

A transient kinetics study of Fischer-Tropsch synthesis mechanism on cobalt catalysts

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A Transient Kinetics Study of Fischer–Tropsch Synthesis Mechanism on Cobalt Catalysts

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus prof.dr.ir. F.P.T. Baaijens, voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op woensdag 29 november 2017 om 16:00 uur

door

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geboren te Zhejiang, China

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"真実はいつも一つ" "真相只有一个" "One truth prevails" 江戸川 コナン 江戸川村南 Edogawa Konan

To the miracle of my life—Zhenbo and Albert



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Science is a paper plane riding on the wind.

Chapter 1

Introduction

1.1 A historical review

The first observation of the conversion of synthesis gas (a mixture of carbon monoxide and hydrogen) into methane on heated nickel was reported by Sabatier in 1902 [1]. In the 1920s, Franz Fischer and Hans Tropsch further developed this process and showed that passing syngas over iron or cobalt below 300°C can lead to the formation of higher hydrocarbons, now known as the Fischer-Tropsch (F-T) process [2, 3]. Rapidly following the development of high-pressure process for ammonia synthesis (Haber–Bosch process [4]), the F-T process was first commercialized in Germany in 1936. The plants provided wartime Germany with liquid fuels. In the late 1940s, the F-T plants were replaced by the direct coal liquefaction process that is out of favor today [5]. After World War II, the US Bureau of Mines launched extensive investigations based on the knowledge acquired from defeated Germany. This resulted in new technology and began a demonstration program in 1953. During the period of 1955–1970, the world energy scene was governed by a plenty of cheap oil until the energy crises of 1973-74 and 1978-81 [6]. All the major development and research in F-T synthesis ceased except in petroleum boycotted South Africa, the plants run by Sasol remained the only operational commercial-size F-T plants in the 1970s. Besides the energy crises, several factors triggered revival of the development of F-T:

- (i) increasing demand in liquid fuel;
- (ii) recognition of the abundant of natural gas and depleting petroleum reserves;
- (iii) need of converting methane on remote natural gas production sites;
- (iv) desire for converting alternative carbon sources including biomass, into liquid fuels;
- (v) new developments in F-T technology.

These led to new commercial plants [7]: Shell in Malaysia (1992), PetroSA in South Africa (1993), Sasol–Qatar Petroleum in Qatar (2007), Shell in Qatar (2011), Sasol–Chevron in Nigeria (2013). Today, 90 years after Fischer and Tropsch claimed their discovery, the F–T process draws increasing attention for more general reason, *i.e.*, the F–T process represents a universal reaction that converts nearly all carbon sources, via syngas, into the entire cosmos of the organic chemistry [8].

1.2 Process

The F–T process is the heart of the XTL technology, which represents an overall process from original carbon sources to liquid fuels, where "X" is named after the feedstock employed. So CTL refers the "coal-to-liquids", GTL refers the "gas-to-liquids", and BTL refers the "biomass-to-liquids". Given the worldwide availability and high operational efficiency of natural gas, GTL is preferred CTL except for countries or places that are short of natural gas reserve but rich of cheap coal like China and South Africa [9]. The GTL process [10] consists of the following three steps (see Figure 1.1): (1) syngas production, (2) F-T synthesis, and (3) product upgrading.



Figure 1.1. Schematic representation of the GTL process.

1.2.1 Syngas production

As presented in Figure 1.1, the syngas production comprises a large proportion of the whole GTL process. The syngas production section typically accounts 60–70% of the capital and running costs of the total plant [9]. Taking into account the factors including availability, efficiency of carbon conversion, sulfur content, plant cost and environmental impact *etc.*, natural gas is preferred to coal for syngas production. Based on natural gas, three basic

approaches are employed to produce syngas, *i.e.*, steam reforming, autothermal reforming and partial oxidation (including non-catalytic and catalytic). The reactions can be described in the following equations [<u>11</u>]:

Steam reforming:

 $CH_4 + H_2O \to CO + 3H_2$ $\Delta H = 206 \text{ kJ mol}^{-1}$ (1.1)

Autothermal reforming.

 $4CH_4 + O_2 + 2H_2O \rightarrow 4CO + 10H_2$ $\Delta H = 85 \text{ kJ mol}^{-1}$ (1.2)

Partial oxidation:

$$CH_4 + \frac{1}{2}O_2 \to CO + 2H_2$$
 $\Delta H = -36 \text{ kJ mol}^{-1}$ (1.3)

The H₂/CO ratio of synthesis gas strongly depends on the carbon source and the reforming process used to produce it. For natural gas, it ranges from about 2 to 3, for coal and biomass it is less than 1. The water-gas shift reaction (Eq. 1.4) is used to adapt the H₂/CO ratio to meet the requirements of the catalysts. For a cobalt based F–T catalyst, the H₂/CO usage ratio is 2.15 [12]. The ratio is typically 1.7 when an iron catalyst is used since the water-gas shift reaction occurs considerably at elevated temperatures [13].

Water-gas shift:

 $CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H = -41.2 \text{ kJ mol}^{-1}$ (1.4)

1.2.2 Fischer–Tropsch synthesis

The reaction temperature plays a crucial role in the performance of the F–T synthesis. Based on the reaction temperature, two operation modes are distinguished: high-temperature F–T ($300-350^{\circ}$ C) on iron based catalysts for lower molecular weight products and low-temperature F–T ($200-240^{\circ}$ C) on either iron or cobalt based catalysts for higher molecular weight products [10]. Increasing temperature not only leads to a higher reaction rate, but also to quicker deactivation and a higher selectivity to undesired methane. Furthermore, the large amount of reaction heat formed by the highly exothermic F–T reaction can cause an inhomogeneous temperature distribution in the reactor, which must be taken into account in the choice and design of the reactor.

In the F–T reaction system, the reactor must be able to remove the heat quickly and keep the temperature constant inside the reactor to obtain optimal performance in terms of selectivity and stability [10]. The first commercial-size Ruhrchemie® atmospheric fixed

bed reactor consisted of vertical metal sheets and horizontal cooling pipes crossing the sheets for heat removal [14]. The reaction heat vaporizes the cooling medium, pressurized water in this case, which is useful in the steam reforming stage. The temperature of the cooling medium is constant in the reactor, so guarantees the gradient-free temperature distribution. This technology is the basis of the Shell F–T process in Malaysia. A large advantage of using tubular fixed bed reactor is that there is no need for catalyst separation from the products. Therefore, this type of reactor is suitable for wax products, as the liquid products can simply trickle down through the catalyst bed. However, using narrow tubular reactor causes a high pressure drop over the reactor, requiring an extra gas compression operation for recycling the exhaust gas. Moreover, replacing the catalysts in narrow tubes is difficult and time consuming, causing high operational cost.

Fluidized bed reactors with high gas velocity are also used to achieve the rapid heat removal from catalyst particles surface. The turbulent gas movement results in a near homogeneous temperature distribution in the reactor. In addition, the online removal/refilling of catalyst allows longer production runs without interrupting the process. However, the fluidized system is very sensitive to sulfur poisoning since the impurity can reach all the catalysts in the reactor and accumulates easily in time. Other disadvantages include more complicated operation and difficult catalyst separation compared with fixed bed reactor. The fluidized bed reactor is considered to be a promising technology for the production of C_2-C_7 light olefins on iron catalysts at high temperature conditions [15].

Recent years have witnessed a considerable progress in slurry bubble column reactor technology [16-18]. Small catalyst particles are suspended in the products that are liquid under reaction conditions. The syngas is fed by a gas distributor and reaches the catalyst particles through the liquid products. Not only is the capital cost of slurry reactor 20–40% lower than that of a fixed bed reactor [19], but also the reaction conditions are more flexible than in fixed or fluidized bed reactors [20]. As a benefit of using small catalyst particles, the diffusion resistance in particle pore is eliminated, resulting in a high activity per unit mass of catalyst [12]. However, similar with the fluidized bed reactor, the catalyst inside the slurry bubble column reactor suffers from the contamination more than in a fixed bed reactor as the catalysts at the top layer of the fixed bed adsorbs and scavenges the poison, leaving the rest unaffected. Separating the catalyst particles from the wax in a slurry reactor is more difficult than in fluidized bed reactor, since the smaller catalyst particles are suspended in wax.

1.2.3 Product upgrading

The mixture leaving the F-T bubble column reactor is referred to as F-T wax that inevitably consists of a wide range of products, requiring a considerable downstream upgrading process. The high quality of F-T wax is a very positive factor for the application in the food industry, cosmetic chemicals and medicines. The sulfur- and aromatic-free linear

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paraffins directly obtained from F–T are excellent choice for high quality lubricants. F–T wax up-grading basically shares the same technology with crude oil refinery [21]. The gasoline-range products can be maximized by oligomerization of C_3/C_4 , hydrogenation and isomerization of C_5/C_6 , catalytic reforming of C_7-C_{10} and severe reforming of the naphtha products. Furthermore, the naphtha-range F–T products can be used as cracker feedstock for ethylene and propylene production. The selectivity for diesel in the products from cobalt catalyzed F–T can be 20%. Hydrocracking at mild condition raises this proportion further. The final diesel has a cetane number of 70 [9]. The F–T diesel therefore is frequently used to upgrade low quality diesel fuel by blending.

1.3 Catalysts

Most group VIII metals are more or less active in CO hydrogenation. Among them, ruthenium shows the most attractive catalytic performance in terms of activity, selectivity and stability, but its low availability and high price limit extensive utilization. The same counts for Rh, which is selective towards oxygenated hydrocarbons. Nickel is more active than iron or cobalt in CO conversion. However, the unacceptably high selectivity of methane prevents its application in F-T reaction. Consequently, iron and cobalt are the most studied and used catalysts in large-scale F-T processes. Although the original German plants used a cobalt based catalyst, various iron catalysts were widely tested in the early years of F-T synthesis [5]. A brief comparison of cobalt and iron catalysts is presented in Table 1.1 [22]. A simplified conclusion drawn from this comparison is that cobalt catalysts show better performance but operate only in a narrow range of temperature, pressure and feedstock composition. Iron catalysts are more flexible and cheaper, however their overall performance is not as good as for cobalt. In general cobalt is a good choice for the longchain hydrocarbons production in the low-temperature F-T process. Whereas iron is mainly used for producing low molecular weight hydrocarbons and oxygenates in the hightemperature F-T process.

Factors	Cobalt catalysts	Iron catalysts
Cost	~1000 times more expensive	cheap
Preparation	impregnation or precipitation	precipitation
Reaction temperature	200–240°C	250–350°C
Carbon sources	natural gas	coal, natural gas, biomass
H ₂ /CO ratio	~2	0.5–2.5
Activity	high	relatively low
Chain-growth probability	0.94	0.95
Stability	durable	coking, poisoning aging, attrition etc.
Sulfur tolerance	<0.1 ppm	<0.2 ppm
Products	wax	C ₁ –C ₁₅ , olefins, oxygenates
Side reaction	negligible	water-gas-shift

Table 1.1. Comparison of cobalt and iron F-T catalysts [5, 21, 22].

1.4 Product distribution

One of the most important features of the F-T reaction is that the formation of long-chain hydrocarbons involves stepwise incorporation of a carbon-containing monomer. The main products of this reaction are therefore linear paraffins, linear olefins and, on rhodium, linear 1-alcohols. In the case of olefins, the overall reaction equation is [23]:

 $n \operatorname{CO} + 2n \operatorname{H}_2 \to n(\operatorname{CH}_2) + n\operatorname{H}_2 \operatorname{O} \qquad \Delta H = -165 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$ (1.5)

Lowering reaction temperature may lead to more branched hydrocarbons and internalolefins, which are considered to be secondary reaction products. Pioneering work of product analysis by Schulz [24], who showed that the composition of primary products is quite similar to the product distribution of other polymerization processes, *i.e.*, the Anderson–Schulz–Flory (ASF) distribution [23-28]:

$$F_n = \frac{n(1-\alpha)\alpha^{n-1}}{\sum_{1}^{\infty} \alpha^{i-1}} = n(1-\alpha)^2 \alpha^{n-1}$$
(1.6)

where F_n is the fraction of the carbon number within the hydrocarbon chain containing *n* carbon atoms with respect to total product and α the probability that an intermediate undergoes chain growth by reaction with a monomer. Assuming the chain-growth probability is chain-length independent, the chain-growth probability α can be defined as:

$$\alpha = \frac{r_{\rm p}}{r_{\rm p} + r_{\rm t}} \tag{1.7}$$

where r_p and r_t are the rates of chain propagation and termination, respectively. The theoretical product distribution as a function of the chain-growth probability is presented in Figure 1.2. However, this assumption seldom holds. Some well-known discrepancies between ideal ASF distribution and experimental observation are as follows. The selectivity of CH₄ is higher than predicted by the ASF distribution. This deviation is usually explained by either the thermodynamic preference for methane formation as compared with C–C coupling reactions, or the kinetically preferred C₁ hydrogenation as compared with long-chain termination [29]. It can also be because methane is formed via a different pathway than the F–T products [30]. This aspect will be addressed later in this thesis. The selectivity of C₂ is lower than predicted by the ASF distribution. A recent theoretical study attributed this deviation to the stronger binding and easier chain growth of ethylene as compared to longer hydrocarbon chains [31]. Also the selectivity of heavy hydrocarbons frequently deviates from the ASF distribution as illustrated in Figure 1.3. Typically, chain-growth probability of C₇₊ is higher than that of C₁-C₇. This could be caused by a chain-length dependent chain-growth probability. Kuipers *et al.* [32] reported that an exponential

increase in paraffin/olefin ratio with chain length, which was attributed to a chain-lengthdependent heat of physisorption of the olefins on catalyst [33] as well their heat of dissolution in [34, 35] and their diffusivity [36-39] through the product wax. They further pointed out that chain-length-dependent reinsertion of α -olefins into the chain-growth process results in an increase of chain-growth probability with chain length [40]. Van Dijk claimed that the condensation of higher hydrocarbons prior to the product analysis is a common systematic error, causing similar deviation and which is erroneously ascribed to mechanistic issues [41].



Figure 1.2. Theoretical product distribution as a function of chain-growth probability.



Figure 1.3. Experimental product distribution in comparison with the theoretical ASF distribution (dotted line). Conditions: $T = 220^{\circ}$ C, $p_{H_2} = 400$ mbar, $p_{CO} = 200$ mbar, on a Co/SiO₂ catalyst.

1.5 Mechanisms

To optimize the yield of the desired products, many efforts have been made to identify the mechanism underling the F–T reaction. Despite the complexity of the F–T mechanism, there is a consensus that the elementary steps involved in the FT reactions can be categorized into (a) CO/H_2 adsorption, (b) initiation, (c) propagation, (d) termination and desorption of hydrocarbons, and (e) oxygen removal. A number of reviews concerning the F–T mechanism have been published previously [12, 27, 42-49]. Therefore, only the most important aspects are discussed here.

1.5.1 CO dissociation

The activation of adsorbed CO initiates the F–T synthesis. The earliest hypothesis was made by Fischer and Tropsch [2]. They proposed that the adsorbed CO reacts directly with the metal resulting in a bulk carbide and oxygen. Later on, a more detailed version of this mechanism was described by Craxford and Riedel, now known as the carbide mechanism [50, 51]. They proposed that adsorbed CO directly dissociates into adsorbed C and O. The

former one is subsequently hydrogenated to methylene, which is either further hydrogenated to methane or involved in the chain propagation reaction. The O is dominantly removed as H₂O. Emmett *et al.* carried out extensive studies, indicating that bulk phase carbide participates only to a negligible extent in the F–T synthesis [52, 53]. Therefore, even though the carbide mechanism kept its original name, only the chemisorbed carbon atoms are considered as reactive intermediates.

The CO dissociation as a key step in F-T reaction was extensively studied. Like N₂ [54, 55] and NO [56] dissociation, CO dissociation is strongly dependent on the local structure of the active site. A key interpretation was made by Liu and Hu [57], who decomposed the structure sensitivity into two terms, *i.e.*, electronic effect and geometric effect. Hammer et al. suggested that the upshift of the d-band on coordinatively unsaturated sites helps to stabilize adsorbates [58]. The geometric effect is interpreted in the following manner. The transition state for CO dissociation on flat surfaces involves four metal atoms, and the C and O share bonding with one metal atom. On the other hand, the transition state involves five atoms on steps and kinks with no metal atoms being shared, leading low energy of the transition state [57]. This topic has been further discussed by Van Santen [59]. Experimental results showed that the dissociation of molecularly adsorbed CO on flat Ru surface is difficult [60]. Note that Ru is the most active metal for F-T synthesis. A theoretical study by Shetty and Van Santen showed that the energy of CO dissociation on the Ru(0001) surface is 227 kJ mol⁻¹ and only 89 kJ mol⁻¹ on a step-edge site [61]. Similarly high CO dissociation barriers of 260 kJ mol⁻¹ and 232 kJ mol⁻¹ were reported for the Co(0001) surface by Gong et al. [62] and Ge et al. [63], respectively. The barrier on a $Co(10\overline{1}0)$ surface is 68 kJ mol⁻¹ [61]. In general, extensive experimental [56, 60, 64] and theoretical studies [57, 65-67] confirmed that stepped and corrugated surfaces are responsible for the low barrier of the cleavage of the π bonds in diatomic molecules such as CO.

In addition to the direct CO dissociation path mentioned above, hydrogen-assisted CO dissociation path have also been considered. This pathway was originally proposed by Pichler and Schulz [68]. They suggested that the hydrogenation of adsorbed CO into HCO, H_2CO or HCOH precedes CO bond scission. Experimental work by Mitchell *et al.* showed that exposing gas-phase hydrogen on a CO saturated Ru(0001) surface yields HCO and H_2CO species [69]. Tuxen *et al.* recently observed a strong increase in the CO dissociation rate of adsorbed CO upon exposure to hydrogen, explained by the H-assistance of CO dissociation on Co nanoparticles [70]. Ojeda *et al.* provided experimental and theoretical evidence of the significant role of H-assisted CO dissociation pathway on both Fe and Co at conditions required for chain growth [71]. Yang *et al.* using an isotopic transient technique combined with DFT calculations to identify the formation of HCOH species as the rate-limiting step on Co catalyst [72, 73]. Hibbitts *et al.* observed water-induced rate enhancement for a Ru catalyst [74]. They explained that H₂O mediates the kinetically-

relevant H-transfer required for O-H bond formation in pathways involving HCOH intermediates.

The reaction path via HCO was explored in more detail by Ciobîcă and Van Santen using density functional theory [48]. They showed that the formation of HCO intermediate on Ru(0001) surface requires an activation energy of 146 kJ mol⁻¹ or 106 kJ mol⁻¹ depending on the local structure and is strongly endothermic, while the CO bond cleavage energy from the HCO intermediate was only 30 kJ mol⁻¹. These results suggest that the assistance of H effectively decreases the barrier of C-O bond cleavage. This low dissociation barrier of HCO is consistent with the observation that HCO decomposes to CO and H upon annealing to 180–220 K [69], implying further that the HCO group is highly unstable above 180 K. Shetty compared the barriers of direct CO dissociation and HCO dissociation on Ru(11 $\overline{2}$ 1), and found the former has the lower overall energy barrier [67]. Liu found the same trend for a Co surface [75]. Although the overall barrier for direct CO dissociation on step-edge is lower than for H-assisted CO dissociation, it is important to consider both reactions as the effect of CO coverage on CO dissociation has not been investigated yet. More specifically, the dominant CO dissociation mode may depend on the surface coverage, the lateral interactions, and the relative occurrence of different sites on the catalyst surface.

1.5.2 Chain propagation

Another mechanistic debate concerns whether the chain-growth monomer is CH_x or CO. In the former case the C–O bond is cleaved before and in the latter after insertion in the growing chain. These two mechanisms are schematically presented in Figure 1.4

Fischer and Tropsch originally proposed that the carbon monomer is formed by direct dissociation of molecularly adsorbed CO [2]. The chain propagation would proceed via insertion of a C_1 species into the metal-carbon bond of a growing chain. An evidence of the participation of carbidic carbon in chain growth was reported by Rabo et al. They showed that passing hydrogen over carbon deposits on Ni, Co or Ru induced by CO disproportionation leads to the production of ethane, propane, butane, in addition to methane [76]. Biloen et al. exposed ¹³C pre-covered catalysts to $^{12}CO/H_2$ mixture and observed the incorporation of ¹³C in the hydrocarbon chains [77]. They concluded that oxygen-free CH_x is the intermediate in F–T synthesis. Ekerdt and Bell observed that the production of hydrocarbons continued when chemisorbed CO was absent [78]. Within the carbide mechanism, different chain-growth modes were proposed. Brady and Pettit proposed a mechanism involving the insertion of CH_2 into alkyl groups [79, 80]. Maitlis contented that chain propagation involves the insertion of CH₂ into an alkenyl group followed by H transfer to from a new alkenyl group [81]. The Gaube mechanism is similar with the Maitlis mechanism, in which the growing chain is an alkylidene group [82]. Accordingly, the termination steps are different in these chain-growth modes.

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Alternatively, Pichler and Schulz proposed the CO insertion mechanism, in which CO is activated by hydrogen followed by consecutive insertion of CO or CHO into the growing chain [68]. The cleavage of C–O bond occurs after the insertion. The growing chains are terminated either before or after C–O scission as oxygenates or hydrocarbons, respectively. However, the calculated activation energy of CO insertion into RCH₂ group as originally proposed for the CO insertion mechanism is too high to account for the rapid chain growth in F-T synthesis [83, 84]. Therefore, Zhuo et al. proposed an alternative mechanism starting with CO insertion into RCH groups with an energy barrier of 80 kJ mol⁻¹ [84].⁶⁸ The RCHCO is subsequently hydrogenated to RCH₂CHO followed by C–O cleavage with a barrier of 50 kJ mol⁻¹. Zhao et al. proposed that HCO insertion exhibits comparable activity with the CO insertion and the CH_2 insertion routes on dense surfaces of Rh and Co [85]. Notably, the energy cost of HCO group formation is high. Kinetic analysis by Van Santen and Markvoort indicates that the rate of CO consumption according to the CO insertion mechanism strongly depends on the rate of chain propagation, whereas the most kinetically relevant step in carbide mechanism is CO dissociation [86]. They also pointed out that whether the chain growth can proceed via CO or CH_x insertion depends on the relative rate of oxygenate removal versus that of C-O bond cleavage, and that the dominant chaingrowth mode may vary depending on the catalyst composition and structure.

1.5.3 Chain termination

The chain termination step in the view of carbide mechanism involves the hydrogenation of the alkylidene species (R–CH=M) to the corresponding alkyl species (R–CH₂–M), which can then undergo hydrogen addition yielding n-paraffins or β -H-elimination yielding α -olefins [87]. Both have been identified as primary products in F–T synthesis [88-90]. β -hydrogen elimination is a reversible reaction, allowing for the re-incorporation of primarily formed olefins into longer-chain hydrocarbons, causing the deviation from theoretical ASF distribution. Suggested by DFT studies [71, 73], the rate of chain termination involving several hydrogenation or dehydrogenation steps can be expressed as

$$r_{\rm t} = k_{\rm t} \theta_{\rm C_n} (\theta_{\rm H})^n \tag{1.8}$$

where k_t is the rate constant for chain termination, θ_{C_n} and θ_H are surface coverage of Cn intermediate and adsorbed H, *n* is the reaction order with respect to the H_{ads}. Since the last step for paraffin formation and olefin formation is H-addition and H-elimination, one expects that the *n* value in Eq 1.8 for paraffin is higher than that for olefin. Ledesma *et al.* using a steady state isotopic transient technique, which will be discussed in detail in Chapter 2, and reported values of 2.2 and 0.7 for propane and propylene, 1.4 and 0.3 for butane and butylene, respectively [91]. They also observed a chain-length-independent rate constant for olefin formation and a chain-length-dependent rate constant for paraffin

formation. Recalling the strong chain-length-dependence of olefin involved secondary reaction [32, 40], this observation could be due to the factor that a large fraction of paraffin in this case is formed by olefin re-adsorption and hydrogenation.



Figure 1.4. Schematic presentation of the carbide mechanism (upper) and the CO insertion mechanism (bottom).

1.6 Structure sensitivity

The F–T synthesis is highly structure dependent [59]. The turnover frequency (TOF) of CO consumption sharply decreases when the cobalt particle size decreases below a certain size (Figure 1.5). As the same trend is found for several supports including inert carbon nanofibers, metal-support interactions can be excluded as the cause. As mentioned earlier, the stepped surfaces containing B_5 sites provide a relatively low barrier for CO dissociation

[56, 64]. Accordingly, two kinds of explanations have been considered for structure sensitivity of F-T synthesis:

- (i) Step sites provide high adsorption energy for CO and its dissociation products and, accordingly, they will be poisoned by strongly adsorbed CO or intermediates. Consequently, small particles with a high fraction of step sites deactivate faster [92, 93]. Alternatively, C–O cleavage can occur on terrace sites via H-assisted CO dissociation. This route contributes most to the activity at steady state. The fraction of terrace sites increases with particle size and becomes nearly constants above a certain size, resulting in a size-independent *TOF*.
- (ii) Step sites that account for the CO dissociation in F–T synthesis can only be formed on particles with a minimum size. This explains the increase in turnover frequency at increasing particle size. As CH_x species from multiple step-edge sites may be involved in chain growth, methane selectivity and chain-growth probability might also depend on the relative proportion of step-edge and terrace sites. In addition, surface reconstruction on large particles creates active step sites during the F–T reaction, leading to a constant *TOF* at increasing particle size [94, 95].



Figure 1.5. TOF for the F-T synthesis based on CO consumption, as a function of cobalt particle size (adapted from Ref [99]).

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For supported Ru catalysts, similar trends have been observed, but with a leveling off at about 10 nm [<u>96</u>]. The decrease in activity for ruthenium nanoparticles at decreasing particle size is explained in two ways, either the lack of specific step edge sites on smaller particles [<u>97</u>] or poisoning by reactants of the step sites of smaller particles [<u>98</u>].

Besides the CO consumption rate, also the selectivity of F–T products strongly depends on the size of metal particles. Barbier *et al.* reported that increasing the cobalt particle size from 4.5 to 9.5 nm leads to an increase in chain-growth probability from 0.74 to 0.87 at 170°C and 1 bar [100]. Bian *et al.* reported that increasing the cobalt particles from 11 to 29 nm enhances the chain-growth probability from 0.85 to 0.89 [101]. Bezemer *et al.* showed that the CH₄ selectivity at 220°C and 1 bar is constant (40%) for cobalt particles larger than 6 nm, but increases sharply for smaller particles [102]. Interestingly, the effect of cobalt particle size on activity levels off above 10 nm. However, the size effect on selectivity extents over a wider range. As the dependence of activity and selectivity on the particle size differ, it can be concluded that there are different elementary steps that control activity and selectivity, of which each has its own structure sensitivity.

1.7 Aim and scope

The F–T synthesis presents a truly universal reaction that converts a wide range of carbon sources into the entire cosmos of organic chemistry via synthesis gas. However, as briefly described above, the complexity of the mechanism underlying the F–T synthesis leads to debates being as old as this nearly one-century-old reaction itself. The aim of this thesis is to provide detailed data about the mechanism and kinetics of CO dissociation and chain growth in the F–T reaction. In order to gain new insights, for the first time a combination of several transient techniques and model fitting was employed.

Transient techniques, based on an abrupt change in the reaction feed, provide a unique way to furnish mechanistic information in a less ambiguous way than steady state kinetics. On top of this, fitting the transient data and subsequently estimating the kinetic rate constants bring us deeper insight into the F–T reaction. The methodology of transient techniques is described in **Chapter 2**.

A fundamental question regarding the CO dissociation, which initiates the F–T reaction, is whether adsorbed CO dissociates directly into adsorbed C and O species or whether the dissociation is assisted by co-adsorbed H to form H-bonded intermediates. ${}^{12}C^{16}O/{}^{13}C^{18}O$ scrambling experiments performed to probe the CO dissociation in the absence of hydrogen on cobalt catalyst are reported in **Chapter 3**. To study further CO dissociation and the influence of hydrogen, *in situ* infrared spectroscopy assisted by DFT calculations was employed. This enabled us to identify the dominant CO dissociation mode.

Chapter 4 focuses on the F–T reaction at conditions leading mainly to methane at elevated temperature. Transient experiments involving chemical transient and isotopic steady state transient were carried out for this methanation reaction. Combining all the

transient data resulted in a fitted model without the usual pre-assumption on the rate-liming step(s). Two mechanisms via direct CO dissociation and H-assisted CO dissociation, respectively, are proposed and compared. Together with results of separate transient experiments, the rate controlling steps in the methanation reaction have been determined.

The chain growth of higher hydrocarbons, being the core of F–T synthesis, is investigated in **Chapter 5** by steady state isotopic transient kinetic analysis (SSITKA) combined with additional isotopic labeling experiments and model fitting. The hydrogenation of carbon pre-deposited on cobalt was used to provide new clues for chain-growth mechanism. In addition, the use of ${}^{12}C_{3}H_{6}$ co-feeding with ${}^{13}C$ -labelled CO shed light on the mechanism and kinetics of chain growth.

With the assistance of SSITKA, we studied the mechanistic influence of carbon deposits (**Chapter 6**), as well as some noble metals (**Chapter 7**), on the cobalt catalyzed FT reaction. Finally, the main conclusions of this thesis are summarized in **Chapter 8**.

References

- [1] P. Sabatier, J.B. Senderens, C. R. Acad. Sci. Paris 134 (1902) 514–516.
- [2] F. Fischer, H. Tropsch, Brennst. Chem. 7 (1926) 97–104.
- [3] F. Fischer, H. Tropsch, Brennst. Chem. 4 (1923) 276–285.
- [4] V. Smil, Nature 400 (1999) 415–415.
- [5] A.N. Stranges, Stud. Surf. Sci. Catal. 163 (2007) 1–27.
- [6] H. Schulz, Appl. Catal., A 186 (1999) 3–12.
- [7] D.J. Moodley, On the Deactivation of Cobalt-based Fischer–Tropsch Synthesis Catalysts, PhD, Einhdven Unversity of Technology, Eindhoven, 2008.
- [8] B. List, Angew. Chem. Int. Ed. 53 (2014) 8528–8530.
- [9] M.E. Dry, Catal. Today 71 (2002) 227–241.
- [10] M.E. Dry, J.C. Hoogendoorn, Catal. Rev. –Sci. Eng. 23 (1981) 265–278.
- [11] S.H. Chan, O.L. Ding, D.L. Hoang, Int. J. Green Energy 1 (2004) 265–278.
- [12] M.E. Dry, Appl. Catal., A 138 (1996) 319–344.
- [13] L. Xu, S. Bao, R.J. O'Brien, D.J. Houpt, B.H. Davis, Fuel Sci. Technol. Int. 12 (1994) 1323–1353.
- [14] H. Pichler, O. Roelen, F. Schnur, W. Rottig, H. Kölbel, in: Ullmanns Enzyklopädie der technischen Chemie, Urban & Schwarzenberg, München–Berlin, 1957, pp. 685.
- [15] A.P. Steynberg, R.L. Espinoza, B. Jager, A.C. Vosloo, Appl. Catal., A 186 (1999) 41–54.
- [16] J.W.A. de Swart, R. Krishna, Chemical Engineering and Processing 41 (2002) 35– 47.

- [17] M.R. Rahimpour, S.M. Jokar, Z. Jamshidnejad, Chem. Eng. Res. Des. 90 (2012) 383–396.
- [18] R.L. Espinoza, A.P. Steynberg, B. Jager, A.C. Vosloo, Appl. Catal., A 186 (1999) 13-26.
- [19] G.N. Choi, S.J. Kramer, S.S. Tam, J.M. Fox III, in: Coal Liquefaction and Gas Conversion Contractors Review Conference, US Department of Energy, Pittsburgh, PA, 1995, pp. 269–282.
- [20] T.M. Leib, P.L. Mills, J.J. Lerou, J.R. Turner, Chem. Eng. Res. Des. 73 (1995) 690– 696.
- [21] M.E. Dry, Catal. Today 6 (1990) 183–206.
- [22] A.Y. Khodakov, W. Chu, P. Fongarland, Chem. Rev. 107 (2007) 1692–1744.
- [23] R.B. Anderson, The Fischer-Tropsch synthesis, Academic Press Inc., Orlando, Florida, 1984.
- [24] G.V.Z. Schulz, Phys. Chem. Abt. B 43 (1939) 25-46.
- [25] R.A. Friedel, R.B. Anderson, J. Am. Chem. Soc. 72 (1950) 1212–1215.
- [26] V.H. Pichler, H. Schulz, M. Elstner, Brennst. Chem. 48 (1967) 78-87.
- [27] J.P. Hindermann, G.J. Hutchings, A. Kiennemann, Catal. Rev. –Sci. Eng. 35 (1993) 1–127.
- [28] G. Henrici–Olivé, S. Olivé, Angew Chem Int Ed Engl 15 (1976) 136–141.
- [29] H. Schulz, Top. Catal. 26 (2003) 73-85.
- [30] H. Schulz, Catal. Today 214 (2013) 140–151.
- [31] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [32] E.W. Kuipers, I.H. Vinkenburg, H. Oosterbeek, J. Catal. 152 (1995) 137–146.
- [33] G.P. Van Der Laan, A.A.C.M. Beenackers, Catal. Rev. -Sci. Eng. 41 (1999) 255-318.
- [34] L.M. Tau, H.A. Dabbagh, B.H. Davis, Energy & Fuels 5 (1991) 174–179.
- [35] H. Schulz, K. Beck, E. Erich, Stud. Surf. Sci. Catal. 36 (1988) 457–471.
- [36] E. Iglesia, S.C. Reyes, R.J. Madon, S.L. Soled, Adv. Catal. 39 (1993) 221-302.
- [37] R.J. Madon, S.C. Reyes, E. Iglesia, J. Phys. Chem. 95 (1991) 7795-7804.
- [38] E. Iglesia, S.C. Reyes, R.J. Madon, J. Catal. 129 (1991) 238–256.
- [39] R.J. Madon, E. Iglesia, J. Catal. 139 (1993) 576–590.
- [40] E.W. Kuipers, C. Scheper, J.H. Wilson, I.H. Vinkenburg, H. Oosterbeek, J. Catal. 158 (1996) 288–300.
- [41] H.A.J. van Dijk, The Fischer–Tropsch synthesis A mechanistic study using transient isotopic tracing, Eindhoven University of Technology, Eindhoven, 2001.
- [42] H. Pichler, Adv. Catal. 4 (1952) 271–341.
- [43] G.A. Mill, F.W. Steffgen, Catal. Rev. -Sci. Eng. 8 (1973) 159-210.
- [44] M.A. Vannice, Catal. Rev. –Sci. Eng. 14 (1976) 153–191.
- [45] V. Ponec, Catal. Rev. –Sci. Eng. 18 (1978) 151–171.

- [46] A.T. Bell, Catal. Rev. –Sci. Eng. 23 (1981) 203–232.
- [47] C.K. Rofer–DePoorter, Chem. Rev. 81 (1981) 447–474.
- [48] R.A. van Santen, I.M. Ciobîcă, E. van Steen, M.M. Ghouri, Adv. Catal. 54 (2011) 127–187.
- [49] R. Van Santen, A.J. Markvoort, I.A.W. Filot, M.M. Ghouri, E.J.M. Hensen, Phys. Chem. Chem. Phys. 15 (2013) 17038–17063.
- [50] S.R. Craxford, E.K. Rideal, J. Chem. Soc. (1939) 1604–1614.
- [51] S.R. Craxford, Trans. Faraday Soc. 42 (1946) 576–580.
- [52] J.T. Kummer, T.W. DeWitt, P.H. Emmett, J. Am. Chem. Soc. 70 (1948) 3632–3643.
- [53] L.C. Browning, T.W. DeWitt, P.H. Emmett, J. Am. Chem. Soc. 72 (1950) 4211– 4217.
- [54] S. Dahl, A. Logadottir, R.C. Egeberg, J.H. Larsen, I. Chorkendorff, E. Törnqvist, J.K. Nørskov, Phys. Rev. Lett. 83 (1999) 1814–1817.
- [55] S. Dahl, E. Törnqvist, I. Chorkendorff, J. Catal. 192 (2000) 381–390.
- [56] T. Zambelli, J. Wintterlin, J. Trost, G. Ertl, Science 273 (1996) 1688–1690.
- [57] Z.-P. Liu, P. Hu, J. Am. Chem. Soc. 125 (2003) 1958-1967.
- [58] B. Hammer, Phys. Rev. Lett. 83 (1999) 3681–3684.
- [59] R.A. van Santen, Acc. Chem. Res. 42 (2009) 57-66.
- [60] T. Zubkov, G.A. Morgan, J.T. Yates, O. Kühlert, M. Lisowski, R. Schillinger, D. Fick, H.J. Jänsch, Surf. Sci. 526 (2003) 57–71.
- [61] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.
- [62] X.-Q. Gong, R. Raval, P. Hu, Surf. Sci. 562 (2004) 247-256.
- [63] M.N. Qingfeng Ge, J. Phys. Chem. B 110 (2006) 15368–15380.
- [64] K. Honkala, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Norskov, Science 307 (2005) 555–558.
- [65] J. Chen, Z.-P. Liu, J. Am. Chem. Soc. 130 (2008) 7929–7937.
- [66] F.B. de Mongeot, A. Toma, A. Molle, S. Lizzit, L. Petaccia, A. Baraldi, Phys. Rev. Lett. 97 (2006) 056103.
- [67] S. Shetty, A.P.J. Jansen, R.A. van Santen, J. Am. Chem. Soc. 131 (2009) 12874– 12875.
- [68] H. Pichler, H. Schulz, Chem. Ing. Tech. 42 (1970) 1162–1174.
- [69] W.J. Mitchell, J. Xie, T.A. Jachimowski, W.H. Weinberg, J. Am. Chem. Soc. 117 (1995) 2606–2617.
- [70] A. Tuxen, S. Carenco, M. Chintapalli, C.H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A.P. Alivisatos, G. Thornton, W.F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, J. Am. Chem. Soc. 135 (2013) 2273–2278.
- [71] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, J. Catal. 272 (2010) 287–297.
- [72] Y. Qi, J. Yang, X. Duan, Y.-A. Zhu, D. Chen, A. Holmen, Catal. Sci. Technol. 4 (2014) 3534–3543.

- [73] J. Yang, Y. Qi, J. Zhu, Y.-A. Zhu, D. Chen, A. Holmen, J. Catal. 308 (2013) 37-49.
- [74] D.D. Hibbitts, B.T. Loveless, M. Neurock, E. Iglesia, Angew. Chem. Int. Ed. 52 (2013) 12273–12278.
- [75] J.-X. Liu, H.-Y. Su, W.-X. Li, Catal. Today 215 (2013) 36–42.
- [76] J.A. Rabo, A.P. Risch, M.L. Poutsma, J. Catal. 53 (1978) 295–311.
- [77] P. Biloen, J.N. Helle, W.M.H. Sachtler, J. Catal. 58 (1979) 95-107.
- [78] J.G. Ekerdt, A.T. Bell, J. Catal. 58 (1979) 170–187.
- [79] R.P. Robert C. Brady III, J. Am. Chem. Soc. 102 (1980) 6182–6184.
- [80] R.P. Robert C. Brady III, J. Am. Chem. Soc. 103 (1981) 1287–1289.
- [81] P.M. Maitlis, V. Zanotti, Catal. Lett. 122 (2008) 80-83.
- [82] J. Gaube, H.F. Klein, J. Mol. Catal. A: Chem. 283 (2008) 60-68.
- [83] P.H. Jun Cheng, Peter Ellis, Sam French, Gordon Kelly, and C. Martin Lok, J. Phys. Chem. C 112 (2008) 6082–6086.
- [84] M. Zhuo, K.F. Tan, A. Borgna, M. Saeys, J. Phys. Chem. C 113 (2009) 8357–8365.
- [85] Y.-H. Zhao, K. Sun, X. Ma, J. Liu, D. Sun, H.-Y. Su, W.-X. Li, Angew. Chem. Int. Ed. 50 (2011) 5335–5338.
- [86] R.A. van Santen, A.J. Markvoort, ChemCatChem 5 (2013) 3387–3397.
- [87] M. Claeys, E. van Steen, Stud. Surf. Sci. Catal. 152 (2004) 601–680.
- [88] H. Pichler, H. Schulz, F. Hojabri, Brennst. Chem. 45 (1964) 215–221.
- [89] D.B. Bukur, D. Mukesh, S.A. Patel, Ind. Eng. Chem. Res. 29 (1990) 194–204.
- [90] R.J. Madon, S.C. Reyes, E. Iglesia, J. Phys. Chem. 95 (1991) 7795–7804.
- [91] C. Ledesma, J. Yang, E.A. Blekkan, A. Holmen, D. Chen, ACS Catal. 6 (2016) 6674–6686.
- [92] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P.d. Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [93] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Langmuir 26 (2010) 16558–16567.
- [94] R.A. van Santen, M.M. Ghouri, S. Shetty, E.M.J. Hensen, Catal. Sci. Technol. 1 (2011) 891–911.
- [95] P. van Helden, I.M. Ciobîcă, R.L.J. Coetzer, Catal. Today 261 (2016) 48-59.
- [96] J.M. González–Carballo, F.J. Pérez–Alonso, M. Ojeda, F.J. García–García, J.L.G. Fierro, S. Rojas, ChemCatChem 6 (2014) 2084–2094.
- [97] X.-Y. Quek, I.A.W. Filot, R. Pestman, R.A. van Santen, V. Petkov, E.J.M. Hensen, Chem. Commun. 50 (2014) 6005–6008.
- [98] J.M. González-Carballo, F.J. Pérez-Alonso, F.J. García-García, M. Ojeda, J.L.G. Fierro, S. Rojas, J. Catal. 332 (2015) 177–186.
- [99] J. van de Loosdrecht, F.G. Botes, I.M. Ciobîcă, A. Ferreira, P. Gibson, D.J. Moodley, A.M. Saib, J.J. Visagie, C.J. Weststrate, J.W. Niemantsverdriet, in: J. Reedijk, K. Poeppelmeier (Eds.) Reference Module in Chemistry, Molecular Sciences and Chemical Engineering: Comprehensive Inorganic Chemistry II, Elsevier, Amsterdam, 2013.

- [100] A. Barbier, A. Tuel, I. Arcon, A. Kodre, G.A. Martin, J. Catal. 200 (2001) 106–116.
- [101] G.-Z. Bian, N. Fujishita, T. Mochizuki, W.-S. Ning, M. Yamada, Appl. Catal., A 252 (2003) 251–260.
- [102] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. van Dillen, K.P. de Jong, J. Am. Chem. Soc. 128 (2006) 3956–3964.

Chapter 2

Transient methods

2.1 Introduction

Resolving reaction kinetics, which are closely interwoven with catalysis, is usually applied to analyze the correlation between catalyst performance and controllable parameters, such as temperature, pressure, and feeding rate [1]. From a practical viewpoint, purely empirical correlations are useful for design, control, and optimization of chemical processes, especially for commercial-scale reactor design. Industrial experience has indicated that overall conversion in a chemical process can often be adjusted by reasonable manipulation of space velocity, temperature, etc. Selectivity in a complex system, like Fischer–Tropsch (F–T) synthesis, is usually more difficult to be controlled, therefore requiring deeper understanding of the reaction system at a molecular level, *i.e.*, reaction mechanism based kinetics or intrinsic kinetics [2, 3]. Unraveling the mechanism and kinetics behind the F–T synthesis reaction network is, therefore, of both practical and scientific interest.

In kinetic analysis, a common practice is to postulate first a number of expected mechanistic models, and subsequently check which is most consistent with experimental observations [4]. Unfortunately, there is always a possibility that a better fitting model is left out of consideration. There may also exist different mechanisms leading to approximately the same rate expression. Transient kinetics provides a unique way to furnish mechanistic information in a less ambiguous way than steady state kinetics, which strongly depend on pre-assuming one elementary step as rate limiting [5]. In a transient experiment, a perturbation is imposed on a system by changing abruptly the partial pressure of one reactant, after which system relaxation is measured. The transient response of the system as it approaches a new steady state exhibits a characteristic behavior reflecting the nature of the sequence of elementary steps which underlie the reaction. Although any parameter that controls the kinetics can be applied to impose a perturbation upon the system, only an abrupt change in gas-phase composition is practically possible. Pioneering work of transient techniques was carried out by Wagner and Hauffe in 1939 [6]. Two decades later, Tamaru applied this technique in a number of reactions to measure the adsorption during the reaction [7]. Later, the groups of Kobayashi [4, 8], Wagner [9], Bennet [5], Happel [10], Biloen [11], and Bell [12] performed extensive kinetic and mechanistic studies using transient experiments. Recent progress was made by Kruse and co-workers [13-18].

Based on the change in gas-phase composition imposed upon the system, two kinds of transient experiments can be defined: chemical transient kinetic analysis (CTKA) and steady state isotopic transient kinetic analysis (SSITKA). The former one, CTKA, is

performed by abruptly changing the inlet flow rate of one of the reactants. Kruse and coworkers used CTKA to study the H₂-CO reaction extensively [<u>13-18</u>], in which H₂ + He gas mixture was abruptly replaced by H₂ + CO flow, or vice versa while keeping constant the H₂ flow as well as the flow rate. SSITKA, which was initially developed by Happel [<u>10</u>, <u>19</u>, <u>20</u>] and Biloen [<u>21-23</u>], is based on monitoring transient responses of the reactants and products following an abrupt switch from a feedstock to its isotopic counterpart at steady state conditions, therefore allows the study of steady state kinetics. SSITKA technique is widely used to obtain information about the reaction mechanism and catalyst surface at steady state conditions, enabling the decoupling of the rate constant and surface coverage [<u>24-33</u>]. Recent progress and applications are reviewed by Shannon and Goodwin [<u>34</u>], Qi [<u>35</u>] and Ledesma [<u>36</u>].

