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Unravelling the influence of catalyst properties on light olefin production via Fischer–Tropsch synthesis: A descriptor space investigation using Single-Event MicroKinetics

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ABSTRACT

Kinetic models constitute a useful tool to provide fundamental insights for catalyst development. Single-Event MicroKinetic modelling (SEMK) is a versatile strategy to assess complex reactions with a limited number of parameters. Particularly for Fischer–Tropsch synthesis SEMK modelling has focused on explaining the performances of individual catalysts within a wide range of operating conditions. In this work, we extend the capabilities of the SEMK modelling approach to investigate the influence of variation in catalyst properties i.e. catalyst descriptors, on the yield of desired component, light olefins ($C_2-C_4=$). We explore the catalyst descriptor space around three literature-reported iron-based catalysts. The three catalyst descriptors, i.e. atomic chemisorption enthalpies of hydrogen (Q_H), carbon (Q_C), and oxygen (Q_O) in the SEMK modelling approach have a combined effect on the conversion, whereas the selectivity to light olefins is found to be less sensitive to Q_0 . These effects can be rationalized in terms of relative surface coverages of different species, leading to different dominant reaction pathways, and thus resulting in product yield variations. Using this approach, a "promising catalyst" with catalyst descriptors, $Q_H \approx 234$ kJ/mol, $Q_C \approx 622$ kJ/mol and $Q_O \approx 575$ kJ/mol resulting in 55% light olefins yield with lower methanation and long-chain hydrocarbon formation, is identified.

1. Introduction

Fischer–Tropsch synthesis (FTS) is one of the most promising approaches to obtain non-petroleum-based hydrocarbons. While, most of the current plants rely on coal [1] or natural gas [2,3] to produce syngas, the feedstock for FTS, various chemical recycling techniques can be used as an alternative to produce syngas with non-conventional H_2/CO (e.g. from plastic waste via gasification) [4]. With the current urge for circular economy [5,6] and, hence, the need to reduce plastic waste and associated pollution, save primary resources and preserve our natural ecosystem, the use of syngas with non-conventional H_2/CO has gained popularity. Technological developments with emphasis on better catalysts can help to increase the competitiveness of the FTS process [7] to produce value-added chemicals such as light olefins from plastic waste. The light olefins so produced could in turn be used for plastic production [8], thus leading to a true circular economy. Therefore, high-temperature FTS has been of interest in the last decades

due to the opportunity to convert plastics and organic waste into valueadded chemicals such as light olefins rather than other hydrocarbon products such as methane, paraffins, and other long-chain hydrocarbons [9,10]. Studies also concentrate on the influence of different catalysts in enhancing the activity and selectivity. A comprehensive review of early catalyst development is reported by Vannice et al. [11] and Anderson et al. [12].

At present, the FTS process mostly uses iron-based (low- and hightemperature operation modes) and cobalt-based (low-temperature operation mode) catalysts. Both cobalt [13–15] and iron [16,17] catalysts yield higher hydrocarbons. Higher activity, light olefin selectivity, and lower costs make iron-based catalysts a better candidate in FTS even though they also lead to proportionally more oxygenates. Due to their potential water gas shift (WGS) activity, iron-based catalysts find merit in processing syngas with varying H2/CO ratio, more particularly hydrogen deficient syngas [12,18,19].

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Nomenclature			
$\Delta ilde{S}^0_r$	Single-event surface reaction entropy, $J(K \text{ mol})^{-1}$		
Δ	The difference between experimental and		
	simulation results in percentage		
F _{CO,in}	Carbon monoxide molar flow rate at the		
	reactor inlet, mol/s		
F _{CO,out}	Carbon monoxide molar flow rate at the		
	reactor outlet, mol/s		
Fi	The molar flow rate of component i at the		
	reactor outlet, mol/s		
n _{C,i}	The number of carbon atoms in component		
6			
s _i	The selectivity toward a gas-phase compo- $n_{C}:F_{i}$		
	nent i, $S_i = \frac{C_i \Gamma_i}{F_{CO} \Gamma_i - F_{CO}}$		
X _{CO}	Carbon monoxide conversion at the reactor		
	outlet, $X_{CO} = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,out}}$		
	F _{CO,in}		
Ea	Forward activation energy, kJ/mol		
A _i	Affinity for elementary reaction i, J mol ⁻¹		
K _{eq}	Thermodynamic equilibrium coefficient,		
ĩ	[-]		
	Pre-exponential factor, 1/s or 1/MPa s		
GN I ETC	Carbon nanotube		
F15	Coo hourly groop valuation L_{1}		
GHSV	Gas nourly space velocity, Lg ⁺ n ⁺		
n	Number of virtual catalysts		
P	Pressure, bar		
K	Cincle Event MicroVinctic modelling		
SEIVIK			
	Temperature, K		
vv	Catalyst weight, g		

The investigations on iron-based catalysts have focused mainly on operating conditions such as temperature, gas flow rate, pressure, gas type, as well as on the promoters. The improvement in catalyst performance with addition of promoters in iron-based catalysts [16,17] has attracted recent research interests. The study of the promoter effect is rather complex as it is done with different supports and at different reaction conditions. Recent studies investigate the effect of iron-promoted catalysts [9,10] on performance. Gu et al. [9] report a higher light olefin selectivity, specifically on promotion by Bi and Pb on carbon nanotube support, over unpromoted Fe catalyst.

