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Carbon Number Dependency of Reaction Mechanism and Kinetics in CO Hydrogenation on a Co-based Catalyst

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# Abstract

A detailed mapping of the kinetic parameters involved in the reaction network of CO hydrogenation on a Co-Re/CNT catalyst has been performed. Multicomponent Steady-State Isotopic Transient Kinetic Analysis (SSITKA) has been used to deconvolute the rates of chain growth and termination to olefins and paraffins with various carbon numbers into the concentration of the surface intermediates and their reactivity, expressed as their rate constants  $k_{g}$ ,  $k_{o}$  and  $k_{p}$ , respectively at a molecular level. The site coverage of the different products ( $\theta_{Cn}$ ) measured by the multicomponent analysis of their isotopic distribution allows the study of their effect on chain growth, as well as on olefin and paraffin formation. The insights into the reaction mechanism were gained from the kinetic dependency of different reaction steps on the hydrogen pressure. The results revealed a significant carbon number dependency of the mechanism for the chain growth and termination to paraffin and olefin reactions: an enol-like intermediate is dominating for the formation of C<sub>3</sub> hydrocarbons, while the alkenyl intermediate is dominating for the formation of  $C_4$  hydrocarbons. Moreover, the SSITKA assisted kinetic study provided the carbon number dependency of the rate constants of various reaction steps for the paraffin formation and chain growth, both decrease concurrently with increasing carbon number. However, the rate constant for the olefin formation is constant, regardless of the carbon number, suggesting the formation rate of olefins with different carbon number depends mainly on the concentration of the corresponding surface intermediates.

# Keywords: CO hydrogenation, multicomponent SSITKA, isotopic labelling, kinetic study, mechanism

# List of Symbols

C <sub>n</sub> *	precursors for chain termination and chain growth	[-]
$D_{Co}$	Cobalt dispersion	$[g_{Co,s} g_{Co}^{-1}]$
F <sub>CO,in</sub>	molar flow rate of CO at the inlet of the reactor	$[\mu mol s^{-1}]$
F <sub>CO,out</sub>	molar flow rate of CO at the outlet of the reactor	$[\mu mol s^{-1}]$
F <sub>Cn</sub>	molar flow of the compound with carbon number n	$[mol s^{-1}]$
F <sub>Cn</sub> (t)	normalized curve of the compound with carbon number n	[-]
$f_{ij}^{\ ref}$	intensity of the fragmentation pattern of a given isotopic combination at its m/e value	[-]
$f_i^{obs}$	intensity of the fragmentation pattern observed in the GC-MS for each m/e value of a given isotopic combination	[-]
$F_{T}$	total flow in the reactor	[NmL min <sup>-1</sup> ]
GHSV	Gas Hourly Space Velocity	$[mL h^{-1} g_{cat}^{-1}]$
i.d.	internal diameter	[-]
kg	rate constant of the chain growth reaction	[s <sup>-1</sup> ]
k <sub>g,n</sub>	rate constant of the chain growth reaction of the compound with carbon number n	[s <sup>-1</sup> ]
ko	rate constant of the olefin formation reaction	[s <sup>-1</sup> ]
k <sub>o,n</sub>	rate constant of the olefin formation reaction of the compound with carbon number n	[s <sup>-1</sup> ]
k <sub>p</sub>	rate constant of the paraffin formation reaction	[s <sup>-1</sup> ]
k <sub>p,n</sub>	rate constant of the paraffin formation reaction of the compound with carbon number n	[s <sup>-1</sup> ]
k <sub>s,g,n</sub>	rate constant of the chain growth reaction for the simple kinetic model of the compound with carbon number n	[s <sup>-1</sup> ]
k <sub>s,o,n</sub>	rate constant of the olefin formation reaction for the simple kinetic model of the compound with carbon number n	[s <sup>-1</sup> ]
k <sub>s,p,n</sub>	rate constant of the paraffin formation reaction for the simple kinetic model of the compound with carbon number n	[s <sup>-1</sup> ]

k <sub>s,n</sub>	rate constant lumped with the site coverage that cannot be measured experimentally	[s <sup>-1</sup> ]
k" <sub>o,n</sub>	k lumped including $k_{o,n}$ ; $K_{H2}^{m2/2}$ and $\theta^{*m2}$	[-]
k" <sub>p,n</sub>	k lumped including $k_{p,n}$ ; $K_{H2}^{m1/2}$ and $\theta^{*m1}$	[-]
$K_{\rm H2}$	hydrogen adsorption equilibrium constant	[-]
K <sub>25a</sub>	equilibrium constant for the reaction step Eq. 25a	[-]
K <sub>25b</sub>	equilibrium constant for the reaction step Eq. 25b	[-]
k <sub>25c</sub>	rate constant for the reaction step Eq. 25c	$[s^{-1}]$
m	number of different m/e values for each hydrocarbon	[-]
m1	reaction order with respect to adsorbed atomic hydrogen for the paraffin formation reaction	[-]
m2	reaction order with respect to adsorbed atomic hydrogen for the olefin formation reaction	[-]
$M_{Co}$	molecular weight of Cobalt	$[g mol^{-1}]$
n	number of isotopic combinations	[-]
N <sub>Cn</sub>	concentration of adsorbed compounds with carbon number n	$[\text{mol } g_{\text{cat}}^{-1}]$
Ns	concentration of total active sites in the catalyst	$[\text{mol } g_{\text{cat}}^{-1}]$
P <sub>T</sub>	total pressure	[bar]
P <sub>CO</sub>	CO partial pressure	[bar]
P <sub>H2</sub>	H <sub>2</sub> partial pressure	[bar]
r <sub>Cn</sub>	reaction rate of the compound with carbon number n	$[mol (g_{cat} s)^{-1}]$
R <sub>CO</sub>	molar rate of CO consumption per gram of catalyst	$[mol (g_{cat} s)^{-1}]$
r <sub>o,n</sub>	reaction rate of the olefin formation for the compound with carbon number n	[s]
r <sub>p,n</sub>	reaction rate of the paraffin formation for the compound with carbon number n	[s]
$\mathbf{S}_{Cn}$	carbon based selectivity to compound with carbon number n	[mol mol <sup>-1</sup> ]
S(x)	objective function to minimize	[-]
Т	temperature	Κ

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Wcat	catalyst mass	[g <sub>cat</sub> ]
$\mathrm{TOF}_{\mathrm{g},\mathrm{n}}$	turnover frequency for chain growth reaction	$[s^{-1}]$
TOF <sub>o,n</sub>	turnover frequency for olefin formation reaction	[s <sup>-1</sup> ]
TOF <sub>p,n</sub>	turnover frequency for paraffin formation reaction	[s <sup>-1</sup> ]
wt.	weight	[-]
X <sub>CO</sub>	CO conversion	[µmol µmol <sup>-1</sup> ]
X <sub>Co</sub>	Cobalt loading on the catalyst	[g <sub>Co</sub> g <sub>cat</sub> <sup>-1</sup> ]
x <sub>ij</sub>	contribution of a given isotopic combination to the mixture at its m/e value	[-]
$ heta_{Cn}$	site coverage of species with carbon number n	[-]
$ heta_{C^*}$	site coverage of the monomer to be incorporated in the growing chain	[-]
$ heta_{o,n}$	site coverage of intermediates with carbon number n corresponding to the formation of olefins	[-]
$ heta_{p,n}$	site coverage of intermediates with carbon number n corresponding to the formation of paraffins	[-]
$oldsymbol{ heta}_{ m H}$	site coverage of hydrogen	[-]
$ heta_{ m RCH2CH2}$	site coverage of the alkyl intermediate	[-]
$ heta_{ ext{RCHCH}}$	site coverage of the alkenyl intermediate	[-]
$ heta_{ m RCH2CH0}$	site coverage of the enol-like intermediates	[-]
$\pmb{ heta}^*$	site vacancy	[-]
$ au_{Cn}$	residence time of compounds with carbon number n	[s]