In spite of the ability to determine the intrinsic kinetics, unambiguous interpretation of transient kinetics results strongly depends on whether the transient responses is only determined by intrinsic kinetic process. Besides the reaction kinetics, the measured transient response is also influenced by the flow characteristics of the experimental system. To obtain purely intrinsic kinetics, the experimental setup as well as the data acquisition and processing must be optimized. These topics are addressed in this chapter



2.2 Instrumentation

Figure 2.1. Flow sheet of the transient experiment setup.

The setup used in the transient experiments consists of a feed, a reaction and an analysis section. The flow sheet is shown in Figure 2.1. In a typical transient experiment, one feed is abruptly replaced by another one. To minimize perturbations in total pressure and flow characteristics, a completely symmetrical setup is used in which the left part is used for the initial feed and the right part for the feed that replaces the initial feed. Both feeds contain an inert tracer and have exactly the same pressure and total flow rate. The response is monitored in time by an online mass spectrometer (MS) and/or a gas-chromatograph-mass-spectrometer (GCMS), and bears the kinetic and mechanistic information about the reaction. For the optimal interpretation of transient data, the evolution of reactants and products following the switch should be fully determined by intrinsic kinetic features only, and not by mixing and mass transfer rates or pressure fluctuations. Therefore, the setup is designed and constructed to diminish these issues, which will be discussed in detailed below:

- (i) Switch-induced pressure disturbance: pressure perturbations have an undesired effect on the flow rate and molar concentrations measured by the mass spectrometer.
- (ii) Axial gas mixing: this occurs mainly in the dead volume parts of the setup *i.e.*, the dead volume after the 4-way valve and in the reactor. Obviously, the axial mixing can be eliminated by minimizing the dead volume.

2.2.1 Feeding section

Two feeding systems, namely for normal gases and labeled gases respectively, are symmetrically built to structurally ensure the identical flow characteristics of two feed streams. Well-calibrated mass flow controllers guarantee the identical total volumetric flow rate of each feed. In each feed system, an inert gas (neon, argon or helium) is used as tracer to monitor the gas phase hold-up in the system. A 4-way valve (Valco, N4WE) with small internal volume (100 μ L) driven by compressed air, enables the fast switch between the two feed streams. The needle valves in the upstream allows for equalizing the pressure drops through the lines. Two back pressure regulators downstream the reactor and in the vent fix the pressure of both feed streams. By this means, the pressures of two feed streams can be controlled and equalized. Besides, another feed stream is connected to the system between the 4-way valve and reactor. By this line, an extra constant feed stream can be introduced into the reactor. The function of this constant flow is twofold:

- (i) Introduction of a constant inert gas flow dilutes the reactants, therefore increases the flow velocity without changing feeding rate. Consequently, the mass transport is enhanced and the thermal effect of the reaction is diminished, achieving the intrinsic activity measurement.
- (ii) Co-fed components that are not replaced during the transient can be introduced through this line. Decreasing the ratio of switched flow to constant flow further minimizes the pressure effect; therefore improves the transient data quality.

2.2.2 Reaction section

The stainless steel tubular fixed bed reactor has a 5 mm I.D. \times 80 mm length reaction zone. The catalyst bed is housed between two sealing rings and supported on a sintered metal filter. The use of two screwed-in thick-wall tubes placed in the reactor minimizes the dead volume. Two stainless steel capillaries (1/16 inch O.D., 0.25 mm I.D.) extend directly to the filters above and below the catalyst bed, through the thick-wall tubes.

T-pieces are used to connect the inlet and outlet lines to the MS capillaries that enter the reactor. With a 3-way valve, the capillaries can be connected to the online MS via another stainless steel capillary (1/16 inch O.D., 0.25 mm I.D., 1.5 m long). All the capillaries, including the 3-way valve, are heated to 120°C to prevent the condensation of water and light hydrocarbons. The reactor is heated by an electric oven. A movable K-type thermocouple placed inside the reactor wall monitors and controls the reactor temperature.

To inspect the transient data quality of the system, the forcing and mixing curves that bear the flow characteristics of the system are measured at the inlet and outlet of the catalytic bed, respectively. A typical result is shown in Figure 2.2, in which a 1 mL min⁻¹ Ne flow is abruptly replaced by a 1 mL min⁻¹ Ar flow in a constant 49 mL min⁻¹ Ar flow (220°C, 3 bar). The following is observed:

- (i) The time constant of the forcing curve measured at the inlet of the reactor (squares in Figure 2.2) is 1.6 s. This parameter is an indicator of the flow characteristics of the piping system at given condition, *i.e.*, pressure, flow rate, and tracing temperature, *etc.*, being independent of reactor configuration and catalytic bed.
- (ii) The transient response measured at the outlet of the catalytic bed is defined as the mixing curve (circles in Figure 2.2). The integral area between the forcing curve and mixing curve represents the average gas phase hold-up time of the feed stream in catalytic bed, which is 2.0 s in this case.



Figure 2.2. The forcing (squares) and mixing (circles) curves measured at 220°C, 3 bar.

2.2.3 Analysis section

The analysis section consists of three instruments: an online gas-phase chromatograph (GC), an online mass spectrometer (MS) and a gas-phase-chromatograph-mass-spectrometer (GCMS). The GC is used to determine the conversion, selectivity at steady state be analyzing the gas-phase components. The MS provides a real-time monitoring of light molecules, e.g. H_2 , He, Ne, Ar, CH_4 , H_2O or CO. To analyze the isotopic composition of the C_{2+} species, a GCMS with sample loops is needed. A detailed discussion is given below:

Online gas-phase chromatograph

The catalytic activity in steady state is determined by analyzing the gas-phase on a GC (VARIAN CP-3800) equipped with two detectors:

- (i) TCD (CP-Molsieve 5A + CP-PoraBOND Q column) for CO₂, CO, N₂, H₂ and CH₄;
- (ii) FID (Rt@-Q-BOND) for the analysis of C_1 to C_8 hydrocarbons.

A N_2 flow controlled by an MFC is used as internal standard that allows the quantification of the molar flow rate in the TCD line.

Online mass spectrometer

The online mass spectrometry (GeneSys) is used to monitor the transient responses of light molecules, including Ar, Ne, He, N₂, H₂, D₂, H₂O, ¹²CO₂, ¹³CO₂, ¹²CO, ¹³CO, ¹²CH₄ and ¹³CH₄. The *m/z* values used to monitor these compounds are listed in Table 2.1. Notably, different inert tracers are chosen in different cases. For instance, Ne and Ar are used in ¹²CO/H₂ to ¹³CO/H₂ switch experiments since Ne and Ar have comparable diffusion behavior. In the ¹³CO/H₂ to ¹³CO/D₂ switch experiments N₂, instead of Ne or He, is used, since Ne and ¹³CD₃H both produce the signal at *m/z* = 20, and He and D₂ produce the signal at *m/z* = 4. He and Ar are needed if the CO₂ is the main product, since both Ar and Ne produce the signal at *m/z* = 20 and CO₂ gives rise to the signal at *m/z* = 22 which is the second most intensive MS signal of Ne. Because of the overlap of the fragmentation patterns, the responses of higher hydrocarbons are measured by GCMS, which will be discussed in next section.

Table 2.1. The overview of the m/z values used for online MS analysis

component	m/z	component	m/z	component	m/z
He, Ne, Ar	4, 22, 40	H ₂ , D ₂	2,4	¹² CH ₄ , ¹³ CH ₄	15, 17
N_2, H_2O	28, 18	¹² CO, ¹³ CO	28, 29	$^{12}CO_2$, $^{13}CO_2$	44, 45

Noteworthy is the limited usefulness of the transient responses of H_2 , D_2 and, because the pump capacity of the mass spectrometry is insufficient for the effective removal of these small molecules. This causes a significant delay in transient responses.

Online gas-phase-chromatograph-mass-spectrometry

The overlap in the fragmentation patterns of the FT products requires separation of the mixture before the mass spectrum analysis. A typical SSITKA transient at FT conditions lasts 15–60 minutes before reaching steady state. However, a GC analysis program for F-T products is typically 1 hour. Therefore, a 16-loop valve (Valco) is equipped for collecting 16 gaseous samples during the transient, making the measurement of fast transient by GCMS (Shimazu GCMS-QP 2010) possible. The sampling process programed by Shimazu Real Time Analysis software is initiated or finalized by switching the 6-way valve before the 16-loop valve. The valves are placed in a heated box (120°C) to prevent the condensation of products.

2.3 Data analysis

2.3.1 GC analysis

The catalytic performance in terms of conversion and selectivity at steady state is determined by online GC. The CO conversion is calculated by:

$$X_{\rm CO} = 1 - \frac{A_{\rm CO,out}/A_{\rm N_2,out}}{A_{\rm CO,in}/A_{\rm N_2,in}}$$
(2.1)

where A refers the peak area in chromatograms. The selectivity towards the individual hydrocarbon is determined as:

$$S_{C_{i}} = \frac{\frac{A_{CH_{4},TCD}K_{CH_{4},TCD}}{A_{N_{2},out}}}{\frac{A_{CO,in}K_{CO,TCD}}{A_{N_{2},in}} \frac{A_{CO,out}K_{CO,TCD}}{A_{N_{2},out}}} \times \frac{n_{C_{i}}A_{C_{i},FID}K_{C_{i},FID}}{A_{CH_{4},FID}K_{CH_{4},FID}}$$
(2.2)

where *A* refers the peak area in corresponding detector; *K* denotes the calibration factor that is obtained by measuring calibration gas (1% CO, 1% CO₂, 1% H₂, 1% CH₄, 1% C₂H₄, 1% C₂H₆, 1% C₃H₆, 1% C₃H₈, balanced by He). n refers to the carbon number of C*i* product. The calibration factors for C₃₊ species are assumed to have linear correlation with carbon number. The first term refers the CH₄ selectivity determined by calibrated TCD detector. The second term refers the ratio of C_i and CH₄ determined by FID detector. By this means, the component measured by FID is correlated to CH₄ measured by TCD.

2.3.2 Online mass spectrometer analysis

The transient responses are normalized between the initial time of the transient and the moment when the system reaches the steady state again:

$$N = \frac{s - S_{\text{final}}}{S_{\text{ini}} - S_{\text{final}}} \left(\text{or } 1 - \frac{s - S_{\text{final}}}{S_{\text{ini}} - S_{\text{final}}} \right)$$
(2.3)

where *s* is the MS signal to be normalized; S_{ini} is signal intensity at the initial time of the transient; S_{final} is the signal intensity when reaching the steady state. The residence times (τ) of CO were calculated by integrating the normalized transient curves, N_{CO} , over time-on-stream and corrected for the gas phase hold-up tracing the Ne inert (Figure 2.3).

$$\tau_{\rm CO} = \int_0^\infty (N_{\rm CO} - N_{\rm Ne}) \mathrm{d}t \tag{2.4}$$

The residence time of ${}^{12}CH_x$ (surface intermediates leading to methane) was first determined in a similar way as CO and then corrected for the chromatographic effect of CO by subtracting half of CO residence time [22].

$$\tau_{\rm CH_x} = \int_0^\infty (N_{\rm CH_4} - N_{\rm Ne}) dt - \frac{1}{2} \tau_{\rm CO}$$
(2.5)

The residence time of higher hydrocarbons in principle can be determined similarly, but needs the correction for the diffusion in the tubing connecting the GCMS, which is discussed in next section.

The amount of reversible adsorbed CO and CH_x species can be determined from the residence time and exit flow of those species. Taking into account the metal surface area, the surface coverage of CO and CH_x can be calculated.

$$\theta_{\rm CO} = \tau_{\rm CO} \frac{F_{\rm CO}(1 - X_{\rm CO})}{A_{\rm Co}} \tag{2.6}$$



Figure 2.3. Representation of the interpretation of a typical transient responses.

$$\theta_{\rm CH_x} = \tau_{\rm CH_x} \frac{F_{\rm CO} X_{\rm CO} S_{\rm CH_4}}{A_{\rm Co}} \tag{2.7}$$

where F_{CO} refers to the CO feed rate; A_{CO} is the amount of accessible cobalt metal atoms measured by H₂-chemisorption; X_{CO} and S_{CH4} are CO conversion and CH₄ selectivity, respectively in steady state measured by GC.

2.3.3 GCMS data analysis

In the SSITKA experiment, the hydrocarbons, which are separated by GC (column (CP-PoraBOND Q) contain molecules with different numbers of labeled carbon. The fragmentation patterns measured by GCMS is supposed to be a linear combination of the individual fragmentation patterns of all the isotopologues of the hydrocarbon. Notably, isotopologues are only distinguished on the base of the number of isotopically labeled carbon number, but not on its position in the molecule, *e.g.* ${}^{13}CH_{3}{}^{12}CH_{2}{}^{12}CH_{3}$ is not differentiated from ${}^{12}CH_{3}{}^{13}CH_{2}{}^{12}CH_{3}$. The fractional contribution of each isotopologue can be determined by minimizing the difference between the measurement and calculated MS pattern. The objective function can be written as [<u>32</u>]

$$S(x) = \left\|\sum_{i=0}^{n} (x_{i,n} F_{i,n}) - M_n\right\|_2$$
(2.8)

where S(x) is the objective function to be minimized; *n* is the chain length of a given product; *i* is the number of isotopic carbons contained in product molecule; M_n refers to the measured MS pattern of the C_n product; $F_{i,n}$ refers to the MS pattern of the C_n product containing *i* isotopic carbon atoms; $x_{i,n}$ is the fractional contribution of C_n with *i* isotopic carbon atoms. It is assumed that the relative intensity of the MS pattern doesn't change when replacing the ¹²C by ¹³C. Accordingly, the MS patterns of the labeled products can be derived from the unlabeled product patterns. Notably, only the molecular fragments without undergoing the C–C breaking were taken into account in the S(*x*) calculation. For instance, m/z values from 24 to 32 were employed to analyze the fraction of ¹²CH₃¹²CH₃, ¹²CH₃¹³CH₃, and ¹³CH₃¹³CH₃ in the C₂ product.

The reference fragmentation patterns are first obtained by measuring the products from ¹²CO cylinder (Linde), and then corrected for the natural abundance of ¹³C (1.1%) by eliminating the contribution of ¹³C. Taking into account the isotopic purity of ¹³CO cylinder (Euriso-Top, 99% ¹³C), a thorough isotopic replacement leads to the following isotopic composition: 99% ¹³CH₄, 2% ¹²C¹³CH₆, 98% ¹³C₂H₆, 3% ¹²C¹³C₂H₈, 97% ¹³C₃H₈, *etc.* However, the typically measured ¹³C content is 0.5~1.5% lower than the estimation above(higher hydrocarbons show greater discrepancy). This discrepancy could be caused by (1) the negligence of the influence of ¹³C-labeling on fragmentation patterns; (2) the negligence of the kinetic influence of the ¹³C-labeling on hydrocarbon formation; or (3) the underestimated isotopic impurity in ¹³CO cylinder. Therefore the products are measured

sufficiently long after the SSITKA switch to make correction the deviation from 100% labeling possible.

Unfortunately, the GCMS equipped with CP-PoraBond Q column (Agilent, 10m x 0.53 mm x 10 um) is not able to measure Ne and CO, which are needed to correct for the gas-phase hold-up and chromatographic effect of CO, respectively. Furthermore, the tubing connecting the GCMS retards the gradient of gaseous concentration, causing the response measured by GCMS to be slower than that by online MS (shown in Figure 2.4). Therefore, the transient response measured by GCMS needed to be correlated to that by online MS. To this end, the methane response, which can be measured by both online MS and GCMS, was chosen to correct the GCMS results by the minimizing the following objective equation:

$$S(x) = \int_{t=0}^{t=t_{end}} F_{L} dt - x \int_{t=0}^{t=t_{end}} F_{S} dt$$
(2.9)

where S is the objective function to be minimized; x is the variable to be determined; t_{end} refers to the time of the last GCMS point; F_L refers to the ¹²CH₄ response measured by online MS; F_S refers to the ¹²CH₄ response measured by GCMS. Thereafter, the time scale of GCMS points were multiplied by a constant factor x to fit MS time scale. The result is presented in the bottom of Figure. 2.4. We assume that all the products are subject to the same transient signal broadening. So, this correction is applied to the transient response of all the products.



Figure 2.4. Correction of transient responses of methane by Equation (2.9).

2.4. Validation of differential operation

For an unambiguous interpretation of the SSITKA results, the experiments should be operated at differential conditions usually obtained at low conversion. Measuring under differential conditions requires that the influence of the decrease in partial pressures of CO and H_2 throughout the catalytic bed on the reaction rates is negligible, implying that the reaction rate remains constant throughout the catalyst bed. In this situation, the reaction can be modeled with a CSTR model. Furthermore, experiments should be performed in the absence of mass and heat transfer limitation. The validation is in Appendix I.

Typical results obtained with varying amount of catalyst in the reactor are presented in Figure 2.5, which shows that the steady state CO conversion increases linearly with catalyst loading up to 18% conversion with 50 mg catalyst. The figure also suggests that the operation with the conversion below 20% guarantees differential conditions. The maximum catalyst loading appears to increase with decreasing reaction temperature (not shown). Typically, 20 mg, 100 mg and 200mg catalyst is used at 260°C, 240°C and 220°C, respectively. The linear relationship between the conversion and catalyst loading implies that the reaction rate is constant over the reactor bed. This result allows us to ignore the mass gradients along the catalytic bed and describe the reaction by an ordinary differential equation set based on a CSTR model.



Figure 2.5. CO conversion as a function of catalyst loading. The red spot refers the typical catalyst loading. Conditions: $p_{CO} = 45$ mbar, $p_{H_2} = 450$ mbar, $T = 260^{\circ}$ C.

References

- I. Chorkendorff, J.W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, Wiley, Weinheim, 2003.
- [2] R.L. Gorring, V.W. Weekman, Ind. Eng. Chem. 58 (1966) 18–19.
- [3] J.M. Smith, Ind. Eng. Chem. Fundam. 21 (1982) 327–332.
- [4] H. Kobayashi, M. Kobayashi, Catal. Rev. –Sci. Eng. 10 (1974) 139–176.
- [5] C.O. Bennett, Catal. Rev. –Sci. Eng. 13 (1976) 121–148.
- [6] C. Wagner, K. Hauffe, Z. Elektrochem. 45 (1939) 409–425.

- [7] K. Tamaru, Adv. Catal. 15 (1965) 65–90.
- [8] M. Kobayashi, Chem. Eng. Sci. 37 (1982) 393–401.
- [9] C. Wagner, Adv. Catal. 21 (1970) 323–381.
- [10] J. Happel, E. Walter, Y. Lecourtier, Ind. Eng. Chem. Fundam. 25 (1986) 704-712.
- [11] Y. Soong, P. Biloen, Langmuir 1 (1985) 768–770.
- [12] P. Winslow, A.T. Bell, J. Catal. 86 (1984) 158–172.
- [13] A. Frennet, C. Hubert, J. Mol. Catal. A: Chem. 163 (2000) 163–188.
- [14] A. Frennet, T. Visart de Bocarmé, J.-M. Bastin, N. Kruse, J. Phys. Chem. B 109 (2005) 2350–2359.
- [15] A. Bundhoo, J. Schweicher, A. Frennet, N. Kruse, J. Phys. Chem. C 113 (2009).
- [16] J. Schweicher, A. Bundhoo, A. Frennet, N. Kruse, H. Daly, F.C. Meunier, J. Phys. Chem. C 114 (2010) 2248–2255.
- [17] E. Vesselli, J. Schweicher, A. Bundhoo, A. Frennet, N. Kruse, J. Phys. Chem. C 115 (2011) 1255–1260.
- [18] J. Schweicher, A. Bundhoo, N. Kruse, J. Am. Chem. Soc. 134 (2012) 16135–16138.
- [19] J. Happel, S. Kiang, J.L. Spencer, S. Oki, M.A. Hnatow, J. Catal. 50 (1977) 429-440.
- [20] J. Happel, Chem. Eng. Sci. 33 (1978) 1567.
- [21] P. Biloen, J. Mol. Catal. 21 (1983) 17–24.
- [22] P. Biloen, J.N. Helle, F.G.A. van den Berg, W.M.H. Sachtler, J. Catal. 81 (1983) 450–463.
- [23] Y. Soong, K. Krishna, P. Biloen, J. Catal. 97 (1986) 330–343.
- [24] J. Yang, Y. Qi, J. Zhu, Y.-A. Zhu, D. Chen, A. Holmen, J. Catal. 308 (2013) 37-49.
- [25] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Langmuir 26 (2010) 16558–16567.
- [26] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P.d. Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [27] V. Frøseth, S. Storsæter, Ø. Borg, E.A. Blekkan, M. Rønning, A. Holmen, Appl. Catal., A 289 (2005) 10–15.
- [28] S. Vada, B. Chen, J.G. Goodwin, J. Catal. 153 (1995) 224–231.
- [29] N. Lohitharn, J. Goodwin Jr, Catal. Commun. 10 (2009) 758–762.
- [30] N. Lohitharn, J. Goodwin, J. Catal. 257 (2008) 142–151.
- [31] N. Lohitharn, J. Goodwin, J. Catal. 260 (2008) 7–16.
- [32] H.A.J. van Dijk, The Fischer–Tropsch synthesis A mechanistic study using transient isotopic tracing, Eindhoven University of Technology, Eindhoven, 2001.
- [33] N.S. Govender, Mechanistic study of the High- Temperature Fischer-Tropsch Synthesis using transient kinetics, Eindhoven University of Technology, Eindhoven, 2010.
- [34] S.L. Shannon, J.G. Goodwin, Chem. Rev. 95 (1995) 677–695.
- [35] Y. Qi, J. Yang, D. Chen, A. Holmen, Catal. Lett. 145 (2015) 145–161.
- [36] C. Ledesma, J. Yang, D. Chen, A. Holmen, ACS Catal. 4 (2014) 4527–4547.


Science is a twinkle star, like a diamond in the sky.

Chapter 3

Mechanism of CO dissociation on a cobalt Fischer– Tropsch catalyst

Abstract

The way how the triple bond in CO is dissociated, a key reaction step in the Fischer– Tropsch (F–T) reaction, is a subject of intense debate. Direct CO dissociation on a Co catalyst was probed by ${}^{12}C^{16}O/{}^{13}C^{18}O$ scrambling in the absence and presence of H₂. The initial scrambling rate without H₂ is significantly higher than the rate of CO consumption under CO hydrogenation conditions, indicating that the surface contains sites sufficiently reactive to dissociate CO without H-assistance. Only a small fraction of the surface is involved in CO scrambling. The minor influence of CO scrambling and CO residence time on H₂ partial pressure shows that CO dissociation is not affected by the presence of H₂. The positive H₂ reaction order is correlated to hydrogenation of adsorbed C and O atoms being slower than CO dissociation. Temperature-programmed *in situ* IR spectra underpin the conclusion that CO dissociation does not require H atoms.



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3.1 Introduction

CO bond dissociation is the initiating step of the Fischer–Tropsch (F–T) reaction, which is at the heart of rapidly growing industrial gas-to-liquids technology to convert synthesis gas into clean transportation fuels [1-3]. There has been considerable debate on the mechanism of CO dissociation. Density functional theory (DFT) calculations have demonstrated that step-edge sites of sufficiently reactive metals such as cobalt [4, 5] and ruthenium [6] can directly dissociate CO with much lower activation barriers than terrace sites. This mechanism is similar to the well-accepted mechanism of N₂ dissociation on step-edge sites of ruthenium nanoparticles relevant to NH_3 synthesis [7]. However, whether these coordinatively unsaturated sites are active during the F-T reaction has been questioned as they are vulnerable to poisoning by strongly adsorbed CO or reaction intermediates [8, 9]. H-assisted CO dissociation on terrace sites is therefore considered as an alternative pathway in which CO is hydrogenated to HCO [10] or HCOH [11-13] intermediates prior to C-O bond cleavage. This CO dissociation pathway has been invoked in mechanisms that take place on highly CO-covered terraces [14, 15]. Besides, the way of CO dissociation also depends on the crystallographic structure of the catalyst nanoparticles [16]. So far, convincing experimental evidence for either of these two pathways is still lacking. In this chapter, we employ ${}^{12}C^{16}O/{}^{13}C^{18}O$ scrambling and *in situ* infrared spectroscopy to provide new insights into the mechanism of CO dissociation on cobalt Fischer-Tropsch catalyst.

3.2 Experimental and computational methods

3.2.1 Preparation

A silica-supported cobalt catalyst promoted by platinum in the present study was prepared by incipient wetness impregnation method with SiO₂ (120–250 μ m) using an aqueous solution of Co(NO₃)₂·6H₂O (Merck, 99.99%) and Pt(NH₃)₄·(NO₃)₂ (Alfa Aesar, 99.995%) as precursor. Pt was added as a reduction promoter. The metal loadings as determined by ICP–OES (Spectroblue, AMETEK Inc.) analysis after dissolving the catalyst in a mixture of nitric acid and hydrogen fluoride were 17.1 wt% cobalt and 0.04 wt% platinum. The catalyst was dried at 110°C for 12 h and then calcined at 350°C in air for 2 h with a ramp of 1°C min⁻¹.

3.2.2 Characterization

H₂-chemisorption

The amount of accessible surface cobalt atoms was measured by H₂-chemisorption on Micromeritics ASAP 2010. Typically, 200 mg sample was *in situ* reduced at 450°C and measured at 110°C. The total H₂ uptake was determined by extrapolating the straight-line

portion of adsorption isotherm to zero pressure. The adsorption stoichiometry factor of H_2 is assumed to be 2, *i.e.*, one H on per cobalt atom. The result shows that there are 116.7 µmol surface cobalt atoms per gram of Co/SiO₂ catalyst. This number was employed to calculate the sites normalized rate, *i.e.*, turn over frequency (*TOF*).

Temperature-programmed reduction

The reduction degree of cobalt was determined by temperature-programmed reduction on ASAP 2920 II (Micromeritics), in which typically 10 mg sample was reduced in diluted H_2 flow (10% H_2 in Ar) using a heating rate of 10°C min⁻¹. The results are shown in Figure 3.1. A silver oxide reference sample (provided by Micromeritics) was used as reference to calibrate the H_2 consumption. It was found that addition of 0.04 wt% platinum enhances the reduction degree of cobalt from 64% to 93%.



Figure 3.1. TPR profiles of Co/SiO₂ and Pt promoted Co/SiO₂ samples.

Transmission electron microscopy

Transmission electron microscopy (TEM) images recorded on a FEI Tecnai 20 transmission electron microscope at an acceleration voltage of 200 kV using a LaB6 filament allow estimating the volume-averaged cobalt particle size at 15 nm [<u>17</u>, <u>18</u>]. A TEM image and a statistical analysis are presented in Figure 3.2.

In situ X-ray diffraction

In situ X-ray diffraction (XRD) patterns were obtained on a D/max-2600 X-ray diffraction instrument (Rigaku). The ground sample was *in situ* reduced in a 10% H₂ flow with a heating rate of 5°C min⁻¹. The XRD patterns were recorded every 25°C. As shown in Figure 3.3, cobalt reduction proceeds through two stages, *i.e.*, Co₃O₄ to CoO at 210°C and CoO to

metallic Co at 390°C. This is fully consistent with TPR result. The XRD pattern recorded at 450°C exhibits the characteristic of face-centered cubic (*fcc*) crystalline structure cobalt (PDF 15-0806 [19]). The crystallite size of reduced cobalt estimated by Scherrer equation is 14.7 nm, which is consistent with the result of TEM.



Figure 3.2. TEM image (a) and Co particle size distribution (b) of SiO₂ supported cobalt catalyst.



Figure 3.3. XRD patterns obtained in a 10% H₂ flow with increasing temperature.

Infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were recorded by Bruker Vertex V70v instrument. Typically, 18~20 mg of ground Co/SiO₂ catalyst was pressed into a self-supporting wafer that was placed in a controlled-environment infrared transmission cell, which is capable of heating and cooling, gas dosing and evacuation. For reduction, the catalyst wafer was first heated to 450°C at a rate of 5°C min⁻¹ in H₂ flow and kept at this temperature for 2 h. Then, the cell was evacuated at 450°C for 1 hour, then cooled to 35°C in vacuum. The IR spectrum at this condition was recorded as background spectrum. The gases can be introduced by either 6-way valve dosing or by needle valve (LEYBOLD).

To record the IR spectra with increasing temperature, the cell with catalyst wafer was first pressurized to 10 mbar of CO, during which the IR spectra were recorded at different CO pressures. After that, the IR cell was heated to 300°C at a rate of 5°C min⁻¹. The IR spectra were recorded every 5°C at a 2 cm⁻¹ resolution and averaged over 16 accumulations. The *in situ* IR experiments in the presence of H₂ in cell, as well as the reference experiment on Pt/SiO₂ catalyst, were carried out by the similar procedure as described above.

To obtain C pre-covered Co/SiO₂ catalyst, reduced sample was first exposed to 0.05 mbar of C_2H_2 at 50°C for 15 minutes. Subsequently, the cell was heated to 130°C in vacuum, and kept at this temperature for 30 minutes to decompose adsorbed C_2H_2 . After that, the cell was cooled to 35°C, and ready for the upcoming IR measurement. To get O pre-covered Co/SiO₂ catalyst, reduced sample was exposed to 0.5 mbar of N₂O at 50°C for 15 min, followed by evacuation at 50°C for 30 minutes to decompose N₂O. After that, the cell was cooled to 35°C.

Temperature-programmed hydrogenation

To study the influence of H_2 partial pressure on the amount of carbon deposits formed during the F–T reaction, the catalysts were subjected to the F–T reaction for 45 h at 220°C with H_2 /CO ratio of 1 and 2, respectively. The catalysts were subsequently flushed by H_2 at 220°C for 6 h to remove the carbonaceous species that cannot be hydrogenated during the reaction, then cooled to 35°C in Ar flow. The temperature-programmed hydrogenation (TPH) experiments were then conducted by heating the reactor to 550°C with the ramp of 5°C min⁻¹ in diluted H_2 flow (10% H_2 in Ar, 50 mL min⁻¹ in total). The product of hydrogenation, *i.e.*, CH₄, was monitored by online MS with *m/z* value of 15. To determine the exact CH₄ flow rate, the MS signal was calibrated by measuring a known gas mixture. The amount of the carbon deposits was determined by integrating the CH₄ flow over timeon-stream, and normalized based on the amount of Co surface atoms.

3.2.3 Catalytic test and ¹²C¹⁶O/¹³C¹⁸O scrambling

In a typical experiment, 200 mg Co/SiO₂ catalyst was loaded into a tubular reactor and diluted by SiC. An *in situ* reduction was performed in a diluted H_2 flow (10% H_2 in Ar, 50

mL min⁻¹ in total) at 450°C (with a ramp of 2°C min⁻¹) and atmospheric pressure for 16 h. To remove adsorbed H, the catalyst was flushed by an Ar flow (50 mL min⁻¹) at 470°C for 2 h. The reactor was subsequently cooled to 220°C in Ar flow and the pressure was increased to 1.5 bar. The scrambling experiments in the absence of H₂ were performed by switching from Ar (4 mL min⁻¹) to a ${}^{12}C^{16}O/{}^{13}C^{18}O/Ne$ (Cambridge Isotope Laboratories, ${}^{13}C$ 99%, ${}^{18}O$ 95%) mixture (1.5/1.5/1 mL min⁻¹), in which the Ne was used as inert tracer. In the scrambling experiments with H₂, a ${}^{12}C^{16}O/{}^{13}C^{18}O/H_2/Ne$ feed was used, in which the H₂ flow rate varies to meet different H₂/CO ratios. Besides, an extra Ar flow was used to dilute feeding and keep the total flow at 50 mL min⁻¹.

The catalytic activity was determined online by analyzing the effluent gas on a GC (VARIAN CP-3800) equipped with TCD (CP-Molsieve 5A + CP-PoraBOND Q column) for CO₂, CO, H₂ and CH₄, FID (Rt@-Q-BOND column) for hydrocarbons. A calibrated online quadrupole mass spectrometry (ESS, GeneSys Evolution) was used to monitor the transient responses of ¹²C¹⁶O (m/z = 28), ¹³C¹⁶O (m/z = 29), ¹²C¹⁸O (m/z = 30), ¹³C¹⁸O (m/z = 44), ¹³C¹⁶O₂ (m/z = 45), ¹²C¹⁶O¹⁸O (m/z = 46), ¹³C¹⁶O¹⁸O (m/z = 47), ¹²C¹⁸O₂ (m/z = 48) and ¹³C¹⁸O₂ (m/z = 49). A GCMS (Shimazu GCMS-QP 2010) equipped with a 16-loop valve (Valco) was used to analyze the isotopic composition of CO and CO₂. Detailed data analysis procedure is provided in Section 2.3.



Figure 3.4. Schematic presentation of ¹³C¹⁸O/¹²C¹⁶O scrambling.

During the scrambling experiment, the ${}^{12}C^{16}O/{}^{13}C^{18}O$ mixture can dissociate and recombine into four CO isotopologues (schematically shown in Figure 3.4). As the ${}^{12}C^{16}O$ or ${}^{13}C^{18}O$ in the effluent can be formed via scrambling with the same rate (ignoring the isotopic effects) as ${}^{13}C^{16}O$ or ${}^{12}C^{18}O$, the scrambling rate is twice as high as the ${}^{13}C^{16}O$ or ${}^{12}C^{18}O$ formation rate, and defined as following:

$$TOF_{\text{scrambling}} = 2 \times \frac{F_{\text{CO}}([{}^{13}\text{C}{}^{16}\text{O}] + [{}^{12}\text{C}{}^{18}\text{O}])}{A_{\text{Co}}}$$
(3.1)

where the F_{CO} refers to the effluent CO flow determined by GC; $[{}^{13}C^{16}O]$ and $[{}^{12}C^{18}O]$ refer to the isotopic composition of ${}^{13}C^{16}O$ and ${}^{12}C^{18}O$, respectively, determined by GCMS,

and corrected for the 0.1mol% ¹³C natural abundance in ¹²C¹⁶O cylinder, and 1% ¹²C and 5% ¹⁶O in ¹³C¹⁸O cylinder; A_{Co} refers to the amount of Co surface atoms measured by H₂-chemisorption. Based on these, the signals of CO isotopologues obtained by online MS can be quantified.

3.2.4 Steady state isotopic transient kinetic analysis

Steady state isotopic kinetic analysis (SSITKA) has been used to determine the residence time and coverage of reaction intermediates.² Typically, 200 mg Co/SiO₂ catalyst diluted with SiC was loaded in a low dead-volume stainless steel tubular reactor with 5 mm inner diameter and 80 mm bed length. The sample was *in situ* reduced in a diluted H₂ flow (10% H₂ in Ar, 50 mL min⁻¹ in total) at 450°C using a heating rate of 2°C min⁻¹ and atmospheric pressure for 16 h. Subsequently, the reactor was cooled to 220°C in Ar flow and the pressure was increased to 3 bar. Thereafter, the feed was switched to a mixture of ¹²CO, H₂, and Ar for 16 h to obtain steady state conversion of the Fischer–Tropsch (F–T) reaction. The H₂ flow was adjusted to obtain the desired H₂/CO ratios. The Ar flow was used to dilute the feed and keep the total flow constant at 50 mL min⁻¹.

The SSITKA experiment was performed by switching from ¹²CO/H₂/Ar to ¹³CO/H₂/Ne. An extra Ar flow was used to keep the total flow at 50 mL min⁻¹. The transients of ¹²CO (m/z = 28) and ¹³CO (m/z = 29), the main hydrocarbon product ¹²CH₄ (m/z = 15) and ¹³CH₄ (m/z = 17), and the inert tracers (Ne, m/z = 22) were recorded by online mass spectroscopy (quadrupole mass spectrometer, ESS, GeneSys Evolution). From the mass spectrometer signals during the switch, the surface residence times were calculated via the area under the normalized transient curves N_i , and corrected for the gas phase hold-up with the use of the Ne inert tracer:

$$\tau_{\rm i} = \int_0^\infty (N_{\rm i} - N_{\rm Ne}) \mathrm{d}t \tag{3.2}$$

The CH_x (intermediates of CH₄) residence time was corrected for the chromatographic effect of CO by subtracting half of the CO residence time by the following [9, 20, 21]: τ_{CH_4} (corrected) = $\tau_{CH_4} - \frac{1}{2}\tau_{CO}$ (3.3)

The number of reversibly adsorbed CO and CH_x species thereafter can be estimated from the residence time and effluent flow of these species. The coverage of the two species (θ_i) was calculated by dividing the number of relevant adsorbed species by the number of Co surface atoms (based on H₂-chemisorption).

$$\theta_{\rm CO} = \frac{\tau_{\rm CO}.F_{\rm CO}.(1-X_{CO})}{A_{\rm CO}}$$

$$\theta_{\rm CH_4} = \frac{\tau_{\rm CH_4}.F_{\rm CO}.X_{\rm CO}.S_{CH_4}}{A_{\rm CO}}$$

$$(3.4)$$

where F_{CO} refers to the CO feeding, X_{CO} and S_{CH_4} refer to the CO conversion and CH₄ selectivity, respectively, determined by GC.

Transient experiment consisting of a switch from Ne (1.5 mL min⁻¹) to ¹²CO/Ar (0.5/1 mL min⁻¹) on *in situ* reduced catalyst was performed to measure the total CO coverage at 35°C. The coverage of reversibly adsorbed CO at 35°C was measured by performing a switch from ¹²CO/Ar (0.5/1 mL min⁻¹) to ¹³CO/Ne (0.5/1 mL min⁻¹). In both cases, an extra 48.5 mL min⁻¹ Ar flow was used to dilute the CO partial pressure to 15 mbar (with respect to 1.5 bar total pressure), which is close to the CO pressure used in FTIR experiment. The transient responses of ¹²CO (m/z = 28), ¹³CO (m/z = 29), and Ne (m/z = 22) were monitored by online MS. The CO coverage was calculated by the same approach as mention above (Eq. 3.2 and Eq. 3.4).

3.2.5 Infrared modeling by DFT

All quantum chemical calculations were performed using a plane-wave density functional theory approach with the projector-augmented wave (PAW) method, as implemented in the Vienna ab initio simulation package (VASP). For exchange-correlation, the Perdew-Burke-Ernzerhof (PBE) functional was used. For the plane wave basis set the kinetic energy cutoff was set at 400 eV. A Monkhorst–Pack mesh k-points of $(5 \times 5 \times 1)$ was used for both cobalt surface slabs. The Co(0001) slab is a 3×3 supercell with 5 layers of metal, corresponding to 45 Co atoms. The Co(11 $\overline{2}$ 1) slab is a 2 × 2 supercell with 3 layers of metal, corresponding to 48 Co atoms. The periodic images of the slabs in the z-direction are separated using a 15 Å vacuum layer. Adsorptions on the Co(0001) surface slab were done mirrored over the xy-plane to avoid dipole-dipole interaction between the super cells. For the Co(11 $\overline{2}$ 1) surface slab the adsorbates were placed using an offsetted inversion. The calculations were performed spin polarized and the degrees of freedom of the system were optimized using the conjugate-gradient technique. The lattice parameters giving the lowest bulk energy for our calculations are 2.49 Å, 2.49 Å and 4.03 Å for a-, b- and c-directions, respectively. For calculation of the CO gas phase reference, only the γ -point was used. The gas phase reference was calculated using a $10 \times 10 \times 10$ Å cell containing one CO.

To obtain the vibrational modes of CO we carried out frequency calculations using the finite displacement technique. This is done by calculating the change in force of atom i upon a displacement of atom j. The corresponding Hessian matrix (Eq. 3.6) is massweighted (Eq. 3.7) and undergoes diagonalization. The eigenvalues are then used to get the frequencies (Eq. 3.8). The resulting dipoles upon displacement (Eq. 3.9) were calculated to obtain a relative measure of the infrared intensities [22, 23]. The electronic potential was not explicitly corrected for these dipoles, as this is not necessary when CO is placed on both sides of the surface symmetrically.

$$H_{i,j} = \frac{\partial^2 E}{\partial x_i \partial x_j} \tag{3.6}$$

$$H_{i,j}^m = \frac{H_{i,j}}{\sqrt{M_i \cdot M_j}} \tag{3.7}$$

$$\boldsymbol{\nu}_{i} = \frac{1}{2\pi c} \sqrt{\boldsymbol{\varepsilon}_{i}}$$

$$\boldsymbol{I}_{\nu} \propto \left| \frac{\partial \vec{\mu}}{\partial q_{i}} \right|^{2}$$
(3.8)
(3.9)

The reported stretching frequencies correspond to the particular vibrational mode where the vibration on the top side of the surface is in-phase with the vibration on the bottom side of the surface. This is illustrated in Figure 3.5. For the gas phase reference, we computed a stretching frequency of 2125 cm⁻¹. This is an underestimation of the experimentally found frequency of 2143 cm⁻¹. Therefore, the reported frequencies have been systematically increased by 0.85%. For a perfectly symmetrical system, the in-phase vibration should give an intensity of zero because of the cancelling dipoles. Therefore, we used the combined intensity of the in-phase and out-phase vibrations.



Figure 3.5. An illustration of the in-phase and out-phase vibrations of CO adsorbed on both sides of a terrace Co(0001) or step $Co(11\overline{2}1)$ unit cell.

3.3 Results and discussion

3.3.1 ¹³C¹⁸O/¹²C¹⁶O scrambling

Following the isotopic scrambling of a ${}^{12}C^{16}O/{}^{13}C^{18}O$ mixture provides a means of investigating C–O bond dissociation in the absence of H₂ [24]. This reaction leads to scrambled ${}^{13}C^{16}O$ and ${}^{12}C^{18}O$ products, demonstrating that CO dissociates and atomic C+O recombine in the absence of H₂. In addition, CO₂ is obtained due to the recombination of CO with O, which is usually termed the Boudouard reaction. Both scrambling and CO₂ formation require CO dissociation. These two reactions may share the same type of active site [25]. These reactions lead to a Co surface covered with C and lesser extent O atoms.

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The CO consumption rate (equal to two times the CO₂ formation rate) and the scrambling rate expressed as turnover frequencies (*TOF*) are displayed in Figure 3.6. The results show that both rates decrease rapidly with time. As the surface of the reduced Co catalyst was initially empty, the C atoms that are deposited during the Boudouard reaction inhibit both CO₂ formation and CO scrambling [26]. Due to the chromatographic effect of CO, the first measurable scrambling rate was determined after 15 s. The *TOF* of 1.6×10^{-2} s⁻¹ is five times higher than the rate of CO consumption in the presence of H₂ (H₂/CO ratio = 2, *TOF* = 3×10^{-3} s⁻¹, see Figure 3.7). The significantly higher scrambling rate implies that the intrinsic rate of direct CO dissociation is sufficiently high to provide the C monomers for hydrocarbon formation during CO hydrogenation in the presence of H₂. We stress that CO dissociation can still control the overall rate at the higher CO coverage encountered under actual F–T conditions [27].



Figure 3.6. Dependence of CO consumption, CO scrambling rate (expressed as turnover frequency (*TOF*), left axis), and carbon coverage (right axis) on time-on-stream (*TOS*) at 220°C (conditions: $p_{12}_{C^{16}_{O}} = p_{13}_{C^{18}_{O}} = 45$ mbar). Lines correspond to MS measurements and data points correspond to GC-MS measurements.

Figure 3.7. Dependence of CO consumption and scrambling rate in the presence of H₂ on time-on-stream at 220°C (conditions: $p_{12}C^{16}O = p_{13}C^{18}O = 45$ mbar, $p_{H_2} = 180$ mbar).

As CO₂ and C are formed in equimolar amounts, it becomes possible to quantify the amount of C atoms deposited as a function of time-on-stream. About 90% of the activity for CO dissociation is lost when less than 1/5 of the Co metal surface is covered by C atoms. Based on a statistical analysis [28, 29], 15 nm *fcc* particles comprise about 20% coordinatively unsaturated atoms. Considering the size of the particles, step-edge sites will dominate over edge and corner sites. This result indicates that not terrace sites but a minority site is involved in C-O bond dissociation, and that the observed rapid deactivation of CO bond dissociation in the absence of H₂ is resulted from the blocking of step-edge

sites by adsorbed C atoms. Considering that a large part of the rate stems from a small fraction of surface sites, it can be inferred that step-edge sites are responsible for the CO activation. This is in line with the microkinetic simulations results [30, 31].

In order to study the CO dissociation under conditions more relevant to the F–T reaction, we also investigated CO scrambling in the presence of H₂ by co-feeding H₂ with ${}^{12}C^{16}O/{}^{13}C^{18}O$ mixtures at 220°C at different H₂/CO ratios. A typical result obtained at H₂/CO = 2 is shown in Figure 3.7. CO is mainly converted into hydrocarbons and only a small amount of CO₂ (Table 3.1). The scrambling rate is initially comparable with CO consumption, but rapidly decreases due to the build-up of reaction intermediates. The scrambling rate at steady state (0.95×10^{-3}) is slightly lower than that in experiment without H₂ (1.4×10^{-3}). This small decrease in CO scrambling rate can be explained by hydrogenation of C and O surface intermediates being relatively slow compared with CO dissociation. The presence of H₂ therefore only slightly affects recombination rate. We note that the CO dissociation rate equals the sum of the CO consumption rate and the scrambling rate relates to the recombination rate.

