

Kinetic study of Fischer-Tropsch synthesis on Fe-carbide

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Kinetic study of Fischer-Tropsch synthesis on Fe-carbide

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 28 september 2022 om 11:00 uur

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Het onderzoek of ontwerp dat in dit thesis wordt beschreven is uitgevoerd in overeenstemming met de TU/e Gedragscode Wetenschapsbeoefening.

To my family

Kinetic study of Fischer-Tropsch synthesis on Fe-carbide

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Chapter 1

Introduction

1.1 Fischer-Tropsch synthesis

Fischer-Tropsch (FT) process has been widely investigated for almost 100 years. In the 1920s, German scientists Franz Fischer and Hans Tropsch first developed this process, in which a mixture of H_2 and CO (synthesis gas) can be converted to valuable long-chain hydrocarbons like gasoline, diesel fuel and chemicals.[1, 2] The FT process was first commercialized in Germany prior to the Second World War. It could offer synthetic fuel for the German war machine due to the abundant domestic coal supplies used for producing synthesis gas.[3] After the Second World War, the development of this process stalled because low crude oil prices led to a strong growth and dominance of the petroleum oil industry.[4] The interest in the FT synthesis was revived in South Africa during the Apartheid regime in the 1970s. During that period, supply of oil in South Africa was cut off due to international sanctions, but through the FT synthesis South Africans were still able to produce the required fuels and chemicals from coal. At the same time, the energy crises in 1973 and 1978 have also stimulated the global interest and exploration of alternative fuel production by expanding the commercialization of FT processes.[5] Besides coal, natural gas and biomass are also considered as important alternatives. The process to convert these carbon sources to valuable chemicals is often referred to as X to Liquid (XTL), in which X stands for the feedstock from which synthesis gas is derived, e.g., coal (CTL), natural gas (GTL) or biomass (BTL).[6] Although most of these embodiments still rely on fossil resources, CTL and GTL enable the production of clean transportation fuels that are free of heavy metals, aromatics or contaminants such as nitrogen and sulfur. Currently, large XTL processes are operated in Malaysia by Shell, in Qatar by Shell and Sasol, in South Africa by Sasol, Uzbekistan and Nigeria by Sasol and in China by Shenhua. Among them, CTL is of large interest in areas with abundant coal resources, for example China and South Africa.[7]

The CTL process generally consists of 4 chemical conversion steps (Fig. 1.1). In the first step, coal gasification is done in gasifiers to produce synthesis gas, a mixture of CO and H₂. Due to the low H/C ratio of coal, the derived synthesis gas has a typical H₂/CO ratio below 1.[8] In the second step, the water-gas shift (WGS) reaction (Eq. 1.1) is used to increase the H₂/CO ratio tailored for the desired product distribution in the subsequent FT synthesis step. Usually, a constant amount of CO₂ is removed in the overall CTL process, either in a WGS step prior to the FT synthesis or in the FT synthesis reactor itself when a catalyst is used that exhibits sufficient WGS activity. CO₂ produced in the FT reactor not only decreases CO conversion,

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but also leads to a higher energy consumption for separating the gas effluent from the reactor. When the main WGS conversion is done in a separate WGS reactor, CO₂ capture becomes more viable.[9] After cooling and purification, the synthesis gas is introduced into the FT synthesis reactor and converted into long-chain hydrocarbons (Eq. 1.2). Traditionally, these processes are realized in either fixed and fluidized bed reactors or slurry bubble reactors. Fixed beds are suitable for wax production as for instance done in Shell FT plants in Malaysia and Oatar.[10] Separation of products from catalysts are more cost-effective in fixed bed reactors. On the other hand, the pressure drop in such reactors leads to higher operational costs than other reactors. Moreover, as it is costly to replace the catalyst inventory, catalysts should exhibit a long lifespan. As the FT reaction is highly exothermic, it is important to rapidly remove the heat of reaction in order to avoid overheating the catalyst.[11] Compared to fixed bed reactors, fluidized bed reactors can realize a very homogenous temperature distribution because of the rapid and turbulent gas/liquid movement. Another important advantage of fluidized bed reactors is that deactivated catalyst can be removed continuously, and new catalysts can be added for longer production runs. A drawback of such reactors is the difficulty in separating the catalyst from the products. Fluidized bed reactors are a promising technology to produce lower-molecular-weight products on Fe-based catalysts at high temperature.[12] Similar to fluidized bed reactors, slurry bubble reactors can meet the requirement of online removal/addition of catalyst and can be operated under isothermal conditions. Catalysts that feature high mechanical strength and attrition resistance are required for slurry bubble reactors. As the catalysts are suspended in the wax, separating the catalyst from wax is a major challenge.[13] The final step of the overall CTL process is product upgrading. The mixture of products formed during the FT process (e.g., long-chain hydrocarbons or oxygenates) need to be processed to obtain high-value transportation fuels and base chemicals using processes such as hydrotreating, hydrocracking and hydro isomerization. In-reactor upgrading of the products of FT reactions by adding zeolites to Febased catalysts has also been investigated.[14, 15]

1.2 Catalysts

A general aspect of FT chemistry is the dissociation of CO in atomic C and O on metal surface, [16] although there are also pathways that involve hydrogenation of CO prior to C-O bond cleavage. Group VIII metals with unoccupied d-orbitals are capable for CO dissociation. Based on Brønsted-Evans-Polanyi (BEP) relations, transition metals with a lower d-band filling that will bind the dissociated C and O atoms strongly will lead to low activation barriers for CO dissociation.[17] Termination of the chain-growth reactions are also important as they determine the length of the hydrocarbons obtained.[16]



Figure 1.1. Schematic representation of the CTL process.

$$CO + H_2O \rightarrow CO_2 + H_2$$
 (Eq. 1.1)

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \tag{Eq. 1.2}$$

From left to right in the periodic table, the d band of transition metals is filled.[18] Catalysts with lower C and O binding energy to the right will hardly produce long-chain hydrocarbons, because the CH_x growth monomers are easily hydrogenated by H_2 , resulting in high CH_4 selectivity. Therefore, CO hydrogenation on Ni mainly produces CH_4 . Metals such as Ru, Co and Fe bind C and O stronger than Ni, resulting in a higher probability for CH_x intermediate to couple to long-chain hydrocarbons. Hence, Ru-, Co- and Fe-based catalysts are the most suitable for the FT reaction.[19]

Ru-based catalysts display outstanding performance for CO hydrogenation in terms of activity, selectivity, and stability. Despite this, Ru cannot serve as a base for catalysts at the industrial scale because of the high price of this noble metal.[20] So far, only Co and Fe have been used as the active phase for industrial FT catalysts.

Co-based catalysts outperform Fe-based catalysts at low temperature (200-240 °C), often referred to low-temperature Fischer-Tropsch (LTFT). Moreover, the WGS activity of Co is much lower than that of Fe, limiting undesired CO₂ formation. On the other hand, the higher CH₄ selectivity on Co-based catalysts restricts its application at higher temperature (250-350 °C), which is referred to as high-temperature Fischer-Tropsch (HTFT). In HTFT, Fe-based catalysts are preferred to reduce the amount of CH₄ formed.[21] Another advantage of

Fe catalysts is that they can handle the low H₂/CO ratio of synthesis gas derived from coal and biomass owing to the substantial WGS activity.[22] On the other hand, Co-based catalysts are typically used in combination with natural gas as a source of the synthesis gas feedstock. Overall, the operation conditions for Fe-based catalyst are more flexible. Paraffins, such as wax, is the main product for Co-based catalyst in the LTFT, whereas Fe is mainly used for producing olefins and oxygenates. Metallic Co is regarded as the active phase for the FT reaction, while Fe has a high tendency to form Fe-carbide because of a strong Fe-C bond. The most significant differences between Co- and Fe-based catalysts are shown in Table 1.1.

Property	Со	Fe
Cost	expensive	cheap
Reaction temperaure	200-240 °C	250-350 °C
FT activity	high	relativley low
WGS activity	neglible	active
Carbon source	natural gas	coal and biomass
H ₂ /CO ratio	~2	0.5-2.5
Active phase	metallic Co	Fe-carbides
Methane selectivity	high	low
Products	wax (paraffins)	C_1 - C_{15} , olefins, oxygenates
Sulfer tolerance	very sensitive	sensitive

Table 1.1	. Comparison	of Co- and	Fe-based FT	catalysts.[23, 24]
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1.3 Fe-based catalysts

In the earth's crust, Fe is the fourth most abundant element, mainly existing in the form of Fe-oxide. This abundance means that Fe is very cheap and an excellent choice for the FT catalysis. For the FT synthesis, precipitated or fused Fe in unsupported form are mainly used as catalyst precursors.[24, 25] The poor mechanical stability of unsupported catalysts may lead to plugging of the catalyst bed in fixed bed operation or to fouling of downstream equipment in fluidized bed operation. Supported Fe catalysts display enhanced dispersion of the active phase and may withstand the mechanical degradation that threatens unsupported catalysts.[21] Upon activation, Fe-oxide precursor is usually converted into a mixture of metallic Fe, Fe-carbides and Fe-oxides and the composition of catalyst depends on many parameters such as the catalyst precursor, catalyst pretreatment and the FT reaction

conditions.[26] Despite the complexity of the composition in the working condition, a correlation between Fe-carbide content and FT activity has been widely observed and Fe-carbide formation is believed to be the necessary step to obtain good FT activity.[27] Fe-oxide, on the other hand, is considered to be active for the WGS reaction, which leads to the production of excessive CO₂.[28] In itself, CO₂ production represents a loss of valuable carbon product. As some WGS operation is needed in CTL and BTL processes, it can be worthwhile to remove CO₂ to reduce the greenhouse gas emissions of the process.[9] A distinct feature of Fe-carbide is that it is air sensitive and readily oxidized in air at room temperature, leading to the formation of Fe-oxide.[29] Thus, activation or carbide formation is preferably done *in situ* before starting the FT reaction.[30] For research purposes, passivation of the catalyst in a diluted O₂ is usually employed.[31]

During the FT reaction, $\varepsilon(')$ -carbide, χ -Fe₅C₂, and Θ -Fe₃C are commonly observed in Febased FT catalysts.[32, 33] They are classified as interstitial carbides, because C atoms occupy the interstices of the Fe lattice. According to way C atoms occupy the hexagonally close packed (hcp) lattice, their structure can be divided into two categories. In $\varepsilon(')$ -carbide, C atoms occupy Fe octahedral interstices, ascribed to octahedral carbides, while C atoms in Θ -Fe₃C and χ -Fe₅C₂ are situated in trigonal prismatic interstices, ascribed to trigonal prismatic carbides. The main differences between these three Fe-carbides are listed in Table 1.2.

	ε(´)-carbide	χ-Fe ₅ C ₂	Θ -Fe ₃ C
Space group	P6 ₃ /mmc	C2/c	pnma
Crystal structure	hexagonal	monoclinic	orthorhombic
C/Fe	0.45~0.5	0.4	0.33
Required carbon chemical potential	high (low T, high H_2/CO)	low (high T, low H ₂ /CO)	low (high T, low H_2/CO)

Table 1.2. Comparison of $\varepsilon(')$ -carbide, χ -Fe₅C₂ and Θ -Fe₃C.

Among these three carbides, $\varepsilon(')$ -carbide is the generic term for ε -Fe₂C and ε' -Fe_{2.2}C. ε -Fe₂C and ε' -Fe_{2.2}C share the same space group and lattice parameter but differ in the chemical environment of Fe atoms.[33, 34] The site occupancy of C in ε -Fe₂C and ε' -Fe_{2.2}C is 0.5 and 0.45, respectively. $\varepsilon(')$ -carbide is favored at a high carbon chemical potential, which represents the condition of low temperature and high CO partial pressure.[26] However, kinetic factors (lattice deformation, carbon diffusion) can prevent its formation at low temperature. Hence, they are commonly observed in catalysts with relatively small particle and when a support material or chemical promoters are present.[35, 36] If temperature exceeds 250 °C, $\varepsilon(')$ -carbide will transform to χ -Fe₅C₂.[37, 38] χ -Fe₅C₂ is the most observed

carbide phase in the context of FT catalysis. Several works show that χ -Fe₅C₂ is the main active phase constituent at moderate FT conditions, owing to its relative thermodynamic stability at low carbon chemical potential. When temperature is further increased, χ -Fe₅C₂ will transform to Θ -Fe₃C.[39] The less active Θ -Fe₃C can also evolve into more active χ -Fe₅C₂.[40] The common feature of carbon-poor Θ -Fe₃C is that it can contribute to the buildup of carbonaceous deposits because of its near-metallic nature.[26, 41] Excessive carbonaceous deposits like graphite will cause deactivation of the catalyst.[42]

Despite extensive research, it is still uncertain which phase is the most active in the FT reaction. The intrinsic activity comparison between $\varepsilon(')$ -carbide and χ -Fe₅C₂ is widely investigated.[43, 44] Usually, a mixture of several Fe-carbides is obtained during reaction, making it impossible to correlate activity with specific phase.[26, 45] Chang *et al.* found that the intrinsic activity of χ -Fe₅C₂ is higher than $\varepsilon(')$ -carbide through changing the pretreatment condition.[43] However, Chun *et al.* found that $\varepsilon(')$ -carbide performs better than χ -Fe₅C₂ by introducing CO₂ in the feed, which increased the amount of $\varepsilon(')$ -carbide.[46] Lu *et al.* also found that the content of $\varepsilon(')$ -carbide is more active than χ -Fe₅C₂.[47] Another exploration by Wezendonk *et al.* pointed out that the weight-normalized activities of χ -Fe₅C₂ and $\varepsilon(')$ -carbide are virtually identical.[48] There also exist controversial conclusions in terms of the product distribution on different Fe-carbide phases in the FT reaction.[26, 43, 48, 49] The observed differences are probably caused by various factors, such as particle size, exposed facet (phase morphology), surface carbon deposition, support effect and the interference of other phases.

1.4 Product distribution

The formation of long-chain hydrocarbons is a key part of the FT chemistry involving a polymerization-like events of C1 monomers. The ideal product distribution follows the Anderson-Schulz-Flory (ASF) statistics.[19] The fraction of the carbon number within the hydrocarbon chain containing n carbon atoms with respect to total carbon numbers is expressed in Eq. 1.3:

$$S_{n} = \frac{Cn}{\sum_{1}^{\infty} Cn} = \frac{n (1-\alpha)\alpha^{n-1}}{\sum_{1}^{\infty} \alpha^{i-1}} = n (1-\alpha)^{2} \alpha^{n-1}$$
(Eq. 1.3)

where α is the chain-growth probability. Assuming it is independent of chain length, it can be expressed as the rate of chain propagation (r_p) over the rate of chain termination (r_t) plus chain propagation (r_p), shown in Eq. 1.4.

$$\alpha = \frac{r_p}{r_p + r_t} \tag{Eq. 1.4}$$

Depending on the catalyst and operation conditions, α value varies, which in turn results in different product distribution. The theoretical product distribution as a function of chaingrowth probability α is shown in Fig. 1.2. The lower temperature regime at which the selectivity towards higher hydrocarbons is favorable is where mainly Co-based catalysts are used for producing wax as precursor to high-quality transportation fuels. On the other hand, at the high temperatures used in the HTFT process, C_{5-20} hydrocarbons or lower olefins (C_{2-1} 4) are the major products and Fe is most often used as a catalyst.[21, 50] Notably, the undesired CH₄ selectivity monotonously decreases with increasing α . However, there is some deviation from the ASF distribution with regards to CH_4 selectivity. The higher CH_4 selectivity than predicted by the ASF distribution can have different origins such as a thermodynamic preference to form CH_4 , the kinetic preference for CH_x hydrogenation compared to C-C coupling or the involvement of specific surface sites that are selective to CH_4 . [51-53] On the other hand, C_2 selectivity is often lower than predicted by ASF, which is explained by the strong binding of ethylene with the catalyst surface. [54] Moreover, it has been observed that the chain-growth probability of C_{7+} products is higher than that of C_{1-7} ones. The chain-length dependent chain-growth probability α has been discussed. [55] Hydrogenolysis, on the other hand, could shorten produced long hydrocarbons by successive demethylation.[56] A high reversibility of chain growth on Co catalysts has been described by Chen et al..[57]



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

1.5 Reaction mechanism

FT reaction has been widely studied for almost 100 years, but there is still debate with regard to the reaction mechanism. Generally, it can be divided into a sequence of elementary reaction steps, characteristic for a polymerization reaction (i) chain initiation, (ii) chain propagation, and (iii) chain termination.

Chain initiation involves CO dissociative adsorption. Two types of mechanisms were proposed. The adsorbed CO on metal sites can directly dissociate into C and O atoms, referred to as direct CO dissociation. The C atoms will participate following chain-growth reactions as preliminary intermediates, while O atoms will be removed as H₂O or CO₂ as FT by-products.[58] In addition to direct CO dissociation, hydrogen-assisted CO dissociation pathways were also proposed. Such pathways can provide HCO or COH intermediate originating from the hydrogenation of adsorbed CO before the C-O bond breaks.[59] It is likely that the CO dissociation pathway depends on the surface coverage, the lateral interactions of intermediates and the relative occurrence of different sites on the catalyst surface.[60]

During chain propagation, carbide mechanism and CO insertion mechanism are differentiated in terms of whether the chain-growth monomer is CH_x or CO. The carbide mechanism, first proposed by Fischer and Tropsch, entails CH_x species inserted into the growing hydrocarbon chain.[1] Although Kummer *et al.* later proved that chemisorbed C is the dominant reactive intermediate rather than bulk carbide,[61] the mechanism is still referred to as the carbide mechanism. However, the formation of oxygenates during the FT reaction is not in keeping with this mechanism. Accordingly, Pichler *et al.* proposed CO insertion mechanism, in which an HCO intermediate or adsorbed CO can be inserted into the hydrocarbons chain.[62] In this mechanism, the C-O bond scission occurs after the C-C coupling, whereas for the carbide mechanism it is believed that the cleavage of C-O bond precedes the C-C coupling.[63]

Chain termination of the adsorbed alkyl group can occur in two different ways. It can either be hydrogenated to form n-paraffin or undergo β -H elimination to form α -olefin.[64] The reversibility of β -H elimination could cause the re-insertion of the α -olefin into a different growing chain, thereby deviating from the theoretical product distribution.[60] In addition, re-adsorption of the α -olefin could lead to the formation of more paraffin and isomer by secondary hydrogenation and isomerization reactions.[55] In the carbide mechanism, termination by CO insertion into a growing hydrocarbon chain is claimed to be the source of oxygenates.[65]

Introduction

1.6 Fe carburization kinetics and the FT mechanism on Fe-carbide

Usually, Fe-carbide is regarded as the active phase for the FT reaction. The formation of Fecarbide is accompanied by hydrocarbon production.[66] It suggests that the C atoms from CO dissociation can either go into the bulk Fe structure or be hydrogenated to CH_x, which is either hydrogenated to CH₄ or involved into chain-growth reaction. Tuning carburization behaviors of Fe-based catalysts is indispensable to realize optimized FT performances. A higher degree of carburization causes the Fe atoms to be in a more electron deficient state, which enhances the σ donation from CO to the surface and weakens the π back-donation for CO adsorption.[67] Carburization rate is highly dependent on reaction conditions and the composition of the catalyst. [45, 68] Ribeiro et al. found that adding alkali promotor could shorten the carburization time span, because it provided higher CO surface coverage for higher carburization rate.[69] The adsorption of Cl⁻ weakened the bonding between Fe and C atoms, thus inhibiting the diffusion of C atoms into the Fe structure.[70] The strong interaction between highly dispersed Fe-oxide and an oxidic support impedes the conversion of Fe-oxide into Fe-carbide.[71] Zhou et al. found that Fe carburization rate was faster when Fe is supported on a silicon substrate than on a silica substrate, because the former could provide an alternative way for O-removal. [72] Butt et al. proposed that increasing H₂ partial pressure promoted carburization of metallic Fe because it could assist O-removal.[73] Similar results were observed by Niu *et al.* that H_2/CO has a higher carburization capability than CO alone on α -Fe.[45] The rate of carburization of Fe-oxide is typically controlled by O diffusion from the oxide core to the surface.[74] The pretreatment environment can influence the initial catalytic activity. It was observed that a precipitated Fe-based catalyst pretreated in H₂ was more active and reached steady state more rapidly than the corresponding catalyst treated in CO.[75] The initial and steady-state catalyst activities were inextricably correlated with the carburization rates to form active surface carbide nodules.[76]

Lohitharn *et al.* pointed out that the FT activity on Fe-carbide is dependent on the number of active intermediates.[77] Temperature-programmed hydrogenation (TPH) was used to establish the correlation between structural type and reactivity of C species in the Fe-based samples.[78] In order of decreasing reactivity, (i) adsorbed atomic C species and surface carbide, (ii) polymeric, amorphous C species (iii) bulk C, and (iv) graphitic C are distinguished. Xu *et al.* revealed that the initial catalytic activity of FePtK/SiO₂ was positively correlated with the amount of adsorbed atomic C species.[79] An atomic C species could also convert to polymeric carbonaceous species on the surface. Herranz *et al.* suggested that the polymeric surface carbonaceous species was more closely related to the FT activity than atomic C species.[40] Ding *et al.* found that the combination of atomic C species and polymeric surface carbonaceous species resulted in graphitic-type C species, restricting

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active sites for the FT activity.[80] Reactive adsorbed C, graphitic C, and carbidic C in the bulk of the Fe-carbide could also be distinguished by electron energy loss spectroscopy (EELS).[81]

Govender et al. found two active pools of C on the surface of Fe-based catalysts to be responsible for the formation of CH_4 . The less active pool occupied the majority of total CH_x coverage, while the more active pool was scarce on the surface. The C-C coupling reaction involved both C pools.[82] Graf et al. also suggested that multiple pools existed on Fe-based catalyst for CH_4 formation and the addition of K would block the fast channel.[83] It was suggested that the slow pool is from C atoms that diffuse from the interior of Fe-carbide.[84] The involvement of lattice C can be described by a Mars-van Krevelen (MvK) mechanism, which has initially been described for oxidation catalysis by Mars and Van Krevelen.[85] This mechanism was also used for describing the reaction cycle to CH_4 on the carbonterminated Fe_5C_2 (100) surface. [86] The hypothesis entails the threefold hydrogenation of a lattice carbide, followed by the creation of a surface vacancy (fourfold site) where a CO molecule from the gas phase can dissociate. Kummer et al. first partially carburized a catalyst by ¹²CO and then fully by radioactive ¹⁴CO, leading to a ¹⁴C-enirched surface. By carrying out the FT reaction in ¹²CO/H₂, it was found that the hydrocarbons produced at 260 °C contained only 10% ¹⁴C as established by measuring their radioactivity. It indicates that the pathway following an MvK mechanism has a minor contribution to hydrocarbons formation.[87] Ordomsky et al. later found that C atoms in Fe-carbide are involved in the chain-growth initiation events of the FT reaction via isotope labeling experiments.[88] The Langmuir-Hinshelwood (L-H) mechanism is currently favored in describing the FT reaction on Co and Ru catalysts, [89, 90] where the metal-carbon bond is not as strong as on Fe. [91] Catalytic reactions predominantly occur between adsorbed species. A brief description of the discrepancy between these two mechanisms on Fe-carbide is presented in Fig. 1.3. Typically, the intrinsic activity of Co and Ru is higher than that of Fe-carbide, [92] suggesting that reaction pathways that follow the L-H mechanism are faster than those involving MvK steps.



Figure 1.3. Schematic representation of the L-H mechanism and MvK mechanism on Fecarbide for CO hydrogenation.

1.7 Deactivation of Fe-based catalysts

As Fe-based catalysts are usually used at high temperature in slurry bubble reactors, they will inevitably face catalyst deactivation because of catalyst sintering, particle agglomeration and attrition.[93] To avoid physical deterioration, a support is needed to disperse and stabilize the active phase.[94] Strong support-metal interactions can inhibit sintering of the catalyst.[95]

Some structural promoters are also added to enhance such interactions.[96] The change in the chemical state of the catalyst also poses a negative effect on the catalytic activity. Oxidation of metallic Fe and/or Fe-carbide phases is believed to be one of the factors for catalyst deactivation, especially at high CO conversion.[97] The formation of Fe-oxide will cause higher CO₂ selectivity owing to WGS reaction.[9] Apart from oxidation, formation of coke will also lead to a decrease in the FT activity. The accumulation of graphite-like carbonaceous species on the catalyst surfaces will restrict the availability of active sites and block the pores.[26] It may also lead to undesired side reactions.[52] A slight increase in CH₄ selectivity during deactivation was observed, but lack of explanation.[98]

Eliason *et al.* proposed two deactivation paths occurring in parallel and/or coupled. First, the transformation of atomic C species to amorphous polymeric C species followed by the formation of graphitic C. Second, the transformation of highly active χ -Fe₅C₂ to less active $\epsilon(')$ -carbide.[78] Jung *et al.* found that the transformation of $\epsilon(')$ -carbide to χ -Fe₅C₂ is accompanied by deactivation, because the decomposition of metastable $\epsilon(')$ -carbide can lead to a buildup of coke. The detached C from $\epsilon(')$ -carbide seems to serve as the nucleation site for the Boudouard reaction (2CO \rightarrow C + CO₂).[36, 99] The transformation between reactive

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C species and graphitic C was reported to be reversible. [52, 100] Increasing H coverage by increasing H₂ partial pressure or decreasing CO partial pressure will constrain the formation of amorphous/graphitic C.[101, 102] Only elevated total pressure in combination with a high H₂/CO ratio was found to provide a sufficient H coverage to restrict C deposition. When the H₂/CO ratio is as low as unity, increasing the total pressure increases C deposition rate.[103] Rising temperature can retard C deposition thermodynamically, but accelerate carburization kinetically.[44] Increasing H₂O vapor content could also inhibit C deposition by inhibiting the formation of Boudouard-type carbonaceous species. [104, 105] However, local high H₂O vapor partial pressure formed by the WGS reaction may also irreversibly oxidize the catalyst, leading to the deactivation of the catalyst. [106] Smaller particles showed a lower tendency to build up inactive surface carbonaceous species on the catalyst surface.[107] The introduction of promoters (Na + S) could result in significant C deposition by facilitating Fe carburization over the initial hours of the FT reaction.[108] However, the use of S, in the absence of Na, could increase the resistance against C deposition. The support effect on carbonaceous deposits formation was also studied by Galuszka et al.[109] It suggested that strong metal-support interaction might counter deactivation by maintaining a balance between active and inactive C species.

1.8 Structure-activity relationships

As in all heterogeneous catalysts in which nanoparticles are used, there is a profound interest in establishing structure-activity relationship for catalyst optimization. For Co- and Ru-based catalysts, the turnover rate of the CO dissociation is dependent on particle size.[110, 111] It has been observed that the turnover rate increases with particle size and shows maximum at intermediate size. This structure-sensitive phenomenon is usually interpreted in terms of geometric effects of the surface metal atoms. It is predicated that below a particle size of 6 nm the density of step-edge sites decreases. The metal atoms on step-edge sites are more reactive to CO dissociation owing to lower coordination number. This can be understood in terms of an electronic effect, because the decrease in coordination number of metal atoms tends to back-donate more electrons to the antibonding orbital of CO, thus lowering the activation energy for CO dissociation. Geometrically, the CO molecule can align with stepedge sites without bending, which is more favorable for CO dissociation than on planar surface. CO dissociation is usually regarded as the rate-limiting step for smaller Co particle because low-coordination sites at corners and edges are poisoned by CO.[112] Hence, the enhanced CO dissociation ability on larger Co particle size will subsequently increase the overall FT activity. Generally, larger Co particles favor chain growth, producing heavier hydrocarbons.[113] Some publications also observed a similar particle size effect for Fe with

Introduction

smaller particles presenting lower TOF and higher CH₄ selectivity than large particles.[114, 115]

Torres Galvis *et al.* observed an opposite particle size effect. In the initial state, when the surfaces are relatively clean, smaller particle size presents higher surface-specific activity because more corner and edge atoms reside on small, promoted Fe-carbide particles, which are beneficial for CH₄ formation.[116] The formation of C₂₊ hydrocarbons are independent of particle size, whereas the TOF for CH₄ formation decreases when larger particle is used. However, small particle suffers more from deactivation because of the loss of active surface area from sintering or C deposition. For unpromoted Fe-carbide, the apparent TOF increases with decreasing particle size, albeit with no difference in terms of selectivity.[116] The fact that not all published work finds the same particle size effect for Fe may be due to the sensitivity of carbon over-layers built up during activation. The different trend for Fe-carbide in terms of structure-activity relationship is probably caused by the intrinsic nature of chemical bonding of metal carbide. On the Fe catalysts, the binding strength of C atoms is stronger than Co. The weaker Fe-C bond corresponds to higher activity on Fe-carbide because it requires less energy needed for C removal through hydrogenation. [54, 91, 117] It indicates that the removal of C atoms by hydrogenation is a rate-limiting step for Fe-carbide rather than CO dissociation.[104]

Theoretical work pointed out that H adsorption also plays an important role in determining product selectivity.[118] Xie *et al.* observed that CH_4 formation occurs equally fast on edge and terrace sites for unprompted Fe-based catalysts, but it slows down on the terrace sites of promoted catalysts. There is a linear relationship between apparent TOF and CH_x coverage, the latter is more abundant on small particle size. In addition, the increase in particle size leads to an increase in H surface residence time and a decrease of H coverage, indicating hydrogenation is suppressed at large particle size.[84]

1.9 Aim and scope

The goal of this thesis is to understand the mechanism and kinetics of Fe carburization and its relevant FT reaction on Fe-carbide. As briefly described above, the complexity of the phase composition of Fe-based catalyst hinders an unequivocal understanding of how Fe-carbide is formed *in situ*, what the role of Fe-carbide in the FT reaction and how the surface composition of the Fe-carbide impacts the FT performance. In order to gain insight into the underlying mechanisms, a model Raney-Fe catalyst was used in this study as a catalyst precursor from which phase-pure carbides could be formed without the interference from Fe-oxide.

Chapter 1

In **Chapter 2**, the effects of temperature and gas phase composition on Fe-carbide formation were investigated. As first step of the carburization, C deposition by CO dissociation at different temperature was studied by IR spectroscopy, XPS and CO-TPR. The phase composition of carbide can be influenced by the rate of C diffusion into Fe lattice. The role of H_2 in Fe carburization rate was investigated by TPH, XRD, XPS and Mössbauer spectroscopy. In particular, this chapter will show how TPH was applied to quantitatively determine the amount of C atoms in a carburized Fe sample.

A fundamental question is whether lattice C of Fe-carbide takes part in the hydrocarbon formation during the FT reaction. Isotopic switch experiments involving ¹²CO/H₂ and ¹³CO/H₂ during carburization in combination with following TPH were performed to study the kinetic and mechanistic issues of Fe carburization and the FT reaction in **Chapter 3**. This enabled us to understand the role of lattice C in the FT reaction. Steady state isotopic transient kinetic analysis (SSITKA) was employed to identify different pathways for C hydrogenation on Fe-carbide and its relevant reaction mechanism.

In **Chapter 4**, the relationship between surface C species distribution of Fe-carbide and the FT activity and selectivity was investigated. The evolution of C species of Fe-carbide during the low-pressure FT reaction was analyzed by XPS, TPH and Raman spectroscopy. Combined with activity data, the rate-limiting step of Fe-carbide in the FT reaction was determined. The underlying mechanism of C deposits on the change of product selectivity was illustrated by SSITKA. The effect of increasing the H₂/CO ratio or the total synthesis gas pressure on inhibiting deactivation was further explored. The concomitant impact of exposure time to synthesis gas at low pressure on the catalytic induction period, activity and selectivity under high-pressure FT conditions was explained by differences in C deposits.

