H_{ads} , which is not observed.

Termination to paraffin

The rate coefficients for termination to paraffin all increase with increasing H_2/CO feed ratio. This is to be expected for hydrogenation reactions, since the surface concentration of H_{ads} , which increases with the H_2/CO ratio, is lumped into the rate coefficients.

The rate coefficients for the termination to the C_{2+} paraffins increase stronger than the termination coefficient for methane. Different dependencies are expected in this case. The net termination to methane is the difference between a hydrogenation and a dehydrogenation reaction, while the terminations to the C_{2+} paraffins are irreversible reactions. For methane, the rate of hydrogenation depends on the surface concentrations of H_{ads} and CH_x, where x=0-2, while the rate of dehydrogenation depends on the surface concentration of vacant surface sites and CH_x, with x=1-3:

$$R_{t,1} = k_{hydro}^* L_{CH_{i-1}} L_H - k_{dehydro}^* L_{CH_i} L_{vacant} = k_{t,1} L_{C_{\beta}} \quad \text{for } 1 \le i \le 3$$
(8.5)

where k_{hydro} and $k_{dehydro}$ are the true rate coefficients for hydrogenation and dehydrogenation, respectively.

In figure 8.16, the rate coefficient for the termination to ethane and propane are more or less equal at every H_2/CO ration. However, going from propane to pentane, the rate coefficient increases at every H_2/CO ratio. This increase is ascribed to the occurrence of chain-branching and bond-shift reactions. These secondary reactions transform reactive 1-olefins into less reactive internal- and iso-olefins and nonreactive iso- and normal-paraffins, causing an increase of the effective termination coefficient to paraffin.

Termination to olefin

The rate coefficient for termination to ethene is significantly lower than the rate coefficients for the termination to the C_{3+} olefins. The latter coefficients all have the same order of magnitude. All rate coefficients in figure 8.17 are independent of the H₂/CO feed ratio. This suggests that the rate of termination to olefin is independent of the surface concentration of H_{ads} or vacant sites, which both increase with increasing H₂/CO ratio.

In literature, controversy concerning the chemical identity of the monomer species and of the growing hydrocarbon chain in the carbene mechanism still exists. The proposals for the chemical identity of the growing hydrocarbon chain for the carbene mechanism are:

- 1. $C_i H_{2i+1,ads}$ species, or so-called alkyl species.
 - chain initiation proceeds via C-C coupling of CH_{2,ads} and CH_{3,ads};
 - termination to olefin proceeds via β-hydride abstraction;
 - termination to paraffin proceeds via a single step hydrogenation.
- 2. C_iH_{2i,ads} species, or so-called alkylidene species.
 - chain initiation proceeds via C-C coupling between two CH_{2,ads};
 - termination to olefin proceeds via desorption;
 - termination to paraffin proceeds via a double step hydrogenation.
- 3. C_iH_{2i-1,ads} species, or so-called alkenyl species.
 - chain initiation proceeds via C-C coupling of CH_{ads} and CH_{2,ads};
 - termination to olefin proceeds via a single step hydrogenation;
 - termination to paraffin proceeds via a triple step hydrogenation.

The $C_i H_{2i-1,ads}$ species is first proposed by the group of Maitlis [Maitlis, 1995; Quyoum *et al.*, 1996], based on the decomposition of Rh-organometallic complexes, which are believed to be model systems for the Fischer-Tropsch intermediates. Characteristic for this mechanism is that both the termination to olefin and the termination to paraffin are hydrogenation reactions. From our results it is clear that the termination to paraffin is indeed a hydrogenation, but that this is not the case for the termination to olefin. On these grounds, the alkenyl Fischer-Tropsch mechanism is discarded.

The $C_i H_{2i+1,ads}$ species is most widely supported in literature [e.g. Hindermann *et al.*, 1993]. Termination to olefin of the $C_i H_{2i+1,ads}$ species occurs via a β -hydride abstraction, in which the presence of a vacant surface site is required. Since the experimental results presented in this work suggest that the surface concentration of vacant sites increases with H_2/CO feed ratio, this proposed termination

reaction to olefin is not supported. Therefore, the chemical composition of the growing hydrocarbon chain is not represented by an alkyl surface species.

The $C_i H_{2i,ads}$ species is used by Dry [1990; 1996] and Andesina [1996] in their reviews on the Fischer-Tropsch reaction. The formation of olefins is represented by a desorption step. The independence of the termination coefficient to olefin of the H₂/CO feed ratio suggests that the termination to olefin is not associated with either H_{ads} or vacant surface sites, which both increase with increasing H₂/CO feed ratio. This is in good agreement with a termination step represented by desorption of a C_iH_{2i,ads} species.

Readsorption

The rate coefficient for readsorption of ethene is larger than for the C_{3+} 1-olefins. The latter is independent of the H₂/CO ratio. The major difference between the modeling of the readsorption coefficients for ethene and for the C₃₊ 1-olefins is that the former is based on the gas-phase concentrations of ethane and ethene alone, while the latter is based on the gas-phase concentrations of all the C₃-C₉ hydrocarbons. The accuracy of $k_{re,2}$ is therefore lower than of $k_{re,3+}$ This is especially true for $k_{re,2}$ at H₂/CO=5, since the ethene yield is lowest at these reaction conditions, resulting in a large experimental error in the steady state concentration for ethene. It is reasonable to assume that $k_{re,2}$, in accordance with $k_{re,3+}$, is independent of the H₂/CO ratio.

The readsorption of a reactive olefin is believed to initially involve a π -complex, which is transformed into the single or double σ -bonded C_iH_{2i,ads} as species mentioned in the foregoing paragraph. For the readsorption to take place, a single vacant surface site or an ensemble of vacant surface sites is required. The concentration of these sites is lumped into the rate coefficient for readsorption. The independence of the lumped rate coefficient for readsorption of the H₂/CO feed ratio, however, implies that this coefficient is independent of the surface concentration of empty sites. This, in turn, implies that the rate of readsorption is not associated with the surface concentration of empty sites. This discrepancy is not understood yet.

8.5 Quantitative comparison with other studies

The model results in sections 8.3 and 8.4 demonstrated that only a small fraction of the metal surface area is active for the C-C coupling reaction and the intrinsic activity of these particular sites is high. From pulse experiments, Dautzenberg *et al.* [1977] conclude that the chain growth process occurs at a rate of one $C_{1,ads}$ unit per minute and that the low activity of their Ru/Al₂O₃ catalyst is due to this intrinsic slow process and not to a limited number of active surface sites. Their conclusions are complete opposite to ours, which are in closer agreement with the observations based on ¹³CO SSITKA experiments by Biloen *et al.* [1983], Mims and McCandlish [1987], and Komaya and Bell [1994a]. They conclude that the chain growth process is fast and that the surface coverage with sites that contain a growing surface chain is low. The estimates for the rate of chain growth based on turnover frequencies and non-steady state techniques are 2 to 3 orders of magnitude lower [Mims and McCandlish, 1987]. This illustrates the power of the SSITKA technique: it enables the steady state rate to be expressed by a rate coefficient and the corresponding surface concentration.

Komaya and Bell [1994a] model ¹³CO SSITKA results obtained on a Ru/TiO₂ catalyst at 523 K, 1 bar, and He/D₂/CO=6/3/1, using a CSTR reactor model. Their mechanism and the corresponding parameter estimates are shown in figure 8.18, where the dashed arrows indicate equilibrium. A few comments on their mechanism are made:

- On the basis of ¹³CO SSITKA experiments alone, the distinction between a CH_{2,ads} and a CH_{3,ads} pool in series cannot be made.
- The mechanisms for termination to olefin and to paraffin are different and the assumption that both processes proceed via identical rate coefficients is an oversimplification of the model.

• Although only reactive olefins can readsorb onto the catalyst surface, their definition of the rate equation for readsorption suggests that both olefins and paraffins participate in this reaction.



Figure 8.18: Chain growth mechanism and parameter estimates by Komaya and Bell [1994a], based on ¹³CO SSITKA experiments.

In table 8.2, the definitions of the rate equations used by Komaya and Bell [1994a] are compared to the definitions used in this work. They use surface coverages, whereas surface concentrations are used in the present study. To relate the rate coefficients of both studies, our rate coefficients are converted to turn-over-frequencies, applying the specific surface of the Co/Ru/TiO₂ catalyst (= $6.2 \cdot 10^{-2}$ mole·kg_{cat}⁻¹). Second, a temperature correction is performed, assuming a global activation energy of 80 kJ·mole⁻¹ for every reaction step [Johnson *et al.*, 1990; Geerlings *et al.*, 1991a, 1991b; Lathinen *et al.*, 1993]. In table 8.3 the rate coefficients from Komaya and Bell [1994a] and the converted parameter estimates from this work are compared. All our parameter estimates are less than one order of magnitude larger than the parameter estimates by Komaya and Bell [1994a], with the readsorption coefficient for C₃₊ as exception, which is nearly four orders of magnitude larger.

	Komaya and Bell [1994a] $r \text{ in s}^{-1}$	This study <i>R</i> in mole kg _{cat} ⁻¹ ·s ⁻¹
Chain initiation to $C_{2,ads}$	$r_{ini}^{eff} = k_p \theta_{CH_2} \theta_{CH_3} - k_{dp} \theta_{C_2H_5}$	$R_{ini} = k_{ini} L_{C_{\beta}}^{2}$
	$= k_{ini} \; \theta_{CH_2} \; \theta_{CH_3}$	
Chain growth	$r_p = k_p \theta_{CH_2} \theta_{C_i H_{2i+1}}$	$R_{p} = k_{p} L_{C_{\beta}} L_{C_{i}}$
Termination	$r_t = \kappa_t \theta_{C_i}$	$R_{t,o,i} = k_{t,o,i} L_{C_i}$
		$R_{t,p,i} = K_{t,p,i} L_{C_i}$
Readsorption C₂ ⁼	$r_{re,2} = k'_{re} \theta_{C_2}^{ph}$	$R_{re,2} = k_{re,2} L_{C_2H_4}^{ph}$
Readsorption C ₃ [⁼]	$r_{re,3} = k_{re} \theta_{C_3}^{ph}$	$R_{re,3} = k_{re,3} L^{ph}_{C_3H_6}$

 Table 8.2: Comparison of the definitions for the rate equations in the Fischer-Tropsch model by Komaya and Bell [1994a]

 and the present study.

According to Komaya and Bell [1994a] the rate coefficient for ethene readsorption is four orders of magnitude larger than the rate constant for the reentry of C_{3+} olefins. They concluded that only the readsorption of ethene is important and that the readsorption of higher olefins can be neglected at their experimental conditions. Our results indicate that the readsorption of the C_{3+} olefins is not negligible. Moreover, if the readsorption of C_{3+} is eliminated from the model, the continuous decrease of the olefin to paraffin ratio, as illustrated in graph C in figures 8.1 to 8.3, cannot be predicted.

According to Komaya and Bell [1994a] the strong readsorption of ethene together with the depolymerization of $C_{2,ads}$ are the reasons for the low total C_2 concentration in the ASF product distribution. Our results indicate that the depolymerization is not a significant reaction and that besides the strong readsorption of ethene, the low termination rate to ethene is responsible for the low C_2 contribution in the ASF plot.

		Komaya and Bell	Present work	ratio
k _ρ	s⁻¹	1.4·10 ⁺⁰	1.3·10 ⁺¹	9.3
, K _{ini}	s⁻¹	1.3·10 ⁻¹	4.2·10 ⁻¹	3.2
k_t	s⁻¹	1.8·10 ⁻¹	2.3·10 ⁻¹ – 1.4·10 ⁺⁰	1.3 – 7.7
			4.0·10 ⁻¹ – 2.0·10 ⁺⁰	2.2 – 11
$k'_{re} = k_{re,2}$	s⁻¹	1.5·10 ⁺²	7.3·10 ⁺²	4.8
$k_{re} = k_{re,3}$	s⁻¹	1.5·10 ⁻²	1.0·10 ⁺²	6700

Table 8.3: Comparison between the rate coefficients for the Fischer-Tropsch model of Komaya and Bell [1994a] and the parameter estimates for the model used in the present work, converted to 523 K and based on turn-over-frequencies.