In order to provide fundamental insights on catalyst development, kinetic models can be recurred to account for properties in the modelling procedure [20]. Microkinetic models, which represent the occurring chemistry at the elementary step level [21-23] help to study the reaction kinetics of complex reactions such as Fischer-Tropsch reaction [24], oligomerization [25], autoxidative curing [26], etc. To model reaction systems with a large number of elementary steps using a microkinetic approach, the single event concept can be employed. In the Single-Event MicroKinetic (SEMK) methodology the reactive moieties are considered to determine the reactivity of individual molecules. Accordingly, the elementary reactions are classified into reaction families to reduce the number of parameters [27]. The single-event kinetic coefficient is unique for a reaction family and the adsorption enthalpies of surface species are calculated via the UBI-QEP method [28,29]. In the SEMK framework, the catalysts are differentiated in terms of model parameters referred to as catalyst descriptors. Single-Event MicroKinetic models have been developed for alkylation [30], hydrocracking [31], catalytic cracking [32] and reforming [33]. Specifically for FTS, studies using the SEMK modelling approach concentrate mostly on identifying the descriptors values corresponding to the catalysts used in a particular experimental investigation [34–39]. However less attention was dedicated to explain how a change in the catalyst properties and, hence, in the descriptor values, would influence the performances. Screening of the descriptor space could help us in identifying the surface reactions that mostly impact the selectivity toward the desired products.

The scope of the current work is, hence, to identify the catalyst descriptor values that enhance the yield of light olefins, within a broad, yet realistic descriptor space. For our study, the descriptor space is identified by taking into account the experimental performances of three iron-based catalysts. We carry out SEMK simulations using different combinations of descriptors, also denoted as virtual catalysts [40]. The SEMK simulations with virtual catalysts aim at assessing how the model explains the difference in the behaviour of catalysts in terms of the microkinetic phenomena and identifying a "promising catalyst" within the descriptor space.

2. Single Event MicroKinetic modelling approach

Before discussing the current work in detail, the SEMK methodology as applied to FTS is briefly explained. The elementary steps and reaction families considered in the SEMK reaction network, are summarized in Table 1. The forward activation energies listed in Table 1 constitute the kinetic descriptors of the model, which are independent of the catalyst descriptors. The forward activation energies reported in the table, along with the standard surface reaction enthalpies, are used to calculate the reverse activation energies for the elementary steps by applying the principle of microscopic reversibility. The surface reaction enthalpies are calculated starting from those of the corresponding gas phase reactions and by accounting for the enthalpy change induced by chemisorption [37]. Chemisorption enthalpies of various surface species are calculated as a function the atomic chemisorption enthalpies using the UBI-QEP method [29,41]. The single-event forward preexponential factors reported in Table 1 are determined via statistical thermodynamics calculations. The calculation involves gas phase entropies of the components and the single-event standard entropy change related to chemisorption [42]. The gas phase entropies are obtained either from databases [43] or using group additivity methods [44]. The calculation of the entropy change related to the chemisorption step is based on the loss of translational entropy of a gas phase component, which is in turn calculated with the Sackur-Tetrode equation [45]. The reverse pre-exponential factors are calculated using the forward preexponential factors (Ã^{for}) and single event surface reaction entropies $(\Delta \tilde{S}_r^0)$ as:

$$\tilde{A}_{j}^{rev} = \frac{\tilde{A}_{j}^{for}}{exp\left(\frac{\Delta \bar{S}_{r,j}^{0}}{R}\right)}$$
(1)

The pre-exponential factors are used for determining the rate coefficients of the reaction families in Table 1. All the above calculations are explained in detail by Lozano-Blanco et al. [34,36]. A sample calculation of the above is reported in Supplementary material.

In the SEMK model, the considered catalyst and corresponding reaction mechanism are quantified in terms of both catalyst and kinetic [27] descriptors. Kinetic descriptors are model parameters that are specific to the reaction families considered and are independent of the catalyst properties. While catalyst descriptors are model parameters that specifically account for the impact of the catalyst on the kinetics. In the case of Fischer–Tropsch synthesis, atomic chemisorption enthalpies of carbon (Q_C in carbide phase), hydrogen (Q_H and Fe₃O₄ – H corresponding to carbide and oxide phase respectively), and oxygen (Q_O in carbide phase) are the catalyst descriptors [36]. The atomic chemisorption

Table 1

Elementary reactions and reaction families in the reaction network [36], where E_a^{for} represent the kinetic descriptors, M represents the metal surface, and \tilde{A}^{for} , represent the forward pre-exponential factors, and $a\tilde{S}_r^0$ represent surface reaction entropies, respectively. The surface reaction enthalpies is a function of catalyst descriptors. The calculations of enthalpies and entropies are reported by Lozano-Blanco et al. [34,36].