Table 3.1. The catalytic performance of the F–T using a mixture of ${}^{12}C^{16}O$, ${}^{13}C^{18}O$, H₂ and Ar (balance) on Co/Sio₂ catalyst. The data presented below were determined by online GC after 1 h time-on-stream. Selectivity is determined on the basis of carbon balance. Condition: $p_{12}_{C^{16}O} = p_{13}_{C^{18}O} = 45$ mbar; T = 220 °C.

p_{H_2}	TOF	Sel(CH ₄)	$Sel(C_2-C_4)$	$Sel(C_5+)$	$Sel(CO_2)^a$	$\alpha^{\rm b}$
mbar	s ⁻¹	%	%	%	%	
90	0.0021	26	35	31.2	7.8	0.55
180	0.0035	29	34	32	5	0.55
270	0.0049	32	33	31.5	3.5	0.56

^a based on carbon balance.

^b chain-growth probability, determined based on C₃-C₇.





Figure 3.8. CO consumption (squares) and scrambling (circles) rates as a function of H₂ partial pressure at 220°C (conditions: $p_{^{12}C^{16}O} = p_{^{13}C^{18}O} = 45$ mbar).

Figure 3.9. Residence times (solid symbols, left axis) and surface coverages (open symbols, right axis) of CO (squares) and CH_x (circles) as a function of H₂ partial pressure (SSITKA, $p_{CO} = 180$ mbar, $T = 220^{\circ}$ C).

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Figure 3.8 presents the CO scrambling and consumption rates as function of the H₂ partial pressure after 1 h on stream. The strong dependence of the CO consumption rate on H₂ pressure (H₂ reaction order ≈ 0.7) is typically observed during CO hydrogenation on Co catalysts [12]. On the other hand, the steady state CO scrambling rate hardly changes with H₂ partial pressure. Our steady state isotopic transient kinetic analysis (SSITKA) results (Figure 3.9) reveal that the CO residence time (τ) and CO coverage (θ) are nearly independent of the H₂ partial pressure, which is consistent with previous work [12]. Taking into account the observation that C and O atoms can recombine, the measured residence time of CO not only depends on reversible adsorption of CO but also on CO dissociation and recombination reactions. As reversible CO adsorption is not expected to be dependent on the H₂ pressure, a constant residence time implies that the reversible dissociation rate is practically independent of H₂ pressure. Below we provide further evidence that H₂ is not involved in CO dissociation, although based on Figure 3.8 alone a parallel mechanism involving H atoms cannot be excluded.



Figure 3.10. Temperature-programmed hydrogenation profiles of the spent catalysts, which are subjected to the F–T reaction (top: $p_{H_2} = 200$ mbar, $p_{CO} = 200$ mbar, $T = 220^{\circ}$ C; bottom: $p_{H_2} = 400$ mbar, $p_{CO} = 200$ mbar, $T = 220^{\circ}$ C) for 45 h followed by H₂ flush at reaction temperature for 6 h. The amount of carbon deposits was determined by integrating CH₄ flow, and normalized based on the amount of Co surface atoms.

The findings described above lead to the conclusion that the overall process of CO adsorption/desorption accompanied by reversible CO dissociation is independent of the presence of H_2 . On the contrary, the residence time of CH_x reaction intermediates strongly depends on H_2 partial pressure, which demonstrates that not CO dissociation but hydrogenation of adsorbed C causes the positive H_2 reaction order. In view of literature [32, 33] O hydrogenation also controls the overall reaction rate. In this sense, the increase in CO dissociation rate (consumption + scrambling) with H_2 partial pressure is interpreted in terms of increasing rate of C and O removal. The relatively minor increase in the scrambling rate with H_2 partial pressure is also likely due to more rapid surface species removal. Separate

TPH experiments (Figure 3.10) clearly show that the total amount of C deposited, which is not explicitly involved in CO hydrogenation and not measurable by SSITKA, increases with decreasing H_2 partial pressure. This further underpins the strong dependence of C removal on H_2 partial pressure. A major kinetic implication of these results is that (i) direct CO dissociation is sufficiently fast and (ii) the H_2 pressure only affects overall CO consumption rate, as adsorbed H atoms increases the hydrogenation rate of adsorbed C and O, regenerating surface vacancies that are needed for CO dissociation and hydrogen adsorption.

3.3.2 Infrared spectroscopy

Additional proof for the possibility of direct CO dissociation on Co was obtained by *in situ* IR spectroscopy in transmission mode. We followed the IR absorption bands of CO chemisorbed on the reduced Co catalyst, which was extensively evacuated at elevated temperature prior to CO adsorption. The catalyst was exposed to CO at 35°C, followed by heating at 5°C/min to 300°C. Figure 3.11 shows the evolution of the IR spectra for three cases: (a) without H₂ and in the presence of (b) 5 mbar H₂ and (c) 10 mbar H₂. After exposure to CO, a prominent band appears at 2026 cm⁻¹ due to CO adsorbed on top sites of metallic Co [34-36]. With increasing temperature, this band undergoes a blue-shift to 2060 cm⁻¹, which starts at 150°C [37]. At high temperature, the intensity becomes lower, presumably due to desorption of CO [38]. The observation of the asymmetric stretching vibration of gaseous CO₂ at 2360 cm⁻¹ (Figure 3.12) accompanied by the blue-shift of adsorbed CO suggests that these two changes are correlated. The formation of CO₂ implies that CO dissociates and C atoms remain on the surface. In a reference experiment using a SiO₂-supported Pt catalyst, we did not observe a blue-shift as observed for Co (Figure 3.13),



Figure 3.11. IR spectra of CO adsorption band on the cobalt-based F–T catalyst as a function of temperature (a) in the absence of H_2 and in the presence of (b) 5 mbar and (c) 10 mbar H_2 . The normalized signal intensity is presented by contour labels.

consistent with the notion that Pt cannot dissociate CO under these conditions [<u>39</u>]. Accordingly, we speculate that the blue-shift for the Co catalyst is due to lateral interactions of CO with adsorbed C and, possibly, O atoms released from CO dissociation.

To verify that lateral CO–C and CO–O interactions cause the CO frequency shift, we recorded IR spectra of CO adsorption on Co surfaces where either C or O atoms were predeposited. We also used DFT calculations to determine the influence of co-adsorbates on the stretching frequency of top-adsorbed CO. C was deposited on the surface by exposure to 0.05 mbar C_2H_2 at 50°C, followed by evacuation at 130°C to decompose adsorbed C_2H_2 to C and H_2 , a procedure taken from surface science studies [40]. The O atoms were adsorbed by exposing the reduced catalyst to 0.5 mbar N_2O at 50°C, followed by evacuation at the same temperature. C and O coverages obtained in this way could not be quantified in these experiments in the IR cell. The effect of co-adsorbates is, however, clear.

The reference spectra depicted in Figure 3.14a relate to an initially clean Co surface. Without co-adsorbates, the CO band appears at 1996 cm⁻¹ at the lowest CO coverage, which shifts to 2018 cm⁻¹ with increasing coverage (final CO pressure: 10 mbar). Based on the IR results of CO adsorption on a Co(0001) single crystal by Weststrate *et al.* [41], we estimate the CO coverage to be 0.35 ML. In good agreement with this, we determined the total CO coverage and the reversibly adsorbed CO coverage of 0.38 ML and 0.31 ML at a CO partial pressure of 15 mbar by Ne \rightarrow ¹²CO and ¹²CO \rightarrow ¹³CO switches, respectively, on the reduced Co catalyst at 35°C (shown in Figure 3.15). These experimental data are in good agreement with DFT calculations of CO adsorbed on a Co(0001) terrace (Table 3.2 and 3.3); the CO stretch frequency occurs at 1988 cm⁻¹ for a CO coverage of 0.11 ML. This band will shift to 2007 cm⁻¹ and 2026 cm⁻¹ at 0.22 ML and 0.33 ML CO coverages, respectively. At a slightly higher CO coverage of 0.67 ML, the frequency shifts to 2109 cm⁻¹. Saeys and co-workers reported that the maximum CO coverage is limited to 7/12 ML under practical F–T conditions [42].





Figure 3.12. IR spectra of CO adsorbed on Co/SiO_2 as a function of temperature in the presence of 10 mbar CO with region of gaseous CO_2 . The dashed line refers the normalized intensity of CO_2 band.

Figure 3.13. IR spectra of CO adsorbed on Pt/SiO_2 as a function of temperature in the presence of 10 mbar CO. The dashed line refers to the peak position of the IR band of adsorbed CO.



Figure 3.14. IR spectra of CO adsorption band on a cobalt-based F–T catalyst at 35°C: (a) reduced at 450°C, (b) pre-coverage by C atoms following acetylene adsorption on the clean Co surface and decomposition at 130°C, (c) pre-coverage by O atoms following nitrous oxide adsorption on the clean Co surface and decomposition at 50°C.



Figure 3.15. Normalized transient responses after switch (a) from Ne (45 mbar) to 12 CO/Ar (15/30 mbar) and (b) from 12 CO/Ar (15/30 mbar) to 13 CO/Ne (15/30 mbar), respectively, on *in situ* reduced Co/SiO₂ catalyst at 35 °C.

Experimental IR spectra at low CO coverage for the Co catalyst, partially pre-covered with atomic C and O species, show similar bands at 1998 cm⁻¹ and 1995 cm⁻¹, respectively. With increasing CO coverage, the blue-shift is, however, much stronger for the pre-covered surfaces (2053 cm⁻¹ and 2058 cm⁻¹ for partially C- and O-covered surfaces, respectively) than for the initially clean surface (2018 cm⁻¹). Qualitatively, these data are in agreement with the CO IR data for Co(0001) with frequency shifts of 47 cm⁻¹ and 42 cm⁻¹ for 0.5 ML C and 0.2 ML O, respectively, with respect to an initial CO frequency of 2026 cm⁻¹ corresponding to 0.5 ML CO [<u>41</u>]. These results demonstrate that C and O atoms exert larger lateral repulsions on adsorbed CO than CO itself. DFT calculations (Table 3.4) confirm that co-adsorbed C and O atoms can cause the strong blue-shift. The results show

	Co(0001) - 0.11 ML			Co(1121) - 0.08 ML					
	top	fcc	bridge	hcp	top	bridge	3 <i>f</i> -a	3 <i>f</i> -b	B_5
C-O stretch	1988	1770	1804	1757	1979	1885	1729	1446	1147

Table 3.2. C–O bond vibrational frequencies $[cm^{-1}]$ and relative intensities (normalized to the top mode) at different adsorption sites on extended cobalt surfaces.

Table 3.3. C–O bond vibrational frequencies $[cm^{-1}]$ and relative intensities (normalized to the 0.11 ML coverage) at different CO coverages of the top sites on an extended Co terrace surface.

	Co(0001) - Top sites					
	0.11 ML	0.22 ML	0.33 ML	0.67 ML	1.0 ML	
C-O stretch	1988	2007	2026	2109	2152	

Table 3.4. C–O bond vibrational frequencies $[cm^{-1}]$ and relative intensities (normalized to the reference without co-adsorbates) of 0.25 ML top adsorbed CO on an extended Co terrace surface with C or O co-adsorbates on the hollow sites.

	Co(0001) - CO on top sites, C/O on three-fold sites						
	0.25 ML CO	+ 0.25 ML C	+ 0.50 ML C	+ 0.25 ML O	+ 0.50 ML O		
C–O stretch	2011	2039	2052	2049	2070		

that CO stretches at 2011 cm⁻¹ for a unit cell containing 0.25 ML CO in the absence of coadsorbates. The frequency shifts to 2052 cm⁻¹ and 2058 cm⁻¹ after adding 0.50 ML C and 0.25 ML O, respectively.

Taken together, these findings show that the shift observed during temperatureprogrammed CO dissociation can be explained by lateral interactions with C and O atoms. Accordingly, we interpret the onset of the CO frequency shift at 150°C in Figure 3.11a as the start of C–O bond dissociation on the clean Co surface. Figures 3.11b and 3.11c depict similar data recorded in the presence of 5 and 10 mbar H₂, respectively. Clearly, the onset of CO dissociation occurs at nearly the same temperature irrespective of whether H₂ is present. Based on these data, we infer that CO dissociation does not involve H₂.

Theoretical studies indicate that step-edge B_5 -type sites provide a unique low-barrier pathway for direct CO dissociation [43-45]. Alternatively, CO intermediates involving H have been proposed to be relevant to CO dissociation on less active terrace sites [10-15]. It has been shown that the overall barrier for direct CO dissociation on step edges is lower than those for the H-assisted pathways on step-edge and terrace sites[44, 45]. The IR and kinetic results discussed above demonstrate that H atoms need not be involved in the CO dissociation reaction. Accordingly, it is likely that step-edge sites are the sites at which CO dissociation occurs. This is in keeping with the finding that during CO scrambling in the absence of H₂, most of the activity is lost by covering the surface with a small number of C atoms. These C atoms migrate to the terrace and exert lateral interactions on co-adsorbed CO as demonstrated by IR spectroscopy. Under actual CO hydrogenation conditions, these C atoms will be hydrogenated, resulting in hydrocarbon formation, thereby regenerating the active sites for CO dissociation. We point out that the data of the present work do not exclude the parallel path of CO dissociation.

3.4 Conclusions

In summary, ${}^{12}C^{16}O/{}^{13}C^{18}O$ scrambling experiments in the absence of H₂ reveal that CO dissociation on a reduced Co catalyst is intrinsically fast and reversible. Only a minor fraction of the metallic Co surface, likely coordinatively unsaturated sites, are involved in direct CO dissociation. In the presence of H₂, the scrambling rate is slightly lower as slow C and O hydrogenation lower the coverage of C and O. The CO scrambling rate and CO residence time depend only weakly on H₂ partial pressure, implying that reversible CO adsorption and CO dissociation are only weakly affected by H₂. *In situ* IR spectroscopy confirms that CO dissociation is not affected by H₂. These findings indicate that the explanation for the near unity reaction order with respect to H₂ during the F–T reaction need not the involvement of H atoms in the assumed rate-limiting CO dissociation step. Instead, we propose that the removal of C and O species from the surface by hydrogenation controls the CO consumption rate. Removing these atoms from the surface regenerates the vacancies required for the F–T reaction.

References

- [1] F. Fischer, H. Tropsch, Brennst. Chem. 7 (1926) 97–104.
- [2] F. Fischer, H. Tropsch, Brennst. Chem. 11 (1930) 489–500.
- [3] M.E. Dry, J.C. Hoogendoorn, Catal. Rev. –Sci. Eng. 23 (1981) 265–278.
- [4] Q. Ge, M. Neurock, J. Phys. Chem. B 110 (2006) 15368–15380.
- [5] J.-X. Liu, H.-Y. Su, W.-X. Li, Catal. Today 215 (2013) 36–42.
- [6] S. Shetty, A.P.J. Jansen, R.A. van Santen, J. Phys. Chem. C 112 (2008) 14027– 14033.
- [7] K. Honkala, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Norskov, Science 307 (2005) 555–558.
- [8] J.M. González–Carballo, F.J. Pérez–Alonso, M. Ojeda, F.J. García–García, J.L.G. Fierro, S. Rojas, ChemCatChem 6 (2014) 2084–2094.
- [9] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P.d. Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [10] W.J. Mitchell, J. Xie, T.A. Jachimowski, W.H. Weinberg, J. Am. Chem. Soc. 117 (1995) 2606–2617.

- [11] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, J. Catal. 272 (2010) 287–297.
- [12] J. Yang, Y. Qi, J. Zhu, Y.-A. Zhu, D. Chen, A. Holmen, J. Catal. 308 (2013) 37-49.
- [13] Y. Qi, J. Yang, X. Duan, Y.-A. Zhu, D. Chen, A. Holmen, Catal. Sci. Technol. 4 (2014) 3534–3543.
- [14] D. Hibbitts, E. Iglesia, Account in Chemical Research 48 (2015) 1254–1262.
- [15] B.T. Loveless, C. Buda, M. Neurock, E. Iglesia, J. Am. Chem. Soc. 135 (2013) 6107–6121.
- [16] J.-X. Liu, H.-Y. Su, D.-P. Sun, B.-Y. Zhang, W.-X. Li, J. Am. Chem. Soc. 135 (2013) 16284–16287.
- [17] A. Borodziński, M. Bonarowska, Langmuir 13 (1997) 5613–5620.
- [18] J.M.G. Carballo, J. Yang, A. Holmen, S. García–Rodríguez, S. Rojas, M. Ojeda, J.L.G. Fierro, J. Catal. 284 (2011) 102–108.
- [19] H.-J. Zhang, H.-C. Kong, X. Yuan, Q.-Z. Jiang, J. Yang, Z.-F. Ma, Int. J. Hydrogen Energy 37 (2012) 13219–13226.
- [20] P. Biloen, J.N. Helle, F.G.A. van den Berg, W.M.H. Sachtler, J. Catal. 81 (1983) 450–463.
- [21] H.A.J. van Dijk, The Fischer–Tropsch synthesis A mechanistic study using transient isotopic tracing, Eindhoven University of Technology, Eindhoven, 2001.
- [22] D. Porezag, M.R. Pederson, Phys. Rev. B 54 (1996) 7830–7836.
- [23] M. Preuss, F. Bechstedt, Phys. Rev. B 73 (2006) 155413.
- [24] C. Strebel, S. Murphy, R.M. Nielsen, J.H. Nielsen, I. Chorkendorff, Phys. Chem. Chem. Phys. 14 (2012) 8005–801212.
- [25] I.M. Ciobîcă, R.A. van Santen, J. Phys. Chem. B 107 (2003) 3808–3812.
- [26] J. Nakamura, I. Toyoshima, K.-i. Tanaka, Surf. Sci. 201 (1988) 185-194.
- [27] M.E. Dry, in: I.T. Horvath (Ed.) Encyclopedia of Catalysis, Elsevier, Amsterdam, 2003, pp. 347–401.
- [28] R. van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189–230.
- [29] P. van Helden, I.M. Ciobîcă, R.L.J. Coetzer, Catal. Today 261 (2016) 48-59.
- [30] I.A.W. Filot, R.J.P. Broos, J.P.M. van Rijn, G.J.H.A. van Heugten, R.A. van Santen, E.J.M. Hensen, ACS Catal. 5 (2015) 5453–5467.
- [31] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Catal. Sci. Technol. 4 (2014) 3129– 3140.
- [32] C.J. Weststrate, P. van Helden, J. van de Loosdrecht, J.W. Niemantsverdriet, Surf. Sci. 648 (2016) 60–66.
- [33] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [34] M.J. Heal, E.C. Leisegang, R.G. Torrington, J. Catal. 51 (1978) 314–325.
- [35] G.A. Beitel, A. Laskov, H. Oosterbeek, E.W. Kuipers, J. Phys. Chem 100 (1996) 12494–12502.

- [36] J. Schweicher, A. Bundhoo, A. Frennet, N. Kruse, H. Daly, F.C. Meunier, J. Phys. Chem. C 114 (2010) 2248–2255.
- [37] J. Couble, D. Bianchi, J. Phys. Chem. C 117 (2013) 14544–14557.
- [38] G.R. Johnson, S. Werner, A.T. Bell, ACS Catal. 5 (2015) 5888–5903.
- [39] F. Kitamura, M. Takahashi, M. Ito, Surf. Sci. 223 (1989) 493–508.
- [40] A.B. T. Ramsvik, H.J. Venvik, F. Hansteen, M. Kildemo, T. Worren, Surf. Sci. 499 (2002) 183–192.
- [41] C.J. Weststrate, J. van de Loosdrecht, J.W. Niemantsverdriet, J. Catal. 342 (2016) 1– 16.
- [42] A. Banerjee, A.P. van Bavel, H.P.C.E. Kuipers, M. Saeys, ACS Catal. 5 (2015) 4756–4760.
- [43] R.A. van Santen, I.M. Ciobîcă, E. van Steen, M.M. Ghouri, Adv. Catal. 54 (2011) 127–187.
- [44] S. Shetty, A.P.J. Jansen, R.A. van Santen, J. Am. Chem. Soc. 131 (2009) 12874– 12875.
- [45] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.





Science is a rocket, by which I can go to the moon and back.

Chapter 4

Mechanism of cobalt-catalyzed CO hydrogenation: 1. Methanation

Abstract

The mechanism of CO hydrogenation to CH_4 at 260°C on a cobalt catalyst is investigated using steady state isotopic transient kinetic analysis (SSITKA) and backward and forward chemical transient kinetic analysis (CTKA). The dependence of CH_x residence time is determined by ${}^{12}CO/H_2 \rightarrow {}^{13}CO/H_2$ SSITKA as a function of the CO and H₂ partial pressure and shows that the CH₄ formation rate is mainly controlled by CH_x hydrogenation rather than CO dissociation. Backward $CO/H_2 \rightarrow H_2$ CTKA emphasizes the importance of H coverage on the slow CH_x hydrogenation step. The H coverage strongly depends on the CO coverage, which is directly related to CO partial pressure. Combining SSITKA and backward CTKA allows determining that the amount of additional CH₄ obtained during CTKA is nearly equal to the amount of CO adsorbed to the cobalt surface. Thus, under the given conditions overall barrier for CO hydrogenation to CH4 under methanation condition is lower than the CO adsorption energy. Forward CTKA measurements reveal that O hydrogenation to H₂O is also a relatively slow step compared to CO dissociation. The combined transient kinetic data are used to fit an explicit microkinetic model for the methanation reaction. The mechanism involving direct CO dissociation represents the data better than a mechanism in which H-assisted CO dissociation is assumed. Microkinetics simulations based on the fitted parameters confirms that under methanation conditions the overall CO consumption rate is mainly controlled by C hydrogenation and to a smaller degree by O hydrogenation and CO dissociation. These simulations are also used to explore the influence of CO and H₂ partial pressure on possible rate-controlling steps.



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4.1 Introduction

Fischer–Tropsch synthesis is a heterogeneously catalyzed reaction whereby synthesis gas (a mixture of carbon monoxide and hydrogen) is converted into liquid fuels and chemicals [1-3]. Known since the seminal works of Franz Fischer and Hans Tropsch in the 1920s [4, 5], the Fischer–Tropsch (F–T) reaction has led to large-scale industrial applications to upgrade carbonaceous feedstock such as coal and natural gas into more valuable liquid products. Supported cobalt is the preferred catalyst for the F-T reaction due to its high activity, high chain-growth probability, low water-gas shift activity and moderate deactivation [$\underline{6}$]. A key challenge of F-T technology in practice is to combine high yield of long-chain hydrocarbons with low methane selectivity. Even for methane, the simplest hydrocarbon product of the F-T reaction, the exact reaction mechanism has not been resolved yet. Mechanisms proposed for the F–T reaction are often based on postulated rate-determining steps leading to Langmuir-Hinshelwood equations [7] or have been developed using empiric rate equations [8]. Some of these models for the F–T reaction are very sophisticated in their ability to describe important kinetic parameters such as CO consumption rate [9], chain-growth probability [10], and other aspects such as olefin re-adsorption and hydrogenation [11, 12]. Nevertheless, given the complexity of the F–T reaction, the large number of involved reactants, products and reaction intermediates and the uncertainty about the reaction mechanism, there is a great need to investigate this important reaction in more detail.

Detailed insight into reaction mechanism, specifically into the way particular elementary reaction steps control reaction rate and selectivity, can be obtained by transient experiments. Transient techniques involving isotopes were developed by Happel [13-15], Bennett [16, 17] and Biloen [18-20]. Steady state isotopic transient kinetic analysis (SSITKA) allows extracting kinetic information under steady state conditions. The unique feature of SSITKA is that the chemical composition of the surface is not changed by the abrupt replacement of one reactant by its isotope [21]. Using this technique surface coverages and kinetic rate constants of rate-controlling steps can be determined unperturbed by changes in surface coverage. This sets SSITKA apart from chemical transient kinetic analysis techniques. Reviews of the SSITKA methodology are given by Shannon and Goodwin [22] and Ledesma *et al* [23].

SSITKA has already been used before to investigate the mechanism of F–T catalysts [24-27]. The majority of these studies focused on methanation [28-34], because the involved molecules are small enough to be traced online by mass spectrometry and also because the reaction network leading to methane can be formulated robustly in terms of elementary reaction steps. Regarding cobalt-catalyzed F–T synthesis, it is usually assumed that CO dissociation is the rate-determining step based on the observation that the reaction order with respect to CO is negative. Matsumoto [17] and Biloen [18] made early attempts to understand the F–T mechanism by transient kinetics. Another important work by

Winslow and Bell combined isotopic transient kinetic analysis with *in situ* infrared spectroscopy to investigate the F–T mechanism for supported ruthenium [35]. Winslow and Bell showed the existence of two different carbon species, one being a reactive surface intermediate and the other one involved in deactivation. These two pools of carbidic carbon have also been observed by others such as Happel *et al.* for nickel [15] and van Dijk *et al.* for cobalt [36] albeit that, different from the work of Winslow and Bell, all of the species could be hydrogenated to methane. Van Dijk *et al.* reported that C hydrogenation is the slow step in the mechanism of CO hydrogenation to methane by supported cobalt [24, 36]. More recently, Yang *et al.* attributed the H₂ partial pressure dependence of the methanation reaction to the H-assisted nature of CO dissociation [30]. Den Breejen *et al.* [31] and Yang *et al.* [32] interpreted the cobalt particle size effect in terms of strongly bonded C and O atoms on small cobalt particles on the basis of SSITKA data. SSITKA investigations of promoter effects of rhenium and zinc on cobalt were reported by Yang *et al.* [33] and Enger *et al.* [34], respectively. Recent progresses in understanding the F–T mechanism by SSITKA has been reviewed by Qi *et al* [37].

An important related aspect of the F–T mechanism in this regard is the mode of CO dissociation. With the advent of density functional theory, the sensitivity of dissociation of molecules like CO [38-42], NO [43] and N₂ [44, 45] to the topology of metal surfaces that enclose catalytic nanoparticles has been extensively investigated. Accordingly, it has been realized that direct CO dissociation is highly likely on step-edge sites [39-42], because the terrace sites, which dominate the surface of sufficiently large nanoparticles [46, 47], are not reactive enough. Another view is that CO activation takes place on terrace sites through an H-assisted mechanism [30, 48-52]. Although it is difficult to disprove a H-assisted CO dissociation mechanism on a surface that contains adsorbed CO and H, we have recently demonstrated by isotopic exchange of a ${}^{12}C{}^{16}O/{}^{13}C{}^{18}O$ mixture that CO dissociation is fast and reversible on an empty cobalt surface [53].

The purpose of the present work is to provide new mechanistic insight into the CO methanation reaction based on direct CO dissociation employing transient kinetic techniques. We discuss an interpretation of the H₂ pressure dependence of the methanation reaction that is different from H-assisted CO dissociation. We employ two different types of transients, a SSITKA switch involving a change in the isotopic labelling of the feed, ${}^{12}CO/H_2/Ar \rightarrow {}^{13}CO/H_2/Ne)$, and forward and backward CTKA transients involving Ne \rightarrow CO/H₂, Ne/H₂ \rightarrow CO/H₂ and CO/H₂ \rightarrow Ne/H₂ switches. The coverage dependence of the kinetic parameters extracted from these transient measurements was evaluated by varying the CO and H₂ pressures. The obtained steady state and transient data are modelled using the two CO dissociation mechanisms. The direct CO dissociation model that describes the data better is then used to carry out microkinetics simulations to identify the elementary reaction steps that control the CO consumption rate and the chain-growth probability. An important corollary of this study will be that CO dissociation is not the rate-controlling step under methanation conditions at 260°C. Instead, hydrogenation of O and especially of C

atoms deriving from CO dissociation are identified as the slow steps. The consequences of applying different conditions (H_2 /CO ratios and partial pressures) on surface composition and major rate-controlling steps will be discussed.

4.2 Experimental

4.2.1 Preparation and characterization

A silica-supported cobalt catalyst containing 17.1 wt% cobalt and 0.04% platinum was used in this study. Detailed preparation and characterization are provided in Section 3.2.

4.2.2 Catalytic activity measurements

Catalytic activity measurements were performed in a setup that is capable of transient experiments. A low dead-volume stainless-steel tubular reactor of 5 mm inner diameter and 80 mm bed length was used. The catalytic activity in steady state was determined by online gas chromatography (VARIAN CP-3800 equipped with TCD and FID). Instrumental information is provided in Section 2.2.

Typically, 20 mg of sample diluted with SiC was loaded in the stainless-steel reactor. Prior to reaction, the sample was *in situ* reduced in a diluted H₂ flow (10% H₂ in Ar, 50 mL min⁻¹ in total) at 450°C using a heating rate of 2°C min⁻¹ and atmospheric pressure for 16 h. Subsequently, the sample was cooled to 260°C in an Ar flow and the pressure was increased to 1.5 bar. Thereafter, the feed was switched to a flow containing a mixture of ¹²CO, H₂, and Ar for 16 h to obtain steady state conversion of the synthesis gas feed.

4.2.3 Transient kinetic experiments

Three types of transient kinetic analyses were performed, *i.e.*, forward and backward chemical transient kinetic analysis (CTKA) [21, 54-56] involving a change in the chemical composition of the gas phase (forward transient involving Ne \rightarrow CO/H₂ or Ne/H₂ \rightarrow CO/H₂; backward transient involving CO/H₂ \rightarrow Ne/H₂) and a steady state isotopic transient kinetic analysis (SSITKA) involving a change in the isotopic labelling of the feed (12 CO/H₂/Ar \rightarrow 13 CO/H₂/Ne). In CTKA experiments, the Ne flow was used as balance to keep the total flow rate unchanged after switch. In SSITKA, the Ne was used as tracer to determine the gas-phase hold-up of the reactor. In all the experiments, an additional Ar flow was used as balance to keep H₂ partial pressure and total flow rate at50 mL min⁻¹ when the CO/H₂ ratio was varied. The concentrations of H₂ (*m*/*z* = 2), H₂O (*m*/*z* = 18), ¹²CO (*m*/*z* = 28), ¹³CO (*m*/*z* = 29), ¹²CH₄ (*m*/*z* = 15), ¹³CH₄ (*m*/*z* = 17), Ne (*m*/*z* = 22), and Ar (*m*/*z* = 40) were monitored by an online quadrupole mass spectrometer (GeneSys). The residence time of CO and CH_x

are determined by Eq. 2.4 and Eq. 2.5, and coverages are calculated by Eq. 2.6 and Eq. 2.7. Detained interpretation is provided in Section 2.3.

4.3 Results and discussion

4.3.1 Steady state kinetic measurements

We first investigated the steady state kinetics of the Co/SiO₂ catalyst at a temperature of 260° C in order to determine reaction orders with respect to CO and H₂. The dependences of the reaction rates (expressed as turnover frequency, TOF) of CO consumption, CH_4 formation, C₂₊ formation, CO₂ formation and the chain-growth probability on CO and H₂ partial pressures are presented in Figure 4.1. The CO and H₂ partial pressures were varied between 90-900 mbar and 270-1350 mbar, respectively. At 260°C, the main product of CO hydrogenation is CH_4 . Under such methanation conditions, the chain-growth probability is low. Apparent reaction orders with respect to CO and H2 are listed in Table 4.1. In line with literature [30], the methanation rate decreases with increasing CO partial pressure, while the reverse holds true for the dependence on H_2 partial pressure. The negative reaction order with respect to CO can be interpreted in terms of a decrease in free sites needed for CO dissociation [57]. An alternative interpretation is a lack of H atoms needed for methanation. The reaction order with respect to H₂ is slightly higher than unity, implying that hydrogenation of CO or hydrogenation of C or O atoms are rate-controlling steps. We observe that the reaction order with respect to H₂ based on the CH₄ formation rate is higher than the corresponding reaction order based on the formation rate of C_{2+} -hydrocarbon products. This suggests that the H_2 partial pressure dependence at least in part originates from the rate-controlling nature of hydrogenation of C atoms, as less C hydrogenation steps



Figure 4.1. Turnover frequencies of CO consumption (squares), CH₄ formation (circles), C₂₊ formation (triangles), CO₂ formation (diamonds) and chain-growth probability (open squares) as a function of CO partial pressure (a) and H₂ partial pressure (b). Conditions: $T = 260^{\circ}$ C, $p_{H_2} = 450$ mbar at varying CO partial pressure, $p_{CO} = 90$ mbar at varying H₂ partial pressure.

Pata basad on	Reaction order			
Kate based off	$\rm CO^a$	H ₂ ^b		
CO	-0.61	1.08		
CH ₄	-0.72	1.20		
$C_{2^+}^{c}$	-0.32	0.45		
CO_2	0.95	-1.09		

Table 4.1. Apparent reaction orders with respect to CO and H_2 based on CO consumption rate and formation rates of CH₄, C_{2+} and CO₂ determined at 260°C. Data were acquired after 16 h time-on-stream.

^a p_{H_2} = 450 mbar, p_{CO} varied from 15 mbar to 150 mbar.

^b $p_{CO} = 90$ mbar, p_{H_2} varied from 270 mbar to 1350 mbar.

^c C₂₊ refers to all hydrocarbons containing two or more carbon atoms.

are involved in formation of C_{2+} -hydrocarbon products than in the formation of CH_4 . The rate of CO_2 formation increases with CO partial pressure and decreases with H_2 partial pressure. These dependencies point to competition of O removal pathways via CO_2 and H_2O . Although CO_2 formation cannot be neglected especially at high CO partial pressure, the dominant O removal pathway is via H_2O . It is interesting to note that the chain-growth probability only changes significantly with CO partial pressure, implying a strong influence of surface coverage on the chain-growth process. This observation will be discussed in more detailed in a companion paper that focuses on similar measurements under F–T conditions at a temperature of 220°C.

4.3.2 Steady state isotopic transient kinetic analysis (SSITKA)

After attaining steady state in a 12 CO/H₂ mixture, the catalyst was subjected to a SSITKA switch from 12 CO/H₂ \rightarrow 13 CO/H₂ in order to determine residence times (τ) of CO and CH_x (intermediates leading to CH₄) by use of Eqs. 2,4 and 2.5. Long residence time indicates low activity, and *vice versa*. Together with the site-normalized rates, CO and CH_x coverages can then be obtained by use of Eqs. 2.6 and 2.7. These residence times and coverages are plotted as a function of the CO and H₂ partial pressure in Figure 4.2. In good agreement with other studies [<u>30</u>], a higher CO partial pressure leads to a longer residence time of CH_x. The reverse holds for changes in the H₂ partial pressure. As widely assumed in literature, CH₄ formation rate is a pseudo-first-order process with respect to the coverage of CH_x (θ_{CH_x}) [<u>22, 28-34</u>]:

$$r_{CH_4} = k'_{CH_x} \theta_{CH_x}$$
(4.1)
where k' is a pseudo-first-order rate constant and, together with Eq. 2.7, we can state that
$$k'_{CH_x} = \frac{1}{\tau_{CH_x}}$$
(4.2)

However, the pseudo-first-order assumption is not valid as the residence time also depends on the reactant partial pressure. Accordingly, we employed a more detailed analysis of the SSITKA results in which we assume that either C hydrogenation or CO



Figure 4.2. Residence times (left panels) and equivalent coverages (right panels) of CO (squares), CH_x (circles), and extra-CH₄ (triangles, defined in Figure 4.4.) as a function of CO partial pressure (a) and H₂ partial pressure (b). Conditions: $T = 260^{\circ}C$, $p_{H_2} = 450$ mbar at varying CO pressure, $p_{CO} = 90$ mbar at varying H₂ pressure.

dissociation is limiting the rate of CH_4 formation. The first assumption leads to decoupling of the pseudo-first-order rate constant via

$$r_{\rm CH_4} = k'\theta_{\rm CH_x} = k_{\rm CH_x}\theta_{\rm H}\theta_{\rm CH_x} \tag{4.3}$$

where $k_{\rm H}$ is the rate constant of hydrogenation and $\theta_{\rm H}$ the H coverage. Therefore,

$$k_{\mathrm{CH}_{x}}\theta_{\mathrm{H}} = \frac{1}{\tau_{\mathrm{CH}_{x}}} \tag{4.4}$$

It should be noted that, at constant H_2 partial pressure, an increase in CO partial pressure will considerably reduce the H coverage, because the CO adsorbs much stronger than H_2 [58, 59]. On the other hand, changing H_2 partial pressure affects CO coverage less profoundly as is evident from Figure 4.2b. Therefore, the dependence of τ_{CHx} on either CO partial pressure or H_2 partial pressure should be largely due to a change in the H coverage, even though this cannot be exactly measured.

Alternatively, when CO dissociation is assumed to be rate-limiting, the rate can be approximated by

$$r_{\rm CH_4} = k_{\rm diss} \theta_{\rm v} \theta_{\rm CO} \tag{4.5}$$

where k_{diss} is the rate constant of CO dissociation and θ_v and θ_{CO} the surface coverages of free sites and CO, respectively. However, this assumption fails in interpreting the SSITKA observations as a function of H₂ partial pressure. We observe that CO coverage changes only slightly with varying H₂ partial pressure (Figure 4.2b). Considering the constant CO

partial pressure, the amount of vacant sites is not expected to significantly change with increasing H₂ partial pressure. Consequently, the product of slightly changed θ_v and θ_{CO} cannot explain the seven-fold-increase in CH₄ formation rate with increasing H₂ partial pressure from 270 mbar to 1350 mbar (Figure 1).

We therefore conclude that CH_4 formation under methanation conditions is most likely controlled by hydrogenation steps that involve H atoms rather than by a CO dissociation step that involves vacancies. We should take care here, as analysis based on SSITKA alone is not able to distinguish an H-assisted CO dissociation mechanism from C hydrogenation as the rate-determining step, because both depend on the H coverage. As outlined above, we have demonstrated that direct CO dissociation on the same Co/SiO₂ catalyst is possible [53]. We also emphasize that the surface coverage plays an important role in determining the rate-controlling steps. SSITKA results show the coverage of CO, the most abundant surface species, is typically no more than 0.30 under methanation conditions, implying there are sufficient free sites for C-O bond scission. Considering the intrinsically high activity of direct CO dissociation on stepped cobalt surfaces [40-42], the overall rate of CO hydrogenation on the cobalt surface with low coverage will not be limited by the rate of C-O bond scission, but rather by hydrogenation steps. It is to be expected that the F–T reaction will occur in a different regime as CO coverage will be higher at the typically used lower temperature. This scenario will be discussed in a companion paper.

The SSITKA results reveal the strong influence of hydrogenation on the overall CO consumption rate. Both C and O hydrogenation should be considered. We therefore combine the results from SSITKA with those obtained in forward and backward CTKA and use them to fit a microkinetic model for CO hydrogenation to CH_4 . From this analysis, we can identify rate-controlling steps.

4.3.3 Backward chemical transient kinetic analysis

The backward CTKA experiment comprises a $CO/H_2 \rightarrow Ne/H_2$ switch. Figure 4 shows that this switch leads to an increase in the CH_4 formation rate followed by a decline towards zero. This phenomenon was first observed for a fused iron catalyst by Matsumoto and Bennett [<u>17</u>]. Later, Cant *et al.* reported similar behavior for a Ru catalyst [<u>60</u>], attributing the increased methane formation rate to increased H coverage. Biloen also observed the same for a Ru catalyst and suggested that the initial increase in rate of methane formation is due to an increasing pseudo-first-order rate constant of methane formation [<u>19</u>]. Kruse and co-workers discussed similar backward transient phenomena for a Co/MgO catalyst [<u>54-56</u>]. They interpreted these CTKA data as evidence for the CO-insertion mechanism. Recently, Ralston *et al.* explained cobalt particle size-dependent CTKA data in terms of structure sensitivity, *i.e.*, lack of B₅-B sites for CO dissociation on small Co nanoparticles [<u>61</u>].



Figure 4.3. Backward transient at different CO pressures (a) and H₂ pressures (b) after a switch from CO/H₂ to H₂. Conditions: $T = 260^{\circ}$ C, $p_{H_2} = 450$ mbar at varying CO pressure, $p_{CO} = 90$ mbar at varying H₂ pressure.

The CTKA transients obtained at different CO and H_2 partial pressures are shown in Figure 4.3. The maximum CH₄ formation rates during the transient coincide with an optimum surface coverage ratio of vacancies, CO, CH_x, and H, of which the latter two determine the CH₄ formation rate. At constant H_2 pressure, the H coverage will depend linearly on the fraction of free sites according to the adsorption equilibrium of CO. Accordingly, the optimum rate is achieved at optimum ratio of CO and vacancies. This ratio is independent of the initial steady state coverage of CO, but is reached later in time when the starting coverage is higher (Figure 4.3a). However, when the CO partial pressure is constant and the H₂ partial pressure is varied, the H₂ adsorption equilibrium will lead to increasing H coverage at higher H₂ partial pressure. This will lead to higher and earlier maximum CH₄ formation rate (Figure 4.3b). Evidently, the CH₄ formation rate is highly dependent on the H coverage.

Here, we combine for the first time SSITKA with backward CTKA in order to construct Figure 4.4. In this figure, we compare CH_4 formation from two different transient experiments, *viz*. SSITKA and backward CTKA measurements. As only CH_4 formed during SSITKA can be assigned to CH_x species present on the surface during steady state, we define the difference as "extra- CH_4 ". We quantified this amount and converted it to an equivalent surface coverage by using the available Co surface area as determined by H_2 -chemisorption. This surface coverage of species generating extra- CH_4 is compared to the CO coverage as determined by SSITKA. These data are displayed in Figure 4.2. Notably, at sufficiently high H_2/CO ratios (either at relatively low CO partial pressure or relatively high H_2 partial pressure), the amount of extra- CH_4 is equivalent to the amount of CO adsorbed on the Co surface during the steady state preceding the CTKA switch. This result indicates that the extra- CH_4 formed during the backward CTKA switch at high H_2/CO ratio can be attributed solely to conversion of adsorbed CO to methane. At low H_2/CO ratio, the amount of extra- CH_4 is slightly higher than the amount of adsorbed CO. This cannot be accounted for by higher hydrocarbon fragments present on the surface that would dissociate and



10.5 $p_{CO} = 150 \text{ mbar}$ p_{CO} = 90 mbar 10.0 CH₄ signal / a.u. $p_{CO} = 45 \text{ mbar}$ p_{CO} = 30 mbar 9.5 $p_{CO} = 15 \text{ mbar}$ = 450 mbar 9.0 8.5 100 200 300 400 500 °C Τ/

Figure 4.4. Normalized responses in SSITKA and backward CTKA. The extra-CH₄ is defined by as the filled area between SSITKA (squares) and backward CTKA (circles) responses. Steady state conditions: $T = 260^{\circ}$ C, $p_{H_2} = 450$ mbar, $p_{CO} = 90$ mbar.

Figure 4.5. TPH profiles of the catalysts subjected to the methanation reaction at 260°C for 16 h time-on-stream followed by an Ar purge at 260°C for 6 h. The partial pressures presented in the graph relate to the reaction feed before the H_2 purge.

hydrogenate to CH_4 , because even at the lowest H_2/CO ratio the CH_4 selectivity is higher than 60% with the CH_x coverage being approximately 5% (Figure 4.2). As higher hydrocarbons formation typically follows an Anderson-Schulz-Flory distribution, the coverage of C_{2+} -products must be even lower than 5%. In this way, a pool of higher hydrocarbons cannot explain the extra- CH_4 formed relative to the amount of adsorbed CO.

Another point worth mentioning about the data in Figure 4.4 is that the CO signal during the SSITKA switch exhibits a delay of 1 s with respect to the inert tracer gas. This delay is caused by the adsorption/desorption equilibrium of CO in the catalyst bed, also known as the chromatographic effect. The CO response in the $CO/H_2 \rightarrow H_2$ backward CTKA switch did not exhibit this delay. Close inspection reveals that the CO signal precedes the inert tracer signal. It implies that all CO adsorbed on the Co surface is consumed and leaves the reactor predominantly as CH_4 . An important corollary of this finding is that the overall barrier for CO hydrogenation to CH_4 is lower than the CO adsorption energy under methanation condition.

In order to understand the deviation between the amount of extra-CH₄ and adsorbed CO, we carried out temperature-programmed hydrogenation (TPH) experiments of samples in which the flow was switched from CO/H₂ to Ar, followed by flushing in Ar for 6 h at 260°C. After cooling to room temperature, a TPH experiments was carried out. As shown in Figure 4.5, there are likely two carbon-containing surface species that are hydrogenated at relatively low temperature that is below 220°C. The data show that this carbon pool is not present at high H₂/CO ratio, but is formed in increasing amounts when the H₂/CO ratio is lowered. The nature of these carbon-containing surface intermediates remains unclear, but a particular property is that they can only be hydrogenated at sufficiently high H coverage as occurs during TPH and during the backward CTKA. Clearly, the surface will also contain

even less-reactive C species as demonstrated by the reduction feature above 300°C. Similar observations have been reported by Winslow and Bell [35]. Flushing a working Ru catalyst in He followed by temperature-programmed reduction in D_2 led to two CD_4 peaks designated as C_{α} and C_{β} , which are assigned to reactive intermediate and less reactive species causing deactivation, respectively.

4.3.4 Forward chemical transient kinetic analysis

We use forward CTKA to distinguish between rates of C and O hydrogenation. As the H coverage during methanation is high, both C and O hydrogenation reactions are fast. It is thus difficult to differentiate between the rates of these two reactions. Therefore, we decreased the H_2 partial pressure (200 mbar) and increased CO partial pressure (200 mbar) to amplify differences in C and O hydrogenation.