In a pioneering ¹³CO SSITKA investigation of the chain growth reaction during the Fischer-Tropsch synthesis, Biloen *et al.* [1983] publish lower limits for the rate of C-C bound formation on Ni/SiO₂, unsupported Co, and Ru/Al₂O₃ at 488 K and 3 bar. The lower limits are $\ge 0.014 \text{ s}^{-1}$ for Ni/SiO₂, $\ge 0.05 \text{ s}^{-1}$ for Co, and $\ge 0.5 \text{ s}^{-1}$ for Ru/Al₂O₃. Although, the accuracy of the transients is poor and the method of data analysis is disputable, Biloen *et al.* [1983] are the first to show experimentally that the surface coverage of growing hydrocarbon chains is small and that the chain growth is not the rate determining step in the Fischer-Tropsch synthesis.

Later, Zhang and Biloen [1986] publish estimates of the surface coverages and rate coefficients obtained from ¹³CO SSITKA on unsupported Co and on a Ru/SiO₂ catalyst at 483 K and 1 bar. The rate of C-C bond formation is $\geq 1 \text{ s}^{-1}$ for Ru/SiO₂ and $\leq 0.1 \text{ s}^{-1}$ for Co. An unexpected decrease of the rate coefficient for C-C formation with increasing D₂/CO ratio is observed, probably caused by the negligence of olefin readsorption in the model. Moreover, fragmentation during on-line MS detection of the deuterated C₁-C₃ hydrocarbons negatively influences the accuracy of the results. Correcting their values to 498 K results in a rate coefficient for C-C bond formation of 2 s⁻¹ for Ru and 0.2 s⁻¹ for Co.

Mims and McCandlish [1987] monitor the ¹³C incorporation into the C₃ and C₄ 1-olefins by ¹³C NMR and GCMS during ¹³CO SSITKA on a Co/SiO₂ catalyst and a precipitated Fe/K catalyst at 475 K and 1.2 bar. Based on the intramolecular ¹³C distributions obtained by ¹³C NMR, their rate coefficient for C-C coupling is $\ge 2 \text{ s}^{-1}$ for both catalysts. Correcting their value to 498 K leads to k_p =5 s⁻¹ for Co.

8.6 Simulation of product distribution at industrial conditions

In chapter 5 it was concluded that the influence of the hydrocarbon chain length on the kinetic parameters is larger in the case of dry operation of the Fischer-Tropsch reaction than in the presence of a wax layer. This was attributed the occurrence of chain-branching and bond-shift reactions [Schulz and Claey, 1999]. In this section, the modeling results at dry operation are used to predict the steady state performance of the catalyst in the presence of a wax layer. Dry operation of the Fischer-Tropsch reaction is typical for laboratory studies at low pressure, while wax formation is typical for industrial operation at high pressure.

The generally observed increased activity in terms of syngas conversion with increasing pressure [Anderson, 1984] is neglected. The goal is to predict the change in product spectrum. In order to simulate high-pressure conditions, the model parameters at 498 K, 1.2 bar, and H₂/CO=2 are taken chain length independent starting from C₃ (see section 5.3). An overview of the parameters for the simulations is given in table 8.4. For the high-pressure case, the wax behaves as a liquid and the effective desorption energy per CH₂ unit, E_{des}/R conform equation (7.19) in section 7.2.4, represents the gas–liquid equilibrium at T=498 K and amounts to 230 K. The simulated steady state performances at low and at high pressure are shown in figures 8.19 to 8.22.

The chain growth probability is defined as (see also section 5.3):

$$\alpha_{i} = \frac{r_{p,i}}{r_{p,i} + r_{t,p,i}^{\text{eff}} + r_{t,p,i}^{\text{eff}}} = \frac{r_{p,i}}{r_{p,i} + r_{t,p,i}^{\text{eff}} + r_{t,p,i} - r_{re,i}}$$
(8.6)

The chain growth probability reaches its asymptotic value when the effective termination rate to olefin becomes zero, *i.e.* when $r_{t,o,i}=r_{re,i}$ [Iglesia *et al.*, 1991, 1993a]:

$$\alpha_{\infty} = \frac{r_{\rho}}{r_{\rho} + r_{t,\rho}^{\text{eff}}}$$
(8.7)

Table 8.4: Overview of the kinetic parameters for the simulation of the steady state performance at low reaction pressure and high reaction pressure at 498 K, W_{cat}/F =36.6 kg_{cat}'s mole⁻¹.

			low pressure	high pressure
physisorption	E _{des} /R	K	374	230
	κ^{o}	kg _{cat} ⋅m _g - ³	1.4·10 ⁺⁵	1.4·10 ⁺⁵
CO sorption	k _{ads}	m _g ³ ·kg _{cat} -1·s ⁻¹	6·10 ⁻²	6·10 ⁻²
	k _{des}	s ⁻¹	9·10 ⁺⁰	9·10 ⁺⁰
Methanation	<i>k</i> _{m,1}	S ⁻¹	2·10 ⁻²	2·10 ⁻²
	<i>k</i> _{m,2}	s⁻¹	6·10 ⁻³	6·10 ⁻³
	<i>k</i> _{<i>m</i>,3}	s⁻¹	3·10 ⁻²	3·10 ⁻²
	$k_{t,1}$	s ⁻¹	5·10 ⁻²	5·10 ⁻²
C ₂ formation	k _{ini}	kg _{cat} ·mole ⁻¹ ·s ⁻¹	3·10 ⁺⁰	3·10 ⁺⁰
	$k_{t,p,2}$	s ⁻¹	1·10 ⁻²	1·10 ⁻²
	$k_{t,o,2}$	s⁻¹	1.5·10 ⁻¹	1.5·10 ⁻¹
	k _{re,2}	s ⁻¹	3·10 ⁺²	3·10 ⁺²
C ₃ formation	k _ρ	kg _{cat} ·mole ⁻¹ ·s ⁻¹	9·10 ⁺¹	9·10 ⁺¹
	$k_{t.p.3}$	s ⁻¹	1·10 ⁻¹	1·10 ⁻¹
	$k_{t.o.3}$	s ⁻¹	8·10 ⁻¹	8·10 ⁻¹
	k _{re.3}	s ⁻¹	4·10 ⁺¹	4·10 ⁺¹
C ₄ formation	<i>К</i> _{t.р.4}	s ⁻¹	3·10 ⁻¹	-
	$K_{t,o,4}$	s ⁻¹	8·10 ⁻¹	-
C ₅₊ formation	$k_{t.p.5}$	s ⁻¹	6·10 ⁻¹	-
	Kt o 5	s ⁻¹	4.10^{-1}	-



Figure 8.19: Simulations of the total yield plots at low pressure versus high pressure according to the parameters in table 8.4.



 1.E+01
 high pressure

 1.E-01
 low pressure

 1.E-03
 low pressure

 1.E-05
 0
 5
 10
 15
 20

 carbon number /

Figure 8.20: Simulations of the olefin to paraffin ratio plots at low pressure versus high pressure according to the parameters in table 8.4.



Figure 8.21: Simulations of the olefin and paraffin yield plots at low pressure versus high pressure according to the parameters in table 8.4.



For the higher hydrocarbon formation at low pressure the rate coefficient for termination to paraffin is relatively high ($k_{t,p,5+}=6\cdot10^{-1} \text{ s}^{-1}$) and the rate coefficient for termination to olefin is relatively

low ($k_{t,o,5+}=4\cdot10^{-1} \text{ s}^{-1}$). The corresponding olefin to paraffin ratio is low. In this situation, the capability of the olefin readsorption reaction to reverse the overall termination probability is limited, *i.e.* $r_{t,o,i}^{\text{eff}} < r_{t,p,i}^{\text{eff}}$ for all i. In this case the chain growth probability is determined by the termination to paraffin and is independent of the chain length for C₅₊, as is observed in figure 8.22.

At high pressure, the rate coefficient for termination to olefin increases ($k_{t,o,3+}$ =8·10⁻¹ s⁻¹) and rate coefficient for termination to paraffin decreases ($k_{t,p,3+}$ =1·10⁻¹ s⁻¹). The olefin selectivity increases and the ability of the readsorption reaction to reverse the overall termination probability becomes apparent. For the low hydrocarbons, the effective rate of termination to olefin is no longer smaller than the rate of termination to paraffin. Because the readsorption increases with chain length and the termination is chain length independent, the effective rate of termination to olefin decreases with increasing chain length. The chain growth probability increases and reaches a higher asymptotic value than at low pressure.

The typical S-shape of the paraffin yield plot at low pressure is attributed to the presence of chain branching that converts reactive 1-olefins into unreactive paraffins, internal-olefins, and iso-olefins [chapter 5; Schulz and Claey, 1999]. The simulations in this section indicate that the suppression of chain branching at high pressure leads to an increased olefin selectivity and a higher C_{5+} selectivity. It is concluded that the lower the chain branching probability of a catalyst at low pressure, the higher the wax formation tendency at high pressure.

8.7 Modeling the alcohol formation

In sections 6.3.2 and 6.3.3, the mechanism of alcohol formation is described by means of ¹³CO and C¹⁸O SSITKA experiments on the Co-sponge catalyst. With this model catalyst it proved possible to assess the kinetics of the formation of oxygenates. The qualitative interpretation of these experiments led to the conclusion that:

the formation of oxygenates involves small surface concentrations of O-containing intermediates;

all surface species participating in hydrocarbon formation are not associated with oxygen.

These two conclusions are verified by modeling the alcohol formation during the ¹³CO SSITKA experiments in section 8.7.1.

In contrast to the Co-sponge catalyst, the alcohol transients on the Co/Ru/TiO₂ catalyst in section 6.2.3 are dominated by the formation of alcoxy species on the TiO₂ support. The Co/Ru/TiO₂ catalyst therefore does not provide information about the formation mechanism of oxygenates on the active Co metal. These results are modeled in section 8.7.2 in terms of the sorption behavior of the TiO₂ support. The concentration of the alcoxy species on the TiO₂ surface and the adsorption and desorption rate coefficients are assessed. Modeling indicates that the spillover of oxygenate intermediates from the Co-metal to the TiO₂ support is important.

The experimental steady state data used for modeling in these sections are summarized in appendixes 4 and 5.

8.7.1 CO-insertion versus CH_yO-insertion

In section 6.3.2, the qualitative interpretation of the transients for methanol and ethanol on the Co-sponge catalyst led to the conclusion that the formation of oxygenates proceeds either via a COor a CH_yO-insertion mechanism. For both mechanisms, the surface concentrations of the oxygenate intermediates, represented as $C_xH_yO_{ads}$, is small. In this section, modeling of the experimental results validates these conclusions. Because the modeling is based on ¹³CO and C¹⁸O SSITKA experiments, no information is obtained about the H-content of the pools of oxygenate intermediates. The pool of methanol intermediates is represented as CH_yO_{ads} and the pool of ethanol intermediates as C₂H_zO_{ads}.

Mechanistic considerations

In figure 8.23 the CO-insertion and the CH_yO -insertion mechanism, are shown. Both mechanisms are based on the Fischer-Tropsch mechanism A of section 7.4.3. As described there, a net consumption term represents the C_{2+} hydrocarbon formation. In both models, methanol is formed via the stepwise hydrogenation of CO_{ads} :

$$CO_{ads} \xrightarrow{H_{ads}} CH_y O_{ads} \xrightarrow{H_{ads}} CH_3 OH$$
 (R-1)

In the CO-insertion mechanism, ethanol is formed from the reaction of $C_{\beta,ads}$ with CO_{ads} and the hydrogenation of the resulting $C_2H_zO_{ads}$ species, via:

$$CO_{ads} + C_{\beta,ads} \xrightarrow{(H_{ads})} C_2 H_z O \xrightarrow{H_{ads}} C_2 H_5 O H$$
(R-2)

In the CH_yO-insertion mechanism, ethanol is formed via the reaction of $C_{\beta,ads}$ with the intermediate towards methanol, CH_yO_{ads}, and the hydrogenation of the resulting C₂H_zO_{ads} species, via:

$$CH_{\gamma}O_{ads} + C_{\beta,ads} \xrightarrow{(H_{ads})} C_2H_zO \xrightarrow{H_{ads}} C_2H_5OH$$
(R-3)

No assumptions are made on the participation of H_{ads} in the two latter surface reactions. However, the termination reactions to methanol and ethanol are bound to involve H_{ads} .



