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Methane, formaldehyde and methanol formation pathways from carbon monoxide and hydrogen on the (001) surface of the iron carbide $\chi$-Fe$_5$C$_2$

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**Article info**

**Abstract**

Formation of CH$_x$(O) monomers and C$_x$ products (CH$_x$, CH$_x$O, and CH$_x$OH) on C-terminated $\chi$-Fe$_5$C$_2$(001) (Hägg carbide) surfaces of different carbon contents was investigated using periodic DFT simulations. Methane (CH$_4$) as well as monomer (CH$_x$) formation follows a Mars–van Krevelen-like cycle starting with the hydrogenation of surface carbodic carbon, which is regenerated by subsequent CO dissociation, while oxygen is removed as H$_2$O. In cases where surface carbon is readily available, the apparent barrier for CH$_4$ formation was found to be $\sim$95 kJ/mol. However, different rate-determining steps show that different propagation mechanisms may be possible for actual chain growth, depending on the carbon content of the surface. Hydrogen addition to CO forms formyl (HCO), which is a precursor for both H-assisted CO activation and oxygenate formation. Further hydrogenation of HCO yields adsorbed formaldehyde and methoxy, rather than hydroxymethyl (HCOH) that would give C–O bond splitting. Full hydrogenation to gas-phase methanol faces a high barrier, suggesting that CH$_x$O formation in a full Fischer–Tropsch mechanism or that the C–O bond does not break until the CHO fragment has been incorporated in a C$_2$ species, a route for which precedents are available in the literature.

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**1. Introduction**

Fischer–Tropsch synthesis (FTS) enables the production of clean transportation fuels and chemicals from virtually any source of carbon, such as natural gas, shale gas, coal, or biomass. In the process, synthesis gas (CO + H$_2$) obtained from these resources, is converted into hydrocarbons and oxygenated products using transition metal catalysts such as iron, cobalt, and ruthenium [1].

When iron is used in the industrial application, catalyst activation is achieved by reducing the iron oxide phase either in hydrogen or in synthesis gas [2–4]. The latter converts the catalyst into iron carbides. Among the mixture of carbide and oxide phases [5–8] present under process conditions, the Hägg carbide ($\chi$-Fe$_5$C$_2$) is generally regarded as the active phase for FTS [2,5,6,9–18], although other phases such as c-Fe$_2$C or $\theta$-Fe$_3$C may exhibit activity as well [9]. Mechanistic studies on CO hydrogenation and FTS on metallic iron surfaces are available in the literature [4,14,19–29], but studies on the catalytic properties of iron carbides in FTS are scarce, we refer to de Smit and Weckhuysen [13] for a recent review and to other literature [3,5,8–11,13,15,24,30–36].

In order for a surface to exhibit Fischer–Tropsch activity, it needs to enable C–O bond breaking, either before or following reaction with hydrogen. For CO dissociation, the activation barrier depends strongly on the catalyst surface [19–22,37,38] and particularly on its structure [6,8,21–24,39]. Hydrogen addition to surface carbon forms CH$_x$, which is the monomer for chain propagation in the carbene mechanism proposed by Fischer and Tropsch [25,26,40].

On the other hand, in cases where the CO bond cannot be broken directly, (partial) hydrogenation of CO can occur, as in the case of hydroxyl-carbene [41] and CO-insertion [42] mechanisms. Such reaction steps are likely to be involved in the formation of oxygenated products in iron-catalyzed FTS through the growth of CH$_x$O intermediates, similar as in the carbene mechanism. Indeed, metals such as copper or palladium with limited reactivity toward CO are known to produce methanol selectively [43].