Based on the understanding of Fe carburization kinetics, the FT reaction mechanism on Fecarbide and the effect of C deposits on the FT performance established from **Chapter 2 to 4**, **Chapter 5** focuses on comparing the intrinsic activity of $\varepsilon(')$ -carbide and χ -Fe₅C₂ in the FT reaction. To exclude the interference by other phases, pure $\varepsilon(')$ -carbide and χ -Fe₅C₂ were synthesized. The surfaces property of these two carbides were compared. It was revealed that subtle differences in surface chemistry between these two carbides ultimately result in relatively small differences in product distribution. The higher MvK pathway to CH₄ formation on $\varepsilon(')$ -carbide was confirmed by SSITKA. These two carbides also share similarities in primary CO₂ selectivity. The underlying mechanism was investigated by IR spectroscopy and isotopic switching experiments.

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Chapter 2

The role of H₂ in Fe carburization by CO in Fischer-Tropsch catalysts

Abstract

The formation of Fe-carbide phases is relevant to the synthesis of Fischer-Tropsch synthesis catalysts. We investigated the carburization of Raney-Fe as a model catalyst using spectroscopic and temperature-programmed techniques. IR spectroscopy shows that CO dissociation already occurs at -150 °C, while C diffusion into metallic Fe requires much higher temperature (~180 °C). The carburization rate increases with increasing H₂/CO ratio, which can be attributed to the lower overall barrier for O removal as H₂O as compared to CO₂. O removal frees vacancies that are needed for CO dissociation. The resulting higher C coverage increases the driving force for Fe-carbide formation. A higher driving force leads to predominant formation of the more carbon-rich $\epsilon(')$ -carbide, while χ -Fe₅C₂ is formed at lower H₂/CO ratio. The removal of surface O appears to be the rate-limiting step under all conditions. Initially, most of deposited C is used for Fe-carbide formation with a small contribution to hydrocarbons formation.



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2.1 Introduction

Fischer-Tropsch (FT) synthesis is an increasingly important technology for producing liquid fuels and chemicals *via* synthesis gas, which can be obtained from coal, natural gas, or biomass.[1, 2] While group 8 and 9 metals show good catalytic activity in the FT synthesis, only the most abundant first-row transition metals Fe and Co are used in commercial FT catalysts.[3-5] Fe has several advantages over Co: it is cheaper, can be used in a wider temperature and pressure window, and is more flexible with respect to feedstock composition. Fe is particularly preferred in coal-to-liquids (CTL) processes due to its higher sulfur tolerance and better ability to deal with the low H₂/CO ratio of coal-derived synthesis gas.[6]

The active phase of Fe-based FT catalysts comprises Fe-oxides (especially Fe₃O₄), Fecarbides and metallic Fe.[7] Despite the heterogeneous composition of these catalysts, it has been established that the FT activity correlates strongly with the Fe-carbide content.[8] Therefore, the conversion of the usual Fe-oxide catalyst precursor into the active Fe-carbide form has received widespread attention. $\varepsilon(')$ -carbide, χ -Fe₅C₂ and Θ -Fe₃C are typical Fecarbides active in FT synthesis.[9] The structure of Fe-carbides can be divided into two categories according to the occupation of C atoms in the hexagonally close packed (hcp) Fe lattice.[10] In ε (')-carbide (octahedral carbide), the C atoms are located in the octahedral interstices of the Fe lattice. ε -Fe₂C and ε '-Fe_{2.2}C can be distinguished by a slightly different C content. In γ -Fe₅C₂ and Θ -Fe₃C, the C atoms are located in the trigonal prismatic interstices of the Fe lattice. The formation of specific Fe-carbides depends on many factors such as the crystallite size, morphology, surface texture, the presence of promoters (or inhibitors), and the carburization conditions (temperature, pressure and gas composition).[11, 12] De Smit et al. studied the stability and interconversion of these Fe-carbide phases as a function of the "carbon chemical potential", which can be linked to the gas-phase composition and the temperature.[13] A higher H₂/CO (lower carbon chemical potential) is predicted to lead to carbon-poor phases such as γ -Fe₅C₂ and Θ -Fe₃C. The methods used to predict these stabilities are rooted in thermodynamics. The stability of the different phases under actual FT conditions will also depend on kinetic factors. Specifically, the diffusion of C atoms derived from CO dissociation from the surface into the bulk of reduced Fe, should be considered. It has been established that the presence of H₂ facilitates carburization, resulting in carbon-richer $\varepsilon($)carbide.[14]

Most research on Fe carburization has focused on bulk chemical issues in metallurgic context. Generally, the rate of carburization is strongly influenced by the composition of the carburizing gas.[15, 16] Fundamental studies often employ high temperature (>500 °C) and iron foil or electrolytic iron as substrates,[17] which are not representative for Fe-carbides

relevant to the FT reaction. Moreover, the carbon content in steel (typically 0.05~0.35% [18]) is much lower than in Fe-carbide phases in FT catalysts. The unsteady kinetic regimes during carburization make it difficult to correlate bulk carbide formation with the processes and carbon-type intermediates present at the surface. In this context, it is important to develop a better understanding of the carburization mechanism of Fe-based catalysts and, specifically, about the correlation between solid-phase reactions involved in carburization of the bulk of Fe nanoparticles and the catalytic reactions occurring at the surface during carburization.

Mechanistically, Fe-carbide formation involves CO dissociation followed by C diffusion into the bulk as well as C and O removal by surface reactions, regardless of whether carburization is applied to metallic Fe or Fe-oxide. A recent previous work showed that careful control of the carburization process of fully reduced Fe leads to pure Fe-carbide.[19] When the Fe precursor is not fully reduced before carburization, it will lead to a mixture of Fe-oxide and Fe-carbides. The remaining Fe-oxide, usually present as hematite (Fe₃O₄), can catalyze the water-gas shift (WGS) reaction, which involves the conversion of CO with H₂O to CO₂ and H₂.[6, 7, 20] It should also be noted that the effect of O diffusion can be excluded during the carburization of metallic Fe, as the diffusivity of O atoms into the Fe lattice is much lower than that of C atoms.[21] Hence, the aim of this work is to study the diffusion of C in metallic Fe relevant to Fe carburization.

Mössbauer spectroscopy [22] and X-ray diffraction [23] are the most used techniques to analyze the phase composition of Fe-carbides (and other forms of Fe). These techniques provide only qualitative insight into the actual C content of the phases formed upon carburization.[24-26] In the present work, these two bulk techniques have been complemented with temperature-programmed hydrogenation measurements, allowing to quantitatively determine the amount of C atoms in a carburized Fe samples. IR spectroscopy and XPS are used to investigate the surface composition of such samples in more detail. Especially the impact of H_2 on carburization by CO has been studied using Raney-Fe as a porous and support-free precursor with a reasonable surface area,[19] rendering it an ideal model catalyst to investigate the carburization process.

2.2 Experimental methods

Catalyst preparation

Raney-Fe catalyst Raney-Fe was prepared from an aluminum-iron (Al50/Fe50) alloy (Goodfellow, 150-micron powder). A 25 ml 9 M KOH (Sigma-Aldrich) solution was prepared in a round-bottom flask. After heating the solution to 70 °C, 5 g of the Al-Fe alloy powder was slowly added. Caution is needed, as this reaction produces hydrogen. After 40 min of stirring at 70 °C, the mixture was cooled to room temperature. The suspension was

washed with water and ethanol 7 times each in order to remove potassium and aluminum hydroxide/oxide ions and retrieve the precipitated Raney-Fe. Due to the pyrophoric character of the fine Fe powder, the catalyst was passivated in a 1% O_2 /He flow for 24 h at room temperature for safe handling.

Fe/SiO₂ catalyst SiO₂-supported Fe sample was prepared by incipient wetness impregnation method of an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (AR, Sinopharm Chemical Reagent Co.) on a silica support (SiO₂ Q15, 120 mesh, Sasol). The sample was sequentially dried at 80 °C for 12 h and 120 °C for 24 h and then calcined at 500 °C for 5 h in static air.[19] Fe/SiO₂ was used to carry out *in situ* IR spectroscopy.

Catalyst characterization

Inductively coupled plasma optical emission spectroscopy (**ICP-OES**) The elemental composition of Raney-Fe was determined by ICP-OES analysis on a Spectroblue spectrophotometer of AMETEK Inc. Typically, 25 mg sample was dissolved in 10 ml concentrated HCl. The mixture was heated until the sample was fully dissolved. Samples were measured in duplo against a standard curve. The Fe content of the Raney-Fe material was 85 wt. %. This value was used to determine the C/Fe ratio of carburized samples. The Al content was 4 wt. %, the remained being attributed to O, most likely in the form of residual aluminum (hydr)oxides and surface Fe-oxide due to passivation.

Transmission electron microscopy (**TEM**) A few milligrams of catalyst powder were suspended in ethanol. The suspension was sonicated to fully suspend all particles. Afterwards, a few drops of the suspension were applied on a carbon-coated copper grid. TEM images were captured using a FEI Technai 20 transmission electron microscope using an acceleration voltage of 200 kV with a LaB6 filament. ImageJ was used to process the images and determine the average particle size.

In situ **IR spectroscopy** Infrared spectroscopy was carried out on a Bruker Vertex 70v spectrometer equipped with DTGS detector by averaging 8 spectra at a 2 cm⁻¹ resolution. IR spectra were recorded in a controlled environment cell with CaF₂ windows. Typically, the samples were pressed into self-supporting wafers of ca. 10 mg. *In situ* reduction of the Raney-Fe sample required slightly milder conditions (50/50 vol% H₂/N₂, 430 °C, 1 h, 1 bar) in comparison with Fe/SiO₂ (50/50 vol% H₂/N₂, 550 °C, 6 h, 1 bar). After reduction, the sample was outgassed (250 °C, 10 min) and the cell was cooled to about -170 °C using liquid N₂. Then, CO was dosed to the cell in small increments. After a CO pressure of 50 mbar was reached, a background IR spectrum was recorded followed by a slow increase of the temperature of the sample by halting the cooling. IR spectra were recorded every 10 °C.

Quasi in situ X-ray photoelectron Spectroscopy (XPS) XPS spectra were recorded in a Kratos AXIS Ultra 600 spectrometer equipped with a monochromatic Al K_a X-ray source (hv = 1486.6 eV). Region scans were recorded at a pass energy of 40 eV (step size 0.1 eV) and survey scans were recorded at a pass energy of 160 eV (step size 0.5 eV) with the background pressure kept below 5×10^{-9} mbar. A high-temperature reaction cell (Kratos, WX-530) was used to pretreat the sample, which was pressed into a pellet placed on a stainless-steel stub. This allowed *in vacuo* sample transfer into the XPS analysis chamber. Reduction was performed in a 100% H₂ flow (50 ml/min, at 1 bar) at atmospheric pressure at 550 °C for 12 h (heating rate 5 °C/min). After reduction, the sample was cooled to 30 °C or 250 °C. Synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min, 1 bar) or CO (8% CO in Ar, 50 ml/min, 1 bar) was used for carburization. After a certain time, the reaction was stopped, and the sample was transferred to the XPS analysis chamber after evacuation. Fitting of the XPS spectra was done using Voigt functions after a Shirley background subtraction using the CasaXPS software (2.3.18PR1.0).

In situ X-ray diffraction (XRD) XRD was carried out on a Rigaku D/max-2600/PC apparatus equipped with a D/teX ultrahigh-speed detector and scintillation counter. The X-ray generator consisted of a Cu rotating anode target with a maximum power of 9 kW. All the tests were operated at 40 mA and 40 kV. *In situ* XRD patterns were recorded in an Anton Paar XRK-900 cell equipped with a CO/H₂/inert gas inlet system.

In situ Mössbauer spectroscopy Transmission ⁵⁷Fe Mössbauer spectra were collected at 120 K and 300 K with a sinusoidal velocity spectrometer using a ⁵⁷Co (Rh) source. Velocity calibration was carried out using an α -Fe foil at room temperature. The source and the absorbing samples were kept at the same temperature during the measurements. The Mössbauer spectra were fitted using the Mosswinn 4.0 software. Carburization experiments were performed in a state-of-the-art high-pressure Mössbauer *in situ* cell. The high-pressure beryllium windows used in this cell contain 0.08% Fe, whose spectral contribution was fitted and removed from the final spectra.

Pre-treatment

In each experiment, 50 mg catalyst precursor was loaded in a quartz tubular flow reactor. The gas feed was controlled by thermal mass flow controllers. The effluent mixture was analyzed using an online mass spectrometer (MS, Balzers TPG-300) and an online gas chromatograph (GC, Compact GC 4.0). Samples were first reduced in a diluted H₂ flow (20% H₂ in Ar, 50 ml/min, 1 bar) at 430 °C using a rate of 5 °C/min followed by a dwell of 1 h. After reduction, the reactor was cooled in Ar to the temperature for investigation of the influence of temperature, duration and gas-phase composition on the carburization process.

A first set of experiments involved carburization in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min) or CO (8% CO in Ar, 50 ml/min) at 1 bar for 40 min at varying temperatures. The second set of carburization experiments were carried out either in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min) or CO (8% CO in Ar, 50 ml/min) at 1 bar and 250 °C for varying durations. In a third set of experiments, carburization was done in synthesis gas with varying H₂/CO ratio ((0-64) % H₂ and 8% CO in Ar, 50 ml/min) at 1 bar and 250 °C for 40 min. After carburization, the catalyst was flushed in Ar and cooled to room temperature. TPH experiments were then conducted by heating the reactor to 750 °C at a rate of 5 °C/min in diluted H₂ flow (20% H₂ in Ar, 50 ml/min). During TPH, the main hydrocarbon product was CH₄ (> 96 %), which was followed by online MS. To quantitatively determine the CH₄ flow rate, the reactor effluent was analyzed by an online GC at regular intervals. The amount of released C atoms was calculated by integrating the CH₄ flow during the experiment.

Carburization kinetics

The kinetics of the carburization process were followed in a steady state isotopic transient kinetic analysis (SSITKA) setup. Details of this setup can be found in the literature.[27] For each catalytic test, 50 mg Raney-Fe mixed with SiC was loaded into the reactor and reduced in a diluted H₂ flow (20% H₂ in Ar, 50 ml/min) at 430 °C (with a ramping rate 5 °C/min) and 1.5 bar for 1 h. After reduction, the reactor was cooled to the targeted temperature (210, 230, 250, or 270 °C). H₂ was removed by flushing the catalyst bed for an additional 15 min. The carburization experiments were performed by switching from the inert Ne gas (6 + x ml/min)to a $H_2/CO/Ar$ mixture (x/4/2 ml/min), in which x was either 0, 2, 8, or 16 ml/min. Ar was added to balance the total flow to 50 ml/min. During carburization, the transient response of $H_2(m/z = 2)$, $CH_4(m/z = 15)$, $H_2O(m/z = 18)$, Ne(m/z = 22), CO(m/z = 28), Ar(m/z = 40), and CO_2 (m/z = 44) were monitored by online MS (ESS Catalysys). The catalytic activity was determined by online GC (Thermo Scientific Trace 1300, extended with Trace 1310 auxiliary oven). A combination of an MXT-QBond column (60 m \cdot 0.53 mm) with a thermal conductivity detector was used to determine the concentrations of CO_2 , CO, H_2 and CH_4 , while a combination of a Rt-SilicaBond column (60 m \cdot 0.32 mm) with a flame ionization detector was used to analyze hydrocarbons. The total amounts of CO effluent (unreacted), CO_2 and C_xH_y were calculated by integrating their flow during the experiment. The CO consumption amount was calculated by subtracting the total CO amount in a blank experiment with the unreacted CO amount. The total amount of H₂O was based on the O balance. After carburization, the catalyst was flushed in Ar and cooled to room temperature for TPH measurements. The procedure to quantify the amount of C atoms was similar as described above for TPH. The activation energy of carbide formation, CO₂ formation, H₂O

formation, C_xH_y formation and CO consumption were determined based on their averaged formation or consumption rate in 40 min.



2.3 Results and discussion

Figure 2.1. *In situ* IR spectroscopy of CO adsorbed on reduced Fe/SiO₂ during heating from -170 °C to 70 °C.

As metallic Fe is typically carburized by CO, *in situ* IR spectroscopy was used to investigate the interaction of metallic Fe with CO. Fig. 2.1 shows the evolution of IR spectra of reduced Fe/SiO₂ upon exposure to CO at liquid N₂ temperature followed by a slow increase of the temperature. A corresponding experiment conducted on reduced Raney-Fe gave comparable results, however with a significantly lower signal-to-noise ratio due to the low transmission through this sample (Appendix Fig. 2.10). A prominent band appearing in the range of 2200-2100 cm⁻¹ in Fig. 2.1 can be ascribed to overlapping contributions of CO physiosorbed on the surface and gaseous CO. During heating, CO₂ is formed at -150 °C as follows from the appearance of the IR band at 2340 cm⁻¹. CO₂ can be formed through the Boudouard reaction (2 CO \rightarrow C + CO₂) on metallic Fe,[28] which will result in poisoning of the Fe surface by C atoms. The CO₂ IR band shows a maximum intensity at -130 °C, which can be explained by the desorption of CO₂ at higher temperatures. The absence of features due to chemisorbed CO at these low temperatures and the formation of CO₂ indicates that CO rapidly dissociates on metallic Fe. Only at a temperature of -20 °C, a weak IR band in the range of 2000-2050 cm⁻¹ is observed, which can be assigned to linear CO adsorption on Fe.[29] A further increase of the temperature results in a lower intensity of this IR band. These data show that CO dissociation occurs very fast on metallic Fe. Part of the O atoms are released as CO_2 , while the remaining C and O atoms on the surface will delay CO dissociation. Their presence is also evident due to the higher wavenumber of the IR band of adsorbed CO in the presence of co-adsorbates, which is due to lateral CO-C and CO-O interactions.[30]



Figure 2.2. *Quasi in situ* XPS spectra of C 1s region and Fe 2p after (a) reduction, (b) carburization with CO for 15 min at 25 °C, (c) carburization with CO for 3 h at 25 °C.

Additional evidence of facile CO dissociation on metallic Fe at low temperature was obtained by *quasi in situ* XPS (Fig. 2.2). The XPS spectrum of reduced Raney-Fe was used as a reference, as there was practically no C present on the surface. The Fe 2p spectrum shows that a small fraction of Fe remains in the oxidized state, which is due to the difficulty in removing all O atoms from Raney-Fe, even at a high reduction temperature of 550 °C. CO adsorption on Fe²⁺ is much weaker than on Fe⁰.[31] Upon introduction of CO at room temperature for 15 min, a weak C 1s peak at ~284.8 eV appears, which can be attributed to sp³ and sp² amorphous carbon species.[32] Prolonging CO exposure leads to a slight increase of this C signal and the formation of Fe²⁺ due to the oxidation of Fe⁰. Although the XPS spectra do not contain the typical C 1s feature of Fe-carbide at ~283 eV,[33] its presence in very small amounts cannot be excluded given the very low overall C 1s intensity. Nevertheless, the current data indicate that the C atoms derived from CO dissociation remain at the surface and do not diffuse into the Fe lattice under these conditions. Thus, at relatively low temperatures C can already be deposited on metallic Fe by CO dissociation and CO₂ is formed by recombination of CO with O atoms.

We next investigated the influence of temperature on the carburization process, which is determining the rate of C diffusion from the surface into the Fe lattice. For this purpose,

temperature-programmed reaction (TPR) experiments in a CO atmosphere on reduced Raney-Fe were performed (Fig. 2.3). As CO₂ is formed by the Boudouard reaction, the evolution of CO₂ is a suitable indicator of C accumulation. It shows that CO₂ formation readily occurs at 30 °C, directly after CO is introduced. The CO₂ profile shows a maximum in this isothermal regime consistent with the notion that C remains on the surface and blocks sites for CO dissociation. Upon ramping the temperature to 175 °C, CO₂ formation increases in an exponential manner. This can be explained by the diffusion of C atoms from the surface to the bulk of Fe, freeing surface sites for further CO dissociation. It has been mentioned that the deformation energy needed to release the structural strain gives rise to the diffusion barrier for Fe-carbide formation.[13]



Figure 2.3. CO-TPR on reduced Raney-Fe (8% CO in Ar, 50 ml/min).

Next, TPH was employed to determine the amount of C present in the catalyst after carburization of Raney-Fe in CO. First, the carburization in CO for 40 min at different temperatures was studied (Fig. 2.4a). CH₄ is the main product of TPH with minor amounts of other hydrocarbons as by-products. The TPH profiles obtained for samples carburized below 190 °C only show a weak broad CH₄ feature at temperatures between 200 °C and 350 °C, which can be attributed to the hydrogenation of surface C. The maximum of this feature shifts to higher temperature with increasing carburization temperature, suggesting that the C phase at the surface becomes more difficult to reduce. Upon carburization at 190 °C, the amount of CH₄ is substantially higher than at lower carburization temperatures, which indicates the onset of Fe-carbide formation. When the carburization temperature is increased,

the CH₄ peak shifts to higher temperatures and increases. The shift to higher temperature can be ascribed to the lower reactivity of C atoms in Fe-carbide than C atoms at the surface.[34] The presence of a high-temperature feature after carburization at 350 °C can be explained by graphite, which can only be hydrogenated at relatively high temperature.[35] Moreover, graphite will also impede the accessibility of the Fe-carbide surface, lowering the hydrogenation of bulk C atoms.[36] This can explain the significant shift to higher temperatures of the bulk reduction feature. Fig. 2.4c shows the atomic C/Fe ratio obtained by integration of these TPH profiles. Consistent with CO-TPR, a low carburization temperature (35-170 °C) results in the deposition of a very small amount of C. Based on the average particle size and dispersion of the Raney-Fe catalyst of 29 nm and 3.5%, respectively (Appendix Fig. 2.11), the C/Fe ratio (~ 0.03) suggests that a monolayer coverage of C is reached. It is also consistent with previous XPS data (Fig. 2.2) that C atoms deposited at 25 °C remain at the surface and do not diffuse into the Fe lattice. When the temperature exceeds 170 °C, deposited C can easily enter the Fe lattice and the C/Fe ratio increases with increasing carburization temperature. The TPH method allows determining the carburization degree in a facile manner.

As in practice carburization is carried out in synthesis gas mixtures, the influence of temperature on the carburization process in the presence of H_2 was also investigated (Fig. 2.4b). Comparison of the TPH profiles recorded with and without H_2 shows that carburization at intermediate temperatures (190-300 °C) results in more CH₄. This shows that H_2 facilitates the carburization process. The carburization rate will depend on the concentration gradient of carbon.[37] As the presence of H_2 in the gas phase will not influence the diffusion rate of C in bulk Fe, the positive effect of H_2 on the carburization kinetics can be ascribed to a higher C coverage. Similar findings have been reported earlier.[14, 38] Figure 2.4c shows that the presence of H_2 accelerates the formation of Fe-carbide.



Figure 2.4. TPH of carburized Raney-Fe at different carburization temperature: (a) after carburization in CO, (b) after carburization in $H_2/CO = 2$, and (c) the C/Fe ratio based on integration of the CH₄ signal. The carburization time was 40 min.

The positive effect of H_2 on Fe carburization was also investigated by varying the H_2/CO ratio using a carburization time of 40 min and a temperature of 250 °C. The results in Appendix Fig. 2.12 show that more C diffuses into the Fe lattice with increasing H_2/CO ratio. Niemantsverdriet *et al.* proposed that there is competition between C diffusion into the Fe lattice and C hydrogenation.[8] It can be expected that, with increasing H_2/CO ratio, the removal of C from the surface in the form of gaseous products becomes faster than the rate of C diffusion into the surface. As the opposite is observed in our study, the carburization process was studied in more detail below.

Fig. 2.5 shows the C/Fe ratio determined by TPH as a function of the carburization time for different H_2/CO ratios. During the first 40 min, the carburization rate at a H_2/CO ratio of 2
(8% CO, 16% H₂) is higher than in 8% CO. This confirms the positive effect of H₂ on the carburization rate. It also explains that catalysts activated in CO need a longer induction time than those activated in synthesis gas.[39] *In situ* Mössbauer spectra during carburization were also recorded at a H₂/CO ratio of 2. The corresponding spectra and the results of spectra deconvolution are given in Appendix Fig. 2.13 and Appendix Table 2.1, respectively. The thereof derived C/Fe ratios are added to Fig. 2.5. These *in situ* Mössbauer results are in good agreement with the TPH data.



Figure 2.5. C/Fe of carburized Raney-Fe as a function of carburization time under different carburization conditions at 250 °C (the inset shows a zoom of the initial 40 min).

In situ techniques are best equipped to study gas phase-solid phase reactions. Therefore, *in* situ XRD and *in situ* Mössbauer spectroscopy were applied here to investigate closely the positive effect of H₂ on Fe carburization. *In situ* XRD shows that, after reduction and before carburization, the catalyst is completely reduced as only the typical reflections of α -Fe can be observed (Fig. 2.6). This is confirmed by *in situ* Mössbauer spectra, which only shows a spectral contribution of pure Fe⁰ (Appendix Fig. 2.13 and Appendix Table 2.1).

In pure CO, *in situ* XRD patterns recorded with increasing temperature show that carburization starts at 220 °C. At this temperature, new reflections due to χ -Fe₅C₂ appear (Fig. 2.6a). Thermodynamically, the formation of $\varepsilon(')$ -carbide is favored at low temperature and low H₂/CO ratio.[13] The observation of χ -Fe₅C₂ instead of $\varepsilon(')$ -carbide can be an indication of a kinetic limitation, leading to the formation of the Fe-carbide with a lower C/Fe ratio. When synthesis gas (H₂/CO = 2) is used, carburization proceeds differently (Fig. 2.6b). Metallic Fe is converted into Fe-carbide at a lower temperature and $\varepsilon(')$ -carbide becomes the

dominant Fe-carbide phase. Above 320 °C, $\epsilon(')$ -carbide transforms to χ -Fe₅C₂ and the latter becomes the main Fe-carbide phase at higher temperatures, because $\epsilon(')$ -carbide formation is entropically not favored.[13] Above 380 °C, χ -Fe₅C₂ transforms to Θ -Fe₃C, which is expected at high temperature.[40] Haglund *et al.* reported that Θ -Fe₃C has a metallic character and is susceptible to the buildup of surface C species.[41] It has indeed been reported that Θ -Fe₃C formation is typically accompanied by graphite growth.[13, 25, 42] This can explain the relatively high C/Fe ratios observed in Fig. 2.4c obtained after carburization at higher temperatures in a H₂/CO = 2 mixture and the asymmetric TPH peaks in Fig. 2.4.



Figure 2.6. *In situ* XRD patterns of carburization of reduced Raney-Fe in (a) CO (20% CO in Ar, 50 ml/min, 1 bar) and (b) H_2/CO (8% CO -16% H_2 in Ar, 50 ml/min, 1 bar).

De Smit *et al.* reported that the formation of $\varepsilon(')$ -carbides is kinetically limited by the diffusion of C atoms into α -Fe due to the higher C/Fe ratio of this phase in comparison to χ -Fe₅C₂.[13] This can explain why $\varepsilon(')$ -carbides are typically formed in catalysts containing small Fe particles [43] or having a structure with an expanded lattice obtained during rapid quenching of Fe.[9] The pretreatment conditions have a pronounced effect on the carbide phase formed upon carburization. It has been found that H₂ reduction of the Fe precursor leads to $\varepsilon(')$ -carbide during the FT reaction, while reduction in CO or synthesis gas preferentially results in χ -Fe₅C₂ formation.[44] Our observations show that the presence of H₂ in the carburizing gas mixture enhances the rate of carburization, which may account for the formation of the carbon-richer $\varepsilon(')$ -carbide phase.

Additional *in situ* Mössbauer spectroscopy measurements were carried out to understand how ϵ (')-carbide formation depended on the presence of H₂. As Fig. 2.7 shows, upon carburization

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without H₂, only a small amount (~22%) of a disordered Fe-carbide phase is formed. The broad signal lines do not allow accurate identification of the formed Fe-carbide. Most likely, these disordered Fe_xC species are a mixture of χ -Fe₅C₂ and ϵ (')-carbide. The Mössbauer data show that Fe-oxides are absent, which can be attributed to the much lower diffusion constant of O in Fe in comparison with C.[21] The introduction of H₂ substantially increases the carburization degree. As a result, a mixture of 19% χ -Fe₅C₂ and 37% ϵ (')-carbide is obtained. The higher carburization degree is consistent with the TPH results. A further increase in the H₂ partial pressure increases the total spectral contribution of the Fe-carbides. The increase is largest for ϵ -Fe₅C₂ is formed and only the spectral contribution of ϵ (')-carbide increases. It was also observed that carburization in a mixture of 8% CO and 16% H₂ leads to more ϵ (')-carbide than carburization in 8% CO (details in Appendix Fig. 2.13, Fig. 2.14 and Appendix Table 2.1, Table 2.2). These results further confirm that the presence of H₂ favors the formation of the carbon-richer ϵ (')-carbide phase.



Figure 2.7. Fe-carbide phase composition as a function of H_2/CO ratio after carburization at 250 °C, 1 bar for 1 h (data obtained from Mössbauer spectra shown in Appendix Fig. 2.14 and Appendix Table 2.2).

Based on the strong correlation between the carburization rate and the H_2 partial pressure, we speculate that the higher C diffusion rate is due to a higher C coverage of the surface. The underlying mechanism for this promotion remains unknown considering the complex nature of the reactions on the surface. This led us to investigate the influence of H_2 on the surface C

and O coverages. The surface reactions involve many elementary reaction steps, some of which are sensitive to the H_2 partial pressure. Among them, H_2 may assist carbide formation in two ways, i.e., by (i) removing O from the surface thus creating vacancies for CO dissociation [45] or (ii) enhancing CO dissociation via H-assisted CO dissociation. According to DFT calculations for the Fe(100) surface, direct CO dissociation is the preferred pathway with only a small contribution of H-assisted pathways. Only on close-packed surfaces such as Fe(110), which are less active in CO dissociation and, thus, contribute less to the total activity, H-assisted routes might also play a role. [46] In addition, Broos et al. reported that CO dissociation proceeds via direct C-O bond scission on the stepped sites on the Fe-carbide surface, while H-assisted CO dissociation is only preferred on surfaces with a large occupancy of subsurface C atoms. [47] As in our case carburization starts from the Cfree metallic Fe surface, direct CO dissociation is expected to be the dominant pathway. As can be appreciated from Fig. 2.5, the C content increases nearly linearly with time on stream (TOS) during the first 40 min both in the presence and absence of H_2 . During this period, the surface will gradually be covered by C. As the carburization rate hardly changes in time, it can be assumed that the mechanism of CO dissociation is not changed dramatically in the initial stage of the reaction and dominated by direct CO dissociation, which is preferred on metallic Fe and carbon-poor Fe surfaces. This conclusion is also in line with the IR results shown above, evidencing that direct CO dissociation can already occur in the absence of H_2 at sub-ambient conditions. Taken together, it is unlikely that H_2 plays an important role in CO dissociation. Therefore, it is reasonable to speculate that enhanced removal of O from the surface accelerates CO dissociation and thus carburization.