E ₂ ^{for}	\tilde{A}^{for}	$\Delta \tilde{S}_{r}^{0}$
(kJ/mol)	$(s^{-1} \text{ or } (MPa \ s)^{-1})$	$(J(K mol)^{-1})$
0	3.1×10^{8}	-63.5
0	2.2×10^{7}	-165.7
56.81 ± 0.53	1.3×10^{13}	-17.34
77.66 ± 0.70	8.8×10^{14}	+35.08
11.94 ± 0.10	5.9×10^{11}	-25.6
61.88 ± 0.50	2.2×10^{11}	-33.5
44.79 ± 0.43	8.3×10^{9}	-60.69
117.75 ± 0.67	3.3×10^{10} (n=2)	+64.3
	2.0×10^{10} (n=3–10)	
96.27 ± 0.50	1.0×10^{10}	+12.32
63(n=2)	1.3×10^{13}	+118.6
61(n=3-10)		
138.95 ± 1.15	1.7×10^{14}	+53.2
103.80 ± 0.96	1.3×10^{12}	+33.92
86.22 ± 0.62	2.4×10^{11}	+73.7
	$\begin{array}{c} E_{a}^{/or} \\ (kJ/mol) \\ \hline 0 \\ 0 \\ 56.81 \pm 0.53 \\ 77.66 \pm 0.70 \\ 11.94 \pm 0.10 \\ 61.88 \pm 0.50 \\ 44.79 \pm 0.43 \\ 117.75 \pm 0.67 \\ 96.27 \pm 0.50 \\ 63(n=2) \\ 61(n=3\cdot10) \\ 138.95 \pm 1.15 \\ 103.80 \pm 0.96 \\ 86.22 \pm 0.62 \\ \end{array}$	$\begin{array}{rl} F_a^{for} & \tilde{A}^{for} \\ (kJ/mol) & (s^{-1} \ or \ (MPa \ s)^{-1}) \\ \hline 0 & 3.1 \times 10^8 \\ 0 & 2.2 \times 10^7 \\ 56.81 \pm 0.53 & 1.3 \times 10^{13} \\ 77.66 \pm 0.70 & 8.8 \times 10^{14} \\ 11.94 \pm 0.10 & 5.9 \times 10^{11} \\ 61.88 \pm 0.50 & 2.2 \times 10^{11} \\ 44.79 \pm 0.43 & 8.3 \times 10^9 \\ 117.75 \pm 0.67 & 3.3 \times 10^{10} \ (n=2) \\ & 2.0 \times 10^{10} \ (n=3-10) \\ 96.27 \pm 0.50 & 1.0 \times 10^{10} \\ 63(n=2) & 1.3 \times 10^{13} \\ 61(n=3-10) \\ \hline 138.95 \pm 1.15 & 1.7 \times 10^{14} \\ 103.80 \pm 0.96 & 1.3 \times 10^{12} \\ 86.22 \pm 0.62 & 2.4 \times 10^{11} \\ \hline \end{array}$

enthalpies are reported in absolute value, with an increase corresponding to more pronounced exothermicity. The atomic chemisorption enthalpies of the iron catalyst discussed by Lozano-Blanco et al. [36] i.e. Q_C , Q_H , Fe_3O_4-H and Q_O are 630.03 \pm 2.47 kJ/mol, 252.40 \pm 0.63 kJ/mol, 233.83 \pm 1.28 kJ/mol and 579.19 \pm 1.77 kJ/mol, respectively. In our discussion below, a "virtual catalyst" corresponds with a specific combinations of these catalyst descriptors, while the ones actually synthesized and experimentally tested are referred to as real catalysts.

3. Methodology

The current work on FTS using SEMK simulations aims at identifying a "promising catalyst" (catalyst descriptors) that leads to enhanced yield of light olefins. The kinetic descriptor values listed in Table 1 based on previous work [36]. The catalyst descriptors are identified as discussed later in this section. The experimental results reported by Gu et al. [9] are used to determine the catalyst descriptor values corresponding to Bi and Pb promoted and non-promoted Fe catalysts. These are used as a benchmark to explore the parametric catalyst descriptor space. The comparison between the numerical simulation results and the experimental data serves to identify the relevant part of the space within which the real catalysts are situated. A "promising catalyst" that leads to enhanced yield of light olefins, is then identified within the catalyst descriptor space enclosing the three literaturereported iron-based catalysts. Thus our methodology is split into two subsections.

3.1. Identification of realistic descriptor space

To identify and analyse the catalyst descriptors space corresponding to Fe/CNT, FeBi/CNT, and FePb/CNT catalysts used by Gu et al. [9], we follow the steps discussed below:

• Step 1: Generation of virtual catalyst library:

A library with a large number of virtual catalysts is generated by varying the catalyst descriptors (Fig. 1). The investigated range of catalyst descriptors is chosen around the descriptor values for an Fe catalyst, as previously investigated [36]. To generate a diverse virtual catalyst library, the virtual space is sampled via an experimental design. In order to account for this deterministic system with various factors (descriptors), we make use of space-filling design [40,46]. The combination of descriptors generated by this procedure forms a virtual catalyst library. The virtual catalysts are used to carry out numerical simulations.

• Step 2: Numerical simulations with a virtual catalyst library: In the second step of the proposed methodology numerical simulations are performed with FTS Single-Event MicroKinetic model incorporated in a plug flow reactor model for all virtual catalysts generated in **Step 1**. The set of ordinary differential equations (mass balances for the molecules) and nonlinear algebraic equations (pseudo-steady state approximation for the surface species) in the reactor model is solved with the DASPK [47] from the Netlib [48] software library as discussed by Lozano-Blanco et al. [36]. In order to ensure convergence, the numerical subroutine DNSQE within Netlib library is used to initialize the variables associated with the algebraic equations (solved using DASPK). In this work, DASPK is used with variable-stepsize backward differentiation formulas applying a direct linear method.

The simulations are performed at the following operating conditions: 623 K, 10 bar, GHSV = $3.4 \text{ Lg}^{-1} \text{ h}^{-1}$, W = 0.2 g, and H₂/CO molar inlet ratio of 1, as reported in [9].