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The present paper is part of a series in which we investigate the FTS mechanism on iron carbide surfaces by computational modeling. Starting point is the question how an iron carbide surface, which is “passivated” compared to a clean metal surface due to structural carbon (C\textsuperscript{\textdegree}), can exhibit sufficient reactivity to activate the CO molecule. To address this problem rigorously, we use the carbon-rich \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\) surfaces with different C\textsuperscript{\textdegree} contents. The results showed that the perfect (non-vacant) \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\) surface is not expected to be a successful FT catalyst as it cannot activate CO. However, C\textsuperscript{\textdegree} hydrogenation to form CH is a feasible reaction. In this way, the carbide surface develops vacancies and increases its reactivity. On such a C\textsuperscript{\textdegree}-vacant surface, both CO dissociation to C\textsuperscript{\textdegree}+O and hydrogenation to HCO are possible. Upon consumption of all C\textsuperscript{\textdegree}, the surface is Fe terminated and shows metallic-like properties, where the only feasible reaction is the dissociation of CO to regenerate C\textsuperscript{\textdegree} and thus the carbide surface. Thus, through the consumption and regeneration of C\textsuperscript{\textdegree}, the active surface shows dynamic behavior, similarly as in the case of the Mars–van Krevelen (MvK) mechanism [44].

Furthermore, in cases where HCO forms, no energetically feasible route for C–O bond breaking could be found, suggesting that this intermediate may play a key role in production of oxygenated products.

Purpose of this paper was to explore hydrogenation routes of surface carbide carbon (C\textsuperscript{\textdegree}), the products of CO dissociation, and the HCO intermediate, on the \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\) iron carbide surfaces of different carbon contents. These reactions show the routes and feasible pathways for the CH\textsubscript{x} and CH\textsubscript{3}O monomers that produce the hydrocarbon and oxygenate products as proposed in the carbene mechanism. We have chosen the C\textsubscript{1} products CH\textsubscript{4}, CH\textsubscript{3}O, and CH\textsubscript{3}OH as the end point. Although CH\textsubscript{4} is an undesired product in FTS, understanding the selectivity trends for CH\textsubscript{4} formation and chain growth is essential. We will consider chain growth reactions to longer hydrocarbons in the next and final paper of the series.

2. Computational details

Periodic DFT computations were performed using the VASP package [45,46], with plane-wave basis sets and RPBE functionals [47–49]. The cutoff energy used was 400 eV. Necessary dipole corrections due to the asymmetric usage of slabs were included in the computations. All the results presented are the output of spin-polarized computations that were obtained by relaxing the structures until the net force acting on the ions was <0.015 eV/Å. The reaction paths were generated using the climbing image nudged elastic band (CI-NEB) method [50].

A C-terminated \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\) surface was used as the starting point for representing the (dynamical) active catalyst surface. The p(1 x 1) surface model (slab) contains 20 Fe and 8 C atoms and is 10.3 Å in height. The vacuum height separating the periodic slabs is 12 Å. In the computations, 10 Fe and 4 C bottom atoms were kept fixed, where all the remaining atoms were relaxed. The k-point sampling was generated by the Monkhorst–Pack procedure with a (4 x 4 x 1) mesh. The total energies of gas-phase molecules were calculated using a single k-point (gamma point), where the periodic molecules were separated with a minimum of 10 Å vacuum distances.

The vibrational frequencies of ground and transition states were computed by calculating the Hessian matrix based on a finite difference approach where the individual atoms were displaced with a step size of 0.02 Å along each Cartesian coordinate. During the frequency computations, symmetry was excluded explicitly. The frequencies of the surface ions were excluded based on the frozen phonon approximation. The transition states were verified by a single imaginary frequency along the reaction coordinate.

The relative energies were calculated with respect to CO\textsubscript{2} and H\textsubscript{2}(g) (\(E_{\text{DFT}} = E_{\text{system}} - (E_{\text{CO}_2(g)} + nE_{\text{H}_2(g)} + E_{\chi\text{-}Fe\text{\textsubscript{5}}\text{C}_2\text{\textsubscript{2}}})\)). Zero-point energy (ZPE) corrections were calculated using the harmonic approximation and the positive modes of the vibrational data (\(E_{\text{ZPE}} = \sum h\nu/2\)), and included in all the energies reported herein (\(E = E_{\text{DFT}} + E_{\text{ZPE}}\)).