To confirm whether H_2 enhances O removal, TPH and XPS were employed to determine the bulk and surface composition as a function of the carburization conditions. In the TPH profiles, the intensities of the H_2O and CH_4 signals were used as respective indicators of the amounts of O and C left on the catalyst after carburization (Appendix Fig 2.12 and Appendix Fig 2.15). These data show that a higher H_2/CO ratio during carburization results in a lower O and a higher C content. The positive effect of H_2 on O removal can also be followed by XPS (Fig. 2.8). Carburization with only CO at 250 °C leads to a Fe²⁺/Fe⁰ ratio of 0.45. In the presence of H_2 ($H_2/CO = 2$), this ratio decreases to 0.18, indicating a lower extent of oxidation. The more metallic nature of the surface in the presence of H_2 goes in parallel with a higher C 1s signal. The C 1s binding energy of the Fe-carbide at 283.1 eV did not very with the C/Fe ratio. These data indicate that H_2 leads to an increased rate of O removal and a higher C coverage implies a larger driving force for C diffusion into bulk Fe, which can explain the higher carburization rate observed with increasing H_2 pressure. This fits with near-ambient-pressure XPS results that indicated that O atoms derived from CO

dissociation can block part of the Fe surface and decrease C diffusion into bulk Fe.[48] A recent report mentioned that pre-deposited C on metallic Fe preferentially leads to $\varepsilon(')$ -carbide formation.[19] This agrees with the finding that a higher C coverage due to the presence of H₂, leads to formation of $\varepsilon(')$ -carbide instead of χ -carbide (Fig. 2.7).



Figure 2.8. *Quasi in situ* XPS spectra of Fe 2p region and C 1s region after carburization at 250 °C at 1 bar for 20 min as a function of H₂/CO ratio.

To better understand the effect of H_2 on the carburization kinetics, additional experiments with varying carburization temperature and H_2/CO ratio were performed. Fig. 2.9 shows Arrhenius plots for the carburization reaction as a function of the H_2/CO ratio. In the absence of H_2 ($H_2/CO = 0$), CO_2 formation is the only pathway for O removal. The similar apparent activation energies of CO_2 formation and carburization (78 and 79 kJ/mol, respectively) suggest that these reactions share the same rate-limiting step. Removal of O is a likely candidate for the rate-limiting step. In the presence of H_2 , O is expected to be removed faster.[49] This is experimentally reflected by the decrease of the apparent activation energy for carburization. The value ranges between 28 and 34 kJ/mol depending on the H_2/CO ratio. These values are close to the apparent activation energy for H_2O formation (31-33 kJ/mol), suggesting that under these conditions H_2O formation is the rate-controlling step in the overall carburization process. The slower removal of O *via* CO_2 formation as compared to H_2O is in line with DFT calculations, which showed that the activation energy for O removal *via* H_2O formation is significantly lower than *via* CO_2 formation. Since the apparent activation energies for carburization are in the same range as the activation energy for O removal independent of the presence of H_2 , it can be inferred that O removal is likely limiting the overall carburization process. As furthermore O removal *via* H₂O is easier than *via* CO₂, H₂ can accelerate the carburization of Fe.

Hydrocarbons were observed in the effluent stream already during carburization. Thus, there is competition for surface C intermediates between hydrocarbon formation and carburization. Comparison of the measured apparent activation energies for these two reactions (Fig. 2.9a and 2.9d) shows that hydrocarbon formation is much more difficult than carburization. In line with this, the overall activation energy for CO consumption is close to the averaged apparent activation energy for H₂O removal is lower than that of hydrocarbon formation under all conditions. Hence, it can be concluded that the predominant role of H₂ is the removal of O and not of C. In summary, increasing the H₂ partial pressure results in faster removal of O, freeing vacancies needed for CO dissociation. This results in a higher C coverage, benefiting the rate of carburization. This is in accordance with the results obtained by *in situ* XRD and Mössbauer spectroscopy.



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Figure 2.9. Kinetic parameters derived from carburization during 40 min at different H_2/CO ratios: (a) accumulation of C in bulk Fe, (b) CO₂ formation, (c) H_2O formation, (d) hydrocarbon formation, and (e) CO consumption.

2.4 Conclusions

The mechanism of the carburization of Raney-Fe used as a model catalyst for Fe FT catalysts was investigated by spectroscopic and temperature-programmed techniques. Carburization of reduced Fe can be divided into two stages: C deposition on the surface and C diffusion into the Fe bulk. *In situ* IR spectroscopy of adsorbed CO verified the high reactivity of metallic Fe towards CO dissociation. Under such conditions, O can be removed as CO₂ and C atoms remain on the surface of reduced Fe. CO-TPR and TPH indicate that the temperature

for overcoming the barrier for C diffusion into the Fe lattice is about 180 °C. The Fe-carbide phase and the rate of its formation depends on the temperature and the composition of the carburizing gas. While at low H₂/CO ratio χ -Fe₅C₂ is formed, $\varepsilon(')$ -carbide is dominant at higher H₂/CO ratio as determined by *in situ* XRD and Mössbauer spectroscopy. H₂ increases the rate of carburization rate, because it accelerated the removal of O *via* H₂O (as opposed to CO₂), regenerating surface vacancies for CO dissociation and thus providing a higher C coverage. The rate of carburization is much faster than the rates of surface hydrogenation reactions of C into hydrocarbons in the early stage of carburization. Intrinsically, all these phenomena stem from the strong Fe-C bond and the low C diffusion barrier. This work sheds light on how bulk C diffusion is affected by surface reactions and how $\varepsilon(')$ -carbide or χ -Fe₅C₂ can be formed by adjusting the carburization conditions.

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Figure 2.10. In situ IR of CO adsorption on reduced Raney-Fe from -170 to 70 °C.



Figure 2.11. TEM image of passivated Raney-Fe.



Figure 2.12. (a) TPH of carburized Raney-Fe at different H_2/CO ratio at 250 °C, 1 bar for 40 mins, (b) C/Fe ratio of carburized Raney-Fe as a function of H_2/CO ratio.



Figure 2.13. *In situ* Mössbauer spectroscopy of Raney-Fe catalyst. (a) Reduced at 20% H₂/Ar, 1 bar, 430 °C for 1 h; (b) Carburized at H₂/CO = 2, 1 bar, 250 °C for 10 min; (c) Carburized at H₂/CO = 2, 1 bar, 250 °C for 30 min; (d) Carburized at H₂/CO = 2, 1 bar, 250 °C for 1 h; (e) Carburized at H₂/CO = 2, 1 bar, 250 °C for 6 h.

Sample treatment	IS (mm/s)	Hyperfi ne field (T)	Г (mm/s)	Phase	Spectral contribution (%)	C/Fe
A. Raney-Fe reduction $H_2/Ar =$ 20%/80% 430 °C, 1 h	0.00	33.8	0.35	Fe ⁰	100	0
B. Raney-Fe carburization CO/H ₂ /Ar = 8%/16%/76 % 250 °C, 10 min.	0.00 0.15 0.18	33.8 26.4 18.5	0.37 0.72 0.72	Fe ⁰ ε-Fe ₂ C (I) ε-Fe ₂ C (II)	73 8 19	0.13
C. Raney-Fe carburization $CO/H_2/Ar =$ 8%/16%/76 % 250 °C, 30 min.	0.00 0.15 0.23 0.19 0.21 0.17 0.18	33.8 26.4 19.0 17.7 24.6 21.4 10.3	$\begin{array}{c} 0.33 \\ 0.46 \\ 0.46 \\ 0.46 \\ 0.43 \\ 0.43 \\ 0.43 \\ 0.43 \end{array}$	Fe ⁰ ϵ -Fe ₂ C (I) ϵ -Fe ₂ C (II) ϵ '-Fe _{2.2} C χ -Fe ₅ C ₂ (I) χ -Fe ₅ C ₂ (II) χ -Fe ₅ C ₂ (III)	45 8 18 13 8 5 3	0.25
D. Raney-Fe carburization CO/H ₂ /Ar = 8%/16%/76 % 250 °C, 1 h	0.00 0.19 0.23 0.22 0.23 0.19 0.18	34.6 27.2 19.4 18.0 25.1 21.3 10.3	$\begin{array}{c} 0.38\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ \end{array}$	$Fe^{0} \\ \epsilon -Fe_{2}C (I) \\ \epsilon -Fe_{2}C (II) \\ \epsilon' -Fe_{2.2}C \\ \chi -Fe_{5}C_{2} (I) \\ \chi -Fe_{5}C_{2} (II) \\ \chi -Fe_{5}C_{2} (III)$	15 11 27 19 13 11 4	0.38
E. Raney-Fe carburization CO/H ₂ /Ar = 8%/16%/76 % 250 °C, 6 h	0.00 0.21 0.23 0.22 0.23 0.17 0.18	33.8 26.1 19.3 17.7 24.1 21.4 10.1	0.30 0.35 0.35 0.39 0.39 0.39 0.39	Fe^{0} ϵ -Fe ₂ C (I) ϵ -Fe ₂ C (II) ϵ '-Fe _{2.2} C χ -Fe ₅ C ₂ (I) χ -Fe ₅ C ₂ (II) χ -Fe ₅ C ₂ (III)	5 12 29 29 12 9 4	0.43

Table 2.1. The Mössbauer fitted parameters of Raney-Fe sample, obtained at -153 °C.

Experimental uncertainties: Isomer shift: IS \pm 0.02 mm/s; Line width: $\Gamma \pm$ 0.03 mm/s; Hyperfine field: \pm 0.1 T; Spectral contribution: \pm 3%.



Figure 2.14. *In situ* Mössbauer spectroscopy of Raney-Fe catalyst. (a) Reduced at 20% H₂/Ar, 1 bar, 430 °C for 1 h; (b) Carburized at H₂/CO = 0, 1 bar, 250 °C for 1 h; (c) Carburized at H₂/CO = 1, 1 bar, 250 °C for 1 h; (d) Carburized at H₂/CO = 2, 1 bar, 250 °C for 1 h; (e) Carburized at H₂/CO = 8, 1 bar, 250 °C for 1 h; (f) Carburized at H₂/CO = 0, 1 bar, 250 °C for 24 h.

Sample treatment	IS (mm/s)	Hyperfin e field (T)	Г (mm/s)	Phase	Spectra l contrib ution (%)	ε(')-carbide /χ-Fe5C2
A. Raney-Fe reduction $H_2/Ar =$ 20%/80% 430 °C, 1 h	0.00	34.5	0.36	Fe ⁰	100	-
B. Raney-Fe carburization CO/Ar = 8%/92% 250 °C, 1 h	0.00 0.20 0.25	34.4 26.3 18.9	0.35 0.72 0.72	Fe ⁰ Fe _x C (I) Fe _x C (II)	78 9 13	-
C. Raney-Fe carburization CO/H ₂ /Ar = 8%/4%/88% 250 °C, 1 h	0.00 0.17 0.23 0.23 0.21 0.19 0.18	34.6 27.4 19.6 18.0 25.3 21.5 10.3	$\begin{array}{c} 0.38\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ \end{array}$	Fe^{0} ϵ -Fe ₂ C (I) ϵ -Fe ₂ C (II) ϵ '-Fe _{2.2} C χ -Fe ₅ C ₂ (I) χ -Fe ₅ C ₂ (II) χ -Fe ₅ C ₂ (III)	44 7 15 15 9 7 3	1.9
D. Raney-Fe carburization CO/H ₂ /Ar = 8%/16%/76 % 250 °C, 1 h	$\begin{array}{c} 0.00\\ 0.19\\ 0.23\\ 0.22\\ 0.23\\ 0.19\\ 0.18\end{array}$	34.6 27.2 19.4 18.0 25.1 21.3 10.3	$\begin{array}{c} 0.38\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ 0.41\\ \end{array}$	$\begin{array}{c} Fe^{0} \\ \hline e -Fe_{2}C (I) \\ \hline e -Fe_{2}C (II) \\ \hline e' -Fe_{2.2}C \\ \chi -Fe_{5}C_{2} (I) \\ \chi -Fe_{5}C_{2} (II) \\ \chi -Fe_{5}C_{2} (III) \end{array}$	15 11 27 19 13 11 4	2.0
E. Raney-Fe carburization CO/H ₂ /Ar = 8%/64%/28 % 250 °C, 1 h	$\begin{array}{c} 0.00 \\ 0.20 \\ 0.23 \\ 0.22 \\ 0.22 \\ 0.19 \\ 0.22 \end{array}$	34.7 26.5 19.5 18.0 24.4 21.1 11.2	$\begin{array}{c} 0.45\\ 0.39\\ 0.39\\ 0.39\\ 0.39\\ 0.39\\ 0.39\\ 0.39\\ 0.39\\ 0.39\end{array}$	Fe^{0} ϵ -Fe ₂ C (I) ϵ -Fe ₂ C (II) ϵ '-Fe ₅ C ₂ (I) χ -Fe ₅ C ₂ (I) χ -Fe ₅ C ₂ (II) χ -Fe ₅ C ₂ (II)	3 13 31 26 12 11 4	2.6
F. Raney-Fe carburization CO/H ₂ /Ar = 8%/16%/76 % 250 °C, 6 h	0.00 0.21 0.23 0.22 0.23 0.17	33.8 26.1 19.3 17.7 24.1 21.4	0.30 0.35 0.35 0.39 0.39 0.39	Fe^{0} ϵ -Fe ₂ C (I) ϵ -Fe ₂ C (II) ϵ '-Fe _{2.2} C χ -Fe ₅ C ₂ (I) χ -Fe ₅ C ₂ (II)	5 12 29 29 12 9	2.8

Table 2.2. Fit parameters of the Mössbauer spectra (spectra recorded at -153 °C).

0.1810.10.39 χ -Fe ₅ C ₂ (III)4G. Raney-Fe0.0034.30.38Fe ⁰ 4carburization0.1526.00.37 ϵ -Fe ₂ C (I)6							
G. Raney-Fe0.0034.30.38 Fe^0 4carburization0.1526.00.37 ϵ -Fe ₂ C (I)6	0.1		0.18 10	.1 0.39	χ -Fe ₅ C ₂ (III)	4	
carburization 0.15 26.0 0.37 ϵ -Fe ₂ C (I) 6	-Fe 0.0	. Raney-Fe	e 0.00 34	.3 0.38	Fe^0	4	
	tion 0.1	arburizatio	on 0.15 26	.0 0.37	ϵ -Fe ₂ C (I)	6	
$CO/Ar = 0.20$ 19.9 0.37 ϵ -Fe ₂ C (II) 19	0.2	O/Ar =	0.20 19	.9 0.37	ϵ -Fe ₂ C (II)	19	
8%/92% 0.23 18.2 0.37 ε'-Fe _{2.2} C 33 1.5	0.2	%/92%	0.23 18	.2 0.37	€'-Fe _{2.2} C	33	1.5
250 °C, 24 h 0.26 24.7 0.37 χ-Fe ₅ C ₂ (I) 15	4 h 0.2	50 °C, 24 h	n 0.26 24	.7 0.37	χ -Fe ₅ C ₂ (I)	15	
0.17 21.4 0.37 χ -Fe ₅ C ₂ (II) 15	0.1		0.17 21	.4 0.37	χ -Fe ₅ C ₂ (II)	15	
0.18 13.8 0.37 χ -Fe ₅ C ₂ (III) 8	0.1		0.18 13	.8 0.37	χ -Fe ₅ C ₂ (III)	8	

Experimental uncertainties: Isomer shift: IS \pm 0.02 mm/s; Line width: $\Gamma \pm$ 0.03 mm/s; Hyperfine field: \pm 0.1 T; Spectral contribution: \pm 3%.



Figure 2.15. H_2O evolution during TPH after carburization with different H_2/CO at 250 °C, 1 bar for 40 mins.

Chapter 3

An isotopic exchange study on the kinetics of Fe carburization and the mechanism of the Fischer-Tropsch reaction

Abstract

The kinetics of the transformation of metallic Fe to the active Fe-carbide phase at the start of the Fischer-Tropsch (FT) reaction were studied. The diffusion rates of C atoms going in or out of the lattice were determined using ¹³C-labelled synthesis gas in combination with measurements of the transient ¹²C and ¹³C content in the carbide by temperature-programmed hydrogenation. In the initial 20 minutes, C diffuses rapidly into the lattice occupying thermodynamically very stable interstitial sites. The FT reaction starts already during these early stages of carburization. When reaching steady state, the diffusion rates of C in and out of the lattice converge and the FT reaction continues *via* two parallel reaction mechanisms. It appears that the two outer layers of the Fe-carbide are involved in hydrocarbon formation *via* a slow Mars-Van Krevelen-like reaction contributing to ~10% of the total activity, while the remainder of the activity stems from a fast Langmuir-Hinshelwood reaction occurring over a minor part of the catalyst surface.



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3.1 Introduction

Since the invention of the Fischer-Tropsch (FT) process, Fe-based catalysts have been studied intensively.[1] They are used in commercial plants by Sasol in South Africa and Shenhua in China,[2] mainly because of their ability to convert coal-derived synthesis gas with a relatively low H₂/CO ratio. As active Fe catalysts typically contain Fe-carbides as well Fe-oxides and metallic Fe,[3] many studies have dealt with the changes in the catalyst composition during the FT reaction aiming at resolving the nature of the active phase.[4, 5] Nowadays, Fe-carbides are generally considered to be the active ingredient of Fe-based FT catalysts.[6-9] Among these, $\varepsilon(')$ -carbide, χ -Fe₅C₂ and Θ -Fe₃C are typically formed under FT process conditions.[10-13]

Because of their pyrophoric character, Fe-carbides are commonly synthesized *in situ* prior to or during the FT reaction. Typically, synthesis gas is used for the conversion of Fe-oxide precursor to Fe-carbides. Despite the importance of Fe-carbides for the FT reaction, relatively little is known about the kinetics and mechanism of carbide formation. This is especially important when trying to identify correlations between catalyst activation, which mainly involves Fe carburization, and the FT reaction. An early experimental study of Fe carburization relevant to FT synthesis by Niemantsverdriet and Van der Kraan [6] showed that the FT activity correlated with bulk Fe-carbide formation. It has been widely reported that during catalyst activation hydrocarbons can already be formed. While initially most C derived from CO dissociation is consumed by the carburization process, C hydrogenation to gaseous products becomes more dominant when the bulk of the active phase is saturated by C.[14] Thus, the formation of adsorbed C species by CO dissociation is relevant to both the carburization and FT reaction.

Once the active Fe-carbide is formed, CH_x intermediates are assumed to be formed on the surface. Chain growth is assumed to proceed *via* the insertion of CH_x monomer into the carbon-metal bond of a growing chain.[15] This mechanism, known as the carbide mechanism, has been proposed by Fischer and Tropsch in 1926 [1] and is supported by various experiments.[16-18] The rupture of a carbon-metal bond in the carbide mechanism shows some similarities with the removal of C from the carbide lattice as occurs in the Mars-Van Krevelen (MvK) mechanism, which has initially been described for oxidation catalysis.[19] In this mechanism, atoms of the surface lattice are directly involved in the catalytic cycle and replenished by reactants from the gas phase. A possible FT reaction path following the MvK mechanism on a C-saturated Fe-carbide surface was theoretically proposed by Niemantsverdriet and co-workers.[20] Their hypothesis entails the hydrogenation of a lattice carbide C, resulting in the formation of a surface vacancy where a

CO molecule from the gas phase can dissociate. This mechanistic cycle is different from the Langmuir-Hinshelwood (L-H) mechanism, in which the reaction occurs between neighboring adsorbed C species, and which is normally used to describe the FT reaction on Co and Ru catalysts. Theoretically, both L-H and MvK mechanisms can occur on Fe-carbide.

The involvement of C atoms of the carbide surface as reaction intermediates in the FT reaction *via* an MvK mechanism has amongst others been investigated by using isotopic labeling experiments. For instance, Kummer *et al.*[21] partially carburized a catalyst with ¹²CO followed by complete carburization with radioactive ¹⁴CO, leading to a ¹⁴C-enirched surface. By carrying out the FT reaction in a ¹²CO/H₂ mixture, it was found that the hydrocarbons produced at 260 °C contained only 10% ¹⁴C as established by measuring their radioactivity. This led to the conclusion that lattice C atoms do not play a major role in hydrocarbons formation. A similar approach was taken by Ordomsky *et al.*,[22] who also found that Fe-carbide did not participate appreciably in the FT reaction.

However, all these studies were performed using catalysts containing a mixture of Fe metal, Fe-carbides, and Fe-oxides. By solely analyzing the gas-phase composition, the role of each separate iron compound in the FT synthesis cannot be discerned. Hence, it remains elusive if and to which extent C atoms in the FT products originate from the Fe-carbide lattice via an MvK mechanism or from adsorbed CO via an L-H mechanism. Therefore, a model Raney-Fe catalyst, which contains no oxidic Fe phases, was used in this study. A concomitant advantage of using pure metallic Fe is that the carburization could be studied without the interference of an oxidic Fe phase.[23] Compared to earlier works that only analyzed the gasphase composition, [21, 22] we also studied changes in the Fe-carbide composition, enabling an accurate demonstration of the existence of any C exchange between lattice and the gas phase. The possible occurrence of either an MvK or an L-H mechanism in the FT reaction was studied by quantifying the occurrence of C exchange followed by comparison of the FT reaction rate with the rates of C diffusing in and out of the carbide lattice, which were determined by using ¹³C-labelled synthesis gas in combination with analysis of the transient (labelled) C content of the Fe-carbide by temperature programmed hydrogenation. Subsequently, steady state isotopic transient kinetic analysis (SSITKA) was used to verify the existence of multiple parallel routes and to determine the corresponding reaction rates.

3.2 Experimental methods

Preparation

Raney-Fe was prepared from an aluminum-iron (Al50/Fe50) alloy (Goodfellow, 150-micron powder). To remove aluminum, 5 g alloy powder was slowly added to 25 mL 9 M KOH solution (Sigma-Aldrich) under stirring at 70 °C for 40 min. The suspension was washed with

water and ethanol 7 times each to remove potassium and aluminum ions and retrieve the Raney-Fe. Leaching aluminum results in a porous structure with a higher surface area than the initial powder. The as-prepared porous Fe powder was transferred into a sealable quartz tube. Due to the pyrophoric character of the fine Fe powder, the catalyst was passivated in a 1% O₂/He flow for 24 h at room temperature for safe handling. According to ICP-OES (Spectroblue, AMETAK) measurements, the weight composition of the passivated sample was as follows Fe/Al/O = 85/4/11. Earlier work has shown that Al left behind after Raney-Fe synthesis has no strong influence on Fe carburization.[23] The volume-weighted average size of the passivated Raney-Fe particles was measured on a FEI Tecnai 20 microscope. The average size was 29 ± 2 nm, corresponding, assuming spherical nanoparticles, to a dispersion of 3.5% and a specific surface area of $26.3 \text{ m}^2 \text{ g}^{-1}$.

Pretreatment and characterization

The reducibility of the as-prepared Raney-Fe was determined by temperature-programmed hydrogenation (H₂-TPR) using a Micromeritics AutoChem II setup. An amount of 30 mg sample was loaded into a quartz U-tube between two quartz wool layers. The sample was pretreated at 100 °C for 1 h in a He flow of 50 mL/min before the measurements. The TPR profile was recorded by heating the sample from 40 to 800 °C at the rate of 10 °C/min in a 4 vol % H₂ in a He flow of 50 mL/min.

Ar physisorption (ASAP 2020, Micromeritics) was carried out to determine the surface area of the unsupported precursor and activated catalyst. Typically, 200 mg sample was treated separately in a sealable reactor, followed by transfer into a sealable measurement tube in a glove box. Prior to measurements, a reduction was performed at 430 °C in H₂ for 1 h (20% H₂ in Ar, 50 ml/min, 1 bar), followed by carburization at 250 °C in H₂/CO for 40 min (8% CO + 16% H₂ in Ar, 50 ml/min, 1 bar). The surface areas of the passivated, reduced, and carburized samples are 30 ± 6 m² g⁻¹, 31 ± 5 m² g⁻¹ and 29 ± 5 m² g⁻¹, respectively. The surface area of the passivated catalyst corresponds to the average particle size determined by TEM analysis. Moreover, these data show that there is no sintering of the Raney-Fe precursor particles during reduction and carburization.

The number of active sites per gram of the catalyst was determined by CO chemisorption (ASAP 2010, Micromeritics). The same pretreatment procedure was applied as for the Ar physisorption measurements. Since it can be expected that part of the surface will still contain adsorbed CO upon carburization, the sample was exposed to a H₂ flow at 250 °C for 10 min (20% H₂ in Ar, 50 ml/min, 1 bar) to remove adsorbed CO. CO chemisorption measurements were conducted at 30 °C. The adsorbed amounts on reduced and carburized catalysts are 0.12 mmol/g and 0.015 mmol/g, respectively. Thus, about 12% of the surface of the carburized

sample can adsorb CO.

Transmission ⁵⁷Fe Mössbauer spectra were collected at 120 K and 300 K with a sinusoidal velocity spectrometer using a ⁵⁷Co (Rh) source. Velocity calibration was carried out using an α -Fe foil at room temperature. The source and the absorbing samples were kept at the same temperature during the measurements. The Mössbauer spectra were fitted using the Mosswinn 4.0 software. Carburization experiments were performed in a high-pressure Mössbauer *in situ* cell. The high-pressure beryllium windows used in this cell contain 0.08% Fe, whose spectral contribution was removed from the final spectra.

Carburization and isotopic transient experiments

The carburization and the FT reactions were studied in a previously described setup,[24] in which synthesis gas feeds containing either ¹³CO (99.30% ¹³C, Eurisotop) or ¹²CO (>99.997% with 1.1% ¹³C natural abundance, Linde) could easily be interchanged at constant reaction conditions. For each test, 100 mg Raney-Fe diluted by SiC was loaded. The catalyst was first reduced at 430 °C in H₂ for 1 h (20% H₂ in Ar, 50 ml/min, 1.5 bar), followed by cooling to 250 °C and subsequently carburized for varying times in synthesis gas (8% CO + 16% H₂ in Ar, 50 ml/min, 1.5 bar). The gas-phase effluent was analyzed by an online gas chromatograph (GC, Thermo Fischer Scientific Trace GC 1300 equipped with a Trace 1310 Auxiliary Oven). A combination of an MXT-QBond column (60 m × 0.53 mm) with a thermal conductivity detector was used to determine the concentrations of CO₂, CO, H₂ and CH₄, while a combination of a Rt-SilicaBond column (60 m × 0.32 mm) with a flame ionization detector was used to analyze hydrocarbons.

Temperature-programmed hydrogenation (TPH) performed in the same setup was used to determine the C content of carburized catalysts. After carburization, the catalyst was flushed in Ar and cooled to room temperature. TPH was conducted by heating the reactor to 630 °C at a rate of 5 °C/min in a diluted H₂ flow (20% H₂ in Ar, 50 ml/min, 1.5 bar). During TPH, the main hydrocarbon product was CH₄ (> 96 %). The CH₄ flow rate was monitored continuously by online MS (ESS Catalysys). A GC taking sample at regular intervals was used to calibrate the MS signal. The carburization degree (C/Fe ratio) were calculated based on the absolute amount of CH₄ evolved during the TPH.

The C exchange of Fe-carbide in time was investigated by transient operation, involving switches between ${}^{13}CO/H_2$ and ${}^{12}CO/H_2$ followed by TPH measurements. The protocol for these measurements is shown in Scheme 3.1. In a first reference experiment, the catalyst was exposed to ${}^{13}CO/H_2$ (8% ${}^{13}CO + 16\%$ H₂ in Ar, 50 ml/min, 1.5 bar) at 250 °C for 1 h. Afterwards, TPH was conducted. Subsequently, the catalyst was exposed to the same treatment with the same labeled synthesis gas mixture for 1 h, followed by a switch to

¹²CO/H₂ with varying exposure time (1-5 h). The switch between ¹³C and ¹²C labelled synthesis gas does not chemically alter the reaction, because pressure and flow rate were kept the same. Then, a TPH analysis was applied to determine the C/Fe and ¹²C/¹³C ratios of the carburized samples. The ¹²C/¹³C ratio was determined by online MS. Due to the overlap of signals of fragmented species and the presence of isotopic impurities in the feed gas, the MS signals were corrected by performing reference experiments using only ¹²CO and ¹³CO.



Scheme 3.1. Schematic representation of isotopic transient experiment in which carburization is divided into blocks of 1 h in either ${}^{13}CO/H_2$ (pink) or ${}^{12}CO/H_2$ (blue). The experiments were performed with varying time of ${}^{12}CO/H_2$ exposure (blue blocks) after 1 h exposure to ${}^{13}CO/H_2$ (pink block).

To determine the rate of C exchange in Fe-carbide, a second set of experiments according to Scheme 3.2 was performed. In the first set of reference experiments, the catalysts were exposed to ${}^{12}CO/H_2$ (8% ${}^{12}CO + 16\%$ H₂ in Ar, 50 ml/min, 1.5 bar) at 250 °C for varying times (0.33-5 h). Afterwards, TPH was conducted. In subsequent experiments, the catalyst was exposed to the same treatment with unlabeled synthesis gas for varying times, followed by a switch to ${}^{13}CO/H_2$ for 1 h. Again, TPH analysis was employed to determine the C/Fe and ${}^{12}C/{}^{13}C$ ratios of the carburized samples.

To determine the decarburization rate in Fe-carbide, a third set of experiments was performed. The catalyst was first exposed to ${}^{12}CO/H_2$ (8% CO + 16% H₂ in Ar, 50 ml/min, 1.5 bar) at 250 °C for 5 h, followed by a switch to ${}^{13}CO/H_2$ for 1 h. Then, the fed was switched to H₂ (16% H₂ in Ar, 50 ml/min, 1.5 bar) for different times, followed by a TPH measurement to determine C/Fe and ${}^{12}C/{}^{13}C$ ratios of the decarburized sample.



Scheme 3.2. Schematic representation of isotopic transient experiment in which carburization is divided into blocks of 1 h in either ${}^{13}CO/H_2$ (pink) or ${}^{12}CO/H_2$ (blue). The experiments were performed with varying time of ${}^{12}CO/H_2$ exposure (blue blocks) preceding 1 h exposure to ${}^{13}CO/H_2$ (pink block).

3.3 Results and discussion

Carburization kinetics

The H₂-TPR profile of as-prepared Raney-Fe contains a single reduction feature at \sim 390 °C (Appendix Fig. 3.8). This feature is due to the reduction of the Fe-oxide layer on air-exposed Raney-Fe to metallic Fe. Based on this, a temperature of 430 °C was used for complete reduction of the Raney-Fe precursor in diluted H₂. Reduced Raney-Fe was carburized and subjected to TPH characterization according to Scheme 3.1. In Fig. 3.1, we compare three TPH profiles of Raney-Fe carburized according to the following protocols (i) 1 h in 13 CO/H₂. (ii) 1 h in ${}^{13}CO/H_2 + 1$ h in ${}^{12}CO/H_2$ and (iii) 1 h in ${}^{13}CO/H_2 + 2$ h in ${}^{12}CO/H_2$. The CH₄ formation peak maximum shifts to higher temperature with increasing carburization time, pointing to a lower reactivity of C atoms in Fe-carbide with increasing carburization degree. Compared to carburization in ¹³CO/H₂ for 1 h, additional carburization in ¹²CO/H₂ for 1 h and 2 h results in a comparatively small amount of ¹²CH₄. This implies that a high carburization degree is already achieved in the first hour of carburization. The C content of in situ formed Fe-carbide as determined by TPH is shown in Fig. 3.2. The evolution of the C/Fe ratio with carburization time is very similar to the results in our previous work.[25] We also used Mössbauer spectroscopy to study the phase composition of Raney-Fe as a function of the duration of carburization under similar conditions. Mössbauer spectra were recorded at -153 °C to determine the relative contributions of the various Fe species. The resulting spectra are shown in Appendix Fig. 2.13, the fit results in Appendix Table 2.1. The excellent agreement between the results from TPH and Mössbauer spectroscopy demonstrates that TPH is suitable to measure the C content of *in situ* formed Fe-carbides.



Figure 3.1. TPH profiles of the samples carburized for 1 h in 13 CO/H₂ (blue), carburized for 1 h in 13 CO/H₂ followed by 12 CO/H₂ for 1 h (red), and carburized for 1 h in 13 CO/H₂ followed by 12 CO/H₂ for 2 h (green).