Figure 8.23: Schematic representations of the CO- and CH_yO -insertion models, both based on the methanation model A of section 7.4.3.

Modeling considerations

In sections 6.3.2 and 6.3.3 it is concluded that once methanol is formed on the Co-sponge catalyst, it does not display any significant interaction with the Co-metal surface. The same is expected for ethanol. Because these reaction products do not display secondary reactions initiated by readsorption, and because the physisorption equilibrium coefficient for these products is no less than one order of magnitude lower than for the corresponding hydrocarbons, negligence of a physisorbed state for the C_1 - C_3 oxygenates in the modeling is acceptable. The hydrogenation of $C_xH_yO_{ads}$ species to the corresponding growing hydrocarbon surface chains is not included in the model, since it is not an essential step for the explanation of the experimental results.

CO-insertion mechanism

For the CO-insertion model, the estimates of the reaction rate coefficients and the values of the surface concentrations of the participating species are shown in table 8.5. The model predictions of the transients of methane and methanol are given in figure 8.24, and of the isotopic variants of ethanol in figure 8.25. The model correctly describes:

- the fast response for methanol;
- the location in time of the maximum of the calculated ¹²CH₃¹³CH₂OH transient;
- the small contribution of the intermediate labeled ¹³CH₃¹²CH₂OH variant.

<i>k_{ads}</i>	m _g ³ ·kg _{cat} ⁻¹ ·s ⁻¹	8.2·10 ⁻³	L _{CO}	mole · kg _{cat} -1	4.9·10 ⁻³	
k _{des}	s⁻¹	7.3·10 ⁺⁰	$L_{C_{\alpha}}$	mole kg _{cat} -1	1.6·10 ⁻³	
<i>k</i> _{m,1}	s⁻¹	5.0·10 ⁻²	$L_{C_{\beta}}$	mole kg _{cat} -1	1.1·10 ⁻³	
<i>k</i> _{m.2}	s⁻¹	4.1·10 ⁻³	L _{C1,tot}	mole kg _{cat} -1	2.7·10 ⁻³	
<i>к_{т,3}</i>	s ⁻¹	1.3·10 ⁻²	$L_{C_{\alpha}}$ /($L_{C_{\alpha}}$ -	$+L_{C_{\beta}})$	58%	
<i>k</i> _{t.1}	s⁻¹	8.0·10 ⁻²	L _{CHyO}	mole · kg _{cat} -1	2.4·10 ⁻⁶	
<i>k</i> ₁	s ⁻¹	4.8·10 ⁻⁴	$L_{C_2H_zO}$	mole kg _{cat} -1	1.4·10 ⁻⁶	
<i>k</i> ₂	s ⁻¹	9.9·10 ⁻¹			data	model
k ₃	kg _{cat} ·mole ⁻¹ ·s ⁻¹	9.7·10 ⁻²	C_{CH_4}	mole ·m _g ⁻¹	2.19·10 ⁻¹	2.19·10 ⁻¹
<i>k</i> ₄	S⁻¹	3.8·10 ⁻¹	C _{CH₃OH}	mole ·m _g ⁻¹	8.25·10 ⁻³	8.25·10 ⁻³
			$C_{C_2H_5OH}$	mole ·m _g -1	1.24·10 ⁻³	1.26·10 ⁻³

Table 8.5: Parameter estimates of the CO-insertion model on the Co-sponge catalyst as presented in figure 8.23. Experimental conditions: 498 K, 1.2 bar, $H_2/CO=4$, $W_{cat}/F=135$ kg_{cat}'s·mole⁻¹.



Figure 8.24: Normalized responses of Ne, methane, and methanol for the Co-sponge catalyst at 498 K, 1.2 bar, H₂/CO=4, W_{cal}/F =135 kg_{cat} s mole⁻¹.

Figure 8.25: Normalized responses of ethanol for the Cosponge catalyst at 498 K, 1.2 bar, $H_2/CO=4$, $W_{cat}/F=135$ kg_{cat}·s·mole⁻¹.

The parameter estimates for the methanation reaction are in good agreement with the estimates presented for the methanation model A for the Co/Ru/TiO₂ catalyst in section 7.3.3. The parameter estimates differ only slightly between the two catalysts, which is to be expected, since the surface concentrations of H_{ads} and vacant sites are likely to differ. Values of the surface concentrations cannot be compared directly between the Co/Ru/TiO₂ catalyst and the Co-sponge catalyst. However, on the Co-sponge catalyst, the two intermediates $C_{\alpha,ads}$ and $C_{\beta,ads}$ constitute 35% of the total amount of C-containing surface species, which is in good agreement with the 30% obtained with the Co/Ru/TiO₂ catalyst. The reducibility of the Co-sponge at reaction conditions is low, evidenced by a total surface coverage for CO_{ads}, $C_{\alpha,ads}$, and $C_{\beta,ads}$ of 58%. The remaining 42% of the Co-metal surface is probably reoxidized, in accordance with the low stability of the unpromoted Co-sponge catalyst.

Compared to the rate coefficient for the hydrogenation of $C_{\beta,ads}$, $k_{t,1}$, the rate coefficient for the hydrogenation of CO_{ads} to CH_yO_{ads} , k_1 , is two orders of magnitude lower. The hydrogenation of molecular absorbed CO_{ads} is not easy on cobalt.

Based on turn-over-frequencies, the rate coefficient for the formation of $C_2H_2O_{ads}$ (k_3 in table 8.5) is compared to the rate coefficient for chain initiation (k_{ini} in table 8.1). The latter is larger by a factor of 130 (k_3 =1.3·10⁻³ s⁻¹, k_{ini} =1.7·10⁻¹ s⁻¹). The C-C coupling reaction between two CH_{2,ads} species towards a growing hydrocarbon chain is much easier than the coupling of a CH_{2,ads} species with CO_{ads} towards an alcohol intermediate.

The calculated surface concentrations of the methanol and ethanol intermediates, *i.e.* CH_yO_{ads} and $C_2H_zO_{ads}$, are small compared to the surface concentrations of the corresponding hydrocarbon

species on the catalyst surface, *i.e.* $L_{C_{\beta}}/L_{C_{1}HO} = 5 \cdot 10^{+2}$ and $L_{C_{2}}/L_{C_{2}HO} = 1 \cdot 10^{+2}$. This is in good agreement with the conclusions drawn on the basis of the qualitative interpretation of the experimental results in section 6.3.2.

CH_yO-insertion mechanism

The CH_yO -insertion model in figure 8.23 is not able to predict the experimental transients nor the steady state rate of methanol and ethanol formation. The parameter estimates for k_1 , k_2 , and k_3 are not significant. Additional, the model underestimates the steady state concentration of methanol in the gas phase and on the catalyst surface. Based on these statistical observations, the CH_yO -insertion model is discarded as the mechanism for alcohol formation.

CO-insertion versus CH_yO-insertion

The alcohol formation on the Co-sponge catalyst proceeds via a CO-insertion mechanism. The hydrogenation of CO_{ads} is a slow reaction and the surface concentrations of alcohol intermediates are two orders of magnitude lower than the surface concentrations of the corresponding hydrocarbon species. Although not presented in this section, modeling of C¹⁸O experiments supports the results presented in this section.

These observations imply that:

• the most probable mechanism for the formation of the monomeric building block in the carbene mechanism, $CH_{2,ads}$, proceeds via the dissociation of CO_{ads} followed by the stepwise hydrogenation of C_{ads} , rather than the hydrogenation of CO_{ads} and the decomposition of the resulting enolic species, $CHOH_{ads}$ [Anderson, 1984];

• no O-containing species (other than CO_{ads} for the generation of $C_{\alpha,ads}$ and $C_{\beta,ads}$) participates in the formation of hydrocarbons on Co-based catalysts;

• the formation of oxygenates is seen as a termination reaction via C-C coupling of growing hydrocarbon chains with CO_{ads}, followed by a partial hydrogenation to aldehydes and ketones or a complete hydrogenation to alcohols.

8.7.2 Alcoxy formation on TiO₂ support

The transients of methanol and ethanol on the $Co/Ru/TiO_2$ catalyst in section 6.2.3 are dominated by the formation of alcoxy species on the support. The sorption capacity for the oxygenate reaction products of the partially reduced TiO₂ support of the Co/Ru/TiO₂ catalyst is modeled in this section.

Mechanistic considerations

A schematic representation of the mechanism for ethanol formation is represented in figure 8.26. The intermediate towards ethanol, C_2HO_{ads} , is formed on the Co-surface via the CO-insertion mechanism. Besides the termination of this intermediate to the gas phase, the spillover to the TiO₂ support to form an alcoxy species is also considered. Ethanol from the gas phase can exchange with the alcoxy species on the TiO₂ support by adsorption and desorption.

Model considerations

For the modeling, the following considerations are made:

- The rate parameters corresponding to the hydrocarbon formation, *i.e.* k_{ads}, k_{des}, k_{m,1} till k_{m,3}, k_{t,1}, and the net consumption rate for C_{β,ads}, are fixed. Their values correspond to the parameter estimates for the methanation model A in table 7.5 of section 7.3.3 at H₂/CO=2.
- The rate coefficients for the alcohol formation on the Co-metal, *i.e.* k_1 till k_4 , are fixed, based on the CO-insertion mechanism from the former section:
 - i. The values for k_1 and k_3 are obtained from to the steady state production rates of methanol and ethanol on the Co/Ru/TiO₂ catalyst, via:

$$R_{w,CH_3OH}^{SS} = k_1 L_{CO}^{SS}$$

$$R_{w,C_2H_5OH}^{SS} = k_3 L_{CO}^{SS} L_{C_\beta}^{SS}$$

$$(8.8)$$

$$(8.9)$$

where the surface concentrations and the steady state production rates are known. This procedure accounts for the different product spectra of the Co/Ru/TiO₂ catalyst and the Co-sponge, which partially originates from a different H₂/CO feed ratio. For the Co-sponge catalyst H₂/CO=4 and for the Co/Ru/TiO₂ catalyst H₂/CO=2.aaa

ii. The coefficients for alcohol formation on the Co-metal, k_2 and k_4 , are based on the parameter estimates for the CO-insertion model of table 8.5. For simplicity, one value is assumed, valid for both parameters.

The remaining model parameters are:

- the rate coefficients for the spillover from the Co-metal to the TiO₂ support;
- the rate coefficients for adsorption from the gas phase to the TiO₂ support;
- the rate coefficients for desorption from the TiO₂ support to the gas phase.

For simplicity reasons, it is assumed that these parameters are identical for methanol and ethanol, leading to a total of three model parameters.