3. Results and discussion

Fig. 1 shows the \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\) surface at different C\textsuperscript{\textdegree} contents, as they were used in our previous study on CO and H\textsubscript{2} activation [39]. We repeat the main findings here. Depending on the surface carbon (C\textsuperscript{\textdegree}) concentration, different reaction paths are available for CO and H\textsubscript{2} [39]. On the perfect surface (\(\theta_{\text{Fe}} = 0.5\) ML), C\textsuperscript{\textdegree} hydrogenation is the most feasible path. On the C\textsuperscript{\textdegree}-free surface (\(\theta_{\text{Fe}} = 0.00\) ML), owing to the complete Fe termination, the surface favors direct CO splitting, which regenerates the C\textsuperscript{\textdegree} and the carbide surface. In the intermediate phases with C\textsuperscript{\textdegree}-vacancies (\(\theta_{\text{Fe}} = 0.25\) ML) addition to both C\textsuperscript{\textdegree} and CO is possible, along with direct CO dissociation. Following these two directions for CO activation, we have further explored the formation of CH\textsubscript{4} and CH\textsubscript{3}O intermediates/monomers up to C\textsubscript{1} compounds (CH\textsubscript{4} and CH\textsubscript{3}OH) starting from C\textsuperscript{\textdegree} and CO to gain insight in the selectivity between desired and undesired products. The details of CH\textsubscript{4} formation, where C\textsuperscript{\textdegree} is readily available, and similarly CH\textsubscript{3}OH formation, where HCO formation is possible, are presented below.

3.1. CH\textsubscript{4} formation

When surface carbide carbon (C\textsuperscript{\textdegree}) is available, its hydrogenation is a feasible route, especially on the perfect (non-vacant) \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\) surface [11,39]. Here, we simulate the hydrogen addition to C\textsuperscript{\textdegree}, which is a facile reaction on the non-vacant (\(\theta_{\text{Fe}} = 0.5\) ML) and C\textsuperscript{\textdegree}-vacant (\(\theta_{\text{Fe}} = 0.25\) ML) surfaces of \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\). Fig. 2 shows the relative energies of the intermediates and transition states along the methanation path on non-vacant (perfect) and C\textsuperscript{\textdegree}-vacant \(\chi\text{-}Fe\text{\textsubscript{5}}\text{C}\text{\textsubscript{2}}(001)\) in a MvK-like cycle. The respective geometries can be seen in Figs. 3 and 4 (a larger set of figures is available in Supporting Information). The three major stages in Fig. 2 are as follows: (i) the formation of CH\textsubscript{4} through the hydrogenation of the surface carbon that leaves a C\textsuperscript{\textdegree}-vacancy, (ii) adsorption of CO on top of a Fe atom and its dissociation to regenerate the surface carbon in the C\textsuperscript{\textdegree}-vacancy, and (iii) formation of H\textsubscript{2}O through the hydrogenation of oxygen. As CH\textsubscript{4} and H\textsubscript{2}O adsorption are weak, these products desorb upon formation.

CH\textsubscript{4} formation on the perfect surface is exothermic by 43 kJ/mol with respect to the gas-phase reactants. As Fig. 2 and Table 1 show, the highest barrier (\(E_a = 93\) kJ/mol) for methanation is faced for the CH\textsubscript{2} hydrogenation step, similar to the situation on Fe(100) [28,29,51]. This suggests that this step may be important in determining the selectivity between the desired chain growth (i.e., CH\textsubscript{4} addition) and undesired methanation, as we address in a forthcoming paper on C\textsubscript{2} hydrocarbons. Indeed, a CH\textsubscript{2} coupling route appears feasible compared to CH\textsubscript{2} hydrogenation, which supports this point.