For these measurements, we analyzed both CH_4 and H_2O as primary products by online mass spectrometer (MS). However, the strong adhesion of water causes significant systematic delay time. This is confirmed by our systematic water delay test (Figure 4.6). We conclude our testing as following. First of all, water molecules not only adsorb on metallic Co, but also on SiO₂ support, reactor wall, tubing and capillary linking MS. The water delay time caused by MS capillary was measured by bypassing reactor. The results are plotted as downward triangles in Figure 4.6, showing that water adhesion in capillary causes considerable delay time and that heating capillary can reduce delay time to some extent, but not completely. Secondly, like the chromatographic effect of CO, the delay time of water is a function of water partial pressure, *i.e.*, water with low partial pressure relates to long residence time, and vice versa. Therefore, measuring the systematic delay time caused by



Figure 4.6. Systematic water delay measured on calcined catalyst (\blacksquare), SiO₂ support (\bullet), reduced catalyst (\blacktriangle), capillary linking the MS only (\blacktriangledown), and forward transient experiments (\blacklozenge).

adsorption/desorption on Co, which is defined as chromatographic effect. The circles in Figure 4.6 were determined on reactor filled with SiC and SiO₂ support (same amount with normal experiment), showing similar water delay with the result without reactor. The squares were measured over calcined catalyst, containing the water delay from the whole system including tubing, reactor, capillary, SiC, SiO₂ support and cobalt oxide. Therefore, the water delay on calcined catalyst as a function of water partial pressure can be used as a calibration line to correct the water transient response with various water partial pressure. The upward triangle denotes the delay time on reduced Co/SiO₂ catalyst, showing Co reduction does not result in additional delay time. The diamonds in Figure 4.6 are raw water delay results of forward transient experiments on empty surface, H covered surface and ¹³C pre-covered, corresponding to Figure 4.7. The corrected water delay times are obtained by subtracting the water delay on calcined catalyst from experimental determined water delay with same water partial pressure. The H₂O delay values discussed below have been corrected for this systematic delay, as well as the delay caused by the chromatographic effect of CO. As before, the CH₄ delay has also been corrected for the chromatographic effect of CO.



Figure 4.7. Forward transient on the initially empty cobalt surface (a), the H-covered surface (b), and the ¹³C precovered surface (c). The signal intensities are normalized based on the flow rate before and after the gas switch. Steady state conditions: $T = 260^{\circ}$ C, $p_{H_2} = 200$ mbar, $p_{CO} = 200$ mbar.

As a reference case, we performed the forward CTKA switch on an empty cobalt surface. We obtained this state by flushing the *in situ* reduced Co catalyst in Ar for 2 h, followed by cooling to reaction temperature in Ar. The forward transient involved an Ar/Ne \rightarrow H₂/CO switch. Figure 4.7a shows that CH₄ formation was delayed 2.5 s with respect to Ne, while H₂O was delayed approximately 6.5 s with respect to Ne. The specific evolution of the CH₄, H₂O and H₂ signals also evidence that H₂ is more rapidly consumed for hydrogenation of C towards CH₄ on an initially empty cobalt surface.

The same transient experiment was also performed on a catalyst that was pre-covered by H₂ followed by a H₂/Ne \rightarrow CO/H₂ switch. In this case, the H coverage before the switch is much higher than that at reaction condition. The corresponding results in Figure 4.7b show a shorter H₂O delay of 0.5 s, while the decrease in the CH₄ delay (2 s) is less pronounced. This comparison implies that the H₂O delay on an empty surface is caused by a lack of adsorbed H, and that the O hydrogenation profits more from higher H coverage than C hydrogenation.

We also carried out an experiment in which we pre-covered the surface with ¹³C atoms by exposure to ¹³CO flow at 260°C for 0.5 h, followed by Ar flushing to remove adsorbed ¹³CO. As demonstrated earlier, this procedure results in the deposition of C atoms on the Co surface [62, 63]. As shown in Figure 4.7c, the forward transient Ar/Ne \rightarrow H₂/CO of this ¹³C-atom pre-covered surface results in a significant longer H₂O delay of 10 s, 3.5 s longer than on the empty surface and 9.5 s longer than on the H pre-covered surface. This increase in H₂O delay is caused by two factors. On one hand, since the surface was partially covered by ¹³C deposits, ¹²CO adsorption and dissociation cannot proceed until a certain fraction of ¹³C has been removed by hydrogenation. The correspondence between the H₂ and ¹³CH₄ signals shown in Figure 4.7b represents the strong dependence of C hydrogenation on H coverage. On the other hand, the pre-adsorbed ¹³C deceases H coverage. In line with the observation that an increase in H coverage effectively shortens the H₂O delay, the extra consumption of adsorbed H atoms caused by hydrogenation of precovered ¹³C results in a longer H₂O delay with respect to ¹²CH₄ on a ¹³C pre-covered cobalt surface (6 s) as compared to the empty surface (4 s). We stress that the competition between C and O hydrogenation is partially due to the low H₂/CO ratio in this case. The findings above also suggest that the strong dependence of H_2O formation on the H coverage significantly contributes to the reaction order with respect to H₂.

4.3.5 Microkinetic modeling

A common approach to distinguish mechanisms is to fit steady state catalytic data to a microkinetic model based on a mechanism consisting of elementary reaction steps. A major limitation of transient kinetic studies of CO hydrogenation is that the H coverage cannot be explicitly measured. This dependence is therefore often lumped into hydrogenation reaction rate constants. Here, we take a different approach in which we use transient data to fit a

microkinetic model for CO hydrogenation involving H explicitly as a surface species. The elementary reaction steps involving two different mechanisms for CO hydrogenation, namely direct CO dissociation and H-assisted CO dissociation, are given in Figure 4.8. We will first discuss the set of coupled non-linear differential equations that describes reaction path based on direct CO dissociation. The equation describing the H-assisted CO dissociation mechanism is in Appendix II. The surface coverage of CO can be described as follows:

$$\frac{d\theta_{\rm CO}}{dt} = k_{\rm ads,CO} p_{\rm CO} \theta_{\rm v} - k_{\rm des,CO} \theta_{\rm CO} - k_{\rm diss}^{\rm f} \theta_{\rm v} \theta_{\rm CO} + k_{\rm diss}^{\rm b} \theta_{\rm C} \theta_{\rm O} - k_{\rm CO_2}^{\rm f} \theta_{\rm CO} \theta_{\rm O} + k_{\rm CO_2}^{\rm b} \theta_{\rm v} \theta_{\rm CO_2}$$

$$\tag{4.6}$$

The balance for CH_x species involves CH_x hydrogenation/dehydrogenation steps and also the CO dissociation for the C intermediate:

$$\frac{d\theta_{\rm C}}{dt} = k_{\rm diss}^{\rm f} \theta_{\rm v} \theta_{\rm CO} - k_{\rm diss}^{\rm b} \theta_{\rm C} \theta_{\rm O} - k_{\rm CH}^{\rm f} \theta_{\rm H} \theta_{\rm C} + k_{\rm CH}^{\rm b} \theta_{\rm v} \theta_{\rm CH}$$
(4.7)

$$\frac{d\theta_{\rm CH}}{dt} = k_{\rm CH}^{\rm f} \theta_{\rm H} \theta_{\rm C} - k_{\rm CH}^{\rm b} \theta_{\rm v} \theta_{\rm CH} - k_{\rm CH_2}^{\rm f} \theta_{\rm H} \theta_{\rm CH} + k_{\rm CH_2}^{\rm b} \theta_{\rm v} \theta_{\rm CH_2}$$
(4.8)

$$\frac{d\theta_{\rm CH_2}}{dt} = k_{\rm CH_2}^{\rm f} \theta_{\rm H} \theta_{\rm CH} - k_{\rm CH_2}^{\rm b} \theta_{\rm v} \theta_{\rm CH_2} - k_{\rm CH_3}^{\rm f} \theta_{\rm H} \theta_{\rm CH_2} + k_{\rm CH_3}^{\rm b} \theta_{\rm v} \theta_{\rm CH_3}$$
(4.10)

$$\frac{d\theta_{\rm CH_3}}{dt} = k_{\rm CH_3}^{\rm f} \theta_{\rm H} \theta_{\rm CH_2} - k_{\rm CH_3}^{\rm b} \theta_{\rm v} \theta_{\rm CH_3} - k_{\rm CH_4} \theta_{\rm H} \theta_{\rm CH_3}$$
(4.11)

The balance for OH_x intermediates involves CO dissociation and O removal:

$$\frac{d\theta_{\rm O}}{dt} = k_{\rm diss}^{\rm f} \theta_{\rm v} \theta_{\rm CO} - k_{\rm diss}^{\rm b} \theta_{\rm C} \theta_{\rm O} - k_{\rm OH}^{\rm f} \theta_{\rm H} \theta_{\rm O} + k_{\rm OH}^{\rm b} \theta_{\rm v} \theta_{\rm OH} + k_{\rm 2OH}^{\rm f} \theta_{\rm OH} \theta_{\rm OH} - k_{\rm 2OH}^{\rm b} \theta_{\rm OH} \theta_{\rm H} - k_{\rm 2OH}^{\rm b} \theta_{\rm OH} \theta_{\rm OH} - k_{\rm 2OH}^{\rm b} \theta_{\rm OH} - k_{\rm 2OH}^{\rm$$

$$\frac{d\theta_{\rm OH}}{dt} = k_{\rm OH}^{\rm f}\theta_{\rm H}\theta_{\rm O} - k_{\rm OH}^{\rm b}\theta_{\rm v}\theta_{\rm OH} - 2k_{\rm 2OH}^{\rm f}\theta_{\rm OH}\theta_{\rm OH} + 2k_{\rm 2OH}^{\rm b}\theta_{\rm O}\theta_{\rm H_{2}O} - k_{\rm H_{2}O}^{\rm f}\theta_{\rm H}\theta_{\rm OH} + k_{\rm H_{2}O}^{\rm b}\theta_{\rm v}\theta_{\rm H_{2}O}$$

$$\tag{4.13}$$

$$\frac{d\theta_{H_2O}}{dt} = k_{H_2O}^{f}\theta_{H}\theta_{OH} - k_{CO_2}^{b}\theta_{v}\theta_{H_2O} + k_{2OH}^{f}\theta_{OH}\theta_{OH} - k_{2OH}^{b}\theta_{O}\theta_{H_2O} - k_{des,H_2O}\theta_{H_2O}$$
(4.14)

The balance for adsorbed CO₂ is given by:

$$\frac{d\theta_{\rm CO_2}}{dt} = k_{\rm CO_2}^{\rm f} \theta_0 \theta_{\rm CO} - k_{\rm CO_2}^{\rm b} \theta_{\rm v} \theta_{\rm CO_2} - k_{\rm des, CO_2} \theta_{\rm CO_2}$$
(4.15)



(a) Direct CO dissociation

Figure 4.8. Schematic presentation of reaction model based on direct CO dissociation mechanism (a) and H-assisted CO dissociation mechanism.

Finally, we provide the balance for the H surface intermediate:

$$\frac{d\theta_{\rm H}}{dt} = 2k_{\rm ads,H_2}p_{\rm H_2}\theta_{\rm v}\theta_{\rm v} - 2k_{\rm des,H_2}\theta_{\rm H}\theta_{\rm H} - \theta_{\rm H}(k_{\rm CH}^{\rm f}\theta_{\rm C} + k_{\rm CH_2}^{\rm f}\theta_{\rm CH} + k_{\rm CH_3}^{\rm f}\theta_{\rm CH_2} + k_{\rm CH_3}^{\rm f}\theta_{\rm CH_2} + k_{\rm H_2O}^{\rm f}\theta_{\rm OH}) + \theta_{\rm v}(k_{\rm CH}^{\rm b}\theta_{\rm CH} + k_{\rm CH_2}^{\rm b}\theta_{\rm CH_2} + k_{\rm CH_3}^{\rm b}\theta_{\rm CH_3} + k_{\rm OH}^{\rm b}\theta_{\rm OH} + k_{\rm H_2O}^{\rm b}\theta_{\rm OH})$$

$$(4.16)$$

where θ_v refers the vacant sites on surface. An additional constraint is that the sum of all coverages is unity:

$$\theta_{\rm CO} + \theta_{\rm C} + \theta_{\rm CH} + \theta_{\rm CH_2} + \theta_{\rm CH_3} + \theta_{\rm O} + \theta_{\rm CO_2} + \theta_{\rm OH} + \theta_{\rm H_2O} + \theta_{\rm H} + \theta_{\rm v} = 1 \qquad (4.17)$$
The transient experiments involved in model fitting comprise 4 different transients experiment, therefore four initial conditions were implemented to solve the ordinary differential equation of the reaction model.

(1) ¹³CO exposure

$$t = 0, p_{H_2} = 0 \text{ mbar}, p_{12}_{CO} = 0 \text{ mbar}, p_{13}_{CO} = 0 \text{ mbar}$$

 $t > 0, p_{H_2} = 0 \text{ mbar}, p_{12}_{CO} = 0 \text{ mbar}, p_{13}_{CO} = F \times 45 \text{ mbar}$
(2) ¹³CO to 12CO/H₂
 $t = 0, p_{H_2} = 0 \text{ mbar}, p_{12}_{CO} = 0 \text{ mbar}, p_{13}_{CO} = 45 \text{ mbar}$
 $t > 0, p_{H_2} = F \times 450 \text{ mbar}, p_{12}_{CO} = F \times 45 \text{ mbar}, p_{13}_{CO} = (1 - F) \times 45 \text{ mbar}$
(3) ¹²CO/H₂ to ¹³CO/H₂
 $t = 0, p_{H_2} = 450 \text{ mbar}, p_{12}_{CO} = 45 \text{ mbar}, p_{13}_{CO} = 0 \text{ mbar}$
 $t > 0, p_{H_2} = 450 \text{ mbar}, p_{12}_{CO} = (1 - F) \times 45 \text{ mbar}, p_{13}_{CO} = F \times 45 \text{ mbar}$
(4) ¹³CO/^{H2} to H₂
 $t = 0, p_{H_2} = 450 \text{ mbar}, p_{12}_{CO} = 0 \text{ mbar}, p_{13}_{CO} = 45 \text{ mbar}$
 $t > 0, p_{H_2} = 450 \text{ mbar}, p_{12}_{CO} = 0 \text{ mbar}, p_{13}_{CO} = 45 \text{ mbar}$

where E is an empirical function for the unideal step change, which is obtained by fitting normalized Ne transient:

$$E = \sum_{i} a_{3,i} \left(1 + e^{\frac{a_0 - t}{a_{1,i}}}\right)^{a_{2,i}}$$
(4.18)

where $\sum a_{3,i} = 1$, meaning *E* is a linear combination of several terms. More term will be automatically added until the determination coefficient, R^2 , is larger than 0.99. The ODEs are solved by build-in ODE15S in Matlab2014b (The MathWork, Inc). We choose transient data obtained at a high H₂/CO ratio of 15 ($p_{CO} = 30$ mbar, $p_{H_2} = 450$ mbar and T =260°C) so as to ensure a high CH₄ selectivity of approximately 90% and a chain-growth probability smaller than 0.1. A least-squares objective function is used as following:

$$\varepsilon = \sum \left(F_{\text{forward}}^{\text{model}} - F_{\text{forward}}^{\text{exp}} \right)^2 + \sum \left(F_{\text{SSITKA}}^{\text{model}} - F_{\text{SSITKA}}^{\text{exp}} \right)^2 + \sum \left(F_{\text{backward}}^{\text{model}} - F_{\text{backward}}^{\text{exp}} \right)^2 + w \left(\left(n_{\text{CO}}^{\text{model}} - n_{\text{CO}}^{\text{exp}} \right)^2 + \left(n_{\text{H}_2}^{\text{model}} - n_{\text{H}_2}^{\text{exp}} \right)^2 \right)$$

$$(4.19)$$

in which *F* denotes the normalized transient response of methane, *n* the reaction order and *w* is a factor for giving a similar weight to the reaction orders as that to the transient data. To decrease the number of unknown variables, we introduced equilibrium constants (Table 4.2) for several surface reactions based on DFT calculations for the $Co(11\overline{2}1)$ surface. Finally, a total of 16 rate constants were fitted.

The differential equations describing the kinetics are highly nonlinear. It is very probably that typical fitting procedures will identify a local minimum rather than the global minimum. Accordingly, we employed a two-stage parameter estimation approach [64]. The procedure is schematically present in Figure 4.9. In the first stage, we searched the multidimensional space spanned by the unknown parameters by the Latin hypercube sampling method, which represents a near-random sampling of parameter values. The initial searching space was roughly determined by DFT calculation. In each iteration, a million uniformly distributed points were generated and evaluated by Eq. 4.19. Based on residual analysis, we shifted, shrank, or broadened searching space. After several iterations, the approximate location of the global minimum was identified. In the second stage, The 10 most promising candidates were then subjected to a standard Levenberg-Marquardt algorithm. The fitting results are listed in Table 4.3. The good correspondence between the model and the experimental data is shown in Figure 4.10.



Figure 4.9. Schematic presentation of the global optimization approach.

		, , ,
	Direct CO dissociation	H-assisted CO dissociation
$\rm CO* + H* \rightleftarrows CHO* + *$		2.1×10 ⁻⁵
$\mathrm{CHO}^* + \mathrm{H}^* \rightleftarrows \mathrm{CH}_2\mathrm{O}^* + *$		3.3×10^5
$\mathrm{C}^* + \mathrm{H}^* \rightleftarrows \mathrm{C}\mathrm{H}^* + {}^*$	8.9×10^{1}	
$\mathrm{CH}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{CH}_{2}^{*} + {}^{*}$	8.8×10 ⁻¹	
$\mathrm{CH}_2^* + \mathrm{H}^* \rightleftarrows \mathrm{CH}_3^* + *$	2.7×10^{1}	9.1×10^{1}
$\mathrm{O}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{OH}^{*} + {}^{*}$	1.8×10^4	4.1×10^2
$\mathrm{OH}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{H}_{2}\mathrm{O}^{*} + {}^{*}$	3.0×10^{3}	5.6×10 ⁴
$2 \text{ OH}^* \rightleftarrows \text{H}_2\text{O}^* + \text{O}^*$	1.8×10^4	1.1×10^{2}

Table 4.2. DFT calculated equilibrium constants ($K = k_f / k_b$) of the hydrogenation steps in direct CO dissociation and H-assisted CO dissociation mechanisms (schematically presented in Figure 4.8) on Co(11 $\overline{2}$ 1) surface.

Table 4.3. Rate constants determined by model fitting.

	Direct CO dissociation		H-assisted CO dissociation		
	$k_{\rm f}({\rm s}^{-1})$	$k_{\rm b}~({\rm s}^{-1})$	$k_{\rm f}({\rm s}^{-1})$	$k_{\rm b} ({\rm s}^{-1})$	
adsorption/desorption					
$CO + * \rightleftharpoons CO*$	4.8×10^{1}	8.1×10 ⁻¹	1.7×10^{1}	2.8×10 ⁻¹	
$\mathrm{H}_2 + 2 \ * \rightleftarrows 2 \ \mathrm{H} *$	7.2×10^{3}	2.5×10^{6}	6.6×10^2	5.8×10^4	
$\mathrm{H_2O} + * \rightarrow \mathrm{H_2O} *$		7.7×10^{1}		1.4×10^{1}	
$\text{CO}_2 + * \rightarrow \text{CO}_2 *$		7.7×10^3		1.4×10^{3}	
CO hydrogenation					
$\mathrm{CO}^* + \mathrm{H}^* \rightleftarrows \mathrm{CHO}^* + *$			3.8×10^{1}	1.8×10^{6}	
$\mathrm{CHO}^* + \mathrm{H}^* \rightleftarrows \mathrm{CH}_2\mathrm{O}^* + *$			2.1×10^{7}	6.4×10^{1}	
CO dissociation					
$\mathrm{CO}^* + * \rightleftharpoons \mathrm{C}^* + \mathrm{O}^*$	5.2×10 ⁻¹	7.3×10^{1}			
$\mathrm{CH}_{2}\mathrm{O}^{*} + * \rightleftarrows \mathrm{CH}_{2}^{*} + \mathrm{O}^{*}$			2.0×10^{1}	1.9×10^{2}	
Methane formation					
$\mathrm{C}^* + \mathrm{H}^* \rightleftarrows \mathrm{C}\mathrm{H}^* + *$	2.3×10^{3}	2.6×10^{1}			
$\mathrm{CH}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{CH}_{2}^{*} + ^{*}$	1.9×10^4	2.2×10^4			
$\mathrm{CH}_2{}^* + \mathrm{H}{}^* \rightleftarrows \mathrm{CH}_3{}^* + {}^*$	2.8×10^{3}	1.0×10^{2}	3.9×10^2	4.3×10^{0}	
CH_3 * + H* \rightleftharpoons CH_4 + 2 *	8.7×10^2		2.4×10^{1}		
Water formation					
$\mathrm{O}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{OH}^{*} + {}^{*}$	1.7×10^{2}	9.3×10 ⁻³	3.7×10^{0}	9.1×10 ⁻³	
$\mathrm{OH}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{H}_{2}\mathrm{O}^{*} + ^{*}$	4.7×10^2	1.5×10 ⁻¹	2.6×10^5	4.7×10^{0}	
$2 \text{ OH}^* \rightleftarrows \text{H}_2\text{O}^* + \text{O}^*$	2.8×10^{6}	2.1×10^{7}	4.5×10^{3}	4.1×10^{1}	
CO ₂ formation					
$CO^* + O^* \rightleftharpoons CO_2^* + *$	1.1×10 ⁻¹	5.9×10 ⁻⁶	7.3×10 ⁻³	1.8×10 ⁻⁵	



Figure 4.10. Combined transient data (points) and model fitting based on direct CO dissociation mechanism (red) and H-assisted CO dissociation mechanism (blue).

Reaction	X _{DRC}
CO adsorption	-4.9×10^{-2}
H ₂ adsorption	3.6×10^{-4}
CO dissociation	0.15
C hydrogenation	0.62
O hydrogenation	0.24
CO ₂ formation	3.2×10^{-2}

Table 4.4. Lumped degree of rate control values obtained at 30 mbar CO and 450 mbar H₂.

Based on the fitted data, we then analyzed the different kinetic regimes of the CO hydrogenation reaction by determining the degree of rate control, which is defined as [65, 66]:

$$X_{DRC,i} = \left(\frac{\partial \ln r}{\partial \ln k_i}\right)_{k_{j\neq i},K_i}$$
(4.20)

$$\sum_{i} X_{\text{DRC},i} = 1 \tag{4.21}$$

where only the rate constant of step *i* is changed. Equilibrium constant K_i is kept constant, so forward and backward rate constants are changed by equal factors. A positive $X_{DRC,i}$ value implies that the overall reaction rate increases when the rate of the corresponding elementary step is raised. Steps with negative $X_{DRC,i}$ value are called inhibition steps that slow down the overall rate. By this method, multiple rate-controlling steps can be identified. Summation over all steps leads to conservation of the DRC.

Lumped DRC values for key reaction steps are listed in Table 4.4, full DRC results are listed in Table 4.5. The X_{DRC} of carbon hydrogenation steps for direct CO dissociation and H-assisted CO dissociation are 0.62 and 0.51, respectively, showing significant rate

Table 4.5. DRC val	lues of elementary	steps.
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	Direct CO dissociation	H-assisted CO dissociation				
adsorption/desorption						
$CO + * \rightleftharpoons CO$	-4.8×10^{-2}	-5.8×10^{-2}				
$H_2 + 2 * \rightleftharpoons 2 H^*$	3.6×10^{-4}	1.4×10^{-3}				
$\mathrm{H_{2}O}+* \rightarrow \mathrm{H_{2}O}*$	-8.2×10^{-2}	-1.8×10^{-1}				
$CO_2 + * \rightarrow CO_2^*$	2.1×10^{-7}	6.1×10^{-7}				
CO hydrogenation						
$CO^* + H^* \rightleftharpoons CHO^* + *$		1.3×10^{-2}				
$\mathrm{CHO}^* + \mathrm{H}^* \rightleftarrows \mathrm{CH}_2\mathrm{O}^* + *$		1.5×10^{-2}				
CO dissociation						
$CO^* + * \rightleftharpoons C^* + O^*$	0.15					
$\mathrm{CH}_{2}\mathrm{O}^{*}+^{*}\rightleftarrows\mathrm{CH}_{2}^{*}+\mathrm{O}^{*}$		5.3×10^{-2}				
Methane formation						
$\mathrm{C}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{C}\mathrm{H}^{*} + {}^{*}$	9.2×10^{-3}					
$\mathrm{CH}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{CH}_{2}^{*} + {}^{*}$	$6.5 imes 10^{-4}$					
$\mathrm{CH}_2^* + \mathrm{H}^* \rightleftarrows \mathrm{CH}_3^* + *$	0.14	0.12				
$CH_3^* + H^* \rightleftharpoons CH_4 + 2 *$	0.47	0.37				
Water formation						
$\mathrm{O}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{O}\mathrm{H}^{*} + {}^{*}$	0.15	0.43				
$\mathrm{OH}^{*} + \mathrm{H}^{*} \rightleftarrows \mathrm{H}_{2}\mathrm{O}^{*} + *$	0.18	9.6×10^{-6}				
$2 \text{ OH}^* \rightleftarrows \text{H}_2\text{O}^* + \text{O}^*$	2.2×10^{-6}	0.18				
CO ₂ formation						
$\mathrm{CO}^* + \mathrm{O}^* \rightleftarrows \mathrm{CO}_2^* + *$	3.2×10^{-2}	4.8×10^{-2}				

control of C hydrogenation in both mechanisms. The X_{DRC} of O hydrogenation (0.24 and 0.46 for direct CO dissociation and H-assisted CO) suggests considerable rate control of O removal. The DRC values of C–O bond scission are relatively small, which are only 0.15 and 0.05 for direct CO dissociation and H-assisted CO dissociation, respectively, showing weak relevance to overall rate. These results clearly show that the strong correlation between hydrogenation and overall rate is independent of the mechanism of CO dissociation. These conclusions are in good agreement with a recent theoretical study [67] and also the forward transient experiments in this study.

An important conclusion from this kinetic analysis is that CO dissociation is not the rate-limiting step during the methanation reaction on cobalt. Instead, the hydrogenation of the O and especially C species deriving from CO dissociation control the reaction rate. This finding is consistent with the experimental observation that the absolute value of H_2 reaction order for CH₄ formation is larger than that of CO reaction order, implying H_2 partial pressure affects the reaction more strongly than CO does. The influence of H_2 partial pressure on the reaction rate is larger, as the H coverage is directly related to the H_2 partial

pressure; while CO partial pressure indirectly influences the reaction by hindering H_2 adsorption.

The present work demonstrates that multiple elementary reaction steps can contribute to the rate control of the methanation reaction. The positive order with respect to H_2 is due to the rate-controlling nature of C and O hydrogenation steps. The negative CO reaction order is due to the competition between CO and H_2 adsorption, in which an increase in CO coverage decreases the H coverage that is needed for catalyzing the rate-controlling C and O hydrogenation steps.

4.3.6 Microkinetics simulations

We employ the fitted microkinetic model to explore the effect of a wider range of CO and H_2 partial pressures, *i.e.*, from 0.06–20 bar and 0.03–10 bar, respectively. The output of these microkinetic simulations is presented in Figure 4.11 in the form of a DRC analysis, surface coverages and CO₂ selectivity. Four regimes can be distinguished on the basis of the DRC values. In regime 1, the H_2 partial pressure is substantially higher than the CO partial pressure. Consequently, CO coverage is low and H coverage high. In this regime, C and O atoms derived from CO dissociation are rapidly removed as CH₄ and H₂O, respectively, and CO dissociation becomes increasingly rate-controlling with increasing H₂ pressure. Thus, C and O hydrogenation steps do not limit the CO conversion rate, but CO dissociation does. In regime 2, the surface contains a significant amount of CH_x intermediates as the lack of H atoms limits their hydrogenation. Regime 3 presents the conditions with moderate H₂/CO ratio (the diagonal lines in Figure 4.11 refer to a H₂/CO ratio of 2), a condition close to the F-T condition. CO dissociation and C hydrogenation steps largely contribute to the overall rate control. Due to the accumulation of OH_x intermediates on the surface, H₂O formation considerably controls the CO conversion rate in this regime. This is in line with recent DFT-based microkinetic simulations [67]. Meanwhile, Regime 4 refers to the lean H condition, under which the cobalt surface is fully covered by CO. In this case, O is predominantly removed as CO₂ (Figure 4.11i), as the surface lacks H atoms for O hydrogenation.

These regimes provide us some insight into the different kinetic regimes one might encounter when varying the H₂/CO ratio. Notably, regime 4 is an extreme case, stemming from the higher CO₂ selectivity observed at 260°C than at the actual F–T temperature. As expected, the rate-controlling steps at conditions close to F–T conditions (upper right corner in Figure 4.11) differ from those under methanation conditions (lower right corner in Figure 4.11). It appears that the very different composition of the surface adsorbed layer at lower temperature will have a significant impact on the rate-controlling nature of the different elementary reaction steps. These aspects are the focus of our companion paper which uses similar transient methodologies to interrogate the reaction mechanism of the Co/SiO₂ catalyst under conditions close to those encountered in practical F–T synthesis.



Figure 4.11. Degree of rate control (a–d), surface coverage (e–h) and CO_2 selectivity (i) as a function of CO and H_2 partial pressures based on a microkinetic model using parameters obtained by fitting of transient data for the methanation reaction on Co/SiO₂.

4.4 Conclusions

The mechanism of CO hydrogenation to CH_4 at 260°C on a cobalt catalyst is interrogated by different types of transient kinetic measurements including SSITKA and backward and forward CTKA. The dependence of CH_x residence time as determined by SSITKA $(^{12}CO/H_2 \rightarrow ^{13}CO/H_2)$ on CO and H₂ partial pressure indicates that the CH₄ formation rate is mainly controlled by CH_x hydrogenation rather than CO dissociation. The backward $CO/H_2 \rightarrow H_2$ CTKA emphasizes the importance of H coverage on the slow CH_x hydrogenation step. The H coverage strongly depends on the CO coverage, which is mainly determined by CO partial pressure. By combining SSITKA and backward CTKA, it is established that the additional CH_4 obtained during CTKA in comparison to SSITKA is nearly equal in amount to the amount of CO adsorbed on the cobalt surface. This implies that under the given conditions the overall barrier for CO hydrogenation to CH_4 is lower than the CO adsorption energy. Forward CTKA measurements also qualitatively show that O hydrogenation is relatively slow compared to CO dissociation. The combined transient kinetic data are captured in an explicit microkinetic model for the methanation reaction. The model fitting shows that a mechanism involving direct CO dissociation better represents the data than a mechanism in which H-assisted CO dissociation is assumed. Microkinetics simulations based on the fitted parameters shows the highest DRC for C hydrogenation and lower DRC for O hydrogenation and CO dissociation at typical methanation conditions. These simulations are also used to explored different conditions depending on CO and H₂ partial pressure. This leads to four kinetic regimes in which CO consumption rate is controlled by CO dissociation, C hydrogenation, O hydrogenation and CO₂ formation.

References

- [1] M.E. Dry, J.C. Hoogendoorn, Catal. Rev. -Sci. Eng. 23 (1981) 265-278.
- [2] M.E. Dry, Catal. Today 71 (2002) 227–241.
- [3] B. List, Angew. Chem. Int. Ed. 53 (2014) 8528-8530.
- [4] F. Fischer, H. Tropsch, Brennst. Chem. 4 (1923) 276–285.
- [5] F. Fischer, H. Tropsch, Brennst. Chem. 7 (1926) 97–104.
- [6] A.Y. Khodakov, W. Chu, P. Fongarland, Chem. Rev. 107 (2007) 1692–1744.
- [7] I.C.Y.a.C.N. Satterfield, Energy & Fuels 5 (1991) 168–173.
- [8] G.P. Van Der Laan, A.A.C.M. Beenackers, Catal. Rev. –Sci. Eng. 41 (1999) 255–318.
- [9] A. Haghtalab, M. Nabipoor, S. Farzad, Fuel Process. Technol. 104 (2012) 73-79.
- [10] B.W. Wojciechowski, Catal. Rev. -Sci. Eng. 30 (1988) 629-702.
- [11] E. Iglesia, S.C. Reyes, R.J. Madon, S.L. Soled, Adv. Catal. 39 (1993) 221-302.
- [12] E.W. Kuipers, I.H. Vinkenburg, H. Oosterbeek, J. Catal. 152 (1995) 137-146.
- [13] J. Happel, S. Kiang, J.L. Spencer, S. Oki, M.A. Hnatow, J. Catal. 50 (1977) 429-440.
- [14] J. Happel, I. Suzuki, P. Kokayeff, V. Fthenakis, J. Catal. 65 (1980) 59-77.
- [15] J. Happel, H.Y. Cheh, M. Otarod, S. Ozawa, A.J. Severdia, T. Yoshida, V. Fthenakis, J. Catal. 75 (1982) 314–328.
- [16] C.O. Bennett, Catal. Rev. -Sci. Eng. 13 (1976) 121-148.
- [17] H. Matsumoto, C.O. Bennett, J. Catal. 53 (1978) 331-344.
- [18] P. Biloen, J.N. Helle, W.M.H. Sachtler, J. Catal. 58 (1979) 95-107.
- [19] P. Biloen, J. Mol. Catal. 21 (1983) 17-24.
- [20] Y. Soong, P. Biloen, Langmuir 1 (1985) 768-770.

- [21] A. Frennet, C. Hubert, J. Mol. Catal. A: Chem. 163 (2000) 163–188.
- [22] S.L. Shannon, J.G. Goodwin, Chem. Rev. 95 (1995) 677-695.
- [23] C. Ledesma, J. Yang, D. Chen, A. Holmen, ACS Catal. 4 (2014) 4527-4547.
- [24] H.A.J. van Dijk, The Fischer-Tropsch synthesis A mechanistic study using transient isotopic tracing, TU/e, Eindhoven, 2001.
- [25] N.S. Govender, Mechanistic study of the High Temperature Fischer-Tropsch Synthesis using transient kinetics, Eindhoven, 2010.
- [26] J.V. Fletcher, Mechanistic Pathways of the High Temperature Fischer-Tropsch Synthesis, Eindhoven, 2016.
- [27] C. Ledesma, J. Yang, E.A. Blekkan, A. Holmen, D. Chen, ACS Catal. 6 (2016) 6674– 6686.
- [28] N. Lohitharn, J. Goodwin, J. Catal. 257 (2008) 142-151.
- [29] N. Lohitharn, J. Goodwin, J. Catal. 260 (2008) 7-16.
- [30] J. Yang, Y. Qi, J. Zhu, Y.-A. Zhu, D. Chen, A. Holmen, J. Catal. 308 (2013) 37-49.
- [31] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P.d. Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [32] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Langmuir 26 (2010) 16558-16567.
- [33] J. Yang, D. Chen, A. Holmen, Catal. Today 186 (2012) 99–108.
- [34] B.C. Enger, V. Frøseth, J. Yang, E. Rytter, A. Holmen, J. Catal. 297 (2013) 187–192.
- [35] P. Winslow, A.T. Bell, J. Catal. 86 (1984) 158-172.
- [36] H.A.J. van Dijk, J.H.B.J. Hoebink, J.C. Schouten, Top. Catal. 26 (2003) 111-119.
- [37] Y. Qi, J. Yang, D. Chen, A. Holmen, Catal. Lett. 145 (2015) 145-161.
- [38] F.B. de Mongeot, A. Toma, A. Molle, S. Lizzit, L. Petaccia, A. Baraldi, Phys. Rev. Lett. 97 (2006) 056103.
- [39] S. Shetty, A.P.J. Jansen, R.A. van Santen, J. Am. Chem. Soc. 131 (2009) 12874– 12875.
- [40] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.
- [41] M.N. Qingfeng Ge, J. Phys. Chem. B 110 (2006) 15368-15380.
- [42] J.-X. Liu, H.-Y. Su, W.-X. Li, Catal. Today 215 (2013) 36-42.
- [43] B. Hammer, Phys. Rev. Lett. 83 (1999) 3681-3684.
- [44] S. Dahl, A. Logadottir, R.C. Egeberg, J.H. Larsen, I. Chorkendorff, E. Törnqvist, J.K. Nørskov, Phys. Rev. Lett. 83 (1999) 1814–1817.
- [45] K. Honkala, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Norskov, Science 307 (2005) 555–558.
- [46] R. van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189-230.
- [47] P. van Helden, I.M. Ciobîcă, R.L.J. Coetzer, Catal. Today 261 (2016) 48-59.
- [48] Y. Qi, J. Yang, X. Duan, Y.-A. Zhu, D. Chen, A. Holmen, Catal. Sci. Technol. 4 (2014) 3534–3543.
- [49] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, J. Catal. 272 (2010) 287–297.

- [50] B.T. Loveless, C. Buda, M. Neurock, E. Iglesia, J. Am. Chem. Soc. 135 (2013) 6107– 6121.
- [51] A. Tuxen, S. Carenco, M. Chintapalli, C.H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A.P. Alivisatos, G. Thornton, W.F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, J. Am. Chem. Soc. 135 (2013) 2273–2278.
- [52] W.J. Mitchell, J. Xie, T.A. Jachimowski, W.H. Weinberg, J. Am. Chem. Soc. 117 (1995) 2606–2617.
- [53] W. Chen, B. Zijlstra, R. Pestman, E. Hensen, ChemCatChem, DOI: 10.1002/cctc.201701203.
- [54] J. Schweicher, A. Bundhoo, N. Kruse, J. Am. Chem. Soc. 134 (2012) 16135–16138.
- [55] N. Kruse, J. Schweicher, A. Bundhoo, A. Frennet, T. Visart de Bocarmé, Top. Catal. 48 (2008) 145–152.
- [56] J. Schweicher, A. Bundhoo, A. Frennet, N. Kruse, H. Daly, F.C. Meunier, J. Phys. Chem. C 114 (2010) 2248–2255.
- [57] S.G. Shetty, I.M. Ciobîcă, E.J. Hensen, R.A. van Santen, Chem. Commun. 47 (2011) 9822–9824.
- [58] P. Winslow, A.T. Bell, J. Catal. 94 (1985) 385-399.
- [59] I. Toyoshima, G.A. Somorjai, Catal. Rev. -Sci. Eng. 19 (1979) 105-159.
- [60] N.W. Cant, A.T. Bell, J. Catal. 73 (1982) 257-271.
- [61] W.T. Ralston, G. Melaet, T. Saephan, G.A. Somorjai, Angew. Chem. Int. Ed. 56 (2017) 7415–7419.
- [62] J. Nakamura, K.-i. Tanaka, I. Toyoshima, J. Catal. 108 (1987) 55-62.
- [63] J. Nakamura, I. Toyoshima, K.-I. Tanaka, Surf. Sci. 201 (1988) 185-194.
- [64] P. Azadi, G. Brownbridge, I. Kemp, S. Mosbach, J.S. Dennis, M. Kraft, ChemCatChem 7 (2015) 137–143.
- [65] C. Campbell, J. Catal. 204 (2001) 520-524.
- [66] C. Stegelmann, A. Andreasen, C.T. Campbell, J. Am. Chem. Soc. 131 (2009) 8077– 8082.
- [67] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.



Science is the mechanism of how time flies.

Mechanism of cobalt-catalyzed CO hydrogenation: 2. Fischer–Tropsch synthesis

Abstract

Fischer-Tropsch (F-T) synthesis is one of the most complex catalyzed chemical reactions in which the chain-growth mechanism that leads to formation of long-chain hydrocarbons is not well understood yet. The present work provides deeper insight into the relation between the kinetics of the F-T reaction on a silica-supported cobalt catalyst and the composition of the surface adsorbed layer. Co-feeding experiments of ¹²C₃H₆ with ¹³CO/H₂ evidence that CH_x surface intermediates are involved in chain growth and that chain growth is highly reversible. We present a model-based approach of steady state isotopic transient kinetic analysis measurements at F-T conditions involving hydrocarbon products containing up to 5 carbon atoms. Our data show that the rates of chain growth and chain decoupling are much higher than the rates of monomer formation and chain termination. An important corollary of the microkinetic model is that the fraction of free sites, which is mainly determined by CO pressure, has opposing effects on CO consumption rate and chaingrowth probability. Lower CO pressure and more free sites leads to increased CO consumption rate, but decreased chain-growth probability because of an increasing ratio of chain decoupling over chain growth. The preferred F-T condition involves high CO pressure in which chain-growth probability is increased at the expense of the CO consumption rate.



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5.1 Introduction

The Fischer–Tropsch (F–T) process encompasses a collection of chemical reactions that converts mixtures of CO and H₂ (synthesis gas) into liquid hydrocarbon fuels and chemicals [<u>1-4</u>]. It is currently primarily used to add value to large reserves of natural gas and coal by producing low-sulfur diesel or gasoline fuels. When natural gas is the feedstock for producing synthesis gas, cobalt is the preferred metal [<u>5</u>]. Alternatively, coal-derived synthesis gas is usually upgraded by iron-containing catalysts, mainly because of their higher water-gas shift activity [<u>6</u>]. In future energy scenarios, similar chemistry may also be used to upgrade resources such as biomass via synthesis gas [<u>7</u>, <u>8</u>] and to convert CO₂ with renewable H₂ into liquid fuels and chemicals [<u>9</u>, <u>10</u>]. Besides these practical aspects, catalytic F–T synthesis of hydrocarbons continues to be of substantial scientific interest, because it involves a large number of elementary surface reaction steps, in which different sorts of surface intermediates participate, giving rise to CO dissociation, chain growth into long-chain olefins and paraffins and removal of oxygen in the form of water [<u>11-13</u>].

The complexity of the F–T reaction has led to an intense debate on the underlying mechanism, which is as old as this nearly one-century-old reaction itself [14-16]. The mostdiscussed one is arguably the way the long-chain hydrocarbons are formed at the catalytic surface. It not only pertains to the chain-growth step itself but also to the mode of CO bond dissociation. The original idea proposed by Fischer and Tropsch was that metal carbide reacts with H₂ to produce methylene, acting as chain-growth monomer for long-chain hydrocarbon formation via polymerization [2]. This idea was later supported by experimental data [17-21], and has been retained up to now [12, 13]. Alternatively, Pichler and Schulz proposed a chain-growth pathway that proceeds via insertion of CO into the growing chains, followed by cleavage of the C–O bond [22]. Zhuo *et al.* [23] and Schweicher *et al.* [24] presented theoretical and experimental data, respectively, to support this mechanism. Also, other chain-growth monomers have been invoked such as the formyl group [25]. So far, there is no consensus on the dominant mechanism, essentially because it is difficult to design experiments that allow distinguishing the two pathways.

Independent of the exact mechanism, a general feature of the F–T reaction is that it proceeds as a surface polymerization process with in situ generation of chain-growth monomer, as reflected by the relative ratios of hydrocarbons of different length usually following a typical Anderson–Schulz–Flory (ASF) distribution [26-28]. Typically, this distribution is discussed in terms of a single parameter, the chain-growth probability α , defined as:

$$\alpha = \frac{r_{\rm p}}{r_{\rm p} + r_{\rm t}} \tag{5.1}$$

where r_p and r_t refer to the rates of propagation and termination of the hydrocarbon chain, respectively. As typically the aim of the F–T process is to produce long-chain hydrocarbons, it is important to understand the kinetic aspects of this chain reaction in which monomer formation (initiation), chain growth (propagation) and chain termination are involved. These insights will help to improve activity and selectivity of F–T catalysts.

Regarding F-T reaction mechanism, most attention has been devoted to understanding CO bond dissociation on F-T active metals such as cobalt and ruthenium. Kinetically, CO bond dissociation should occur at a sufficient rate to provide enough monomers for chaingrowth [12, 13]. As the activation barrier of CO dissociation on cobalt [29-32] and ruthenium [32, 33] terraces is too high to be consistent with F-T reactivity, H-assisted CO bond dissociation on terraces has been considered involving HCO [34] or HCOH [35-38] intermediates. This mechanism can explain the positive reaction order with respect to H_2 assuming that CO dissociation is the rate-determining step. The alternative view is that step-edges are the active sites involved in CO dissociation. Density functional theory (DFT) calculations have shown that stepped sites can dissociate CO with low barrier without the involvement of H atoms [31-33]. We have recently confirmed that reversible CO dissociation can occur on cobalt nanoparticles without the assistance of hydrogen and that this reaction involves a relatively small fraction of the cobalt metal surface [39]. An important kinetic implication of this earlier work is that the near-unity reaction order with respect to H₂ observed during CO methanation is not caused by rate-determining CO dissociation but, instead, by slow hydrogenation of C atoms relative to CO dissociation [40].

In this work, we focus on the chain-growth mechanism over the same silica-supported cobalt catalyst. We provide support for the importance of CH_x species as chain-growth monomer and present experimental evidence for the earlier discussed hypothesis that chain growth is reversible [41-44]. The reversibility of chain growth has profound implications on the relation between the composition of the surface adsorbed layer and the chain-growth probability. We employ steady state isotopic transient kinetic analysis to investigate chain growth by carefully examining the coverage of carbon-containing reaction intermediates and transient responses of F–T products. These unique data show that forward and backward chain-growth reactions are very fast in comparison to other elementary reaction steps including chain termination. The obtained steady state and transient data are used to fit a simplified microkinetic model. Microkinetics simulations are used to understand in detail the influence of particular reaction steps on activity and selectivity. Specifically, we will demonstrate how CO consumption rate strongly decreases with the fraction of free sites, while the reverse holds true for the chain-growth probability.

5.2 Experimental

5.2.1 Preparation and basic characterization

The Co/SiO₂ catalyst prepared by incipient wetness impregnation method containing 17.1 wt% cobalt and 0.04 wt% platinum as determined by ICP–OES (SpectroBlue, Ametek Inc.), where Pt was used as reduction promoter. The catalysts were dried at 110°C for 12 h and then calcined at 350°C in static air for 2h using a heating rate of 1°C min⁻¹. Cobalt dispersion was measured by H₂-chemisorption on Micromeritics ASAP 2010 after reaction at 450°C for 6 h. The average cobalt particle size is 15 nm as determined by TEM (FEI Tecnai 20, LaB6, 200 kV) and *in situ* XRD (D/max-2600, Rigaku). More details of experimental information can be found in Section 3.2.