Table 8.6: Parameter estimates for the sorption of methanol and ethanol and the resulting surface concentrations of the corresponding species for the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H₂/CO=2, and $W_{cat}/F=28$ kg_{cat}'s mole⁻¹. Fixed rate coefficients: k_{ads} , k_{des} , $k_{m,1}$, $k_{m,2}$, $k_{m,3}$, $k_{t,1}$, k_1 , k_2 , k_3 , k_4 Italic values: insignificant parameter estimates.

k _{ads}	m _g ³ ·kg _{cat} ⁻¹ ·s ⁻¹	fixed	6.2·10 ⁻²	L _{CO}	mole·kg _{cat} -1	4.0·10 ⁻²	
k _{des}	S ⁻¹	fixed	9.1·10 ⁺⁰	$L_{C_{\alpha}}$	mole·kg _{cat} -1	8.6·10 ⁻³	
<i>k</i> _{m.1}	S⁻¹	fixed	1.7·10 ⁻²	$L_{C_{\beta}}$	mole·kg _{cat} -1	7.1·10 ⁻³	
<i>k</i> _{<i>m</i>,2}	S ⁻¹	fixed	6.6·10 ⁻³	L _{C1,tot}	mole kg _{cat} -1	1.6·10 ⁻²	
<i>к_{т,3}</i>	S⁻¹	fixed	3.0·10 ⁻²	$L_{C_{\alpha}}$ /(L	$C_{\alpha} + L_{C_{\beta}}$)	55%	
<i>k</i> _{t, 1}	S ⁻¹	fixed	5.2·10 ⁻²	L _{CHy} O	mole·kg _{cat} -1	9.0·10 ⁻⁸	
<i>k</i> ₁	s ⁻¹	fixed	4.9·10 ⁻⁵	$L_{C_2H_zO}$	mole·kg _{cat} -1	2.0·10 ⁻⁷	
<i>k</i> ₂	S ⁻¹	fixed	5.0·10 ⁻¹	L _{CH_yO,TiO₂}	mole·kg _{cat} -1	7.5·10 ⁻⁴	
<i>k</i> 3	kg _{cat} ·mole ⁻¹ ·s ⁻¹	fixed	1.5·10 ⁻²	$L_{C_2H_zO,TiO_2}$	mole·kg _{cat} -1	1.7·10 ⁻³	
<i>k</i> 4	s ⁻¹	fixed	5.0·10 ⁻¹			data	model
k _{ads,alc}	m _g ³ ⋅kg _{cat} ⁻¹ ⋅s ⁻¹		1.8·10 ⁻⁷	C _{CH4}	mole · mg ⁻¹	2.88·10 ⁻¹	3.01·10 ⁻¹
k _{des.alc}	S ⁻¹		2.5·10 ⁻³	C _{CH3OH}	mole · mg ⁻¹	1.59·10 ⁻³	1.60·10 ⁻³
k _{spill}	S⁻¹		2.1·10 ⁺¹	$C_{C_2H_5OH}$	mole·mg ⁻¹	3.54·10 ⁻³	3.55·10 ⁻³

The transients are shown in figure 8.27 for methanol and in figure 8.28 for ethanol. The comparison with the experimental data is satisfying. Besides the fit for the fully labeled isotopic variant of ethanol, the model correctly describes the low contribution for the ${}^{12}CH_{3}{}^{13}CH_{2}OH$ labeled variant and the virtual absence of the ${}^{13}CH_{3}{}^{12}CH_{2}OH$ labeled variant. The parameter estimates for the spillover, the adsorption and the desorption, together with the calculated surface concentrations of the intermediates on the Co-metal as well as on the TiO₂ support are represented in table 8.6.



Figure 8.27: Normalized responses of methanol according to the model in figure 8.22 for the Co/Ru/TiO₂ catalyst at 498 K, 1.2 bar, H_2 /CO=2, and W_{cat}/F =28 kg_{cat}·s·mole⁻¹.



Figure 8.29: Normalized responses of methanol according to the model without spillover.



Figure 8.28: Normalized responses of ethanol according to the model in figure 8.22 for the Co/Ru/TiO₂ catalyst.



Figure 8.30: Normalized responses of ethanol according to the model without spillover.

From table 8.6 the surface concentration of alcoxy species on the TiO₂ support resulting from methanol and ethanol amounts to $2.4 \cdot 10^{-3}$ mole·kg_{cat}⁻¹. If the total alcohol product spectrum is taken into account, the total surface concentration is estimated to rise to $4 \cdot 10^{-3}$ mole·kg_{cat}⁻¹. In a sorption study of methanol on Degussa P25 TiO₂ powder, Taylor and Griffin [1988] report that a surface concentration in the order of 30 µmole·g_{cat}⁻¹ is stable on the surface to a temperature of 673 K. Adjusting this value for the difference in surface area between their TiO₂ powder (=47 m²·g⁻¹) and the Co/Ru/TiO₂ catalyst (=21 m²·g⁻¹) and for the metal loading of the Co/Ru/TiO₂ catalyst (12 wt% Co and 0.2 wt% Ru), results in a typical capacity of $1.2 \cdot 10^{-2}$ mole·kg_{cat}⁻¹ for the Co/Ru/TiO₂ catalyst. The total surface concentration of the alcoxy species on the TiO₂ support according to the model represents 30% of the saturation coverage.

From table 8.6 it is observed that the surface concentrations of the alcohol intermediates are three orders of magnitude lower than the corresponding hydrocarbon surface species, *i.e.* $L_{C_{\beta}} / L_{C_{1}HO} = 8 \cdot 10^{+4}$ and $L_{C_{2}} / L_{C_{2}HO} = 1 \cdot 10^{+3}$. This is in accordance with the observations on the Cosponge catalyst in the former section.

Compared to the termination of the alcohol intermediate on the Co-surface, k_2 , the direct spill over from the Co-metal to the TiO₂ support, k_{spill} , is 40 times faster. Moreover, the parameter estimate for the adsorption from the gas phase on the TiO₂ surface, $k_{ads,alc}$, is insignificant, indicating that this is
not an important step in the mechanism to describe the results. These observations imply that the major route for alcohol evolution is:

- · the formation of the alcohol intermediate on the Co-metal surface;
- the spillover from the Co-metal surface to the TiO₂ support to form an alcoxy species;
- the desorption of this alcoxy species from the TiO₂ support.

The inverse spill over of alcoxy species from the TiO_2 support to the Co-metal is believed to be more difficult because of the low fraction of vacant sites on the Co-surface.

Because of the high surface concentration of alcoxy species on the TiO_2 support compared to the alcohol intermediates on the Co-metal, the methanol and ethanol transients in figures 8.27 and 8.28 correspond to a single pool mechanism. Eliminating the spillover, an oxygenate first terminates from the Co-metal surface into the gas phase before it forms an alcoxy species on the TiO_2 support. In this case the adsorption from the gas phase is the only route for the formation of alcoxy species on the TiO_2 support. Because of the low residence time, this results in an immediate breakthrough of ¹³C-labeled methanol and ethanol, which is illustrated in figures 8.29 and 8.30, respectively. The breakthrough causes the fast onset of all transients directly at the initiation of the isotopic step change. This is not observed experimentally, and it is concluded that the spill over of the alcohol intermediate from the Co-metal to the TiO_2 support is an essential step in the mechanism.

8.8 Conclusions

The mechanism for the Fischer-Tropsch synthesis as presented in figure 8.31 is capable of describing the steady state performance of the Co/Ru/TiO₂ catalyst as well as the transients for the isotopic variants of CO, the C₁-C₅ hydrocarbons, and the C₁-C₃ alcohols. The main features of the model are:

- surface heterogeneity on the level of the single C-species;
- the presence of a physisorbed state;
- the possibility for 1-olefins to reenter the chain growth process by readsorption from the physisorbed state;
- alcohol formation via a CO-insertion termination reaction.

The conclusions for the hydrocarbon formation are:

- The surface concentrations of the growing hydrocarbon chains increase with increasing residence time due to the readsorption of 1-olefins. The total surface coverage of growing hydrocarbon chains is typically 1.4%.
- The low surface concentration of active sites for chain growth is believed to involve surface defect.
- Chain initiation and chain growth are not the rate determining processes during the Fischer-Tropsch synthesis. The rate constants are independent of the surface concentrations of H_{ads} and vacant sites, as expected for a bimolecular reaction between two C-containing species studied by ¹³C-labeling. Lower limits for the rate constants are k_{ini}≥0.2 s⁻¹ and k_p≥5 s⁻¹ at 498 K and 1 bar, which are in good agreement with values reported in literature.
- If it is assumed that the true rate coefficients for chain initiation and chain growth are equal, 3% of the pool of C_{β,ads} consists of CH_{2,ads} species and the true rate of C-C coupling rises to 1.7·10⁺² s⁻¹.
- The surface concentrations of hydrocarbons in the physisorbed state increase with increasing
 residence time due to the formation of reaction products. It is limited to 0.3% of a monolayer until
 C₂₀. Despite this low surface coverage, its presence is essential to describe the experimental
 carbon number dependency of the olefin to paraffin ratio. A too large capacity of the physisorbed
 layer prevents SSITKA experimentation at high pressures.
- The total termination rate is constant starting at C₃, while a shift is observed from a preferential termination to olefin to a preferential termination to paraffin going from C₃-C₅. This shift is

responsible for the S-shaped paraffin yield plot, which is not observed if the physisorbed layer exceeds the monolayer coverage.

- The rate coefficient for termination to paraffin depends on the surface concentration of H_{ads}, as expected for a hydrogenation reaction.
- The rate coefficient for termination to olefin is independent of the surface concentration of H_{ads} and vacant sites. The reaction represents a desorption process.
- Ethene readsorption is faster than the readsorption of C_{3+} 1-olefins. The rate coefficients for readsorption are independent of the surface concentrations of H_{ads} and vacant sites.
- The dependencies of the rate coefficients on the surface concentrations of H_{ads} and vacant sites suggests that the growing hydrocarbon chain is a C_iH_{2i,ads} species and that chain initiation starts via the coupling of two CH_{2,ads} species.



Figure 8.31: Schematic representation of the Fischer-Tropsch mechanism based on the ¹³CO SSITKA investigation. The main features of the mechanism are:

- surface heterogeneity on the level of the single C-species;
- the presence of a physisorbed state;
 - the possibility for 1-olefins to reenter the chain growth process by readsorption from the physisorbed state;
 - alcohol formation via a CO-insertion termination reaction.

The conclusions for the simulation of the industrial product distribution are:

- The obedience to the ASF product distribution must be interpreted as an abnormality of the Fischer-Tropsch mechanism rather than the positive deviation of the ASF product distribution at large carbon numbers.
- The rate of termination to olefin and the rate of readsorption of olefins do not influence the asymptotic chain growth probability. The rate of termination to paraffin and the rate of propagation solely determine this value.

The conclusions for the alcohol formation are:

- Alcohol formation is a termination reaction, proceeding via a CO-insertion mechanism, while hydrocarbon formation proceeds via O-free surface species.
- In the carbene mechanism, the monomeric building blocks, CH_{2,ads}, are formed via the reversible stepwise hydrogenation of C_{ads} following CO_{ads} dissociation. The direct hydrogenation of CO_{ads} to CH_{2,ads} via an enolic intermediate is unlikely to occur on Co-based catalysts.
- The interaction of alcohols with the partially reduced TiO₂ support leads to the formation of alcoxy species. The calculated surface coverage on the TiO₂ support is 30% of the stable saturation coverage.
- The formation of the alcoxy species on the TiO₂ support mainly proceeds via the spillover of alcohol intermediates on the Co-metal to the TiO₂ support.

9

General conclusions

The work described in this thesis was focused on the reaction kinetics of the Fischer-Tropsch synthesis. The literature review indicated that there is an ongoing debate on the reaction mechanism. In relation to this, relatively little is known about the chemical identity, abundance, and reactivity of the participating species in the Fischer-Tropsch mechanism. Steady state kinetic investigations proved unsuccessful in the identification of a feasible reaction mechanism. Transient kinetic techniques are more promising in that respect. In this study it is shown that isotopic tracing techniques are powerful to assess the reaction mechanism of the complex Fischer-Tropsch synthesis. This is realized by applying a large variety of experimental conditions and an extensive product analysis. Moreover, the experimental results are not only interpreted qualitatively but also quantitatively via reactor modeling.