Figure 3.2. C/Fe ratio of carburized Raney-Fe as a function of carburization time as derived from TPH (red squares) and Mössbauer spectroscopy (blue dots).

As shown in Fig. 3.2, the C/Fe ratio is 0.37 after 1 h carburization, corresponding to 88% of the final C/Fe ratio (0.42). While the C/Fe ratio is already 0.4 after 2 h, it takes another 3 h to increase the C/Fe ratio from 0.4 to 0.42. As can be deduced from Appendix Table 2.1, Mössbauer spectroscopy shows that the reduction step preceding the carburization results in the complete reduction of the precursor to metallic Fe. After 10 min carburization, 27% metallic Fe is converted to $\varepsilon(')$ -carbide. After 30 min, 16% χ -carbide and 39% $\varepsilon(')$ -carbide are formed. After 6 h, Fe is nearly fully carburized with only 5% metallic Fe (Fe⁰) left. This sample contains 70% $\varepsilon(')$ -carbide and 25% χ -Fe₅C₂. Under these carburization conditions, $\varepsilon(')$ -carbide is more stable than χ -Fe₅C₂ as reported before.[25] Notably, no Fe-oxides are observed during the carburization process, which indicates that O removal from the surface as either H₂O or CO₂ is fast compared to C removal. In the following, we refer to all $\varepsilon(')$ - and χ -Fe₅C₂ phases collectively as Fe-carbides.

Lattice C exchange

A possible involvement of an MvK mechanism in the FT reaction implies the participation of one or more of the top layers of the catalytic surface in C hydrogenation and coupling reactions. This can be investigated by considering that C vacancies will be occupied by C derived from CO dissociation. We studied the exchange of lattice C by exposure of the Raney-Fe sample to ¹³CO/H₂ and ¹²CO/H₂ mixtures for varying times according to Scheme 3.1, followed by TPH measurements to determine the total amount of C as well as the isotopic ¹²C/¹³C distribution. Fig. 3.3a shows the ¹²C/Fe and ¹³C/Fe ratios for two experiments involving exposure of Raney-Fe to (i) a ¹³CO/H₂ mixture for 1 h and (ii) a ¹³CO/H₂ mixture for 1 h followed by exposure to a ${}^{12}CO/H_2$ mixture for 1 h. By comparing the total C/Fe, ¹²C/Fe and ¹³C/Fe ratios, we can determine how much C was deposited in the first hour and how much ¹³C was exchanged in the second hour. In this way, the amount of C removed from the Fe-carbide (C_{out}) can be determined, which is defined as the difference between the amount of ${}^{13}C$ present in the sample after the original exposure to ${}^{13}CO/H_2$ for 1 h and the amount of ¹³C left after exposure to ¹²CO/H₂. C_{net} is the difference between the total amounts of C between the two experiments. C_{in} is the sum of C_{out} and C_{net} and represents the net amount of ¹²C accumulated during the exposure to ¹²CO/H₂. In theory, the amount of C exchanged could be higher than determined in this way, because the replacement of ${}^{13}C$ in carbide by ¹³CO still present in the gas phase after the switch is not taken into account. The error due to the replacement of the gas phase during the switch is however very low, because ¹³CO gas in the reactor is entirely replaced by ¹²CO within 5 s after the switch (Appendix Fig. 3.9).



Figure 3.3. The C/Fe ratio of carburized samples. (a) The samples carburized with 1 h 13 CO/H₂ followed by 1 h 12 CO/H₂. (b) The samples carburized with 1 h 13 CO/H₂ followed by *x* h 12 CO/H₂ (*x* varies from 0-5).

Fig. 3.3b shows the results of experiments where an initial exposure to ${}^{13}CO/H_2$ for 1 h was followed by exposure to ${}^{12}CO/H_2$ for longer times. The total C/Fe ratios derived from these experiments agree with those shown in Fig. 3.2. After 2 h carburization, the total C/Fe ratio is 0.4, indicating nearly complete carburization. In the period between 1 h and 2 h, the contribution of ¹³C decreases from 0.37 to 0.34. A rough estimation based on the amount of C exchanged (7%) and the dispersion of Raney-Fe (3.5%) indicates that the first two layers are involved in C exchange events, hinting at the involvement of an MvK-like mechanism. To determine how ¹³C was extracted from the carbide, the gas-phase composition was monitored directly after the switch (Appendix Fig. 3.9). The instantaneous drop of the 13 CO and ${}^{13}CO_2$ signals in parallel with the inert implies that CO hardly interacts with the carbide and is not responsible for the removal of 13 C. On the other hand, the slow decay of the 13 CH₄ signal shows that ¹³C from lattice position is removed by hydrogenation to CH₄. Prolonging the ${}^{12}CO/H_2$ carburization time to 5 h yields a nearly fully carburized sample (C/Fe = 0.42) and results in a nearly twofold increase of the amount of exchanged ¹³C, evidencing that C atoms deeper into the bulk can be exchanged. Fig. 3.3b shows that the exchange rate slows down with carburization degree but does not vanish. This points to a slow but continuous involvement of C atoms of the Fe-carbide in the FT reaction *via* an MvK mechanism.

Mössbauer spectroscopy can be used to determine the overall C/Fe ratio based on the relative contributions of the main bulk Fe-carbide phases. The C/Fe ratio can also be determined by TPH analysis. It can be expected that the C/Fe ratio determined by TPH is higher than the

ratio determined by Mössbauer spectroscopy, because the former technique also titrates surface adsorbed carbonaceous species. The close agreement between the two methods indicates that the contribution of surface adsorbed species to the overall C/Fe ratio is minor. Adsorbed species can play a role in the exchange of C atoms from the bulk Fe-carbide with the gas phase. To understand this aspect in more detail, the TPH profiles were deconvoluted into separate contributions for surface C and bulk C. This is possible, because during TPH different carbon-containing intermediates are hydrogenated at specific temperatures, viz., in order of decreasing reactivity (i) adsorbed carbon-containing species and surface carbide, (ii) bulk C, and (iii) graphitic C.[26] The TPH results present contain distinct features. The one observed at the lowest temperature is ascribed to surface C species, while the second feature in the range between 380 and 480 °C can be related to bulk C, which includes all lattice C atoms in the inner layers of the Fe-carbide. The absence of a clear peak above 500 °C indicates that there is not much graphitic C present. The TPH profiles of ¹²CH₄ and ¹³CH₄ for an experiment involving varying ${}^{12}CO/H_2$ exposure times (1-5 h) after a preceding 1 h 13 CO/H₂ carburization step are displayed in Appendix Fig. 3.10a and 3.10b. As expected, the increase in the amount of ${}^{12}CH_4$ with reaction time (Appendix Fig. 3.10a) goes at the expense of the amount ¹³CH₄ (Appendix Fig. 3.10b), consistent with an MvK mechanism. To distinguish the contribution of surface C and bulk C in the C exchange, the TPH profiles of 12 CH₄ and 13 CH₄ were deconvoluted (Appendix Fig. 3.11). The profiles of the experiments involving 0 h and 1 h of exposure to ¹²CO/H₂ could be fitted by two features that are due to hydrogenation of surface and bulk C species. Prolonged exposure to ¹²CO/H₂ required fitting with three peaks, namely surface C and two bulk C features, the latter two denoted by C1 and C_2 . The nature of these two bulk carbide species remains unknown. We tentatively ascribe C1 to a Fe-carbide that features moderate hydrogenation ability and the smaller C2 peak to Fe-carbide whose hydrogenation is hindered by oligomeric C or a very small amount of graphitic C.

Fig. 3.4 summarizes the results of the TPH analyses in which the ¹²C and ¹³C contributions to bulk C (Fig. 3.4a) and surface C (Fig. 3.4b) of the Fe-carbide are differentiated. The amount of bulk ¹³C declines with prolonged ¹²CO exposure, implying that C from the carbide lattice can be exchanged. Simultaneously, the contribution of bulk ¹²C gradually increases as more ¹²C from the gas phase enters the bulk of Fe-carbide. As the total amount of bulk C also increases, ¹²C does not only replace ¹³C but also increases the C content of the Fe-carbide. It should be noted that ¹³C atoms that are exchanged by ¹²C leave the bulk by passing through the surface layer. Fig. 3.4b displays the isotopic composition of the surface C layer. ¹²C is built up on the surface when the sample is exposed longer to ¹²CO. This points to the accumulation of surface C species. The nearly constant ¹³C content of the surface suggests

that the surface C species formed during the first hour of exposure to 13 CO are replenished by 13 C from the bulk. These observations highlight the dynamic behavior of C both at the surface and in the bulk of Fe-carbide. Contrary to the theory that anticipates bulk C is a spectator in the FT reaction,[27] our results strongly indicate surface C can be supplied by the outward diffusion of bulk C.



Figure 3.4. The ¹³C/Fe and ¹²C/Fe distribution in the bulk (a) and surface (b) of Fe-carbide as a function of exposure time to 12 CO/H₂ following exposure for 1 h to 13 CO/H₂.

C exchange and diffusion rates

The experiments presented in Fig. 3.3 and 3.4a reveal that C atoms from the carbide bulk can be exchanged by C atoms from gas-phase CO. However, no detailed information about the rate of this exchange is obtained from these experiments. Therefore, we set up another series of experiments, where the catalysts were first treated in ${}^{12}CO/H_2$ for periods of 0.33-5 h followed by exposure to ${}^{13}CO/H_2$ for 1 h (Scheme 3.2). For comparison, the catalysts were also only treated in ${}^{12}CO/H_2$ for the same periods without subsequent exposure to the labeled synthesis gas mixture. The total C/Fe ratios determined by TPH before as well as after 1 h exposure to 13 CO/H₂ are shown in Fig. 3.5a. The reaction rate of lattice C atoms leaving and entering the catalyst in 1 h, respectively denoted as rout and rin, can now be derived by dividing the amounts C_{in} and C_{out} by the exposure time to ${}^{13}CO/H_2(1 h)$. Fig. 3.5b shows the difference between these two rates, which is the net carburization rate (r_{net}), as a function of the ¹²CO/H₂ carburization treatment. The figure also includes the evolution of the total C/Fe ratio. The carbide formation rate based on the derivative of the total C content as a function of carburization time is also shown in Fig. 3.5b and matches well the values of r_{net} derived from the isotopic measurements. r_{in} decreases rapidly with time on stream from the very beginning. At the same time, rout slowly increases. After about 6 h, an equilibrium is reached where rin and r_{out} converge to the same value, representing the stage that the catalyst attains its final

C/Fe ratio under the given conditions. The fact that r_{in} is much higher than r_{out} at the early stage of carburization indicates that, at this stage, practically all C atoms entering the catalyst migrates to lattice position. This inhibits C exchange reactions. At later stages of the carburization process, r_{in} and r_{out} converge expectedly.

To better understand the early stages of carburization, additional experiments were performed at a shorter time scale. For this purpose, the catalyst was carburized for only 20 min by $^{13}CO/H_2$ preceding a switch to $^{12}CO/H_2$. The results presented in Appendix Fig. 3.12 show that C atoms entering the catalyst during the initial 20 min cannot be replaced by C atoms entering later, even after extending the exposure time to 100 min. Clearly, the C atoms entering the fresh Fe catalyst in the first 20 min (about 50% of the saturated C concentration in Fe-carbide) are bound very tightly to the lattice. This contrasts with the results shown in Fig. 3.3, which show that, after 1 h carburization, nearly 85% of the maximum C/Fe ratio is reached. About 7% of these C atoms, which is equivalent to the first two layers, can be exchanged during the following 1 h exposure to $^{12}CO/H_2$. After 6 h carburization when the catalyst is fully carburized, approximately 5% C can be exchanged within 1 h (Fig. 3.5b). In conclusion, all the C atoms that diffuse into the Fe in the first 20 min cannot be exchanged. This suggests that C diffuses to energetically stable interstitial sites. C atoms entering at a later stage occupy less stable positions, allowing for facile exchange.



Figure 3.5. Isotope compositions change and carburization rates of experiments following Scheme 3.2: carburization by ${}^{12}CO/H_2$ for varying times, followed by 1 h ${}^{13}CO/H_2$ (a) the isotope composition, represented by the colored areas and the C/Fe ratio after ${}^{12}CO/H_2$ exposure only (middle black line). (b) evolution of total C/Fe ratio (squares), carbide formation rate based on the derivative of the C/Fe ratio (black curve), carbon entering rate (downward triangles), carbon leaving rate (upward triangles) and the net accumulation rate

 r_{net} (circles) as a function of time on stream in the carburization process (8% CO + 16% H₂, 250 °C).

To study the decarburization rate, the following transient experiment was performed: a reduced Fe catalyst was fully carburized in ¹²CO/H₂ for 5 h, followed by a 1 h treatment with 13 CO/H₂. TPH analysis showed that the carburized catalyst contained 95% 12 C and 5% 13 C. As the last hour of carburization was conducted in 13 CO/H₂, it can be expected that the 13 C atoms predominantly reside in the top layers, while the ¹²C sits atoms mostly occupy the bulk. This is confirmed by ¹³CH₄ and ¹²CH₄ TPH analyses shown in Appendix Fig. 3.13. After 6 h carburization, an abrupt switch was made to a flow containing only H_2 . The remaining amounts of ¹²C and ¹³C in the Fe-carbide were followed in time by TPH analysis. The respective decarburization rates were determined by calculating the derivatives of the ¹²C, ¹³C, and total C amounts as a function of decarburization time. The resulting rates are presented in Fig. 3.6 together with the decay in the total C/Fe ratio. Notably, the initial overall decarburization rate at the start of the decarburization is approximately equal to r_{out} at the end of the carburization experiment shown in Fig. 3.5b, amounting to $1.8 \cdot 10^{-4}$ mol C/mol Fe_{surface} s⁻¹. Both rates represent the rate of C removal after 6 h carburization. Even though the rates are obtained in different gas atmospheres, they are nearly equal, which suggests that the ratelimiting step in the decarburization process is independent of the gas-phase composition and, consequently, the surface coverage. A possible explanation for this is that the slow step in the overall decarburization process is the migration of C from interstitial sites to sites close to the surface. It takes 95 h to remove 86% of the C in the carbide, while introducing this amount of C in reduced Raney-Fe at the same temperature takes only 1 h. This difference reflects the high thermodynamic stability of C in the Fe-carbide lattice, leading to a lower overall activation barrier for carburization than for the reverse decarburization process. It should be noted that, in order to take part in the FT reaction via an MvK mechanism, a C atom has to leave the Fe-carbide lattice. As can be seen in Fig. 3.6, the overall decarburization rate slows quickly at the start and gradually afterwards. The high rate at the beginning can be ascribed to fast removal of ¹³C atoms that are located in the outermost layers of the Fe-carbide particles. After the fast decay, the overall C removal rate overlaps completely with the ¹²C removal rate. Thus, after the ¹³C-containing top layers were removed, the remaining ¹²C atoms diffuse slowly to the surface to complete the decarburization process.



Figure 3.6. Decarburization rate as a function of time on stream in a reaction with H_2 (16% H_2 , 250 °C, 1.5 bar) of a catalyst carburized in 12 CO/ H_2 for 5 h followed by 1 h exposure to 13 CO/ H_2 : decarburization rate of 12 C (blue curve) and 13 C (green curve) and the overall decarburization rate (black curve). The total C content expressed as the atomic C/Fe ratio is provided as well (brown curve).

Comparison with FT rates

As the carburization reaction studied above competes with hydrocarbons formation from the same surface C species, it is useful to compare these two reactions by following how they change directly after exposure to synthesis gas. The carburization rate as calculated by the derivative of the total C content as a function of carburization time and the C_xH_y formation rates are plotted in Fig. 3.7. The latter carbon-based rate is determined based on all analyzed hydrocarbons (C₁-C₁₀). The reaction was started by switching from H₂ to CO/H₂. Carbide formation, which starts immediately and is the dominant reaction in the early stages of carburization, slows with increasing C/Fe ratio. By contrast, the rate of C_xH_y formation rate goes up as the carburization degree increases. The C_xH_y formation rate reaches a maximum after *ca*. 1500 s, when the C/Fe ratio is 0.3. This corresponds to a carburization degree of 72%. Qualitatively, these trends can be explained by variations in the Fe-C bond energy as a function of the C/Fe ratio of the active phase. The initial reduced Fe phase has a very strong affinity for C,[28] which can explain the preferential diffusion of the C atoms into the Fe lattice over their hydrogenation. The average Fe-C bond energy in the bulk and at the surface will decrease with increasing C/Fe ratio.[29] A lower Fe-C bond energy favors hydrocarbons

formation and lowers the rate of carburization. The latter rate also decreases with increasing C/Fe content because less lattice sites are available.



Figure 3.7. The CO consumption rate, carbide formation rate, C_xH_y formation rate, r_{out} , and the C/Fe ratio as a function of time on stream at 250 °C, 1.5 bar, $H_2/CO = 2$ (note that r_{out} and the carbide formation rate are taken from Fig. 3.5).

After 80 min, about 10% of the C atoms in C_xH_y formation comes from Fe-carbide (r_{out}). This result is in qualitative agreement with the study by Kummer *et al.*.[29] These authors observed a radioactive ¹⁴C content of ~10% among hydrocarbon products during the FT reaction with ¹²CO/H₂ at 260 °C after carburization in a ¹⁴CO/H₂ mixture. This result confirms that C exchange *via* an MvK-like mechanism takes place and contributes to the overall FT activity. The major FT pathway responsible for the remaining 90% of the FT activity is likely a parallel L-H pathway involving surface adsorbed intermediates. Thus, it is interesting to study the role of these two reactions in more detail by steady state transient isotopic kinetic analysis (SSITKA), as this technique allows estimating the rates and relative contributions of parallel reaction pathways.[30]

Parallel reaction pathways

SSITKA was performed by switching from ¹²CO/H₂ to ¹³CO/H₂ after 5 h carburization (H₂/CO = 2). The response of the reaction products was followed by online MS. Interpretation of such SSITKA measurements is usually based on the assumption that the reaction occurs on the catalytic surface *via* an L-H mechanism. When considering a contribution of an MvK mechanism, parameters like residence time and surface coverage become less meaningful.

Nevertheless, the transient response of the products still bears important kinetic information. The usual approach is to describe the evolution of the simplest hydrocarbon CH_4 by a pseudofirst order process.[31-33] In this way, kinetic information about parallel reaction pathways can be obtained. [31, 33, 34] Details of the data modeling are provided in the Appendix 3. A reasonable fit was obtained involving 4 pools of active sites, each exhibiting a different activity (Appendix Table 3.2). Table 3.1 lists for each of these pools the fitted pseudo-first order rate constant k_i , the corresponding fractional contribution x_i to the total reaction rate and the fractional contribution y_i to the total number of active sites. The rate constants span several orders of magnitude ranging from $3.2 \cdot 10^{-4}$ to $2.8 \cdot 10^{-1}$ s⁻¹. The most abundant active sites have a rate of 3.2·10⁻⁴ s⁻¹, representing 89% of the total amount of active sites and contributing 17% to the total rate. Note that the fitted rate constant of this slow reaction path is in the same range as the experimentally observed exchange rate of C atoms in the Fecarbide catalyst in steady state, *i.e.*, $2 \cdot 10^{-4}$ s⁻¹ (Fig. 3.5, for $r_{out} = r_{in}$). We tentatively attribute this relatively slow reaction pathway to CH₄ formation via an MvK mechanism, which involves the difficult extraction of C from the surface lattice. This assumption is consistent with the result from Fig. 3.7 that the rate of C removal from the lattice is around 10% of the C_xH_y formation rate. The other faster pathways occupy together about 10% of the surface area but have a much larger contribution to the total activity. According to CO chemisorption, only 12% of the surface Fe sites is accessible for adsorption. Hence, we suggest that the fast reaction pathways can be associated with L-H reactions involving adsorbed C species on Fe sites. The proposed assignment of MvK and L-H reaction mechanisms to slow and fast reaction pathways fits with the notion that extraction of C from the carbide is slower than reactions between adsorbed species. The existence of multiple L-H reactions with different rates could be due to the presence of more than one active sites on the Fe-carbide nanoparticles. Overall, these data show that the CH₄ activity over Fe-carbide is dominated by a reaction path following the L-H mechanism with a small contribution of an MvK mechanism. The existence of more than one pool of C atoms (C_{α} and C_{β}) in CH₄ formation on Fe-based FT catalysts was already proposed by Govender et al.. [30] They also pointed out that a slow pool (C_{α}) makes a small contribution to the total activity but takes up most of the surface. Their kinetic analysis did however not reveal the origin of the C pools. In another study by Graf *et al.*, the possibility of multiple pools was mentioned but not linked to specific reaction routes.[35] The transient kinetic analysis in this work deals exclusively with CH₄ formation. This implies that we cannot draw conclusions about the impact of C exchange on the formation of hydrocarbons with more than one C atom. It is however worthwhile to point out that it has been shown that C-C coupling reactions involve both fast and slow C pools,[30, 36] suggesting that the current results would also be relevant to the FT reaction. Ordomsky et al. found that labelled C atoms in Fe-carbide are only involved in the chain growth 63

initiation events of the FT reaction.[22] Based on this insight, it can be speculated that the slow C pool, which involves lattice C, provides the CH_x species for chain-growth initiation *via* an MvK mechanism while the fast C pool provides chain-growth monomers by CO hydrogenation *via* an L-H mechanism occurring on a small fraction of the total surface area. It cannot be excluded that CH_x species obtained by hydrogenation of surface carbide C atoms migrate to other sites where they are involved in L-H type reactions that give rise to higher hydrocarbons. In any case, the small contribution of surface carbide C atoms must stem from the relatively strong binding to Fe as compared to adsorbed C atoms.

Table 3.1. Modeling of SSITKA CH_4 response with 4 pseudo-first-order reaction rate constants with x_i the fractional contribution to the total CH_4 rate and y_i the fraction contribution to the total number of active sites.

pathway <i>i</i>	rate constant k_i (s ⁻¹)	x_i (%)	<i>y</i> _i (%)
1	3.23.10-4	16.5	89.8
2	4.23·10 ⁻³	19.9	8.2
3	2.15.10-2	20.8	1.7
4	2.76.10-1	41.3	0.2

3.4 Conclusions

Iron carburization of a fully metallic Fe catalyst and the FT reaction mechanism were studied with alternating non-labelled and ¹³C-labelled synthesis gas streams. By analyzing the transient change in labelled C composition of the carbide over time, not only the carburization rate but also the diffusion rate of C entering and leaving the carbide could be determined. Initially, carburization dominates over hydrocarbon formation because of the high stability of C atoms in the Fe lattice. After about 20 min, half of the maximum C/Fe ratio was obtained. The C atoms dissolved during this stage can hardly be exchanged. After 6 h, the rates of C leaving and entering the carbide converge, indicating that maximum carburization is obtained. At this steady state, a limited amount of C atoms representing roughly the two outermost layers of the Fe-carbide particles can be exchanged and about 10% of the total FT activity is attributed to this C diffusing out of the carbide. A SSITKA measurement involving a switch of ¹²CO/H₂ to ¹³CO/H₂ over a completely carburized catalyst points to the existence of four parallel reaction paths expanding several orders in rate for CH₄ formation. The slowest reaction path occurs on the largest fraction of the surface and its rate has the same order of magnitude as the rate at which C diffuses out of the lattice during the steady state. The fast reaction path dominates the CH₄ formation rate but runs over only about 10% of the catalyst surface which coincides with the percentage of CO adsorption sites. In contrast to previous

literature, which does not link reaction rates to mechanisms nor reaction sites, it can thus be proposed that the slow path corresponds to a C hydrogenation pathway *via* an MvK mechanism and that the dominant fast pathway involving only a small part of the surface can be attributed to CO hydrogenation *via* an L-H mechanism.

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Appendix 3

Section I. Supplementary figures



Figure 3.8. H₂-TPR profile of as-prepared Raney-Fe.



Figure 3.9. Transient response of Ne, 13 CO, 13 CO₂, and 13 CH₄ after a switch from 13 CO/H₂ to 12 CO/H₂ after 1 h carburization (8% CO + 16% H₂, 250 °C, 1.5 bar).



Figure 3.10. TPH profiles for (a) 12 CH₄ and (b) 13 CH₄ component in carburized samples with 1 h 13 CO/H₂ followed by x h 12 CO/H₂ (8% CO + 16% H₂, 250 °C, 1.5 bar).



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Figure 3.11. Deconvolution of (a-d) 13 CH₄ TPH profiles after carburization in (a) 1 h 13 CO/H₂, (b) 1 h 13 CO/H₂ + 1 h 12 CO/H₂, (c) 1 h 13 CO/H₂ + 2 h 12 CO/H₂, (d) 1 h 13 CO/H₂ + 5 h 12 CO/H₂ and (e-g) 12 CH₄ TPH profiles after carburization in (e) 1 h 13 CO/H₂ + 1 h 12 CO/H₂, (f) 1 h 13 CO/H₂ + 2 h 12 CO/H₂, (g) 1 h 13 CO/H₂ + 5 h 12 CO/H₂ (8% CO + 16% H₂, 250 °C, 1.5 bar).



Figure 3.12. C/Fe ratio after carburization in 13 CO/H₂ for 20 min followed by *x* min 12 CO/H₂ (8% CO + 16% H₂, 250 °C, 1.5 bar).



Figure 3.13. TPH profiles for (a) 13 CH₄ and (b) 12 CH₄ in samples carburized in 12 CO/H₂ for 5 h followed by 1 h 13 CO/H₂ (8% CO + 16% H₂, 250 °C, 1.5 bar).

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Section II. SSITKA data analysis

The transient ¹²CH₄ response was first corrected for catalyst deactivation. The deactivation was assumed to follow an exponential decay behavior due to the loss of active sites. It is assumed that the deactivation behavior before and after switch is the same. Therefore, determining the deactivation rate prior to the switch gives a measure for the correction factor of the transient response after the switch. k_{deact} before the switch can be obtained by Eq. 3.1, in which R_0 represents the reaction rate of a fresh catalyst and R_t the reaction rate over time before the switch. It should be mentioned that k_{deact} is not a variable used in the fitting procedure.

$$\mathbf{R}_{t} = \mathbf{R}_{o} \cdot \boldsymbol{e}^{(-k_{deact} \cdot t)} \tag{Eq. 3.1}$$

The reaction rate r after the switch can be described as a product of steady state rate \overline{r} at the moment of the switch (t = 0), the transient response F, and exponential deactivation evolution (Eq. 3.2).

$$\mathbf{r} = \overline{\mathbf{r}} \cdot \mathbf{F} \cdot \mathbf{e}^{(-k_{deact} \cdot t)}$$
(Eq. 3.2)

$$F = \frac{r / \bar{r}}{e^{(-k_{deact} \cdot t)}}$$
(Eq. 3.3)

Thus, the transient response after the switch can be corrected by k_{deact} (Eq. 3.3). The corrected transient response was subsequently analyzed following previously described procedures for transient data treatment.[1-3]

The formation rate of ¹²CH₄ is assumed to be pseudo-first order in the coverage of CH_x (θ_{CHx}):

$$\mathbf{r}_{\mathrm{CH4}} = \mathbf{k}_{\mathrm{CHx}} \ \theta_{\mathrm{CHx}} \tag{Eq. 3.4}$$

where k_{CHx} is a pseudo-first-order rate constant with unit s⁻¹.

The isotopic switch will lead to an exponential decay of the ${}^{12}CH_4$ signal. The transient response over time is given in Fig. 3.14. It is evident that the signal cannot be described by a single exponential factor. We attribute this to the presence of multiple active sites with different intrinsic activities in CH₄ formation.

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Figure 3.14. Semi-logarithmic plot of the normalized transient response of ${}^{12}CH_4$ over time from ${}^{12}CO/H_2$ to ${}^{13}CO/H_2$ after carburized in ${}^{12}CO/H_2$ for 5 h (8% CO + 16% H₂, 250 °C, 1.5 bar).

The normalized transient response of the ${}^{12}CH_4$ after the isotopic switch, *F*, can be expressed as:

$$F = \sum x_i e^{(-k_i t)} \tag{Eq. 3.5}$$

Each path rate r_i contributes x_i to the overall reaction rate r with a pseudo-first-order rate constant k_i :

$$x_i = \frac{r_i}{r} \tag{Eq. 3.6}$$

The parameter sets x_i and k_i can then be determined by non-linear least square fitting. Fig. 3.15 shows the transient response of ¹²CH₄ after a switch from ¹²CO/H₂ to ¹³CO/H₂ in combination with a line fitted by a varying number of exponential decay functions. The fitted rate constants and their fractional contribution to the overall rate are listed in Table 3.2. As can be seen, increasing the number of the reaction paths leads to a better fit as the value of coefficient of determination (R²) approaches 1. The use of 4 paths yields a reasonably good fitting result. Further increasing the number of the reaction paths 4 hardly reduces the fitting error but increases the number of unknown parameters. Therefore, 4 paths have been used for fitting the SSITKA results. The reciprocal of the k_i indicates the residence time τ_i of the intermediate in the *i*th path. So the amount of the active site, N_i , is

$$N_i = x_i r \tau_i = x_i r k_i^{-1}$$
 (Eq. 3.7)

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And the total amount of the active site, N, is

TOS (s)

0.0

$$N = \sum N_i = r \sum x_i k_i^{-1} \tag{Eq. 3.8}$$

TOS (s)

For the *i*th path, the fraction number of the active sites y_i, can be calculated as







Figure 3.15. The normalized transient response of ${}^{12}CH_4$ after a switch from ${}^{12}CO/H_2$ to ${}^{13}CO/H_2$, fitted by (a) 1 path, (b) 2 paths, (c) 3 paths, (d) 4 paths, (e) 5 paths and (f) 6 paths.

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number of paths	rate constant k_i (s ⁻¹)	activity contribution x_i	sum of activity contributions	\mathbb{R}^2
1	9.52.10-4	0.330	0.330	0.7285
2	5.46.10-4	0.225	0.624	0.9602
	$1.32 \cdot 10^{-2}$	0.399	0.624	
3	4.29.10-4	0.192		0.9892
	7.23·10 ⁻³	0.289	0.938	
	$1.65 \cdot 10^{-1}$	0.457		
4	3.23.10-4	0.165		0.9915
	$4.23 \cdot 10^{-3}$	0.199	0.085	
	2.15.10-2	0.208	0.985	
	$2.76 \cdot 10^{-1}$	0.413		
5	$1.01 \cdot 10^{-4}$	0.094		0.9916
	1.20.10-3	0.131		
	6.12·10 ⁻³	0.184	0.989	
	2.96.10-2	0.178		
	$2.94 \cdot 10^{-1}$	0.402		
6	8.33.10-5	0.089		
	1.18.10-3	0.066		0.0016
	$1.17 \cdot 10^{-3}$	0.068	0.000	
	6.13.10-3	0.185	0.988	0.9910
	$2.95 \cdot 10^{-2}$	0.178		
	2.94.10-1	0.402		

Table 3.2. Fitted parameters with an increasing number of parallel reaction paths.

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Chapter 4

Influence of carbon deposits on Fe-carbide for the Fischer-Tropsch

reaction

Abstract

A well-known observation in the Fe-catalyzed Fischer-Tropsch (FT) synthesis of hydrocarbons is that the Fe-carbide catalysts deactivate due to carbon deposition. However, there is lack of knowledge on how such carbon deposits influence the product distribution. The present work investigates the relationship between the kinetics of the FT reaction for a carburized Raney-Fe catalyst and the catalyst surface composition with a focus on carbon deposits. The deposition of carbon during the ongoing FT reaction at low pressure decreases FT activity and increases CH₄ selectivity. Steady state transient isotopic kinetic analysis (SSITKA) at low pressure shows that the buildup of C deposits affects fast CO conversion sites on the Fe-carbide surface, mainly responsible for C-C coupling via a Langmuir-Hinshelwood mechanism, more than slow sites which mainly produce CH_4 via a Mars-Van Krevelen mechanism. Hindrance of migration of chain-growth monomers by carbon deposits decreases the amount of longer hydrocarbons. Nevertheless, SSITKA shows that C₂ products form faster, which is likely since such products increasingly derive from growth monomers formed at proximate CO dissociation sites when the amount of carbon deposits increases. Carbon deposition can be suppressed and reversed by increasing the H_2/CO ratio at constant pressure or by increasing the total pressure at constant H_2/CO ratio. As such, the FT performance can be stabilized by operating at elevated pressure, even if initially the reaction was started at low pressure. Nevertheless, prolonged operation at low pressure leads to a less reactive character of the C deposits that cannot be removed anymore during high-pressure operation.



