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Methane, formaldehyde and methanol formation pathways from carbon monoxide and hydrogen on the (001) surface of the iron carbide χ -Fe₅C₂

M. Olus Ozbek^{a,b,1}, J.W. (Hans) Niemantsverdriet^{a,b,*}

^a Laboratory for Physical Chemistry of Surfaces, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

^b Syngaschem BV, Nuenen, The Netherlands

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ABSTRACT

Formation of CH_x(O) monomers and C₁ products (CH₄, CH₂O, and CH₃OH) on C-terminated χ -Fe₅C₂(001) (Hägg carbide) surfaces of different carbon contents was investigated using periodic DFT simulations. Methane (CH₄) as well as monomer (CH_x) formation follows a Mars–van Krevelen-like cycle starting with the hydrogenation of surface carbidic carbon, which is regenerated by subsequent CO dissociation, while oxygen is removed as H₂O. In cases where surface carbon is readily available, the apparent barrier for CH₄ formation was found to be ~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_xO species may be involved in higher oxygenate 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 C₂ 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 + H₂) 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 (χ -Fe₅C₂) is generally regarded as the active phase for FTS [2,5,6,9–18], although other phases such as ϵ -Fe_{2.2}C or θ -Fe₃C

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 CH₂, 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_xO 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].

* Corresponding author at: Laboratory for Physical Chemistry of Surfaces, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands. Fax: +31 40 245 5054.

E-mail addresses: m.o.ozbek@yeditepe.edu.tr (M.O. Ozbek), J.W.Niemantsverdriet@tue.nl (J.W. (Hans) Niemantsverdriet).

¹ Present address: Department of Chemical Engineering, Yeditepe University, Istanbul, Turkey.

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^*), can exhibit sufficient reactivity to activate the CO molecule. To address this problem rigorously, we use the carbon-rich χ -Fe₅C₂(001)_{-0.05} surface [7], which has one carbidic carbon, denoted as C^* , per two iron atoms ($\theta_{C^*} = 0.5$ ML) and investigate how removal of C^* from this surface affects its reactivity in CO hydrogenation reactions.

The previous study [39] concerned the elementary reactions of CO and H₂ on the χ -Fe₅C₂(001)_{-0.05} surfaces with different C^* contents. The results showed that the perfect (non-vacant) χ -Fe₅C₂(001)_{-0.05} surface is not expected to be a successful FT catalyst as it cannot activate CO. However, C^* hydrogenation to form CH is a feasible reaction. In this way, the carbide surface develops vacancies and increases its reactivity. On such a C^* -vacant surface, both CO dissociation to $C^* + O$ and hydrogenation to HCO are possible. Upon consumption of all C^* , the surface is Fe terminated and shows metallic-like properties, where the only feasible reaction is the dissociation of CO to regenerate C^* and thus the carbidic surface. Thus, through the consumption and regeneration of C^* , 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 carbidic carbon (C^*), the products of CO dissociation, and the HCO intermediate, on the χ -Fe₅C₂(001)_{-0.05} iron carbide surfaces of different carbon contents. These reactions show the routes and feasible pathways for the CH_x and CH_xO monomers that produce the hydrocarbon and oxygenate products as proposed in the carbene mechanism. We have chosen the C₁ products CH₄, CH₂O, and CH₃OH as the end point. Although CH₄ is an undesired product in FTS, understanding the selectivity trends for CH₄ 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 χ -Fe₅C₂(001) surface was used as the starting point for representing the (dynamical) active catalyst surface. The $p(1 \times 1)$ 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 $(4 \times 4 \times 1)$ 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_(g) and H_{2(g)} ($E_{DFT} = E_{\text{system}} - (E_{\text{CO(g)}} + nE_{\text{H2(g)}} + E_{\chi\text{-Fe5C2}})$). Zero-point energy (ZPE) corrections were calculated using the harmonic approximation and the positive modes of the vibrational data ($E_{\text{ZPC}} = \sum h\nu_i/2$), and included in all the energies reported herein ($E = E_{\text{DFT}} + E_{\text{ZPC}}$).