# Introduction

Fischer-Tropsch (FT) synthesis is one of the most important industrial processes to convert synthesis gas into valuable chemicals and clean liquid fuels. Although the process is known since the 1920s, the reaction mechanism for CO activation, chain growth and termination is still in debate<sup>1-3</sup>. The FT product spectrum, which can be generally described by the Anderson-Schulz-Flory (ASF) model for chain polymerization kinetics, contains a complex mixture of linear and branched hydrocarbons and oxygenated products, as a result of several intermediate steps: reactant adsorption, chain initiation, chain growth, chain termination, product desorption, readsorption and further reaction  $4^{-6}$ . Several mechanisms have been developed over the years to explain the different product distribution obtained in this process, and they can be summarized in three different groups: the carbide mechanism<sup>7</sup>, originally proposed by Fischer-Tropsch; the CO insertion mechanism<sup>8</sup> and the hydroxycarbene mechanism<sup>9</sup>. The key surface intermediates (Cn\*) responsible for the chain growth and the termination to hydrocarbons with different carbon number could depend on the reaction mechanism. The nature of the intermediates corresponding to the chain growth and termination, together with the reaction mechanism of FT synthesis remains in debate.

The identity of metal, particle size, support and promoter, as well as reaction conditions have been intensively studied, and observed to largely influence the catalyst activity and selectivity<sup>10–16</sup>. However, about the nature of such effects very little is known. As an important step towards a rational design of FT catalysts, a kinetic diagnostic tool is highly desired, which could provide fundamental understanding of the catalyst properties and reaction conditions on adsorption and

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surface reactions in the steps involved in CO activation, methane formation, chain growth and termination by olefin and paraffin formation.

SSITKA is a powerful technique known since the 1970s that can give valuable kinetic information about the adsorption and surface reactions at the molecular level by providing the site coverage and rate constants simultaneously at steady-state conditions. This technique has been applied to many reaction systems, including  $FT^{17,18}$ . Most of the work deals with the conventional SSITKA, limited to analysis of C<sub>1</sub> compounds only, such as CO conversion and methane formation<sup>19–21</sup>. Developments in SSITKA have recently been reviewed<sup>18</sup>, and one of the progresses has been the implementation of the multicomponent SSITKA where the responses of heavier hydrocarbons can be evaluated. Schouten and co-workers developed a mathematical method based on different assumptions to identify and discriminate efficiently between different mechanistic models for methane formation as well as for higher hydrocarbon (C<sub>2+</sub>) formation in FT synthesis over cobalt<sup>22–24</sup> and iron-based catalysts<sup>25–27</sup>. This type of transient kinetic model of the SSITKA response curves in combination with Density Functional Theory (DFT) calculations was found to effectively elucidate the reaction mechanism of CO activation and methane formation over cobalt-based catalysts under methanation conditions<sup>19–21</sup>.

In the current work, a new method is developed to extend our previous kinetic studies on methane formation by using multicomponent SSITKA. This method makes it possible to determine the site coverage of  $C_{2+}$  hydrocarbons and provide a mapping of the kinetic parameters of the CO hydrogenation reaction network over a Co-Re catalyst supported on carbon nanotubes. It deconvolutes the rates of chain growth and termination by olefin and paraffin formation with various carbon numbers into the concentration of the surface intermediates and their reactivity. Combining the kinetic analysis in terms of the concentration of the intermediates on Co surfaces,

the reaction mechanism and the chemical identity of intermediates leading to chain growth and termination are proposed.

# **Experimental section**

The CO hydrogenation reaction has been performed using a fixed-bed quartz reactor (4 mm i.d.) over a 20% wt. Co and 0.5% wt. Re supported on carbon nanotubes. Previous investigations have pointed out that Re has little effect in the intrinsic site activity and apparent activation energy for the catalysts<sup>21</sup>. The Co-Re/CNT behaves almost identical as the Co/CNT catalyst. CNT as a support has showed a high surface area and low interaction with cobalt, where the cobalt particles can be completely reduced<sup>28–30</sup>. The dispersion of cobalt is 5.1% and the cobalt particle size is 18.9 nm based on H<sub>2</sub> chemisorption. The crystallite size of cobalt is 11.7 nm found by X-ray diffraction. The detailed preparation method, full characterization of the catalyst and the procedures for H<sub>2</sub> chemisorption and X-ray diffraction have been described previously<sup>21</sup>. The CNT supported Co catalyst with relatively large Co particle size and support on the reaction mechanism<sup>31</sup>. Therefore, the mechanistic insight obtained in this study reflects the CO hydrogenation mechanism on industrial relevant Co catalysts with relatively large Co particles.

Prior to reaction 25 mg of catalyst were reduced in 10 NmL/min H<sub>2</sub> at 623 K for 16 h using a ramping rate of 1 K/min. The catalyst was then cooled down to 483 K, H<sub>2</sub>/CO/Ar (15/1.5/33.5 NmL/min) mixture was introduced and the pressure was adjusted to 1.85 bar (absolute pressure), which corresponds to a Gas Hourly Space Velocity (GHSV) of 3600 mL<sub>CO</sub>/h/g<sub>cat</sub>. Once steady state was achieved after 6 hours on stream, the catalytic performance was evaluated. Comparing

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the amount of the different components in the reactor outlet to the composition of the feed gas, the conversion and selectivity were calculated as shown in Eqs. 1 and 2, respectively.

$$\chi_{co} = \frac{F_{co,in} - F_{co,out}}{F_{co,in}} \cdot 100 \quad [\%]$$
(Eq. 1)

$$S_{Cn} = \frac{F_{Cn}}{\sum_{i}^{n} F_{Cn}} \cdot 100 \quad [\%]$$
 (Eq. 2)

where the terms  $F_{co,in}$  and  $F_{co,out}$  correspond to  $\mu$ mol/s CO flow rate of the feed gas and at the reactor outlet, respectively;  $F_{Cn}$  corresponds to the carbon based mol/s of the hydrocarbon n produced in the reaction and  $S_{Cn}$  corresponds to the carbon based selectivity of the n product in %.

SSITKA experiments were carried out at 483 K and a total pressure ( $P_T$ ) of 1.85 bar by switching between  $H_2/^{12}CO/Ar$  and  $H_2/^{13}CO/Kr$ . The reaction order of the reactants has been determined by varying their partial pressure. The transient responses of Ar, Kr, <sup>12</sup>CO, <sup>13</sup>CO, <sup>12</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> were monitored with a Balzers QMG 422 quadrupole mass spectrometer (MS). The concentrations of H<sub>2</sub>, CO, Ar and C<sub>1</sub>-C<sub>6</sub> hydrocarbons were analyzed with a GC-MS (Agilent GC7890B – MSD5977A) equipped with TCD, FID and MSD detectors. The isotopic distribution of C<sub>2</sub>-C<sub>5</sub> hydrocarbons were calculated as a linear combination of the fragmentation patterns of the corresponding isotopic products<sup>26</sup>. At the conditions tested mass or heat transfer limitations are not observed experimentally<sup>32</sup>, which were also verified via adequate correlations<sup>33</sup>. A repeated set of experiments indicates that the experimental relative error is typically less than 5%.