• Step 3: Comparison and screening to identify realistic catalyst descriptors:

From the simulation results, we find a pool of virtual catalysts with different combinations of catalyst descriptors resulting in comparable conversion (Δ < 5%) and light olefin selectivity (Δ < 10%) with respect to the experimentally observed ones. This reduces the number of virtual catalyst candidates by \approx 90%. This is followed by a screening of the selectivities toward other components namely, CO2, CH4, and long-chain hydrocarbons (on a carbon-dioxide-free basis), to identify the range of realistic catalyst descriptors. This screening process in the order mentioned above leaves us with less than 5%, 2% and 0.5% virtual catalysts initially generated, respectively. We identify the range of catalyst descriptors that represent the above 0.5% of virtual catalysts. More virtual catalysts are generated in this confined range, and the Step 1-Step 3 are carried out iteratively, until there is no difference between consecutive iterations. The catalyst descriptors which result in a match of conversion and selectivity between experiments and simulations are thus identified. The process discussed above is carried out to identify the catalyst descriptors of the three real catalysts, Fe/CNT, FePb/CNT, and FeBi/CNT.

3.2. Identification of a "promising catalyst"

To identify a "promising catalyst" with maximum light olefins yield, the descriptor space around the catalyst descriptors of the three literature-reported real catalysts is analysed. The descriptor space is



Fig. 1. Identification of descriptors in SEMK simulations that explain the performance behaviour of real experimental catalysts. SEMK simulations are carried out at different combinations of descriptors and the resulting performance is compared with experimental results. The descriptor combinations explaining the performance obtained with experiments using different catalysts are identified.

analysed using 2D parametric planes and 3D iso-surfaces of conversion, selectivity, and yield. We also compare reaction pathways as simulated for various virtual catalyst to understand how the corresponding descriptor values determine the selectivities/yields. Reaction pathway analysis (RPA) serves as an important tool to analyse the occurring phenomena, e.g., elementary steps, both in a qualitative and quantitative manner, and identify the prevailing reaction routes [39]. In this work, the reaction pathway analysis is performed by determining the affinities of elementary reactions.

For an elementary reaction, $aA + bB \approx cC + dD$, we define affinity of the elementary reaction as,

$$A_i = RT \times ln\left(K_{eq} \frac{A^a B^b}{C^c D^d}\right),\tag{2}$$

where, R, T and Kee are universal gas constant, temperature and thermodynamic equilibrium coefficient, respectively. If the affinity is close to zero, the elementary reaction occurs very fast and can be assumed to be in quasi-equilibrium. In the reaction pathway analysis carried out, an elementary reaction is considered to be in quasi-equilibrium when the affinity, $|A_i| < 1000 \text{ J mol}^{-1}$ [39]. Kinetically relevant reactions will have an affinity exceeding this value. The corresponding reaction rate will then allow determining what fraction of the reactant is consumed via this elementary reaction. In the current study, the reactions in quasi-equilibrium are represented with solid black arrows, while the thickness of the kinetically relevant steps (coloured arrows) are scaled logarithmically. Thickness of the coloured arrows are chosen such that, Thickness, $t = k \times |logx|^{-1}$, where, x = forward or backward reaction rate and k = multiplication factor. The value of k is chosen to be 11.5 for discrimination of arrows. Each reaction family is given a separate colour.

From our analysis above, we then identify a "promising catalyst" with maximum light olefins yield, within the investigated descriptor space.

Table 2

Catalyst descriptors, i.e atomic chemisorption enthalpies for Fe, FeBi/CNT and FePb/CNT catalysts.

Atomic chemisorption enthalpies	Fe/CNT (kJ/mol)	FeBi/CNT (kJ/mol)	FePb/CNT (kJ/mol)
$Q_{\rm H}$ (Fe _x C – H) $Q_{\rm H}$ (Fe _x C – C)	249.5	247.7	248.4
$Q_C (Fe_x C - C)$ $Q_O (Fe_x C - O)$	601.0	589.1	577.1

4. Results and discussion

4.1. Identification of realistic catalyst descriptors

To find the catalyst descriptor range corresponding to the catalysts Fe/CNT, FePb/CNT, and FeBi/CNT reported in [9], we compare the simulated performance of virtual catalysts with the experimental ones. In Fig. 2(a) each blue dot corresponds to the conversion and light olefin selectivity obtained with a virtual catalyst. As seen from the scatter plot (Fig. 2(a)), different virtual catalysts, result in a wide conversion and selectivity range. However, only a few virtual catalysts result in conversion and light olefins selectivity comparable to that with the real catalysts (experiments) namely, Fe/CNT (brown), FePb/CNT (green) and FeBi/CNT (red).

As discussed in **Step 3** of our methodology, the catalyst descriptors which best reproduced the experimental performances (see Fig. 2(b), Fig. 2(c)–(e)) are identified for both non-promoted and promoted catalysts. The descriptor values for the three real catalysts are reported in Table 2. The atomic chemisorption enthalpy of oxygen (Table 2) is lower for the promoted Fe based catalysts compared to the non-promoted Fe catalyst. It leads to an enhanced CO dissociation and, hence, higher conversion, in line with the experimental observations. This has been denoted in the literature as an increase in the scavenging of oxygen atoms [9]. It is ensured from Fig. 2(c)–(e) that the simulated



Fig. 2. (a) CO Conversion vs light olefin selectivity ($C_2 - C_4 =$) obtained with different virtual catalysts (blue dots). The experimental results obtained with real catalysts Fe/CNT, FePb/CNT and FeBi/CNT are represented with brown, green and red square dots respectively. The light coloured boxes around real catalysts represent the virtual catalysts with comparable conversion and light olefin selectivity. The screening of the virtual catalysts within the light coloured boxes is carried out to obtain the virtual catalyst matching real catalyst. (b) Conversion obtained with experiments (real catalyst) are compared with simulated conversion obtained with the best matching virtual catalyst after screening. Selectivity of CH₄ (Methane), $C_2 - C_4 =$ (light olefin), C_5 + (long-chain hydrocarbons) and CO₂ (Carbon dioxide) with (c) Fe/CNT catalyst (conversion 57%), (d) FeBi/CNT catalyst (conversion 96%) obtained with experiments are matched with that of simulations using the best matching virtual catalyst. The experiments and simulations are reported at operating condition of 623 K, 10 bar, GHSV = 3.4 Lg⁻¹ h⁻¹, W = 0.2 g and H₂/CO molar inlet ratio of 1. The values in the figure are reported in a scale between 0 and 1.

selectivity toward the other hydrocarbons and CO_2 (Fig. 2(c)–(e)) using the catalyst descriptor values in Table 2 is also comparable with experimental results of Gu et al. [9].