On the C\textsuperscript{\textdegree}-vacant surface, as Fig. 2 and Table 1 show, CH\textsubscript{4} formation is exothermic by 67 kJ/mol. Furthermore, compared to the perfect surface, CH formation does not compete with H\textsubscript{2} desorption. On this surface, the most difficult step is the hydrogenation of CH to CH\textsubscript{2}, with an activation barrier of 55 kJ/mol.
Along the methanation path, CH₄ hydrogenation to form CH₃ is usually reported to have the highest barrier of ~90 to ~100 kJ/mol [6,28,29,52–56]. Although the highest barriers were not faced at this stage, the apparent barriers for the perfect and C⁺-vacant surfaces (93 and 95 kJ/mol, respectively) agree with this. On the other hand, here again, the dependency of the surface reactivity on the C⁺ content is obvious. Also, changes in the reaction steps with the highest barriers point to the possibility of having parallel mechanistic steps in FTS, as on the Fe(100) surface [28].

During the methane formation stage of the catalytic cycle, the carbide surfaces become more reactive due to the removal of surface carbon, C⁺. Removal of the C⁺ through hydrogenation renders the perfect surface (θc⁺ = 0.5 ML) into a C⁺-vacant surface (θc⁺ = 0.25 ML), and similarly, the vacant surface into a C⁺-free surface. The C-atom of CO replaces C⁺ through dissociation and recovers the carbicid nature. As the middle part of Fig. 2 shows, CO adsorption on the C⁺-vacant and C⁺-free surfaces releases similar energies (~130 kJ/mol) and its dissociation faces similar barriers (84 kJ/mol). However, the dissociation is highly exothermic on the C⁺-free surface, which is Fe terminated and has metallic characteristics. More detail on the CO adsorption and activation can be found in [39]. Note that on both carbide surfaces, the O-atom after CO dissociation goes to a bridged position and does not compete with carbon for the higher coordination sites, see Figs. 3 and 4.

The third part of Fig. 2 concerns the removal of the oxygen from the surface in the form of H₂O. This part of the catalytic cycle faces the highest barriers, namely 100 and 146 kJ/mol on perfect and C⁺-vacant surfaces, respectively. There are notable differences in barriers for the first and second hydrogenation steps between the two surfaces. On the perfect surface, the first H addition faces a higher barrier than the second, while the order is reversed on the C⁺-vacant surface. These are higher compared to previously reported values for the Fe(110) surface [57], which are ~60 kJ/mol and 70 kJ/mol for the first and second H additions. Govender et al. demonstrated that water formation on Fe(100) can also occur by reaction of two OH groups [27]. This step appears less likely on the carbide surfaces. The results indicate that oxygen removal forms a part of the mechanism, that is far from trivial, and could very well limit the rate of the Fischer–Tropsch reaction. Of course, scenarios are conceivable in which the O-atoms formed from CO dissociation diffuse away to sites where the reaction to OH and H₂O is more facile than on the ones considered in this paper. Studies to investigate diffusion and reaction of O-atoms on carbide surfaces are definitely in order.

A second alternative mechanism for the removal of O-atoms is their combination with adsorbed CO to form CO₂, and the third one is the formation of the oxygen molecule (O₂ads). These paths were not tested for all C⁺ coverages considered in
this work. However, for the calculated cases, Table 1 shows that water formation through subsequent hydrogenation is the most feasible path. We conclude that atomic oxygen is less reactive on the carbide surfaces of $v$-Fe$_5$C$_2$(001)/C$_{0.05}$ than on metallic iron.

The three stages in methanation of CO on $v$-Fe$_5$C$_2$(001)/C$_{0.05}$, as depicted in Fig. 2, namely hydrogenation of surface carbon to methane, regeneration of the surface by direct dissociation of CO, and oxygen removal by subsequent hydrogenation to water, together form a Mars–van Krevelen-like catalytic cycle, in which the surfaces switch composition to first loose and next regain structural carbon (C$^*$). The catalytic cycle from CO + 3H$_2$ to CH$_4$ + H$_2$O is exothermic by −223 kJ/mol, in good agreement with the experimental value of 206 kJ/mol [58].