**Results and discussion** 

# 1. Effect of CO and $H_2$ pressures on chain growth and termination to olefin and paraffin

The kinetic study of CO hydrogenation reaction has been performed on Co-Re/CNT catalyst at methanation conditions using a mixture of  $H_2$ /CO/Ar at 483 K and 1.85 bar. The present work focuses on gaining a better mechanistic understanding of CO hydrogenation, and the experiments were performed at constant temperature, but at various CO and  $H_2$  pressures. The results are summarized in Table 1.

**Table 1.** Performance of the Co-Re/CNT catalyst in CO hydrogenation at T = 483 K and  $P_T = 1.85$  bar under different partial pressures of the reactants, CO and H<sub>2</sub>;  $F_T = 50$  NmL/min

$\frac{(bar) (bar) (mL_{CO}/h/g_{cat})}{0.05(-0.5(0) - 2(00) - 4.8 - 2.2 - 0.5 - 5.7 - 2.8 - 2.2 - 2.0 - 1.5 - 1.2 - 0.8 - 0.0}{(\%)}$	`
	(%)
0.056 0.560 3600 4.8 72.3 8.2 0.5 5.7 3.8 2.2 3.9 1.5 1.2 0.8 0.0	
0.111 0.560 1800 3.6 62.6 8.1 0.5 7.3 4.6 3.9 5.9 2.9 2.6 1.7 0.0	1
0.137 0.560 2220 3.1 58.0 7.5 0.6 6.5 7.3 4.1 7.3 3.3 3.5 2.0 0.0	I
0.166 0.560 2700 2.4 53.3 6.9 0.8 5.4 10.1 3.9 8.1 3.4 4.2 2.1 1.8	
0.056 0.296 3600 2.4 69.9 7.1 1.3 4.0 7.1 1.6 5.5 1.3 1.8 0.4 0.0	1
0.056 0.370 3600 2.7 66.6 7.6 1.1 4.4 7.1 2.0 5.6 2.4 1.2 0.0 0.0	1
0.056 0.444 3600 3.3 70.8 7.9 0.8 5.2 4.9 2.1 4.4 1.4 1.6 0.9 0.0	I

Based on the product distribution, a simplified reaction network including monomer formation,

 $C_1$ - $C_6$  paraffin and olefin formation is depicted in Scheme 1, where the intermediates of  $C_n^*$  are generally defined as the precursors for the chain growth and termination<sup>5,35–45</sup>.



Scheme 1. Reaction network of CO hydrogenation, where the rates for chain growth and termination to paraffin and olefin are marked for each intermediate.

The turnover frequency for olefin formation  $(TOF_{o,n})$ , paraffin formation  $(TOF_{p,n})$  and chain growth  $(TOF_{g,n})$  are obtained from the formation rates of all the products and the mass balance. The formation rates of olefin and paraffin, expressed as turnover frequency (TOF) based on the Co active sites measured by hydrogen chemisorption, are calculated by Eq. 3.

$$TOF_{p(o),n} = \frac{S_{Cn} \cdot R_{CO} \cdot M_{Co}}{D_{Co} \cdot x_{Co}} [s^{-1}]$$
 (Eq. 3)

where  $S_{Cn}$  is the carbon based selectivity of the product n,  $R_{CO}$  corresponds to the molar rate of CO consumption per gram of catalyst (mol/g<sub>cat</sub>/s), which was estimated from the conversion by the differential reactor design equation,  $M_{Co}$  corresponds to the molecular weight of cobalt (g/mol),  $D_{Co}$  is the Co dispersion obtained from H<sub>2</sub> chemisorption and  $x_{Co}$  corresponds to the cobalt loading on the catalyst ( $g_{Co}/g_{cat}$ ).  $S_{Cn}*R_{CO}$  is the formation rate of the hydrocarbon with

carbon number n (mol/g<sub>cat</sub>,s).  $D_{Co}x_{Co}/M_{Co}$  represents mole of surface Co per gram of catalyst (mol<sub>Co,s</sub>/g<sub>cat</sub>). The turnover frequencies for paraffin and olefin formation are plotted as a function of CO and H<sub>2</sub> partial pressures in Figure 1.



**Figure 1.** Turnover frequencies of paraffin formation  $(TOF_{p,n})$  (a, b) and olefin formation  $(TOF_{o,n})$  (c, d). (a,c) were measured at different CO pressures and constant H<sub>2</sub> pressure of 0.56 bar and (b,d) at different H<sub>2</sub> pressures and constant CO pressure of 0.06 bar. T = 483 K and P<sub>T</sub> = 1.85 bar.

The effect of CO pressure on the paraffin formation is presented in Figure 1 a). The effect depends obviously on the carbon number. Results indicate that the rate of paraffin formation

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generally decreases with the carbon number. The methane formation rate shows a monotonic decrease with increasing CO pressure. For  $C_2$ - $C_5$  paraffin, the formation rates increases with increasing CO pressure following a decrease at high CO pressures. A maximum rate exists for each paraffin at a CO pressure of about 0.11 bar. The decrease in the TOF<sub>p,n</sub> with increasing CO pressure is less pronounced when the carbon number increases. The effect of H<sub>2</sub> pressure on the paraffin formation is presented in Figure 1 b). The forming rates of all the paraffins increase almost monotonically with increasing H<sub>2</sub> pressure.

The effects of CO and H<sub>2</sub> pressure on the olefin formation are presented in Figure 1 c) and d), respectively. The amount of ethylene formed at the different conditions tested is very small (Table 1, Figure 1), possibly due to strong adsorption of ethylene. The ethylene formation rate did not vary significantly with CO pressure, while the formation rate decreased slightly with increasing H<sub>2</sub> pressure. There are also maxima in the curves for C<sub>4</sub>-C<sub>5</sub> olefin formation with CO pressure, but the optimum rates appear at a slightly higher CO pressure of about 0.14 bar compared to the paraffin formation (Figure 1a).

The effective chain growth turnover frequency (TOF<sub>g,n</sub>) for C<sub>n</sub> is calculated based on Eqs. 4 and 5, where the chain growth is generally assumed to be irreversible. Since no significant C<sub>6+</sub> hydrocarbon were detected, TOF<sub>g,5</sub>, the chain growth from C<sub>5</sub> is equal to the formation TOF of C<sub>6</sub> paraffin (TOF<sub>p,6</sub>), with no C<sub>6</sub> olefins observed above the GC detection limit. The TOF<sub>g,n</sub> for C<sub>n</sub> (n=1-5) is calculated based on the mass balance as described by Eq. 5, comprising the formation rate to C<sub>n+1</sub> paraffin and olefins and chain growth rate of C<sub>n+1</sub> towards C<sub>n+2</sub>, where the insertion of C<sub>1</sub> unit as the chain growth monomer in the chain growth of C<sub>n+1</sub> is subtracted from the chain growth rate by applying a factor of n+1/n+2.

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$$TOF_{g,5} = TOF_{p,6} \tag{Eq. 4}$$

$$TOF_{g,n} = TOF_{p,n+1} + TOF_{o,n+1} + \frac{n+1}{n+2}TOF_{g,n+1}; n = 1 - 4$$
 (Eq. 5)

The dependence of the chain growth with CO and H<sub>2</sub> partial pressures is depicted in Figure 2.



**Figure 2.** Turnover frequency of chain growth (TOF<sub>g,n</sub>; n=1-5) at a) different CO pressures and constant H<sub>2</sub> pressure of 0.56 bar and b) different H<sub>2</sub> pressures and constant CO pressure of 0.06 bar. T = 483 K and P<sub>T</sub> = 1.85 bar.

Figure 2 indicates that the chain growth rate depends significantly on the carbon number and the rate decreases with increasing carbon number. Furthermore, a maximum in the curve was also observed for the chain growth rate with the CO pressure, and the maximum chain growth rate was located at a CO pressure between 0.11-0.14 bar (Figure 2a). The position of this is identical to the peak position of the CO activation rate. The chain growth rate increases concurrently with increasing hydrogen pressure (Figure 2b), and the effect of hydrogen is more significant for hydrocarbons with lower carbon number.