Low pressure operation

The kinetic investigation was performed on a Co(12wt%)/Ru(0.18wt%)/TiO₂ catalyst, a Co(12wt%)/TiO₂ catalyst, and a full metal Co-sponge catalyst at 498 K and 1.2 bar. The conversions were kept low and the build-up of wax on the catalyst surface was prevented. Nevertheless, the presence of a physisorbed state for the hydrocarbon reaction products caused the olefin to paraffin ratio to decrease with carbon number. The readsorption of 1-olefins from the physisorbed state into the chemisorbed state on the catalyst surface was observed, while the readsorption of internal- and iso-olefins was less pronounced. At a pressure of 1.2 bar, the readsorption led to the formation of ultimate-bonded species as well as penultimate-bonded. Ultimate-bonded hydrocarbon chains on the catalyst surface terminated as paraffin, terminated as olefin, or participated in chain growth. Penultimate-bonded hydrocarbon chains, however, led to the formation of internal-olefins, iso-olefins, and iso-paraffins. These isomerization and bond-shift reactions were characteristic for the operation of the Fischer-Tropsch synthesis at low pressure. At high pressure, these two secondary reactions were supposed to be suppressed, resulting in chain initiation of readsorbed 1-olefins as the most important secondary reaction. This was confirmed by simulations using the kinetic parameter estimates obtained by regression analysis of the experimental results.

Surface heterogeneity

A qualitative interpretation of the experimental results indicated that the catalyst surface was heterogeneous towards the formation of both methane as higher hydrocarbons. Modeling showed that the assumption of two single-C species, denoted as $C_{\alpha,ads}$ and $C_{\beta,ads}$, suffices. Modeling did not support the concept of multiple chain growth sites. Moreover, the depolymerization reaction of growing hydrocarbon chains was not a necessary reaction to explain the experimental results.

The combination of C-labeling and O-labeling experiments indicated that all surface species participating in hydrocarbon formation (including $C_{\alpha,ads}$ and $C_{\beta,ads}$) are O-free, excluding the formation

of enolic species. The additional H-labeling experiments called for a twofold interpretation. If the surface hydrogenation steps for C_{ads} to CH_4 were assumed to be irreversible, the experiments indicated that the surface concentrations of CH_x , where x=1-3, are low and the hydrogenation of C_{ads} to CH_{ads} was rate determining. If reversible hydrogenation steps were assumed, the hydrogenation and dehydrogenation reactions were faster than the net methane formation reaction and the individual surface concentrations of CH_x , where x=0-3, were not accessible. Apparently, $C_{\alpha,ads}$ and $C_{\beta,ads}$ had comparable chemical compositions and the difference between them was reflected in the presence of different surface sites. These results conform the carbene mechanism, in which the surface intermediates are C_xH_y species.

Surface concentrations of reaction intermediates

The catalyst surface was largely covered by CO_{ads} , $C_{\alpha,ads}$, and $C_{\beta,ads}$, having a total fractional coverage of 90%. The surface concentration of CO_{ads} was independent of the H₂/CO feed ratio, whereas the surface concentration of $C_{\alpha,ads} + C_{\beta,ads}$ decreased. The surface concentrations of H_{ads} and vacant sites increased with H₂/CO feed ratio. The total surface coverage with growing hydrocarbon chains was low at 1.4% and the surface concentrations of the individual growing hydrocarbon chains decreased rapidly with increasing carbon number. The concentrations of the light hydrocarbons (up to C_{10}) in the physisorbed state were several orders of magnitude lower than the concentrations of the corresponding growing hydrocarbons in the chemisorbed state. Nevertheless, the inclusion of a physisorbed state was essential for modeling. Moreover, the concentrations of the individual hydrocarbons in the physisorbed state increase slightly with carbon number. At high operating pressure, the capacity of the physisorbed state increased due to wax formation and SSITKA transients would no longer contain kinetic information.

Kinetics of hydrocarbon formation

The C-C coupling reaction was fast compared to the formation of monomer building-blocks and chain initiators from CO_{ads} . The surface concentration of active sites that display C-C coupling was low. Thus, the productivity of Co-based catalysts was not limited by the low activity of surface sites for C-C coupling, but by the low number of highly active surface sites. In literature, these highly active sites are associated with surface defects. Stabilizing surface defects would increase the productivity of Fischer-Tropsch catalysts.

The termination of a growing hydrocarbon chain to paraffin was a hydrogenation reaction, as expected. However, the termination of a growing hydrocarbon chain to an olefin was a desorption reaction rather than a β -hydride abstraction reaction. The chemical identity of the growing hydrocarbon chain was established as a C_xH_{x,ads} species rather than a C_xH_{x+1,ads} species.

Kinetics of alcohol formation

Alcohols formed via the insertion of CO_{ads} into a growing hydrocarbon chain on the catalyst surface. The rate coefficient for this termination reaction was two orders of magnitude slower than the coupling of a $CH_{2,ads}$ with a growing hydrocarbon chain. Spillover of the alcohol intermediates from the Co-metal to the partially reduced TiO₂ support resulted in the formation of alcoxy species. The inverse spillover and the subsequent decomposition towards hydrocarbons was not observed.

Catalyst development

The bottleneck for catalyst development for the Fischer-Tropsch synthesis was identified as: despite the high surface concentration of monomeric building blocks and the high activity of the active site for C-C coupling, the catalyst productivity is limited to a low surface concentration of active sites for C-C coupling.

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Nomenclature

as	specific surface	mole⋅kg _{cat} -1
Ai	gas chromatographic peak area for component i	counts
Ci	gas phase concentration of component i	mole·mg ⁻³
D	metal dispersion	mole _{surf} ·mole _{tot} '
E	tractional contribution of an isotopic variant	- I mala ⁻¹
⊏des ⊏		J.IIIOIE
F	total molar feed	- mole·s ⁻¹
f(t)	input function for the SSITKA experiment	-
Fi	molar flow rate	mole·s⁻¹
f _i	intensity of fragmentation pattern at i th m/e value	-
Fi	molar flow of component I	mole·s⁻¹
f _{i,j}	intensity of fragmentation pattern at i th m/e value of j ^{ih} isotopic variant	-
Fn	fraction of C-atoms within a chain containing n C-atoms	- 3 1
F _V	total volume flow	mg°·s⁻′
H ^r	pre-exponential factor for Henry coefficient	-
ni I	mentry coefficient for component i	-
י חו	internal diameter	mm
k	reaction rate coefficient	situation dependent
K ⁰	pre-exponential factor for physisortion	kg _{cat} ·m _g ⁻³
Ki	calibration factor for gas chromatography	mole·s ⁻¹ ·count ⁻¹
Ki ^{ph}	physisorption equilibrium coefficient for component i	kg _{cat} ·m _g -3
L.	length	m 1
Li	surface concentration of component i	mole·kg _{cat}
m	number of m/e values in the fragmentation pattern of a component	-
IVI n		-
D		- bar
ı P:	partial pressure of component i	bar
Ρi ^σ	saturation pressure of component i	bar
r	reaction rate	s ⁻¹
R	gas constant (=8.3144)	J·mole ⁻¹ ·K ⁻¹
R _{w,i}	production rate of component i	mole·kg _{cat} -1·s ⁻¹
S	object function for regression analysis	-
Si	selectivity for component i	mole C%
t T	time	S
	temperature	K
	total volume of reactor	s m_ ⁻¹
VR Waat	weight of catalyst in reactor bed	knoot
X	fractional axial position within catalyst bed	-
Xi	mole fraction of component i in the liquid phase	-
X _{i,j}	fractional contribution of the j th isotopic variant to the mixture at the i th m/e	-
	value	
Xi	conversion of component i	mole C%
yi	mole fraction of component i in the gas phase	-
Graak		
Greek	fractional ourface coverage for component i	
Θ _i	chain growth probability	-
a	asymptotic chain growth probability	-
u _∞ α	critical chain growth probability	_
и _с В	chain termination probability	_
ρ βσ	vanor pressure decline factor	_
۲ ۲	hed norosity	$m_a^3 \cdot m_b^{-3}$
Φ:	mole fraction of products containing i C-atoms	-
ρ _b	bed density	kg _{cat} ·m _b ⁻³
σ	saturation	-
Φi	isotopic fraction of component i on the surface	-
γi	isotopic fraction of component i in the gas phase	-
τ	bed residence time	S
$ au_i$	surface residence time of component i	S

Subscripts

ads	adsorption
b	bed
С	critical
des	desorption
g	gas phase
ini	initiation
m	monomer formation
0	olefin
ov	overall
р	paraffin
р	propagation
ph	physisorption
R	reactor
re	readsorption
surf	surface

t termination tot total

Superscripts

G/L	gas-liquid equilibrium
L	liquid
obs	observed
ph	physisorption
ref	reference
SS	steady state
TIO	an TiO aunnart

 $\begin{array}{lll} TiO_2 & on \ TiO_2 \ support \\ V & vapor \end{array}$

Abbreviations

ASF	Anderson Schulz Flory
ATR	Autothermal Reforming
CFBR	Circulating Fluidized Bed Reactor
CPO	Catalytic Partial Oxidation
CSTR	Continuous Stirred Tank Reactor
FBR	Fluidized Bed Reactor
FC	Flow Controller
FI	Flow Indicator
GC	Gas Chromatograph
GCMS	Gas Chromatograph Mass Spectrometer
I.D.	Internal Diameter
L.	Length
LPG	Liquefied Petroleum Gas
MS	Mass Spectrometer
ParSEC	Paraffin Selective Efficient Catalyst
PFR	Plug Flow Reactor
PI	Pressure Indicator
PO	Partial Oxidation
SBCR	Slurry Bubble Column Reactor
sccm	standard cubic centimeter per minute
SR	Steam Reforming
SSITKA	Steady State Isotopic Transient Kinetic Analysis
TC	Temperature Controller
TFBR	Tubular Fixed Bed Reactor
TI	Temperature Indicator
TIC	Temperature Indicator Controller
TOF	Turn-over Frequency
TPR	Temperature Programmed Reduction

Specifications of the product analysis by gas chromatography (GC) and gas chromatography mass spectrometry (GCMS)

The specifications of the gas chromatographic analysis using the Hewlett Packard 5890 series II GC are given in table A-1. The analysis is schematically represented in figure A-1. The analysis system contains two lines:

- two packed Porapak Q columns in series with a packed Molesieve 13X column for the TCD detection of N₂, CO, CH₄, CO₂, C₂ to C₄ hydrocarbons, and C₁ to C₃ oxygenates;
- a capillary Pona column for the FID detection of C₄ to C₁₀ hydrocarbons and C₁ to C₄ oxygenates.

Tuble A 1. Opeomodulono of the CO and the Como analysis systems.							
	GC analysis		GCMS analysis				
Gas chromatograph	Hewlett Packa	ard 5890 series II	Hewlett Packard 5890 series II/5971 GCMS				
Carrier gas	He		He				
Detection	First line: TCE)	Total ion count in m/e range 20 to 80				
	Second line: F	FID					
Flow	First line: 50 ml min ⁻¹		HP-Plot/Al ₂ O ₃ column: 1 ml·min ⁻¹				
	Second line: 1	ml min⁻¹	CP-PoraBOND-Q column: 1 ml·min ⁻¹				
Columns	First line:	Porapack Q 80/100 mesh 12 ft	HP-Plot/Al ₂ O ₃ ID 0.32 mm 50m				
		PONA ID 0.32mm 50 m	CP-PoraBOND-Q ID 0.32mm 50m				
	Second line Molesieve 13X 40/60 1 ft						
Temperature program	8 min at 308 K, ramp 10 K·min ⁻¹ to 448 K, 30 min at		6 min at 303 K, ramp 5 K·min ⁻¹ to 423 K, 40 min				
	448 K		at 423 K				
Time program	0.1 min valve 1 on, valve 2 on		-				
	2.5 min valve 2 off						
	5.0 min valve 3 on, TCD sensitivity high						

 Table A-1: Specifications of the GC and the GCMS analysis systems.

The specifications of the gas chromatograph mass spectrometric analysis using the Hewlett Packard 5890 series II/5971 GCMS are given in table A-2. A schematic representation of the analysis is given in figure A-2. One of two columns is used:

- capillary HP-Plot/Al₂O₃ column for the detection of the C₂ to C₅ hydrocarbons;
- a capillary CP-PoraBOND-Q column for the detection of the C₂ to C₅ hydrocarbons and the C₁ to C₃ oxygenates.





Sample in



Figure A-2: Schematic representation of the GCMS analysis.