### 3.2. CH$_3$OH formation

Our previous results [39] showed that both direct and H-assisted CO activation routes are possible on the C$^*$-vacant and C$^*$-free surface, although these are not feasible on the perfect surface. Among the several H-assisted routes initiated by different CO adsorption modes, we found that H addition to adsorbed CO to form an HCO intermediate (Fig. 5a) is the most feasible process, in agreement with [56]. Following its formation, two routes are possible for the further hydrogenation of HCO, depending on whether the second H-atom binds to carbon or oxygen in HCO. In Fig. 5b, we show the energetics when the H-atom binds to the O side of HCO and forms HCOH. This is associated with appreciable activation energies on the order of 104 kJ/mol on the C$^*$-free surface of...
Table 1: Activation ($E_a$, kJ/mol) and reaction energies ($\Delta H$, kJ/mol) along methanation routes on perfect (0.50 ML C$^\ast$) and C$^\ast$-vacant (0.25 ML C$^\ast$) $\chi$-Fe$_3$C$_2$(001)$_{-\text{ao}}$.

<table>
<thead>
<tr>
<th>Route</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}^\ast + 2\text{H} \rightarrow \text{CH} + \text{H}$</td>
<td>58</td>
<td>26</td>
</tr>
<tr>
<td>CH + H + CH$_2$</td>
<td>-</td>
<td>28</td>
</tr>
<tr>
<td>CH$_2 + 2\text{H} \rightarrow \text{CH}_2 + \text{H}$</td>
<td>93</td>
<td>6</td>
</tr>
<tr>
<td>CH$_3 + \text{H} \rightarrow \text{CH}_4$</td>
<td>59</td>
<td>-24</td>
</tr>
<tr>
<td>CO$_{(\text{HCO})}$ + C$^\ast$ + O</td>
<td>83</td>
<td>16</td>
</tr>
<tr>
<td>O + $\text{H} \rightarrow \text{O} + \text{H}$</td>
<td>100</td>
<td>-112</td>
</tr>
<tr>
<td>O + CO + CO$_2$</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>O + O + O$_{(\text{ad})}$</td>
<td>-</td>
<td>335</td>
</tr>
<tr>
<td>OH + OH + H$<em>2$O$</em>{(\text{ad})}$</td>
<td>121</td>
<td>50</td>
</tr>
<tr>
<td>OH + H + H$<em>2$O$</em>{(\text{ad})}$</td>
<td>77</td>
<td>20</td>
</tr>
</tbody>
</table>

n.a.: not available (i.e., not computed).

Fe$_3$C$_2$ and 131 kJ/mol on its surface with C$^\ast$ vacancies. In the following reaction step, HCO$_2$ splits into CH + OH, thus breaking the CO bond, which is easy on the C$^\ast$-free surface, but activated on the surface with C$^\ast$ vacancies ($E_a = 72$ kJ/mol). Hence, once HCO$_2$ is present, immediate dissociation of its CO bond is anticipated on C$^\ast$-free patches of the carbide surface. However, CH$_2$O formation from HCO$_2$ is substantially activated. The relevant energies for these reactions are summarized in Fig. 5a, b and Table 2, and the geometries are given in Figs. 6 and 7.

Starting from the easily formed HCO$_2$ in this H-assisted CO activation mechanism, a second route is possible that forms adsorbed formaldehyde (CH$_2$O), see Fig. 5c. Its desorption would cost 139 kJ/mol (Table 2). As Fig. 5c and Table 2 show, formation of CH$_2$O faces lower barriers than the route to CO bond breaking via HCO$_2$ formation. Although it is easily formed, formaldehyde is not observed in the products. This is probably due to the easier route to dehydrogenation or consumption in a reaction such as chain growth to oxygenates.