5.2.2 In situ FTIR spectroscopy

FTIR spectra were recorded on Bruker Vertex V70v instrument. Typically, 15 mg of finely ground Co/SiO₂ catalyst was pressed into a self-supporting wafer and placed in an environmental transmission IR cell, which can be subjected to heating, cooling, gas dosing and evacuation. Before IR measurements, the catalyst wafer was reduced *in situ* at 450°C in a H₂ flow for 2 h. Subsequently, the cell was evacuated at 450°C for 1 h to remove adsorbed hydrogen, followed by cooling to 35°C in vacuum. Then, an IR spectrum was recorded as background for subsequent measurements. In a typical experiment, the cell was pressurized with 10 mbar CO using a needle valve. After 0.5, h the cell was evacuated to a pressure lower than 10⁻⁵ mbar and heated to 300°C at a rate of 5°C min⁻¹. IR spectra were recorded every 5°C at a resolution of 2 cm⁻¹. Each spectrum involved 16 accumulations that were averaged.

5.2.3 Steady state isotopic transient kinetic analysis (SSITKA)

Steady state isotopic transient kinetic analysis (SSITKA) experiments were performed by a ${}^{12}\text{CO/H}_2 \rightarrow {}^{13}\text{CO/H}_2$ switch when steady state CO conversion was obtained. The catalytic activity in steady state was determined online by analyzing the effluent gas on a Varian CP-3800 gas chromatograph equipped with TCD and FID detectors. The transient responses of Ne, ${}^{12}\text{CH}_4$, ${}^{13}\text{CH}_4$, ${}^{12}\text{CO}$ and ${}^{13}\text{CO}$ were monitored by an online mass spectrometer (ESS, GeneSys Evolution) using *m/z* values of 22, 15, 17, 28 and 29, respectively. The transients of higher hydrocarbons were measured by a gas chromatograph equipped with a mass spectrometer (Shimazu, GCMS-QP 2010) and a 16-loop sample holder for storage of gas samples. In this way, the isotopic composition of higher hydrocarbons formed in during a short reaction period can be analyzed. Detailed experimental and data analysis procedures can be found in Section 2.2 and 2.3.

5.3 Results and discussion

SSITKA is uniquely suited to determine the coverage of reversibly adsorbed surface species during heterogeneous reactions [45-47]. In a companion paper, we already discussed CO hydrogenation to CH₄ at 260°C on the same Co/SiO₂ catalyst. At this temperature, the formation of higher hydrocarbons is limited. The SSITKA data show that CO coverage under methanation conditions is relatively low ($\theta_{CO} < 0.30$) [40]. As a consequence, CO dissociation is intrinsically fast as compared to the hydrogenation of C and O species. It is important to establish how this picture changes when the temperature is decreased to 220°C, which is a temperature close to the F–T condition. We will first show SSITKA data from which steady state reaction rates, surface coverages and other relevant kinetic parameters are derived. Then, we will provide evidence for the reversibility of chain growth, which is decoupling of chains into shorter chains and C₁ monomers, and the importance of high CO coverage to the F–T condition. In the last part, we will discuss a microkinetic model fitted to experimental transient data and employ simulations based on this model to identify rate- and selectivity-controlling steps.

5.3.1 Steady state kinetics

Figure 5.1 shows the kinetic data derived from steady state measurements at different temperatures. We include data obtained at 260°C to highlight the influence of temperature. The overall apparent activation energy is about 74 kJ mol⁻¹ at $p_{CO} = 90$ mbar, which is higher than the value of 57 kJ mol⁻¹ obtained at $p_{CO} = 450$ mbar. It is also notable that the apparent activation energies based on the CH₄ formation rate are higher than those based on CO conversion. This is consistent with the higher CH₄ selectivity at lower CO partial pressure or when the temperature is raised. A necessary condition for F–T synthesis is that CH₄ formation has a higher activation energy than C₂₊-hydrocarbons formation. This difference also explains the observation that the reaction orders for CH₄ formation with respect to CO partial pressure are more negative than those for CO conversion. We observe that the chain-growth probability strongly decreases with temperature. Notably, the chain-growth probability is in the range of 0.52–0.85 under the conditions applied for model fitting (*vide infra*).

SSITKA experiments were carried out at 220°C and 260°C to determine steady state CO and CH_x surface coverages as a function of CO and H₂ partial pressure. A typical SSITKA result following a 12 CO/H₂ \rightarrow 13 CO/H₂ switch at 220°C is presented in Figure 5.2. Figure 5.3 reports the steady state CO coverages obtained from SSITKA at 220°C and 260°C as a function of the CO and H₂ partial pressure. In agreement with literature [<u>38</u>], the CO coverage increases with CO partial pressure following a Langmuir isotherm dependence. The CH_x coverage does not vary strongly with CO partial pressure and a small decrease is noted. Figure 5.3b shows that the CO coverage only weakly depends on the

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Figure 5.1. Kinetic parameters derived from steady state measurement as a function of temperature ($p_{CO} = 90-450$ mbar, $p_{H_2} = 900$ mbar): (a) turnover frequency (*TOF*) of CO conversion, (b) *TOF* of CH₄ formation, (c) reaction order with respect to CO, and (d) chain-growth probability.



Figure 5.2. Typical transient responses following a ${}^{12}\text{CO/H}_2 \rightarrow {}^{13}\text{CO/H}_2$ switch. Condition at steady state: $T = 220^{\circ}\text{C}$, $p_{\text{H}_2} = 900$ mbar, $p_{\text{CO}} = 180$ mbar.

 H_2 partial pressure between 180 mbar and 1800 mbar, whereas the CH_x coverage is hardly affected. As outlined in our companion paper [40], this result is consistent with the stronger adsorption of CO in comparison with H.

At 220°C, the CO coverage reaches a maximum of 0.46 at a CO partial pressure of 450 mbar. A further increase does not further raise the CO coverage. The remainder of the surface is covered by CH_x species, growing chains (adsorbed C_{2+}) and, probably, irreversibly adsorbed species that cannot be determined by SSITKA and free sites. This result indicates that a CO coverage of about 0.5 ML is close to the saturated CO coverage at this temperature. This is consistent with recent single crystal Co(0001) data using a Kelvin probe to determine CO coverage [<u>48</u>]. DFT calculations of the group of Saeys show that on the Co(0001) surface a maximum coverage of about 7/12 ML can be obtained [<u>49</u>].



Figure 5.3. Coverage of CO (squares) and C_1 (circles) species as determined by SSITKA over the cobalt catalyst as a function of (a) CO pressure and (b) H_2 pressure at 220°C (solid symbols) and 260°C (open symbols).



Figure 5.4. Chain-growth probability as a function of $\theta_v K_{CO}$ (= θ_{CO}/p_{CO}) at 220°C (squares) and 260°C (circles) as a function of CO pressure (denoted as solid symbols, $p_{H_2} = 900$ mbar, $p_{CO} = 90-900$ mbar) and varying H₂ pressure (denoted as open symbols, $p_{H_2} = 180-1800$ mbar, $p_{CO} = 180$ mbar), where θ_{CO} is the CO coverage determined by SSITKA and p_{CO} is CO pressure applied.

To gain insight into the fraction of free sites, which cannot be measured explicitly, we assume that the adsorption-desorption equilibrium of CO is established. Then, we can express the vacancy density, θ_v , as

$$\theta_{\rm v} K_{\rm CO} = \theta_{\rm CO} / p_{\rm CO} \tag{5.2}$$

where θ_{CO} is the CO coverage, K_{CO} the equilibrium constant of CO adsorption, which is assumed to be independent of surface coverage, and p_{CO} CO partial pressure. Using actual values for the applied CO partial pressure and the SSITKA-measured CO coverage leads to the result that the fraction of vacancies is reduced by a factor of 7 when the CO partial pressure increases from 90 mbar to 900 mbar, while this fraction only decreased by less than 20% when the H₂ partial pressure increases from 180 mbar to 1800 mbar. This is expected as CO binds much stronger to the cobalt surface than H. Importantly, within the range of conditions we study here, a decrease in the fraction of free sites is strongly correlated to the CO partial pressure, while it hardly depends on the H₂ partial pressure.

Based on this correlation, Figure 5.4 shows how chain-growth probability depends on $\theta_v K_{CO}$. It emphasizes the strong correlation between free sites and chain-growth probability. Kruse and co-workers linked higher chain-growth probability to higher CO coverage (and thus, CO partial pressure) in the framework of the CO insertion mechanism [24]. In the CO insertion mechanism, CO dissociation provides the C₁ species that initiates chain growth. Thus, a decreased CO dissociation rate with increasing CO coverage is also consistent with the observation that CO consumption rate decreases. In the following section, we will discuss an alternative interpretation of these data following the carbide mechanism, involving reversibility of the chain-growth step.

5.3.2 Chain-growth monomer

The two essentially different reaction paths proposed for the chain-growth mechanism in the F–T reaction differ by the chain-growth monomer, a CH_x species in the carbide mechanism [2] and CO in the CO-insertion mechanism [22]. First-principles-based microkinetics simulations on a stepped ruthenium surface operating under F–T conditions have demonstrated that CH insertion is the dominant growth mechanism [50]. For both mechanisms, a necessary condition is that the chain growth should be relatively fast compared to chain termination [51].

We investigated the possibility of chain growth via CH_x species in the following manner. An *in situ* reduced catalyst was first exposed to CO flow at 260°C for 0.5 h to deposit C atoms, and then evacuated (< 10⁻⁵ mbar) at 300°C for 1 h to remove adsorbed CO, eliminating a possible contribution of CO insertion into growing hydrocarbons. The absence of molecularly adsorbed CO was confirmed by IR spectra of adsorbed CO on the Co/SiO₂ catalyst recorded with increasing temperature (Figure 5.5a). After cooling to



Figure 5.5. (a) IR spectra of adsorbed CO recorded in vacuum at increasing temperature showing that adsorbed CO is removed by evacuation at 300°C. (b) Evolution of MS signals after H₂-exposure at 200°C (bottom), 220°C (middle) and 260°C (top) over the cobalt catalyst, which was exposed to a CO flow at 260°C for 30 min, followed by evacuation at 300°C for 1 h.

200°C, 220°C or 260°C, the catalyst was exposed to a H₂ flow. As shown in Figure 5.5b, H₂-exposure at 260°C led mainly to CH₄ and a small amount of C₂. When decreasing the hydrogenation temperature, the MS signals related to C₂ and C₃ hydrocarbons increased. Considering the absence of molecular CO, we conclude that the pre-deposited C species are involved in the formation of higher hydrocarbons. This further demonstrates that the carbide mechanism can contribute to chain growth in the F–T reaction.

5.3.3 Co-feeding of ¹³CO and ¹²C₃H₆

In most experimental kinetic studies of the F–T reaction, it is assumed that the chaingrowth step is irreversible. Quantum-chemical studies of chain growth on metallic cobalt and ruthenium surfaces according to the carbide mechanism show that the activation barriers for the insertion of the C₁ monomer into a growing chain and the reverse decoupling are of the same magnitude [43]. Microkinetics simulations based on the carbide mechanism predict that this reversibility should occur under F–T conditions [44]. In order to experimentally verify the reversibility of chain growth, we carried out experiments in which ${}^{12}C_{3}H_{6}$ was co-fed with ${}^{13}CO/H_{2}$.

Figure 5.6 shows that ${}^{12}CH_4$ appears in the hydrocarbon product mixture during ${}^{13}CO$ hydrogenation in the presence of ${}^{12}C_3H_6$. This evidences that the cobalt nanoparticle surface can decompose C–C bonds under F–T conditions. Additionally, the simultaneous presence of ${}^{12}C$ and ${}^{13}C$ in C₂-products shows that the ${}^{12}C$ atoms obtained from ${}^{12}C_3H_6$ can be coupled to form higher products. We also observe that hydrocarbons with more than three C atoms contain different amounts of ${}^{12}C$, indicating that ${}^{12}CH_x$ species are involved in the reaction as chain-growth monomers. Thus, this intermediate is both involved in chain growth and chain decoupling.



number of ¹²C atoms in a given molecule

Figure 5.6. Isotopic content of alkane products when co-feeding ${}^{12}C_{3}H_{6}$ with ${}^{13}CO/H_{2}$ as a function of the CO partial pressure. The colors indicates the number of ${}^{12}C$ atoms in a given hydrocarbon. The markers show the total ${}^{12}C$ fraction for each product. Conditions: $T = 220^{\circ}C$, $p_{H_{2}} = 600$ mbar, $p_{{}^{12}C_{3}H_{6}} = 60$ mbar.

To gain an understanding into the chain-growth behavior of C_1 monomers derived from co-fed ${}^{12}C_3H_6$, ASF-plots are presented in Figure 5.7. A mixture of ${}^{12}C_3H_6/H_2$ without CO gives rise to a hydrocarbons product distribution qualitatively similar to the distribution obtained with a CO/H₂ mixture. It should be noted that the C₃ products are an exception because of the co-feeding of propene. A substantial fraction of the ${}^{12}C_3H_6$ is hydrogenated to ${}^{12}C_3H_8$. This observation proves that similar chain growth as in the F–T reaction occurs with ${}^{12}C_1$ species derived from ${}^{12}C_3H_6$. Figure 5.7 also shows that the addition of ${}^{12}C_3H_6$ to a ${}^{13}CO/H_2$ mixture facilitates the formation of higher hydrocarbons, both in terms of yield and chain-growth probability. Thus, the higher formation rate of higher hydrocarbons can be attributed to ${}^{12}C_1$ species obtained by ${}^{12}C_3H_6$ decoupling. As the ${}^{12}C_1$ species obtained by ${}^{12}C_3H_6$ decoupling are free of O, the CO-insertion mechanism cannot explain this specific case of chain growth. Considering furthermore that the product distribution in the presence

Table 5.1. Chain-growth probability (α , based on C₄–C₇ products) with and without 60 mbar co-fed ¹²C₃H₆ at different ¹³CO partial pressure, Condition: $T = 220^{\circ}$ C, $p_{H_2} = 600$ mbar.

$p_{^{13}\mathrm{CO}}$	$p_{^{12}\mathrm{C}_3\mathrm{H}_6}$	α	
(mbar)	(mbar)		
60	0	0.44	
120	0	0.62	
300	0	0.81	
0	60	0.23	
60	60	0.66	
120	60	0.76	
300	60	0.84	



Figure 5.7. Logarithmic products distribution as a function of carbon number (ASF plot) obtained at 220°C (squares: $p_{H_2} = 600 \text{ mbar}$, $p_{^{12}C_3H_6} = 60 \text{ mbar}$; circles: $p_{H_2} = 600 \text{ mbar}$, $p_{^{13}CO} = 60 \text{ mbar}$; triangles: $p_{H_2} = 600 \text{ mbar}$, $p_{^{13}CO} = 60 \text{ mbar}$; $p_{H_2} = 600 \text{ mbar}$, $p_{^{12}C_3H_6} = 60 \text{ mbar}$).

of ${}^{12}C_{3}H_{6}$ (except for C₃) is almost similar to the product distribution obtained without cofed ${}^{12}C_{3}H_{6}$, we conclude that chain growth will proceed via an O-free C₁ species, that is to say via the carbide mechanism. The chain-growth probability values based on C₄–C₇ products obtained at different conditions are summarized in Table 5.1. Comparing the values with and without ${}^{12}C_{3}H_{6}$, one can see that the increase in chain-growth probability upon addition of ${}^{12}C_{3}H_{6}$ is limited by the increase in ${}^{13}CO$ partial pressure. Considering the fact that the CO partial pressure significantly influences the fraction of free sites [52, 53]. both ${}^{13}CO$ dissociation and ${}^{12}C_{3}H_{6}$ decomposition will be facilitated by a decrease in the CO partial pressure, and both reactions will supply chain-growth monomers, namely ${}^{13}C_{1}$ and ${}^{12}C_{1}$ monomers, respectively. We observe in Figure 5.6 that the ${}^{12}C$ optent rather than the ${}^{13}C$ optent in the hydrocarbon products increases with decreasing ${}^{13}CO$ pressure. This suggests that the ${}^{12}C_{3}H_{6}$ decomposition profits more from free sites than ${}^{13}C-O$ bond scission. A kinetic implication is that, although C_1 supply via CO dissociation is promoted, an increasing fraction of free sites due to lowering of the CO partial pressure lowers the chain-growth probability due to faster chain decoupling.

5.3.4 Transient response of F-T products

In the context of the F–T reaction, SSITKA has been most frequently used at conditions resulting in high methane selectivity (*i.e.*, $H_2/CO > 2$) [<u>38</u>, <u>54-58</u>]. In this section, SSITKA will be used to study the transient behavior of the hydrocarbon products during the F–T reaction, including CH₄ and higher hydrocarbons. Typical transients of the isotopologues of C₅H₁₂ following a ¹²CO/H₂ \rightarrow ¹³CO/H₂ switch are presented in Figure 5.8. All responses of partially labeled products display a maximum. The position of the maximum shifts in time with increasing isotope content of partially labeled C₅ hydrocarbon. The higher the ¹³C content, the later the maximum occurs. Taking into account the ¹³C content of all the isotopologues allows inspecting the evolution of ¹³C fraction within a given product. An example is presented by the open symbols in Figure 5.8. This evolution is determined in the following manner

$$E_n(t) = \sum_{i=1}^n \frac{i}{n} N_{i,n}(t)$$
(5.3)

where *n* is the chain length of the given product, *i* the number of ¹³C atoms in the product molecule, and $N_{i,n}$ refers to the normalized transient response of the C_n product with *i* ¹³C atoms. The fractional ¹³C evolution of C₁–C₅ alkanes are plotted in Figure 5.9. The result



Figure 5.8. Normalized SSITKA responses (${}^{12}\text{CO/H}_2$) to ${}^{13}\text{CO/H}_2$) of the isotopologues of pentane with different number of ${}^{13}\text{C}$ atoms. The open squares represent the evolution of ${}^{13}\text{C}$ content of pentane molecules (E_n) using the equation above. Conditions: $T = 220^{\circ}\text{C}$, $p_{\text{H}_2} = 900$ mbar, $p_{\text{CO}} = 180$ mbar.

Figure 5.9. Evolution of ¹³C content in F–T products. Transient was performed by a switch from ¹²CO/H₂ to ¹³CO/H₂ at steady state. Conditions: $T = 220^{\circ}$ C, $p_{H_2} = 900$ mbar, $p_{CO} = 180$ mbar.

shows that the evolution of the ${}^{13}C$ content of C_1-C_5 alkanes with time-on-stream after the switch are almost identical and thus independent of chain length. The ^{13}C content of CH₄ can be directly correlated to the ${}^{13}C$ fraction of C_1 species on surface, as the formation of CH₄ does not involve C–C coupling steps but only CO dissociation and C hydrogenation. An implication of the overlapping of the ¹³C evolution curves is that the ¹³C content of all formed hydrocarbons is strongly correlated to the ${}^{13}C/{}^{12}C$ ratio of C₁ species on the surface. This further underpins that the C_1 species is the chain-growth monomer, rather than CO. Typically, the ¹³CO/¹²CO transient in SSITKA, which is directly correlated to the adsorbed ¹³CO/¹²CO ratio on the surface, is significantly shorter than the ¹³CH₄/¹²CH₄ transient (see Figure 5.2). If weakly adsorbed CO is the chain-growth monomer, as proposed by Schweicher *et al.* in the CO-insertion mechanism [24], one expects more rapid introduction of ¹³C fraction into C_{2+} products than in CH₄. The observation that the ¹³C content evolution is independent of chain length of the hydrocarbon including CH₄ therefore demonstrates that CO insertion cannot be the dominant chain-growth mechanism. Regarding the process of chain growth, the formation of a long-chain hydrocarbon will take more time than the formation of a shorter one. The chain-length-independent ¹³C evolution suggests that the chain-growth and decoupling steps are very fast in comparison to monomer formation. In this way, the ¹³C content of the growing chains is dictated by that of the C_1 species. An important corollary of this finding is that the chain-growth rate is mainly limited by the supply of C₁ monomers under the F-T condition on the cobalt catalyst. This is in agreement with microkinetics simulations showing that, within the carbide mechanism, chain- rowth may occur on sites with high CO coverage as long as the rate of chain growth is fast compared to the rate of chain monomer supply [12, 51]. Together with the inverse correlation between the amount of free sites and the chain-growth probability (Figure 5.4) and the reversibility of chain-growth evidenced in the previous section, we conclude that the chain-growth probability is largely controlled by the rate of chain growth vs. chain decoupling. More free sites implies a higher rate of chain decoupling, while a higher rate of monomer formation leads to higher chain-growth probability. Recalling enhanced ¹²C₃H₆ decomposition by a decrease in the ¹³CO partial pressure, the fraction of free sites influences chain decoupling more significantly than C-O scission. This issue will also follow from microkinetic modeling to be discussed below.

Figure 5.10 plots the transients of unlabeled and fully labeled C_1-C_5 alkanes following a ${}^{12}CO/H_2 \rightarrow {}^{13}CO/H_2$ switch. We observed that the transient of unlabeled short chain hydrocarbon is slower than that of longer ones and that ${}^{12}CH_4$ decays slowest amongst all unlabeled products. The fully labeled products appear in the other way around, *i.e.*, the transient responses of fully labeled products become slower with increasing carbon number. The noteworthy aspect is that the responses of unlabeled and fully labeled isotopologues of all products cross each at the same time (~7 s). At this moment, as shown in Figure 5.9, the overall ${}^{13}C$ content is ~50% in all products. A similar observation was recently reported by Ledesma *et al* [59]. Its reason has been discussed above, *i.e.*, fast chain propagation/decomposition reactions result in a chain-length-independent ¹³C evolution within a given product.

The residence time of unlabeled and fully labeled hydrocarbons measured at different CO partial pressure are presented as a function of chain length in Figure 5.11. The residence time of unlabeled products decreases with chain length, while the fully labeled products shows an opposite trend in residence time. The physical meaning of the residence time of CH₄ is clear [45, 56-58]. However, the meaning of the residence time of higher hydrocarbons is less evident, as the intermediates of long-chain hydrocarbon can be formed via multiple routes on the catalytic surface. For instance, C_2H_6 can be formed via either hydrogenation of adsorbed C_2 species, or C–C coupling followed by hydrogenation, implying that the measured residence time of C_2H_6 is a combination of several paths. In other words, it is not possible to directly derive intrinsic formation rate of C_{2+} -hydrocarbons as is customarily done for CH₄ on the basis of its residence time. Therefore, a model fitting approach is employed to extract kinetic parameters that intrinsically control the activity and selectivity of the F–T reaction on the Co/SiO₂ catalyst.



Figure 5.10. Normalized SSITKA responses of unlabeled (open symbols) and fully labeled (solid symbols) alkanes. The green lines are the response curves for methane. The arrows point into the direction with increasing length up to the response curves for pentane in red. Conditions: $T = 220^{\circ}$ C, $p_{H_2} = 900$ mbar, $p_{CO} = 180$ mbar.



Figure 5.11. Residence time of fully labeled (upper) and unlabeled (bottom) alkanes measured at different CO partial pressure. The spots and lines represent the measurement and model fitting results, respectively. Transient was performed by a switch from ¹²CO/H₂ to ¹³CO/H₂ at steady state. Conditions: $T = 220^{\circ}$ C, $p_{H_2} = 900$ mbar, $p_{C0} = 90-900$ mbar.

5.3.5 Microkinetic modeling

Based on the mechanistic insights described in the previous sections, a lumped kinetic model [44, 60] was established and fitted with steady state kinetic and SSITKA data obtained at the following conditions: $p_{CO}=90-900$ mbar, $p_{H_2}=900$ mbar and $T=220^{\circ}$ C. The model, which is schematically shown in Figure 5.12, takes into account the carbide



Figure 5.12. Schematic representation of the F–T mechanism, where θ_{CO} presents adsorbed CO, θ_{Ci} adsorbed chains of *i* carbon atoms, C_i desorbed product of *i* carbon number, and θ_v vacant sites. k_{ads}/k_{des} presents the CO adsorption/desorption rate constants, k_{diss} the CO dissociation rate constant, k_{tm} the methane termination rate constant, k_i the chain termination rate constant and k_i/k_b the forward/backward chain-growth rate constants.

mechanism and reversible chain-growth. As compared to our earlier microkinetic model based on experimental transient kinetic data determined under methanation conditions [40], hydrogenation steps are not explicitly involved but lumped into the rate constants. This is mainly done because involving hydrogenation steps into the reaction model would dramatically increase the number of unknown variables, but also because the H coverage before and after the SSITKA switches remains unchanged [60].

In the microkinetic model, CO adsorbs and desorbs with rate constants k_{ads} and k_{des} , respectively. Adsorbed CO dissociates with rate constant k_{diss} to yield C and O species. Notably, k_{diss} implicitly involves the H coverage for the C \rightarrow CH_x reaction. The latter one is denoted by C₁ and is the chain-growth monomer. All chain-growth reaction steps, incorporating a C₁ species into a growing chain C_i, are considered to be reversible with rate constants k_f and k_b , respectively. These rate constants are assumed to be independent of the chain length. The intermediate that leads to CH₄ and the chain-growth monomer are assumed to be the same C₁ species. C₁ and C_i desorb as CH₄ and long-chain hydrocarbons in single lumped steps with rate constant k_{tm} and k_t , respectively. The value of k_{tm} is expected to be larger than that of k_t , as the selectivity of CH₄ is always higher than the expected CH₄ selectivity on the basis of the ASF distribution [<u>26-28</u>]. Adsorbed O is hydrogenated and removed as water with a lumped rate constant k_w . Re-adsorption of products is not considered in this model. The site balance is expressed by

$$\theta_{\rm CO} + \theta_{\rm O} + \theta_{\rm v} + \sum_{i=1}^{\infty} \theta_i = 1 \tag{5.4}$$

The chain-growth probability is assumed to be chain-length independent and is determined by $\alpha = \theta_{C_{i+1}}/\theta_{C_i}$ [44, 60]. Accordingly, the site balance can be rewritten as

$$\frac{\theta_1}{1-\alpha} + \theta_{\rm CO} + \theta_0 + \theta_{\rm v} = 1 \tag{5.5}$$

Together with the site balance (Eq. 5.4), there are 6 differential equations that describe this model in terms of the evolution of surface coverage. In steady state, the differential equations are equal to zero.

$$\frac{d\theta_{\rm CO}}{dt} = k_{\rm ads} P_{\rm CO} \theta_{\rm v} - k_{\rm des} \theta_{\rm CO} - k_{\rm diss} \theta_{\rm CO} \theta_{\rm v} = 0$$
(5.6)

The C₁ and O coverages are given by

$$\frac{d\theta_{C_1}}{dt} = k_{diss}\theta_v\theta_{CO} - k_{tm}\theta_1 + (k_b\theta_v - k_f\theta_1)\frac{\theta_1}{1-\alpha} - k_f\theta_1^2 + k_b\theta_v\theta_1(\alpha - 1) = 0 (5.7)$$

$$\frac{d\theta_O}{dt} = k_{diss}\theta_{CO}\theta_v - k_w\theta_O = 0$$
(5.8)

As the coverage with growing chain is also constant, we can write:

$$\frac{d\theta_{C_i}}{dt} = k_f \theta_1 + k_b \theta_v \alpha^2 - \alpha (k_f \theta_1 + k_b \theta_v + k_t) = 0$$
(5.9)

The carbon balance yields:

$$k_{\rm ads} P_{\rm CO} \theta_{\rm v} - k_{\rm des} \theta_{\rm CO} - k_{\rm tm} \theta_1 - \frac{k_{\rm f} \theta_1}{(1-\alpha)^2} + k_{\rm f} \theta_1 = 0$$
(5.10)

Numerically solving this set of 6 equations will lead to the steady state coverages θ_{CO} , θ_{O} , θ_{C_1} , and θ_v and the chain-growth probability. The experimental data to be fitted include transient data (data points in in Figs. 11) and steady state CO conversion rates and chain-growth probabilities measured at different CO partial pressure (90 – 900 mbar) at constant H₂ partial pressure (900 mbar) (Figure 5.1). The mathematical description of the SSITKA model and fitting procedure are described in the Appendix III.

The curves in Figure 5.11 show the good correspondence between experimental SSITKA data and model fitting. The rate constants determined by fitting the data obtained at different CO partial pressure are listed in Table 5.2. These data normalized based on the data obtained at the condition of p_{CO} = 90 mbar and p_{H_2} = 900 mbar are plotted in Figure 5.13 as a function of CO partial pressure. As expected, the rate constants of CH₄ formation (k_{tm}) and chain termination (k_t) decrease with rising CO pressure, because increasing CO pressure is accompanied by a decrease in the H coverage that is implicitly involved in k_{tm} and k_t . We observe that k_{tm} decreases more pronounced than k_t . This difference is in line with the experimentally observed more negative CO reaction order on the basis of CH₄ than on the basis of CO conversion. Note that the forward and backward chain-growth rates are



Figure 5.13. Rate constants determined by model fitting ($T = 220^{\circ}$ C, $p_{H_2} = 900$ mbar, $p_{CO} = 90-900$ mbar). The data are normalized based on the values obtained at $p_{CO} = 90$ mbar.

$p_{\rm CO}$ (mbar)	$k_{\rm ads}{}^{\rm a}$	kdes	kdiss	$k_{ m tm}$	<i>k</i> t	$k_{ m f}$	$k_{ m b}$	$k_{ m w}$
90	3.7	0.033	1.30	0.60	0.22	4.1×10^{3}	2.1×10^{3}	0.163
137	3.6	0.034	1.31	0.52	0.18	4.5×10^{3}	2.1×10^{3}	0.135
180	3.4	0.036	1.32	0.43	0.16	4.7×10^{3}	2.2×10^{3}	0.143
300	2.9	0.038	1.39	0.28	0.13	4.7×10^{3}	2.4×10^{3}	0.144
450	2.8	0.039	1.38	0.19	0.10	4.8×10^{3}	2.5×10^{3}	0.148
900	2.6	0.042	1.40	0.079	0.076	5.1×10^{3}	2.6×10^{3}	0.149

Table 5.2. Rate constants [s⁻¹] determined by model fitting.

^a Unit: [s⁻¹ bar⁻¹]

orders of magnitude higher than the other rates. This is in accordance with a high exchange rate of C_1 monomer in the growing chain (*vide infra*). The rate constant for CO dissociation (k_{diss}) depends slightly on CO pressure, which can be explained by the implicit involvement of the $C \rightarrow CH_x$ reaction. The changes in CO adsorption and desorption can be explained by increasing lateral interactions at higher CO coverage, which also explains the minor changes of the other rate constants. It can be seen that the chain-growth and reversed chaindecoupling rates are much larger than the rate of monomer formation and termination. This is in line with the nearly identical evolution of isotopic inclusion in C_1 – C_5 products as determined in the SSITKA experiment above (Figure 5.8).

Figure 5.14 shows model predictions of the steady state kinetic parameters as a function of CO partial pressure. Figure 5.14a highlights the strong dependence of the CO consumption rate and chain-growth probability on CO coverage. Values for the degree of rate control (DRC, defined by Eq. 4.20) [<u>61</u>, <u>62</u>] are presented in Figure 5.14b. We also we define the degree of chain-growth control (DCGC) by Eq. 5.11, which quantitatively

indicates the influence of individual steps on the chain-growth probability as shown in Figure 5.14c.

$$X_{DCGC,i} = \left(\frac{\partial \alpha_i}{\partial \ln k_i}\right)_{k_{j\neq i},K_i}$$
(5.11)

Similar with DRC, a positive $X_{DCGC,i}$ value means speed up step *i* increases the chaingrowth probability, a negative $X_{DCGC,i}$ value indicates an inverse relation between step *i* and chain-growth probability. By this means, the influence of individual step on chain-growth probability can be quantitatively studied. Finally, Figure 5.14d presents the predicted activity (expressed as turnover frequency, *TOF*), the chain-growth probability (α , defined as $\theta_{C_{i+1}}/\theta_{C_i}$) and the product distribution as a function of the free sites fraction. We note that a near-unity CO coverage in these models represents saturated CO adsorption in the practical situation rather than monolayer coverage of CO.



Figure 5.14. Microkinetics simulations at conditions of $T = 220^{\circ}$ C, $p_{H_2} = 900$ mbar, $p_{CO} = 90-900$ mbar: (a) surface coverage and chain-growth probability (α); (b) degree of rate control analysis; (c) degree of chain-growth control analysis; (d) turnover frequencies (*TOFs*) of CO consumption, CH₄ formation, C₂-C₄ formation, C₅₊ formation and chain-growth probability (α) as a function of the free sites fraction.

CO coverage markedly increases with CO pressure, resulting in a continuous loss of free sites. Concomitantly, the influence of CO adsorption on the overall rate becomes increasingly negative, which is consistent with the negative CO reaction order. CO adsorption inhibits the F–T reaction by (i) hampering CO dissociation and (ii) slowing hydrogenation because of the strong influence of CO adsorption on H coverage [52, 53]. Compared with methanation conditions [40], CO dissociation becomes the most rate-controlling step as there is a lack of free sites and competes with O removal.

The increase in chain-growth probability with CO partial pressure is caused by two factors, *i.e.*, slow termination by hydrogenation and inhibited chain decoupling. The former one is confirmed by the relation between CO pressure and k_t and k_{tm} as shown in Figure 5.13. A nearly one order of magnitude decrease in the fraction of free sites (from 0.2 to 0.02) results in corresponding decrease of the chain-decoupling rate. In comparison, the increase in C1 coverage (from 0.036 to 0.023 by SSITKA and from 0.051 to 0.019 predicted by microkinetic simulation) is relatively small, causing relatively small increase in chaingrowth rate. Consequently, the net rate of chain-growth decreases as CO pressure increases. The positive correlation between chain-growth probability and CO adsorption becomes less pronounced when the fraction of free sites decreases. Then, CO dissociation becomes more important to the DCGC. The effect of O removal on the chain-growth probability is limited, as there are two opposing aspects. When more free sites become available by removing O, the CO dissociation rate and monomer supply increase, but it also enhances chain decoupling and hydrogenation. Accordingly, the DCGC values of O removal are only slightly positive. Expectedly, faster chain termination or methanation lowers chain-growth probability. It is noteworthy that changing the chain-growth rate constant (k_f) , while fixing the equilibrium constant (k_f/k_b , Eq. 5.11) does not affect the chain-growth probability.

As schematically presented in Figure 5.12, the C_i species can be form by chain propagation of C_{i-1} or chain decoupling og C_{i+1} . The mass balance of θ_{C_i} can expressed as:

$$r_{f,C_{i-1}} - r_{b,C_i} = r_{t,C_i} + r_{f,C_i} - r_{b,C_{i+1}}$$
(5.12)

where

$$r_{f,C_{i-1}} = k_f \theta_{C_1} \theta_{C_{i-1}}$$
(5.13)

$$r_{\mathrm{b},\mathrm{C}_{i}} = k_{\mathrm{b}}\theta_{\mathrm{v}}\theta_{\mathrm{C}_{i}} \tag{5.14}$$

$$r_{\mathrm{t},\mathrm{C}_i} = k_{\mathrm{t}}\theta_{\mathrm{C}_i} \tag{5.15}$$

$$r_{\mathrm{f},\mathrm{C}_i} = k_{\mathrm{f}} \theta_{\mathrm{C}_1} \theta_{\mathrm{C}_i} \tag{5.16}$$

$$r_{b,C_{i+1}} = k_b \theta_v \theta_{C_{i+1}}$$
(5.17)

Taking into the relation $\alpha_i = \theta_{C_{i+1}}/\theta_{C_i}$ yields:

$$r_{\mathbf{b},\mathsf{C}_{i+1}} = r_{\mathbf{b},\mathsf{C}_i}\alpha_i \tag{5.18}$$

$$r_{f,C_{i-1}} = r_{f,C_i} / \alpha_i \tag{5.19}$$

Substituting Eq. 5.18 and 5.19 into Eq. 5.12 yields an expression of chain-growth probability that involves chain decoupling.

$$\alpha_i = \frac{r_{\mathbf{f},i} - \alpha_i r_{\mathbf{b},i}}{r_{\mathbf{f},i} - \alpha_i r_{\mathbf{b},i} + r_{\mathbf{t},i}} \tag{5.20}$$

where the term $r_{f,i} - \alpha_i r_{b,i}$ represents the net rate of $C_i + C_1 \rightarrow C_{i+1}$. To analytically determine the influence of the rates of termination, forward and backward chain-growth on the chain-growth probability, we calculate the derivative with respect to $r_{t,i}$ $r_{f,i}$, and $r_{b,i}$ as following.

$$\frac{\partial \alpha_i}{\partial r_{\mathbf{t},i}} = \frac{-r_{\mathbf{f},i} + \alpha_i r_{\mathbf{b},i}}{\left(r_{\mathbf{f},i} - \alpha_i r_{\mathbf{b},i} + r_{\mathbf{t},i}\right)^2 + r_{\mathbf{b},i} r_{\mathbf{t},i}}$$
(5.21)

$$\frac{\partial \alpha_i}{\partial r_{f,i}} = \frac{r_{t,i}}{\left(r_{f,i} - \alpha_i r_{b,i} + r_{t,i}\right)^2 + r_{b,i} r_{t,i}}$$
(5.22)

$$\frac{\partial \alpha_i}{\partial r_{b,i}} = \frac{-\alpha_i r_{t,i}}{\left(r_{f,i} - \alpha_i r_{b,i} + r_{t,i}\right)^2 + r_{b,i} r_{t,i}}$$
(5.23)

Since k_f and k_b are four orders of magnitudes larger than k_t , the rates of chain growth $(r_{f,i})$ and chain decoupling $(r_{b,i})$ are much higher than the rate of chain termination $(r_{t,i})$, while the net rate of chain growth $(r_{f,i} - \alpha r_{b,i})$, according to Eq. 5.20, is of the same order of magnitude as $r_{t,i}$. In this way, practical values of the chain-growth probability can be obtained. This approach shows the importance of chain decoupling on the chain-growth probability. Chain decoupling significantly decreases the values of $\frac{d\alpha_i}{dr_{t,i}}$, $\frac{d\alpha_i}{dr_{f,i}}$ and $\frac{d\alpha_i}{dr_{b,i}}$ through the term $r_{b,i}r_{t,i}$ in Eqs. 5.21–5.23. Notably, Eqs. 20–23 are consistent with the conventional definition of α_i (Eq. 5.1) when $r_{b,i}$ goes to zero.

As we discussed above, all the F–T parameters can be directly or indirectly correlated to the amount of free sites. As a consequence, the reaction kinetics depend strongly on coverage as presented in Figure 5.11. As free sites play an important role in several crucial elementary steps in the F–T reaction, their presence or absence is decisive in directing the selectivity towards desired F–T products. As shown in Figure 5.14d, a certain fraction of free sites is needed to activate CO molecules, reflected by the negative reaction order with respect to CO. Concerning selectivity, reducing the fraction of free sites leads to high chain-growth probability by suppressing chain-decoupling. Thus, chain-growth probability and CO conversion rate are inversely correlated on the cobalt surface under F–T reaction conditions. As commonly observed in catalysis [50, 63], the balance between activity and

selectivity implies that there is an optimal surface composition leading to optimum performance in terms of higher hydrocarbons yield (see C_{5+} trace in Figure 5.14d). We find that CO pressure has the strongest influence on surface coverage. In industrial practice, CO pressures in the 10–15 bar are usually employed to achieve high chain-growth probability (0.85 < α < 0.95) on a highly CO-covered surface [64, 65]. As suggested by Figure 5.14d, high chain-growth probability comes at the expense of CO consumption rate.

5.4 Conclusions

The present work provides deeper insight into the relation between the kinetics of the F-T reaction on a silica-supported cobalt catalyst and the composition of the surface adsorbed layer. We provide experimental data that unequivocally show that CH_x surface species are involved in chain growth and that chain growth is reversible. The latter chain decoupling reaction benefits more from an increase in free sites than CO dissociation itself. SSITKA measurements at F-T conditions involving hydrocarbons products up to C₅ show that the rates of chain growth and chain decoupling are much higher than the rates of monomer formation and chain termination. As reversible CO dissociation is slower than chain-growth and the inclusion of isotopic C in growing chains is independent of chain length, CO cannot be the chain-growth monomer. A microkinetic model based on the carbide mechanism and involving reversible chain growth is fitted and used to understand several intricacies of the F-T reaction. The fraction of free sites plays a crucial role in determining the CO consumption rate and the chain-growth probability. A high fraction of free sites leads to high CO consumption rate but decreases chain-growth probability because of a high ratio of chain decoupling over chain growth. Therefore, we understand the practical F-T process, viz. high CO pressure, in terms of conditions that maximize the selectivity to heavy hydrocarbons (high chain-growth probability) at the expense of CO consumption rate.

References

- [1] F. Fischer, H. Tropsch, Brennst. Chem. 4 (1923) 276–285.
- [2] F. Fischer, H. Tropsch, Brennst. Chem. 7 (1926) 97–104.
- [3] M.E. Dry, Catal. Today 71 (2002) 227–241.
- [4] B. List, Angew. Chem. Int. Ed. 53 (2014) 8528–8530.
- [5] A.Y. Khodakov, W. Chu, P. Fongarland, Chem. Rev. 107 (2007) 1692–1744.
- [6] M.E. Dry, Catal. Lett. 7 (1990) 241–251.
- [7] H. Jahangiri, J. Bennett, P. Mahjoubi, K. Wilson, S. Gu, Catal. Sci. Technol. 4 (2014) 2210–2229.
- [8] R.D. Cortright, R.R. Davda, J.A. Dumesic, Nature 418 (2002) 964–967.
- [9] W.-H. Wang, Y. Himeda, J.T. Muckerman, G.F. Manbeck, E. Fujita, Chem. Rev. 115 (2015) 12936–12973.

- [10] T. Avanesian, G.S. Gusmão, P. Christopher, J. Catal. 343 (2016) 86–96.
- [11] A.T. Bell, Catal. Rev. –Sci. Eng. 23 (1981) 203–232.
- [12] R.A. van Santen, I.M. Ciobîcă, E. van Steen, M.M. Ghouri, Adv. Catal. 54 (2011) 127–187.
- [13] R. Van Santen, A.J. Markvoort, I.A.W. Filot, M.M. Ghouri, E.J.M. Hensen, Phys. Chem. Chem. Phys. 15 (2013) 17038–17063.
- [14] C.K. Rofer–DePoorter, Chem. Rev. 81 (1981) 447–474.
- [15] M.E. Dry, Appl. Catal., A 138 (1996) 319–344.
- [16] M. Claeys, E. van Steen, Stud. Surf. Sci. Catal. 152 (2004) 601–680.
- [17] P. Biloen, J.N. Helle, W.M.H. Sachtler, J. Catal. 58 (1979) 95–107.
- [18] J.G. Ekerdt, A.T. Bell, J. Catal. 58 (1979) 170–187.
- [19] R.P. Robert C. Brady III, J. Am. Chem. Soc. 102 (1980) 6182–6184.
- [20] R.P. Robert C. Brady III, J. Am. Chem. Soc. 103 (1981) 1287–1289.
- [21] W.A.A. van Barneveld, V. Ponec, J. Catal. 88 (1984) 382–387.
- [22] H. Pichler, H. Schulz, Chem. Ing. Tech. 42 (1970) 1162–1174.
- [23] M. Zhuo, K.F. Tan, A. Borgna, M. Saeys, J. Phys. Chem. C 113 (2009) 8357–8365.
- [24] J. Schweicher, A. Bundhoo, N. Kruse, J. Am. Chem. Soc. 134 (2012) 16135–16138.
- [25] Y.-H. Zhao, K. Sun, X. Ma, J. Liu, D. Sun, H.-Y. Su, W.-X. Li, Angew. Chem. Int. Ed. 50 (2011) 5335–5338.
- [26] H. Schulz, Catal. Today 214 (2013) 140–151.
- [27] A. Tavakoli, M. Sohrabi, A. Kargari, Chem. Eng. J. 136 (2008) 358–363.
- [28] G. Henrici-Olivé, S. Olivé, Angew. Chem. Int. Ed. 15 (1976) 136-141.
- [29] M.N. Qingfeng Ge, J. Phys. Chem. B 110 (2006) 15368–15380.
- [30] J.-X. Liu, H.-Y. Su, W.-X. Li, Catal. Today 215 (2013) 36-42.
- [31] J. Cheng, X. Gong, P. Hu, C. Lok, P. Ellis, S. French, J. Catal. 254 (2008) 285–295.
- [32] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.
- [33] S. Shetty, A.P.J. Jansen, R.A. van Santen, J. Am. Chem. Soc. 131 (2009) 12874– 12875.
- [34] W.J. Mitchell, J. Xie, T.A. Jachimowski, W.H. Weinberg, J. Am. Chem. Soc. 117 (1995) 2606–2617.
- [35] B.T. Loveless, C. Buda, M. Neurock, E. Iglesia, J. Am. Chem. Soc. 135 (2013) 6107–6121.
- [36] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, J. Catal. 272 (2010) 287–297.
- [37] Y. Qi, J. Yang, X. Duan, Y.-A. Zhu, D. Chen, A. Holmen, Catal. Sci. Technol. 4 (2014) 3534–3543.
- [38] J. Yang, Y. Qi, J. Zhu, Y.-A. Zhu, D. Chen, A. Holmen, J. Catal. 308 (2013) 37-49.
- [39] W. Chen, B. Zijlstra, R. Pestman, E.J.M. Hensen, ChemCatChem, DOI: 10.1002/cctc.201701203.
- [40] W. Chen, R. Pestman, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen, ACS Catal. (accepted)

- [41] J. Cheng, P. Hu, P. Ellis, S. French, G. Kelly, C. Lok, J. Catal. 257 (2008) 221–228.
- [42] P.H. Jun Cheng, Peter Ellis, Sam French, Gordon Kelly, and C. Martin Lok, J. Phys. Chem. C 112 (2008) 6082–6086.
- [43] I.A.W. Filot, R.J.P. Broos, J.P.M. van Rijn, G.J.H.A. van Heugten, R.A. van Santen, E.J.M. Hensen, ACS Catal. 5 (2015) 5453–5467.
- [44] A.J. Markvoort, R.A. van Santen, P.A. Hilbers, E.J. Hensen, Angew Chem Int Ed Engl 51 (2012) 9015–9019.
- [45] S.L. Shannon, J.G. Goodwin, Chem. Rev. 95 (1995) 677–695.
- [46] C. Ledesma, J. Yang, D. Chen, A. Holmen, ACS Catal. 4 (2014) 4527–4547.
- [47] Y. Qi, J. Yang, D. Chen, A. Holmen, Catal. Lett. 145 (2015) 145–161.
- [48] C.J. Weststrate, J. van de Loosdrecht, J.W. Niemantsverdriet, J. Catal. 342 (2016) 1– 16.
- [49] M. Zhuo, A. Borgna, M. Saeys, J. Catal. 297 (2013) 217–226.
- [50] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [51] R.A. van Santen, A.J. Markvoort, M.M. Ghouri, P.A.J. Hilbers, E.J.M. Hensen, J. Phys. Chem. C 117 (2013) 4488–4504.
- [52] I. Toyoshima, G.A. Somorjai, Catal. Rev. –Sci. Eng. 19 (1979) 105–159.
- [53] P. Winslow, A.T. Bell, J. Catal. 94 (1985) 385–399.
- [54] N. Lohitharn, J. Goodwin, J. Catal. 257 (2008) 142–151.
- [55] N. Lohitharn, J. Goodwin, J. Catal. 260 (2008) 7–16.
- [56] J. Yang, D. Chen, A. Holmen, Catal. Today 186 (2012) 99–108.
- [57] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Langmuir 26 (2010) 16558–16567.
- [58] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P.d. Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [59] C. Ledesma, J. Yang, E.A. Blekkan, A. Holmen, D. Chen, ACS Catal. 6 (2016) 6674–6686.
- [60] R.A. van Santen, A.J. Markvoort, Faraday Discuss. 162 (2013) 267–279.
- [61] C. Stegelmann, A. Andreasen, C.T. Campbell, J. Am. Chem. Soc. 131 (2009) 8077– 8082.
- [62] C. Campbell, J. Catal. 204 (2001) 520–524.
- [63] J. Cheng, P. Hu, J. Am. Chem. Soc. 130 (2008) 10868–10869.
- [64] M.E. Dry, in: I.T. Horvath (Ed.) Encyclopedia of Catalysis, Elsevier, Amsterdam, 2003, pp. 347–401.
- [65] J.B. Van de Loosdrecht, F. G.; Ciobîcă, I. M.; Ferreira, A.; Gibson, P.; Moodley, D. J.; Saib, A. M.; Visagie, J. L.; Weststrate, C. J.; Niemantsverdriet, J. W., Fischer-Tropsch Synthesis: Catalysts and Chemistry, in: J.P. Reedijk, K. (Ed.) Reference Module in Chemistry, Molecular Sciences and Chemical Engineering: Comprehensive Inorganic Chemistry II, Amsterdam, 2013, pp. 525–557.