Carobon deposit-rich Fe-carbide surface



Carobon deposit-poor Fe-carbide surface

4.1 Introduction

The interest in the Fischer-Tropsch (FT) process has not diminished since it was developed about 100 years ago. [1] In this process, a mixture of H_2 and CO is converted to hydrocarbons like gasoline, diesel, or chemicals.[2, 3] Only Co- and Fe-based catalysts are used in industrial FT synthesis because of cost reasons. Fe-based catalysts are currently used in coalto-liquids (CTL) technology, because they can better handle coal-derived synthesis gas with a low H₂/CO ratio.[4] In the future, Fe could also find utility in converting synthesis gas with a low H₂/CO ratio derived from renewable carbon-containing sources such as biomass or waste. During the FT reaction, Fe-based catalysts are usually a mixture of metallic Fe, Fecarbides and Fe-oxides.[5] The composition varies on parameters such as the catalyst precursor, catalyst pretreatment and the FT reaction conditions.[6] A correlation between the carbide content and the FT activity has been widely observed and the formation of Fe-carbide is believed to be a necessary step to obtain high FT activity.[7] Fe-oxide is considered to be active in the water-gas shift (WGS) reaction, contributing to an increase of the H₂/CO ratio by converting CO in the feed with product H_2O to CO_2 and H_2 . A too high WGS activity results in excessive CO_2 production, [8] which not only limits the carbon efficiency of the overall process but also increases operational costs.[9]

Another challenge for Fe-based catalysts is the high CH₄ selectivity.[10] CH₄ formation can be suppressed by adding alkali promoters, which suppress H₂ dissociation while enhancing CO dissociation.[11] Both effects lead to more coupling C-C reactions, thus lowering CH₄ formation. Torres et al. reported that increasing the particle size of promoted Fe₂C₅ particles lowers the CH₄ selectivity.[12] Xie et al. found that the decrease in the CH₄ selectivity observed for larger promoted Fe_2C_5 particles correlates with a lower H coverage.[13] Density functional theory (DFT) calculations have shown that the presence of surface and interstitial C atoms near the Fe atoms results in a higher CO dissociation barrier.[14] Surfaces with more reduced Fe atoms exhibit a lower activation energy for CO dissociation and bind adsorbed C stronger, which is unfavorable for CH₄ formation.[15-19] These studies indicate that controlling the surface Fe and C composition can help tuning the activity and selectivity of Fe-carbides for the FT reaction. Despite modeling efforts of CO dissociation and CH₄ formation on some relevant surface terminations, formulating a comprehensive microkinetic model of the complete FT mechanism for Fe-carbide is challenging because several Fecarbide surfaces can contribute to the overall catalytic performance.[20] The influence of surface C and the coverage of carbon-containing adsorbates on the CH₄ selectivity and activity of Fe-carbide catalysts has never been studied experimentally in detail. In this contribution, catalyst performance is followed as a function of reaction time and thus buildup of carbonaceous species.

Catalytic deactivation during the FT reaction poses another threat to the efficient utilization of Fe-based catalysts. Oxidation of metallic Fe or Fe-carbide to Fe-oxide is believed to be one of the factors causing catalyst deactivation.[21] Another possible factor is coke formation,[22] which can block active sites and pores.[23] For Co, it was confirmed that more-reactive carbidic C species can reversibly transform into less-reactive C deposits, which are preferentially located on flat surfaces.[24, 25] As planar surfaces contribute relatively strongly to CH₄ formation, C deposits on Co can suppress CH₄ formation rate, while hardly affecting the higher hydrocarbons formation rate, which is linked to stepped surface sites where CO dissociation and C-C coupling take place. However, the impact of C deposits on the FT product distribution on Fe-carbide remains elusive due to the complexity of surface C species and bulk C composition of Fe-based catalysts.

In our earlier work, it was found that carburization of reduced Raney-Fe with synthesis gas leads to the formation of phase-pure Fe-carbide, which is practically free of Fe-oxide (Chapter 3). However, the formed Fe-carbide suffers from rapid deactivation under the applied FT conditions. In the present work, the cause for the deactivation was investigated by XPS, Raman spectroscopy, temperature-programmed hydrogenation (TPH), and isotopic transient kinetic analysis. By simultaneously following the development in catalyst activity and selectivity during the deactivation process, a unique opportunity was created to correlate catalytic performance with the composition and the amount of C species on the catalyst surface. The reaction rates on Fe-carbide were evaluated by varying H₂ and CO partial pressures. Furthermore, the rate-limiting step of the FT reaction on Fe-carbide was determined. To counter deactivation, the importance of increasing H₂/CO ratio or synthesis gas pressure was investigated. The impact of exposing a Fe-based catalyst to low-pressure synthesis gas prior to the high-pressure reaction on the final FT activity and product distribution was illustrated.

4.2 Experimental methods

Catalyst preparation

Raney-Fe catalyst Raney-Fe was prepared from an aluminum-iron (Al50/Fe50) alloy (Goodfellow, 150-micron powder). A 25 ml 9 M KOH (Sigma-Aldrich) solution was prepared in a round-bottom flask. After heating the solution to 70 °C, 5 g of the Al-Fe alloy powder was added slowly. Caution is needed, as this reaction produces hydrogen. After stirring 40 min at 70 °C, the mixture was cooled to room temperature. The suspension was washed with water and ethanol 7 times each to remove potassium and aluminum ions and retrieve the precipitated Raney-Fe. Due to the pyrophoric character of the fine Fe powder, the catalyst was passivated in a 1% O₂/He flow for 24 h at room temperature for safe handling.

Catalyst characterization

Before TEM, XRD and Raman spectroscopy characterization, the as-prepared or spent catalyst was first passivated in a 1 vol% O_2 in He flow for 24 h at room temperature.

Transmission electron microscopy (TEM)

The particle size of the spent catalysts was studied by TEM using a FEI Technai 20 transmission electron microscope using an acceleration voltage of 200 kV with a LaB6 filament. A few milligrams of catalyst powder were suspended in ethanol. The suspension was sonicated to fully suspend all particles. Afterward, a few drops of the suspension were applied on a carbon-coated copper grid. ImageJ was used to process the images and determine the average particle size.

The carbon deposits on spent catalyst samples were investigated by HRTEM/STEM images using a JEOL JEM ARM200F with a Cs-corrected scanning probe operated at 200 kV. The passivated samples for high-resolution imaging were dispersed on lacey carbon films supported on copper grids. Energy-dispersive X-ray spectroscopy (EDS) analysis data were obtained using an Oxford X-max 100TLE system.

Raman spectroscopy

The spent catalysts were studied by Raman spectroscopy using a Witec Alpha 300 R Raman microscope equipped with a CCD1 detector, a Zeiss 10x, NA = 0.25 objective and a 300 g/mm grating. Spectra were acquired using a laser power of 2 mW at $\lambda_{exc} = 532$ nm with a collection time of 40 s by averaging 20 scans.

X-ray diffraction (XRD)

The crystal structure of the spent catalysts was analyzed using a Bruker D2 Phaser diffractometer with Cu K α radiation. XRD patterns were recorded in the 2 θ range of 30–60° using a step size of 0.02° and a step time of 1 s.

Quasi in situ X-ray photoelectron Spectroscopy (XPS)

The surface chemical composition of the catalysts af*ter reaction* was studied using a Kratos AXIS Ultra 600 spectrometer equipped with a monochromatic Al K_a X-ray source (hv = 1486.6 eV). Region scans were recorded at a pass energy of 40 eV (step size 0.1 eV) and survey scans were recorded at a pass energy of 160 eV (step size 0.5 eV) with the background pressure being kept below 5×10^{-9} mbar. A high-temperature reaction cell (Kratos, WX-530) was used to pretreat the sample, which was pressed into a pellet placed on a stainless-steel stub for *in vacuo* sample transfer into the XPS analysis chamber. Reduction was performed

in a 100 % H₂ flow (50 ml/min, at 1 bar) at 550 °C for 12 h (heating rate 5 °C/min). After reduction, the sample was cooled to 250 °C. In the same reaction cell, pretreatments were carried out that included carburization, FT reaction and decarburization. The low-pressure FT reaction was caried out at 1 bar in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min), while the high-pressure FT reaction was conducted at 5 bar in synthesis gas (66% H₂ and 33% CO, 50 ml/min). Decarburization was performed in H₂ (16% H₂ in Ar, 50 ml/min, 1 bar). Low-pressure carburization was conducted in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min, 1 bar). Low-pressure carburization was conducted in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min, 1 bar) for 1 h, while high-pressure carburization was conducted at 5 bar in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min, 1 bar) for 1 h, while high-pressure carburization was conducted at 5 bar in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min) for 1 h. After reaction or (de)carburization, the sample was evacuated and transferred to the XPS analysis chamber. Fitting of the XPS spectra was done using Voigt functions after a Shirley background subtraction with CasaXPS software (2.3.18PR1.0).

Catalytic activity measurements

Low-pressure FT reaction

An amount of 50 mg Raney-Fe mixed with SiC was loaded into a steady state isotopic transient kinetic analysis (SSITKA) reactor setup, which was used for the low-pressure FT reaction and transient kinetic experiments. Details of this setup have been described elsewhere.[26] The catalyst was first reduced in a dilute H₂ flow (20% H₂ in Ar, 50 ml/min, 1.5 bar) at 430 °C (with a heating rate 5 °C/min) for 1 h. This pre-treatment leads to the complete reduction of Raney-Fe into metallic Fe.[27] After reduction, the reactor was cooled to 250 °C. The reaction was started by substituting the diluted H₂ flow (24% H₂ in Ar, 50 ml/min, 1.5 bar) by an H_2 /CO/Ar mixture (16% H_2 and 8% CO in Ar, 50 ml/min, 1.5 bar). During reaction, the transient responses of H₂ (m/z = 2), CH₄ (m/z = 15), H₂O (m/z = 18), CO (m/z = 28), Ar (m/z = 40), and CO₂ (m/z = 44) were monitored by online MS (ESS Catalysys). The catalytic activity was determined by analyzing the effluent gas with an online GC (Thermo Scientific Trace 1300, extended with a Trace 1310 auxiliary oven). A combination of an MXT-QBond column (60 m \cdot 0.53 mm) with a thermal conductivity detector was used to determine the concentrations of CO_2 , CO_1 , H_2 and CH_4 , while a combination of a Rt-SilicaBond column (60 m \cdot 0.32 mm) with a flame ionization detector was used to analyze hydrocarbons.

High-pressure FT reaction

For each high-pressure experiment, 20 mg catalyst precursor mixed with SiC was loaded in a stainless-steel tubular flow reactor (Microactivity-Reference unit). The setup is operated in down-flow mode and is equipped with MFCs to supply gases to the top of the reactor. Sample was first reduced in a diluted H_2 flow (20% H_2 in He, 50 ml/min, 1 bar) at 430 °C using a rate

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of 5 °C/min followed by a dwell of 1 h. After reduction, the reactor was cooled in He to 250 °C for reaction. The catalyst was first exposed to low-pressure synthesis gas (16% H₂ and 8% CO in He, 50 ml/min, 1 bar) for 0, 0.5 or 24 h. Subsequently, the pressure in the reactor was built up to 20 bar for high-pressure reaction in synthesis gas (16% H₂ and 8% CO in He, 50 ml/min, 20 bar) for 36 h. A combination of an XL-Sulfur column (1.25 m \cdot 1.59 mm) and Molsieve 5A column (2 m \cdot 1.59 mm) equipped with a thermal conductivity detector was used to determine the concentrations of CO₂, CO, H₂, and CH₄. A Rtx-1 column (25 m \cdot 0.15 mm) equipped with a flame ionization detector was used to analyze the hydrocarbons.

Temperature-programmed hydrogenation (TPH)

The characteristics of carbon in and on the Fe-carbide were studied using TPH. In a typical experiment, 50 mg sample was loaded in a quartz tubular flow reactor. The gas feed was controlled by a thermal mass flow controller (MFC). The TPH was conducted by heating the reactor from room temperature to 750 °C at a rate of 5 °C/min in a diluted H₂ flow (20% H₂ in He, 50 ml/min, 1 bar). During TPH, the main hydrocarbon product was CH₄ (> 96 %), which was followed by online MS (MS, Balzers TPG-300). For *in situ* TPH, the catalyst sample was introduced in a quartz tubular flow reactor and subjected to a reaction according to a procedure similar to the above-described low-pressure activity test with varied time. After reaction, the catalyst was flushed in He and cooled to room temperature before starting the TPH as described above. For *ex situ* TPH, a catalyst sample was first subjected to a reaction, the catalyst was flushed in a 1 vol% O₂ in He and cooled to room temperature in ambient pressure for 24 h. The spent catalyst was transferred to the quartz tubular flow reactor for TPH.

Transient isotopic kinetic experiments

Transient isotopic kinetic experiments were performed using the SSITKA setup with the same reduction and reaction procedure as described for low-pressure FT activity testing. The transient experiment was performed by switching abruptly from a H₂/¹²CO/Ar mixture (8/4/2 ml/min) to a H₂/¹³CO/Ne mixture (8/4/2 ml/min) or from a H₂/CO/Ar mixture (8/4/2 ml/min) to a D₂/CO/Ne mixture (8/4/2 ml/min). An additional Ar was added to balance the total flow to 50 ml/min. The transient responses of H₂ (m/z = 2), HD (m/z = 3), D₂ (m/z = 4), ¹²CH₄ (m/z = 15), ¹³CH₄ (m/z = 17), H₂O (m/z = 18), ¹²CO (m/z = 28) and ¹³CO (m/z = 29) were monitored by online MS (ESS CatalySys).

4.3 Results and discussion

Catalyst performance with time on stream at low pressure

The initial stage of the FT reaction at low pressure was studied using a reduced model Raney-Fe catalyst. Metallic Fe was obtained by reducing Raney-Fe in a H₂ flow at a temperature of 430 °C and a pressure of 1.5 bar.[27] Fig. 4.1a shows the reaction rates as a function of time on stream directly after switching the feed from H₂ to a synthesis gas with a H₂/CO ratio of 2. Initially, CO is mainly consumed for the conversion of metallic Fe to Fe-carbide in line with our earlier findings. With time, the carburization rate decreases to negligible values within 1 h, indicative of the completion of the carburization process. Concomitantly, the FT reaction rate increases gradually, becoming the main CO-consuming reaction after 0.5 h. It is also observed that the hydrocarbons formation rate exhibits a maximum at 0.5 h, after which it declines gradually, implying that catalyst deactivation already sets in during the early stages of the FT process. O is removed mainly as H₂O directly after the switch to synthesis gas. Very likely, this is due to some remaining H atoms from the reduction step. However, the CO₂ formation quickly becomes the dominant O-consuming reaction after these H atoms have been removed.

We studied in more detail the activity and selectivity after 1 h of FT reaction, when the rate of carburization has become negligible. The corresponding catalytic data after 1 h are shown in Fig. 4.1b. In line with Fig. 4.1a, Fig. 4.1b also shows a declining FT activity with time on stream. Niemantsverdriet and Van der Kraan speculated that such a gradual decrease of the activity over prolonged time is most likely due to a slow loss of active sites.[28] Concomitantly, the olefins/paraffins ratio increases with time on stream. Experimental[6] and theoretical[29] studies have provided support for the idea that olefins are the primary products of the FT reaction, while paraffins are mainly obtained by hydrogenation of olefins after re-adsorption. The slowly increasing olefins/paraffins ratio is thus in keeping with the suggested loss of active sites, which would result in a lower probability of re-adsorption of primary reaction products. The catalytic data also show a slight increase in the CH₄ selectivity at the expense of the C_{2+} selectivity with time on stream. The slight increase in CH₄ selectivity during deactivation was also observed by other authors, but lack an adequate explanation.[30] In addition, most of the literature on Fe-carbide catalysts have evaluated the FT performance after 12 h or longer, when the conversion has become much more stable. [3, 9, 31] However, in this contribution, variations in the activity and product distribution were studied during the very first hours of the FT reaction, when changes in the composition of the surface species are more substantial, offering an opportunity to study in-depth the correlations between the changing catalyst surface composition and the catalytic performance.

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Figure 4.1. (a) CO consumption rate, CO₂ formation rate, carbide formation rate (based on the derivative of the total C content as a function of time on stream), C_xH_y formation rate, and H₂O formation rate as a function of time on stream at 250 °C, 1.5 bar, and H₂/CO = 2. (b) CO conversion, CH₄ selectivity, C₂₊ selectivity, CO₂ selectivity and C₂-C₃ olefins/paraffins ratio as a function of time on stream at 250 °C, 1.5 bar, and H₂/CO = 2 after 1 h reaction.

TEM analysis shows that the particle size of the catalyst does not change during the FT reaction at low pressure (Appendix Fig. 4.11). This means that sintering as a cause of deactivation is unlikely. The surface composition of the catalyst was investigated by quasi in situ XPS at 250 °C, 1 bar, and $H_2/CO = 2$. The Fe 2p XPS spectra show a decreasing Fe signal with time on stream (Fig. 4.2a). Besides sintering, the lower Fe signal can also be explained by the formation of C-containing species on the catalyst surface. The latter explanation is supported by the C 1s XPS spectra (Fig. 4.2b), which show, together with the decrease in Fe 2p intensity, a strong increase in the C 1s signal due to C-C/C=C groups. These features can be related to hydrocarbon fragments with hybridized sp^3 bonds and sp^2 bonds.[32] The C 1s signal at 283.1 eV due to Fe-carbide decreases in parallel with the Fe intensity. From the observation that the C-C/C=C signal increases at the expense of the Fe signal, it can be inferred that active site is partially covered by carbonaceous species during the FT reaction, providing an explanation for catalyst deactivation shown in Fig. 4.1a and 4.1b. To confirm the formation of carbonaceous species, high-resolution TEM imaging combined with EDX was performed on a passivated sample after reaction at 250 °C, 1bar, and $H_2/CO = 2$ for 24 h. The EDX maps in Appendix Fig. 4.12 show the presence of a carbonaceous layer around Fe-carbide. No crystalline graphitic C species could be observed in HAADF-STEM and BF-STEM images (representative images in Appendix Fig. 4.13). HRTEM in Appendix Fig. 4.14 also elaborates the structure of the carbon formed, emphasizing the presence of curved fringes of amorphous C. Appendix Fig. 4.15 shows that surface Fe was not completely reduced at

the start of the *quasi in situ* XPS experiment. During the experiment, the degree of oxidation decreases. Introduction of synthesis gas apparently enhances Fe reduction, likely because CO has a higher reducing ability than H_2 .[32] The decrease in the oxidation degree of Fe over time implies that removal of O species is faster than C species and thus not a rate-limiting step nor a cause for deactivation during the reaction.



Figure 4.2. *Quasi in situ* XPS spectra of (a) the Fe 2p region and (b) the C 1s region at 250 °C, 1 bar, and $H_2/CO = 2$ for different times on stream.

The buildup of C-containing species indicates that C removal is slow and possibly ratelimiting in the FT reaction network. To understand this aspect better, the dependences of the reaction rates for CO consumption, CH₄ formation, C₂₊ formation, and CO₂ formation on the CO and H_2 partial pressures were determined. The results are shown in Fig. 4.3. The reaction orders in CO are positive for all products except for CH_4 (Fig. 4.3a). This contrasts with the behavior observed on Co catalysts, which show a negative order in CO for the overall reaction rate. The negative order for Co catalysts is typically ascribed to a high surface coverage of strongly adsorbed CO, which leaves no space for the CO dissociation needed for the FT reaction.[26] The positive orders in CO on Fe-carbide suggest that, in agreement with previous findings (Chapter 3), the surface coverage of CO on Fe-carbide is low under the applied reaction conditions. An increase in CO pressure would lead to a higher coverage of adsorbed CO species, as likely CO dissociation is not limiting the rate, and a higher coverage with adsorbed C species. Hence, chain-growth probability is expected to increase with increasing CO pressure at the expense of CH₄ formation, which agrees with the observed positive order in CO for the longer hydrocarbons (C_{2+}) and negative order for CH₄. The reaction orders in H₂ related to CH₄ and C₂₊ formation are strongly positive (Fig. 4.3b),

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suggesting that hydrogenation of C atoms is a rate-controlling step. This is in line with literature that proposes that CH_x formation by hydrogenation of surface C is the rate-determining step in the low-pressure regime.[33] An alternative explanation involving H-assisted CO dissociation would not explain the different reaction orders in H₂ for different hydrocarbons. Therefore, it can be concluded that the removal of C from the surface by hydrogenation is limiting the overall rate. Notably, the reaction order with respect to H₂ for CH₄ formation is higher than the H₂ reaction order for C₂₊ formation. This is expected since removal of C as CH₄ requires more H atoms per adsorbed C atom than the removal as C₂₊ hydrocarbons. We propose that slow hydrogenation of adsorbed C species compared to the fast CO dissociation not only makes it a rate-limiting step but also bears the risk of carbonaceous species accumulation on the catalyst surface.



Figure 4.3. CO consumption rate (squares), CH₄ formation rate (circles), C₂₊ formation rate (up-triangles) and CO₂ formation rate (down-triangles) as a function of (a) CO partial pressure (b) and H₂ partial pressure. Conditions: T = 250 °C, $pH_2 = 0.9$ bar at varying CO partial pressure, pCO = 0.3 bar at varying H₂ partial pressure.

The accumulation of C species during the FT reaction can also be observed by Raman spectroscopy (Fig. 4.4). Upon prolonged reaction time, the Raman spectra display a significant increase in the signal intensities in two regions, namely between 1000 and 1500 cm⁻¹ and between 1500 and 1800 cm⁻¹. The D band (1374 cm⁻¹) is typically ascribed to the presence of disorder/defects in cyclic compounds with sp² C, while the G band (1571 cm⁻¹) is characteristic of cyclic and/or chain structures with sp² C.[23, 34, 35] The observation of broad D and G bands indicates the formation of sp² C-containing species with disordered structures.[36] This finding is in line with the HRTEM result that no crystalline graphitic C could be observed on catalysts used in the atmospheric FT reaction at 250 °C for 24 h.



Figure 4.4. Raman spectra of Fe catalyst after reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for different times on stream.

TPH can be used to identify C species with different reactivities. The C-containing species include, in order of decreasing reactivity towards H_2 , (i) adsorbed atomic C, surface carbide or oligomeric C, (ii) bulk carbide C, and (iii) disordered or moderately-ordered graphitic C.[37] TPH profiles of catalysts exposed for times on stream are shown in Fig. 4.5. The TPH peak at the lowest temperature belongs to the most reactive C species (adsorbed atomic, surface carbide, and oligometric C), which are easiest hydrogenated and are partly the reactive intermediates during the FT reaction. The second peak can be assigned to bulk carbide C, which takes up the majority of C in the catalyst. With increasing time on stream, the bulk carbide peak shifts to higher temperature. This delay of structural carbon hydrogenation is likely caused by the accumulation of deposited C with a disordered structure blocking part of the surface. In the following discussion, this stable C species is denoted as C deposits. This is in accordance with literature that showed that C deposition renders Fe-carbide more stable.[22, 30] The hydrogenation peak of the deposited C itself cannot be discriminated in these TPH profiles, as it overlaps with the peak of bulk carbide C. The asymmetry of the peaks after 8 h reaction is likely caused by this overlap or by incomplete coverage of the surface by C deposits. The amount of the most reactive C species as well as the ease of their hydrogenation are suppressed simultaneously when the time on stream is prolonged, as indicated by the decrease in the peak height and its shift to higher temperature (see inset of Fig. 4.5). The diminishing amount of active C species observed could be the result of a slow transformation of active C species into a more stable C deposits.[37]



Figure 4.5. In situ TPH of Fe catalyst after reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for different times on stream.

To further confirm the decreasing reactivity of surface C species, a series of SSITKA experiments was performed. The transient response of CH₄ after an isotopic switch from 12 CO/H₂ to 13 CO/H₂ can provide information about the reactivity of surface C species.[38] Although the used catalysts suffer from deactivation, the transient response of CH₄ can still provide information about the reaction kinetics. The details of data treatment needed to take into account the ongoing catalyst deactivation can be found elsewhere (Chapter 3). As the deactivation rate is not constant over time, the transient responses after switches at different times on stream were corrected by a k_{deact} correlated to the specific deactivation rate at the moment of the switch. The values for k_{deact} with varying times on stream are listed in Appendix Table 4.2. Fig. 4.6a shows the normalized ¹²CH₄ curves upon a switch from ¹²CO/H₂ to ¹³CO/H₂ after different times on stream. Clearly, the CH₄ signal declines slower after prolonged time on stream. This implies that the residence time of CH_x species (τ_{CHx}) increases due to a lower rate constant for the hydrogenation to CH₄ ($k = 1/\tau_{CHx}$)[26] decreases. This agrees with the TPH results, in which the peak for reactive species hydrogenation shifts to higher temperatures. Unfortunately, it is not possible to determine the amount of adsorbed CH_x species reliably by SSITKA for Fe-carbides, because the presence of slowly reacting surface lattice C causes tailing, precluding reliable integration of the signal. To extract more information from the SSITKA results, the transient responses were fitted by three exponential decay functions, which correspond to three parallel reaction paths. The use of three paths was found to result in the best fit with the lowest possible number of parameters. The fitted rate constant k_i , the corresponding fractional contribution to the total reaction rate, x_i the fractional contribution to the total number of active sites, v_i and the goodness-of-fit measure (\mathbb{R}^2) are listed in Appendix Table 4.2. Fig. 4.6b shows the fractional contribution of each path to the total reaction rate against the corresponding rate constants. In a previous study, the slow and fast reaction paths were linked to reactions occurring via a Mars-Van Krevelen (MvK) and Langmuir-Hinshelwood (L-H) mechanisms, respectively (Chapter 3). As can be seen in Appendix Table 4.2, the fast reaction paths involving adsorbed C species on Fe sites contribute most to the total reaction rate, while the slow path involving extraction of C from the surface lattice has a relatively small contribution. This dominance of fast sites to the overall activity does not change with increasing time on stream. On the other hand, it is observed that the rate constants decrease for all the contributing pathways. For example, the k of the slowest path decreases from $1.4 \cdot 10^{-3}$ to $9.8 \cdot 10^{-4}$ s⁻¹, whilst the fastest path decreases from 1.1.10⁻¹ to 8.8.10⁻² s⁻¹. The total decrease in intrinsic activity observed in Fig. 4.6a can thus be attributed to a simultaneous decrease in activity for all parallel reaction routes. Obviously, this decrease is due to blocking of part of the surface by C deposits. Moreover, we speculate that the decrease is due to a shift in the equilibrium from reactive C species to more stable oligomerized C deposits.

The changes in selectivity over time depicted in Fig. 4.1b still need an explanation. The SSITKA experiments presented in Fig. 4.6b and 4.6c also show that the fractional contribution to the overall activity of the slow sites and their relative contribution increases with time on stream at the expense of faster sites. These results indicate that the slow sites are less influenced by the buildup of C deposits during the reaction. The decrease in C_{2+} selectivity can thus be tentatively correlated to the decrease in the contribution of fast sites. It can be speculated that the slow MvK sites are prone to CH₄ formation, whereas fast sites are mainly involved in C-C coupling *via* an L-H mechanism. Such supposition is based on the ideas that the C atoms in the surface carbide are more strongly bonded than the adsorbed C on the fast sites (Chapter 3). DFT calculations demonstrated that CH₄ formation becomes faster compared to chain growth with increasing metal-C interaction energy. [29] It can be thus deduced that the relatively higher CH_4 selectivity on slow sites is inherent to the stronger Fe-C bond from lattice C. Our previous work revealed about 10% of the C atoms in the hydrocarbons formed comes from lattice C atoms of Fe-carbide (rout) via an MvK mechanism. r_{out} corresponds to the CO consumption rate on slow sites at later stages of the carburization process (Chapter 3). The comparison of r_{out} with the overall C_{2+} formation rate in Appendix Fig. 4.16 also indicates that slow sites make a small contribution to longer hydrocarbons formation.

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We also considered other explanations for the decreasing C_{2+} selectivity with time on stream. For instance, a higher H coverage would also enhance CH₄ formation and suppress chain growth. To investigate this, the H coverage was estimated by following H/D exchange following a CO/H₂ \rightarrow CO/D₂ switch. Appendix Fig. 4.17 shows an almost constant HD peak area, which means the H coverage does not change with increasing time on stream (Appendix Table 4.3). Thus, changes in the H coverage cannot explain the changing product distribution with time on stream. Another explanation would be a decrease in the coverage of reactive C species because this decreases the chain-growth probability. Although we cannot directly determine the amount of reactive C species, Fig. 4.5 illustrates that the total amount of active surface C species diminishes over time because of a slow transformation of active C species into more stable C deposits. It is reasonable to assume that C deposits are more likely to build up on surface facets with fast CO dissociation sites, because C-C coupling is a prerequisite for the formation of heavier C deposits. Thus, fast sites would be more affected by C deposition than slow sites which are mostly leading to CH₄, thus explaining the decreasing chain-growth probability.

Another possibility is that migration of CH_x growth monomers is hindered by immobile C deposits, thus causing the decreasing C2+ selectivity. To further investigate this, the transient response of C₂ products (*i.e.*, ethane and ethylene) was investigated (Appendix Fig. 4.18). The interpretation of residence time of C_2 products is not as straightforward as the residence time for CH₄, because C₂ product formation involves CO dissociation, C-C coupling as well as hydrogenation reactions of C_1 and C_2 species.[39] Nevertheless, the transient response of C_2 products still bears important kinetic information. Notably, the C_2 residence time decreases with time on stream, which shows the opposite behavior of the CH₄ residence time. This means that hydrogenation reactions, presumed to be the slow steps for Fe-carbide, are not likely causing the observed difference. It is reasonable that the C-C coupling rate will depend on the migration of CH_x species between sites where CO is dissociated followed by hydrogenation to mobile CH_x species. Coverage of the surface by immobile C-containing deposits would hinder such migration, explaining the overall decreased C2 selectivity. We speculate that the faster C_2 formation observed by SSITKA is due to the fact that the decreasing amount of C_2 products originates from C_1 species formed relatively close together. This provides a tentative explanation for the smaller amount of C_2 products (and hydrocarbons with more than two C atoms) that are nonetheless formed faster due to their proximity with increasing coverage of C deposits.

In summary, SSITKA data with increasing time on stream illustrate that the impact of deposited C on the product distribution can be ascribed to two factors. First, the CH₄ transient response indicates that fast sites mainly responsible for C-C coupling *via* an L-H mechanism

are more suppressed by deposited C than slow sites which mainly lead to CH_4 *via* an MvK mechanism. This is expected as formation of such deposits also involves C-C coupling reactions. Second, data on the FT product distribution (less C_{2+} hydrocarbons) and the C_2 transient response (faster C_2 formation) indicate that C deposits limit the migration of chaingrowth monomers, resulting in less C_2 products. Their faster formation can be explained by C-C coupling of growth monomers obtained from proximate CO dissociation sites, because migration is hindered by C deposits.