From Table 2 we could see that, in addition to the difference in atomic chemisorption enthalpy of $oxygenQ_O$, the non-promoted and two promoted catalysts also exhibit differences in atomic chemisorption enthalpies of hydrogen Q_H and carbon Q_C . It was observed in some preliminary simulations that the atomic chemisorption enthalpy of hydrogen in oxide phase (Fe₃O₄ – H = 220 kJ/mol), affecting the WGS reaction did not lead to major differences in the targeting results. Hence, this value was fixed throughout the procedure. As expected, from the above discussion, we see that the catalyst performance is well captured by the catalyst descriptors without the adjustment of any of the kinetic descriptors discussed in Table 1. To assess the effect of the differences in catalyst properties on their performance, we thus examine the catalyst descriptor space of Q_H , Q_C , and Q_O .

4.2. Analysis of catalyst performance

In this section we analyse the catalyst performance as a function of catalyst descriptors to understand their influence on conversion and light olefins selectivity.

4.2.1. Conversion

To analyse the catalyst descriptor effect on the CO conversion, we investigate $Q_H - Q_C$ descriptor planes at three different Q_O (Fig. 3). The planes are considered at atomic chemisorption enthalpies of oxygen, $Q_O = (601, 589.1, 577.1)$ kJ/mol, corresponding to the three real catalysts (Fe/CNT, FeBi/CNT, and FePb/CNT) reported in Table 2. The

ranges of ${\rm Q}_{\rm H}$ and ${\rm Q}_{\rm C}$ are chosen such that the plane encloses the three real catalysts, Fe/CNT, FeBi/CNT, and FePb/CNT. From Fig. 3(a)-(c), we see a combined influence of the catalyst descriptors on the simulated conversions. In the descriptor planes (Fig. 3(a)-(c)), the intersection of dotted lines (red) indicate the location of the real catalysts, namely Fe/CNT, FeBi/CNT, FePb/CNT. As we traverse along the horizontal dotted line with fixed atomic chemisorption enthalpies of carbon and oxygen, respectively we observe an increase in conversion followed by a decrease. As expected, this observation follows Sabatier's principle also referred to as a volcano-curve [39]. It is also seen from the parametric plots of conversion (Fig. 3) that the effect of the atomic chemisorption enthalpy of hydrogen (Q_H) is more pronounced (especially at $Q_H > 260$ kJ/mol) than that of the atomic chemisorption enthalpy of carbon (Q_C). A too high value of Q_H results in higher hydrogen surface coverages, which causes the coverage of CO to decrease and, hence, results in a decrease in CO conversion, while a too low value of Q_H leads to lower surface coverage of hydrogen thus adversely affecting the initiation and chain growth reactions discussed in Table 1. On the other hand, too high values of atomic chemisorption enthalpy of carbon ($Q_C > 660 \text{ kJ/mol}$, not shown in Fig. 3) lead to lower availability of surface hydrogen (due to higher CO coverage), whereas, too low values lead to lower availability of surface carbon. Both these situations result in a decrease in conversion. However, the conversion is less sensitive to a change in Q_C as compared to Q_H. Along different $Q_H - Q_C$ planes (Fig. 3(a)–(c)) with the decrease in atomic chemisorption enthalpy of oxygen, we obtain a higher conversion for a fixed Q_H and Q_C . Thus, a decrease in Q_O with the addition of Bi and Pb as promoters, means that oxygen is more loosely bound to the surface.



Fig. 3. Conversion as a function of atomic chemisorption enthalpy of hydrogen (Q_H) and carbon (Q_C) for atomic chemisorption enthalpy of oxygen (Q_O) at 601 kJ/mol (a), 589.1 kJ/mol (b) and 577.1 kJ/mol (c). The intersection of dotted red lines corresponds to Fe/CNT (a), FeBi/CNT (b) and FePB/CNT (c) respectively. The simulations are reported at operating condition of 623 K, 10 bar, GHSV = 3.4 Lg⁻¹ h⁻¹, W = 0.2 g and H₂/CO molar inlet ratio of 1. The values in the figure are reported in a scale between 0 and 1.

This reduces the concentration of metal sites being blocked by oxygenates,¹ permitting adequate coverages of surface carbon/hydrogen, in turn increasing the conversion.

4.2.2. Selectivity

In Fig. 4 we look at the light olefin selectivity along the $Q_H - Q_C$ planes, for different values of atomic chemisorption enthalpy of oxygen corresponding to non promoted and promoted Fe catalysts, as discussed earlier in Section 4.2.1. As in the case of conversion, catalyst descriptors have a combined role in the selectivity values (Fig. 4), but the effect of Q_O on the light olefin selectivity is limited, i.e. Fig. 4(a)–(c) are quite comparable. It is observed that higher selectivity for light olefins is observed with Q_H in the range of 230–245 kJ and Q_C in range of 625–630 kJ. However, this not necessarily ensures a higher yield of light olefins ($C_2-C_4 =$) as the CO conversion should also be considered when determining the latter. This trade-off between light olefin selectivity and CO conversion should also be taken into account when engineering promoted catalysts.