Figure 1 and 2 illustrate the complex dependencies of the formation rates of olefins and paraffins as well as the chain growth rates on the CO and  $H_2$  pressures. In order to get a better understanding of such effects and thus provide new insights to the reaction mechanism, multicomponent SSITKA was performed in order to deconvolute these effects to the site coverage and the reactivity of the intermediates.

# 2. Mapping of the kinetic parameters involved in the reaction network

Based on the transient curves of different isotopic labeled products, the site coverages of the intermediates leading to the main products on the catalyst surface were directly obtained. The site coverage of each intermediate produced in FT synthesis is defined by Eq. 6, namely the ratio of the concentration of adsorbed species ( $N_{Cn}$ ) in mol/g<sub>cat</sub> and the concentration of total active sites ( $N_s$ ) in mol/g<sub>cat</sub>, measured by H<sub>2</sub> chemisorption.

$$\theta_{Cn} = \frac{N_{Cn}}{N_s} \tag{Eq. 6}$$

The number of adsorbed species ( $N_{Cn}$ ) is defined by the product of the reaction rate ( $r_{Cn}$ ), which can be calculated by Eq. 7 (mol/g<sub>cat</sub>s), and the mean residence time of each intermediate (s) over the catalytic surface (Eq. 8).

$$r_{Cn} = \frac{F_{CO}X_{CO}}{W_{cat}} \cdot S_{Cn} \qquad \left[\frac{mol}{g_{cat}S}\right] \tag{Eq. 7}$$

$$N_{Cn} = r_{Cn} \cdot \tau_{Cn} \qquad \begin{bmatrix} mol/g_{cat} \end{bmatrix}$$
(Eq. 8)

where  $F_{CO}$  is the CO flow rate in the feed stream (mol/s) and  $X_{CO}$  is the CO conversion level in %.  $S_{Cn}$  is the selectivity of the product n and  $w_{cat}$  corresponds to the weight of catalyst in grams.

The residence time of CO, Ar, Kr, and CH<sub>4</sub> are determined from the area under the normalized curve obtained by SSITKA experiments using the MS (Eq. 9).

$$\tau_{Cn} = \int_0^\infty F_{Cn}(t) dt \tag{Eq. 9}$$

The residence time of higher hydrocarbons is determined by the analysis of the fragmentation pattern of the non-, partially and fully labelled products after the isotopic switch using a GC-MS, following the procedure developed by Van Dijk and co-workers<sup>23–27</sup>. Firstly, the fragmentation pattern of each hydrocarbon produced in the reaction is calculated as a linear combination of the fragmentation patterns of the non-, partially and fully labeled compounds and its contribution to the product. The contribution can be calculated by minimizing the objective function shown in Eq. 10.

$$S(x) = \sum_{i=1}^{m} \left( \sum_{j=1}^{n} \left( x_{ij} f_{ij}^{ref} \right) - f_{i}^{obs} \right)^2 \xrightarrow{x} minimum$$
(Eq. 10)

where S(x) is the objective function, m is the number of different m/e values for each hydrocarbon produced, n is the number of isotopic combinations depending on the number of atoms that can be labelled,  $x_{ij}$  is the contribution of a given isotopic combination to the mixture at its m/e value,  $f_{ij}^{ref}$  is the intensity of the fragmentation pattern of a given isotopic combination at its m/e value, and  $f_i^{obs}$  is the intensity of the fragmentation pattern observed in the GC-MS for each m/e value of a given isotopic combination. Once the contribution of each isotopic combination is calculated, the normalized responses can by depicted over time on stream as shown in Figure 3, which was used to calculate the residence time of the non-, partially and fully-labeled intermediates. The isotopic distribution in ethylene was not shown in Figure 3, due to very low concentration of ethylene at the conditions studied. The overall residence time of a

given hydrocarbon can be calculated by the overall <sup>12</sup>C content of a hydrocarbon with n C-atoms where i atoms are labelled, as shown in Eq. 11.

$$\tau_{Cn} = \frac{1}{n} \sum_{i=1}^{n} i \cdot \tau_{12_{Ci} 13_{Cn-i}}$$
(Eq. 11)





**Figure 3.** Isotopic distribution of the main intermediates  $C_2H_6$  (a),  $C_3H_8$  (b),  $C_3H_6$  (c),  $C_4H_{10}$  (d),  $C_4H_8$  (e),  $C_5H_{12}$  (f),  $C_5H_{10}$  (g) over time on stream at 483 K,  $P_T = 1.85$  bar,  $P_{CO} = 0.17$  bar and  $P_{H2} = 0.56$  bar.



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**Figure 4.** Site coverage of CO, and the intermediates leading to the formation of CH<sub>4</sub> and C<sub>2+</sub> (C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>8</sub>) paraffins (a, b) and to the formation of C<sub>2+</sub> olefins (C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>5</sub>H<sub>10</sub>) (c, d). (a,c) were measured at different CO pressures and constant H<sub>2</sub> pressure of 0.56 bar and (b, d) were measured at different H<sub>2</sub> pressures and constant CO pressure of 0.06 bar. T = 483 K and P<sub>T</sub> = 1.85 bar.

Figure 4 presents the changes of the site coverage of CO and the main surface intermediates leading to the formation of paraffin (Figure 4 a and b) and olefin (Figure 4, c and d) of various carbon numbers with CO and H<sub>2</sub> pressure. Figure 4a shows an increase in CO site coverage with increasing CO pressure, while Figure 4b shows no significant changes in CO site coverage with increasing H<sub>2</sub> partial pressure. The results clearly revealed the adsorbed CO species as the most abundant surface species on Co surfaces at the studied conditions, suggesting a stronger adsorption of CO compared to other species. However, the monotonic increase in CO site coverage is inconsistent with the volcano type of relationship between the CO conversion rate and CO pressure (Table 1). Based on the previously reported CO hydrogenation mechanism, the HCO\*+H\* step is the rate determining step for CO activation<sup>34</sup>, and the CO conversion rate is then proportional to  $\theta_{CO}\theta_{H}^{2}$ . Unfortunately, it is not possible to accurately measure the H surface coverage by  $H_2/D_2$  switch in SSITKA experiments due to exchange reactions with surface and gas phase OH groups. However, the adsorption of CO and H is competitive on the Co surfaces, and CO adsorption is much stronger than H adsorption. It is then expected that increasing CO pressure increases the CO site coverage and consequently decreases the H site coverage. The opposite changes in CO and H site coverages resulted in a volcano type change of the CO conversion rate with CO pressure. The increase of reaction rate with the increase in CO pressure is a result of more significant increase in CO site coverage compared to the decrease in H site coverage. At high CO pressures, increasing CO pressure might result in a more significant decrease in the H site coverage, thus the reaction rate decreases.

In general, the dependency of site coverage of intermediates leading to olefin and paraffin formation with CO and H<sub>2</sub> pressures (Figure 4) corresponds well with the dependencies of olefin and paraffin formation rates (Figure 1). This is expected from a kinetic point of view, the CO and hydrogen pressures should mainly influence their site coverage. Similar to the CO pressure dependency of the paraffin formation rate (Figure 1a), a volcano-shaped curve was also observed for the CO pressure dependency of the site coverage of the intermediates leading to paraffin formation. Although the detailed kinetic expression for the formation of these intermediates could be complicated, the results suggest that the intermediate formation rate is a function of the site coverage of CO and H. The maximum in the site coverage of intermediates at a moderate CO pressure is possibly a result of the positive effect on the CO site coverage and a negative effect on the hydrogen site coverage with increasing CO pressure. Moreover, a more significant decrease in the site coverage of intermediates leading to paraffin formation with increasing CO pressure at relatively high CO pressures was observed, compared to changes in intermediates leading to olefin formation. It is a result of more hydrogen involved in the elementary reactions leading to paraffin formation compared to olefin formation, which will be discussed later in more detail.