3. Results and discussion

Fig. 1 shows the χ -Fe₅C₂(001)_{-0.05} surface at different C^* contents, as they were used in our previous study on CO and H₂ activation [39]. We repeat the main findings here. Depending on the surface carbon (C^*) concentration, different reaction paths are available for CO and H₂ [39]. On the perfect surface ($\theta_{C^*} = 0.5$ ML), C^* hydrogenation is the most feasible path. On the C^* -free surface ($\theta_{C^*} = 0.00$ ML), owing to the complete Fe termination, the surface favors direct CO splitting, which regenerates the C^* and the carbide surface. In the intermediate phases with C^* -vacancies ($\theta_{C^*} = 0.25$ ML), H addition to both C^* and CO is possible, along with direct CO dissociation. Following these two directions for CO activation, we have further explored the formation of CH_x and CH_xO intermediates/monomers up to C₁ compounds (CH₄ and CH₃OH) starting from C^* and CO to gain insight in the selectivity between desired and undesired products. The details of CH₄ formation, where C^* is readily available, and similarly CH₃OH formation, where HCO formation is possible, are presented below.

3.1. CH₄ formation

When surface carbidic carbon (C^*) is available, its hydrogenation is a feasible route, especially on the perfect (non-vacant) χ -Fe₅C₂(001)_{-0.05} surface [11,39]. Here, we simulate the hydrogen addition to C^* , which is a facile reaction on the non-vacant ($\theta_{C^*} = 0.5$ ML) and C^* -vacant ($\theta_{C^*} = 0.25$ ML) surfaces of χ -Fe₅C₂(001)_{-0.05}. Fig. 2 shows the relative energies of the intermediates and transition states along the methanation path on non-vacant (perfect) and C^* -vacant χ -Fe₅C₂(001)_{-0.05} 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 CH₄ through the hydrogenation of the surface carbon that leaves a C^* -vacancy, (ii) adsorption of CO on top of a Fe atom and its dissociation to regenerate the surface carbon in the C^* -vacancy, and (iii) formation of H₂O through the hydrogenation of oxygen. As CH₄ and H₂O adsorption are weak, these products desorb upon formation.

CH₄ 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 CH₂ 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_x addition) and undesired methanation, as we address in a forthcoming paper on C₂ hydrocarbons. Indeed, a CH₂ coupling route appears feasible compared to CH₂ hydrogenation, which supports this point.

On the C^* -vacant surface, as Fig. 2 and Table 1 show, CH₄ formation is exothermic by 67 kJ/mol. Furthermore, compared to the perfect surface, CH formation does not compete with H₂ desorption. On this surface, the most difficult step is the hydrogenation of CH to CH₂, with an activation barrier of 55 kJ/mol.

Fig. 1. Top and side views of χ -Fe₅C₂(001)_{0.05} surface with different surface carbon (C*) contents (Fe: brown and C: black). (For the interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 2. Relative energies of intermediates and transition states along methanation routes on non-vacant ($\theta_{C^*} = 0.5$ ML) and C*-vacant ($\theta_{C^*} = 0.25$ ML) χ -Fe₅C₂(001)_{0.05}.

Along the methanation path, CH₃ hydrogenation to form CH₄ 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 ($\theta_{C^*} = 0.5$ ML) into a C*-vacant surface ($\theta_{C^*} = 0.25$ ML), and similarly, the vacant surface into a C*-free surface. The C-atom of CO replaces C* through dissociation and recovers the carbide 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 (O_{2(g)}). These paths were not tested for all C* coverages considered in

Fig. 3. Top views of the ground and transition states along methanation path on non-vacant ($\theta_{C^*} = 0.5$ ML) χ -Fe₅C₂(001)_{-0.05} (Fe: brown, C: black, O: red, and H: white). (For the interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4. Top views of the ground and transition states along methanation path on C*-vacant ($\theta_{C^*} = 0.25$ ML) χ -Fe₅C₂(001)_{-0.05} (Fe: brown, C: black, O: red, and H: white). (For the interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

this work. However, for the calculated cases, Table 1 shows that water formation through subsequent hydrogenation is the most feasible path. We conclude that that atomic oxygen is less reactive on the carbide surfaces of χ -Fe₅C₂(001)_{-0.05} than on metallic iron.

The three stages in methanation of CO on χ -Fe₅C₂(001)_{-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 + 3H₂ to CH₄ + H₂O is exothermic by −223 kJ/mol, in good agreement with the experimental value of 206 kJ/mol [58].

3.2. CH₃OH 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 (ΔH , kJ/mol) along methanation routes on perfect (0.50 ML C*) and C*-vacant (0.25 ML C*) χ -Fe₅C₂(001)_{-0.05}.