4.3. Understanding the differences in performances using surface level phenomena

In this section, we first compare the change in performance between selected virtual catalysts. It is then followed by discussions at an indepth level, explaining the differences in their performance in terms of surface coverages and reaction pathways.

4.3.1. Comparison of performance

To better understand the impact of descriptors at iso-conversion, in Fig. 5 we more deeply analyse the simulation results at three points in the $Q_H - Q_C$ descriptor plane containing the catalyst with higher conversion, i.e. FePb/CNT. The FePb/CNT catalyst is indicated by mid- Q_H . The points low- Q_H , mid- Q_H and high- Q_H are chosen such that the conversion obtained with the virtual catalysts represented by these three points is comparable (Fig. 5). Thus the variation in the selectivity of these three points directly indicates the variation in light olefins yield because of the change in $Q_{\rm H}$ at a constant value of $Q_{\rm C}$ = 642 kJ/mol and Q_0 = 577.1 kJ/mol. The Q_H values corresponding to points low-Q_H, mid-Q_H and high-Q_H are 240 kJ/mol, 248 kJ/mol, and 252 kJ/mol, respectively. The selectivity of light olefins $(C_2 - C_4 =)$ and the most common product of FTS reaction, methane (CH₄) is compared at these three points, to understand the competing effects among these two products. From the selectivity contour and histogram in Fig. 5, for the three points considered, we observe that the light olefin selectivity is highest at $low\mathchar`Q_H$ (left) and lowest at $high\mathchar`Q_H$

 $^{^1\,}$ For $Q_{\rm H}$ = 248.4 kJ/mol and $Q_{\rm C}$ = 641.5 kJ/mol, with decrease in $Q_{\rm O}$ from 601 kJ/mol to 577.1 kJ/mol the free metal sites increases by a factor of 2.6.



Fig. 4. Selectivity of light olefins as a function of atomic chemisorption enthalpy of hydrogen (Q_H) and carbon (Q_C) for atomic chemisorption enthalpy of oxygen (Q_0) at 601 kJ/mol (a), 589.1 kJ/mol (b) and 577.1 kJ/mol (c). The intersection of dotted red lines corresponds to Fe/CNT (a), FeBi/CNT (b) and FePb/CNT (c) respectively. The simulations are reported at operating condition of 623 K, 10 bar, GHSV = 3.4 Lg⁻¹ h⁻¹, W = 0.2 g and H₂/CO molar inlet ratio of 1. The values in the figure are reported in a scale between 0 and 1.



Fig. 5. Conversion and selectivity as a function of atomic chemisorption enthalpy of hydrogen Q_H for points **low-Q_H** ($Q_H = 240 \text{ kJ/mol}$), **mid-Q_H** ($Q_H = 248 \text{ kJ/mol}$) and **high-Q_H** ($Q_H = 252 \text{ kJ/mol}$) at a constant value of $Q_C = 642 \text{ kJ/mol}$ and $Q_O = 577.1 \text{ kJ/mol}$. The contour plane to the left of the histogram corresponds to the $Q_H - Q_C$ plane of selectivity containing FePb/CNT catalyst. The FePb/CNT catalyst is represented by **mid-Q_H**. The simulations are reported at operating condition of 623 K, 10 bar, GHSV = 3.4 Lg⁻¹ h⁻¹, W = 0.2 g and H₂/CO molar inlet ratio of 1. The values in the figure are reported in a scale between 0 and 1.

(right) when compared to the selectivity with FePb/CNT catalyst (mid- $\mathbf{Q}_{\rm H}$). The simulations with these three set of catalyst descriptors in the

 $Q_H - Q_C$ plane containing FePb/CNT catalyst (Fig. 5), shows that the lower light olefin selectivity at **high-Q_H** occurs at the expense of more

Table 3

Relative surface coverage of species MH, MMCH₂ and MCH₃ for the three virtual points **low-Q_H**, **mid-Q_H** and **high-Q_H** calculated as reported by Van Belleghem et al. [39]. The points are located in the Q_H – Q_C plane containing FePb/CNT catalyst. The atomic chemisorption enthalpies of carbon and oxygen are kept at a constant value of Q_C = 642 kJ/mol and Q₀ = 577.1 kJ/mol. The points **low-Q_H** (Q_H = 240 kJ/mol), **mid-Q_H** (Q_H = 252 kJ/mol) have different atomic chemisorption enthalpy of hydrogen. The simulations are reported at operating condition of 623 K, 10 bar, GHSV = 3.4 Lg⁻¹ h⁻¹, W = 0.2 g and H₂/CO molar inlet ratio of 1.

Surface species	Relative surface coverage [-]		
	low-Q _H	mid-Q _H	high-Q _H
	-	-	-
MH	0.18	0.54	1.0
MMCH ₂	1.0	0.40	0.21
MCH ₃	1.0	0.47	0.25

pronounced methanation. To better understand the differences at these three points, we look at the surface coverage of different species.