Figures 1-4 show that the CO and  $H_2$  pressure dependency of the formation rates of olefin and paraffin and chain growth, as well as the concentration of intermediates, and such dependency is clearly a function of the carbon number. A clearer carbon number dependency of the formation rates of olefin and paraffin and chain growth is presented in Figure 5a. Both paraffin formation and chain growth rates decrease with increasing carbon number, while the olefin formation rate increases with carbon number up to 4, followed by a decrease for higher carbon numbers. The reaction rates follow exactly same trend as the selectivity as a function of carbon number. SSITKA data could provide a better understanding of the carbon number dependency of TOFs in terms of site coverage and the rate constant.

Similar to previous modeling of the SSITKA data<sup>17,18</sup>, the TOF of the formation of olefin, paraffin and chain growth can be expressed by the site coverage of corresponding intermediates and their reactivity, namely the inverse of the corresponding residence time (Eqs. 12-14):

$$TOF_{p,n} = k_{s,p,n}\theta_{p,n} \tag{Eq. 12}$$

$$TOF_{o,n} = k_{s,o,n}\theta_{o,n} \tag{Eq. 13}$$

$$TOF_{g,n} = k_{s,g,n}\theta_{o,n} \tag{Eq. 14}$$

where n represents the intermediate with carbon number of n;  $\text{TOF}_{p,n}$ ,  $\text{TOF}_{o,n}$ , are the turnover frequencies for the formation of paraffin, olefin, respectively,  $\text{TOF}_{g,n}$  is the propagation, and  $k_{s,p,n}$ ,  $k_{s,o,n}$ ,  $k_{s,g,n}$  are the rate constants for the formation of paraffin and olefin and propagation, respectively for the simple kinetic model;  $\theta_{p,n}$ ,  $\theta_{o,n}$  are the site coverage of the intermediate corresponding to the formation of paraffin and olefin, respectively. Table 2 and Figure 5 provide a detailed mapping of the surface coverage and kinetic rate constants of the steps involved in the reaction network of the CO hydrogenation on Co-Re/CNT.

**Table 2.** Compilation of the site coverage, turnover frequency and rate constants for the different compound formation on the catalytic surface of Co-Re/CNT at 483 K,  $P_T = 1.85$  bar,  $P_{CO} = 0.11$  bar and  $P_{H2} = 0.56$  bar.

Compound	TOF $(10^{-3}  \mathrm{s}^{-1})^{[a]}$	$\theta^{[b][e]}$	$k_{s,n} \left( s^{\text{-}1} \right)^{[d]}$
СО		0.6423	
CH <sub>4</sub>	13.2195	0.0811	0.1630
$C_1 - C_2^{[c]}$	5.0849		0.0627
$C_2H_6$	1.7029	0.0365	0.0467
$C_2H_4$	0.0939	0.0021	0.0449
C <sub>2</sub> -C <sub>3</sub>	4.9321		2.3587
$C_3H_8$	1.5444	0.0340	0.0454
$C_3H_6$	0.9712	0.0216	0.0449
C <sub>3</sub> -C <sub>4</sub>	3.2220		0.1490
$C_4H_{10}$	0.8196	0.0183	0.0448
$C_4H_8$	1.2403	0.0276	0.0449
C <sub>4</sub> -C <sub>5</sub>	1.4527		0.0526
$C_{5}H_{12}$	0.6206	0.0142	0.0437
$C_{5}H_{10}$	0.5390	0.0127	0.0425
C <sub>5</sub> -C <sub>6</sub>	0.3517		0.0278
$C_{6}H_{14}$	0.3517	0.0078	

[a] TOF of chain growth, paraffin and olefin formation reactions. [b] Site coverage of the main intermediates adsorbed on the catalytic surface, which were determined by transient response curves of labeled species as shown in Figure 3. [c]  $C_n$ - $C_{n+1}$  represents the chain growth reaction of  $C_n$ , [d]  $k_{s,n}$  is the rate constant lumped with the site coverage which cannot be measured directly, for chain growth  $k_{s,n}=k_{g,n}\theta_{C^*}$ , paraffin formation ( $k_{s,n}=k_{p,n}(\theta_H)^{m1}$ ) and olefin formation ( $k_{s,n}=k_{o,n}(\theta_H)^{m2}$ ) reactions, respectively. ks,n were estimated from measures TOFs and site coverages based on Eq. 12-14; [e] The summary of the site coverages in Table 2 is not 1, and the rest corresponds the site coverage of H, OH, site vacancy and others.

Figure 5 provides a detailed mapping of the surface coverage of intermediates and kinetic rate constants of the steps involved in the reaction network of the CO hydrogenation on Co catalysts, at the conditions of 483 K,  $P_T = 1.85$  bar,  $P_{CO} = 0.11$  bar and  $P_{H2} = 0.56$  bar, as an example.



**Figure 5.** Kinetic data from multicomponent SSITKA and its dependence on carbon number. a) Changes in chain growth rate (•), the formation rate of olefin (•) and paraffin ( $\blacktriangle$ ). b) Evolution of site coverage of intermediates leading directly to the formation of olefin (•) and paraffin ( $\bigstar$ ). c) Rate constants obtained by Eq. 12-14 for the chain growth (•), olefin (•) and paraffin ( $\bigstar$ ) formation in FT synthesis at 483 K, P<sub>T</sub> = 1.85 bar, P<sub>CO</sub> = 0.11 bar and P<sub>H2</sub> = 0.56 bar. Dashed line corresponds to estimated value.

The changes in site coverage of the intermediates leading to paraffin and olefin formation are presented in Figure 5b as a function of the carbon number. As reported previously, the site coverage of intermediates leading to methane is much higher than for intermediates leading to heavier paraffins<sup>19</sup>. The site coverage of the intermediates is reported only up to carbon number 5, since there is too large uncertainty in the measurement of the site coverage of the heavier olefins due to the low concentrations obtained at the conditions tested. The site coverage of the intermediate for ethylene formation is very low, possibly due to the strong adsorption of ethylene and therefore leading to a fast chain growth reaction. It explains a very low observed formation

rate of ethylene. A volcano curve of the intermediates leading to olefin formation is observed with the carbon number and the largest site coverage is found for carbon number 4.

Figure 5c shows the evolution of the rate constants for chain growth, paraffin and olefin formation with the carbon number. The rate constant for the olefin formation is constant regardless of the carbon number, indicating that the carbon number dependency of the olefin formation rate (Figure 5a) is mainly governed by the carbon number dependency of the site coverage of the intermediates, more precisely the adsorption strength of the olefin. It is interesting to note that the rate constants for paraffin formation are very similar to the ones for olefin formation and constant for  $C_2$ - $C_6$ , except for methane, which is higher than the others. Regarding the chain growth, there is a significant decrease in the rate constant with increasing carbon numbers.

It should be noted that the above simple kinetic model deconvolutes the TOF into the site coverage and the reactivity (or rate constant) of the intermediates, which provides a useful tool to study the effect of catalyst properties and operation conditions on the catalytic performance. However, this type of simple kinetic model alone cannot provide any information on the nature of the intermediates, which is a key factor for a better understanding of the mechanism of the formation of paraffin and olefin of each carbon number as well as the chain growth. Furthermore, the rate constants in the simple model are lumped parameters, and the exact physical meaning depends on the detailed reaction mechanism, which will be discussed in the next section.