	0.50 ML C*		0.25 ML C*	
	E_a	ΔH	E_a	ΔH
C* + 2H → CH + H	58	26	44	40
CH + H → CH ₂	–	28	55	12
CH ₂ + 2H → CH ₃ + H	93	6	42	–28
CH ₃ + H → CH _{4(g)}	59	–24	51	7
CO _(1F1) → C*+O	83	16	83	–81
O + 2H → OH + H	100	–112	43	–78
O + CO → CO ₂	n.a.	n.a.	164	15
O + O → O _{2(g)}	–	335	n.a.	n.a.
OH + OH → H + H _{2O(g)}	121	50	n.a.	n.a.
OH + H → H _{2O(g)}	77	20	146	114

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

Table 2

Activation (E_a , kJ/mol) and reaction energies (ΔH , kJ/mol) of H-assisted CO activation and CH₃OH formation on C*-vacant (0.25 ML C*) and C*-free (0.00 ML C*) χ -Fe₅C₂(001)_{-0.05}.

	0.25 ML C*		0.00 ML C*	
	E_a	ΔH	E_a	ΔH
CO _(1F1) + 2H → HCO + H	–	21	–	61
HCO + H → CH + O + H	196	79	132	–53
HCO + H → CHOH	131	88	104	36
HCO + H → CH ₂ O	73	–12	–	–40
CHOH → CH + OH	72	–97	–	–130
CH ₂ O → CH ₂ + O	133	18	78	–66
CH ₂ O → CH _{2O(g)}	–	139	–	139
CH ₂ O + 2H → CH ₂ OH + H	76	–9	86	53
CH ₂ O + 2H → CH ₃ O + H	–	–124	–	–93
CH ₃ O + H → CH ₃ OH _(g)	–	149	–	154

Fe₅C₂ and 131 kJ/mol on its surface with C* vacancies. In the following reaction step, HCOH splits into CH + OH, thus breaking the CO bond, which is easy on the C*-free surface, but activated on the surface with C* vacancies (E_a = 72 kJ/mol). Hence, once HCOH is present, immediate dissociation of its CO bond is anticipated on C*-free patches of the carbide surface. However, CHOH formation from HCO 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 in this H-assisted CO activation mechanism, a second route is possible that forms adsorbed formaldehyde (CH₂O), see Fig. 5c. Its desorption would cost 139 kJ/mol (Table 2). As Fig. 5c and Table 2 show, formation of CH₂O faces lower barriers than the route to C–O bond breaking via HCOH 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 CH₃OH 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, CH₃O, and its formation by hydrogenation of adsorbed formaldehyde is a feasible step on both C*-vacant and C*-free surfaces of Fe₅C₂. 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 CH₃O intermediate is highly stable on the surface. Its hydrogenation and desorption in the form of methanol (CH₃OH) is endothermic by 150 kJ/mol. However, formation of methanol is exothermic by –104 kJ/mol with respect to gas-phase CO and 2H₂. 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 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_xO 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 H₂ were also reported for a metallic iron (110) 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

Fig. 5. Relative energies of intermediates and transition states along H-assisted CO activation and methanol formation on C*-vacant (θ_{C^*} = 0.25 ML) and C*-free (θ_{C^*} = 0.0 ML) χ -Fe₅C₂(001)_{-0.05}.

Fig. 6. Top views of the ground and transition states along H-assisted CO activation path on C^* -vacant ($\theta_{\text{C}^*} = 0.25 \text{ ML}$) $\chi\text{-Fe}_5\text{C}_2(001)_{-0.05}$ (Fe: brown, C: black, O: red, and H: white). (For the interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 7. Top views of the ground and transition states along H-assisted CO activation path on C^* -free ($\theta_{\text{C}^*} = 0.0 \text{ ML}$) $\chi\text{-Fe}_5\text{C}_2(001)_{-0.05}$ (Fe: brown, C: black, O: red, and H: white). (For the interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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 $\text{CO} + \text{H}$. 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_3O , 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_2O , 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 $\text{Co}(0001)$ surfaces [63–65].

As Fig. 5 shows, HCO hydrogenation to form an oxygenate (i.e., CH_2O) is more feasible than breaking of the C–O bond. Even on the more reactive C^* -free surface of Fe_5C_2 , 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 $\text{Co}(0001)$

Fig. 8. Top views of the ground and transition states along methanol formation path on C*-vacant ($\theta_{C^*} = 0.25$ ML) χ -Fe₅C₂(001)_{–0.05} (Fe: brown, C: black, O: red, and H: white). (For the interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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_xO type species in our next paper.