4.3.2. Influence of catalysis descriptors on surface coverage

An analysis on the relation between surface coverages and catalyst performance at different operating conditions is discussed by Van Belleghem et al. [39]. Here we carry out a similar analysis for different (virtual) catalysts at the same operating conditions. The difference in selectivity can be interpreted in terms of evolutions in the relative surface coverage of the dominant species (Table 3) among different surface species reported in Table 1. The relative surface coverage is obtained by dividing the surface coverage of surface species i at a particular Q_H by the maximum surface coverage of surface species i found among the points $low\mathchar`Q_H, mid\mathchar`Q_H$ and $high\mathchar`Q_H.$ The maximum surface coverage of the surface species MH, MMCH₂ and MCH₃ are of order 10^{-2} , 10^{-9} and 10^{-4} respectively. It can be observed that relative surface coverage of MH, i.e hydrogen on the metal surface follows the trend, $high\mathchar`Q_H\mathchar`Z_H\mathc$ surface coverage of the surface species MH increases with an increase in Q_H. The higher MH relative surface coverage for high-Q_H results in increased hydrogenation for high-Q_H followed by mid-Q_H and low- Q_{H} . The surface coverages of MMCH₂ and MCH₃ show a reverse trend, i.e. $low-Q_H > mid-Q_H > high-Q_H$. Thus, the relative surface coverage of metal alkyls (see Table 1) decreases with an increase in Q_H. This trend can result in higher alkanes or alkenes production depending on MH surface coverage. From Table 4 we see that the relative selectivity of total alkenes to total alkanes is higher for low-Q_H followed by mid- \mathbf{Q}_{H} and $high\text{-}\mathbf{Q}_{H}.$ Thus, alkene production is higher if MH surface coverage is lower and vice-versa. Higher surface coverage of MH leads to lower surface coverage of MCH₂ and lower availability of free sites for beta hydride elimination (Table 2, Eq. (9)) and thus results in increased hydrogenation [39]. It is also observed that the 1-alkane (methane) to 2-alkane (ethane) selectivity ratio follows a reverse trend, i.e. high-Q_H has higher methane to ethane production, followed by $\textbf{mid-Q}_{H}$ and $\textbf{low-Q}_{H}.$ This indicates that for a fixed value of $Q_{c},$ the tendency for increase in chain length decrease with increasing Q_H.

A similar analysis on performance at two different atomic chemisorption enthalpies of carbon Q_C ($Q_C = 630$ kJ/mol and 665 kJ/mol) at constant values of Q_H (240 kJ/mol) and Q_O (570 kJ/mol) is carried out. It is observed that the yield of light olefins increases with decreasing Q_C , whereas it follows a reverse trend for the yield of long-chain hydrocarbons. This is attributed to the increased relative surface coverage of MMCH₂ at higher values of Q_C . For the two Q_C values investigated the relative surface coverage of SMCH₂ is 0.61 and 1 respectively where maximum surface coverage is of order of 10^{-9} .

Thus, the yield of light olefins becomes lower due to increased methanation at high values of Q_H and due to long chain hydrocarbon formation at high values of Q_C . At very low values of Q_C , unavailability of surface carbon also leads to lower conversion and thus lower light olefins yield.

Table 4

Relative selectivity of alkanes to alkenes and 1-alkane (methane) to 2-alkane (ethane) at three virtual points **low-Q**_H, **mid-Q**_H and **high-Q**_H. The points are located in the Q_H – Q_C plane containing FePb/CNT catalyst. The atomic chemisorption enthalpies of carbon and oxygen are kept at a constant value of Q_C = 642 kl/mol and Q_O = 577.1 kJ/mol. The points **low-Q**_H (Q_H = 240 kJ/mol), **mid-Q**_H (Q_H = 248 kJ/mol) and **high-Q**_H (Q_H = 252 kJ/mol) have different atomic chemisorption enthalpy of hydrogen. The simulations are reported at operating condition of 623 K, 10 bar, GHSV=3.4 Lg⁻¹ h⁻¹, W=0.2 g and H₂/CO molar inlet ratio of 1.

	Relative selecti	Relative selectivity [-]		
	low-Q _H	mid-Q _H	high-Q _H	
	-	-	-	
$\frac{\sum \text{ alkenes}}{\sum \text{ alkanes}}$	4.0	0.88	0.31	
$\frac{1 - \text{alkane}}{2 - \text{alkane}}$	2.41	3.08	4.39	

4.3.3. Comparison of reaction pathways

A reaction pathway analysis is carried out at virtual catalyst points **low-Q_H** and **high-Q_H**, to indicate the difference in trend in hydrocarbon selectivity as we traverse from lower to higher hydrogenative catalysts with respect to the FePb/CNT catalyst. The affinity calculations are used in Fig. 6 to differentiate the elementary surface reactions which are at quasi-equilibrium (black arrows) and those that are kinetically relevant (coloured arrows). The reactions :

- · chemisorption of CO, H₂ and alkenes
- CO dissociation
- hydrogenation of surface oxygen and carbide

were found to be in quasi-equilibrium for both the virtual catalysts, $low-Q_H$ and $high-Q_H$.

At **low-Q_H** (Fig. 6), it could be noted that MCH hydrogenation is kinetically relevant when compared at **high-Q_H**, where the reaction is in quasi-equilibrium. This leads to a reduced surface coverage of MH at **low-Q_H** (Table 3) and, hence, lower hydrogenation of metal alkyls. Since the MMCH₂ insertion reaction is more prominent at **low-Q_H** along with lower hydrogenation, an enhanced production of chain growth products, more particularly olefins, is observed. However, at **high-Q_H** (Fig. 6), since the MCH hydrogenation is in quasi-equilibrium, the surface coverage of MH is higher, leading to an increased alkane production, particularly methane. Thus, it is explained how a change in catalyst descriptor values can influence the surface coverages (Table 3) of key intermediates, thus altering the prevailing reaction pathways (Fig. 6) and ultimately impacting the product selectivities (Fig. 5).