# 3. Carbon number dependence of reaction mechanism and kinetics

# 3.1 Olefin and paraffin formation

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In order to better understand the carbon number dependency of the kinetics, knowledge of the reaction mechanism and identification of the nature of the intermediates involved in the elementary reactions for each carbon number are essential. Here we will employ a kinetic study at the elementary step level by varying the CO and H<sub>2</sub> pressure and combining a more detailed kinetic modeling, as a tool to elucidate the possible nature of the intermediates in Scheme 1. Based on the reaction network proposed in Scheme 1 and analysis of all the data, intermediates leading to olefin formation was selected as  $C_n^*$  in the kinetic analysis. The elementary reaction steps from the intermediate  $C_n^*$  to the corresponding olefin and paraffin involve several hydrogenation or dehydrogenation reaction steps. The exact number of elementary steps or how many H atoms are involved in the reaction steps depend on the detailed mechanism. Based on the rate determining step of  $C_nH_{2n+1}^*+H^*$  suggested by DFT studies<sup>19,46</sup> and the assumption of reaction orders of m1 and m2 H involved in the elementary reaction steps towards the formation of paraffin and olefin with the carbon number of n, the rate expressions can be described as in Eqs. 15-16, respectively:

$$TOF_{p,n} = k_{p,n}\theta_{Cn}(\theta_H)^{m1}$$
(Eq. 15)

$$TOF_{o,n} = k_{o,n}\theta_{Cn}(\theta_H)^{m2}$$
(Eq. 16)

where  $k_{p,n}$ ,  $k_{o,n}$  are the rate constant for the formation of paraffin and olefin, respectively;  $\theta_{Cn}$  and  $\theta_{H}$ , are the site coverage of the intermediate and hydrogen, respectively, measured by SSITKA; and m1 and m2 are the reaction order with respect to adsorbed atomic hydrogen for the paraffin and olefin formation from the intermediates, respectively. Unfortunately, the site coverage of hydrogen is not directly measureable by  $D_2/H_2$  switches in SSITKA, due to exchange reactions with OH groups on the support as well as in gas phase. By assuming an equilibrium of hydrogen

adsorption and desorption, the site coverage of hydrogen and vacant sites can be expressed as shown in Eqs. 17 and 18, respectively.

$$\theta_H = \sqrt{K_{H2} P_{H2}} \theta^* \tag{Eq. 17}$$

$$\theta^* = \frac{1 - (\sum_{i=1}^n \theta_i)}{1 + \sqrt{K_{H2}P_{H2}}}$$
(Eq. 18)

where  $K_{H2}$  is the H adsorption equilibrium constant, estimated to be 1.68 at 483 K in our previous studies combining transient and steady-state modeling<sup>19</sup>, P<sub>H2</sub> is the hydrogen partial pressure and  $\theta_i$  is the site coverage of all the compounds adsorbed on the catalytic surface except hydrogen, this includes CO, CH<sub>4</sub> and higher hydrocarbons. It was found that site vacancy is almost constant at the conditions studied in this work. It is partially due to opposite changes in site coverage of H and CO when CO or hydrogen pressure changes which compensates each other to a certain degree. Therefore, we could lump the site vacancy ( $\theta^*$ ) together with the rate constant. By rearranging Eqs. 15-16 and combining with Eqs. 17-18, Eqs. 19 and 20 are obtained in order to evaluate the reaction order with respect hydrogen:

$$\ln(TOF_{p,n}/\theta_{Cn}) = lnk''_{p,n} + m_1/2ln (P_{H2})$$
(Eq. 19)

$$\ln(TOF_{o,n}/\theta_{Cn}) = lnk''_{o,n} + m_2/2ln(P_{H2})$$
(Eq. 20)

where k"<sub>p,n</sub>= $k_{p,n}K_{H2}^{m1/2}\theta^{*m1}$  and k"<sub>o,n</sub>= $k_{o,n}K_{H2}^{m2/2}\theta^{*m2}$ , where  $K_{H2}$  is the equilibrium constant of hydrogen adsorption and  $\theta^*$  is the site vacancy.  $\ln(\text{TOF}_{p,n}/\theta_{Cn})$  and  $\ln(\text{TOF}_{o,n}/\theta_{Cn})$  were plotted as a function of  $\ln(P_{H2})$ , as depicted in Figure 6.



**Figure 6.** Plot of  $\ln(\text{TOF}_{i,n}/\theta_{Cn})$  vs.  $\ln(P_{H2})$  for (a) paraffin formation (i=p) and (b) olefin formation (i=o) reactions at different carbon numbers:  $\blacksquare$ : C<sub>3</sub>,  $\blacktriangle$ : C<sub>4</sub>, at: 483 K, P<sub>CO</sub> = 0.06 bar and P<sub>T</sub> = 1.85 bar.

A linear relationship was found both for  $C_3$  and  $C_4$  and the slope of the line gives the reaction order with respect to hydrogen of 2.2 for the paraffin formation and 0.7 for the olefin formation from the  $C_3$  intermediate. Similarly, the reaction order with respect to hydrogen is found to be 1.4 for the paraffin formation and 0.3 for the olefin formation for the  $C_4$  intermediate. The carbon number dependency of the hydrogen reaction order suggests therefore a possible carbon number dependency of the reaction mechanism for the termination reactions of  $C_n^*$  to paraffin and olefin. As discussed above, the reaction order with respect to hydrogen provides the number of H\* involved in the kinetic relevant elementary steps<sup>19,46</sup> from the intermediates to the products. The last hydrogenation step of  $C_nH_{2n+1}^*+H^*$  has been suggested as the rate determining step for paraffin formation. Using that as the starting point, the chemical identity of possible intermediate can be suggested based on the reaction order of hydrogen for the paraffin and olefin formation.

The most probable chemical identity of the intermediates could be related to  $alkyl^{5,37,47}$ ,  $alkenyl^{5,23,47,48}$  or hydroxycarbene<sup>49–51</sup> like species depending on the reaction mechanism. In the carbide mechanism, alkyl and alkenyl intermediates could be formed by the dissociation of adsorbed CO followed by hydrogenation of the carbide species to generate alkylene species (CH<sub>2</sub>-), which finally polymerize to generate alkyl like intermediates. Alternatively they can be

formed by the hydrogen assisted CO activation following decomposition of oxygen containing intermediates and hydrogenation<sup>19,20,36,46</sup>. Brady and Pettit<sup>41</sup> proposed a mechanism for the formation of 1-alkenes through alkyl like intermediates which involves the polymerization of methylene species to produce alkyl intermediates. Paraffin formation occurs by hydrogenation of the intermediate and olefin formation occurs via  $\beta$ -elimination of hydrogen atoms contained in the growing hydrocarbon chain.

The paraffin can be formed from alkyl intermediates ( $RCH_2-CH_2*$ ) through hydrogenation followed by desorption, while the olefin can be formed via  $\beta$ -elimination of hydrogen atoms in  $RCH_2-CH_2*$  to be followed by desorption of the olefin, as shown in Eqs. 21 and 22, respectively.

$$(R - CH_2 - CH_2)^*_{ads} + H_{ads} \rightarrow (R - CH_2 - CH_3)_{ads} + *$$
 (Eq. 21)

$$(R - CH_2 - CH_2 -)_{ads} + * \rightarrow (R - CH = CH_2)_{ads} + H_{ads}$$
 (Eq. 22)

The rate expressions for paraffin and olefin formation reactions are shown in Eqs. 23 and 24 respectively, assuming that Eq. 21 and 22 describe the rate determining steps.

$$r_{p,n} = k_{p,n} \theta_{RCH2CH2} (P_{H2})^{1/2}$$
(Eq. 23)

$$r_{o,n} = k_{o,n} \theta_* \theta_{RCH2CH2} \tag{Eq. 24}$$

where  $r_{p,n}$  and  $r_{o,n}$  are the paraffin and olefin formation rates, respectively;  $k_{p,n}$  and  $k_{o,n}$  are the rate constants for the paraffin and olefin formation, respectively;  $\theta_{RCH2CH2}$  is the site coverage of the alkyl intermediate and  $P_{H2}$  is the partial pressure of hydrogen.