Product spectrum by gas chromatography (GC)

The chromatogram and the corresponding peak identification for the first line of the gas chromatographic analysis of the Fischer-Tropsch product spectrum on the Hewlett Packard 5890 series II GC are listed in figure A-3 and table A-2. The same features for the second line are represented in figure A-4 and table A-3.



Table A-2: Peak identification forthe first line of the GC set-up.

peak	component			
1	hydrogen (- peak)			
2	nitrogen			
3	carbon monoxide			
4	methane			
5	carbon dioxide			
6	ethene			
7	ethane			
8	propene			
9	propane			
10	methanol			
11	ethanol			
12	1-butene			
13	n-butane + 2-butenes			

time /min

Figure A-3: Chromatogram of the first line of the GC set-up for the components of interest. At 5.0 min the intensity of the TCD detector is switched from low to high.



Figure A-4: Chromatogram of the second line of the GC set-up for the components of interest.

peak	component	peak	component	peak	componer
26	i-C ₆ [■]	35	i-C ₇ [⁼]	44	t-2-octene
27	c-2-hexene	36	t-2-heptene	45	c-2-octene
28	$C_6^{=}$	37	c-2-heptene	46	i-C ₈ ⁼
29	i-C ₇ ⁼	38	i-C ₈ ⁼	47	i-C ₉ [⁼]
30	2-methyl-hexane	39	$2-C_8 + 4-C_8$	48	i-C ₉
31	3-methyl-hexane	40	3-methyl-heptane	49	i-C ₉ [⁼]
32	i-C ₇ [■]	41	i-C ₈ ⁼	50	1-nonene
33	1-heptene	42	1-octene	51	n-nonane
34	n-heptane	43	n-octane	52	t-2-nonen
				53	c-2-nonen

Table A-3: Peak identification for the second line of the GC set-up.

peak	component			
1	propane + propene			
2	methanol + ethanal			
3	1-butene			
4	n-butane			
5	t-2-butene			
6	c-2-butene			
7	ethanol			
8	3-methyl-1-butene			
9	i-pentane			
10	1-pentene			
11	2-methyl-1-butene			
12	n-pentane			
13	t-2-pentene			
14	c-2-pentene			
15	2-methyl-2-butene			
16	1-propanol			
17	4-methyl-1-pentene			
18	3-methyl-1-pentene			
19	2-methylpentane			
20				
21	$1-C_6$			
22	n hovene			
23	t-2-hevene			
25				
compor				
t-2-octe	ne			
c-2-octe	ene			
i-C ₈ ⁼				
i-C ₉ ⁼				
i-C ₉				
i-C ₉ ⁼				
1-none	ne			
n-nonai	ne			
t-2-non	ene			
c-2-non	ene			

Product spectrum by gas chromatography mass spectrometry (GCMS)

In the Hewlett Packard 5890 series II/5971 GCMS set-up one of two different columns are used:

- a capillary HP-Plot/Al₂O₃ column for the separation of the C₂ to C₅ hydrocarbons;
- a capillary CP-PoraBOND-Q column for the separation of the C₂ to C₅ hydrocarbons and the C₁ to C₃ oxygenates.

The chromatogram of the HP-Plot/Al₂O₃ column and the identification of the components are represented in figure A-5 and table A-4. The chromatogram of the CP-PoraBOND-Q column and the identification of the components are represented in figure A-6 and table A-5. On this column, the separation of the C₄-hydrocarbons is worse than on the HP-Plot/Al₂O₃ column and the distinction between the two 2-butanes is not made.



Figure A-5: Chromatogram of the capillary HP-Plot/Al_ $2O_3$ column of the GCMS set-up for the components of interest.

Table A-4: Peak identification for the capillary HP-Plot/Al_2O_3 column.

peak	component	peak	component
1	ethane	7	1-butene
2	ethene	8	i-butene
3	propane	9	c-2-butene
4	propene	10	i-pentane
5	n-butane	11	n-pentane
6	t-2-butene		



Figure A-6: Chromatogram of the capillary CP-PoraBOND-Q column of the GCMS set-up for the components of interest.

Table	A-5:	Peak	identification	for	the	capillary	CP-
PoraB	OND-	-Q colu	umn.				

peak	component	peak	component			
1	ethene	10	1-butene			
2	ethane (+water)	11	2-butene			
3	methanol	12	n-butane			
4	propene	13	2-butene			
5	propane	14	propanon			
6	ethanal	15	i-pentene			
7	ethanol	16	1-propanol			
8	i-butane	17	1-pentene			
9	i-butene					

Steady state behavior of the Co/Ru/TiO₂ catalyst

For the experiments on the Co/Ru/TiO₂ catalyst in the SSITKA set-up, the characteristics of the catalyst bed, *i.e.* the bed density and the bed porosity, together with the residence time, are listed in table A-6. The bed density is calculated according to:

$$\rho_b = \frac{W_{cat}}{V_R} \tag{A-1}$$

The bed porosity is calculated from:

$$\varepsilon_{b} = 1 - \frac{1}{V_{R}} \left(\frac{W_{cat}}{\rho_{cat}} (1 - \varepsilon_{cat}) + \frac{W_{SiC}}{\rho_{SiC}} \right)$$
(A-2)

And the residence time is calculated from:

$$\tau = \frac{\varepsilon_b \, V_R}{F_{V,tot}} \tag{A-3}$$

where W_{cat} is the loading of the reactor with catalyst in kg_{cat}; V_R is the total volume of the reactor in m_R³ (=1.51 10⁻⁶ m_R³); ρ_{cat} is the specific density of the catalyst pellets in kg_{cat}·m_p⁻³ (=2990 kg_{cat}·m_p⁻³); ε_{cat} is the porosity of the catalyst pellet in m_g³·m_p⁻³ (=0.37 m_g³·m_p⁻³); W_{SiC} is the loading of the reactor with SiC in kg_{SiC}; ρ_{SiC} is the specific density of the SiC pellets in kg_{SiC}·m_p⁻³ (=3220 kg_{SiC}·m_p⁻³); $F_{V,tot}$ is the total volume flow at reaction temperature (=498 K) and pressure (=1.2 bar) in m_g³·s⁻¹.

 Table A-6:
 Characteristics of the catalyst bed for the different experimental conditions using the Co/Ru/TiO₂ catalyst.

Exp. No.		225-27	225-24	225-22	225-21	225-25	225-23	225-26
$ ho_b$	kg _{cat} ⋅m _R -3	339	904	335	544	856	262	452
\mathcal{E}_b	m _g ³ ⋅m _R ⁻³	0.54	0.61	0.54	0.57	0.61	0.53	0.56
τ	S	0.79	0.89	0.52	0.74	0.76	0.47	0.49

The experimental conditions and the characteristics for the Fischer-Tropsch product spectrum at steady state reaction conditions are listed in table A-7 for H₂ and D₂ as reactants. The CO conversion is based on the GC analysis and is calculated according to equation (2.1) in chapter 2. The H₂ conversion is not measured directly, but calculated from the CO conversion and H/C content of the hydrocarbon reaction products, assuming that the selectivity towards CO_2 is zero. This leads to equation (A-4):

 $X_{H_2} = \frac{F_{CO} X_{CO} \left(\frac{H}{C} + 2\right)}{2F_{H_2}}$ (A-4)

where F_{CO} and F_{H_2} are the molar feed rates of CO and H₂ in mole·s⁻¹ and *H/C* is the average number of H-atoms per C-atom of the hydrocarbon reaction products. The steady state concentrations for the reaction products for H₂ and CO as reactants are listed in table A-8. The concentration for H₂O is calculated assuming an O-balance of unity.

Fable A-7: Steady state characteristics of the Fischer-Tropsch synthesis using the Co/Ru/TiO ₂ catalyst at 498 K a	ind
I.2 bar (n.d. indicates not determined).	

Exp. No		225-27	225-24	225-22	225-21	225-25	225-23	225-26
F _{H2}	mole⋅s⁻¹	9.15E-06	9.15E-06	1.83E-05	1.36E-05	1.42E-05	2.50E-05	2.50E-05
F _{co}	mole⋅s⁻¹	9.15E-06	9.15E-06	9.15E-06	6.80E-06	7.07E-06	4.99E-06	4.99E-06
F _{He}	mole·s⁻¹	1.22E-05	1.22E-05	1.83E-05	1.36E-05	1.42E-05	2.00E-05	2.00E-05
P _{H2}	bar	0.36	0.36	0.48	0.48	0.48	0.60	0.60
P _{co}	bar	0.36	0.36	0.24	0.24	0.24	0.12	0.12
P _{He}	bar	0.48	0.48	0.48	0.48	0.48	0.48	0.48
F _{V,tot}	m _g ³ ·s ⁻¹	1.04 E-6	1.04 E-6	1.56 E-6	1.16 E-6	1.21 E-6	1.70 E-6	1.70 E-6
W _{cat}	g _{cat}	0.512	1.366	0.506	0.822	1.29	0.396	0.683
W _{cat} /F	kg _{cat} ·s·mole⁻¹	16.8	44.8	11.1	24.2	36.6	7.92	13.7
H ₂ /CO		1	1	2	2	2	5	5
X _{co}	%	3.26	7.92	9.37	10.4	15.1	8.51	22.3
H/C	-	2.61	2.74	2.88	2.95	2.99	3.30	3.33
X _{H2}	%	7.52	18.8	7.81	12.9	18.8	6.75	10.4
$lpha_{3-9}$	-	0.62	0.63	0.54	0.55	0.61	0.39	0.43
C _{bal}	-	1.002	0.992	1.009	0.998	1.007	1.019	1.027
D ₂ /CO	-	1	1	2	2	2	5	5
X _{co}	%	4.20	10.4	n.d.	13.7	20.7	16.7	29.4
D/C	-	2.45	2.52	n.d.	2.72	2.73	2.97	2.90
X_{D2}	%	9.34	23.5	n.d.	15.9	24.4	8.22	14.3
α_{3-8}	-	0.75	0.77	n.d.	0.71	0.71	0.60	0.62
C _{bal}		0.977	0.966	n.d.	0.958	0.950	0.987	1.012

Table A-8: Steady state characteristics of the Fischer-Tropsch synthesis using the $Co/Ru/TiO_2$ catalyst at 498 K and1.2 bar (n.d. indicates not determined).