Upon obtaining formaldehyde, we have carried out our computations up to full CO hydrogenation into CH$_2$OH to complete the carbon cycle, although it is a very minor product in the process [59]. In fact, the most stable product along this route in Fig. 5c is the methoxy intermediate, CH$_2$O, and its formation by hydrogenation of adsorbed formaldehyde is a feasible step on both C$^\ast$-vacant and C$^\ast$-free surfaces of Fe$_3$C$_2$. However, its eventual hydrogenation to form gas-phase methanol is strongly endothermic and on the order of 150 kJ/mol. All relevant geometries corresponding to Fig. 5c are shown in Figs. 8 and 9.

As Fig. 5c illustrates, the CH$_2$O intermediate is highly stable on the surface. Its hydrogenation and desorption in the form of methanol (CH$_3$OH) is endothermic by 150 kJ/mol. However, formation of methanol is exothermic by $-104$ kJ/mol with respect to gas-phase CO and H$_2$. Facing the highest barrier in the last step agrees with [56]. Yet it is important to note that the route toward either formaldehyde, methoxy, or methanol depends on the formation of the HCO$_2$ intermediate, which in itself is in competition with the hydrogenation of surface carbon and direct CO dissociation [39]. On the other hand, the high surface stability of the methoxy suggests that the surface should be covered with this intermediate, a case with is not observed physically. We speculate that methoxy is either consumed itself or dehydrogenates to a CH$_3$O species that is subsequently consumed. The latter possibility also precludes formation of methoxy species.

A similar mechanism for the formation of methanol as discussed above was reported for stepped Cu surfaces by Behrens et al. [60]. However, on copper, which is a successful methanol synthesis catalyst, the hydrogenation of the methoxy has a lower barrier (~120 kJ/mol) [60] than what we find on the defect iron carbide surface. Furthermore, easy formation and stability of formaldehyde from CO and H$_2$ were also reported for a metallic iron (1 1 0) surface by Ojeda et al. [57]. This is different than what was concluded on Pd and Pt surfaces [61,62]. As Fig. 5 shows, for...
both the C\(^{-}\)-vacant and C\(^{-}\)-free surfaces, the highest activation barriers are faced for the hydrogenation of the HCO intermediate, either in the direction of CO bond breaking or toward formaldehyde/methanol formation. These steps require considerably higher activation energies than HCO decomposition back to CO + H. However, it is clear that, among the two reactions, both surfaces would favor formaldehyde formation over HCOH, which agrees with Cheng et al.\[56\].

The energy diagram given in Fig. 5 also agrees qualitatively with experimental observations where formaldehyde or methanol decomposition has been studied on cobalt surfaces \[63,64\]. These surface science studies report that methanol adsorbs as methoxy, CH\(_2\)O, which is stable up to 300 K. Further heating decomposes the methoxy into CO and H\(_2\), which is the rate-limiting step. Also, the intermediate species, HCO and CH\(_2\)O, are unstable and rapidly decompose into CO and H\(_2\) \[65\]. As shown in Fig. 5, the higher forward barriers for H-assisted CO activation and methanol formation are in agreement with these experimental observations, be it that these were made on Co(0001) surfaces \[63–65\].

As Fig. 5 shows, HCO hydrogenation to form an oxygenate (i.e., CH\(_2\)O) is more feasible than breaking of the C–O bond. Even on the more reactive C\(^{-}\)-free surface of Fe\(_5\)C\(_2\)(001), the overall barrier to H-assisted dissociation amounts to 160 kJ/mol \[39\], compared to values on the order of 80–90 kJ/mol for direct dissociation (Fig. 2). Hence, we conclude that the hydrogen-assisted routes of Fig. 5 leave the CO bond intact, at least for the C\(_1\) species as studied here. However, chain growth mechanisms have been proposed where the CO bond is kept intact until the formation of C\(_2\) species \[56,66\]. Also, Weststrate et al. \[64\] demonstrated experimentally that the C–O bond in ethanol-derived intermediates on Co(0001)
breaks readily, while in species derived from methanol it does not [66]. We investigate this as well as mechanisms involving combination of CH$_x$ and CH$_x$O type species in our next paper.