It has also been observed that the polymerization of methylene species (CH<sub>2</sub>-) can lead to the formation of alkenyl or vinyl intermediates (RCH=CH\*)<sup>40</sup>, which can be hydrogenated to

produce paraffins and olefins. The elementary steps for paraffin formation from RCH=CH\* to the rate determining step can be described by Eq. 25a-c:

$$(R - CH = CH -)_{ads} + H_{ads} \leftrightarrow (R - CH_2 - CH)_{ads} + K_{25a}$$
(Eq.25a)

$$(R - CH_2 - CH -)_{ads} + H_{ads} \iff (R - CH_2 - CH_2)_{ads} + K_{25b}$$
(Eq.25b)

$$(R - CH_2 - CH_2 -)_{ads} + H_{ads} \rightarrow (R - CH_2 - CH_3)_{ads} + k_{25c}$$
 (Eq.25c)

For a clarity purpose, the above elementary steps are lumped in Eq. 25:

$$(R - CH = CH -)_{ads} + 3H_{ads} \rightarrow (R - CH_2 - CH_3)_{ads} + 3^*$$
 (Eq. 25)

The olefin formation is described by Eq. 26:

$$(R - CH = CH -)_{ads} + H_{ads} \rightarrow (R - CH = CH_2)_{ads} + *$$
(Eq. 26)

The rate expressions for paraffin and olefin formation reactions are shown in Eqs. 27 and 28, respectively.

$$r_{p,n} = k_{p,n} \theta_{RCHCH} (P_{H2})^{3/2}$$
(Eq. 27)

$$r_{o,n} = k_{o,n} \theta_{RCHCH} (P_{H2})^{1/2}$$
(Eq. 28)

where  $k_{p,n} = k_{25c} K_{25a} K_{25b} K_{H2}^{3/2} = k'_{p,n} K_{H2}^{3/2}$ ,  $k_{o,n} = k'_{o,n} K_{H2}^{1/2}$ ,  $K_{25a}$  and  $K_{25b}$  are the equilibrium constants for the reaction steps of 25 a and b, k25c is the rate constant for the step 25c.

Surface science and theoretic calculation have recently suggested alkyne (RCH=CH\*) and alkylidyne  $(RCH_2C^*)^{52,53}$  as the most stable intermediates for chain growth. It should be noted that RCH=CH\* and RCH\_2C\* are species that cannot be distinguished by kinetic analysis alone.

The enol like intermediates ( $RCH_2$ - $CHO_{ads}$ ) are formed via the hydrogenation of associatively adsorbed CO, which generates  $CHOH_{ads}$  (hydroxycarbene) species. Subsequently, the hydroxycarbene species polymerize generating aldehydes, which subsequently can form paraffins and olefins by reaction with hydrogen. The formation of paraffins and olefins from  $RCH_2$ - $CHO_{ads}$  is presented in Eqs. 29 and 30, respectively.

$$(R - CH_2 - CHO -)_{ads} + 4 H_{ads} \rightarrow (R - CH_2 - CH_3)_{ads} + H_2O_{ads} + 3 * (Eq. 29)$$

$$(R - CH_2 - CHO -)_{ads} + 2H_{ads} \rightarrow (R - CH = CH_2)_{ads} + H_2O_{ads} + *$$
 (Eq. 30)

The rate expressions for paraffin and olefin formation reactions are shown in Eqs. 31 and 32, respectively.

$$r_{p,n} = k_{p,n} \theta_{RCH2CH0} (P_{H2})^2$$
 (Eq. 31)

$$r_{o,n} = k_{o,n} \theta_{RCH2CHO} P_{H2} \tag{Eq. 32}$$

**Table 3.** Hydrogen reaction order of the paraffin and olefin formation reaction for the possible intermediates and experimental values obtained for the  $C_3$  and  $C_4$  intermediates.

	<b>Reaction order of H<sub>2</sub></b>		$\mathbf{k}_{\mathbf{p},\mathbf{n}}$	k <sub>o,n</sub>
Intermediates (C <sub>n</sub> *)	Paraffin	Olefin		
	formation	formation		
$R - CH_2 - CH_2$ (alkyl)	0.5	0		
R - CH = CH (alkenyl)	1.5	0.5		
$R - CH_2 - C$ (alkylidyne)	1.5	0.5		
$R - CH_2 - CHO(enol)$	2.0	1.0		
Fynarimantal	Paraffin	Olefin		
	formation	formation		
C <sub>3</sub>	2.2	0.6	335.7	88.1
$C_4$	1.4	0.3	69.3	61.6

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The possible hydrogen reaction orders for the formation of paraffin and olefin are summarized in Table 3 based on the kinetic analysis of the reactions from alkyl, alkenyl or alkylidyne and aldehyde like intermediates. The experimental observed reaction orders of hydrogen are also summarized in Table 3 for comparison.

The experimental reaction orders with respect to hydrogen of 2.2 and 0.6 were observed for the paraffin and olefin formation from  $C_3$  intermediates, respectively. The results suggest that alkyl and alkenyl or alkylidyne like intermediate can be excluded, and the enol like intermediates (CH<sub>x</sub>CHO-) seems to be the intermediates responsible for propane and propene formation. It requires 4 H for the hydrogenation from an enol like intermediate to propane formation. The experimental reaction orders towards hydrogen of 1.4 and 0.3 were observed for the paraffin and olefin formation from C<sub>4</sub> intermediate, respectively. The results indicate that the intermediate responsible for the reactions forming C<sub>4</sub> (Scheme 1) is most likely to be an alkenyl or alkydiyne like intermediate. However, the experimental hydrogen order of 1.4 and 0.3 is slightly lower than the theoretical ones of 1.5 and 0.5 from alkenyl like intermediates. This is within the experimental uncertainty (less than 5%).

The rate constants for the termination reactions to  $C_3$  and  $C_4$  hydrocarbon are also summarized in Table 3. The carbon number dependence of the rate constants for olefin formation is similar to the one in Figure 1c obtained by Eqs. 12-13. However, the carbon number dependence of the rate constants for the paraffin formation is different. It should be noted that the intermediate used in Eq. 12 and 15 is different. The site coverage of the intermediates leading to paraffin formation measured by SSITKA ( $\theta_{p,n}$ ) was used in Eq. (12), while the site coverage of the intermediates leading to the olefin formation is used in Eq. 15. Comparing the carbon number dependence of the two rate constants, it can be concluded that the rate constant for the paraffin formation from

the paraffin like intermediates is independent on the carbon number, but the rate constant for the formation of the paraffin like intermediates from the intermediates leading to olefin formation depends on the carbon number.  $k_{p,3}$  is larger than  $k_{p,4}$ , possibly due to the different chemical nature of the C<sub>3</sub> and C<sub>4</sub> intermediates.