Exp. No		225-27	225-24	225-22	225-21	225-25	225-23	225-26
W _{cat} /F	kg _{cat} ·s·mole⁻¹	16.8	44.8	11.1	24.2	36.6	7.92	13.7
CO ₂	mole ·mg ⁻³	1.06 E-2	2.06 E-2	6.97 E-3	1.11 E-2	1.48 E-2	5.22E -3	6.89 E-3
H ₂ O	mole∙m _g - ³	2.77 E-1	6.69 E-1	3.72 E-1	5.97 E-1	8.75 E-1	3.75 E-1	5.80 E-1
C ₁	mole∙m _g -³	8.87E-02	2.38E-01	1.48E-01	2.53E-01	3.85E-01	2.20E-01	3.46E-01
C ₂	mole∙m _g - ³	3.59E-03	1.22E-02	8.64E-03	1.53E-02	2.27E-02	1.34E-02	2.06E-02
$C_2^{=}$	mole∙m _g - ³	5.69E-03	5.45E-03	3.69E-03	3.53E-03	2.90E-03	1.85E-03	2.54E-03
C ₃	mole∙m _g -³	8.35E-04	3.71E-03	2.87E-03	6.82E-03	1.26E-02	6.90E-03	1.20E-02
$C_3^{=}$	mole∙m _g -³	1.34E-02	2.98E-02	1.85E-02	2.28E-02	2.82E-02	8.45E-03	9.07E-03
C ₄	mole∙m _g - ³	1.89E-03	7.91E-03	5.41E-03	1.08E-02	1.61E-02	6.23E-03	9.55E-03
$C_4^{=}$	mole∙m _g - ³	8.01E-03	1.42E-02	7.34E-03	9.02E-03	1.07E-02	3.42E-03	4.69E-03
C ₅	mole∙m _g -³	3.56E-03	1.12E-02	6.84E-03	1.10E-02	1.69E-02	4.60E-03	7.02E-03
$C_5^{=}$	mole∙m _g -³	4.31E-03	5.88E-03	2.10E-03	1.96E-03	2.22E-03	2.77E-04	2.86E-04
C ₆	mole∙m _g - ³	3.23E-03	8.13E-03	3.97E-03	6.32E-03	1.01E-02	1.71E-03	2.65E-03
$C_6^{=}$	mole∙m _g - ³	1.60E-03	2.25E-03	5.21E-04	4.22E-04	5.74E-04	6.03E-05	5.08E-05
C ₇	mole∙m _g -³	2.18E-03	5.62E-03	1.98E-03	3.24E-03	6.33E-03	6.59E-04	1.28E-03
$C_7^{=}$	mole∙m _g -³	5.47E-04	6.12E-04	1.50E-04	1.13E-04	1.92E-04	1.65E-05	2.08E-05
C ₈	mole∙m _g -³	1.24E-03	3.30E-03	1.16E-03	1.69E-03	3.46E-03	2.44E-04	4.82E-04
$C_8^{=}$	mole∙m _q -³	1.75E-04	1.71E-04	4.34E-05	3.03E-05	3.91E-05	n.d.	n.d.
C ₉	mole∙m _g -3	7.90E-04	2.16E-03	5.37E-04	8.20E-04	3.04E-03	n.d.	n.d.
$C_9^{=}$	mole∙m _g - ³	6.84E-05	7.03E-05	1.66E-05	8.31E-06	3.32E-05	n.d.	n.d.
C ₁ O	mole∙m _g - ³	7.49E-04	1.29E-03	n.d.	n.d.	3.73E-03	n.d.	5.03E-03
C ₂ O	mole ·mg ⁻³	1.32E-03	2.62E-03	n.d.	n.d.	2.93E-03	n.d.	2.48E-03
C ₃ O	mole·m _g -3	2.93E-04	4.33E-04	n.d.	n.d.	4.98E-04	n.d.	4.44E-04

Steady state behavior of the Co-sponge catalyst

The characteristics for the catalyst bed in the SSITKA set-up, according to equations (A1) to (A-3) of appendix 5, for the Co-sponge catalyst are listed in table A-9.

Exp. No		sponge-2	sponge-4	
$ ho_b$	kg _{cat} ·m _R ⁻³	3250	3375	
Eb	m _g - ⁻³ ⋅m _R - ⁻³	0.64	0.61	
τ	S	0.74	0.73	

Table A-9: Characteristics of the catalyst bed for the experiments on the Co-sponge catalyst.

The experimental conditions and the characteristics for the Fischer-Tropsch product spectrum at steady state reaction conditions are listed in table A-10. For the calculation of the H_2 conversion and the H_2O concentration see appendix 5.

Table A-10: Steady state performance of the Co-sponge catalyst at 498 K and 1.2 bar.

Exp	o. No.	spo	onge-2	sponge-4	Exp. No.		sponge-2	sponge-4
F_{H2}	mole⋅s⁻¹	1.7	71E-05	2.27E-05	W _{cat} /F	kg _{cat} ·s·mole⁻¹	135	135
F_{CC}	mole·s⁻¹	5.6	69E-06	5.69E-06	H ₂ /CO		3	4
F_{He}	mole⋅s⁻¹	1.5	52E-05	9.48E-06	X _{co}	%	5.57	21.2
P_{H2}	bar		0.54	0.72	H/C	-	2.56	2.70
P_{cc}	bar		0.18	0.18	X _{H2}	%	4.23	12.4
P_{He}	bar		0.48	0.30	α ₃₋₈	-	0.57	0.62
$F_{V.t}$	ot mg ³ ·s ⁻¹	1.2	29 E-6	1.29 E-6	C _{bal}	-	1.001	0.992
W_{ca}	at g _{cat}		4.91	5.10				

 Table A-11: Steady state characteristics of the Fischer-Tropsch synthesis using the Co-sponge catalyst at 498 K and 1.2 bar (n.d. indicates not determined).

Exp. No.		sponge-2	sponge-4	Exp. No		sponge-2	sponge-4
W _{cat} /F	kg _{cat} ·s·mole⁻¹	135	135	C ₆	mole ·mg ⁻³	2.88E-03	1.38E-02
CO ₂	mole·mg ⁻³	1.02 E-2	1.66 E-2	$C_6^{=}$	mole ·mg ⁻³	5.53E-04	4.48E-04
H ₂ O	mole∙m _g -3	2.35 E-1	9.04 E-1	C ₇	mole∙m _g -3	1.62E-03	8.00E-03
C ₁	mole∙m _q -3	6.07E-02	2.19E-01	C ₇ ⁼	mole∙m _a -³	1.43E-04	2.04E-04
C ₂	mole∙m _g -3	7.98E-03	4.02E-02	C ₈	mole ·m _g ⁻³	8.57E-04	4.83E-03
$C_2^{=}$	mole∙m _g -3	3.90E-03	3.03E-03	C ₈ ⁼	mole ·mg ⁻³	3.66E-05	5.31E-05
C ₃	mole∙m _g -3	2.12E-03	2.36E-02	C ₉	mole∙m _g -³	5.55E-04	-
$C_3^{=}$	mole∙m _g -3	1.31E-02	3.00E-02	C ₉ ⁼	mole∙m _g -³	9.65E-06	-
C ₄	mole∙m _g -3	3.64E-03	2.28E-02	C ₁ O	mole ·m _g -3	2.31E-04	7.77E-03
$C_4^{=}$	mole∙m _g -3	5.59E-03	1.05E-02	C ₂ O	mole∙m _g -³	5.70E-04	1.16E-03
C ₅	mole·m _g -3	4.77E-03	2.37E-02	C ₃ O	mole ·m _g ⁻³	5.76E-05	3.48E-04
$C_5^{=}$	mole∙m _g -3	1.95E-03	1.77E-03				

Model quantification using net consumption rates

The modeling results for the transient responses for ¹³CO and ¹³CH₄ on the CO/Ru/TiO₂ catalyst are represented in figure A-7 for H₂/CO=1. For H₂/CO=5, the results are represented in figure A-8. The experimental results are obtained at 498 K, 1.2 bar, and 40% He-dilution of the syngas. Values for the specific H₂/CO feed ratios and residence times are summoned in the captions of the figures.



Figure A-7: Modeling results for Ne, ¹³CO, and ¹³CH₄ at H₂/CO=1 and W_{cat}/F =16.8 kg_{cat} s mole⁻¹ (left) and W_{cat}/F =44.8 kg_{cat} s mole⁻¹ (right) for the methanation part of the Fischer-Tropsch mechanism as represented by model A and model B in figure 7.18 in section 7.3.3. \Box ¹³CO; \Diamond ¹³CH₄ data.



Figure A-8: Modeling results for Ne, ¹³CO, and ¹³CH₄ at H₂/CO=5 and $W_{cat}/F=7.92$ kg_{cat} s mole⁻¹ (left) and $W_{cat}/F=13.7$ kg_{cat} s mole⁻¹ (right) for the methanation part of the Fischer-Tropsch mechanism as represented by model A and model B in figure 7.18 in section 7.3.3. \Box ¹³CO; \Diamond ¹³CH₄.

Model equations for C-labeled isotopic variants for the C₃₊ hydrocarbon reaction products

An overview of the partial differential equations for the C-labeled isotopic C_{2+} components in the gas phase and on the catalyst surface are given in this appendix. For the C_{3+} hydrocarbon reaction products, the equations are similar in structure and a set of general equations is defined for a hydrocarbon with i C-atoms of which j C-atoms are labeled. The equations presented below are valid for i≥3 and 0≤j≤i.

1. For the paraffin reaction product in the gas phase containing i C-atoms in total of which j Catoms are labeled:

$$\left(1 + \frac{\rho_b}{\varepsilon_b \cdot K_i^{ph}}\right) \frac{\partial C_{i}_{C_j C_{i-j} H_{2i+2}}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{i}_{C_j C_{i-j} H_{2i+2}}}{\partial x} = \frac{\rho_b}{\varepsilon_b} k_{t,p,i} L_{i}_{C_j C_{i-j}}$$
(A-5)

2. For the olefin reaction product in the gas phase containing i C-atoms in total of which j C-atoms are labeled:

$$1 + \frac{\rho_{b}}{\varepsilon_{b} \cdot K_{j}^{ph}} \left(\frac{\partial C_{C_{j}C_{i-j}H_{2i}}}{\partial t} + \frac{1}{\tau} \frac{\partial C_{C_{j}C_{i-j}H_{2i}}}{\partial x} - \frac{\rho_{b}}{\varepsilon_{b}} \left(k_{t,o,i} L_{C_{j}C_{i-j}} - k_{re,i} \frac{C_{C_{j}C_{i-j}H_{2i}}}{K_{j}^{ph}} \right) \right)$$
(A-6)

3-a. For the growing hydrocarbon chain on the catalyst surface containing i C-atoms in total of which no C-atoms are labeled (*i.e.* j=0):

$$\frac{\partial L_{C_i}}{\partial t} = k_p L_{C_\beta} L_{C_{i-1}} - k_{t,p,i} L_{C_i} - k_{t,o,i} L_{C_i} + k_{re,i} \frac{C_{C_i H_{2i}}}{K_i^{ph}} - k_p L_{C_\beta, tot} L_{C_i}$$
(A-7)

3-b. For the growing hydrocarbon chain on the catalyst surface containing i C-atoms in total of which j C-atoms are labeled where 1≤j≤i-1:

$$\frac{\partial L_{C_{j}C_{i-j}}}{\partial t} = \kappa_{p} \left(L_{C_{\beta}} L_{C_{j-1}C_{i-j}} + L_{C_{\beta}} L_{C_{j}C_{i-j-1}} \right) - \kappa_{t,p,i} L_{C_{j}C_{i-j}} - \kappa_{t,o,i} L_{C_{j}C_{i-j}} + \kappa_{re,i} \frac{C_{C_{j}C_{i-j}H_{2i}}}{K_{re,i}^{ph}} - \kappa_{p} L_{C_{\beta},tot} L_{C_{j}C_{i-j}} \right)$$
(A-8)

3-c. For the growing hydrocarbon chain on the catalyst surface containing i C-atoms in total of which all C-atoms are labeled (*i.e.* j=i):

$$\frac{\partial L_{C_i}}{\partial t} = k_p L_{C_j} L_{C_{i-1}} - k_{t,p,i} L_{C_i} - k_{t,o,i} L_{C_i} + k_{re,i} \frac{C_{C_i H_{2i}}}{K_i^{ph}} - k_p L_{C_j,tot} L_{C_i}$$
(A-9)

Regression results for the steady state performance at $H_2/CO=1$ and $H_2/CO=5$

The steady state performance of the Co/Ru/TiO₂ catalyst at the feed ratio H₂/CO=1 is presented in figure A-9 for $W_{cat}/F=16.8 \text{ kg}_{cat} \cdot \text{s} \cdot \text{mole}^{-1}$ and in figure A-10 for $W_{cat}/F=44.8 \text{ kg}_{cat} \cdot \text{s} \cdot \text{mole}^{-1}$. The data are displayed in three plots, individual concentrations (graph A), total concentration (graph B), and olefin to paraffin ratio (graph C). In these graphs, the markers, which are connected via a dotted line, display the individual data points and the solid lines represent the model calculations.

The steady state performance at the feed ratio H₂/CO=5 is presented in figure A-11 for $W_{cat}/F=7.92 \text{ kg}_{cat} \cdot \text{s} \cdot \text{mole}^{-1}$ and in figure A-12 for $W_{cat}/F=13.7 \text{ kg}_{cat} \cdot \text{s} \cdot \text{mole}^{-1}$.







Figure A-12: Steady state performance of the Co/Ru/TiO₂ catalyst at H_2 /CO=5 and W_{cat}/F =13.7 kg_{cat}·s·mole⁻¹.