We conclude that H addition to CO is possible and easily achieved on both non-perfect Fe$_5$C$_2$ surfaces. However, dissociation of the CO bond along this route is unlikely. Instead, the HCO intermediate could be the initiator for the formation of higher oxygenates through CH$_x$O type intermediates. On the other hand, it is also possible that the C–O bond in this intermediate breaks in a later stage when the C–O containing fragment is incorporated in C$_2$ species, as observed in computational [56,66] and experimental studies [64]. Studies to explore this on the present iron carbide surfaces are underway.

4. Mechanistic implications

Limiting ourselves to formation of monomers and products with a single carbon atom from CO and H$_2$ on perfect and defect surfaces of $\chi$-Fe$_5$C$_2$(001)$_{0.05}$, we have reported the energetics for the reactions of CH$_x$ to methane (Fig. 2), and CH$_x$O to formaldehyde and methanol (Fig. 5). We summarize the results as follows:

- The perfect $\chi$-Fe$_5$C$_2$(001)$_{0.05}$ surface (which contains iron and carbon in the ratio 2:1, or 50% C$^*$) enables CO to adsorb, but direct or H-assisted CO activation does not take place. Activation of H$_2$ occurs readily. A reaction cycle can initiate, however, by hydrogenation of a surface carbide carbon atom, in these papers denoted by C$^*$. This leads to CH$_x$ on a surface which now formally contains a C$^*$-vacancy. Further hydrogenation of CH species forms higher CH$_2$ and CH$_3$ intermediates, with the limit being full methanation. This hydrogenation path to methane is also possible on the C$^*$-vacant surface.
- The $\chi$-Fe$_5$C$_2$(001)$_{0.05}$ surface with C$^*$ vacancies (in the DFT simulations this surface has 25% C$^*$), is the most versatile surface in this study, as it allows CO to dissociate directly, as well as to form HCO. In the C$^*$ hydrogenation sequence, CH$_2$ formation has the highest apparent barrier, effectively around 95 kJ/mol, while it is expected to compete with H-assisted route to adsorbed formaldehyde and methoxy. Methanol formation faces a high barrier and seems unlikely. Overall, water formation has the highest barriers, and hence oxygen removal should be considered as a significant process in the overall mechanism.
- The carbon-free $\chi$-Fe$_5$C$_2$(001)$_{0.05}$ surface sustains an energetically facile route to methoxy species. Its overall barrier amounts to about 60 kJ/mol, whereas the lowest barrier for direct dissociation was found to be 73 kJ/mol [39]; hence, these two routes (i.e., direct vs. H-assisted) are expected to compete. Note that CO dissociation changes the metallic C$^*$-free surface to the surface with partial C$^*$ occupation of the previous bullet. Again, the methoxy on the metallic-like surface is expected to be a spectator, as it is highly stable.

A limitation of the present results is associated with CO coverage. Under more realistic conditions of high CO partial pressure, the surface coverage of CO will be high, and many reaction steps will in essence occur in the presence of co-adsorbed CO with consequences for adsorption energies and activation energies.
Incorporation of such effects in DFT studies is in principle possible, but requires the use of computationally demanding procedures with large unit cells, as illustrated in recent studies [67,68].

The formation of CH\textsubscript{x} species is important as they are considered to be the building blocks of the growing hydrocarbon chains in Fischer–Tropsch synthesis. In the case of complete C\textsubscript{2} hydrogenation to CH\textsubscript{4}, the reactions follow a Mars–van Krevelen-like mechanism, as we suggested before [11]. Fig. 10 summarizes the cycle, in which surface carbide C\textsuperscript{*} eventually forms CH\textsubscript{2} and the carbide surface is recovered by CO dissociation. Having different rate-determining steps on perfect (CH\textsubscript{2} → CH\textsubscript{3}) and C\textsuperscript{*}-vacant (CH → CH\textsubscript{2}) surfaces with similar apparent activation barriers brings up the possibility that the step responsible for chain growth may vary among the surfaces, or in practical terms, with C\textsuperscript{*} content of the surface.