Figure 4.6. (a) Normalized transient response of ¹²CH₄ upon a switch from ¹²CO/H₂ to ¹³CO/H₂ (b) fractional contribution to the total activity of the 3 fitted parallel reaction paths and (c) fractional contribution to the total number of active sites, plotted against the corresponding pseudo-first-order rate constant after different times on streams at 250 °C, 1.5 bar, and H₂/CO = 2.

Catalyst regeneration

As we suspected that the buildup of C deposits is due to a too slow hydrogenation of C species, we exposed a catalyst used in the low-pressure FT reaction to pure H_2 . Fig. 4.7a shows the CH₄ evolution before, during and after the H₂ treatment. During the first 6 h FT reaction (16% H_2 and 8% CO in Ar, 50 ml/min, 1.5 bar at 250 °C), the catalyst deactivates as usually observed. When switching to H_2 (24% H_2 in Ar, 50 ml/min, 1.5 bar), a sharp peak in CH₄ formation is observed, which is most likely related to an increasing H coverage as reactive C-containing species are removed from the catalytic surface. A strong CH_4 formation peak was observed for Co catalysts due to a decreasing CO and increasing H coverage. [26] During exposure to pure H₂, the formation of hydrocarbons continues with CH₄ as the main product (selectivity > 90%) (Fig. 4.7b). The hydrocarbons formation rate corresponds to the overall decarburization rate of Fe-carbide (*i.e.*, removal of C atoms in the surface adsorbed layer as well as bulk C), which decays quickly at the start of the reaction followed by a more gradual decrease.(Chapter 3) The high rate directly after the switch to H₂ can be ascribed to the removal of adsorbed reactive C species, while the slow residual formation of hydrocarbons likely originates from various sources such as less reactive C deposits but also from C atoms of the bulk carbide, requiring a very long time to be removed albeit mostly as CH_4 .[40] The removal of C-containing species from the surface by H₂ is confirmed by XPS analysis before and after reaction in H₂ (Appendix Fig. 4.19). The signal related to C species (C-C/C=C) decreases upon exposure to H_2 concomitant with an increase of the Fe and Fe-carbide related Fe 2p XPS signals. Thus, the surface of the Fe-carbide becomes more exposed due to C removal. The removal of C species from the surface is also evident from TPH and Raman spectra shown in Appendix Fig. 4.20 and Fig. 4.21, respectively. TPH shows that the removal of C species leads to easier bulk C hydrogenation. The bulk C/Fe ratios before and after H₂ treatment are comparable, indicating that the Fe-carbide phase itself is relatively stable at the relatively low temperature. After switching back to synthesis gas, another peak in CH₄ formation appears (seen in Fig. 4.7a), which can be explained by fast dissociation of CO on a largely empty surface, which may be partially reduced exposing more reactive Fe sites. Comparison of the hydrocarbons formation rate and the CH₄ selectivity before and after reaction with H₂ in Fig. 4.7b shows that removal of deposited C after H₂ treatment results in a higher activity and lower CH₄ selectivity in the first hour after switching back to the synthesis gas feed. This agrees with the previous finding that deposited C species decreases the FT activity and increases CH₄ selectivity (Fig. 4.1b). However, the catalyst again deactivates and, after some time, the activity and CH₄ selectivity follow the activity trend before the H₂ treatment. The data suggests that subsequent buildup of C deposits leads to a

comparable surface adsorbed layer as before the H_2 treatment. Clearly, atmospheric hydrogenation is not very effective in regenerating the catalyst.



Figure 4.7. (a) Transient response of CH₄ (b) the evolution of hydrocarbons formation rate and CH₄ selectivity before, during, and after reaction in H₂ at 250 °C, 1.5 bar (FT reaction at the same conditions with $H_2/CO = 2$).

As shown in Fig. 4.3, the reactions that lead to hydrocarbons have a higher order in H₂ than in CO. As hydrogenation reactions are thought to be relatively slow on Fe-carbide, we speculated that a higher total synthesis gas pressure at the same H₂/CO ratio will lower the amount of surface deposits, thus reducing deactivation. To verify this supposition, a carburized catalyst was subjected to the FT reaction at total synthesis gas pressures of 1 bar and 5 bar at constant H₂/CO ratio followed by *quasi in situ* XPS analysis. The pressure of 5 bar was determined by the pressure limit of the reaction chamber attached to the XPS analysis chamber. Comparison of the Fe 2p and C 1s XPS signals after 1 h carburization in Fig. 4.8 shows an increase of the total synthesis gas pressure under otherwise similar conditions leads to a decrease of the C-C/C=C signals and an increase of the Fe signal. This experiment demonstrates that a higher synthesis gas pressure leads to a lower coverage of C-containing species.



Figure 4.8. *Quasi in situ* XPS spectra of (a) Fe 2p region and (b) C 1s region after the catalyst is carburized at $250 \text{ }^{\circ}\text{C}$, $\text{H}_2/\text{CO} = 2$ for 1 h at 1 bar and 5 bar.

Based on this insight, we studied operating at elevated synthesis gas pressure to avoid deactivation. When the reaction was operated at 20 bar, the catalyst did not activate at the time scale of the experiment (Fig. 4.9a). The slight drop in CO conversion at the start of the reaction is likely caused by a decline of the initially fast carburization rate. The nearly constant conversion at 20 bar indicates a higher C removal rate is obtained at higher synthesis gas pressure, thus preventing accumulation of C species on the Fe surface. This is in sharp contrast with the data during the FT reaction at low pressure shown in Fig. 4.1, where the removal of C species is too slow. Notably, when the catalyst is deactivated by reaction at 1 bar for 24 h, the activity can be increased by exposure to synthesis gas at 20 bar (Fig. 4.9b). However, the CO conversion does not reach the same value as without preceding reaction in synthesis gas at 1 bar. When the preceding reaction at 1 bar is shortened to 0.5 h, the activity can be recovered fast, and the final obtained activity is higher than observed in the experiment involving 24 h preceding reaction at 1 bar. Despite these differences that underline the possibility to remove C deposits at elevated synthesis gas pressure, the activity remains lower than without any preceding reaction at 1 bar (Fig. 4.9c). This implies that some of the C deposits are not reactive under these conditions and their contribution grows during reaction at low synthesis gas pressure. The recovery of the activity at 20 bar (Fig. 4.9b) can be explained by hydrogenation at elevated H_2 pressure. It was also found that the Fe-carbide catalyst operated at elevated pressure can be easier hydrogenated during TPH (Appendix Fig. 4.22). To exclude that a different bulk phase is formed during the activity recovery at 20 bar, XRD patterns of samples after low- and high-pressure reaction were compared. Appendix

Fig. 4.23 shows that the phase composition does not change after the catalyst is exposed to high-pressure synthesis gas.



Figure 4.9. (a) CO conversion as a function of time on stream at 250 °C, 20 bar, $H_2/CO = 2$, (b) CO conversion as a function of time on stream at 250 °C, 20 bar, $H_2/CO = 2$ after 24 h reaction at 250 °C, 1 bar, $H_2/CO = 2$, (c) CO conversion as a function of time on stream at 250 °C, 20 bar, $H_2/CO = 2$ after 0.5 h reaction at 250 °C, 1 bar, $H_2/CO = 2$.

Steady-state performance at high pressure

For these measurements in Fig. 4.9, when they are reaching steady state, Table 4.1 gives an overview of the catalytic performance of the catalyst at 20 bar after different reaction times at 1 bar. The trends coincide with the those in Fig. 4.1b. An increasing reaction time at low pressure leads to lower steady-state CO conversion, lower chain-growth probability, higher CH_4 selectivity, and higher C_2 - C_4 olefins/paraffins ratio at 20 bar. The reaction orders in H_2

and CO on Fe-carbide at 20 bar synthesis gas (Appendix Fig. 4.24) are very similar to those obtained at 1.5 bar (Fig. 4.3), indicating that the reaction mechanism does not depend on the synthesis gas pressure. It is thus likely that the positive effect of high pressure on maintaining (or recovering) the FT activity is not caused by differences in the FT reaction mechanism such as a shift to another rate-determining step. Instead, the differences are mostly due to the changes in the coverage with C deposits due to higher hydrogenation rates at elevated synthesis gas pressure.

Low-pressure	CO	CO_2	CH_4	Chain-	C ₂₋₄
reaction		selectivity	selectivity	growth	olefins/paraffins
period (h)	conversion	(%)	(%)	probability	ratio
0	0.13	17.2	13.7	0.54	1.30
0.5	0.11	12.5	17.5	0.52	1.35
24	0.10	10.4	18.3	0.51	1.49

Table 4.1. Catalytic performance at steady state (250 °C, 20 bar, $H_2/CO = 2$) after different exposure times to low-pressure synthesis gas (250 °C, 1 bar, $H_2/CO = 2$).

It has been reported that the FT synthesis reaction is a structure-sensitive reaction and that the catalytic performance depends strongly on the active phase composition and size of the nanoparticles.[41] In the present study, the composition of the active phase and the size of the catalytic nanoparticles do not change upon exposure to synthesis gas at low pressure. The XRD patterns of all used catalysts indicate that $\varepsilon(')$ -carbide remains the dominant phase with only a small contribution of γ -carbide, independent of the reaction time at low pressure (Appendix Fig. 4.23). Moreover, the crystallite sizes of the Fe-carbide particles after reaction are very similar according to Scherrer analysis. TEM further underpins this aspect (Appendix Fig. 4.25 and Appendix Table 4.4). As the Fe-carbide structure and particle size are unchanged, any observed difference in catalytic performance can be attributed to changes in the surface composition of the catalyst. Above, we correlated the changing FT activity and product distribution with time on stream at 1 bar (shown in Fig. 4.1b) to the deposition of unreactive C at the surface. Table 4.1 shows the same changes in catalytic performance, *i.e.*, a decrease in the chain-growth probability in parallel with an increase in CH₄ selectivity and an increasing C_2 - C_4 olefins/paraffins after prolonged exposure to low-pressure synthesis gas. Apparently, the effect of C deposits on the selectivity during low-pressure reaction is preserved after reaction at 20 bar. Indeed, Raman spectra demonstrate that prolonging the FT reaction at 1 bar results in more C deposits, even if the reaction is subsequently carried out at 20 bar (Fig. 4.10a), analogous to what is shown in Fig. 4.4. TPH measurements in Fig. 4.10b also demonstrate that the hydrogenation of Fe-carbide shifts to higher temperature with increasing exposure time to low-pressure synthesis gas, as more C deposits are accumulated on the surface. This lowers the FT activity at high pressure.

In summary, during the FT reaction at 1 bar and 250 °C, C deposits accumulate at the Fecarbide surface, which deactivate the catalyst and change the product distribution. Based on the present data, these C deposits likely form on the same facets that are involved in the formation of higher hydrocarbons, *i.e.*, the fast sites that follow a L-H mechanism. The slow MvK sites giving rise to mainly CH_4 are less affected. Subsequent reaction at 20 bar can recover the activity by hydrogenation of some of the C deposits. Some unreactive C deposits, however, whose contribution increases with time on stream at 1 bar cannot be hydrogenated at 20 bar and will therefore continue negatively affecting the catalytic performance.



Figure 4.10. (a) Raman spectra and (b) TPH curves of samples after high-pressure reaction at 250 °C, 20 bar, $H_2/CO = 2$ with varied exposure times to low-pressure synthesis gas (250 °C, 1 bar, $H_2/CO = 2$).

Table 4.1 shows that the CO₂ selectivity at 20 bar increases when the catalyst is exposed for shorter times to synthesis gas at low pressure. *Quasi in situ* XPS C 1s spectra (Appendix Fig. 4.26a) show that this goes in parallel with an increased intensity for the O-C=O component, which has been related to the adsorption of CO or CO₂ on the surface O-containing species.[42, 43] During the FT synthesis, CO₂ can be formed *via* the WGS reaction, which converts the reactant CO with product H₂O to CO₂ and H₂. Fe-oxide is the most active WGS component in Fe-based FT catalysts.[8] Thus, it can be inferred that catalyst is more oxidized when it is less exposed to low-pressures synthesis gas. The XRD patterns in Appendix Fig. 4.23 show that the used catalysts after high-pressure reaction do not contain bulk Fe-oxide.

However, *quasi in situ* XPS data in Appendix Fig. 4.26b point to a higher Fe oxidization degree compared to case where the reaction was carried out at lower synthesis gas pressure (Fig. 4.2). The higher degree of Fe oxidation is most likely due to the larger amount of H₂O produced at higher CO conversion. Furthermore, Appendix Fig. 4.26b shows an increasing degree of reduction, when the low-pressure reaction is prolonged, consistent with the observation in Appendix Fig. 4.26a. Tentatively, the C deposits lower the degree of surface Fe oxidation, leading to a lower CO₂ selectivity. A positive impact of preventing surface Fe oxidation on the CO₂ selectivity was also reported by Xu *et al.*, who observed that a hydrophobic shell can protect Fe-carbide from oxidation.[44]

4.4 Conclusions

The impact of carbon deposits formed during the initial stages of the FT reaction at atmospheric synthesis gas pressure on pure Fe-carbide was investigated. Besides a gradual decrease of the CO conversion, the CH₄ selectivity increased at the expense of the formation of longer hydrocarbons (lower chain-growth probability). Kinetic analysis indicates that the deposition of low-reactive C deposits affects fast CO dissociation sites, mainly responsible for C-C coupling via an L-H mechanism, more than the slow MvK sites involved in CH₄ formation. SSITKA indicates a slowing CH₄ formation when more C is deposited, whereas the smaller amount of C_2 products (a proxy for longer hydrocarbons formation) are formed faster. While the decrease of the chain-growth probability is linked to the overall lower rate of CO dissociation, the different SSITKA responses for C_1 and C_2 products can be explained by hindered migration of growth monomers due to C deposits. The remaining C_2 products are then formed from proximate CO dissociation sites. The deposition of C can be linked to the relatively slow hydrogenation of C on Fe-carbide. Increasing the H_2/CO ratio at constant pressure as well as increasing the total pressure at H_2/CO constant ratio lowers the amount of low-reactive C deposits. Thus, carrying out the reaction at higher synthesis gas pressure can reverse to some extent the initial deactivation caused by low-pressure FT reaction. When the reaction is started at elevated pressure, deactivation can be largely avoided. The longer the FT reaction is carried out at low pressure, the more unreactive C deposits accumulate that cannot be eliminated by high-pressure reaction at typical FT reaction temperatures, leading to lower FT activity and lower chain-growth probability at high synthesis gas pressure.

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Appendix 4



Figure 4.11. TEM images of Fe samples after (a) reduction at 430 °C, 1 bar in H_2 for 1 h, and FT reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for (b) 1 h and (c) 24 h.




Figure 4.12. HAADF-STEM with corresponding EDX mappings of C, O and Fe of catalyst after reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for 24 h.





Figure 4.13. (a) TEM image of catalyst after reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for 24 h. (b) High-resolution BF-STEM image and (c) HAADF-STEM image of the highlighted area showed in the TEM image.



Figure 4.14. (a) TEM image of catalyst after reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for 24 h. (b) HRTEM image of the highlighted area showed in the TEM image.



Figure 4.15. *Quasi in situ* XPS spectra of Fe 2p after reduction (550 °C, 1 bar in H₂ for 12 h) and after 20 min FT reaction (250 °C, 1 bar, and H₂/CO = 2).

Table 4.2. The k_{deact} , fitted rate constant k_i , the corresponding fractional contribution to the total reaction rate, x_i , the fractional contribution to the total number of active sites, y_i , and coefficient of determination (R²) upon a switch from ¹²CO/H₂ to ¹³CO/H₂ on streams at 250 °C, 1.5 bar, and H₂/CO = 2.

Reaction condition	k _{deact} (s ⁻¹)	rate constant k _i (s ⁻¹)	activity contribution x_i	Site contribution y _i	R ²	
2 h ¹² CO	5.20.10-5	1.45.10-3	0.141	0.736		
		1.01.10-2	0.310	0.225	0.9979	
		$1 \cdot 11 \cdot 10^{-1}$	0.567	0.038		
5 h ¹² CO	2.12.10-5	$1.04 \cdot 10^{-3}$	0.156	0.782		
		8.26.10-3	0.301	0.189	0.9985	
		1.02.10-1	0.550	0.028		
15 h ¹² CO	1.04.10-5	9.81.10-4	0.183	0.785		
		5.95.10-3	0.266	0.188	0.9977	
		8.84.10-2	0.546	0.026		



Figure 4.16. The CO consumption rate, C_{2+} formation rate, r_{out} as a function of time on stream at 250 °C, 1.5 bar, $H_2/CO = 2$.





Figure 4.17. Normalized transient response of H_2 , HD and D_2 upon an isotopic switch from CO/H₂ to CO/D₂ after different times on stream at: 250 °C, 1.5 bar, and H₂ (D₂)/CO = 2 (a) 1 h, (b) 2 h, and (c) 5h.

Table 4.3. Residence time of HD and estimated coverage of H based on the transient results shown in Fig. 4.17.

Time on stream (h)	Residence time of HD (s)	Coverage of H (1*10 ⁻²)
1	3.23	4.35
2	3.47	5.15
5	3.15	4.23



Figure 4.18. Normalized transient response of ${}^{12}C_2$ (${}^{12}C_2H_4 + {}^{12}C_2H_6$) upon a switch from ${}^{12}CO/H_2$ to ${}^{13}CO/H_2$ on streams at 250 °C, 1.5 bar, and H₂/CO = 2.



Figure 4.19. *Quasi in situ* XPS spectra of (a) Fe 2p and (b) C 1s region after 6 h reaction (250 °C, 1 bar, and $H_2/CO = 2$) and after subsequent 6 h exposure to 1 bar H_2 at 250 °C.



Figure 4.20. TPH after 6 h reaction (250 °C, 1 bar, and $H_2/CO = 2$) and after subsequent 6 h exposure to 1 bar H_2 at 250 °C.



Figure 4.21. Raman spectra after 6 h reaction (250 °C, 1 bar, and $H_2/CO = 2$) and after subsequent 6 h exposure to 1 bar H_2 at 250 °C.



Figure 4.22. TPH spectra after low-pressure reaction (250 °C, 1 bar, $H_2/CO = 2$ for 24 h) and after subsequent high-pressure reaction (250 °C, 20 bar, $H_2/CO = 2$ for 30 h).



Figure 4.23. XRD patterns of samples after low-pressure reaction (250 °C, 1 bar, and H₂/CO = 2 for 24 h) and high-pressure reaction at 250 °C, 20 bar, and H₂/CO = 2 for 30 h with varied preceding exposure times to low-pressure synthesis gas (250 °C, 1 bar, and H₂/CO = 2).



Figure 4.24. CO consumption rate (down-triangles), CH₄ formation rate (squares), C₂₊ formation rate (circles) and CO₂ formation rate (up-triangles) as a function of (a) CO partial pressure ($pH_2 = 3.2$ bar) (b) and H₂ partial pressure (pCO = 1.6 bar) at 250 °C, at 20 bar total pressure. The numbers n given next to each line are the calculated corresponding reaction orders in CO and H₂.



Figure 4.25. TEM images of samples after high-pressure reaction at 250 °C, 20 bar, and $H_2/CO = 2$ for 30 h with varied preceding exposure times to low-pressure synthesis gas (250 °C, 1 bar, and $H_2/CO = 2$) (a) 0 h, (b) 0.5 h and (c) 24 h.

Table 4.4. Average crystallite size and particle size after high-pressure reaction at 250 °C, 20 bar, and $H_2/CO = 2$ for 30 h with varied preceding exposure times to low-pressure synthesis gas (250 °C, 1 bar, and $H_2/CO = 2$).

Low massive pariod (b)	Average crystallite size	Average particle size (nm)	
Low-pressure period (ii)	(nm) based on XRD	based on TEM	
0	8.9	35.8	
0.5	8.8	35.0	
24	9.2	36.5	



Figure 4.26. *Quasi in situ* XPS spectra of (a) Fe 2p region and (b) C 1s region after highpressure reaction at 250 °C, 5 bar, and $H_2/CO = 2$ for 30 h with varied preceding exposure times to low-pressure synthesis gas (250 °C, 1 bar, and $H_2/CO = 2$).

Chapter 5

Comparison of $\varepsilon(')$ - and χ -carbide in the Fischer-Tropsch reaction

Abstract

Fe-carbides are the active phases in the Fe-based Fischer-Tropsch (FT) reaction. Here, we investigated the surface and catalytic properties of $\varepsilon(')$ -carbide and γ -Fe₅C₂, which are most frequently proposed to be the active phase in the low-temperature FT reaction. Raney-Fe was converted to either phase-pure $\varepsilon(')$ -carbide or γ -Fe₅C₂. To obtain the latter in pure form, a higher carburization temperature was needed, which resulted in a higher coverage with carbonaceous deposits in comparison to $\varepsilon(')$ -carbide. This hinders the direct comparison between these two carbides. By carrying out the FT reaction at high pressure, the carbonaceous deposits are largely removed, resulting in nearly similar steady-state activities of $\varepsilon(\dot{\gamma})$ -carbide and γ -Fe₅C₂. By excluding particle size effects, the presence of other phases, and C deposits on the catalytic performance, the intrinsic activity of ε (')-carbide and γ -Fe₅C₂ in the FT reaction are compared. They share similar FT activity and chain-growth probability. $\varepsilon($)-carbide shows slightly higher CH₄ selectivity. The higher Mars-Van Krevelen pathway contribution to the total CH₄ formation on $\varepsilon($)-carbide can tentatively explain its higher CH₄ selectivity. A high surface oxidization degree of carbide would lead to higher CO₂ selectivity. These two carbides also share similarities in terms of primary CO₂ formation. Compared to metallic Fe or Fe-oxide, Fe-carbide features lower primary CO₂ selectivity.



0

H

5.1 Introduction

Fischer-Tropsch (FT) synthesis is a versatile process to convert synthesis gas, a mixture of CO and H₂, into fuels and chemicals.[1, 2] Fe and Co catalysts are widely used in industrial FT synthesis.[3] Typical reaction conditions for the production of fuels and chemicals are temperatures and pressures in the range of 200-350 °C and 2-4.5 MPa, respectively.[4] A major difference between these two catalysts is the by-product that removes the O atom from CO dissociation. H₂O is the main by-product on Co, whereas the contribution of CO₂ by-product is much larger for Fe due to its significant water-gas shift (WGS) activity.[5] Therefore, Fe-based catalysts are often applied to convert synthesis gas with a relatively low H₂/CO ratio (0.5-1.3) obtained from coal and biomass feedstock.[3, 6, 7] Fe-based catalysts are preferentially used in industrial coal-to-liquids (CTL) technology.[8]

It is well established that Fe-carbide is the active phase in Fe-based FT catalysts. [9, 10] The relevant carbide phases are $\varepsilon(')$ -carbide, γ -Fe₅C₂ (Hägg carbide), Fe₇C₃ (Eckstrom and Adcock carbides), and Θ -Fe₃C (Cementite).[11] The formation of these phases depends strongly on the carburization conditions such as temperature, pressure and H_2/CO ratio.[12, 13] ϵ (')-carbide and χ -Fe₅C₂ are the most reported phases present in catalysts used under lowtemperature FT reaction conditions.[14, 15] A large amount of work has been devoted to compare the activity and product distribution for $\varepsilon(\dot{r})$ -carbide and γ -Fe₅C₂.[16] Chang *et al.* reported a higher activity yet lower chain-growth probability for χ -Fe₅C₂ in comparison to $\varepsilon(\dot{a})$ -carbide.[13] De Smit *et al.* found that a catalyst containing predominantly $\varepsilon(\dot{a})$ -carbide produces more long-chain hydrocarbons.[11] Eliason et al. observed that catalyst deactivation was caused by the transformation of the more active χ -Fe₅C₂ phase to the less active $\varepsilon(')$ -carbide one.[17] On the contrary, Chun *et al.* suggested that $\varepsilon(')$ -carbide is the more active phase in FT synthesis.[18] Wezendonk *et al.* pointed out that $\varepsilon(\dot{})$ -carbide and γ -Fe₅C₂ possess nearly equal catalytic activity under low-temperature FT conditions and reported a higher CH₄ selectivity for $\varepsilon(')$ -carbide, which was attributed to a higher hydrogenation ability.[19] An explanation for these conflicting results is that the used catalysts contained different Fe phases. Comparing the performance of catalysts that contain mixtures of different carbides and, typically, varying amounts of Fe-oxides and metallic Fe makes it difficult to identify the exact role of each Fe-carbide phase during the FT reaction.[20]

Usually, a constant amount of CO_2 is removed in the overall CTL process, either in a WGS step prior to the FT synthesis or in the FT synthesis reactor itself. The first approach allows for efficient capture and storage of CO_2 . Therefore, WGS activity in the FT reactor is undesirable, since CO_2 formed in the FT reactor will increase operational costs.[8] Thus, it is

beneficial to use Fe-based catalysts with an as low as possible CO₂ selectivity during the FT reaction. Fe-oxides are active catalysts for the WGS reaction.[21] The active sites for this reaction involve an Fe²⁺/Fe³⁺ redox couple at the surface of Fe₃O₄ magnetite.[22] Complete reduction of magnetite to metallic Fe or Fe-carbide suppresses the WGS reaction.[23] Typically, primary CO₂ and secondary CO₂ formation are distinguished.[24] The amount of primary CO₂ is independent of CO conversion and can be obtained by extrapolating CO₂ selectivity to zero CO conversion. The amount of secondary CO₂ relates to the WGS reaction between CO and the H₂O by-product and, therefore, increases with CO conversion. Primary CO₂ formation on phase-pure $\varepsilon(')$ -carbide is very small, implying a relatively low CO₂ selectivity during the FT synthesis.[8] It remains unclear whether pure χ -Fe₅C₂ also exhibits such a low primary CO₂ selectivity. Therefore, it is worthwhile to investigate the activity and product distribution of pure $\varepsilon(')$ -carbide and χ -Fe₅C₂ phases for the FT reaction.

In this contribution, we use pure $\varepsilon(')$ -carbide and χ -Fe₅C₂ catalysts to compare their catalytic performance in the FT reaction and understand mechanistic differences by excluding aspects such as the particle size, the presence of other Fe phases and the influence of C deposits built up during carburization. To prepare Fe-carbides without Fe-oxide, Raney-Fe was converted into either pure $\varepsilon(')$ -carbide or χ -Fe₅C₂ by adapted carburization procedures taken from literature.[8, 25] The phase purity of these Fe-carbide catalysts was determined by Mössbauer spectroscopy.[25] The surface and bulk composition of the two carbides were thoroughly compared by XPS, temperature-programmed hydrogenation (TPH), Raman spectroscopy and XRD. The activity and product distribution of the two catalysts in the FT reaction were compared under varying reaction conditions. The kinetics were studied by evaluating the reaction rates as a function of the H₂ and CO partial pressures. To investigate the role of Feoxides in the formation of primary CO₂, two composite catalysts were prepared that contained either a mixture of $\varepsilon(')$ -carbide and χ -Fe₅C₂ [26] or a mixture of $\varepsilon(')$ -carbide, χ -Fe₅C₂ and Fe₃O₄. Isotopic switching experiments and IR spectroscopy on carburized and reduced samples were employed to illustrate the mechanism of the CO₂ formation.

5.2 Experimental methods

Catalyst preparation

The formation of specific Fe-carbide phases strongly depends on the carburization conditions such as temperature, pressure, and gas composition. Also other factors such as crystallite size, morphology, surface texture, promoters or inhibitors can influence carbide formation.[13] We used literature procedures starting from Raney-Fe to prepare phase-pure χ -Fe₅C₂ and ϵ (')carbide as well as a reference material containing a mixture of these two carbides. In addition, a sample was prepared containing a mixture of the two carbides together with magnetite (Fe_3O_4) . The corresponding preparation protocols are given in Scheme 5.1 and described below. Table 5.1 contains fit parameters of the Mössbauer spectra of the first three samples, while XRD data are presented in the results and discussion section to demonstrate the presence of Fe₃O₄ in the latter sample.

Raney-Fe. Raney-Fe was prepared from an aluminum-iron (Al50/Fe50) alloy (Goodfellow, 150-micron powder). 5 g of the Al-Fe alloy powder was slowly added to 25 ml of a 9 M KOH (Sigma-Aldrich) solution in a round-bottom flask at 70 °C. Caution was needed, as this reaction produces hydrogen. After 40 min stirring, the mixture was cooled to room temperature. The suspension was washed with water and ethanol 7 times each, to remove potassium and aluminum ions and retrieve the precipitated Raney-Fe. Due to the pyrophoric character of the fine Fe powder, the catalyst was passivated in a 1 vol% O_2 in He flow for 24 h at room temperature for safe handling.



Scheme 5.1. Protocols used for obtaining pure χ -Fe₅C₂, pure ϵ (')-carbide, a mixture of ϵ (')-carbide and χ -Fe₅C₂, and a mixture of ϵ (')-carbide, χ -Fe₅C₂ and Fe₃O₄ from Raney-Fe.

 χ -Fe₅C₂. The C atoms in χ -Fe₅C₂ reside in trigonal prismatic interstitial sites of the hexagonal Fe lattice.[27] This carbide is stable at relatively high temperatures and low CO partial pressure.[11] Following a procedure as described in literature,[25] Raney-Fe was carburized in a H₂-rich synthesis gas (81% H₂ and 2.7% CO in He, 111 ml/min, 1 bar) at a 350 °C using a rate of 1 °C/min followed by a dwell of 6 h.

 $\varepsilon()$ -carbide. The C atoms in $\varepsilon()$ -carbide are located in the octahedral interstitial sites of the hexagonal lattice structure of Fe atoms. It has been postulated that formation of $\varepsilon($ ')-carbide requires higher deformation energy and is entropically disfavored compared to χ -Fe₅C₂ formation. Due to the slow diffusion of C atoms into the Fe lattice, the formation of the carbon-rich $\varepsilon(')$ -carbide phase is kinetically hindered.[11] Therefore, $\varepsilon(')$ -carbide can only be obtained under conditions that represent a high C coverage. [26] To obtain an Fe surface with high C coverage (and low O coverage), Raney-Fe has to be fully reduced. Two subsequent carburization steps with increasingly higher CO partial pressure are needed to obtain the carbon-rich $\varepsilon(\hat{})$ -carbide. Due to the low stability of $\varepsilon(\hat{})$ -carbide at high temperature both carburization steps have to be performed at maximally 250 °C. Following a procedure from literature, [8] Raney-Fe was reduced in a dilute H_2 flow (20% H_2 in He, 50 ml/min, 1 bar) at 430 °C at a rate of 5 °C/min followed by a dwell of 1 h. After reduction, the reactor was cooled to 170 °C. The sample was pre-carburized in synthesis gas (16% H_2 and 8% CO in He, 50 ml/min, 1 bar) for 40 min to pre-deposit carbon. Subsequently, the gas composition was adjusted to 43% H₂ and 28.5% CO in He, 50 ml/min at 1 bar. The temperature was increased at a rate of 0.5 °C/min to 250 °C and kept at this temperature for 6 h carburization.

Mixture of ϵ (')**-carbide and** χ **-Fe**₅**C**₂**.** Following a procedure as described in literature,[26] Raney-Fe was reduced in a dilute H₂ flow (20% H₂ in He, 50 ml/min, 1 bar) at 430 °C using a ramp of 5 °C/min followed by a dwell of 1 h. After cooling down to 250 °C, the sample was carburized in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min, 1 bar) for 6 h.

Mixture of ϵ **(')-carbide,** χ **-Fe**₅**C**₂ **and Fe**₃**O**₄**.** Raney-Fe was treated in a He flow (50 ml/min, 1 bar) at 250 °C using a ramp of 5 °C/min followed by a dwell of 1 h. Then, the catalyst was exposed to synthesis gas (16% H₂ and 8% CO in He, 50 ml/min, 1 bar) for 1 h carburization. The composition of the catalyst was confirmed by XRD, which will be shown in the results and discussion section.