5. Identification of optimum catalyst

From our discussion above, we observe that the effects of each catalyst descriptor on conversion and selectivity are inter connected to each other. To identify the trends in conversion and selectivity due to the simultaneous variation of the three catalyst descriptors and, hence, to identify the best catalyst leading to maximum yield of light olefins, iso-performance surfaces are presented in Fig. 7. Each sub-figure in Fig. 7 contains two iso-surfaces, one corresponding to a higher value and another to a lower value of the analysed performance indicator. The values of iso-surfaces are chosen such that a clear distinction in trend can be observed. The three catalysts, Fe/CNT, FeBi/CNT, and FePb/CNT are represented with black dots. Depending on the relative location of catalysts *w.r.t.* the iso-surface the black dots representing the catalysts, appear dark (not enclosed by the surface) or light (enclosed by the iso-surface).

As was already evident from Figs. 4(a)–(c) and 7(b), the light olefins selectivity weakly depends on Q_0 with other descriptors being kept constant. However, the conversion significantly increases with decreasing Q_0 , for the range of catalyst descriptors investigated (see also Figs. 3(a)–(c) and 7(a)). This leads to an increased light olefins



Fig. 6. Reaction pathway analysis at **low-Q**_H ($Q_H = 240 \text{ kJ/mol}$) and **high-Q**_H ($Q_H = 252 \text{ kJ/mol}$) is carried out at temperature of 623 K, pressure of 10 bar, GHSV of 3.4 Lg^{-1} h⁻¹, W of 0.2 g and H₂/CO molar inlet ratio of 1. The coloured arrows with a thickness of less than 1 unit are represented with dotted arrows. The rate corresponding to oxidative addition of MCH₃ (in the case of **high-Q**_H), is used as the base (with lines thickness of 1 unit) for the scaling of coloured arrows. The reaction between hydrogen attached to the metal surface and other surface species are not shown, for better visualization.

yield at lower Q_0 . As discussed in Section 4.3.2, the lower light olefins yield at very low values of Q_H and Q_C is attributed to lower surface coverage of hydrogen and carbon, respectively. Increased production of methane at high values of Q_H , and that of long-chain hydrocarbons at high values of Q_C also adversely affect the light olefins yield.

The combined effect of the descriptors mentioned above is evident from the iso-surface of higher yield (yield = 0.5) being enclosed within the iso-surface of lower yield (yield = 0.28). We observe that the FePb/CNT and FeBi/CNT catalysts are close to the iso-surface corresponding to yield = 0.28, while the non-promoted Fe catalyst is situated high above from this iso-surface. From Fig. 7(c) we could infer that the yield of light olefins ($C_2 - C_4$ =) for the given operation conditions, may be increased to a value exceeding 0.5, by engineering the catalyst in such a way that $Q_H \approx 234$ kJ/mol, $Q_C \approx 622$ kJ/mol and $Q_O \approx$ 575 kJ/mol. A catalyst with the above descriptors would result in an increased yield of light olefins close to 55% when compared to Fe/CNT (20%), FeBi/CNT (27%), and FePb/CNT (30%) catalysts.

6. Conclusions

The single-event methodology developed for Fe catalyzed Fischer– Tropsch synthesis is used to differentiate the performance of different catalysts from a micro-kinetic perspective, using catalyst descriptors. The atomic chemisorption enthalpy of hydrogen, Q_H effects the formation of methane vs longer hydrocarbons, and olefins vs paraffins. A

very high value of Q_H leads to higher hydrogenation and thus, higher methanation and lower olefin production. The atomic chemisorption enthalpy of carbon, Q_C relates to carbon species on the surface and, hence, to chain growth by increased methylene insertion at higher values. Whereas, atomic chemisorption enthalpy of oxygen, Q₀ in the investigated range plays an important role in the availability of free metal sites. A lower Q_O, reduces the metal sites being blocked by oxygenates and thus permitting adequate coverage of metal-carbon and metal-hydrogen, resulting in increased CO conversion. With the decrease in Q_H (w.r.t. the real catalysts), the availability of free sites increases, that can provoke enhanced beta hydride elimination. This leads to an increased light olefins yield. At lower value of Q_C (w.r.t. the real catalysts), the yield of long-chain hydrocarbons is reduced. In the investigated range of catalyst descriptors, an enhanced light olefin production is observed at lower values of $Q_{\rm O},\,Q_{\rm H}$ and $Q_{\rm C}$ (w.r.t the real catalysts). For the given operating conditions, we identify that a "promising catalyst" with catalyst descriptors, $Q_{\rm H}\approx 234$ kJ/mol, $Q_{C}\approx$ 622 kJ/mol and $Q_0 \approx 575$ kJ/mol which would result in an increased yield of light olefins (55%) compared to the catalysts Fe/CNT (20%), FePb/CNT (27%), and FeBi/CNT (30%).

The further identification of promoters that modify the catalyst descriptor values close to the values mentioned above can help us to attain enhanced yield of light olefins. This work thus represents a first step to unravel the causes behind the relative performances of catalysts, and thus act as a guideline to engineer promoted catalysts with desired performance traits.



Fig. 7. Iso-surfaces of conversion (a), selectivity $C_2 - C_4 = (b)$, and yield $C_2 - C_4 = (c)$ as a function of atomic chemisorption enthalpy of Q_H , Q_C and Q_O . Each figure has 2 iso-surfaces corresponding to high and low values respectively. The catalysts Fe/CNT, FBi/CNT and FePb/CNT are represented by black dots. The simulations are reported at operating condition of 623 K, 10 bar, GHSV = 3.4 Lg⁻¹ h⁻¹, W = 0.2 g and H₂/CO molar inlet ratio of 1. The iso-surface values are reported in a scale between 0 and 1.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.cej.2021.129633.

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