We could not identify a CO dissociation route on the perfect surface. However, direct CO dissociation can take place with moderate activation barriers on the C\textsuperscript{*}-vacancies of the carbide surfaces. Along with the direct dissociation path, H addition to CO is also possible on these surfaces, which preferably forms the HCO than the COH intermediate [39]. Investigation of the further hydrogenation of HCO revealed that the preferred route is the formation of CH\textsubscript{2}O, rather than HCOH. This is in conflict with a mechanism proposed by Wender et al. in 1958 [69], where HCOH forms prior to C–O bond breaking, and leads to CH\textsubscript{2} groups on the surface.

The Pichler–Schulz mechanism of 1970 [42] proposes the breaking of the C–O bond at the stage of the formaldehyde intermediate to yield CH\textsubscript{2} + O. Several other authors [70–73] supported the idea of C–O bond breaking in HCO or CH\textsubscript{2}O intermediates, without the formation of HCOH [74]. The high barriers found in this work suggest that the C–O bond remains intact in the CH\textsubscript{x}O intermediates. The latter could in principle hydrogenate completely to methanol. However, the high stabilities of CH\textsubscript{2}O and CH\textsubscript{3}O species prevent this and explain the low amounts of C\textsubscript{1} oxygenates observed in the product distribution [75].

The feasibility of the route to methanol in Fig. 5 agrees with the work of Emmett and coworkers [76], who showed that methanol decomposes to (CO + 2H\textsubscript{2}) under reaction conditions. In fact, the surface chemistry proposed here is similar as on other metal surfaces. CH\textsubscript{2}O was previously identified as the intermediate that forms methanol [77] on copper catalyst. A similar reaction
mechanism that forms methanol was previously proposed for Cu catalyst [60]. The major difference with the situation on iron carbide is the high stability of the methoxy on the latter, which prevents substantial methanol formation on iron carbide.

Our investigation on the formation of C2 hydrocarbon and oxygenates is in progress and will be the subject of our next paper. However, following the idea of CH₃ addition as proposed in the carbide mechanism [25,26,40], a similar mechanism may take place starting from CH₂O intermediate by the addition of CH₂ monomers (Fig. 10), leading to oxygenated products, although breaking of the CO bond at this stage needs consideration also.

5. Conclusions

Periodic DFT simulations starting from the carbon-terminated \( \chi\text{-Fe}_2\text{C}_2(001) \) (Hägg carbide) surface with different surface carbon \( (C) \) contents showed that monomer \( (CH_2) \), as well as methane \( (CH_4) \), forms through the hydrogenation of the surface carbon, which is subsequently regenerated by CO dissociation, making the Mars–van Krevelen-like cycle. The oxygen resulting from the direct CO dissociation is then removed from the surface in the form of H₂O. The high barriers faced for the different CH₃ formations on perfect and C-vacant surfaces point to the possibility of different CH₃ coupling pathways for chain growth. In particular, the relatively high barrier for hydrogenation of CH₂ may favor chain growth and limit methane formation. A hydrogen-assisted path for CO hydrogenation via HCO is feasible on carbide surfaces with carbon vacancies and leads to adsorbed formaldehyde and methoxy, while the end product CH₃OH is unlikely to form due to the high stability of the methoxy species. High barriers faced for C–O bond breaking in the oxygenated intermediates suggest that CH₂O species may couple with CH₃ groups to form higher oxygen-containing products, similar as in the carbene mechanism. The carbide carbon \( (C) \) that is part of the carbide lattice participates in CH₄ formation and can be regenerated through CO dissociation. This kind of a C cycle shows that the active catalyst surface is dynamic and switches between carbide structures of moderate reactivity, where hydrogenation and molecular adsorption of CO prevail, and defect, metallic structures of higher reactivity, where CO is activated and chain propagation reactions occur.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.01.018.

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