Fe/SiO₂ catalyst. SiO₂-supported Fe sample was prepared by incipient wetness impregnation method of a silica support (SiO₂ Q15, 120 mesh, Sasol) with an aqueous solution of Fe(NO₃)₃·9H₂O (AR, Sinopharm Chemical Reagent Co.). The sample was sequentially dried at 80 °C for 12 h and 120 °C for 24 h and then calcined at 500 °C for 5 h in static air.[14] Fe/SiO₂ was used to carry out *in situ* IR spectroscopy.

Sample	IS (mm/s)	Hyperfine field (T)	Г (mm/s)	Phase	Spectral contribution (%)
Pure $\varepsilon(')$ -	0.28	18.7	0.56	ε'-Fe _{2.2} C	61
carbide [8]	0.24	25.3	0.86	ε-Fe ₂ C	39
	0.26	25.0	0.48	χ-Fe ₅ C ₂ (I)	42
Pure χ -Fe ₅ C ₂ [25]	0.18	21.8	0.50	χ-Fe ₅ C ₂ (II)	38
	0.14	13.9	0.47	χ-Fe ₅ C ₂ (III)	20
	0.00	33.8	0.30	Fe ⁰	5
Mintune of o(')	0.21	26.1	0.35	ϵ -Fe ₂ C (I)	12
Mixture of $\varepsilon()$ -	0.23	19.3	0.35	ϵ -Fe ₂ C (II)	29
Earbide and χ -	0.22	17.7	0.39	€'-Fe _{2.2} C	29
FE5C2 [20]	0.23	24.1	0.39	χ -Fe ₅ C ₂ (I)	12
	0.17	21.4	0.39	χ -Fe ₅ C ₂ (II)	9
	0.18	10.1	0.39	χ -Fe ₅ C ₂ (III)	4

 Table 5.1. Mössbauer fit parameters of carburized Raney-Fe samples.

Catalyst characterization. Before TEM, XRD and Raman spectroscopy, as-prepared and spent $\epsilon(')$ -carbide and χ -Fe₅C₂ were first passivated in a flow of 1 vol% O₂ in He for 24 h at room temperature.

Transmission electron microscopy (**TEM**). A few milligrams of catalyst powder were suspended in ethanol. The suspension was sonicated to fully suspend all particles. Afterwards, a few drops of the suspension were applied on a carbon-coated copper grid. TEM images were captured using a FEI Technai 20 transmission electron microscope using an acceleration voltage of 200 kV with a LaB6 filament. The ImageJ software was used to process the images and determine the average particle size.

X-ray diffraction (XRD). XRD was carried out on a Bruker D2 Phaser diffractometer equipped with a Cu K_{α} radiation source. XRD patterns were recorded in the 2 θ range of 30-60° using a step size of 0.02° and a step time of 1 s.

Raman spectroscopy. Raman spectroscopy was conducted on a Witec Alpha 300 R Raman microscope equipped with a CCD1 detector, a Zeiss 10x NA = 0.25 objective and a grating of 300 g/mm. Spectra were acquired using a laser power of 2 mW at λ_{exc} = 532 nm with a collection time of 40 s by averaging 20 scans.

Quasi in situ X-ray photoelectron Spectroscopy (XPS). XPS spectra were recorded in a Kratos AXIS Ultra 600 spectrometer equipped with a monochromatic Al K_a X-ray source (hv = 1486.6 eV). Region scans were recorded at a pass energy of 40 eV (step size 0.1 eV) and survey scans were recorded at a pass energy of 160 eV (step size 0.5 eV) with the background pressure being kept below 5×10^{-9} mbar. A high-temperature reaction cell (Kratos, WX-530) was used to carburize Raney-Fe. The Raney-Fe was pressed into a pellet and placed on a stainless-steel stub, allowing *in vacuo* sample transfer into the XPS analysis chamber. High-pressure reaction on as-prepared ϵ (')-carbide or χ -Fe₅C₂ was conducted by increasing the reactor pressure to 5 bar in synthesis gas (66% H₂ and 33% CO, 50 ml/min at 250 °C). Notably, the H₂ and CO pressures used in this 5 bar XPS experiment are the same as the partial pressures used for the 20 bar the catalytic experiments described below, as the 20 bar pressure was obtained by addition of He. The reaction was stopped after a certain time, followed by transfer of the evacuated sample to the XPS analysis chamber. Fitting of the XPS spectra was done using Voigt functions after a Shirley background subtraction using the CasaXPS software (version 2.3.18PR1.0).

Temperature-programmed hydrogenation (TPH). In each experiment, 50 mg sample was loaded in a quartz tubular flow reactor and carburized *in situ* according to the above-described procedures to obtain the desired carbide. After flushing with He and cooling to room temperature, TPH experiments were conducted by heating the reactor from room temperature to 750 °C using a rate of 5 °C/min in a diluted H₂ flow (20% H₂ in He, 50 ml/min). The gas feed was controlled by thermal mass flow controllers. The effluent mixture was analyzed using an online mass spectrometer (MS, Balzers TPG-300) and an online gas chromatograph (GC, Compact GC 4.0). During *in situ* TPH, H₂ (m/z = 2), He (m/z = 4), CH₄ (m/z = 15) and H₂O (m/z = 18) were monitored by online MS. The main hydrocarbon product was CH₄ (> 96 %). For TPH analysis after high-pressure FT activity evaluation, the used catalyst sample was transferred *via* air to the same quartz tubular flow reactor as used above after being passivated in a 1 vol% O₂ in He flow for 24 h at room temperature.

In situ **IR spectroscopy.** IR spectroscopy was carried out on a Bruker Vertex 70v spectrometer equipped with a DTGS detector by averaging 8 spectra at a 2 cm⁻¹ resolution. IR spectra were recorded in a controlled environment cell with CaF₂ windows. Typically, Fe/SiO₂ samples were pressed into self-supporting wafers of *ca.* 10 mg. CO adsorption was conducted on reduced and carburized samples. *In situ* reduction of Fe/SiO₂ was performed in an atmospheric mixture of 50/50 vol% H₂/N₂ at 550 °C for 6 h. After reduction, the sample was outgassed (250 °C, 1 bar) for 10 min. Afterward, the cell was cooled to 30 °C for CO adsorption. A background IR spectrum was recorded before dosing CO in small increments by a sample loop. IR spectra were collected as a function of the CO pressure. For

carburization of the Fe/SiO₂, it also required the same reduction procedure. After reduction, the cell was cooled to 250 °C followed by the introduction of synthesis gas (16% H₂ and 8% CO in N₂, 50 ml/min, 1 bar) for 1 h carburization. Subsequently, the sample was treated in a dilute H₂ flow (20% H₂ in N₂, 50 ml/min, 1 bar) for 10 min to remove the adsorbed C species from the surface. Afterward, the cell was cooled to 30 °C for CO adsorption. The same treatment procedure for CO dose was applied as for the reduced sample.

Transient isotopic kinetic experiments. In a typical experiment, 50 mg Raney-Fe mixed with SiC was loaded in a steady state isotopic transient kinetic analysis (SSITKA) setup. Details of this setup can be found in the literature.[28] In the case of χ -Fe₅C₂, 150 mg Raney-Fe mixed with SiC was loaded to get a decent CH₄ signal. All the experiments were conducted under differential conditions.

ε(')-carbide or χ-Fe₅C₂ was *in situ* synthesized before use. Transient isotopic kinetic measurements were performed on ε(')-carbide and χ-Fe₅C₂ by switching from a H₂/¹³CO/Ne mixture (8/4/2 ml/min, 1.5 bar) to a H₂/¹²CO/Ar mixture (8/4/2 ml/min, 1.5 bar) at 250 °C. In all cases, an Ar flow was added to the feed to keep the total flow rate at 50 ml/min. The transient responses of ¹²CH₄ (m/z = 15), ¹³CH₄ (m/z = 17), H₂O (m/z = 18), Ne (m/z = 22), ¹²CO (m/z = 28), ¹³CO (m/z = 29) and Ar (m/z = 40) were monitored by online MS (ESS CatalySys).

The reduced catalyst was obtained by exposing Raney-Fe in a dilute H₂ flow (20% H₂ in He, 50 ml/min, 1.5 bar) at 430 °C using a rate of 5 °C/min followed by a dwell of 1 h. The carburized catalyst was obtained by cooling the reduced catalyst to 250 °C followed by introduction of synthesis gas (16% H₂ and 8% CO in He, 50 ml/min, 1.5 bar) for 1 h. After reduction and carburization, the reactor was cooled to 30 °C by flushing with Ar. Transient isotopic kinetic measurements were performed by switching from a H₂/¹³CO/Ne mixture (8/4/2 ml/min, 1.5 bar) to a H₂/¹²CO/Ar mixture (8/4/2 ml/min, 1.5 bar) at 30 °C. In all cases, an Ar flow was added to the feed to keep the total flow rate at 50 ml/min. The transient responses of Ne (m/z = 22), ¹²CO (m/z = 28), ¹³CO (m/z = 29) and Ar (m/z = 40) were monitored.

Catalytic activity measurements

Low-pressure FT reaction. An amount of 50 mg catalyst mixed with SiC was loaded in the SSITKA setup. The FT reaction on ϵ (')-carbide or χ -Fe₅C₂ was conducted at 1.5 bar in synthesis gas (16% H₂ and 8% CO in Ar, 50 ml/min) at 250 °C. The catalytic activity and product distribution were determined by an online gas chromatograph (Thermo Scientific Trace 1300 extended with a Trace 1310 auxiliary oven). A combination of an MXT-QBond column (60 m \cdot 0.53 mm) with a thermal conductivity detector was used to determine the 120

concentration of CO₂, CO, H₂ and CH₄, while a combination of a Rt-SilicaBond column (60 $m \cdot 0.32 mm$) with a flame ionization detector was used to analyze hydrocarbons.

High-pressure FT reaction. In a typical experiment, 20 mg catalyst mixed with SiC was loaded in a stainless-steel tubular flow reactor placed in a Microactivity-Reference unit. The setup operated in down-flow mode is equipped with thermal mass flow controllers to supply gases to the top of the reactor. The catalytic performance was determined in synthesis gas (16% H₂ and 8% CO in He, 50 ml/min) at 250 °C and a pressure of 20 bar. The effluent mixture was analyzed by an online gas chromatograph (Thermo Scientific Trace 1300). A combination of an XL-Sulfur column (1.25 m \cdot 1.59 mm) and a Molsieve 5A column (2 m \cdot 1.59 mm) with a thermal conductivity detector was used to determine the concentration of CO₂, CO, H₂, CH₄ and the internal standard gas Ar. A combination of an Rtx-1 column (25 m \cdot 0.15 mm) with a flame ionization detector was used to analyze hydrocarbons. Another reference FT reaction test involved the use of 50 mg catalyst mixed with SiC in synthesis gas (16% H₂ and 8% CO in He, 50 ml/min, 23 bar) at 250 °C.

5.3 Results and discussion

Characterization of ϵ (')-carbide and χ -Fe₅C₂

The XRD patterns shown in Fig. 5.1a confirm that the first two synthesis protocols from Scheme 5.1 result in the formation of phase-pure $\varepsilon(')$ -carbide and χ -Fe₅C₂ samples. The Raman spectra of as-prepared χ -Fe₅C₂ and ε (')-carbide (Fig. 5.1b) show that the D and G bands, [29] typical for disordered and ordered graphitic species respectively, are more pronounced for χ -Fe₅C₂ than for ε (')-carbide. A higher amount of C deposits can be attributed to the higher carburization temperature needed to obtain γ -Fe₅C₂.[11] *Quasi in situ* XPS confirms that the surface of χ -Fe₅C₂ contains more carbon (Fig. 5.1c). The C 1s spectra show a stronger signal in the C-C/C=C region due to hydrocarbon fragments with hybridized sp³ and sp² bonds, [30] while the C 1s signal at a binding energy of 283.1 eV due to C in the Fecarbide [31] is less intense for χ -Fe₅C₂. Both samples exhibit the same Fe 2p signal at 706.9 eV due to reduced Fe. Comparison of the $\varepsilon(')$ -carbide and γ -Fe₅C₂ spectra shows that the intensities of the C 1s peak of Fe-carbide as well as the Fe 2p peaks are lower for χ -Fe₅C₂ than for $\varepsilon()$ -carbide, while the C 1s peak due to hydrocarbon fragments is higher, indicating that a larger part of the catalytic surface of γ -Fe₅C₂ is covered by C deposits, weakening the intensities of Fe and carbidic C. Both samples contain some oxidized Fe species. This can be due to their stabilization by residual Al_2O_3 of the Raney-Fe precursor, [26] but it is also possible that the very reactive (pyrophoric) nature of reduced Fe-carbides will lead to some surface oxidation during the vacuum transfer step from the reaction chamber to the XPS analysis chamber during the XPS experiments. Irrespective of this, the Fe 2p spectra show

that the surface of χ -Fe₅C₂ is more oxidized (Fe^{2+,3+}/Fe⁰ ratio 0.42) than the surface of ε (')carbide (Fe^{2+,3+}/Fe⁰ ratio 0.21). The higher oxidation degree of χ -Fe₅C₂ is most likely related to the absence of a reduction step in the synthesis procedure (see Scheme 5.1). This suggests that surface O species do not hinder the formation of χ -Fe₅C₂.[26] The higher amount of Feoxide at the surface of χ -Fe₅C₂ is in line with the higher H₂O signal during *in situ* TPH after synthesis (see in Appendix Fig. 5.10). Note that the H₂O signal is substantially lower than the CH₄ signal, in line with the predominant formation of Fe-carbide and oxidation being limited to the surface.

TPH was used to identify the different C species in the Fe-carbide samples. The results are shown in Fig. 5.1d. The TPH profile of $\varepsilon(')$ -carbide contains two reduction features. The peak between 200 °C and 400 °C relates to adsorbed atomic C, surface carbide and polymeric amorphous C.[32] Such species can be hydrogenated relatively easily and are further referred to as reactive surface C species.[33] The main peak at higher temperature can be assigned to hydrogenation of C atoms that are part of bulk Fe-carbide. The delayed hydrogenation of χ - Fe_5C_2 compared to $\varepsilon(')$ -carbide can be explained by the higher amount of C deposits blocking the surface of the former catalyst. The hydrogenation of less reactive deposited C and bulk C overlap. The higher stability of χ -Fe₅C₂ during hydrogenation could also be due to more stable lattice C in this carbide compared to $\varepsilon($ ')-carbide as suggested in earlier work.[34] Xu et al. also found that the bulk carbide hydrogenation peak for $\varepsilon($)-carbide appears at lower temperature than the one for γ -Fe₅C₂.[32] The amount of reactive surface C species observed on χ -Fe₅C₂ is very small. This is in agreement with the Raman and XPS data, which show that, compared to $\varepsilon(\dot{z})$ -carbide, more of the surface of χ -Fe₅C₂ is blocked by less reactive C deposits. A possible explanation for the lower amount of reactive surface C species on χ - Fe_5C_2 is the use of H₂-rich synthesis gas (H₂/CO = 30) for carburization, which can remove a larger fraction of reactive C species during Fe-carbide synthesis. In conclusion, the higher temperature, and the use of more H₂-rich synthesis gas for obtaining γ -Fe₅C₂ results in a surface richer in less reactive C deposits.



Figure 5.1. (a) XRD patterns, (b) Raman spectra, (c) *quasi in situ* XPS spectra (Fe 2p and C 1s regions) and (d) *in situ* TPH profiles of as-prepared $\varepsilon(')$ -carbide and χ -Fe₅C₂.

Catalytic activity

The low-pressure catalytic FT performance data (1.5 bar, H₂/CO = 2, and 250 °C) of *in situ* synthesized ε (')-carbide and χ -Fe₅C₂ are shown in Fig. 5.2. As can be seen, ε (')-carbide is much more active than χ -Fe₅C₂ under these reaction conditions. The low activity of χ -Fe₅C₂ is most likely due to the large amount of relatively stable C deposits present on its surface. Both catalysts suffer from deactivation, albeit χ -Fe₅C₂ to a lesser extent (inset in Fig. 5.2). The deactivation can be related to the further deposition of C species during reaction, as C hydrogenation is a slow step in the FT reaction over Fe-carbides under these conditions (Chapter 4).



Figure 5.2. CO conversion as a function of time on stream on ε (')-carbide and χ -Fe₅C₂ at 250 °C, 1.5 bar and H₂/CO = 2.

It is clear that a straightforward comparison between the catalytic properties of the two carbide phases at relatively low pressure (H₂/CO = 2 at 250 °C and 1.5 bar) is hampered by the rapid deactivation of $\varepsilon(')$ -carbide, whereas χ -Fe₅C₂ is already strongly poisoned by C deposits before the start of the reaction. Our previous work showed that operating the FT reaction at elevated pressure can remove C species, thereby decreasing deactivation or even reversing the poisoning effect of C species deposited during carburization (Chapter 4). Therefore, we compared the catalytic performance of as-prepared $\varepsilon(')$ -carbide and χ -Fe₅C₂ at high-pressure conditions (H₂/CO = 2 at 250 °C and 20 bar).

The catalytic activity data at 20 bar as a function of time on stream (Fig. 5.3a) show that the CO conversion for $\varepsilon(')$ -carbide is stable under these conditions. In contrast, the CO conversion over χ -Fe₅C₂ gradually increases and reaches a stable state after approximately 38 h reaction, suggesting that indeed some of the C deposits remaining after catalyst synthesis are slowly removed during reaction at 20 bar (Chapter 4). Fig. 5.3b and 5.3c demonstrate that the CO₂ and CH₄ selectivity, the chain-growth probability α and the C₂₋₄ olefins-to-paraffins ratio on $\varepsilon(')$ -carbide hardly change over time, which is in line with the nearly stable CO conversion. In contrast, the C₂₋₄ olefins-to-paraffins ratio on χ -Fe₅C₂ (Fig. 5.3c) decreases over time along with the increasing CO conversion (Fig. 5.3a). This can be explained by the removal of C deposits on the surface, exposing more active sites for olefin re-adsorption and hydrogenation. It is commonly assumed that olefins are the primary products of the FT reaction, which are subsequently hydrogenated to paraffins.[35, 36] The chain-growth

probability and C₂₋₄ olefins-to-paraffins ratio on ϵ (')-carbide and χ -Fe₅C₂ become nearly similar after prolonged reaction. Another significant change observed for χ -Fe₅C₂ with reaction time is the increasing CO₂ selectivity. We attribute this to the gradually increasing CO conversion, which leads to a higher H₂O partial pressure and a larger contribution of the WGS reaction. After prolonged reaction, the CO₂ selectivity of χ -Fe₅C₂ is lower than for ϵ (')carbide at similar CO conversion. The CH₄ selectivity of χ -Fe₅C₂ is always lower than for ϵ (')-carbide. In conclusion, χ -Fe₅C₂ exhibits a lower CO₂ and CH₄ selectivity, while activity, chain-growth probability, and olefins-to-paraffins ratio are very similar. The final conversion and selectivity values after reaching steady state are presented in Table 5.2. To further confirm ϵ (')-carbide and χ -Fe₅C₂ possess similar activity, we also evaluated these samples at a slightly higher reaction pressure (p = 23 bar) under otherwise similar conditions and found again that they exhibited similar catalytic activity with a lower CO₂ and CH₄ selectivity for χ -Fe₅C₂ in Appendix Table 5.3.



Figure 5.3. (a) CO conversion, (b) CO₂ and CH₄ selectivity, (c) chain-growth probability α and C₂₋₄ olefins-to-paraffins ratio as a function of time on stream at 250 °C, 20 bar and H₂/CO = 2 on ϵ (')-carbide and χ -Fe₅C₂.

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	CO conversion	CO_2	CH ₄	Chain-	C ₂₋₄ olefins-to
		selectivity	selectivity	growth	-paraffins
		(%)	(%)	probability	ratio
ε(')-carbide	0.10	12.2	17.5	0.51	1.50
χ -Fe ₅ C ₂	0.11	10.0	12.3	0.52	1.50
ε(')-carbide					
+ treated in					
Haat 250 °C	0.12	12.0	12.5	0.57	1.28
112 at 250 C					
for 5 h					
ε(')-carbide					
+ treated in					
	0.14	9.4	10.1	0.59	1.25
H_2 at 350 °C					
for 5 min					

Table 5.2. Catalytic performance of ϵ (')-carbide and χ -Fe₅C₂ at steady state (250 °C, 20 bar and H₂/CO = 2).

The TPH profiles of $\varepsilon(')$ -carbide and χ -Fe₅C₂ after the FT reaction at elevated pressure are displayed in Fig. 5.4a. Comparison of TPH profiles of χ -Fe₅C₂ at low pressure (Fig. 5.1d) and elevated pressure (Fig. 5.4a) shows that a new low-temperature peak appears after reaction at elevated pressure, suggesting that a higher amount of reactive surface C species are present during the high-pressure reaction in line with the more exposed nature of the catalytic surface. However, the amount of reactive surface C species on χ -Fe₅C₂ is still lower than on $\varepsilon(')$ -carbide. Notably, it is still easier to hydrogenate bulk C in $\varepsilon(')$ -carbide than in χ -Fe₅C₂, similar to the difference observed at low pressure. Our previous work suggested that lattice C atoms in carbide bulk can also be involved in the FT reaction *via* a Mars-Van Krevelen (MvK) mechanism (Chapter 3).

As mentioned above, the effect of the carbide phase on the FT activity and selectivity has been extensively studied before with contradicting conclusions,[11, 13, 17-19] most likely due to the simultaneous presence of different Fe-carbide phases as well as remaining Feoxides and metallic Fe in the studied catalysts. This significantly hampers proper evaluation of the FT performance of individual Fe-carbide phases. In order to rule out any particle size effect on the catalytic performance in our study, TEM analysis was conducted on spent $\varepsilon(\dot{})$ carbide and γ -Fe₅C₂ catalysts. As shown in Appendix Fig. 5.11, the average particle sizes of $\varepsilon(')$ -carbide and χ -Fe₅C₂(35 and 37 nm, respectively) are nearly the same. The slightly larger particle size of γ -Fe₅C₂ may be explained by some sintering due to the higher carburization temperature. The particle size of the samples is well above the size where structure sensitivity is expected,[37] which allows the estimation of a surface-normalized activity comparison of the product distribution. To evaluate whether the formed $\varepsilon(\dot{z})$ -carbide and χ -Fe₅C₂ are stable under reaction conditions, the structure of the spent catalysts was analyzed by XRD. Comparison of Fig. 5.1a with Fig. 5.4b shows that the XRD patterns of $\varepsilon(')$ -carbide and γ -Fe₅C₂ hardly changes during the FT reaction. Moreover, neither of the two catalysts suffers from severe oxidation, as no typical peaks belonging to Fe-oxides appear. As shown above, the presence of C deposits on γ -Fe₅C₂ before high-pressure reaction hinders direct comparison of the catalytic performance of the two considered carbides. However, after highpressure reaction, the amount and nature of C deposited on $\varepsilon(\dot{r})$ -carbide and γ -Fe₅C₂ are comparable, as follows form the practically overlapping Raman spectra in Fig. 5.4c, indicating that not the C deposits but the higher stability of χ -Fe₅C₂ might be the cause for its delayed hydrogenation showed in Fig. 5.4a. Excluding particle size effects, the presence of other phases and C deposits on the catalytic performance, it is reasonable to expect that the activity and selectivity differences between ϵ (')-carbide and γ -Fe₅C₂ relate to intrinsic differences in carbide properties.

As can be seen in Table 5.2 and Appendix Table 5.3, the CO conversion levels of $\varepsilon(')$ -carbide and χ -Fe₅C₂ at high pressure are comparable. Our previous results suggest that the main reaction pathway leading to hydrocarbons on Fe-carbide involves a small fraction of active sites with a relatively high activity following a Langmuir-Hinshelwood (L-H) mechanism, mainly responsible for long-chain hydrocarbons (Chapter 4). Another fraction of sites that operate via an MvK mechanism mainly leads to CH₄ formation. As it is likely the Fe-carbides operate in the C-removal limit, [36] the nearly similar FT activity and chain-growth probability of $\varepsilon(')$ -carbide and χ -Fe₅C₂ imply that the surface C hydrogenation do not vary much between the two investigated carbides. It is worthwhile to compare these data to results of microkinetics simulations based on DFT energetics of the FT mechanism for reactive stepped surfaces of the two Fe-carbides considered here, namely γ -Fe₅C₂(100) and ϵ -Fe₂C(011).[38] At a temperature of 237 °C and a H₂/CO ratio of 2, Broos et al. predicted a slightly higher rate on χ -Fe₅C₂(100) and nearly similar chain-growth probabilities of 0.52 for both surfaces. This is in qualitative agreement with the present experimental results. These simulations also showed that the CH_4 selectivity was ~25% at 1 bar but decreased to values below 20% at elevated pressure (e.g., 19% at 5 bar). The predicted CO₂ selectivity for the

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two stepped Fe-carbide surfaces in the microkinetic simulations was lower than 1%, indicative of the preference for the removal of O as H_2O . The much higher CO_2 selectivity in the experiment can be explained by the partial oxidation of the surface, resulting in a higher WGS rate than for the fully reduced Fe-carbide surfaces. The observed difference in CO₂ selectivity between the two catalysts is in line with the higher amount of oxidized Fe on the surface of $\varepsilon(')$ -carbide (Fig. 5.4d). The C 1s spectra show that $\varepsilon(')$ -carbide feature a stronger signal intensity for the O-C=O component, which can be directly related to the adsorption of CO or CO_2 on O-containing surface species to form formate or carbonate.[39] Comparison of the Fe 2p spectra in Fig. 5.4d with the spectra in Fig. 5.1c also shows that the surface of both catalysts oxidizes further during the high-pressure FT reaction. Although directly after preparation the surface of $\varepsilon(\dot{\gamma})$ -carbide was less oxidized than the surface of γ -Fe₅C₂, the highpressure reaction leads to a more extensive oxidation of the former surface. This can also be proved by the higher H₂O signal on $\varepsilon($)-carbide during ex situ TPH after reaction (see in Appendix Fig. 5.12). The higher degree of oxidation of the surface can be linked to the higher CO conversion, which leads to a higher H_2O partial pressure. It should be noted that the higher oxidation degree of $\varepsilon(\dot{})$ -carbide as compared to χ -Fe₅C₂ is likely due to its higher activity at the beginning of the high-pressure reaction (Fig. 5.3). While XPS clearly shows that the surface is oxidized, bulk characterization methods like XRD and Mössbauer spectroscopy do not show the formation of Fe-oxide in these samples under high-pressure conditions.[25] This implies that the oxidation is limited to the surface region. The transformation from Fe-carbide to bulk Fe-oxide during the ongoing FT reaction is one of the main concerns with respect to catalyst stability.[40] The absence of bulk Fe-oxide in the spent catalysts is consistent with the stable performance observed in the time frame of the high-pressure FT reaction experiments. The C₂₋₄ olefins-to-paraffins ratio is comparable on $\varepsilon(\dot{r})$ -carbide and γ -Fe₅C₂. It is difficult to explain the differences in CH₄ selectivity. Migration of CH_x growth monomers from stepped surfaces to less reactive terraces can play a role in the higher amount of CH₄ formed compared to Anderson-Schulz-Flory statistics as shown before for Co-based catalysts.[41] On the other hand, at least part of CH₄ originates from MvK sites on Fe-carbides, whose contribution may be different for the two catalysts without strongly affecting the main FT reaction products and total activity.

Fig. 5.4a shows that bulk χ -Fe₅C₂ hydrogenation is delayed in comparison to $\varepsilon(')$ -carbide. The difference in TPH peak maxima between these two carbides can be explained by the overall exothermicity of Fe-carbide decomposition in H₂. The reaction energy was estimated for the reaction of χ -Fe₅C₂ + 4 H₂ $\rightarrow \alpha$ -Fe + 2 CH₄ and ε -Fe₂C + 2 H₂ $\rightarrow \alpha$ -Fe + CH₄ using DFT (see Appendix for computational details). Appendix Table 5.4 shows that hydrogenation of $\varepsilon(')$ -carbide is favored over that of χ -Fe₅C₂. This means that removal of lattice C *via* an MvK mechanism is slower on χ -Fe₅C₂. This is qualitatively in line with the lower amount of CH₄ formed on χ -Fe₅C₂. As the MvK pathway contributes only slightly to the overall FT rate, this increased contribution would not affect the overall rate and product distribution. The small contribution of lattice C hydrogenation to the total activity was further investigated by SSITKA. The deactivation-corrected transient responses of CH₄ after an isotopic switch from ¹²CO/H₂ to ¹³CO/H₂ on $\varepsilon(')$ -carbide and χ -Fe₅C₂ (Appendix Fig. 5.13) were fitted by 4 parallel reaction paths as done before (Chapter 3). The fitted rate constant k_i of each pathway, the corresponding fractional contribution to the total reaction rate, x_{i} , and the fractional contribution to the total number of active sites, y_{i} are listed in Appendix Table 5.5 together with the goodness-of-fit indication (R²). The activity contribution is higher for $\varepsilon(')$ -carbide (0.106) than for χ -Fe₅C₂ (0.059). This suggests that there is a larger contribution of lattice C hydrogenation to CH₄ *via* an MvK mechanism on $\varepsilon(')$ -carbide than on χ -Fe₅C₂.



Figure 5.4. (a) TPH profiles, (b) XRD patterns, (c) Raman spectra of the spent $\varepsilon(')$ -carbide and χ -Fe₅C₂ after reaction at 20 bar and (d) *Quasi in situ* XPS spectra (Fe 2p and C 1s region)

of ε (')-carbide and χ -Fe₅C₂ after reaction at 5 bar, with CO and H₂ partial pressures similar to the high pressure reaction at 20 bar (250 °C, H₂/CO = 2, 38 h).

From the low-temperature feature in the TPH profiles in Fig. 4a, $\varepsilon()$ -carbide contains more surface lattice C than χ -Fe₅C₂. To explore a possible correlation with the CH₄ selectivity during the FT reaction, as-prepared $\varepsilon(')$ -carbide was treated in H₂ either at 250 °C for 5 h or at 350 °C for 5 min in an attempt to selectively remove such species. After such treatments, the low-temperature reduction feature is significantly decreased in the TPH profiles (Appendix Fig. 5.14a), similar as was demonstrated in Chapter 4. Comparison of the C/Fe ratio before and after H_2 treatment (inset Appendix Fig. 5.14a) and considering the dispersion suggest that more than only surface C species were removed by the H_2 treatment (*i.e.*, ca. 20%) of C is removed). After H₂ treatment at 250 °C, it becomes easier to hydrogenate the bulk C species of $\varepsilon(')$ -carbide. However, bulk C hydrogenation shifts to higher temperature when the H₂ treatment was done at 350 °C. XRD patterns in Appendix Fig. 5.14b explain this difference by a phase change from $\varepsilon(\dot{\gamma})$ -carbide to γ -Fe₅C₂ during the H₂ treatment at 350 °C. Such a phase change does not occur during H₂ treatment at 250 °C. This comparison demonstrates that hydrogenation is intrinsically easier for $\varepsilon(')$ -carbide than for χ -Fe₅C₂. Table 5.2 shows that the catalysts are not only more active after the H_2 treatment but also exhibit a higher chain-growth probability and lower CH_4 selectivity in comparison to the $\varepsilon()$ -carbide reference. This provides a link between the CH₄ selectivity and the presence of lattice C species at the surface.