Science is a microscope, in which I see both big and small.

Influence of carbon deposits on the cobalt-catalyzed Fischer–Tropsch reaction: evidence for a two-site reaction model

Abstract

A well-known observations in the Fischer–Tropsch (F–T) reaction is that the CH₄ selectivity for cobalt catalysts is always higher than the prediction of the Anderson-Schulz-Flory (ASF) distribution. Depositing graphitic carbon on a cobalt catalyst strongly suppresses this non-ASF CH₄, while the formation of higher hydrocarbons is much less affected. Carbon was laid down on the cobalt catalyst via the Boudouard reaction. We provide evidence that the carbidic carbon does not influence the F-T reaction as it can be easily hydrogenated under reaction conditions. Graphitic carbon is rapidly formed and cannot be removed. This unreactive form of carbon is located on terrace sites and mainly decreases the CO conversion by limiting methane formation. Despite nearly unchanged higher hydrocarbons yield, the presence of graphitic carbon enhances the chain-growth probability and strongly suppresses olefin hydrogenation. We explain these results by a two-site model on the basis of insights into structure sensitivity of the underlying reaction steps in F-T mechanism: carbidic carbon formed on step-edge sites is involved in chain growth or can migrate to terrace sites, where it is rapidly hydrogenated to methane. The primary olefinic F-T products are predominantly hydrogenated on terrace sites. Covering the terraces by graphitic carbon increases the residence time of CH_x intermediates in line with decreased methane selectivity and increased chain-growth rate. We also demonstrate that graphitic carbon will slowly deposit on the cobalt catalysts during CO hydrogenation, thereby influencing CO conversion and product distribution in a similar way as observed for pre-deposited graphitic carbon.


6.1 Introduction

Since Fischer-Tropsch (F–T) synthesis was discovered in 1925 [<u>1</u>, <u>2</u>], this fascinating reaction has attracted tremendous interest of chemists and chemical engineers [<u>3</u>, <u>4</u>]. Today, it has been commercialized for the conversion of cheap coal and natural gas feedstock to a variety of products including clean transportation fuels and chemicals [<u>5-7</u>]. Given the abundance and low price of natural gas in certain areas, methane is preferred over coal for the production of synthesis gas. Also, synthesis gas production, which accounts for 60–70% of the capital and running costs of a typical F–T plant [<u>7</u>], is cheaper with methane as the feedstock. A central issue in commercial F–T technology is to minimize the production of methane, which has the lowest value among the hydrocarbon products.

The main products of cobalt-catalyzed F–T synthesis are linear olefins and paraffins [8]. A typical hydrocarbons distribution is strongly reminiscent of the Anderson-Schulz-Flory (ASF) distribution that is typically found for the products of oligomerization or polymerization processes [9, 10]. The CH₄ selectivity on cobalt is always higher than the ideal ASF distribution on the basis of higher hydrocarbons predicts. This observation has been attributed to thermodynamically favored formation of methane, since the bond strength of C-H in CH₄ (435 kJ mol⁻¹) is higher than that of C-C bond (376 kJ mol⁻¹ in ethane) [8]. Also, the deviated CH₄ selectivity has been interpreted as the surface CH_x intermediate leading to CH₄ being hydrogenated easier than intermediates of higher hydrocarbons [11]. However, recent simulations using a reversible chain-growth model shows that enlarging the rate constant of CH_x hydrogenation does not lead to a lower propagation rate for CH_x but rather to a lower chain-length independent α [12].

Thorough understanding of the CH₄ formation is fundamentally important to improve performance of cobalt catalysts. Modern computational approaches combined with the development of accurate nanoparticle model systems enable in-depth study of this issue, in which knowledge of structure sensitivity plays a key role [13, 14]. It is widely documented that the dissociation of diatomic molecules with π -bonds such as CO [15, 16], NO [17, 18] and N_2 [19] preferably takes place on step-edge sites. Whereas this is well accepted for N_2 dissociation in the context of ammonia synthesis [20], there is less agreement on the mode of CO dissociation under F-T conditions [21, 22]. Direct CO dissociation is preferred on step-edges over terraces [21]. The main alternative idea is that CO can be dissociated in an H-assisted manner, *i.e.*, involving HCO [23, 24] or HCOH [25, 26] as intermediates. Also, chain growth has been compared on step-edge and terrace sites. Cheng et al. reported that the lowest energy barrier of CH_x - CH_y bond formation involves $CH_2 + CH_2$ reactions, which are strongly favored on a stepped cobalt surface over a flat one [27]. On the contrary, CH_x hydrogenation, in which a σ -bond is formed, is usually regarded as a structure insensitive reaction [13, 14]. As CH_x binds weaker on terrace than on stepped surface, one expects slightly fast CH_x hydrogenation on terraces [28]. Related to this, also the hydrogenation of

growing hydrocarbon chains on the catalytic surface has been suggested to be independent of the surface topology [13, 14]. A microkinetic model that compared different mechanisms for the F–T reaction on a stepped Ru surface showed that hydrocarbons are mainly obtained via direct CO dissociation, CR+CH-type coupling reactions mainly produce olefins as the primary products [29]. A hypothesis born from these insights is that part of the (non-ASF) CH₄ is obtained on terrace sites. However, direct evidence for tis speculation is still absent.

Carbon can be deposited on the surface in different forms, and is linked with a part of catalyst deactivation [30]. It was confirmed that carbidic carbon and less structured carbon deposits can reversibly transform into graphitic carbon, which kinetically and thermodynamically prefers the flat surface of cobalt as compared to stepped surface [31-35]. This accordingly enables the possibility of selectively blocking the flat surface by the Boudouard reaction (2 CO \rightarrow C + CO₂), assuming that carbidic carbon can be easily removed. We have previously shown that CO disproportionation via the Boudouard reaction is a structure sensitivity reaction [36]. It occurs at a high rate in the absence of hydrogen, but suffers from rapid deactivation due to the build-up of carbon. In the present work, we characterized in more detail the carbon deposited during the Boudouard reaction and their propensity towards hydrogenation. In this way, we found that the carbidic carbon can be removed by hydrogenation at intermediate temperature, retaining the graphitic carbon. We investigate the impact of graphitic carbon on the F-T reaction. The reaction data are discussed in terms of a two-site model involving step-edge sites for CO dissociation, chain growth and termination, while the terrace sites are involved in CH₄ formation. Blocking the latter sites by graphitic carbon suppresses CH₄ formation. The concomitant increase in chain-growth probability is explained by the suppressed migration of CH_x intermediates from the step-edge sites to terrace sites.

6.2 Experimental

6.2.1 Preparation

The Co/SiO₂ catalyst containing 17.1 wt% Co and 0.04 wt% Pt (ICP-OES, Spectroblue, Ametek Inc.) was prepared by incipient wetness impregnation of a silica support (120-250 um, provided by Shell) using an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (99.99%, Merck) and Pt(NH₃)₄·(NO₃)₂ (99.995%, Alfa Aesar) as precursors. The detailed preparation of this catalyst can be found in Section 3.2. The accessible surface area of 116.7 µmol Co atoms per gram catalyst was determined by H₂-chemisorption (Micromeritics ASAP 2010). The average cobalt particle size of 15 nm was determined by TEM analysis (FEI Tecnai 20) and confirmed by *in situ* XRD (D/max-2600, Rigaku). Detailed experimental procedures are provided in Section 3.2.

6.2.2 Carbon deposition and temperature-programmed hydrogenation

Carbon deposition and subsequent temperature-programmed hydrogenation (TPH) were performed in a tubular reactor. Typically, 200 mg of the Co/SiO₂ catalyst was *in situ* reduced in a diluted H₂ flow (20% H₂ in Ar, 50 mL min⁻¹ in total) at 450°C (heating rate of 2°C min⁻¹) and atmospheric pressure for 16 h and subsequently flushed in an Ar flow for 2 h. Then, the reactor was cooled to the desired carbon deposition temperature. Carbon was deposited by exposure to a diluted CO flow (10% CO in Ar, 50 mL min⁻¹ in total). After deposition, the catalyst was flushed in Ar for 2 h and cooled to room temperature. The TPH experiments were conducted by heating the reactor to 550°C at a rate of 5°C min⁻¹ in an H₂ flow (10% H₂ in Ar, 50 mL min⁻¹ in total). The main hydrocarbon product of carbon hydrogenation was CH₄ as followed by online mass spectrometer (ESS, GeneSys Evolution). To determine the exact CH₄ flow rate, the mass spectrometer (MS) signal was calibrated using a known gas mixture. The amount of pre-deposited carbon was determined by integrating the CH₄ flow with time-on-stream.

6.2.3 Quasi in situ X-ray photoelectron spectroscopy

Carbon deposition on the Co/SiO₂ catalyst was studied by *quasi in situ* XPS using a Kratos AXIS Ultra 600 spectrometer equipped with a monochromatic Al K α X-ray source (Al K α energy is 1486.6 eV). Survey scans were recorded at a pass energy of 160 eV and 40 eV for detailed region scans. The step size was 0.1 eV in both cases and the background pressure during the experiment was kept below 5×10⁻⁶ mbar. A high temperature reaction cell (Kratos, WX-530) was used to pretreat the sample, which was supported on an alumina stub, allowing *in vacuo* sample transfer into the XPS measurement chamber.

The initial reduction was performed in a 50% H₂ in Ar flow at atmospheric pressure and 450°C for 8 h. After reduction the sample was cooled to 150°C and subsequently transferred to the measurement chamber. For the carbon deposition, the sample was heated in a flow of 50 ml Ar to 260°C at a rate of 5°C min⁻¹. As soon as the target temperature was reached, the gas flow was switched to a flow of 20% CO in Ar. After the desired carbon deposition time, the gas flow was stopped and the reaction cell was immediately evacuated and cooled to room temperature. Energy calibration was done using the Co $2p_{3/2}$ peak at 778.2 eV for the reduced samples, and the Si 2s peak at 103.3 eV of the SiO₂ support for the calcined sample.

6.2.4 Catalytic test

Steady-state and transient catalytic activity measurements were performed in a setup that is capable of switching gas feeding. After reduction at 450°C for 16 h, the reactor was cooled to desired temperature (220°C or 260°C) in an Ar flow and an increase of the pressure to 2

bar. The flow was subsequently switched to a synthesis gas mixture $(CO/H_2/Ar)$. The partial pressure of H₂ and CO were adjusted by varying their flow rates. The total flow rate was fixed at 50 mL min⁻¹ by using Ar as balance. The activity and selectivity were measured by online analysis with a VARIAN CP-3800 gas chromatograph equipped with TCD and FID for analysis of hydrocarbon and permanent gases.

To study the reactivity of pre-deposited carbon, a diluted ¹³CO flow (10% ¹³CO in Ar, 50 mL min⁻¹ in total) was used to deposit isotopically labeled carbon at 260°C for 30 min. Afterward, the ¹³CO flow was replaced by an Ar flow to remove molecularly adsorbed ¹³CO. After flushing in Ar for 2 h, the Ar flow was abruptly switched to a ¹²CO/H₂/Ar feed (5/5/40 mL min⁻¹). The transient responses of H₂ (m/z = 2), ¹²CH₄ (m/z = 15), ¹³CH₄ (m/z = 17), ¹²CO (m/z = 28), ¹³CO (m/z = 29) were monitored by online mass spectrometry.

Steady-state isotopic transient kinetic analysis (SSITKA) as performed by switching from ${}^{12}CO/H_2/Ar$ to ${}^{13}CO/H_2/Ne$ when steady-state conversion is obtained, in which the Ne was used as a tracer to determine the gas-phase hold-up time. Procedures to determine the residence time and coverage of CO and CH_x (intermediates of CH₄) are provided in our earlier work [<u>37</u>].

6.3 Results

6.3.1 Carbon deposition by CO exposure

In order to study the influence of surface carbon on the CO hydrogenation reaction, carbon was deposited by the Boudouard reaction (2 CO \rightarrow CO₂ + C) on the metallic cobalt surface of reduced Co/SiO₂. We employ TPH to determine the reactivity of the deposited carbon species. Figures 6.1a and 1b show the TPH traces as a function of the carbon deposition time and the carbon deposition temperature, respectively. Based on these data, we can distinguish two types of carbon deposits. One type of carbon can be hydrogenated below 260°C and we assign these carbon species to atomic carbon or carbidic carbon on the basis of literature [32, 34, 38, 39]. The temperature at which carbidic carbon can be hydrogenated is within the temperature range employed in the F-T process (200–240°C), meaning that these species are reactive enough to be involved in the F-T reaction. The other type of carbon can only be hydrogenated at temperatures in the 260–550°C range. Accordingly, these carbon species are most likely not involved in the F-T reaction. Figure 6.1a shows that the amount of the less-reactive carbon increases strongly when CO exposure is prolonged. H₂-chemisorption data in Table 6.1 compare the metallic cobalt surface area of freshly reduced Co/SiO₂ with samples exposed to CO and subsequently reduced at 260°C to remove most of the reactive carbon species. Clearly, the deposition of carbon species causes a strong decrease of the metallic cobalt surface area. Importantly, CO exposure at 260° C for 3 h decreases the surface that can be probed by H₂-chemisorption by about 95%.



Figure 6.1. TPH profiles of the carbon deposits obtained by CO exposure at 260°C for different time (a) and at different temperatures for 30 min (b). The amount of carbon was quantified by integrating the CH_4 flow.

Table 6.1. Cobalt surface area measured by H_2 -chemisorption. The carbon pre-deposited catalysts were exposed to a H_2 flow for 6 h at 260°C before the H_2 -Chemisorption measurement.

CO exposure	Co surface	relative loss	Cgraph/Cosurf ^a
	(m^2/g_{Co})	(%)	
-	30.4	-	-
200°C, 30 min	29.8	2	-
220°C, 30 min	22.5	26	0.13
260°C, 30 min	18.5	39	0.39
260°C, 3 h	1.4	95	0.98

^a C_{graph}/Co_{surf} determined by integration of the CH₄ signal above 260°C during TPH (cf. Figure 1).

We also characterized these carbon species by XPS. For this purpose, we carried out similar carbon deposition experiments on the *in situ* reduced Co/SiO₂ catalyst in a reaction chamber directly attached to an XPS spectrometer. A highly oriented pyrolytic graphite reference is used to fit the sp2 carbon in C 1s spectra. Figure 6.2 shows that this procedure leads to sp² and sp³ carbon species. The amount of sp² carbon increases with CO exposure time. Exposure of the carbon deposits to H₂ at 260°C results in a decrease of the amount of sp³ carbon, while the intensity of sp² carbon remains nearly unchanged. This result highlights the low reactivity of sp² carbon. XPS quantification shows that about 81% of the carbon species after 4 h CO exposure at 260°C is sp² carbon. As hexagonal graphite primarily consisting of sp² carbon is commensurate with the hexagonal close-packed surface of cobalt terraces [<u>39</u>, <u>40</u>], we conclude that the less reactive carbon is in graphitic nature.

After CO exposure at 220°C, the TPH profile is different in the sense that more than one type of carbon species can be distinguished below 300°C and a much lower amount of graphitic carbon is formed (Figure 6.1b). One can also see that the total amount of carbidic



Figure 6.2. Quasi *in situ* XPS spectra of the reduced Co/SiO₂ catalyst: after reduction at 450°C (a), subsequent CO exposure at 260°C for 30 min (b) and 4 h (c) and finally hydrogenation at 260°C for 5 min (d).

carbon is much less affected by the deposition temperature or deposition time than the amount of graphitic carbon. This suggests that the more reactive carbidic carbon species are the primary products of CO dissociation and that these species are slowly converted into the more stable graphitic form [<u>32-35</u>]. The transformation between these carbon species was reported to be reversible [<u>32</u>].

Quantifying the deposited carbon reveals that the amount of carbidic carbon does not change markedly neither with the carbon deposition time (Figure 6.1a) nor with the carbon deposition temperature (Figure 6.1b). This is in keeping with a surface science study by Nakamura *et al.*, who investigated carbon deposition on a polycrystalline cobalt foil [33]. Accordingly, we speculate that this type of carbon is closely associated with surface cobalt sites involved in CO activation. Considering the absence of hydrogen during carbon deposition, it is likely that step-edges are the active sites for CO dissociation [41, 42]. In a recent study, we also emphasized the importance of a minority site on the surface involved

in direct CO dissociation [36]. In the absence of hydrogen, the O atoms can only be removed as CO₂, leading to the predominant coverage of the cobalt surface with carbon. Because of the low diffusion barrier, *i.e.* 26 kJ mol⁻¹ on Co(0001) [40, 43], carbon atoms can easily migrate over the cobalt surface and form clusters of carbon atoms through C-C coupling reactions on terraces. Additional DFT calculations estimate the migration barrier for diffusion of a C atom from the four-fold step-edge site to the terrace at 75 kJ mol⁻¹ [29]. According to DFT, the coupling between C atoms is much easier on terraces than on steps with respective activation barriers of 118 kJ mol⁻¹ and 234 kJ mol⁻¹ [31]. Formation of (poly-)aromatic structures containing predominantly sp² carbon explain the low reactivity of these deposits [40]. Figure 6.1b clearly shows that formation of graphitic carbon is facilitated by higher CO exposure temperature [33, 34]. It has also been reported that the hexagonal graphite structure is thermodynamically favored on the closed-packed surface [39, 40]. We therefore conclude that the graphitic carbon formed via CO exposure mainly covers the terrace sites that dominate the surface of the relatively large cobalt nanoparticles in Co/SiO₂. Furthermore, the step-edge sites will also contain a variety of carbon species which are likely more carbidic in nature.

The reactivity of the carbon deposits obtained at 260°C via the Boudouard reaction in the CO hydrogenation reaction is demonstrated in Figure 6.3, where a 12 CO/H₂ flow is passed over the 13 C-pre-covered Co/SiO₂ catalyst. The transient response shows that 13 CH₄ appears concomitantly with H₂, demonstrating the involvement of pre-deposited 13 C in CH₄ formation at 260°C. 12 CO adsorption and hydrogenation cannot proceed until a certain fraction of free sites is regenerated by 13 C hydrogenation. This causes a 1.5 s delay



Figure 6.3. Transient responses of ¹³CH₄ (open squares), ¹²CH₄ (solid squares), ¹²CO (circles), and H₂ (triangles) following an Ar \rightarrow ¹²CO/H₂ switch over a ¹³C-pre-covered Co/SiO₂ catalyst obtained by ¹³CO exposure at 260°C for 30 min followed by Ar flushing for 2 h. Conditions: $p_{H_2} = 200$ mbar, $P_{CO} = 200$ mbar, T = 260°C.

(corrected for the chromatographic effect of CO) of ${}^{12}CH_4$ formation as compared to ${}^{13}CH_4$ formation. Taking into account the TPH profile in Figure 6.1 and by quantifying the amount of ${}^{13}CH_4$ formed, we find that a part of the reactive ${}^{13}C$ deposits is hydrogenated to ${}^{13}CH_4$ after the switch to a H₂-containing feed. The remainder of the ${}^{13}C$ species, mainly in the form of graphitic carbon, stays on the surface. The influence of these residual carbon deposits on the catalyst under model F–T conditions will be discussed below.

6.3.2 Influence if carbon deposits in the CO hydrogenation reaction

As confirmed by Figure 6.1a, the amount of the graphitic carbon strongly increases with the carbon deposition time. This approach allows studying the CO hydrogenation reaction on cobalt catalysts that are pre-covered with different amounts of graphitic carbon. The resulting data are reported in Figure 6.4. The catalytic performance is plotted as a function of graphitic carbon to surface cobalt ratio (denoted as C_{graph}/Co_{surf}). C_{graph} relates to the amount of carbon hydrogenated above 260°C in separate TPH experiments. All the data in Figure 6.4 were obtained after 6 h time-on-stream under model F–T reaction conditions. The model F–T reactions were carried out at 260°C and 220°C and a H₂/CO ratio of 1.

We first verified whether carbidic carbon influences the catalytic performance. The open symbols in Figure 6.4a represent the experiment, in which CO exposure at 260°C for 30 min was followed by hydrogenation at 260°C for 2 h in order to remove most of the carbidic carbon. The resulting reaction data are nearly identical to those obtained without the hydrogenation step at 260°C, demonstrating that pre-deposited carbidic carbon does not influence the F–T performance. This is expected as most of the carbidic carbon can be easily removed below 260°C in a TPH experiment. This leads to the conclusion that the effect of carbon deposition on the model F–T reaction at 260°C to be discussed below is mainly exerted by the presence of graphitic carbon.

Figures 6.4a and 6.4b reveal that graphitic carbon decreases the CO consumption rate at both reaction conditions. The decrease is more evident at 260°C than at 220°C. Strikingly, these data also show that graphitic carbon affects the formation rates of different products in profoundly different ways. While the decrease in CO consumption rate is accompanied by a substantial decrease of the CH₄ yield, the yield of C₂₊-hydrocarbon products (paraffins and olefins containing two or more carbon atoms) remains nearly unchanged. Also, the chain-growth probability increases with the graphitic carbon content of the pre-covered catalyst. At 260°C, the chain-growth probability increases from 0.43 for the clean cobalt surface to 0.61 for the nearly completely poisoned cobalt surface. When the reaction is carried out at 220°C, the chain-growth probability also changes from 0.70 to 0.82 due to the presence of graphitic carbon. Concomitant with the decrease in CH₄ yield, we see that the CO₂ yield is lowered for both cases. Clearly, these data show that partial poisoning of the cobalt surface by graphitic carbon substantially inhibits CO conversion and CH₄ and CO₂



Figure 6.4. The catalytic properties of the F–T reaction over carbon pre-covered Co/SiO₂ as a function of graphitic carbon to surface cobalt ratio (denoted as C_{graph}/Co_{surf}): (a and b) CO conversion (squares), CH₄ yield (circles), C₂₊ yield (triangles), CO₂ yield (diamonds) and chain-growth probability (stars); (c and d) C₂ (left) and C₃ products (right) yields; Conditions: $p_{H_2} = 200$ mbar, $p_{CO} = 200$ mbar, $T = 260^{\circ}C$ (a and c) and $220^{\circ}C$ (b and d).

formation. On the other hand, graphitic carbon hardly affects the formation of higher hydrocarbons, albeit that on average longer hydrocarbons are obtained.

Figures 6.4c and 6.4d illustrate the strong impact of graphitic carbon on the paraffinsto-olefins ratio. For instance, at 260°C its presence suppresses the formation of C_2H_6 and C_3H_8 and slightly increases the formation of C_2H_4 and C_3H_6 . Notably, the C_2H_6/C_2H_4 and C_3H_8/C_3H_6 ratios decrease by more than 95%, *i.e.*, from 13.7 and 0.89 to 0.94 and 0.099, respectively. These relative changes are quantitatively consistent with the relative decrease in the CH₄ yield (88%) and the loss of cobalt surface as determined by the amount of carbon deposited by the TPH experiment (>90%). A similar trend is observed in the data obtained at 220°C (Figure 6.4d). Experimental [8, 44] and theoretical [29] studies have shown that olefins are the primary products of the F–T reaction. Paraffins are therefore mostly obtained by hydrogenation of the primary olefins.



Figure 6.5. Residence time (blue) and coverages (red) of CH_x (squares) and CO (circles) as determined by SSITKA over carbon pre-covered Co/SiO₂ catalysts as a function of C_{graph}/Co_{surf} . Conditions: $p_{H_2} = 200$ mbar, $p_{CO} = 200$ mbar, $T = 260^{\circ}C$.

In order to establish how the graphitic carbon influences CO coverage and the hydrogenation rate, we carried out SSITKA measurements at 260°C. Figure 6.5 compares the resulting residence times and coverages of CO and CH_x coverages. With increasing graphitic carbon content, the CO coverage decreases. There is a strong correlation between the decrease in CO coverage and the loss of cobalt surface area as determined by H₂-chemisorption. The longer CH_x residence time with increasing graphitic carbon content implies slower CH_x hydrogenation to CH_4 . This can be the result of two factors, *i.e.*, (i) a decrease in the H coverage and (ii) a decrease of the amount of surface sites that produce mainly CH_4 .

Consequently, the results presented in this section illustrate a different impact of graphitic carbon on the various reaction routes from synthesis gas to methane and higher hydrocarbons. While CO conversion, CH_4 and CO_2 formation as well as olefins hydrogenation are substantially inhibited by graphitic carbon, the rate of formation of C_{2+} -hydrocarbons is hardly affected. The results imply that the reaction pathway from CO to CH_4 is more suppressed by graphitic carbon than that of CO to higher hydrocarbons. Whilst the yield of higher hydrocarbons only decreases very slightly, the chain-growth probability substantially increases due to the presence of graphitic carbon species also slowly build up on an initially clean cobalt surface during CO hydrogenation and affects the catalytic performance in a similar manner as shown in this section.

6.3.3 Influence of carbon deposits formed during the F-T reaction

To study the build-up of carbon deposits during CO hydrogenation, we carried out model F-T reaction experiments at H₂/CO ratios of 1 and 2 at 220°C and 260°C. Quantification of the carbon deposits by integrating the TPH profiles of spent catalysts allows establishing the correlation between carbon deposition and catalytic performance. In this case, we removed a significant part of the carbidic carbon in a H₂-flow at the reaction temperature for 6 h. Thereafter, the content of graphitic carbon on spent catalysts can be quantified by TPH.



Figure 6.6. The evolution of (a) CO conversion and (b) normalized C₁ yield (left panel) and C₂₊ yield (right panel) as a function of time-on-stream at various conditions: squares: $p_{H_2} = 200$ mbar, $T = 260^{\circ}$ C; circles: $p_{H_2} = 400$ mbar, $T = 260^{\circ}$ C; triangles: $p_{H_2} = 200$ mbar, $T = 220^{\circ}$ C; diamonds: $p_{H_2} = 400$ mbar, $T = 220^{\circ}$ C. $p_{CO} = 200$ mbar in all cases. The lighter blue markers represent experiments run for 5 h, 15 h, and 45 h at the same conditions.

temperature	$p_{\rm CO}$	$p_{ m H_2}$	TOS	Cgraph/Cosurf ^a
(°C)	(mbar)	(mbar)	(h)	
220	200	400	45	0.09
220	200	200	45	0.35
260	200	400	45	0.43
260	200	200	5	0.26
260	200	200	15	0.48
260	200	200	45	0.91

Table 6.2. Graphitic carbon content on spent cobalt catalysts upon different pre-treatment procedures.

^a C_{graph}/Co_{surf} determined by integration of the CH₄ signal above 260°C during TPH (cf. Figure 1).



Figure 6.7. Evolution of selectivity and chain-growth probability (based on C₃–C₆ hydrocarbons) as a function of time-on-stream. Conditions: $p_{H_2} = 200$ mbar, $p_{C0} = 200$ mbar, $T = 260^{\circ}$ C.



Figure 6.8. Relative decrease in CH₄ (solid symbols) and C₂₊-hydrocarbons (open symbols) yield with respect to initial values as a function of the C_{graph}/Co_{surf} ratio. The line is a guide to the eye. Conditions: squares: $p_{H_2} = 200$ mbar, $T = 260^{\circ}$ C; circles: $p_{H_2} = 400$ mbar, $T = 260^{\circ}$ C; triangles: $p_{H_2} = 200$ mbar, $T = 220^{\circ}$ C; diamonds: $p_{H_2} = 400$ mbar, $T = 220^{\circ}$ C. $p_{CO} = 200$ mbar in all cases. The light blue squares represents experiments run for 5 h, 15 h, and 45 h at similar conditions.

As shown in Table 6.2, the amount of graphitic carbon increases with time-on-stream of the F–T reaction. Accordingly, we propose that the initial decrease in the CO consumption rate can be assigned to carbon deposition. Figure 6.6a shows that the CO consumption rate at 260°C decreases much faster with time-on-stream than at 220°C, while the effects are also less pronounced at an H₂/CO ratio of 2. This difference can be explained by the larger amount of graphitic carbon deposited at higher temperature and lower H₂/CO ratio [45]. Notably, there are also differences in the reactivity of the deposited graphitic carbon. Typically, at higher temperature more graphitic carbon is formed. We highlight the effect of the graphitic carbon build-up on the CH₄ and C₂₊-hydrocarbon yields in Figure 6.6b normalized to the initial values as a function of time-on-stream. In all cases, the CH₄ yields decrease much faster than the C₂₊-hydrocarbons yields and the effect is more pronounced at 260°C and at lower H₂/CO ratio.

Figure 6.7 shows the evolution of the selectivity from C1 to C6 and the corresponding chain-growth probability obtained at 260°C and a H2/CO ratio of 1 with time-on-stream, reflecting the impact of graphitic carbon build up during the reaction. Clearly, the CH₄ selectivity decreases substantially, while the influence on the C_{2+} -hydrocarbons yield is much less pronounced. At the same time, the yield of higher hydrocarbons increases with the progressing reaction. Another remarkable observation is that the selectivity of longer hydrocarbons increases more pronouncedly than the selectivity of shorter hydrocarbons, fully consistent with the increasing chain-growth probability. Finally, we plot the relative

decrease in product yields with respect to the initial values as a function of the C_{graph}/Co_{surf} ratio in Figure 6.8. The decrease in CH₄ yield is strongly correlated with the graphitic carbon coverage. In contrast, the correlation is much weaker for the C_{2+} -hydrocarbons yield.

6.3.4 Influence of carbon deposits on chain growth

In order to gain an insight into the impact of graphitic carbon on chain growth, we studied the conversion of a C_3H_6/H_2 mixture on freshly reduced and carbon-covered cobalt catalysts. In an earlier work, we co-reacted ¹³CO/H₂ synthesis gas with ¹²C₃H₆ to investigate the reversibility of chain growth and the inclusion of carbon species resulting from C–C bond cleavage reactions in propene into higher hydrocarbons [46]. In the present experiments, we did not use CO as a reactant in order to exclude any influence of CO coverage [46]. The cobalt catalyst containing graphitic carbon was prepared by ¹³CO exposure at 260°C for 30 min followed by H₂ exposure at 260°C for 30 min. By using labelled ¹³CO to deposit, we can track the origin of the carbon atoms in the hydrocarbon products in subsequent C₃H₆/H₂ reaction experiments. C₃H₆ is completely converted in these experiments and C₃H₈ is the major product for both cases. The other products are lighter and heavier hydrocarbons than C₃-hydrocarbons. The selectivity results are collected in Figure 6.9 as a plot of the logarithmic molar fraction as a function of the carbon number.

These data demonstrate that the product distribution obtained from a C_3H_6/H_2 mixture is qualitatively similar to the typical ASF-type product distribution obtained with synthesis gas. Consistent with our earlier conclusion [46], this result shows that carbon atoms



Figure 6.9. Anderson–Schulz–Flory plot of the products of the reaction of a C_3H_6/H_2 mixture on a clean (squares) and graphitic carbon pre-covered cobalt catalyst (circles) prepared by ¹³CO exposure at 260°C for 30 min followed by H₂ exposure at 260°C for 2 h. C₃ products were excluded from the selectivity calculations. Conditions: $T = 220^{\circ}C$, $p_{H_2} = 600$ mbar, $p_{C_3H_6} = 60$ mbar.

deriving from olefin cracking can give rise to similar chain-growth products as with CO. Figure 6.9 shows a lower CH₄ selectivity for the catalysts that contains graphitic carbon, consistent with the lower hydrogenation activity of the carbon-covered catalyst. At the same time, the chain-growth probability based on the C₄–C₇ hydrocarbon products increases from 0.23 for the initially clean cobalt catalyst to 0.42 for the cobalt catalyst that was pre-covered with graphitic carbon. These results are qualitatively in good agreement with the changes in the chain-growth probability due to the presence of graphitic carbon. Isotopic analysis by GC-MS shows that the ¹³C content in the hydrocarbon products is lower than 0.2%, confirming that the pre-deposited graphitic carbon is not involved in the chain-growth reactions.

6.4 Discussion

The detailed mechanism of the F–T reaction is far from understood. The reaction involves many elementary reaction steps, some of which are structure sensitive while others are expected to depend not significantly on the surface topology. Identifying how blocking of part of the catalyst surface affects activity and selectivity may provide deeper insight into the reaction mechanism and site requirements. In this study, we investigated how carbon deposits on the cobalt surface impact the CO consumption rate and the product distribution of the F–T reaction.

By using the Boudouard reaction to cover a substantial part of the metallic surface by graphitic carbon, we demonstrate that the catalytic surface contains different sites involved in the production of CH₄ and higher hydrocarbons. The used cobalt catalyst contains ~15 nm particles. This size is larger than the minimum size of 6 nm below which the catalytic performance is strongly dependent on particle size [47, 48]. The surface of the nanoparticles in the present work will predominantly contain low-reactive planar surfaces, while about 20% of the surface will be made up of defects in the form of corners, edges, and step-edges [49]. Combining ¹²C¹⁶O/¹³C¹⁸O isotopic scrambling with *in situ* infrared spectroscopy, we have earlier demonstrated that direct CO dissociation proceeds predominantly on step-edges [36]. This is consistent with the expected strong structure sensitivity of the CO dissociation reaction.

The main observation made in this work is that CH_4 and CO_2 formation rates and the paraffins-to-olefins ratio are substantially suppressed by the presence of graphitic carbon, while the rate of higher hydrocarbons formation hardly changes. This result cannot be explained by assuming a surface that contains only one type of sites, as one would expect a decrease in CO conversion without changes in selectivity. Accordingly, we discuss these findings in the framework of a surface that contains both step-edge and terraces as typically assumed in cobalt-catalyzed F–T synthesis [<u>31</u>, <u>41</u>, <u>50</u>]. Our data show a very strong correlation between the CH₄ selectivity, the paraffins-to-olefins ratio and the available

cobalt surface, even for a catalyst in which more than 90% of the available cobalt sites were covered by graphitic carbon. Thus, we infer that a large part of CH_4 originates from CH_x hydrogenation on terrace sites, which is in keeping with the notion that CH_x hydrogenation to CH_4 is not a structure sensitive reaction, which has been well explained by Liu and Hu [13] and van Santen [14]. The observation of significantly inhibited olefin hydrogenation lines up with CH₄ formation rate as a function of graphitic carbon content, while the observation that the yield of C_{2+} -hydrocarbons is less affected is in keeping with the proposal that olefins are the primary product of the F–T reaction [8, 29, 44]. Thus, the terraces are responsible for the hydrogenation of the primary olefin products, which is a structure insensitive reaction as well. Similarly, CO₂ yield correlates with CH₄ yield identifying the terrace surfaces as the active sites for CO₂ formation. On the contrary, the C_{2+} -hydrocarbons formation rate changes only slightly when the more than 90% of the surface is blocked. We therefore conclude that higher hydrocarbon formation occurs on a small fraction of the surface sites, which are most likely step-edge sites [14, 49]. Although C₂₊-hydrocarbons formation rate is hardly affected by graphitic carbon, the chain-growth probability is increased. This is in line with prolonged CH_x residence time, implying that more CH_x species can be built into growing chains. Altogether, our data are consistent with the view that CO dissociation and chain-growth reactions are structure sensitive and preferred on step-edge sites [28, 31], while hydrogenation and oxidation occur on the whole surface [13, 14].

An important aspect to be considered is the migration of surface adsorbates between the different types of surface sites. Based on the strong correlation between cobalt surface area and CH₄ formation rate, we speculate that the terrace sites are the origin of a large part of the production of CH_4 . If we assume that migration of CH_x species from step-edge to terrace sites is not relevant, the CO dissociation leading to CH4 must take place on the terrace sites. CO dissociation with assistance of adsorbed H on planar sites has been extensively discussed as an alternative to direct CO dissociation on step-edges. DFT calculations show that the H-assisted CO dissociation on terrace sites is feasible [23, 26], despite the activation barrier is higher than on step-edge sites [21]. We refer to the work of Iglesia [22, 25, 26], who proposed that the F–T reaction exclusively takes place on cobalt terrace sites. However, this view cannot explain the distinct dependence of CH_4 and C_{2+} formation rates on carbon deposits, as well as the increase in chain-growth probability. Following this one-site model, one would not expect any change in selectivity when the catalyst surface is partially covered. We therefore also consider that H-assisted CO dissociation occurs on terrace sites, which mainly leads to CH₄, while CO dissociation taking place on step-edge sites leads to C_{2+} -hydrocarbons and a small amount of CH₄. In other words, we cannot exclude two independent parallel reaction routs process on terraces and steps. This though provides an explanation for the decreased CO consumption rate in the presence of graphitic carbon. Notably, the CO consumption rate declines with increasing graphitic carbon content but not proportionally with the loss of cobalt surface

area nor with the CO coverage nor with the CH_4 formation rate. This is because the contribution of CO consumption via CO dissociation on step-edge sites is less affected by graphitic carbon as compared to the rout on terraces.

Now, we discuss an alternative scenario taking into account a migration of surface adsorbates between step-edge and terrace sites. We contrast the previous case by assuming that CO dissociation exclusively occurs at step-edges. Then, C and O fragments obtained by CO dissociation can diffuse from the step-edges to the terrace sites. C will be converted to mainly CH₄, because chain growth is disfavored on terraces compared with step-edges [14,31]. In lean hydrogenation conditions, a fraction of the C atoms will be converted to graphitic carbon as we observed in the present work [45]. Similarly, O migrating to terraces will be converted to CO₂ due to the high CO coverage. Graphitic carbon on terrace sites will suppress CH₄ and CO₂ formation in line with experimental observation. Our earlier work shows that the CO consumption rate under methanation conditions is mainly limited by CH_x hydrogenation, meaning that suppression of CH_4 formation will cause a corresponding decrease in CO conversion. It also implies that blocking terrace sites slows CH_x hydrogenation to CH_4 , thereby increasing the residence time of CH_x fragments, meaning that the CH_x fragment will reside longer on step-edge sites. Evidently, the additional CH_x species available at the step-edge sites are involved in chain growth, while the C₂₊-hydrocarbons yield is only moderately affected. The higher coverage at the stepedges suppresses decoupling over chain growth [46], explaining the higher chain-growth probability. This view is also consistent with the C_3H_6/H_2 reaction experiments, in which C–C coupling is facilitated by presence of graphitic carbon terraces, since (i) CH_x migration to terraces is suppressed and (2) higher CH_x coverage on step-edges sites suppresses C–C decoupling. Of equal importance is then the observation that the presence of graphitic carbon during C₃H₆/H₂ conversion decreases the CH₄ selectivity. This directly proves that C species formed at step-edges can migrate to terrace sites and that graphitic carbon suppresses this migration. Having said this, we consider that H-assisted CO dissociation on terraces can play a role in the overall CO consumption, but it will mainly lead to CH₄. Indeed, if C species originating from terrace sites would be involved in chain growth on step-edges via migration, one would expect the C2+-hydrocarbons yield to decrease due to graphitic carbon. Therefore, this scenario can be excluded.

Our approach to selectively poison the surface with graphitic carbon provides new insight into the structure sensitivity of the F–T reaction and enables the assignment of stepedge sites as the main reaction centers for the F–T reaction. We have also shown that graphitic carbon can slowly build up during CO hydrogenation. The build-up of such graphitic carbon occurs faster at higher temperature and at lower H₂/CO ratio. At the time scale of our reaction (45 h), it is observed that at 260°C a considerable amount of graphitic carbon is deposited. At more typical F–T conditions (T = 220°C; H₂/CO = 2), the build-up is much slower. Nevertheless, the *in situ* produced graphitic carbon has a similar effect as pre-deposited graphitic carbon. Figure 6.8 shows that the decrease in CH₄ selectivity strongly correlates with the graphitic carbon content. The decrease in the C_{2+} -hydrocarbons yield is very low and only substantial when nearly the complete surface is poisoned.

In this respect, it is important to discuss CH_4 selectivity is an important parameter in practical F–T technology [7]. It is typically observed that the CH_4 selectivity is higher than expected on the basis of the ASF-distribution observed for the higher hydrocarbons [8, 11]. This discrepancy is usually explained by thermodynamically favored methane formation [11]. Our data show that formation of non-ASF CH₄ should be attributed to the structure sensitivity of the F-T reaction. For instance, Figure 6.10 confirms the formation of non-ASF CH_4 and its decrease with increasing graphitic carbon build-up. It is also consistent with the microkinetics simulations carried out for stepped Ru in which a lower than ASFpredicted CH₄ selectivity is found [29]. In this respect, it is worthwhile to cite two computational works that have involved different surface sites in predicting cobalt catalytic performance [50, 51]. Liu et al. employing DFT together with microkinetic modeling studied the chain-growth mechanism on a $Co(10\overline{1}1)$ surface. The results confirmed that the surface containing step-edge sites exhibits good selectivity towards C₂₊ hydrocarbons [51]. This is consistent our observation that a small fraction of surface sites is responsible for higher hydrocarbon formation. Van Helden et al. explored a combination of step-edge sites for CO dissociation and terrace sites for chain growth using first-principles kinetic parameters obtained for cobalt surfaces [50]. The reactions assigned to the different surface sites in these studies are not consistent with our experimental observations. The insights about structure sensitivity will guide the definition of more appropriate surface models for microkinetics simulations of the F-T reaction.

Finally, we contrast the above interpretation with two important works on the F–T reaction. Schulz has also discussed considerable changes in the CO conversion and product distribution for supported cobalt under typical F–T conditions [8, 52, 53]. Notably, he



Figure 6.10. ASF distribution determined after 1 h (squares), 5 h (circles), 15 h (triangles) and 45 h (diamonds) time-on-stream. Conditions: $p_{H_2} = 200$ mbar, $p_{C0} = 200$ mbar, $T = 260^{\circ}$ C.

observed an increasing paraffins-to-olefins ratio and chain-growth probability and decreasing CH₄ selectivity during the initial stages for a cobalt-rhenium catalyst. This is qualitatively similar to our observations. Schulz attributed these changes in part to the build-up of CO on planar sites, which for longer reaction times caused surface reconstruction [52]. This surface reconstruction led to an increase the fraction of step-edge sites on the catalyst surface. Another relevant study was recently reported by Ralston *et al.* [54], who observed that large cobalt particles (9.5 nm) contain more reactive carbon species and catalyze chain growth more effectively than small particles (4.3 nm). This observation is quantitatively consistent with the fraction of B_5 -B sites, a certain type of step-edge sites [19, 20, 49, 55]. Therefore, the different performance for small and large particles was attributed to the density of step-edge sites. This conclusion is qualitatively in line with our work, as the balance between step-edge sites responsible for CO dissociation and chain propagation and terrace sites for methane formation will determine the product distribution.