# 3.2 Chain growth reaction

It is generally assumed that chain growth is an irreversible reaction. The propagation rate is described as Eq. 33:

$$TOF_{q,n} = k_{q,n}\theta_{Cn}\theta_{C*} = k'\theta_{Cn}$$
(Eq. 33)

where  $\text{TOF}_{g,n}$  is the turnover frequency of chain growth,  $k_{g,n}$  is the rate constant for the propagation rate and  $\theta_{Cn}$  and  $\theta_{C*}$  are the site coverage of intermediate with carbon number of n and the monomer to be incorporated into the growing chain, respectively. It is reasonable to assume that the site coverage of the monomer ( $\theta_{C*}$ ) is constant in all the steps of the chain growth, regardless of the carbon number. Therefore,  $\theta_{C*}$ , can be lumped together with  $k_{g,n}$ , which is a function of the concentration of the chain growth monomer. Eq. 33 was rearranged using chain growth rate of C<sub>3</sub> as the reference to eliminate the effects of  $\theta_{C*}$ . The relative rate constant is described by Eq. 34 and plotted in Figure 7.

$$\frac{k_{g,n}}{k_{g,3}} = \frac{TOF_{g,n}}{TOF_{g,3}}\frac{\theta_{C3}}{\theta_{Cn}}$$
(Eq. 34)



**Figure 7.** a) Ratio of chain growth rate constant as a function of carbon number; b) Chain growth rate divided by the site coverage as a function of the carbon number at different  $P_{CO}$  and  $P_{H2}$  (in bar). T = 483 K and  $P_{T}$  = 1.85 bar.

Figure 7a shows that the  $k_{g,n}/k_{g,3}$  values for each hydrocarbon with different carbon numbers do not depend on CO and H<sub>2</sub> pressures, except for C<sub>2</sub>. The variation of  $k_{g,2}/k_{g,3}$  for C<sub>2</sub> is possibly a result of experimental uncertainty due to very low concentrations of ethylene, which makes it difficult to accurately measure the residence time of the ethylene intermediate. In the estimation of the surface coverage of this compound, it has been assumed that the residence time of ethylene is relatively close to the residence time of propylene. Anyhow, the results in Figure 7a confirm the hypothesis of identical chain growth monomer for all the carbon numbers. Moreover, the results clearly demonstrate that the of reactivity of C<sub>n</sub>\* (rate constant  $k_{g,n}/k_{g,3}$ ) is a function of the carbon number. The significantly higher rate constant for the C<sub>2</sub> chain growth compared to the ones for the chain growth of C<sub>2+</sub> explains the very low ethylene selectivity observed. The decrease in the  $k_{g,n}/k_{g,3}$  with carbon number is also observed for carbon numbers.

The lumped rate constant (k') was obtained by  $\text{TOF}_{g,n}/\theta_{Cn}$  from Eq. 33 and plotted as a function of the carbon number in Figure 7b. The k' values depend on the coverage of chain growth monomer as well as the carbon number (Eq. 33). k' decreases with increasing carbon number, consistent with the observation in Figure 7a. The lumped rate constant k' varied also

with the CO and H<sub>2</sub> pressures (Figure 7b). This suggests that the concentration of chain growth monomer ( $\theta_{C*}$ ) is a function of CO and H<sub>2</sub> pressures. However, the carbon number dependency of the k' appears almost as parallel lines with the carbon number in Figure 7b at different CO and H<sub>2</sub> pressures. The k' value is higher at higher hydrogen pressures. Based on the factor of the dependence of the chain growth monomer on the CO and H<sub>2</sub> pressures, the direct CO insertion mechanism can be excluded. However, in order to distinguish the carbide and the hydroxycarbene or enol mechanism for chain growth, more detailed investigations need to be done.

As discussed above, there are three types of mechanisms such as carbide, CO insertion and enol mechanism dominating in the literature of CO hydrogenation. Although a kinetic study cannot exclusively identify the reaction mechanism, it is reasonably acceptable to use kinetics to eliminate some of the mechanisms and make it possible to suggest the reaction mechanism for the paraffin and olefin formation as well as the propagation in CO hydrogenation. Based on the kinetic analysis of the reactions for  $C_3$  and  $C_4$ , it can be concluded that a single reaction mechanism cannot describe all the reactions of CO hydrogenation, and the mechanism seems to depend on the carbon number. Indeed the results rather suggest a reunified mechanism where alkyl, alkenyl and enol intermediates co-exist on the surface, and dominating intermediates corresponding to the chain growth and termination depends on the carbon number, maybe also on reaction conditions.

It has been demonstrated that the multicomponent SSITKA is a powerful kinetic diagnostic tool to elucidate the kinetics and reaction mechanism of CO hydrogenation at a molecular level at relatively low pressures. It should be noticed that the conditions used here are far from the realistic conditions of industrial FT synthesis. The low total pressure and high  $H_2$ /CO ratios were

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employed in the SSITKA experiments to avoid the formation of heavy products such as wax, to allow the full analysis of all the products, which is essential for the analysis of kinetics of the chain growth. In addition, it eliminates possible effects of the diffusion limitation due to filling of wax in the pore on the product residence time, making it possible to study the intrinsic reaction mechanism and kinetics. However, the relative value of rate constants for chain growth and termination and their dependency on the carbon number could be the same for CO hydrogenation at low pressures and F-T at high pressures. In addition, the mechanic insights for the CO hydrogenation have been obtained at very high CO site coverages. Therefore, it is anticipated that the kinetic and mechanistic insights obtained here, in particular the observed tendencies in the kinetic dependence of carbon number and CO and H<sub>2</sub> pressures, are also applicable at industrial F-T conditions. It has already been demonstrated that the dependence of TOF and methane selectivity on the cobalt particle size agree well with each other both at CO hydrogenation conditions like the ones used for SSITKA here and industrial FT synthesis conditions<sup>54</sup>.

# Conclusions

In this work we have developed a powerful tool to provide the kinetic mapping of the CO hydrogenation network over a Co-based catalyst by analyzing the residence time and site coverage of the main intermediates obtained by multicomponent SSITKA experiments. It demonstrates that the multicomponent SSITKA is a valuable kinetic diagnostic tool, which can not only provide mechanistic and kinetic insights of the reaction network, but also deconvolute the effects of operation conditions on the reaction rates into their effects on the surface concentration of the key intermediates and the reactivity in CO hydrogenation at a molecular

level. Kinetic study by using such a tool suggests a carbon number dependency of the chemical nature of the intermediates (Cn\*) in the reaction network responsible for paraffin and olefin formation as well as chain growth, where enol and alkenyl like species are dominating for  $C_3$  and  $C_4$  reactions, respectively. Our results rather suggest a reunified mechanism, where the alkyl, alkenyl and enol intermediates co-exist on the surface, and dominating intermediates corresponding to the termination and propagation depend on the carbon number, maybe also on reaction conditions.

Moreover, by using such a diagnostic tool, we have a direct experimental measurement of the carbon number dependency of rate constants for olefin and paraffin formation as well as chain growth. The rate constants are identical for the termination reactions of Cn\* to olefin and paraffin, suggesting that the surface coverage, and thus the adsorption strength of the olefin and paraffin is the key parameter to determine the olefin and paraffin ratio. It is anticipated that this tool will be highly valuable in FT catalyst developments, especially for lower olefin production through effective study of effects of catalytic properties, such as the active material and support identity, promoter or particle size on the catalytic performance by quantitative mapping of the surface intermediates and their reactivity.

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# **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

# Notes

The authors declare no competing financial interest.

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# **Table of Contents Graphic**



This work describes a powerful tool for kinetic mapping of the reaction network of CO hydrogenation over a Co-Re-based catalyst by analyzing the site coverage of the main intermediates obtained by multicomponent SSITKA. The results suggest a carbon number dependence of the intermediates in the reaction network responsible for paraffin and olefin formation, showing that aldehyde and alkenyl-like species are dominating for reactions forming C3 and C4, respectively.

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