To further investigate this aspect, we also carried out TPH measurements after high-pressure FT reaction at 20 bar for samples with and without H_2 treatment. These data were slightly different from those in Fig. 5.4a due to the use of a different batch of catalyst. Overall, the results show similar trends with smaller low-temperature peaks for the H₂-treated samples than as-prepared and spent $\varepsilon(')$ -carbide (Fig. 5.5a). The XRD patterns in Fig. 5.5b evidence that in this case both H₂-treated samples underwent a phase change to χ -Fe₅C₂, whereas the untreated sample remains pure $\varepsilon($)-carbide. This explains the shift to higher temperatures of main bulk reduction feature in the TPH profiles for H_2 -treated samples in Fig. 5.5a. The results show that the removal of lattice C species from the surface of $\varepsilon(')$ -carbide renders this phase unstable against γ -Fe₅C₂ when exposed to high-pressure synthesis gas. This finding is consistent with the notion that the presence of pre-deposited C is needed for preparing carbon-rich $\varepsilon(')$ -carbide (Chapter 2). Fig. 5.5b shows that H₂ treatment at 350 °C leads to a more complete transformation to γ -Fe₅C₂ than treatment at 250 °C. As hydrogenation of γ - Fe_5C_2 is harder than that of $\varepsilon($ ')-carbide, one would expect that the main peak appears at a higher temperature for the sample treated at 350 °C. The opposite result in Fig. 5.5a indicates that deposited C could also play a role in determining bulk C hydrogenation. In line with this,

the Raman spectra in Fig. 5.5c show that less C is deposited on the sample treated at 350 °C. Overall, these data show a strong link between the presence of deposited C with the CO conversion and the CH₄ selectivity in Table 5.2. Nevertheless, it appears that the lower CH₄ selectivity of χ -Fe₅C₂ is an intrinsic property, which is most likely related to a smaller amount of surface lattice C species.



Figure 5.5. (a) TPH profiles, (b) XRD patterns and (c) Raman spectra of the spent catalysts after reaction at 20 bar (250 °C, $H_2/CO = 2$, 24 h) with different H_2 pre-treatments.

The kinetic differences presented in Table 5.2 are in agreement with results reported by Wezendonk *et al.*,[19] but not in complete agreement with previous work by Chang *et al.*[13] and De Smit *et al.*[11]. The latter two reports indicated that ε (^)-carbide produced more longer hydrocarbons than χ -Fe₅C₂. The fact that carbonaceous deposits were not taken into account in these studies may explain the contradicting results. Furthermore, the contradicting results between these studies may arise from the presence of mixtures of different Fe phases. A higher CH₄ selectivity on ε (^)-carbide than χ -Fe₅C₂ was also reported by Zhao *et al.*,[40] though they found that χ -Fe₅C₂ displayed a significantly higher CO conversion than ε ()-

carbide. They did, however, not characterize the surface composition of the spent catalyst. Comparison of pure ϵ (´)-carbide and χ -Fe₅C₂ with comparable amounts of C deposits in the present work provides a more convincing approach to determine the intrinsic properties of these two carbides.

To further compare the differences between the two carbides, the reaction orders in CO and H_2 were determined. Fig. 5.6 reports the dependences on H_2 and CO partial pressures of the reaction rates for CO consumption, CH_4 formation, C_{2+} formation, and CO_2 formation for ϵ (')-carbide and γ -Fe₅C₂. The H₂ and CO partial pressures were varied between 1.6-4.8 bar and 0.8-2.4 bar, respectively, while keeping the partial pressures of the other reactant constant. The reaction order of the CO consumption with respect to H_2 on $\varepsilon()$ -carbide is slightly lower than on γ -Fe₅C₂ (Fig. 5.6a and 5.6c), suggesting that C species on γ -Fe₅C₂ are more difficult to be hydrogenated, consistent with slower hydrogenation kinetics of bulk γ -Fe₅C₂. The reaction orders in CO are positive for all products except for CH₄ on both $\varepsilon(')$ -carbide and γ -Fe₅C₂ (Fig. 5.6b and 5.6d). An increase in CO partial pressure will lead to a higher coverage of adsorbed C species and lower coverage of H. Hence, the chain-growth probability is expected to increase with increasing CO pressure at the expense of CH₄ formation, which agrees with the observed positive order in CO for the longer hydrocarbons (C_{2+}) and negative order for CH₄. The CH₄ formation on χ -Fe₅C₂ is more sensitive to CO partial pressure than on $\varepsilon(')$ -carbide. This highlights that CH₄ formation over γ -Fe₅C₂ is more dependent on H coverage than $\varepsilon()$ -carbide and is more easily to be inhibited by higher CO partial pressure. The reaction order based on CO₂ formation in H₂ and CO are close to zero. Apparently, the formation of CO₂ does not share a common rate-determining step with the other FT reactions.





Figure 5.6. CO consumption rate (squares), CH₄ formation rate (up-triangles), C₂₊ formation rate (down-triangles) and CO₂ formation rate (circles) as a function of (a) H₂ partial pressure (pCO = 1.6 bar), (b) CO partial pressure ($pH_2 = 3.2$ bar) on ε (')-carbide, and (c) H₂ partial pressure (pCO = 1.6 bar), (d) CO partial pressure ($pH_2 = 3.2$ bar) on χ -Fe₅C₂ at 250 °C, total pressure = 20 bar. The numbers n given next to each line are the calculated corresponding reaction orders in H₂ and CO.

Primary CO₂

In earlier work, it was shown that pure $\varepsilon(')$ -carbide displays a low primary CO₂ selectivity due to the absence of Fe-oxides.[8] Table 5.2 shows that χ -Fe₅C₂ has a lower CO₂ selectivity than $\varepsilon(')$ -carbide at a slightly higher CO conversion. To compare the primary CO₂ selectivity of these two Fe-carbide phases, we determined the CO₂ selectivity as a function of CO conversion by changing the space velocity at constant H₂/CO ratio. Fig. 5.7 shows the results for $\varepsilon(')$ -carbide and χ -Fe₅C₂ as well as for reference samples composed of a mixture of $\varepsilon(')$ carbide and χ -Fe₅C₂ as well as a mixture of $\varepsilon(')$ -carbide, χ -Fe₅C₂, and Fe₃O₄. The primary CO₂ selectivity obtained by extrapolating the CO₂ selectivity to zero CO conversion was lower for χ -Fe₅C₂ than for $\varepsilon(')$ -carbide. The three catalysts that only contain Fe-carbide, *i.e.*, pure $\varepsilon(')$ -carbide and χ -Fe₅C₂ or their mixture, display a low primary CO₂ selectivity, meaning that O atoms originating from CO dissociation are preferentially removed as H₂O. This is in line with density functional theory predictions that H₂O is the preferred product of O removal on $\varepsilon(')$ -carbide and χ -Fe₅C₂.[38] In contrast, the catalyst containing Fe₃O₄ displays a high primary CO₂ selectivity.

To synthesize a catalyst that contains Fe_3O_4 , unreduced Raney-Fe was directly exposed to synthesis gas at 250 °C and 1 bar and a H₂/CO ratio of 2 for 1 h. XRD spectra presented in Appendix Fig. 5.15 show that Fe₃O₄ remains present after operating the catalyst under high-

pressure conditions at 250 °C, 20 bar, and $H_2/CO = 2$ for 30 h. On the contrary, when the catalyst is pre-reduced in dilute H_2 before exposure to synthesis gas, only carbides, *viz.* a mixture of $\varepsilon(')$ -carbide and χ -Fe₅C₂, remained after high-pressure FT reaction. Based on Fig. 5.7, it is clear that the presence of bulk Fe-oxide leads to a much higher amount of primary CO₂ formation. It must be noted that primary CO₂ formation strongly depends on the reaction pressure in the FT reactor. As an example, the dependence of the CO₂ selectivity over $\varepsilon(')$ -carbide at varying total pressure is shown in Appendix Fig. 5.16. The CO₂ selectivity decreases with increasing pressure. At 23 bar, the primary CO₂ selectivity of pure $\varepsilon(')$ -carbide is as low as values reported previously.[8] The decrease in CO₂ selectivity with increasing pressure can be explained by the kinetics presented in Fig. 5.6: C-consuming reactions have a stronger positive dependence on the partial pressure of CO and H₂ than CO₂ formation. Hence, at increasing pressure the selectivity to hydrocarbons will increase at the expense of CO₂ selectivity.



Figure 5.7. CO₂ selectivity as a function of CO conversion on $\varepsilon(')$ -carbide, χ -Fe₅C₂, a mixture of $\varepsilon(')$ -carbide and χ -Fe₅C₂ and a mixture of $\varepsilon(')$ -carbide, χ -Fe₅C₂ and Fe₃O₄ at 250 °C, 20 bar, H₂/CO = 2, 36 h. The CO conversion is varied by adjusting the flow rate at a constant H₂/CO ratio. The lowest two conversion values per pressure were extrapolated to zero conversion to estimate the primary CO₂ selectivity.

Our previous work demonstrated that metallic Fe has a high propensity for dissociative CO adsorption and is prone to primary CO_2 formation through the Boudouard reaction (2 CO \rightarrow C + CO₂) at the initial stages of Fe carburization.[26] After carburization, Fe-carbides display

a low primary CO_2 selectivity. It has been reported that primary CO_2 formation on Fe-based catalysts can be formed without the involvement of H₂.[24] Thus, it can be speculated that primary CO_2 can only be formed after direct CO dissociation on Fe-based catalysts.

To estimate the extent of CO adsorption on Fe-based catalysts, SSITKA experiments were performed on two catalysts, *i.e.*, metallic Fe and a mixture of $\varepsilon(')$ -carbide and χ -Fe₅C₂. The transient responses after a SSITKA switch from ¹³CO/H₂ to ¹²CO/H₂ at 30 °C are presented in Fig. 5.8. In such experiments, the ¹³CO signal is usually delayed compared to the inert (Ne) because of reversible adsorption of CO or dissociation of CO followed by recombination of dissociated C and O. This behavior is clearly observed for metallic Fe. Experimental and theoretical work indicated that direct CO dissociation is the dominant pathway on metallic Fe than H-assisted pathway.[26, 42] The observed fast decay would be a consequence of ¹³CO being replaced from the gas flow by ¹²CO in the plug flow reactor. On top of that, a slow process is observed which is likely involving the relatively slow recombination of dissociated ¹³C atoms with O. On Fe-carbide, however, the ¹³CO signal nearly coincides with the inert, which implies a very weak interaction of CO with the catalytic surface. The same transient responses were observed on pure $\varepsilon(')$ -carbide and χ -Fe₅C₂ (Appendix Fig. 5.17).



Figure 5.8. Transient responses of Ne, ¹²CO and ¹³CO after a switch from ¹³CO/H₂ to ¹²CO/H₂ on (a) metallic Fe and (b) Fe-carbide (a mixture of ϵ (′)-carbide and χ -Fe₅C₂) at 30 °C, 1.5 bar.

IR spectroscopy was next employed to study the relationship between direct CO dissociation and primary CO₂ formation on Fe-based catalysts. The reduced and carburized samples were exposed to increasing amounts of CO at 30 °C. Fig. 5.9a shows that the IR band belonging to gaseous CO₂ appears immediately upon CO dosing for metallic Fe. This points to a low barrier for direct CO dissociation on metallic Fe.[26] Besides the bands due to gaseous CO in the 2200-2100 cm⁻¹ range, the IR spectra also contains features in the 2000-1850 cm⁻¹ range, which are likely due to chemisorbed CO. The relatively weak signal may be due to the high coverage of C and O species. Thus, under these conditions, the metallic Fe surface will be covered by C atoms and, to a lesser extent, O atoms as well as adsorbed CO. Exposure of the Fe-carbide sample to CO under the same conditions does not lead to CO_2 formation (Fig. 5.9b). This implies that the surface is much less reactive in direct CO dissociation. The most reasonable explanation for this is that the Fe atoms in Fe-carbide are less reactive towards CO dissociation as suggested by DFT modeling.[43] The nearly saturated Fe-carbide surface also has no tendency to interact with CO as no chemisorbed CO can be observed on the carburized sample in the range of 2000-1850 cm⁻¹.



Figure 5.9. FTIR spectra of CO adsorption band on (a) metallic Fe and (b) Fe-carbide (a mixture of $\epsilon(')$ -carbide and χ -Fe₅C₂) at 30 °C.

5.4 Conclusions

The catalytic properties of $\varepsilon(')$ -carbide and χ -Fe₅C₂ were compared in the FT reaction. Comparison at low pressure is hampered by the presence of C deposits on χ -Fe₅C₂ formed during carburization. After high-pressure synthesis gas treatment, the amount and nature of the remaining carbonaceous deposits are similar on both carbides, allowing to compare the intrinsic catalytic properties of these Fe-carbides. While these two carbides present nearly similar FT activity and chain-growth probability, χ -Fe₅C₂ has a slightly lower CH₄ selectivity and CO₂ selectivity. The identical FT activity suggests surface C hydrogenation on these two carbides *via* the L-H kinetics is comparable, consistent with DFT calculations. The difference in CH₄ selectivity is likely due to a larger contribution of MvK sites for that mainly produce CH₄. The removal of surface lattice C on Fe-carbide leads to lower CH₄ selectivity. All carbides display a low primary CO₂ selectivity, which is tentatively assigned to little direct CO dissociation on carbides as compared to metallic Fe. The absence of bulk oxidic Fe in the synthesized pure carbides also accounts for a low primary CO₂ selectivity.

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Appendix 5

Figure 5.10. (a) H₂O and CH₄ evolution during *in situ* TPH of the as-prepared ε (')-carbide and χ -Fe₅C₂. (b) A zoom of the H₂O signal, emphasizing that different O species are present.



Figure 5.11. TEM of ϵ (')-carbide and χ -Fe₅C₂ after high-pressure reaction at 250 °C, 20 bar, H₂/CO = 2.

Chapter 5

Table 5.3. Catalytic performance of ϵ (')-carbide and χ -Fe₅C₂ at steady state (250 °C, 23 bar, and H₂/CO = 2).

	CO conversion	CO ₂ selectivity (%)	CH ₄ selectivity (%)	Chain- growth probability	C ₂₋₄ olefins-to- paraffins ratio
ε(')-carbide	0.21	14.5	17.2	0.52	1.17
χ-Fe ₅ C ₂	0.21	11.6	13.6	0.53	1.02



Figure 5.12. H₂O and CH₄ evolution during *ex situ* TPH of the spent ε (')-carbide and χ -Fe₅C₂ after reaction at 20 bar (250 °C, H₂/CO = 2, 38 h).

Computational modeling method

In this work, density functional theory (DFT) calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA) with the effective ion cores described by projector-augmented wave (PAW) potentials.[1-4] The cut-off energy of the plane wave basis was set to 400 eV. The sampling of the Brillouin zone was done using 5x5x1 and 1x5x5 k-point mesh for $\epsilon(')$ -carbide and χ -Fe₅C₂ bulk calculation separately. Structure optimization was conducted with the convergence criterion for the forces of all atoms were less than 0.05 eV/Å. All atoms are relaxed in all calculations in this work.

The CH₄ formation in different Fe-carbide phase was calculated as:

$$\epsilon\text{-Fe}_{2}\text{C} + 2 \text{ H}_{2} \rightarrow \alpha\text{-Fe} + \text{CH}_{4}$$
$$\gamma\text{-Fe}_{5}\text{C}_{2} + 4 \text{ H}_{2} \rightarrow \alpha\text{-Fe} + 2 \text{ CH}_{4}$$

The electronic reaction energy for CH₄ formation was defined as:

$$E_{rxn} = (E_{CH_4} + \frac{x}{y}E_{\alpha \ Fe} - \frac{x}{y}E_{Fe_x C_y} - 2E_{H_2})$$

Where E_{CH_4} is the electronic energy of CH₄, $E_{\alpha Fe}$ is the electronic energy of Fe in bulk α -Fe, $E_{Fe_xC_y}$ represents the bulk energy ϵ -Fe₂C or χ -Fe₅C₂, and E_{H_2} is the electronic energy of H₂.

Table 5.4. The electronic reaction energy for bulk $\epsilon(')$ -carbide and χ -Fe₅C₂ hydrogenation to CH₄.

Reaction	∆H/eV	∆H/kJ/Mol	\triangle S/kJ/Mol*K	$\triangle G/kJ/Mol$	∆G/kJ/Mol (per Fe)
ϵ -Fe ₂ C + 2 H ₂ $\rightarrow \alpha$ -Fe + CH ₄	-1.52	-146.08	-0.072	-108.42	-54.21
χ -Fe ₅ C ₂ + 4 H ₂ $\rightarrow \alpha$ -Fe + 2 CH ₄	-2.84	-272.48	-0.144	-197.16	-39.43

* Entropies based on NIST values of gas-phase molecules

* Free energy at 523 K



Figure 5.13. Normalized transient response of ${}^{12}CH_4$ upon a switch from ${}^{12}CO/H_2$ to ${}^{13}CO/H_2$ on $\epsilon(')$ -carbide and χ -Fe₅C₂ (250 °C, 1.5 bar, and H₂/CO = 2).

Carbide phase	rate constant k_i (s ⁻¹)	activity contribution <i>x_i</i>	site contribution <i>Y_i</i>	R ²	
ε(´)- carbide	5.77.10-4	0.106	0.705		
	3.48.10-3	0.211	0.232	- 0.0015	
	2.00.10-2	0.293	0.056	- 0.9915	
	$2.78 \cdot 10^{-1}$	0.367	0.005	-	
χ-Fe5C2	5.36.10-4	0.059	0.590		
	3.04.10-3	0.154	0.292	- 0.00 5 6	
	1.69.10-2	0.309	0.105	- 0.9956	
	2.35.10-1	0.483	0.011	-	

Table 5.5. Modeling of SSITKA CH₄ response with 4 pseudo-first-order reaction rate constants with x_i the fractional contribution to the total CH₄ rate and y_i the fraction contribution to the total number of active sites on $\varepsilon(')$ -carbide and χ -Fe₅C₂.



Figure 5.14. (a) *in situ* TPH profiles and (b) XRD patterns of as-prepared ϵ (')-carbide, treated in H₂ (20% H₂ in He) at 250 °C for 5 h or 350 °C for 5 min.



Figure 5.15. XRD patterns of samples (a) after low-pressure reaction (250 °C, 1 bar, and $H_2/CO = 2$ for 1 h) without pre-reduction, (b) after high-pressure reaction at 250 °C, 20 bar, and $H_2/CO = 2$ for 30 h with a proceeding exposure to low-pressure reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for 1 h without pre-reduction, and (c) after high-pressure reaction at 250 °C, 20 bar, 20 bar, and $H_2/CO = 2$ for 30 h with a proceeding exposure to low-pressure reaction at 250 °C, 1 bar, and $H_2/CO = 2$ for 30 h with a proceeding exposure to low-pressure reaction at 250 °C, 1 bar, 20 bar, and $H_2/CO = 2$ for 30 h with a proceeding exposure to low-pressure reaction at 250 °C, 1 bar, 20 bar, and $H_2/CO = 2$ for 30 h with a proceeding exposure to low-pressure reaction at 250 °C, 1 bar, 20 bar, and $H_2/CO = 2$ for 1 h with pre-reduction in diluted H_2 (430 °C, 1 bar for 1 h).



Figure 5.16. CO₂ selectivity as a function of CO conversion on (a) ϵ (')-carbide and (b) χ -Fe₅C₂ at different pressures. The CO conversion is varied by adjusting the flow rate at a constant H₂/CO ratio (250 °C, x bar, H₂/CO = 2). The lowest two conversion values per pressure were extrapolated to zero conversion to estimate the primary CO₂ selectivity.



Figure 5.17. Transient responses of Ne, ¹²CO and ¹³CO after a switch from ¹³CO/H₂ to ¹²CO/H₂ on (a) ϵ (')-carbide and (b) χ -Fe₅C₂ at 30 °C, 1.5 bar.

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Chapter 6

Summary and outlook

Kinetic study of the Fischer-Tropsch reaction on Fe-carbide

Fischer-Tropsch (FT) synthesis is an increasingly important approach for producing sulfurfree and aromatic-free liquid fuels and valuable chemicals *via* synthesis gas (a mixture of CO and H₂) generated from coal, natural gas, or biomass. Fe and Co are the only viable transition metals used in commercial FT catalysts. Although Fe-based catalysts are not as active as Cobased catalysts, they show a broader range of operation windows (pressure, temperature, and feedstock composition), and more importantly, they are much cheaper than Co. Fe-carbides are the active phases of Fe-based catalysts in the FT reaction. Due to the complex changes of Fe phases during reaction, the kinetic and mechanistic understandings of Fe carburization and FT reaction on Fe-carbide are relatively limited. In this thesis, a model Raney-Fe catalyst, which is free of Fe-oxides, was used as starting material. Transient kinetic studies combined with temperature-programmed hydrogenation (TPH) and spectroscopic studies were employed to study the kinetics and mechanism of Fe carburization as well as Fe-catalyzed FT reaction. Special attention was paid to illustrate the existence of parallel reaction pathways in the FT reaction on Fe-carbide by steady state isotopic transient kinetic analysis (SSITKA).

In **Chapter 2**, we investigated the carburization of Raney-Fe using spectroscopic and temperature-programmed techniques. IR spectroscopy showed that CO dissociation on metallic Fe occurs at -150 °C, leaving C species deposited on the Fe surface. To form bulk Fe-carbide, much higher temperature (~180 °C) is required for C diffusion into metallic Fe structure. The Fe-carbide phase and its formation rate were determined by the carburization temperature and the composition of feeding gas. Higher H₂/CO ratio increases the carburization rate in favor of carbon-rich $\varepsilon(')$ -carbide formation, while χ -Fe₅C₂ is formed at lower H₂/CO ratio. H₂ increases the carburization rate since it can accelerate O removal *via* H₂O, regenerating surface vacancies for CO dissociation and thus providing a higher C coverage for Fe-carbide formation. The rate of carburization is much faster than the rates of surface hydrogenation reactions of C into hydrocarbons in the early stage of carburization. This work provides deep insight into how bulk C diffusion is affected by surface reactions and how a specific Fe-carbide is formed by adjusting the carburization conditions.

In **Chapter 3**, the kinetics of the transformation from metallic Fe to Fe-carbide phases at the initial period of FT reaction were studied. The diffusion rates of C atoms going in or out of the Fe lattice were determined using ¹³C-labelled synthesis gas in combination with measurements of the transient ¹²C and ¹³C content in the carbide by temperature-programmed

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hydrogenation. In the first 20 minutes, C atoms diffuses rapidly into the lattice occupying thermodynamically very stable interstitial sites. The hydrocarbons formation rate increases with the increase of bulk C/Fe ratio. When reaching steady state, the diffusion rates of C in and out of the lattice converge and the FT reaction continues *via* two parallel reaction mechanisms. It appears that the two outer layers of C atoms in the Fe-carbide are involved in the FT reaction *via* a slow Mars-Van Krevelen (MvK) reaction contributing to only 10% of the total activity, while the remainder of the activity stems from a fast Langmuir-Hinshelwood (L-H) reaction occurring over only a minor part of the catalyst surface (about 10%). The small contribution of surface carbide C atoms stems from the relatively strong binding to Fe compared to adsorbed C atoms. Compared to earlier works that only focused on analyzing the gas-phase composition, our research not only proved the existence of C exchange between lattice and the gas phase on Fe-carbide in the FT reaction, but also determined its rate by analysis of the labelled C content in Fe-carbide.

The insights obtained thus far suggest that C hydrogenation on Fe-carbide surface is closely linked with the inward- and outward-diffusion rates of C atoms in the carbide structure and reveal the dynamic state of lattice C atoms in the FT reaction. In this sense, besides adsorbed C species, lattice C atoms are an intrinsic component of the catalyst. The question remains on how product selectivity is determined by the composition of surface C species and how to modify the catalyst surface to influence the FT performance. To answer this, Chapter 4 focuses on studying the relationship between C species distribution on Fe-carbide surface and the FT activity and selectivity. Formation of C deposits during the ongoing FT reaction at low pressure was identified by TEM, XPS, TPH and Raman spectroscopy. It was revealed that C-removal is the rate-limiting step on Fe-carbide and the buildup of C deposits not only covers the active site decreasing the FT activity but also increases the CH₄ selectivity. SSITKA at low pressure shows that the C deposits mainly affects more the fast CO conversion sites on Fe-carbide surface, responsible for C-C coupling via an L-H mechanism, than the slow sites which mainly produce CH₄ via an MvK mechanism. C deposits could also hinder the migration of chain-growth monomer decreasing the chain-growth probability though it could accelerate the formation of C_2 products by decreasing the fraction of free sites. Increasing the H_2/CO ratio at constant pressure as well as increasing the total pressure at constant H₂/CO ratio lowers the amount of low-reactive C deposits by accelerating C removal. Running the FT reaction at high pressure appears to reverse the deactivation caused by the buildup of C deposits at low pressure and realizes a stable FT activity. However, the longer the reaction proceeds at low pressure, the more C deposits are accumulated that cannot be eliminated by a high-pressure reaction leading to a lower activity and lower chain-growth probability at high-pressure steady state. The CO_2 selectivity is closely linked with CO

conversion. To some extent, the build-up of C deposits can protect surface Fe from oxidization.

Chapter 4 illustrates that C deposition is an integral part of the Fe catalyzed FT reaction, making it difficult to correlate the intrinsic activity of a specific Fe-carbide to its FT performance. Another interfering factor is the existence of Fe-oxide, which can catalyze the water-gas shift reaction leading to extra CO_2 formation. In **Chapter 5**, we synthesized pure $\varepsilon(\dot{r})$ -carbide and γ -Fe₅C₂ catalysts to compare their catalytic performance in the FT reaction and understand mechanistic differences by excluding aspects such as the particle size, the presence of Fe-oxide and the influence of C deposits during reaction. The as-prepared γ - Fe_5C_2 shows much lower activity than $\varepsilon($)-carbide under low-pressure FT reaction conditions because of the buildup of C deposits on its surface. Reactivation of the catalyst and the absence of deactivation in reaction at high-pressure creates an environment to compare the intrinsic activity of $\varepsilon(\gamma)$ -carbide and γ -Fe₅C₂. Though Fe surface suffers oxidization to some extent under high-pressure FT reaction conditions, both carbides are free from bulk Fe-oxide and experience no phase change. At steady state, $\varepsilon(\hat{})$ -carbide and χ -Fe₅C₂ share similar FT activity and chain-growth probability, while $\varepsilon()$ -carbide shows slightly higher CH₄ selectivity. Based on SSITKA analysis, this difference is tentatively ascribed to a higher MvK contribution to CH_4 formation on ϵ ()-carbide. All carbides display a low primary CO_2 selectivity, which is tentatively assigned to little CO dissociation on carbides as compared to metallic Fe. Also, the absence of bulk oxidic Fe in the synthesized pure carbides accounts for a low primary CO₂ selectivity. A higher surface oxidation degree leads to more CO₂ formation.

The kinetic study presented in this work illustrates the relationship between solid-phase reactions involving Fe carburization and the catalytic reactions occurring at the surface during the FT reaction. To quantitatively determine the amount of C atoms in a carburized Fe sample and to study the role of H_2 in carburization on reduced Raney-Fe, TPH measurement was employed in **Chapter 2.** Such an approach can be expanded towards other similar systems that require the quantification of the amount of C in a catalyst. Although Raney-Fe is not yet used in the industrial FT process, it is a still a valuable model catalyst for studying Fe carburization kinetics and the FT mechanism. Its higher reducibility compared to conventional industrial catalysts enables us to study Fe carburization in the absence of perturbing oxidic phases. We expect that future work may focus on studying Fe carburization as presented in **Chapter 3** revealed the catalytic role of lattice C in the Fe-carbide in the FT reaction. We explicitly mentioned that we did not relate the exchange of surface and bulk C atoms to the formation of higher hydrocarbons in this work because direct measurement of

the contribution of lattice C in the FT reaction is still a challenge, especially when considering chain growth. More carefully designed isotopic transient experiments are needed to address this issue. The accurate interpretation of the occurrence of multiple L-H reaction pathways is not yet possible and likely requires integration of explicit DFT calculations, which suggests CO activation and CH₄ formation rates are strongly dependent on the exposed crystal facets and active site geometry.

In Chapter 4, an endeavor was made to study the site-specific selectivity of Fe-carbide in the FT reaction. Similar to the above, the interpretation of heterogeneous nature of Fe-carbide surface requires a reactivity distribution analysis with SSITKA. The correlation between each active site on Fe-carbide and the corresponding FT activity needs to be studied in more detail by using advanced surface science techniques. Studying the relationship between C deposits on Fe-carbide and the FT activity and selectivity under low- or high-pressure FT conditions could provide a rational way for adjusting the FT performance in the practical process by regulating pretreatment conditions on reduced Fe-based catalysts. Further work could aim at industrial FT catalysts to prevent C deposits buildup. Promoter addition, particle size effect, and the metal-support interaction should be considered to improve the product distribution and inhibit catalyst deactivation. Based on the understanding of Fe carburization kinetics and the FT reaction mechanism on Fe-carbide from Chapter 2 to 4, a comprehensive comparison between $\varepsilon(\gamma)$ -carbide and γ -Fe₅C₂ in the FT reaction was demonstrated in **Chapter 5**. This fundamental study highlighted that the FT activity on Fe-carbide is influenced less strongly by the bulk phase composition of the catalyst as the MvK pathway only makes a small contribution to the total FT activity and that Fe-C bond energies on the surface of these two carbides cannot be too distinct. The similar FT kinetics displayed by these two carbides inspired us to focus more on investigating the effect of surface morphology of Fe-carbide on the FT performance. This aspect is seldomly explored from an experimental viewpoint because of the intricate surface nature of Fe-based catalysts during the FT reaction, let alone complex surface reconstructions. The evolution of C and O intermediates on atomically defined carbide surfaces should be tracked by time-resolved spectroscopy to establish structure-activity relationships. Another approach to systematically studying the facetdependent FT activity and the interaction of the Fe-C bond on different carbides is the inclusion of DFT calculations.

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Jiachun Chai

柴佳春

List of Publications

Journal articles

Publications within the scope of this thesis

<u>J. Chai</u>, R. Pestman, W. Chen, A. I. Dugulan, B. Feng, Z. Men, P. Wang, E. J. M. Hensen, The role of H_2 in Fe carburization by CO in Fischer-Tropsch Catalysts, J. Catal., 400 (2021) 93-102.

J. Chai, R. Pestman, W. Chen, N. Donkervoet, A. I. Dugulan, Z. Men, P. Wang, E. J. M. Hensen, An isotopic exchange study on the kinetics of Fe carburization and the mechanism of the Fischer-Tropsch reaction, ACS Catal., 12 (2022) 2877-2887.

Publications outside the scope of this thesis

L. Meng, G. Vanbutsele, R. Pestman, A. Godin, D. E. Romero, A. J. F. van Hoof, L. Gao, T. F. Kimpel, <u>J. Chai</u>, J. A. Martens, E. J. M, Hensen, Mechanistic aspects of n-paraffins hydrocracking: Influence of zeolite morphology and acidity of Pd(Pt)/ZSM-5 catalysts, J. Catal., 389 (2020) 544-555.

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Curriculum Vitae

Jiachun Chai was born on June 25th, 1990 in Shanxi Province, China. After finishing his high school in 2010, he started his study in Tianjin University in Tianjin, China. In June 2014, he received his bachelor's degree of Applied Chemistry. He continued his master study at Institute of Coal Chemistry, Chinese Academy of Science in Taiyuan, China, working on biomass conversion to high value-added products under supervision of Prof. Weibin Fan. In June 2017, he defended his



thesis entitled "New Routes for Cellulose Conversion to Ethylene Glycol and Ethanol" with A-level. He later joined the group of Inorganic Materials & Catalysis at Eindhoven University of Technology as a Ph.D. student with a scholarship from China Scholarship Council. Under supervision by prof.dr.ir. E.J.M. Hensen, he studied the kinetics and mechanism of Fischer-Tropsch synthesis on iron-based catalysts. The main results of his research are summarized in this thesis.