6.5 Conclusions

The influence of graphitic carbon on the F-T reaction was investigated in detail. Carbon was deposited by the Boudouard reaction, which involves CO dissociation on step-edge sites, diffusion of C atoms to terrace sites and agglomeration of these C atoms. Based on TPH, carbidic and graphitic carbon can be distinguished. Carbidic carbon can be hydrogenated below 260°C, while graphitic carbon can only be removed by hydrogenation at much higher temperature. Consistent with the low temperature at which carbidic carbon can be removed, it does not influence the F-T catalytic performance. The presence of predeposited graphitic carbon, on the other hand, has a profound influence on CO conversion and the product distribution. While CO conversion and CH₄ formation rate decrease, the formation rate of higher hydrocarbon is nearly unaffected by the presence of graphitic carbon. Additional F-T experiments designed to study the effect of *in situ* formed carbon deposits led to the insight that slow build-up of graphitic carbon has similar effects as predeposition of graphitic carbon. The formation of graphitic carbon is more pronounced at higher temperature and at lower H_2/CO ratio. Considering the structure sensitivity of the various elementary reaction steps underlying the F–T reaction, we reach the conclusion that two sites must be involved in the F-T reaction. Step-edge sites catalyze CO dissociation and chain growth. CH_x species formed on step-edge sites are involved in chain growth and CH₄ formation on step-edge sites and can also diffuse to terrace sites, where they are predominantly hydrogenated to CH₄. The terrace sites favor methanation, thereby explaining the occurrence of non-ASF CH₄. Under particular conditions, graphitic carbon can build up on terrace sites which decreases non-ASF CH₄.

References

- [1] F. Fischer, H. Tropsch, Brennst. Chem. 7 (1926) 97–104.
- [2] F. Fischer, H. Tropsch, Brennst. Chem. 11 (1930) 489–500.
- [3] A.N. Stranges, Stud. Surf. Sci. Catal. 163 (2007) 1–27.
- [4] H. Schulz, Appl. Catal., A 186 (1999) 3–12.
- [5] M.E. Dry, Appl. Catal., A 138 (1996) 319–344.
- [6] M.E. Dry, Catal. Today 6 (1990) 183–206.
- [7] M.E. Dry, Catal. Today 71 (2002) 227–241.
- [8] H. Schulz, Top. Catal. 26 (2003) 73–85.
- [9] G. Henrici–Olivé, S. Olivé, Angew. Chem. Int. Ed. 15 (1976) 136–141.
- [10] V.H. Pichler, H. Schulz, M. Elstner, Brennst. Chem. 48 (1967) 78-87.
- [11] H. Schulz, Catal. Today 214 (2013) 140–151.
- [12] A.J. Markvoort, R.A. van Santen, P.A. Hilbers, E.J. Hensen, Angew. Chem. Int. Ed. 51 (2012) 9015–9019.
- [13] Z.-P. Liu, P. Hu, J. Am. Chem. Soc. 125 (2003) 1958–1967.
- [14] R.A. van Santen, Acc. Chem. Res. 42 (2009) 57-66.
- [15] I.M. Ciobîcă, R.A. van Santen, J. Phys. Chem. B 107 (2003) 3808–3812.
- [16] M.N. Qingfeng Ge, J. Phys. Chem. B 110 (2006) 15368–15380.
- [17] B. Hammer, Phys. Rev. Lett. 83 (1999) 3681–3684.
- [18] J. Rempel, J. Greeley, L.B. Hansen, O.H. Nielsen, J.K. Nørskov, M. Mavrikakis, J. Phys. Chem. C 113 (2009) 20623–20631.
- [19] S. Dahl, A. Logadottir, R.C. Egeberg, J.H. Larsen, I. Chorkendorff, E. Törnqvist, J.K. Nørskov, Phys. Rev. Lett. 83 (1999) 1814–1817.
- [20] K. Honkala, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Norskov, Science 307 (2005) 555–558.
- [21] S. Shetty, A.P.J. Jansen, R.A. van Santen, J. Am. Chem. Soc. 131 (2009) 12874– 12875.
- [22] D. Hibbitts, E. Iglesia, Acc. Chem. Res. 48 (2015) 1254–1262.
- [23] W.J. Mitchell, J. Xie, T.A. Jachimowski, W.H. Weinberg, J. Am. Chem. Soc. 117 (1995) 2606–2617.
- [24] C.-F. Huo, Y.W. Li, J. Wang, H. Jiao, J. Phys. Chem. C 112 (2008) 14108–14116.
- [25] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, J. Catal. 272 (2010) 287–297.
- [26] B.T. Loveless, C. Buda, M. Neurock, E. Iglesia, J. Am. Chem. Soc. 135 (2013) 6107–6121.
- [27] P.H. Jun Cheng, Peter Ellis, Sam French, Gordon Kelly, and C. Martin Lok, J. Phys. Chem. C 112 (2008) 6082–6086.
- [28] R.A. van Santen, I.M. Ciobîcă, E. van Steen, M.M. Ghouri, Adv. Catal. 54 (2011) 127–187.

- [29] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [30] D.J. Moodley, J. van de Loosdrecht, A.M. Saib, M.J. Overett, A.K. Datye, J.W. Niemantsverdriet, Appl. Catal., A 354 (2009) 102–110.
- [31] J. Cheng, X. Gong, P. Hu, C. Lok, P. Ellis, S. French, J. Catal. 254 (2008) 285–295.
- [32] J. Nakamura, K.-I. Tanaka, I. Toyoshima, J. Catal. 108 (1987) 55-62.
- [33] J. Nakamura, I. Toyoshima, K.-I. Tanaka, Surf. Sci. 201 (1988) 185-194.
- [34] D.-K. Lee, J.-H. Lee, S.-K. Ihm, Appl. Catal. 36 (1988) 197–207.
- [35] C.J. Weststrate, A.C. Kızılkaya, E.T.R. Rossen, M.W.G.M. Verhoeven, I.M. Ciobîcă, A.M. Saib, J.W. Niemantsverdriet, J. Phys. Chem. C 116 (2012) 11575–11583.
- [36] W. Chen, B. Zijlstra, R. Pestman, E.J.M. Hensen, ChemCatChem, DOI: 10.1002/cctc.201701203.
- [37] W. Chen, R. Pestman, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen, ACS Catal. (accepted)
- [38] J.G. McCarty, H. Wise, J. Catal. 57 (1979).
- [39] K.F. Tan, J. Xu, J. Chang, A. Borgna, M. Saeys, J. Catal. 274 (2010) 121–129.
- [40] J.C.W. Swart, I.M. Ciobîcă, R.A. van Santen, E. van Steen, J. Phys. Chem. C 112 (2008).
- [41] J.-X. Liu, H.-Y. Su, W.-X. Li, Catal. Today 215 (2013) 36–42.
- [42] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.
- [43] L. Joos, I.A.W. Filot, S. Cottenier, E.J.M. Hensen, M. Waroquier, V. Van Speybroeck, R.A. van Santen, J. Phys. Chem. C 118 (2014) 5317–5327.
- [44] R.A. Friedel, R.B. Anderson, J. Am. Chem. Soc. 72 (1950) 1212–1215.
- [45] K. Keyvanloo, M.J. Fisher, W.C. Hecker, R.J. Lancee, G. Jacobs, C.H. Bartholomew, J. Catal. 327 (2015) 33–47.
- [46] W. Chen, I.A.W. Filot, R. Pestman, E.J.M. Hensen, ACS Catal. (accepted)
- [47] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. van Dillen, K.P. de Jong, J. Am. Chem. Soc. 128 (2006) 3956–3964.
- [48] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P.d. Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [49] P. van Helden, I.M. Ciobîcă, R.L.J. Coetzer, Catal. Today 261 (2016) 48–59.
- [50] P. van Helden, J.–A.v.d. Berg, M.A. Petersen, W. Janse van Rensburg, I.M. Ciobîcă, J. van de Loosdrecht, Faraday Discuss. 197 (2017) 117–151.
- [51] H. Liu, R. Zhang, L. Ling, Q. Wang, B. Wang, D. Li, Catal. Sci. Technol. (2017).
- [52] H. Schulz, Z. Nie, F. Ousmanov, Catal. Today 71 (2002) 351–360.
- [53] H. Schulz, Z. Nie, M. Claeys, Stud. Surf. Sci. Catal. 119 (1998) 191–196.
- [54] W.T. Ralston, G. Melaet, T. Saephan, G.A. Somorjai, Angew. Chem. Int. Ed. 56 (2017) 7415–7419.
- [55] R. van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189–230.



Science is the joke that she can never get.

Chapter 7

Silver addition to a cobalt Fischer–Tropsch catalyst

Abstract

Silver is known to promote F-T catalysts as a reduction promoter, although it has also been observed to affect catalytic performance of, for instance, cobalt nanoparticles. In this chapter, a series of silica-supported cobalt catalysts promoted with 0.04 wt% platinum and different amount of silver added to cobalt catalyst were characterized and tested. Characterization shows that silver is covering the surface, resulting in replacement of coordinatively unsaturated sites (as probed by N₂ IR) and also of planar surfaces (as probed by H₂-chemisorption). While at low silver content mainly coordinatively unsaturated sites are substituted, adding more silver leads to nanoparticles mostly enclosed by silver. The presence of silver in the surface affects both structure-sensitive CO dissociation and structure-insensitive hydrogenation reactions. The Boudouard reaction shows that the CO dissociation rate is decreased with increasing silver content. Slow CO dissociation is also apparent from temperature-programmed CO IR spectroscopy. However, even at high silver content at which no coordinatively unsaturated Co atoms are probed anymore by N_2 IR, the surface still contains step-edge sites that can dissociate CO and a small amount of carbon is deposited as graphitic carbon. The presence of silver leads to decreased CH₄ selectivity and enhanced chain-growth probability. This is mainly due to the coverage of terrace hydrogenation sites by silver. Silver affects catalytic performance at 260°C (methanation) and at 220°C (F–T) differently. During methanation where hydrogenation is rate controling step, silver mainly poisons sites for the structure-insensitive CH_x hydrogenation – mostly terrace sites -, thereby suppressing CH4 formation. As accordingly CHx intermediates reside longer on the surface, the chain-growth probability increases as does the C_{2+} selectivity. SSITKA confirms that the steady-state CO coverage strongly correlates to the cobalt surface area. Another effect of slower hydrogenation is that the olefins-to-paraffins ratios are strongly increased when silver is added to the catalyst. At a temperature closer to the F–T condition (220°C), the influence of silver on the product distribution is the same as at higher temperature. However, CO conversion is hardly affected by silver. Transient experiments show that silver accelerates oxygen-removal steps, likely because silver binds oxygen weaker than cobalt. Different from methanation, CO dissociation and oxygenremoval steps control the overall CO consumption rate at F-T conditions. Accordingly, the opposite effects of silver on these two reactions explain why CO conversion is not affected by silver. Importantly, covering the cobalt the silver surface affects the F-T product distribution in a similar manner as graphitic carbon deposited on terrace sites.

7.1 Introduction

One of the approaches to improve the performance of Fischer–Tropsch (F–T) catalysts is addition of small amounts of other elements, known as promoters. Silver, which does not exhibit measurable F-T activity, was initially proposed as a reduction promoter for iron based F-T catalysts. Early work by Wachs et al [1] showed that silver helps iron oxide reduction, but less effectively than copper does, because reduced silver poorly disperses on the iron oxide surface. The poor contact between silver and iron during the F-T reaction results in a moderate influence on the product distribution. Recent investigations on silver as promoter for iron-based F–T catalysts showed that silver facilitates the reduction of Fe^{3+} into magnetite during the pretreatment via either CO or H₂, which was attributed to the ability of silver to spillover hydrogen to iron oxide [2]. The iron-silver catalyst also shows enhanced F-T activity and increased chain growth, but at the expense of an increased CO₂ selectivity [2]. Chuang and Pien studied the effect of silver on a silica-supported rhodium catalyst [3]. The increased activity and selectivity of C_2 and C_3 oxygenates was attributed to a higher ratio of linear CO to bridged CO on the silver-promoted sample than on the unpromoted one. On a ruthenium F-T catalyst, a decreased turnover frequency (TOF) after silver addition was reported by Kelzenberg and King [4], who attributed the decline in TOF to occupation of coordinatively unsaturated sites by silver atoms. Later, this hypothesis was described in more detail by the same group [5]. They proposed that low-coordinated edge and corner sites on the catalyst surface act as reservoirs for highly mobile surface H atoms. Silver atoms preferentially occupy these coordination unsaturated sites, slowing down the supply of atomic hydrogen. Silver addition consequently results in a decreased CO hydrogenation rate due to the lack of surface hydrogen. Jacobs et al. provided detailed characterization and testing of silver-promoted cobalt catalysts [6]. They showed that the silver promoter enhances cobalt reducibility and therefore increases the amount of active sites, leading to enhanced CO conversion. In parallel with the increase in F-T activity, a decrease in CH₄ selectivity and an increase in C₅₊ selectivity were observed. EXAFS characterization showed increased Ag-Ag coordination numbers with increasing Ag content, indicating the formation of a segregated metallic silver phase [7].

In spite of these investigations, fundamental understanding about the role of Ag promoter in cobalt–catalyzed F–T synthesis is still lacking. In this chapter, silica-supported cobalt catalysts with constant platinum content (0.04 wt% based on catalyst weight) with varying silver content were prepared by step-wise impregnation. The effect of silver promotion was studied by means of CO exposure followed by temperature programed hydrogenation (TPH), infrared spectroscopy (IR), steady state isotopic transient kinetic analysis (SSITKA) and F–T performance tests.

7.2 Experimental

7.2.1. Preparation

The silver-promoted cobalt catalysts were prepared by incipient wetness impregnation of reduced platinum-cobalt catalysts (see Section 2.3.1 for the preparation of this catalyst) with a AgNO₃ aqueous solution. Following the impregnation step, the catalysts were dried at 110°C in static air overnight and subsequently calcined at 350°C for 2 h using a heating rate of 1°C min⁻¹. As determined by ICP–OES. The cobalt and platinum content are 17 wt% and 0.04 wt%, respectively. The silver-containing samples are denoted by their silver weight content, *e.g.*, 4.3AgCo stands for a catalyst containing 4.3 wt% Ag, 17 wt% cobalt, and 0.04 wt% platinum on a silica support.

7.2.2 Characterization

Infrared (IR) spectra were recorded on Bruker Vertex V70v FTIR spectrometer. A detailed description of the instrument and the experimental procedure for obtaining IR spectra of CO are provided in Chapter 3. For obtaining IR spectra of adsorbed N₂, the catalyst wafer was first reduced in H₂ flow at 500°C for 2 h followed by cooling in vacuum to -175°C using liquid nitrogen. Small doses of N₂ were admitted to the transmission cell, until the IR band at 2200 cm⁻¹ reached a maximum.

Temperature-programmed reduction (TPR) experiments were carried out on ASAP 2920 II (Micromeritics). Typically 10 mg sample was reduced in diluted H_2 flow (10% H_2 in Ar) using a heating rate of 10°C min⁻¹. A silver oxide reference sample was used to calibrate the H_2 consumption.

Carbon deposition and subsequent temperature-programmed hydrogenation (TPH) were performed in a tubular reactor. Typically, 200 mg *in situ* reduced (20% H₂ in Ar, 450°C, 16 h) Co/SiO₂ was exposed to a diluted CO flow (10% CO in Ar). The subsequent TPH experiments were conducted by heating the reactor to 550°C at a rate of 5°C/min in an H₂ flow (10% H₂ in Ar). The main hydrocarbon product of carbon hydrogenation was CH₄ as determined by online mass spectrometer (ESS, GeneSys Evolution). The amount of deposited carbon was determined by integrating the CH₄ flow with time-on-stream. Details of this procedure are provided in Section 6.2.

Catalytic activity measurements and transient experiments were performed in a setup capable of switching gas feeding. After reduction at 450°C for 16 h, the reactor was cooled to 260°C in an Ar flow and the pressure was increased to 2 bar. The Ar flow was subsequently switched to a synthesis gas mixture (CO/H₂/Ar). The responses after the switch are monitored by online MS. The activity and selectivity were measured on a VARIAN CP–3800 gas chromatograph equipped with TCD and FID detectors.

Steady state isotopic transient kinetic analysis (SSITKA) was performed by switching from a mixture of ¹²CO/H₂/Ar to a mixture of ¹³CO/H₂/Ne, when steady state conversion was reached. In these measurement, Ne was used as a tracer to determine the gas-phase hold-up time. The transient responses of H₂ (m/z = 2), ¹²CH₄ (m/z = 15), ¹³CH₄ (m/z = 17), ¹²CO (m/z = 28), ¹³CO (m/z = 29) were monitored by online mass spectrometry (ESS, GeneSys Evolution). The procedures to determine the residence times and coverages of CO and CH_x are determined by Eq 2.4–Eq2.7.

7.3 Results and discussion

7.3.1 Cobalt reducibility

Temperature-programed reduction (TPR) experiments were performed to trace the influence of silver promotion on the cobalt reducibility. Figure 7.1 shows that as little as 0.3 wt% silver reduces the temperature of CoO to Co reduction by 40°C. Increasing the silver content does not further decrease the reduction temperature of CoO. Quantification of H₂-consumption during the TPR indicates that the presence of silver increases the cobalt reduction degree only slightly. For instance, the cobalt reduction degree of 8.8AgCo is 96%, marginally higher than that of the parent cobalt catalyst. The high reduction degree of the cobalt catalysts is due to the presence of platinum, which acts as a reduction promoter. As outlined earlier, the presence of 0.04 wt% platinum increases the cobalt reduction degree from 64% to 93% (see Section 3.2.2).



Figure 7.1. TPR profiles of silver-promoted cobalt catalysts.

7.3.2. CO exposure followed by TPH

CO disproportionation, known as the Boudouard reaction [8-10] was employed to probe the activity of silver-promoted cobalt catalysts towards CO bond scission [11]. The ${}^{12}C^{16}O/{}^{13}C^{18}O$ isotopic scrambling experiments in Chapter 3 prove that reversible CO dissociation in the absence of H₂ occurs on a small fraction of surface. As previously discussed, the C–O bond can only be broken on step-edge sites, because the barrier of CO dissociation on terrace sites without the assistance of hydrogen is very high [12, 13]. The silver-free cobalt catalyst contains on average 15 nm particles, whose surface is dominated by terrace sites with about 20% coordinatively unsaturated cobalt atoms such as corner, edges and step-edges among which the latter dominate at the given size [14, 15]. Therefore, we attributed the CO bond activation activity to these step-edge sites on the cobalt nanoparticles.



Figure 7.2. CO_2 responses following the switch from Ar to CO at 260°C. The curves are shifted in time for the clarity. The sharp CO_2 increasing occurs simultaneously with CO breaking in.



Figure 7.3. TEM image (left) and EDS mapping (right) of 4.3AgCo catalyst.



Figure 7.4. TPH profiles of the catalysts exposed to CO flow (10% CO in Ar) at 260°C for 30 min. The carbon to surface cobalt ratios were calculated on the basis of unpromoted cobalt catalyst.

Figure 7.5. Cobalt surface area determined by H_2 -chemisorption as a function of silver content.

Figure 7.2 illustrates the response of the Co and AgCo catalysts to an Ar \rightarrow CO switch at 260°C. As for the cobalt catalyst, CO₂ appears immediately after the switch for the AgCo catalysts, followed by a rapid decrease due to the deposition of C atoms which block the active sites for CO dissociation in the absence of hydrogen. These data also show that addition of silver strongly decreases the CO₂ formation rate. For instance, addition of 0.3 wt% Ag results in two times lower activity. This result suggests that silver atoms modify the active sites for CO bond dissociation. A rough estimation shows that 0.3 wt% Ag would occupy about 15% of the cobalt surface sites. The decrease in CO dissociation rate observed for silver-promoted cobalt is consistent with the report that adding a small amount of silver to ruthenium (Ag/Ru = 0.03) suppresses the rate of CO hydrogenation by more than 80% [5]. Increasing the silver content to 8.8 wt% results in a gradual decrease of the CO dissociation activity. For 8.8AgCo, the CO_2 formation rate is suppressed by 90%. The silver loading is significantly higher than the surface of the cobalt catalyst. Thus, the observation that 8.8AgCo still shows significant CO₂ formation implies that not all the cobalt step-edge sites are covered. These findings suggest that addition of silver to the cobalt catalyst preferentially blocks sites involved in CO bond dissociation. Not all of these sites are blocked, even if the silver content becomes very high. With increasing silver content, the silver atoms segregate from the cobalt surface [16] and result in separate silver particles. This is consistent with the TEM/EDS images of reduced 4.3AgCo in Figure 7.3.

The amount of carbon deposited by CO disproportionation was determined by subsequent TPH experiments. The TPH profiles together with the carbon to surface cobalt ratio are presented in Figure 7.4. It was possible to remove all of the carbon by TPH up to 650°C. For the cobalt catalyst, a carbon-to-surface-cobalt ratio of 0.79 was determined, illustrating that nearly the complete surface was covered after CO-exposure for 30 min. The total amount is too large to be accommodated only on the coordinatively unsaturated cobalt

sites of the surface.[14, 15] As discussed in Chapter 6, the C atoms derived from CO dissociation will migrate from step-edge sites to terrace site [17, 18] and aggregate in the form of graphitic carbon [18, 19]. The rate of carbon formation on cobalt surface may be limited by C migration from step-edge to terrace, since CO dissociation on step-edge sites is intrinsically very fast. One can see that the carbon-to-surface-cobalt ratio decreases from 0.8 to 0.32 as the Ag content increases from 0 to 8.8 wt%. The decrease in carbon deposits is therefore likely not only due to inhibited CO dissociation on step-edge sites, but also partial blocking of the terraces, which accommodate graphitic carbon.

We also measured H_2 chemisorption on the Co and AgCo samples (Figure 7.5) and found that the cobalt surface area is decreased by 93% upon addition of 4.3 wt% silver. A catalyst only containing silver was not able to chemisorb H_2 in keeping with earlier studies [20]. Clearly, this large decrease is not only due to coverage of step-edge sites but also due to blocking of terrace sites.

7.3.2 N₂ and CO infrared spectroscopy

Identifying step-edge sites in nanoparticle catalysts has remained a challenging task. Van Hardeveld and Van Montfoort attributed an unusual adsorption feature of N2 on Pt, Ni and other transition metal nanoparticles to strong adsorption of N₂ in the step-edges [21, 22]. Lighart et al. demonstrated a strong correlation between the intensity of a similar IR band of adsorbed N₂ at 2205 cm⁻¹ and the CO bond dissociation activity for zirconia-supported rhodium particle [23]. Complementary DFT calculations showed that the unusual N₂ stretching feature is not due to direct adsorption of N2 in a step-edge site but, instead, due to top adsorption of N_2 on coordinatively unsaturated sites such as the corner, edge and stepedge atoms [23]. The intensity increases with increasing coordinative unsaturation of the surface metal atom to which N_2 binds. We employed here a similar approach to follow the impact of silver on step-edge sites of cobalt nanoparticles. The corresponding N2 IR spectra recorded at liquid nitrogen temperature on a series of silver-promoted cobalt catalysts and the unpromoted one are presented in Figure 7.6. The band observed at 2200 cm⁻¹ is close to perturbed N₂ bands observed on nanoparticles of Ni, Pt, Pd [21, 22], and Rh [23]. A recent study of Dillinger et al. assigned IR frequencies in the 2180-2290 cm⁻¹ range for sizeselected cobalt clusters to coordinatively unsaturated sites [24]. Figure 7.6 illustrates that silver substantially suppresses the intensity of the N₂ band at 2200 cm⁻¹. Addition of 0.3 wt% silver results in a decrease of the intensity by 75%. When the silver content increases to 1.7 wt%, the band is not present anymore. This observation is qualitatively in keeping with the strong decrease in the rate of CO_2 formation during the Boudouard reaction. It is in line with the result of computer simulations [4, 25] and experimental observations [26] showing that group IB group metal atoms preferentially occupy coordinatively unsaturated sites on metal surfaces. Vang et al. observed by STM that silver atoms can selectively block stepedge sites of the Ni(111) surface [27]. The results attest that addition of silver to the cobalt



Figure 7.6. IR spectra of adsorbed N_2 on (silver-promoted) cobalt catalysts. The spectra were recorded at -175 °C. The spectra intensities are normalized based on the Co mass.

nanoparticle catalysts blocks coordinatively unsaturated sites. Although this is qualitatively reflected in a strong decline of the CO dissociation rate, the catalytic data evidence that some step-edge sites are still available. We emphasize that the N_2 binding energy is relatively weak, implying that it is much less sensitive than for instance CO. Therefore, we also characterized the catalysts using CO IR spectroscopy.

In earlier work, we attributed a blue shift in the CO IR adsorption band observed above 150°C to lateral interactions with co-adsorbed C and O atoms derived from CO dissociation [28]. Here, we employ the same approach to determine the influence of silver on CO bond dissociation. Figure 7.7 presents the evolution of the CO IR spectrum as a function temperature for 0AgCo, 0.3AgCo and 1.7AgCo catalysts. The dashed lines guide the eye to the center of the main CO adsorption feature. We use the inflection point of the dashed line as an indication for the temperature at which appreciable CO dissociation occurs. Clearly, the addition of silver to the cobalt catalyst increases this temperature of CO dissociation from 180°C to 230°C. Additional support for this difference is derived from temperature-programmed reaction experiments in a CO flow. Figure 7.8 shows that the temperature at which CO consumption starts is higher (200°C) than for Co (160°C). Together with the N_2 IR data, we infer that silver blocks step-edge sites, thereby decreasing the rate of CO dissociation. For 1.7AgCo, the evolution of the IR spectra is different. Interestingly, increasing silver content to 1.7 wt% does not raise the CO dissociation temperature further. Although the blue-shift of the CO IR band is still observed at nearly the same temperature as in 0.3AgCo, the intensity of this feature is much lower. We attribute this to a substantial coverage of terrace sites by silver atoms. Accordingly, the terrace sites cannot accommodate large amounts of C atoms and the strongly perturbed CO adsorption state observed for 0AgCo is not observed pronouncedly anymore.



Figure 7.7. IR spectra of adsorbed CO on un-promoted (a), 0.3 wt% silver-promoted (b) and 1.7 wt% silver-promoted (c) cobalt catalysts with increasing temperature.



Figure 7.8. Temperature-programmed reaction over 0AgCo and 0.3AgCo in a CO-flow (10 mbar CO in He).

7.3.3 Influence of silver on catalytic performance

We evaluated the catalytic performance of the various catalysts in a model F–T reaction at $T = 260^{\circ}$ C with a H₂/CO ratio of 1 and at $T = 220^{\circ}$ C with a H₂/CO ratio of 5. We verified that the silver-only catalyst showed only negligible CO conversion. Figure 7.9a shows CO conversion, CH₄ selectivity, C₅₊ selectivity and CO₂ selectivity as a function of the silver content at 260°C. While CO conversion and CH₄ selectivity decrease from 6.2% to 4.4% and from 50% to 26%, respectively, the C₂₊ selectivity increases substantially with increasing silver content. Figure 7.9b illustrates the decreasing CH₄ yield and increasing C₂₊ yield. CO₂ yield also decreases. Concomitantly, the chain-growth probability increases



Figure 7.9. Catalytic performance of F–T reaction over Ag promoted cobalt catalysts as a function of silver content. Conditions: (a) and (b): $p_{H_2} = p_{CO} = 200$ mbar, $T = 260^{\circ}$ C; (c) and (d): $p_{H_2} = 450$ mbar, $p_{CO} = 90$ mbar, $T = 220^{\circ}$ C.

significantly with increasing silver content. At 220°C, similar trends are observed (Figure 7.9c and d), although the decrease in CO conversion is only minor. Notably, the influence of silver or carbon deposits on CO conversion and the product distribution is qualitatively similar.

The decrease in CO conversion can be attributed in part to the coverage of step-edge sites by silver atoms. In contrast to the observation that the rate of the Boudouard reaction is suppressed by nearly 90% for the catalyst with the highest silver content, the CO conversion only decreases less than half, comparing the 0AgCo and 8.8AgCo samples. This difference can be explained by the notion that CO methanation at 260°C is not limited by CO dissociation but by C hydrogenation as demonstrated in Chapter 4. This observation also underpins the conclusion reached in Chapter 3, *i.e.*, only a small fraction of the active sites for CO dissociation are directly involved in the CO hydrogenation.



Figure 7.10. SSITKA-determined residence times (a) and coverage (b) as a function of silver content. The SSITKA measurements were performed after 21 h time-on-stream.

To understand this aspect better, we report residence times for CH_x derived from SSITKA measurements at 260°C as a function of the silver content. Figure 7.10a shows that the residence time of CH_x increases as a function of silver content. This trend means that the C hydrogenation rate is decreased when a larger part of the surface is occupied by silver. The longer CH_x residence time can also be correlated to a higher probability of C–C coupling reactions, explaining the enhanced chain-growth probability. It may be noted here that the conversion and selectivity changes impacted by silver are similar with the impact of graphitic carbon on CO hydrogenation reaction as discussed in Chapter 6: graphitic carbon on terraces significantly suppresses the CH_4 production and increases chain growth. Figure 7.10b shows the surface coverages derived from the SSITKA data and cobalt surface area of unpromoted 0AgCo catalyst determined by H₂-chemisorption. The CH_x coverage is only slightly affected at low silver content and decreases more pronouncedly with increasing silver content. The CO coverage can be correlated to the total cobalt surface area.

Figure 7.11 shows that the ethylene/ethane and propylene/propane ratios also strongly increase with silver content. It is well understood from experiment [29-32] and theory [33] that olefins are the primary products of the F–T reaction. Paraffins are mainly obtained by olefin re-adsorption and hydrogenation. Similar to CH_x hydrogenation, olefin hydrogenation is expected to be largely insensitive to active site structure. Therefore, we can argue that the decrease in olefin hydrogenation is well in line with the loss of cobalt surface. It can therefore also be linked to a decreased H coverage. Notably, the increase in the olefin-to-paraffin ratio is relatively minor up to a silver content of 0.9 wt%, but increases steeply when more silver is added. This further underpins the conclusion that low amounts of silver more significantly affect step-edge sites than terrace sites.

Besides cobalt surface blocking, silver facilitates oxygen removal from the surface. This step is one of the rate-controlling step at F–T conditions [33, 34]. Figure 7.12 presents



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Figure 7.11. Ethylene/ethane and propylene/propane ratios over silver-promoted cobalt catalysts as a function of silver content. Conditions: $p_{H2} = p_{CO} = 150$ mbar, 260 °C. The data were obtained after 21 h time-on-stream.

Figure 7.12. Normalized water response after a switch from Ar to CO/H₂ over silver AgCo catalyst. Steady state conditions: $p_{H_2} = p_{CO} = 200$ mbar, $T = 260^{\circ}$ C.

the water response after a Ar \rightarrow CO/H₂ switch on the reduced AgCo catalysts. Adding as little as 0.3 wt% silver significantly reduces the water delay time. Further increasing the silver content, however, prolongs the water delay again. This is not surprising, since the systematic delay time caused by adsorption/desorption (the chromatographic effect) correlates with the flow rate and the amount of surface sites via

$$\tau_{\rm H_2O} = \frac{A}{F_{\rm H_2O}} \tag{7.1}$$

where A is the total surface area of the system and F_{H_2O} the molar flow rate of water, which can be correlated to CO conversion. Considering the fact that the CO conversion deceases by 30% when 8.8 wt% silver is added, the systematic delay time of water accordingly increases. The unpromoted cobalt catalyst showing the highest CO conversion bears the shortest systematic delay time. Consequently, the decrease in water delay time reflects the enhancement of the O removal step. This effect can compensate the decrease of the available cobalt surface, resulting in a less pronounced decrease in CO consumption. Notably, the catalytic data recorded at 260°C show a severe negative effect of silver on CO conversion, consistent with C hydrogenation being the most dominant rate-controlling step under these conditions. The removal of O from the surface as water only contributes slightly to the rate control of the methanation reaction. On the other hand, at 220°C O removal as water will control the overall CO consumption rate more strongly together with CO dissociation. Thus, we speculate that, despite the decrease in CO dissociation rate due to partial deactivation of step-edges, the faster O removal from these step-edge sites will facilitate the reaction. This can explain the observation that the CO conversion does not appreciably change with silver content at 220°C. Notably, the effect of silver on CH4 selectivity and chain-growth probability remains evident as shown in Figure 7.9c and 7.9d.

7.3.4 General discussion

Promoters are widely employed in F–T catalysts to increase the reduction degree of the active transition metal or to improve the intrinsic catalytic performance. We investigated the role of silver as a promoter for cobalt-catalyzed F–T synthesis. All of the catalysts contained platinum, which is effective in reducing cobalt oxide. Therefore, the impact of silver as a promoter will mainly be due to its influence on the elementary reaction steps. Silver was added to a reduced cobalt catalyst followed by calcination and reduction with the purpose of investigating the influence of a low-reactive transition metal on the cobalt-catalyzed F–T reaction. The surface of the reduced catalysts was investigated by N₂ and CO IR spectroscopy. Steady state and SSITKA measurements under model F–T conditions are then used to determine CO conversion and the product distribution.

The addition of silver to the cobalt catalyst results in a decrease of the cobalt surface area, suggesting that part of the added silver covers the surface. In line with surface science model and other studies on supported nanoparticle catalysts, the low-reactive promoter atoms will be preferentially replace or cover coordinatively unsaturated cobalt atoms. Only at higher silver content, an appreciable part of the terrace surfaces will be also covered by silver atoms. The selective coverage of step-edge sites is evident from a strongly decreased intensity of the N₂ IR band, which is characteristic for low-coordinated cobalt atoms. CO disproportionation, which is the main structure-sensitive reaction in F-T catalysis, was used to establish that a large fraction of the step-edge sites are deactivated by silver. Nevertheless, even at the highest silver content, CO dissociation remains possible at an appreciable rate. Temperature-programmed CO IR spectroscopy shows that CO dissociation is shifted to higher temperature, reflecting the lower amount of active sites for CO dissociation. CO IR spectroscopy, H₂-chemisorption and steady-state CO coverage values derived from SSITKA attest to the decreased CO coverage of the bimetallic catalysts. The data suggest that an appreciable part of the cobalt surface is occupied by silver atoms. During the model F–T reaction, the CO coverage of the 8.8AgCo is about half that of the 0AgCo catalyst. We speculate that there are still cobalt atoms at the surface of the terraces but the absence of cobalt ensembles will strongly decrease the binding energy of CH_x intermediates, the ability of the surface to dissociate H_2 , together contributing to the decreased hydrogenation performance.

Addition of silver to the cobalt nanoparticle catalyst has a strong influence on the catalytic performance. The presence of silver decreases CO conversion at methanation conditions (260°C) in spite of the blockage of step-edge sites. This can be understood by taking into account that the CO conversion rate is mainly controlled by C hydrogenation, which occurs on terraces. Moreover, blocking an increasing fraction of terrace sites results in lower CH₄ and higher C_{2+} -selectivity. The lower CH₄ selectivity is due to slower CH_x hydrogenation due to a lower amount of hydrogenation sites. The increased C_{2+} selectivity and chain-growth probability correlate well with the resulting long CH_x residence time.

Finally, hydrogenation of the primary olefin products is also delayed by silver, in line with the notion that also hydrogenation of olefins is a structure-insensitive reaction. All of these results are qualitatively in line with the earlier observed impact of graphitic carbon deposited on terrace sites on F–T performance.

The interpretation presented in this section is mainly based on the structure sensitivity of CO dissociation [13, 35-37] and chain-growth and -decoupling [38] reactions and the structure insensitivity of CH_x hydrogenation reactions. It also involves the migration of C species generated by direct CO bond dissociation on step-edge sites to terrace sites [33]. Given that the catalytic performance data are obtained at 260°C, the main effect of silver on catalytic performance is due to the coverage of terrace sites. This suppresses hydrogenation of CH_x intermediates and, in this way, affects CO conversion and the hydrocarbons product distribution. To be more specific, CO dissociation is sufficiently fast to supply the CH_x intermediates that lead to the dominant CH_4 product, even if a large fraction of step-edge sites are deactivated. The effect of silver on CO conversion is much less pronounced when the F-T reaction is carried out at 220°C. The data show that the water delay is considerably shorter upon addition of silver, proving that the weaker O adsorption on a surface in which silver replaces cobalt atoms leads to easier water formation. Thus, we expect that at 220°C the effect of silver on CO dissociation and oxygen removal steps is opposite leading to only small dependence of CO conversion on the amount of silver. The clear influence of silver on the terrace sites leading to decrease CH₄ selectivity and increased C₂₊-selectivity and chain-growth probability is still observed during the model F-T reaction at 220°C.

7.4 Conclusions

In this chapter, we studied the influence of silver on a cobalt-based F-T catalyst. As platinum is used as a reduction promoter, addition of silver does not further enhance cobalt reduction. Given that the particle size of the promoted catalysts does not strongly vary with silver content, silver mainly impacts catalytic performance through lowering the reactivity of the cobalt surface. H₂-chemisorption shows that silver atoms are covering a large part of the surface, resulting in decreased H₂-chemisorption. At low silver content, mainly coordinatively unsaturated surface cobalt atoms are substituted by silver as follows from low-temperature N2 IR spectroscopy. This results in a strong decrease of the CO dissociation rate as confirmed by a transient switch from Ar to CO leading to CO disproportionation and temperature-programmed CO IR spectroscopy, showing a shift of CO dissociation to higher temperatures as compared to the cobalt-only catalyst. With increasing silver content, a substantial fraction of the cobalt atoms are replaced by silver. The combined characterization and catalytic data suggest some step-edge sites remain active in CO dissociation and the terrace surfaces contain mainly silver with isolated cobalt atoms. During CO hydrogenation at 260°C, the CO conversion is strongly decreased due to the presence of silver. This does not correlate well with the loss in step-edge sites or CO

dissociation rate as probed by CO disproportionation, because the CO consumption rate under methanation conditions is controlled by C hydrogenation. As silver poisons sites for the structure-insensitive CH_x hydrogenation – mostly terrace sites –, the CH_4 formation rate is suppressed. As accordingly CH_x intermediates reside longer on the surface, the chaingrowth probability increases as does the C2+-selectivity. SSITKA confirms that the steadystate CO coverage strongly correlates to the cobalt surface area. Also the CH_x coverage decreases with increasing silver content. Another effect of slower hydrogenation is that the olefins-to-paraffins ratios are strongly increased when silver is added to the catalyst. At a temperature closer to the F-T condition (220°C), the influence of silver on the product distribution is the same as at higher temperature. However, CO conversion is hardly affected by silver. Transient experiments with C18O show that silver accelerates oxygenremoval steps, likely because silver binds oxygen weaker than cobalt. At the F–T condition, CO dissociation and oxygen-removal steps both control the overall CO consumption rate. Therefore, the opposite effects of silver on these two reactions explain why CO conversion is not affected by silver. Importantly, covering the cobalt the silver surface affects the F-T product distribution in a similar manner as graphitic carbon deposited on terrace sites. A difference is that the silver also affects step-edge sites, while C atoms on step-edge sites are removed in the form of hydrocarbon products.

References

- [1] I.E. Wachs, D.J. Dwyer, E. Iglesia, Appl. Catal. 12 (1984) 201–217.
- [2] Z.H. Chonco, A. Ferreira, L. Lodya, M. Claeys, E. van Steen, J. Catal. 307 (2013) 283–294.
- [3] S.S.C. Chuang, S.-I. Pien, J. Catal. 138 (1992) 536–546.
- [4] J.C. Kelzenberg, T.S. King, J. Catal. 126 (1990) 421–433.
- [5] D.P. VanderWiel, M. Pruski, T.S. King, J. Catal. 188 (1999) 186–202.
- [6] G. Jacobs, M.C. Ribeiro, W. Ma, Y. Ji, S. Khalid, P.T.A. Sumodjo, B.H. Davis, Appl. Catal., A 361 (2009) 137–151.
- T. Jermwongratanachai, G. Jacobs, W. Ma, W.D. Shafer, M.K. Gnanamani, P. Gao,
 B. Kitiyanan, B.H. Davis, J.L.S. Klettlinger, C.H. Yen, D.C. Cronauer, A.J. Kropf,
 C.L. Marshall, Appl. Catal., A 464–465 (2013) 165–180.
- [8] D.B.R. Hansong Cheng, Sheldon Dean Jr., Catal. Today 50 (1999) 579–588.
- [9] G.M. Bremmer, E. Zacharaki, A.O. Sjastad, V. Navarro, J.W.M. Frenken, P.J. Kooyman, Faraday Discuss. 197 (2017) 337–351.
- [10] J. Nakamura, I. Toyoshima, K.-I. Tanaka, Surf. Sci. 201 (1988) 185-194.
- [11] I.M. Ciobîcă, R.A. van Santen, J. Phys. Chem. B 107 (2003) 3808–3812.
- [12] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.
- [13] J.-X. Liu, H.-Y. Su, W.-X. Li, Catal. Today 215 (2013) 36-42.
- [14] P. van Helden, I.M. Ciobîcă, R.L.J. Coetzer, Catal. Today 261 (2016) 48-59.
- [15] R. van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189–230.
- [16] F. Dorfbauer, T. Schrefl, M. Kirschner, G. Hrkac, D. Suess, O. Ertl, J. Fidler, J. Appl. Phys. 99 (2006) 08G706.
- [17] L. Joos, I.A.W. Filot, S. Cottenier, E.J.M. Hensen, M. Waroquier, V. Van Speybroeck, R.A. van Santen, J. Phys. Chem. C 118 (2014) 5317–5327.
- [18] J.C.W. Swart, I.M. Ciobîcă, R.A. van Santen, E. van Steen, J. Phys. Chem. C 112 (2008) 12899 - 12904.
- [19] K.F. Tan, J. Xu, J. Chang, A. Borgna, M. Saeys, J. Catal. 274 (2010) 121–129.
- [20] X.-L. Zhou, J.M. White, Surf. Sci. 218 (1989) 201-210.
- [21] R. van Hardeveld, A. van Montfoort, Surf. Sci. 4 (1966) 396–430.
- [22] R. Van Hardeveld, A. Van Montfoort, Surf. Sci. 17 (1969) 90–124.
- [23] D.A.J.M. Ligthart, I.A.W. Filot, A.A.H. Almutairi, E.J.M. Hensen, Catal. Commun. 77 (2016) 5-8.
- [24] S. Dillinger, J. Mohrbach, J. Hewer, M. Gaffga, G. Niedner-Schatteburg, Phys. Chem. Chem. Phys. 17 (2015) 10358-10362.
- [25] J.K. Strohl, T.S. King, J. Catal. 116 (1989) 540-555.
- [26] K.S. Kim, J.H. Sinfelt, S. Eder, K. Markert, K. Wandelt, J. Phys. Chem. 91 (1987) 2337-2342.
- [27] R.T. Vang, K. Honkala, S. Dahl, E.K. Vestergaard, J. Schnadt, E. Lægsgaard, B.S. Clausen, J.K. Nørskov, F. Besenbacher, Nat. Mater. 4 (2005) 160–162.
- [28] W. Chen, B. Zijlstra, R. Pestman, E.J.M. Hensen, ChemCatChem, DOI: 10.1002/cctc.201701203.
- [29] V.H. Pichler, H. Schulz, M. Elstner, Brennst. Chem. 48 (1967) 78-87.
- [30] R.A. Friedel, R.B. Anderson, J. Am. Chem. Soc. 72 (1950) 1212–1215.
- [31] H. Schulz, Top. Catal. 26 (2003) 73–85.
- [32] K.R. Krishna, A.T. Bell, Catal. Lett. 14 (1992) 305–313.
- [33] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [34] C.J. Weststrate, P. van Helden, J. van de Loosdrecht, J.W. Niemantsverdriet, Surf. Sci. 648 (2016) 60–66.
- [35] R.A. van Santen, M.M. Ghouri, S. Shetty, E.M.J. Hensen, Catal. Sci. Technol. 1 (2011) 891–911.
- [36] Z.-P. Liu, P. Hu, J. Am. Chem. Soc. 125 (2003) 1958–1967.
- [37] J. Cheng, X. Gong, P. Hu, C. Lok, P. Ellis, S. French, J. Catal. 254 (2008) 285–295.
- [38] P.H. Jun Cheng, Peter Ellis, Sam French, Gordon Kelly, and C. Martin Lok, J. Phys. Chem. C 112 (2008) 6082–6086.

Chapter 8

Summary and outlook

A Transient Kinetics Study of Fischer–Tropsch Synthesis Mechanism on Cobalt Catalysts

Fischer–Tropsch synthesis is an increasingly important technology to convert various carbon-containing resources, such as natural gas, coal and biomass, into clean transportation fuels. Despite its importance, a large number of questions remain regarding the mechanism underlying the CO hydrogenation reaction. Understanding of this complex reaction is hampered by the many reaction steps involved in the mechanism, which restricts the use of conventional evaluation of the reaction kinetics in which a single rate-determining step is assumed. Transient kinetics provides a unique way to furnish mechanistic information in a less ambiguous way than steady-state kinetics. In this thesis, transient kinetics analysis is combined with spectroscopy and temperature-programmed experiments in order to study the mechanism and kinetics of the cobalt-catalyzed F–T reaction. Transient techniques and the main aspects of data analysis are described in **Chapter 2**.