- A) Individual concentrations of the C_1 to C_9 olefins (\diamondsuit) and paraffins (\square)
- $\begin{array}{lll} B) & \mbox{Total concentration of the C_1 to C_9 hydrocarbons}\\ C) & \mbox{Olefin to paraffin ratio} \end{array}$

Regression results of the transients for C₂ to C₅ paraffins at $H_2/CO=1$ and $H_2/CO=5$

The model descriptions of the transient experimental results for the sets of data at H₂/CO=1 are represented in figures A-13 and A-14 for W_{cat}/F =16.8 kg_{cat}·s·mole⁻¹ and W_{cat}/F =44.8 kg_{cat}·s·mole⁻¹, respectively.

The model descriptions of the transient experimental results for the sets of data at H₂/CO=5 are represented in figures A-15 and A-16 for $W_{cat}/F=7.92$ kg_{cat}·s·mole⁻¹ and $W_{cat}/F=13.7$ kg_{cat}·s·mole⁻¹, respectively.



Figure A-13: Descriptions of the transient responses for ethane, propane, butane, and pentane at $H_2/CO=1$ and $W_{cat}/F=16.8$ kg_{cat}·s·mole⁻¹. Dashed lines and open markers: data ; solid lines and closed symbols: calculations.



Figure A-14: Descriptions of the transient responses for ethane, propane, butane, and pentane at $H_2/CO=1$ and $W_{cat}/F=44.8$ kg_{cat}·s·mole⁻¹. Dashed lines and open markers: data ; solid lines and closed symbols: calculations.



Figure A-15: Descriptions of the transient responses for ethane, propane, butane, and pentane at $H_2/CO=5$ and $W_{cat}/F=7.92$ kg_{cat}·s·mole⁻¹. Dashed lines and open markers: data ; solid lines and closed symbols: calculations.



Figure A-16: Descriptions of the transient responses for ethane, propane, butane, and pentane at $H_2/CO=5$ and $W_{cat}/F=13.7$ kg_{cat}'s-mole⁻¹. Dashed lines and open markers: data ; solid lines and closed symbols: calculations.

Continuity equations for the D-labeling of methane in a plug flow reactor

The continuity equations for the D-labeling of the methanation reaction are based on the general mechanism of figure A-17, where the formation of CH_4 is represented by the reversible stepwise hydrogenation of surface C_{ads} .

$$\begin{array}{c} H_{2,g} + 2 * \overbrace{\frac{k_{ads}}{k_{des}}}^{k_{ads}} 2H_{ads} \\ \hline \\ C_{ads} + H_{ads} \xrightarrow{k_1} CH_{ads} + * \\ \hline \\ CH_{ads} + H_{ads} \xrightarrow{k_2} CH_{2,ads} + * \\ \hline \\ CH_{2,ads} + H_{ads} \xrightarrow{k_3} CH_{3,ads} + * \\ \hline \\ CH_{3,ads} + H_{ads} \xrightarrow{k_4} CH_{4,g} + 2 * \end{array}$$

(A-16)

Figure A-17: Schematic representation of the methanation mechanism, consisting of the reversible stepwise hydrogenation of surface C_{ads} following CO_{ads} dissociation.

(A-23)

Assuming differential operation of the reaction in the absence of H/D kinetic isotope effects, the partial differential equations for the isotopic components in the gas-phase and on the catalyst surface are written in isotopic fractions. The reasoning is highlighted in chapter 3. The definitions for the isotopic fractions are listed below:

gas phase components:

$$C_{H_2} = \chi_1 C_{H_2}^{SS}$$
 (A-10) $C_{H_2} = \chi_2 C_{H_2}^{SS}$ (A-11) $C_{CH_4} = \varphi_1 C_{CH_4}^{SS}$ (A-12)

$$C_{''_{CH_4}} = \varphi_2 C_{CH_4}^{SS}$$
(A-13)
$$C_{'''_{CH_4}} = \varphi_3 C_{CH_4}^{SS}$$
(A-14)
$$C_{'''_{CH_4}} = \varphi_4 C_{CH_4}^{SS}$$
(A-15)

Surface components: $L_{I_H} = \omega L_H^{SS}$

$$L_{_{CH}} = \gamma_1 L_{CH}^{SS}$$
 (A-17) $L_{_{CH_2}} = \gamma_2 L_{CH_2}^{SS}$ (A-18) $L_{_{'CH_2}} = \gamma_3 L_{CH_2}^{SS}$ (A-19)

$$L_{CH_3} = \gamma_4 L_{CH_3}^{SS}$$
 (A-20) $L_{CH_3} = \gamma_5 L_{CH_3}^{SS}$ (A-21) $L_{CH_3} = \gamma_6 L_{CH_3}^{SS}$ (A-22)

Note that the total amount of methane intermediates on the catalyst surface is given by: $L_C^{SS} + L_{CH}^{SS} + L_{CH_2}^{SS} + L_{CH_3}^{SS} = L_{C_1}^{SS}$

The set of continuity equations for the isotopic components in the gas phase is:

$$\frac{\partial \chi_1}{\partial t} + \frac{1}{\tau} \frac{\partial \chi_1}{\partial x} = \frac{\rho_b}{\varepsilon_b} k_a \left(\omega^2 - \chi_1 \right)$$
(A-24)

$$\frac{\partial \chi_2}{\partial t} + \frac{1}{\tau} \frac{\partial \chi_2}{\partial x} = \frac{\rho_b}{\varepsilon_b} k_a (\omega(1-\omega) - \chi_2)$$
(A-25)

$$\frac{\partial \varphi_1}{\partial t} + \frac{1}{\tau} \frac{\partial \varphi_1}{\partial x} = \frac{1}{\tau} \left(\omega \left(1 - \gamma_4 - \gamma_5 - \gamma_6 \right) + \left(1 - \omega \right) \gamma_4 \right)$$
(A-26)

$$\frac{\partial \varphi_2}{\partial t} + \frac{1}{\tau} \frac{\partial \varphi_2}{\partial x} = \frac{1}{\tau} \left(\omega \gamma_4 + (1 - \omega) \gamma_5 \right) \tag{A-27}$$

$$\frac{\partial \varphi_3}{\partial t} + \frac{1}{\tau} \frac{\partial \varphi_3}{\partial x} = \frac{1}{\tau} \left(\omega \gamma_5 + (1 - \omega) \gamma_6 \right)$$
(A-28)

$$\frac{\partial \varphi_4}{\partial t} + \frac{1}{\tau} \frac{\partial \varphi_4}{\partial x} = \frac{1}{\tau} \omega \gamma_6 \tag{A-29}$$

The set of continuity equations for the isotopic components on the catalyst surface is: C^{SS}

$$\frac{\partial \omega}{\partial t} = k_a \frac{C_{H_2}^{SS}}{L_H^{SS}} \left(2\chi_1 - 2\omega^2 + \chi_2 - \omega(1 - \omega) \right)$$
(A-30)

$$\frac{\partial \gamma_1}{\partial t} = \left(\frac{\varepsilon_b}{\rho_b \tau} \frac{C_{CH_4}^{SS}}{L_{CH}^{SS}} + k_{-1}\right) (\omega - \gamma_1) - k_{-2} \frac{L_{CH_2}^{SS}}{L_{CH}^{SS}} (\gamma_1 - \frac{1}{2}\gamma_2 - \gamma_3)$$
(A-31)

$$\frac{\partial \gamma_2}{\partial t} = \left(\frac{\varepsilon_b}{\rho_b \tau} \frac{C_{CH_4}^{SS}}{L_{CH_2}^{SS}} + k_{-2}\right) \left(\omega \left(1 - \gamma_1\right) + (1 - \omega)\gamma_1 - \gamma_2\right) - k_{-3} \frac{L_{CH_3}^{SS}}{L_{CH_2}^{SS}} \left(\gamma_2 - \frac{2}{3}\gamma_4 - \frac{2}{3}\gamma_5\right)$$
(A-32)

$$\frac{\partial \gamma_3}{\partial t} = \left(\frac{\varepsilon_b}{\rho_b \tau} \frac{C_{CH_4}^{SS}}{L_{CH_2}^{SS}} + k_{-2}\right) (\omega \gamma_1 - \gamma_3) - k_{-3} \frac{L_{CH_3}^{SS}}{L_{CH_2}^{SS}} (\gamma_3 - \frac{1}{3}\gamma_5 - \gamma_6)$$
(A-33)

$$\frac{\partial \gamma_4}{\partial t} = \left(\frac{\varepsilon_b}{\rho_b \tau} \frac{C_{CH_4}^{SS}}{L_{CH_3}^{SS}} + k_{-3}\right) \left(\omega \left(1 - \gamma_2 - \gamma_3\right) + (1 - \omega)\gamma_2 - \gamma_4\right)$$
(A-34)

$$\frac{\partial \gamma_5}{\partial t} = \left(\frac{\varepsilon_b}{\rho_b \tau} \frac{C_{CH_4}^{SS}}{L_{CH_3}^{SS}} + k_{-3}\right) \left(\omega \gamma_2 + (1 - \omega)\gamma_3 - \gamma_5\right)$$
(A-35)

$$\frac{\partial \gamma_6}{\partial t} = \left(\frac{\varepsilon_b}{\rho_b \tau} \frac{C_{CH_4}^{SS}}{L_{CH_3}^{SS}} + k_{-3}\right) (\omega \gamma_3 - \gamma_6)$$
(A-36)

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Het is koud in het scriptorium, mijn duim doet me pijn. Ik laat dit geschrift na, ik weet niet voor wie, ik weet niet meer waarover:

stat rosa pristina nomine, nomina nuda tenemus (de roos van weleer bestaat als naam, naakte namen houden we over)

Uit: "De naam van de roos", Umberto Eco, 1984.

Curriculum Vitae

Henricus Adrianus Johannes van Dijk werd geboren op 24 december 1970 te St. Oedenrode. Na het behalen van het VWO diploma aan het Mrg. Zwijsen College te Veghel begon hij in september 1989 met de studie Scheikundige Technologie aan de Technische Universiteit Eindhoven. In september 1995 studeerde hij af bij prof.dr.ir. G.B.M.M. Marin in het Laboratorium voor Chemische Technologie. De titel van het afstudeerwerk was: "Bepaling van de stationaire kinetiek van de CO oxidatie over een commerciële Pt/Rh/CeO₂/Al₂O₃ autouitlaatkatalysator onder invloed van CO₂ en H₂O". In januari 1996 begon hij bij het Laboratorium voor Chemische Technologie met zijn promotieonderzoek wat leidde tot dit proefschrift. Het promotieonderzoek werd geïnitieerd door prof.dr.ir. G.B.M.M. Marin en werd afgerond onder leiding van prof.dr.ir. J.C. Schouten. Tijdens de promotie heeft hij in het academisch jaar 1996/1997 de eenjarige opleiding "Raffinage, Pétrochemie, Gaz" aan het Ecole Nationale Supérieure du Pétrole et des Moteurs (ENSPM) van het Institut Français du Pétrole (IFP) te Rueil-Malmaison, Frankrijk, met succes gevolgd. Vanaf 1 augustus 2000 is hij werkzaam als onderzoeker bij het Energieonderzoek Centrum Nederland (ECN) te Petten binnen de afdeling Schoon Fossiel.

List of reports and publications

- ParSEC JOULE project of the European Commission no. JOF3-CT95-0016, final report, 1999
- Van Dijk, H.A.J.; Hoebink, J.H.B.J.; Schouten, J.C., 2nd Int. Conf. on Refinery Processing, AIChE Spring National Meeting, Houston, 1999, 395-400
- Van Dijk, H.A.J.; Hoebink, J.H.B.J.; Schouten, J.C., Stud. Surf. Sci. Catal., 130, 2000, 1505-1510
- Van Dijk, H.A.J.; Hoebink, J.H.B.J.; Schouten, J.C., accepted in Chem. Eng. Sci., 2001
- Chapters 7 and 8 will be submitted to Ind. Chem. Eng. Sci..