In **Chapter 3**, we introduce the Co/SiO₂ catalyst that is the main subject of the mechanistic studies. We present the basic characterization of this catalyst and show that adding of Pt is sufficient to fully reduce the catalyst at 450°C. CO disproportionation is used to study CO dissociation in the absence of hydrogen. The results reveal an unexpectedly high scrambling rate on initially empty cobalt catalyst, meaning that the direct CO dissociation is reversible and sufficiently fast to activate the CO molecules for all subsequent CO consuming reactions occurring during F–T synthesis. The rapid decrease in scrambling rate is correlated to the blocking of a small fraction of cobalt surface, which can be assigned to the active sites for CO dissociation. In the presence of H₂, the scrambling rate is slightly lower as slow C and O hydrogenation lower the coverage of C and O. The CO scrambling rate and CO residence time are nearly independent of H₂ partial pressure, implying that the reversible CO adsorption and dissociation are only weakly affected by H₂. *In situ* IR spectra of adsorbed CO as a function of temperature confirm that the CO dissociation is independent of the presence of H₂. All these findings strongly indicate that direct CO dissociation is important in the presence of H₂.

In **Chapter 4**, different types of transient experiments are employed to investigate cobalt-catalyzed CO hydrogenation under methanation conditions (260°C, 1.5 bar). Combining data of several transient experiments allowed to fit microkinetic models. The results suggest that the overall methanation rate is not controlled by CO dissociation, but by

surface hydrogenation steps that remove C and O atoms from the surface. Backward transient experiments $(H_2/CO \rightarrow H_2)$ show that an increase in the number of vacancies and surface hydrogen leads to a significant increase in methane formation, until all the surface carbon species are depleted. Forward transient experiments $(Ar \rightarrow CO/H_2 \text{ and } H_2 \rightarrow CO/H_2 \text{ switch})$ further reveal slow O removal. It is noteworthy that models employing direct CO dissociation and hydrogen-assisted CO dissociation result in the similar conclusion that overall reaction rate is highly controlled by hydrogenation steps. It is emphasized that the high dependence of hydrogen cannot be solely correlated to hydrogen-assisted CO dissociation step. Hydrogenation reactions to water and hydrocarbons can be kinetically relevant as long as the CO dissociation step proceeds sufficiently fast, no matter whether it occurs direct or assisted by hydrogen. Hydrogen has an indirect influence on the reaction rate, as hydrogenation of adsorbates creates vacancies and thus increases the overall CO dissociation rate.

The kinetics of the F-T reaction strongly depends on the reaction conditions. In Chapter 5, a lower temperature (220°C) and a higher pressure (3 bar) are applied to approach the F-T condition. An increase in CO partial pressure will increase the CO coverage, resulting in a near fully covered catalyst surface. SSITKA measurements involving hydrocarbons products up to C5 not only reveal relatively fast chain growth compared to monomer formation and chain termination, but also underpin the carbide mechanism for chain propagation. The main observation in keeping with the carbide mechanism is that the evolution of the ${}^{13}C$ content in the hydrocarbon products is in keeping with the ratio of ${}^{13}CH_x/{}^{12}CH_x$ on surface rather than the ratio of ${}^{13}CO/{}^{12}CO$. Experiments of $C_3H_6/^{13}CO/H_2$ show that the CH_x species formed by chain-decoupling can be incorporated into chain growth, and that C-C decoupling reaction can be suppressed by increasing surface coverage. The kinetic analysis at F-T conditions suggests that on a lowcovered surface (low CO partial pressure), the degree of rate control value of CO dissociation is 0.2. This value increases to unity as the surface becomes fully covered. In this situation, the forward reaction of CO dissociation will be greatly hampered by a lack of free sites. Another important step that controls the rate is oxygen removal. Microkinetic modeling highlights the importance of the fraction of free sites: high selectivity of long hydrocarbons can only be obtained by increasing surface coverage, but this is always at the expense of low CO consumption rate.

The insights obtained thus far suggest that modifying the catalyst surface without changing the reaction conditions should also influence the F–T catalytic performance. This idea is developed in **Chapter 6** and **Chapter 7**. In **Chapter 6**, we study the formation of carbon deposits on the cobalt surface during CO disproportionation. We show that carbidic carbon deposits can be easily removed by hydrogenation at temperatures below or close to the F–T conditions. Graphitic carbon (sp2 carbon) as identified by XPS covers mainly the terrace surface and its amount can be controlled by the CO exposure time. During CO hydrogenation, carbidic carbon does not affect catalytic performance. On the other hand,

graphitic carbon results in a decrease of the CH₄ selectivity and increasing chain-growth probability, while the C₂₊-product formation is hardly affected. Catalytic data at model F–T conditions favoring carbon deposition (260°C, H₂/CO = 1) shows that *in situ* formed carbon deposits have similar effect on the catalytic performance as pre-deposited graphitic carbon. The data are interpreted as the involvement of two types of active sites that are responsible for methanation and chain growth, respectively. Taking into account the structure sensitivity of the various elementary reaction steps underlying the F–T reaction, we propose a two site model for the F–T reaction: step-edge sites are essential for CO dissociation and chain-growth reactions, while terrace sites mainly catalyze CH₄ formation. We speculate that the terraces are responsible for the non-ASF CH₄ typically formed in the F-T reaction.

Chapter 7 provides another example of how modification of the cobalt catalyst surface influences the F-T reaction. Silver is chosen as promoter as it does not show activity to the F-T reaction. The combined characterization and catalytic data suggest that silver block step-edge sites and terrace sites. At low silver content, step-edge sites are preferentially blocked, while adding more silver also affects the terrace sites. Even at high silver content some step-edge sites remain active in CO dissociation. The terrace surfaces contain mainly silver with few cobalt atoms. During CO hydrogenation at 260°C, the CO conversion is strongly decreased due to silver. This does not correlate well with the loss in step-edge sites or CO dissociation rate as probed by CO disproportionation, because the CO consumption rate under methanation conditions is controlled by C hydrogenation. As silver poisons mainly sites for the structure-insensitive CH_x hydrogenation, CH_4 formation is suppressed. As accordingly CH_x intermediates reside longer on the surface, the chaingrowth probability increases as does the C_{2+} -selectivity. SSITKA confirms that the steadystate CO coverage strongly correlates with the cobalt surface area. Also the CH_x coverage decreases with increasing silver content. Another effect of slower hydrogenation is that the olefins-to-paraffins ratios are strongly increased when silver is added to the catalyst. At a temperature closer to the F-T condition (220°C), the influence of silver on the product distribution is the same as at higher temperature. However, CO conversion is hardly affected by silver. Transient experiments show that silver accelerates oxygen-removal steps, likely because silver binds oxygen weaker than cobalt. At the F-T condition, CO dissociation and oxygen-removal steps both control the overall CO consumption rate. Therefore, the opposite effects of silver on these two reactions explain why CO conversion is not affected by silver. Importantly, covering the cobalt the silver surface affects the F-T product distribution in a similar manner as graphitic carbon deposited on terrace sites. A difference is that the silver also affects step-edge sites, while C atoms on step-edge sites are removed in the form of hydrocarbon products.

The mechanistic study presented in this thesis is largely based on transient experiments that enable an unambiguous kinetic interpretation as discussed in **Chapter 2**. Compared to merely determining residence time and surface coverage of reaction intermediates, fitting transient data with solid microkinetic models provide additional

detailed information and understanding about the main reaction steps taking place. Although hydrogen plays an important role in the F–T reaction, the H coverage and, accordingly, hydrogenation steps are seldom explicitly involved in such microkinetic models. With the aid of DFT calculations [1, 2], it will be possible to develop more refined microkinetic models with explicit consideration of all relevant surface intermediates. Direct measurement of the H coverage is a challenge since the (i) the considerable kinetic isotopic effect associated with H_2/D_2 switches leads to perturbations of CO conversion and selectivity (although by itself this kinetic isotopic effect can provide useful insight into the mechanism [3, 4]) and (ii) extensive H spillover and H/D exchange with the support give rise to substantial errors in H coverage determination during H_2/CO to D_2/CO switches [5, 6]. The use of metallic sponge catalysts might be a solution. A study of the role of hydrogen in the F–T reaction merits a separate work.

The chain propagation is the core of the F–T reaction although most of the SSITKA works were carried out at methanation condition. In **Chapter 5**, we mainly analyzed the transients of non-labeled and fully labeled higher hydrocarbon products in SSITKA. The transient behavior of the partially products are rich of mechanistic and kinetic information as well. However, the exact interpretation of these data is not yet possible and likely require integration of explicit DFT-based microkinetic models in experimental data analysis.

Advanced transient data interpretation involves deconvolution techniques which allows a reactivity distribution analysis [7]. The inverse Laplace transformation [8] and Tikonov–Fredholm deconvolution [9] provide non-parametric methods. In the context of structure sensitivity, the reactivity distribution analysis of the catalysts provides unambiguous information. However, this requires better data quality, *i.e.*, free from systematic errors and smooth transient signals. The former requirement can be achieved by data correction based on a complete understanding of the responses due to the system. Smooth transient signals relate to high conversion. To obtain intrinsic kinetic data, a lower conversion condition is needed. Carefully choosing the experimental conditions will be essential to achieve suitable data for advanced modeling.

Transient experiments provide unique kinetic information by measuring the changes in the gas phase, which is mainly done by online mass spectrometer. Spectroscopic studies, on the other hand, provide information of the catalytically active solid phase. As the F–T reaction is a typical heterogeneous catalytic process, it is essential to understand the communication between catalyst and gas phase. Combining the transient experiments with vibrational spectroscopy allows to follow the response of a catalyst to the changes in gas phase. Such combinations as SSITKA with IR spectroscopy have already been used and warrant follow-up work, using DFT as a complementary technique to characterize the surface intermediates in full [10, 11].

References

- I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [2] I.A.W. Filot, R.J.P. Broos, J.P.M. van Rijn, G.J.H.A. van Heugten, R.A. van Santen, E.J.M. Hensen, ACS Catal. 5 (2015) 5453–5467.
- [3] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Langmuir 26 (2010) 16558–16567.
- [4] G. Parkin, Acc. Chem. Res. 42 (2009) 315–325.
- [5] J. Schweicher, A. Bundhoo, A. Frennet, N. Kruse, Catal. Lett. 144 (2013) 204–210.
- [6] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P.d. Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [7] S.L. Shannon, J.G. Goodwin, Chem. Rev. 95 (1995) 677–695.
- [8] M. de Pontes, G.H. Yokomizo, A.T. Bell, J. Catal. 104 (1987) 147–155.
- [9] T. Eddy Hoost, J.G. Goodwin, J. Catal. 134 (1992) 678–690.
- [10] P. Winslow, A.T. Bell, J. Catal. 86 (1984) 158–172.
- [11] J. Schweicher, A. Bundhoo, A. Frennet, N. Kruse, H. Daly, F.C. Meunier, J. Phys. Chem. C 114 (2010) 2248–2255.

Appendix I: Calculations on mass and heat transfer limitations

In order to measure intrinsic kinetics, all experiments should be performed in the absence of mass and heat transfer limitations. In this appendix, we verify these assumptions.

External mass transfer

External mass transfer is absent if Mears' criterion for external heat transfer is obeyed. The criterion is given by $[\underline{1}]$:

$$C_{\text{Mears}} = \frac{-r_{\text{A}}\rho_{\text{b}}n}{k_{c}a_{c}\varepsilon_{\text{b}}c_{\text{A},\text{b}}}$$
(A1.1)

in which:

C _{Mears}	Mears' criterion	5.7×10^{-5} [-]
$r_{\rm A}$	Reaction rate of disappearance for limiting reactant A	2.6×10^{-3} [mol kg _{cat} ⁻¹ s ⁻¹]
$ ho_{ m b}$	Catalyst bed density	502.8 [kg _{cat} m _r - ³]
n	Order of the reaction	1 [-]
k _c	Mass transfer coefficient	$0.20 [m_p s^{-1}]$
a _c	Specific surface area	$3.3 \times 10^4 \ [m_p^2 m_p^{-3}]$
ε _b	Catalyst bed porosity	$0.25 \ [m_g^3 \ m_r^{-3}]$
$C_{A,b}$	Bulk concentration of the limiting reactant A	10.4 [mol mg ⁻³]

The limiting reactant for the Fischer–Tropsch reaction is assumed to be CO. Therefore, the reaction rate can be calculated by:

(A1.2)

$$(-r_{\rm CO}) = \frac{F_{\rm CO}^{\rm in} x_{\rm CO}}{W_{\rm cat}}$$

in which:

-r _{co}	Rate of disappearance for the limiting reactant CO	$2.6 \times 10^{-3} \text{ [mol kg_{cat}^{-1} s^{-1}]}$
$F_{\rm CO}^{\rm in}$	Molar flow rate of CO in the reactor feed	$5.12 \times 10^{-6} \text{ [mol s}^{-1}\text{]}$
X _{co}	Conversion of CO	0.1 [-]
W _{cat}	Catalyst mass	$2.0 \times 10^{-4} [kg_{cat}]$

The bed density is calculated by multiplying the catalyst mass with one minus the bed porosity. The reaction order is assumed to be 1 and the mass transfer coefficient can be

obtained from Sherwood relations. The flow in the experiment is laminar since Re < 2300 (Eq. A1.4). Therefore the following relation can be used to determine the mass transfer coefficient, k_c [1]:

Sh
$$= \frac{k_c d_p}{D_{AB}} = 2 + 0.6 R e^{0.5} S c^{0.33}$$
 (A1.3)

in which:

Sh	Sherwood number	2.68 [-]
k _c	Mass transfer coefficient	$0.20 [m_p s^{-1}]$
$d_{ m p}$	Catalyst particle diameter	$1.8 \times 10^{-4} [m_p]$
D_{AB}	Diffusion coefficient of component A in mixture A/B	$1.32 \times 10^{-5} [m^2 s^{-1}]$
Re	Reynolds number	1.29 [-]
Sc	Schmidt number	1.01 [-]

The diffusion coefficient of CO in Ar, which is the most abundant component, is estimated according to Ref [2]. The Reynolds number can be calculated by [3]

$$Re = \frac{\rho_{\rm mix} u_{\rm s} d_{\rm p}}{\mu_{\rm mix}} \tag{A1.4}$$

in which

Re	Reynolds number	1.29 [-]
$ ho_{ m mix}$	Density of the gas mixture	1.96 [kg m ⁻³]
$d_{ m p}$	Catalyst particle diameter	$1.8 \times 10^{-4} \ [m_p]$
u _s	Superficial velocity	0.10 [m s ⁻¹]
$\mu_{ m mix}$	Viscosity of the gas mixture	2.6×10^{-5} [Pa s]

The density of the mixture can be calculated as

$$\rho_{\rm mix} = \sum_{\rm i} y_{\rm i} \, C_{\rm tot} M_{\rm i} \tag{A1.5}$$

with

$$C_{\rm tot} = \frac{p_{\rm tot}}{RT} \tag{A1.6}$$

Appendix I

$ ho_{ m mix}$	Density of the gas mixture	1.96 [kg m ⁻³]
y_{i}	Mole fraction of component <i>i</i> in the gas phase	[-]
$C_{\rm tot}$	The total gas phase concentration	73.2 [mol m ⁻³]
Mi	Molar mass of component i	[kg mol ⁻¹]
$p_{ m tot}$	Total pressure in the reactor	3.0×10^5 [Pa]
R	Gas constant	8.314 [m ² Pa mol ⁻¹ K ⁻¹]
Т	Temperature in the reactor	493 [K]

in which

In these calculations it is assumed that the pressure and temperature are uniform in the reactor. The assumption for the temperature gradient is validated below. The superficial velocity, u_s , can be calculated by dividing the volumetric flow rate with the cross-sectional area of the reactor:

$$u_{\rm s} = \frac{F^{\rm in}}{A_{\rm r}\varepsilon_{\rm b}} \frac{Tp^{\rm o}}{pT^{\rm o}} \tag{A1.7}$$

in which

u _s	Superficial velocity	0.10 [m s ⁻¹]
F^{in}	Volumetric feeding rate at standard condition	$8.3 \times 10^{-7} [m^3 s^{-1}]$
A _r	Reactor cross-sectional area	$1.96 \times 10^{-5} [m^2]$
$\varepsilon_{ m b}$	Catalyst bed porosity	0.25 [-]
Τ°, Т	Standard and reaction temperature	493 [K]
p^{o}, p	Standard and reaction pressure	3 × 10 ⁵ [Pa]

The viscosity of the mixture can be calculated by $[\underline{4}]$:

$$\mu_{\rm mix} = \sum_{i} \left(\frac{y_i \mu_i}{\sum_j y_j \Phi_{ij}} \right) \tag{A1.8}$$

where Φ_{ij} is calculated by

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{\frac{1}{2}} \left(1 + \left(\frac{\mu_i}{\mu_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{1}{4}} \right)^2$$
(A1.9)

in which

$\mu_{ m mix}$	Viscosity of the gas mixture	2.65×10^{-5} [Pa s]
y_i, y_j	Mole fraction of component i, j in the gas phase	[-]
μ_i, μ_j	Viscosity of component i with j	[Pa s]
Φ_{ij}	Interaction parameter of component i with j	[-]
$M_{\rm i}, M_{\rm j}$	Molar mass of component i	[kg mol ⁻¹]

The Schmidt number is calculated by [3]

$$Sc = \frac{\mu_{\rm mix}}{\rho_{\rm mix} D_{\rm AB}} \tag{A1.10}$$

in which

Sc	Schmidt number	1.01 [-]
$\mu_{ m mix}$	Viscosity of the gas mixture	2.6×10^{-5} [Pa s]
$ ho_{ m mix}$	Density of the gas mixture	1.96 [kg m ⁻³]
D_{AB}	Diffusion coefficient of component A in mixture A/B	$1.32 \times 10^{-5} [m^2 s^{-1}]$

The specific surface area can be calculated by dividing the surface area of the catalyst pellet by its volume. This leads to:

$$a_{\rm c} = \frac{6}{d_{\rm p}}$$
 (valid for spheres only) (A1.11)

The bulk concentration of the limiting reactant CO is approximated by

$$C_{\rm CO,b} = y_{\rm CO}^{\rm in} C_{\rm tot} \left(1 - \frac{x_{\rm CO}}{2} \right) \tag{A1.12}$$

in which

C _{CO,b}	Bulk concentration of CO	10.42 [mol mg ⁻³]
$y_{\rm CO}^{\rm in}$	Mole fraction of CO in the feed	0.15 [-]
$C_{\rm tot}$	The total gas phase concentration	73.17 [mol m ⁻³]
X _{co}	Conversion of CO	0.1 [-]

Substituting the parameters above into Eq. A1.1 leads to $C_{Mears} = 7.6 \times 10^{-5}$, which is much smaller than 0.15, demonstrating that external mass transfer can be neglected [1].

Internal mass transfer

To indicate whether the internal mass transfer plays an important role in this reaction, the Weisz-Prater criterion is used. This criterion is given by $[\underline{1}]$:

$$\Phi = \frac{n+1}{2} \frac{-r_A \rho_b}{D_e a_c^2 C_{A,i} \varepsilon_b}$$
(A1.13)

in which

Φ	Weisz-Prater criterion	[-]
п	Reaction order	1 [-]
r _A	Reaction rate of disappearance for limiting reactant A	$2.6 \times 10^{-3} \text{ [mol kg_{cat}^{-1} s^{-1}]}$
$ ho_{ m b}$	Catalyst bed density	502.8 [kg _{cat} ⁻¹ m _r ⁻¹]
D _e	Effective diffusivity	$1.41 \times 10^{-6} [m^2 s^{-1}]$
ac	Specific surface area	$3.3 \times 10^4 \ [m_p^2 m_p^{-3}]$
$C_{\mathrm{A,i}}$	Concentration of component A at the catalyst surface	10.4 [mol m _i ⁻³]
$\varepsilon_{\rm b}$	Catalyst bed porosity	$0.25 \ [m_g^3 m_r^{-3}]$

The effective diffusivity, D_e , which is the diffusion coefficient corrected for the fact that pores are not straight and cylindrical and that the pellet consist of empty space and solid, is calculated by [1]:

$$D_{\rm e} = \frac{D_{\rm AB}\phi_{\rm p}\sigma_{\rm c}}{\tau} \tag{A1.14}$$

D _e	Effective diffusivity	1.41×10^{-6} [-]
D_{AB}	Diffusion coefficient of component A in mixture A/B	$1.32 \times 10^{-5} [m^2 s^{-1}]$
$\phi_{ m p}$	Pellet porosity	0.4 [-]
$\sigma_{ m c}$	Constriction factor	0.8 [-]
τ	Tortuosity	3.0 [-]

We used typical value for the pellet porosity, constriction factor and tortuosity [1]. This results in an effective diffusivity of approximately 10 times smaller than the diffusion coefficient. The interface concentration of CO equals the bulk concentration, since external mass transfer is negligible. This results in $\Phi = 3.3 \times 10^{-4}$, which is much smaller than the criterion 0.15. Thus, internal mass transfer can be neglected.

Axial temperature gradient

The axial temperature gradient can be estimated by determining the maximum adiabatic temperature difference over the reactor. This criterion can be estimated by $[\underline{3}]$:

$$\Delta T_{\max,\text{adia}} = \frac{c_{\text{A},\text{in}}(-\Delta H_{\text{r}})\varepsilon_{\text{b}}}{\rho_{\text{b}}c_{\text{p}}}$$
(A1.15)

in which

$\Delta T_{ m max,adia}$	Maximal adiabatic temperature difference	1.16 [K]
$C_{A,in}$	Concentration of the rate limiting reactant in the feed	$10.4 \text{ [mol m}^{-3}\text{]}$
$\Delta H_{\rm r}$	Reaction enthalpy (based on methane formation)	$-2.09 \times 10^{5} [\text{J mol}^{-1}]$
$ ho_{ m b}$	Catalyst bed density	502.8 [kg _{cat} m ⁻³ _{cat}]
ε_{b}	Catalyst bed porosity	$0.25 [m_g^3 m_r^{-3}]$
C_{p}	Heat capacity of the catalyst (mixture of SiC and SiO ₂)	925 [J kg ⁻¹ K ⁻¹]

Since $\Delta T_{\text{max,adia}} = 1.16$ K, which is very small compared to the reactor temperature, 493 K, the axial temperature gradient is negligible.

Radial temperature gradient

The radial temperature gradient can be estimated using the following Mears criterion [5].

$$T_{\text{Mears}} = \frac{-(1-\varepsilon_{\text{b}})r_{\text{A}}\rho_{\text{b}}(-\Delta H_{\text{r}})T_{\text{a}}d_{\text{b}}^{2}}{4\lambda_{\text{b},\text{eff}}T_{\text{w}}^{2}} \left(1 + \left(\frac{8\lambda_{\text{b},\text{eff}}}{Ud_{\text{b}}}\right)\right) < 0.4$$
(A1.16)

in which

<i>T</i> _{Mears}	Mears criterion for radial temperature gradient	0.008 [-]
$\varepsilon_{\rm b}$	Catalyst bed porosity	$0.25 [m_g^3 m_r^{-3}]$
r _A	Reaction rate of disappearance for limiting reactant A	$2.6 \times 10^{-3} \text{ [mol kg}_{cat}^{-1} \text{s}^{-1} \text{]}$
$ ho_{ m b}$	Catalyst bed density	$502.8 [kg_{cat} m_{cat}^{-3}]$
$\Delta H_{\rm r}$	Reaction enthalpy (based on methane formation)	$-2.09 \times 10^{5} [J \text{ mol}^{-1}]$
T _a	Adiabatic temperature	162 [K]
$d_{ m b}$	Diameter of the catalyst bed	0.005 [m]
$\lambda_{\rm b, eff}$	Effective thermal conductivity for the catalyst bed	1.93 [W m ⁻¹ K ⁻¹]
$T_{\rm w}$	Temperature of the reactor wall	493 [k]
U	Global heat exchange coefficient at the tube wall	$400 [W m^{-2} K^{-1}]$

The reaction rate for the limiting reactant is calculated in a similar manner as above. The tube wall temperature is assumed to be equal inner and outer site and is measured by a thermocouple. A global heat exchange coefficient of the stainless tube wall is $U = 400 Wm^{-2}K^{-1}$ [5], which is a typical value under lab conditions. The adiabatic temperature and the effective thermal conductivity are calculated by:

$$T_{\rm a} = \frac{E_{\rm act}}{R} \tag{A1.17}$$

$$\lambda_{\rm b,eff} = \varepsilon_{\rm b} \lambda_{\rm g} + (1 - \varepsilon_{\rm b}) \lambda_{\rm inert} \left(\frac{1}{\frac{\phi_{\rm b} \lambda_{\rm inert}}{\lambda_{\rm g}} + 2/3} \right)$$
(A1.18)

in which

T _a	Adiabatic temperature	$9.62 \times 10^3 [K]$
E _{act}	Activation energy for the reaction	80 [kJ mol ⁻¹]
R	Gas constant	8.314 [J mol ⁻¹ K ⁻¹]
$\lambda_{\mathrm{b,eff}}$	Effective thermal conductivity for the catalyst bed	1.93 [W m ⁻¹ K ⁻¹]
$C_{\mathrm{P,g}}$	Heat capacity of the gas phase	3402 [J kg ⁻¹ K ⁻¹]
$ ho_{ m mix}$	Density of the gas mixture	1.96 [kg m ⁻³]
$d_{ m p}$	Catalyst particle diameter	$1.8 \times 10^{-4} \text{ [m]}$
d_{b}	Diameter of the catalyst bed	$5 \times 10^{-3} [m]$
$\varepsilon_{\rm b}$	Catalyst bed porosity	$0.25 \ [m_g^3 \ m_r^{-3}]$
λ _g	Effective thermal conductivity of the gas phase	$0.21 [W m^{-1} K^{-1}]$
$\lambda_{ m inert}$	Thermal conductivity of the solid inert phase (SiC)	83.4 [W m ⁻¹ K ⁻¹]
$\phi_{ m b}$	Thermal effectivity parameter [6]	0.08 [-]

Combining these parameters with the values calculated earlier, the radial temperature gradient equals 0.23, which is smaller than the Mears criterion 0.4 [5]. So it can be assumed that there is no strong radial gradient.

References

- [1] H.S. Fogler, Elements of chemical reaction engineering, 4th ed., 1999.
- [2] E.N. Fuller, P.D. Schettler, J.C. Giddings, Ind. Eng. Chem. 58 (1966) 19-27.
- [3] R.B. Bird, W.E. Stewart, Transport phenomena, 2nd ed., 2001.
- [4] J.R. Welty, C.E. Wilson, Fundamentals of momentum, heat and mass transfer, 4th ed., 2001.
- [5] R. Philippe, M. Lacroix, L. Dreibine, C. Pham-Huu, D. Edouard, S. Savin, F. Luck, D. Schweich, Catal. Today 147 (2009) S305-S312.
- [6] D. Kunii, O. Levenspiel, Fluidization Engineering, 2nd ed., Elsevier, 1991.

Appendix II: H-assisted CO dissociation mechanism based reaction model

CO hydrogenation reaction model based on H-assisted CO dissociation mechanism is schematically depicted in Figure 4.8b. The surface concentration of the reaction intermediates are mathematically described by the following equations:

$$\frac{d\theta_{\rm CO}}{dt} = k_{\rm ads,CO} p_{\rm CO} \theta_{\rm v} - k_{\rm des,CO} \theta_{\rm CO} - k_{\rm CHO}^{\rm f} \theta_{\rm H} \theta_{\rm CO} + k_{\rm CHO}^{\rm b} \theta_{\rm v} \theta_{\rm CHO} - k_{\rm CO_2}^{\rm f} \theta_{\rm CO} \theta_{\rm O} + k_{\rm CO_2}^{\rm b} \theta_{\rm v} \theta_{\rm CO_2}$$
(A2.1)

$$\frac{d\theta_{\rm CHO}}{dt} = k_{\rm CHO}^{\rm f} \theta_{\rm H} \theta_{\rm CO} - k_{\rm CHO}^{\rm b} \theta_{\rm v} \theta_{\rm CHO} - k_{\rm CH_2O}^{\rm f} \theta_{\rm H} \theta_{\rm CHO} + k_{\rm CH_2O}^{\rm b} \theta_{\rm v} \theta_{\rm CH_2O}$$
(A2.2)

$$\frac{d\theta_{\rm CH_2O}}{dt} = k_{\rm CH_2O}^{\rm f} \theta_{\rm H} \theta_{\rm CHO} - k_{\rm CH_2O}^{\rm b} \theta_{\rm v} \theta_{\rm CH_2O} - k_{\rm diss}^{\rm f} \theta_{\rm v} \theta_{\rm CH_2O} + k_{\rm diss}^{\rm b} \theta_{\rm O} \theta_{\rm CH_2}$$
(A2.3)

$$\frac{d\theta_{\rm CH_2}}{dt} = k_{\rm diss}^{\rm f} \theta_{\rm v} \theta_{\rm CH_20} - k_{\rm diss}^{\rm b} \theta_0 \theta_{\rm CH_2} - k_{\rm CH_3}^{\rm f} \theta_{\rm H} \theta_{\rm CH_2} + k_{\rm CH_3}^{\rm b} \theta_{\rm v} \theta_{\rm CH_3}$$
(A2.4)

$$\frac{d\theta_{\rm CH_3}}{dt} = k_{\rm CH_3}^{\rm f} \theta_{\rm H} \theta_{\rm CH_2} - k_{\rm CH_3}^{\rm b} \theta_{\rm v} \theta_{\rm CH_3} - k_{\rm CH_4} \theta_{\rm H} \theta_{\rm CH_3}$$
(A2.5)

$$\frac{d\theta_{\rm O}}{dt} = k_{\rm diss}^{\rm f} \theta_{\rm v} \theta_{\rm CH_{2O}} - k_{\rm diss}^{\rm b} \theta_{\rm O} \theta_{\rm CH_{2}} - k_{\rm OH}^{\rm f} \theta_{\rm H} \theta_{\rm O} + k_{\rm OH}^{\rm b} \theta_{\rm v} \theta_{\rm OH} + k_{\rm 2OH}^{\rm f} \theta_{\rm OH} \theta_{\rm OH} - k_{\rm 2OH}^{\rm b} \theta_{\rm O} \theta_{\rm H_{2O}} - k_{\rm CO_{2}}^{\rm f} \theta_{\rm CO} \theta_{\rm O} + k_{\rm CO_{2}}^{\rm b} \theta_{\rm v} \theta_{\rm CO_{2}}$$
(A2.6)

$$\frac{d\theta_{\rm CO_2}}{dt} = k_{\rm CO_2}^{\rm f} \theta_0 \theta_{\rm CO} - k_{\rm CO_2}^{\rm b} \theta_{\rm v} \theta_{\rm CO_2} - k_{\rm des, CO_2} \theta_{\rm CO_2}$$
(A2.7)

$$\frac{d\theta_{\rm OH}}{dt} = k_{\rm OH}^{\rm f}\theta_{\rm H}\theta_{\rm O} - k_{\rm OH}^{\rm b}\theta_{\rm v}\theta_{\rm OH} - 2k_{\rm 2OH}^{\rm f}\theta_{\rm OH}\theta_{\rm OH} + 2k_{\rm 2OH}^{\rm b}\theta_{\rm O}\theta_{\rm H_{2}O} - k_{\rm H_{2}O}^{\rm f}\theta_{\rm H}\theta_{\rm OH} + k_{\rm H_{2}O}^{\rm b}\theta_{\rm v}\theta_{\rm H_{2}O}$$
(A2.8)

$$\frac{d\theta_{\rm H_2O}}{dt} = k_{\rm H_2O}^{\rm f} \theta_{\rm H} \theta_{\rm OH} - k_{\rm CO_2}^{\rm b} \theta_{\rm v} \theta_{\rm H_2O} + k_{\rm 2OH}^{\rm f} \theta_{\rm OH} \theta_{\rm OH} - k_{\rm 2OH}^{\rm b} \theta_{\rm O} \theta_{\rm H_2O} - k_{\rm des, H_2O} \theta_{\rm H_2O}$$
(A2.9)

$$\frac{d\theta_{\rm H}}{dt} = 2k_{\rm ads,H_2}p_{\rm H_2}\theta_{\rm v}\theta_{\rm v} - 2k_{\rm des,H_2}\theta_{\rm H}\theta_{\rm H} - \theta_{\rm H}(k_{\rm CH0}^{\rm f}\theta_{\rm CO} + k_{\rm CH_20}^{\rm f}\theta_{\rm CHO} + k_{\rm CH_3}^{\rm f}\theta_{\rm CH_2} + k_{\rm CH_4}\theta_{\rm CH_3} + k_{\rm OH}^{\rm f}\theta_{\rm O} + k_{\rm H_20}^{\rm f}\theta_{\rm OH}) + \theta_{\rm v}(k_{\rm CH0}^{\rm b}\theta_{\rm CHO} + k_{\rm CH_20}^{\rm f}\theta_{\rm CH_2O} + k_{\rm CH_3}^{\rm f}\theta_{\rm CH_3} + k_{\rm OH}^{\rm b}\theta_{\rm OH} + k_{\rm H_20}^{\rm b}\theta_{\rm H_2O}) \tag{A2.10}$$

$$\theta_{\rm CO} + \theta_{\rm CHO} + \theta_{\rm CH_2O} + \theta_{\rm CH_2} + \theta_{\rm CH_3} + \theta_0 + \theta_{\rm CO_2} + \theta_{\rm OH} + \theta_{\rm H_2O} + \theta_{\rm H} + \theta_{\rm v} = 1$$
(A2.11)

Appendix III: SSITKA modeling

Ordinary differential equations

To model the transient kinetics following the ¹²CO/H₂ to ¹³CO/H₂ switch, isotopic carbon (¹³C) needs to be distinguished from the normal one (¹²C). This was carried out by following the surface concentration of the chains with ¹²C or ¹³C at a given position, denoted as $\theta_n^{p,^{12}C}$ or $\theta_n^{p,^{13}C}$, where *n* refers to the chain length, *p* to the position within the chain.[1] For a given chain length *L*, we can write $\theta_L^{1,^{12}C} + \theta_L^{2,^{12}C} = \theta_L^{2,^{12}C} + \theta_L^{2,^{13}C} = \cdots = \theta_L^{L,^{12}C} + \theta_N^{N,^{13}C} = \theta_N^{SS}$, where θ_N^{SS} refers to the coverage of C_N at steady state, which is constant during the ¹²CO/H₂ to ¹³CO/H₂ transient.

The coverages of ¹²CO and ¹³CO are given by

$$\frac{d\theta_{12}_{\rm CO}}{dt} = k_{\rm ads} P_{12}_{\rm CO} \theta_{\rm v} - k_{\rm des} \theta_{12}_{\rm CO} - k_{\rm diss} \theta_{12}_{\rm CO} \theta_{\rm v}$$
(A3.1)

$$\frac{d\theta_{13}_{\rm CO}}{dt} = k_{\rm ads} P_{13}_{\rm CO} \theta_{\rm v} - k_{\rm des} \theta_{13}_{\rm CO} - k_{\rm diss} \theta_{13}_{\rm CO} \theta_{\rm v}$$
(A3.2)

The transient of ${}^{12}C_1$ and ${}^{13}C_1$ coverage are expressed as

$$\frac{d\theta_{1}^{1,^{12}C}}{dt} = k_{\rm diss}\theta_{1^{2}CO}\theta_{\rm v} + k_{\rm b}\theta_{\rm v}\left(\theta_{2}^{1,^{12}C} + \sum_{i=2}^{\infty}\theta_{i}^{1,^{12}C}\right) - k_{\rm tm}\theta_{1}^{1,^{12}C} - k_{\rm f}\theta_{1}^{1,^{12}C}\left(\theta_{1}^{\rm SS} + \sum_{i=1}^{\infty}\theta_{i}^{\rm SS}\right)$$
(A3.3)

and

$$\frac{d\theta_{1}^{1,13C}}{dt} = k_{\rm diss}\theta_{13}{}_{\rm CO}\theta_{\rm v} + k_{\rm b}\theta_{\rm v}\left(\theta_{2}^{1,13C} + \sum_{i=2}^{\infty}\theta_{i}^{1,13C}\right) - k_{\rm tm}\theta_{1}^{1,13C} - k_{\rm f}\theta_{1}^{1,13C}\left(\theta_{1}^{\rm SS} + \sum_{i=1}^{\infty}\theta_{i}^{\rm SS}\right)$$
(A3.4)

The surface concentration of the chains of length $i \ge 1$ with a ¹²C or ¹³C at the first position (p = 1) are written as

$$\frac{d\theta_i^{1,1^2C}}{dt} = k_b \theta_v \left(\theta_{i+1}^{1,1^2C} - \theta_i^{1,1^2C} \right) + k_f \theta_{i-1}^{SS} \theta_1^{1,1^2C} - k_t \theta_i^{1,1^2C} - k_f \theta_1^{SS} \theta_i^{1,1^2C}$$
(A3.5)

and

$$\frac{d\theta_i^{1,^{13}C}}{dt} = k_b \theta_v \left(\theta_{i+1}^{1,^{13}C} - \theta_i^{1,^{13}C} \right) + k_f \theta_{i-1}^{SS} \theta_1^{1,^{13}C} - k_t \theta_i^{1,^{13}C} - k_f \theta_1^{SS} \theta_i^{1,^{13}C}$$
(A3.6)

The surface concentration of the chains of length $i \ge 1$ with a ¹²C or ¹³C at position $p \ge 2$ are written as

$$\frac{d\theta_i^{p,^{12}C}}{dt} = k_b \theta_v \left(\theta_{i+1}^{p+1,^{12}C} - \theta_i^{p,^{12}C} \right) + k_f \theta_1^{SS} \left(\theta_{i-1}^{p-1,^{12}C} - \theta_i^{p,^{12}C} \right) - k_t \theta_i^{p,^{12}C}$$
(A3.7)

and

$$\frac{d\theta_i^{p,^{13}C}}{dt} = k_b \theta_v \left(\theta_{i+1}^{p+1,^{13}C} - \theta_i^{p,^{13}C} \right) + k_f \theta_1^{SS} \left(\theta_{i-1}^{p-1,^{13}C} - \theta_i^{p,^{13}C} \right) - k_t \theta_i^{p,^{13}C}$$
(A3.8)

The O coverage does not change during the steady state isotopic transient.

Transient responses of isotopologues

The above ordinary differential equations (ODEs) describe the transient behavior of the fraction of 12 C and 13 C at each position of adsorbed hydrocarbons chains. For comparison to the experimental data that do not contain the information on the position of the isotopes in the chain, we need to convert these fractions to the surface concentration of each individual isotopologue for a given hydrocarbon product as a function of time on stream. For the non-labeled isotopologue (all 12 C monomer), the surface concentration is expressed as

$$\frac{d\theta_{12}c_N}{dt} = \theta_N^{SS} \prod_{i=1}^N \frac{\theta_N^{i,12}c}{\theta_N^{SS}}$$
(A3.9)

The analogous expression of fully labeled isotopologue is

$$\frac{d\theta_{13}}{dt} = \theta_N^{SS} \prod_{i=1}^N \frac{\theta_N^{i,13} c}{\theta_N^{SS}} = \theta_N^{SS} \prod_{i=1}^N \frac{\left(\theta_N^{SS} - \theta_N^{i,12} c\right)}{\theta_N^{SS}}$$
(A3.10)

As only the number of labeled carbon atoms can be experimentally identified, all possible partially labeled isotopologue with different ¹³C position need to be taken into account. For instance, the coverage of C_4 with two ¹³C atoms (${}^{13}C_2{}^{12}C_2$) is expressed as:

$$\frac{d\theta_{^{13}C_{2}^{12}C_{2}}}{dt} = \frac{1}{\theta_{^{4}}^{5S^{3}}} \left(\theta_{4}^{^{1,13}C} \theta_{4}^{^{2,13}C} \theta_{4}^{^{3,12}C} \theta_{4}^{^{4,12}C} + \theta_{4}^{^{1,13}C} \theta_{4}^{^{2,12}C} \theta_{4}^{^{3,13}C} \theta_{4}^{^{4,12}C} + \theta_{4}^{^{1,13}C} \theta_{4}^{^{2,12}C} \theta_{4}^{^{3,13}C} \theta_{4}^{^{4,13}C} + \theta_{4}^{^{1,13}C} \theta_{4}^{^{2,12}C} \theta_{4}^{^{3,13}C} \theta_{4}^{^{4,13}C} + \theta_{4}^{^{1,12}C} \theta_{4}^{^{2,12}C} \theta_{4}^{^{3,13}C} \theta_{4}^{^{4,13}C} + \theta_{4}^{^{1,12}C} \theta_{4}^{^{2,12}C} \theta_{4}^{^{3,13}C} \theta_{4}^{^{4,13}C} \right)$$
(A3.11)

To go over all the possible isotopologues of a partially labeled hydrocarbon chain, we employed the Matlab function, C = nchoosek(v, k), which returns a matrix containing all possible combinations of the elements of vector v taken k at a time. Matrix C has k columns and n!/((n-k)! k!) rows, where n is length(v). Accordingly, the number of isotopologues and the position of ¹³C of a hydrocarbon chain of length N with L ¹³C can be presented as

$$nchoosek((1,2,\ldots,N),L) = \begin{pmatrix} C_{1,1} & \cdots & C_{1,L} \\ \vdots & \ddots & \vdots \\ C_{Q,1} & \cdots & C_{Q,L} \end{pmatrix}$$
(A3.12)

where Q = N!/((N-L)! L!) refers to the number of possible isotopologues, the elements of the matrix *C* refer to the position of *L* labeled carbons in each isotopologue. This allows us to calculate the transient responses of partially labeled hydrocarbon chains.

Reference

[1] R.A. van Santen, A.J. Markvoort, Faraday Discuss. 162 (2013) 267-279.

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List of publications

Journal articles

W. Chen, B. Zijlstra, R. Pestman, E.J.M. Hensen: Mechanism of CO dissociation on a cobalt Fischer-Tropsch catalyst, ChemCatChem, DOI: 10.1002/cctc.201701203.

W. Chen, R. Pestman, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen: Mechanism of Cobalt-Catalyzed CO Hydrogenation: 1. Methanation, ACS Catal. (accepted)

W. Chen, I.A.W. Filot, R. Pestman, E.J.M. Hensen: Mechanism of Cobalt-Catalyzed CO Hydrogenation: 2. Fischer-Tropsch Synthesis, ACS Catal. (accepted)

W. Chen, T.F. Kimpel, Y. Song, F.-K. Qiang, B. Zijlstra, R. Pestman, E.J.M. Hensen: Influence of carbon deposits on the cobalt-catalyzed Fischer-Tropsch reaction: evidence for a two-site reaction model (in preparation)

Conference contributions

W. Chen, R. Pestman, E.J.M. Hensen: Transient kinetic study of methanation and Fischer-Tropsch synthesis over supported Co catalyst, *NRSC-Catalysis Workshop*, Utrecht, The Netherlands, 13 February, 2014. (oral)

W. Chen, R. Pestman, E.J.M. Hensen: Determining individual reaction rates in Fischer-Tropsch, *Netherlands Chemistry and Catalysis conference XV*, Noordwijkerhout, The Netherlands, 10–12 March, 2014. (oral)

W. Chen, B. Zijlstra, I.A.W. Filot, R. Pestman, D.A.J.M. Ligthart, E.J.M. Hensen: How CO is activated on cobalt Fischer-Tropsch catalyst, *Netherlands Chemistry and Catalysis conference XV*, Noordwijkerhout, The Netherlands, 3–5 March, 2015. (oral)

W. Chen, B. Zijlstra, I.A.W. Filot, D.A.J.M. Ligthart, A.J.F. van Hoof, R. Pestman, E.J.M. Hensen: CO Activation on cobalt Fischer-Tropsch catalyst, *12th European Congress on Catalysis – EuropaCat-XII*, Kazan, Russia, 30 August–4 September, 2015. (oral)

W. Chen, B. Zijlstra, R. Pestman, I.A.W. Filot, E.J.M. Hensen: Mechanism of the Cobaltcatalyzed Fischer-Tropsch reaction, *Netherlands Chemistry and Catalysis conference XVII*, Noordwijkerhout, The Netherlands, 7–9 March, 2016. (oral)

W. Chen, B. Zijlstra, R. Pestman, I.A.W. Filot, E.J.M. Hensen: Fischer-Tropsch synthesis on cobalt catalyst: A combined transient kinetic and mechanistic study, *11th Natural Gas Conversion Symposium*, Tromsø, Norway, 6–9 June, 2016 (oral)

W. Chen, B. Zijlstra, R. Pestman, E.J.M. Hensen: Probing CO dissociation on cobalt based Fischer-Tropsch Catalyst, *Netherlands Chemistry and Catalysis conference XVIII*, Noordwijkerhout, The Netherlands, 6–8 March, 2017. (poster)

Curriculum Vitae



Wei Chen was born on 30-8-1984 in Hangzhou, Zhejiang, China. After finishing his high school in 2003, he commenced his studies of chemistry and chemical engineering at Zhejiang University of Technology. After the 4-year undergraduate program, he got his bachelor's degree of engineering with A-Level thesis. In 2009, he started catalysis studying at East China Normal University under the guidance of Prof. Yong Lu. His research project was to study dry reforming of methane on nickel catalyst and develop high carbon-resistance catalyst and microfibrous-structured reactor for process intensification. This work was involved in National (China)

863 project and 973 project, and honored with Excellent Masters Thesis of Shanghai Municipality. Part of this work is patented in China. He got Master's degree of Science with Excellent Graduates Award in 2012. In the same year, he moved to Netherlands and started his PhD project at Eindhoven University of Technology, Laboratory of Inorganic Materials Chemistry under the supervision of prof. dr. ir. E.J.M. Hensen. The aim of his research is to study the mechanism and kinetics of Fischer-Tropsch synthesis on cobalt-based catalyst by transient technique. The most important results are presented in this thesis.