We conclude that H addition to CO is possible and easily achieved on both non-perfect Fe₅C₂ 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_xO 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 C₂ 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 H₂ on perfect and defect surfaces of χ -Fe₅C₂(001)_{–0.05}, we have reported the energetics for the reactions of CH_x to methane (Fig. 2), and CH_xO to formaldehyde and methanol (Fig. 5). We summarize the results as follows:

- The perfect χ -Fe₅C₂(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 H₂ occurs readily. A reaction cycle can initiate, however, by hydrogenation of a surface carbidic carbon atom, in these papers denoted by C*. This leads to CH, on a surface which now formally contains a C*-vacancy. Further

hydrogenation of CH species forms higher CH₂ and CH₃ intermediates, with the limit being full methanation. This hydrogenation path to methane is also possible on the C*-vacant surface.

- The χ -Fe₅C₂(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, CH₂ formation amounts to 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 χ -Fe₅C₂(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.

Fig. 9. Top views of the ground and transition states along methanol formation path on C^* -free ($\theta_{C^*} = 0.0$ ML) χ -Fe₃C₂(001)_{-0.05} (Fe: brown, C: black, O: red, and H: white). (For the interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 10. MvK cycle of methanation reaction and the proposed chain growth routes.

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_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^* hydrogenation to CH_4 , the reactions follow a Mars–van Krevelen-like mechanism, as we suggested before [11]. Fig. 10 summarizes the cycle, in which surface carbidic C^* eventually forms CH_4 and the carbidic surface is recovered by CO dissociation. Having different rate-determining steps on perfect ($CH_2 \rightarrow CH_3$) and

C^* -vacant ($CH \rightarrow CH_2$) 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^* 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^* -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_2O , 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_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 $CH_2 + O$. Several other authors [70–73] supported the idea of C–O bond breaking in HCO or CH_2O [70] 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_xO intermediates. The latter could in principle hydrogenate completely to methanol. However, the high stabilities of CH_2O and CH_3O species prevent this and explain the low amounts of C_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 $(CO + 2H_2)$ under reaction conditions. In fact, the surface chemistry proposed here is similar as on other metal surfaces. CH_2O 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 CH_x addition as proposed in the carbide mechanism [25,26,40], a similar mechanism may take place starting from CH_xO intermediate by the addition of CH_x 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 χ -Fe₅C₂(001)_{-0.05} (Hägg carbide) surface with different surface carbon (C*) contents showed that monomer (CH_x), as well as methane (CH₄), 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 CH_x formations on perfect and C*-vacant surfaces point to the possibility of different CH_x coupling paths 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 CH_xO species may couple with CH_x groups to form higher oxygen-containing products, similar as in the carbene mechanism. The carbidic carbon (C*) that is part of the carbide lattice participates in CH_x 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 carbidic 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>.

References

- [1] J.v.d. Loosdrecht, F.G. Botes, I.M. Ciobica, A. Ferreira, P. Gibson, D.J. Moodley, A.M. Saib, J.L. Visagie, C.J. Weststrate, J.W. Niemantsverdriet, Fischer–Tropsch synthesis: catalysts and chemistry, in: J. Reedijk, K. Poeppelmeier (Eds.), *Comprehensive Inorganic Chemistry II*, Elsevier, Oxford, 2013, pp. 525–557.
- [2] T. Herranz, S. Rojas, F.J. Pérez-Alonso, M. Ojeda, P. Terreros, J.L.G. Fierro, Genesis of iron carbides and their role in the synthesis of hydrocarbons from synthesis gas, *J. Catal.* 243 (2006) 199–211.
- [3] J. Xu, C.H. Bartholomew, Temperature-programmed hydrogenation (TPH) and in situ Mössbauer spectroscopy studies of carbonaceous species on silica-supported iron Fischer–Tropsch catalysts, *J. Phys. Chem. B* 109 (2004) 2392–2403.
- [4] S. Li, G.D. Meitzner, E. Iglesia, Structure and site evolution of iron oxide catalyst precursors during the Fischer–Tropsch synthesis, *J. Phys. Chem. B* 105 (2001) 5743–5750.
- [5] D.-B. Cao, F.-Q. Zhang, Y.-W. Li, J. Wang, H. Jiao, Structures and energies of coadsorbed CO and H₂ on Fe₅C₂(001), Fe₅C₂(110), and Fe₅C₂(100), *J. Phys. Chem. B* 109 (2005) 10922–10935.
- [6] C.-F. Huo, Y.-W. Li, J. Wang, H. Jiao, Insight into CH₄ formation in iron-catalyzed Fischer–Tropsch synthesis, *J. Am. Chem. Soc.* 131 (2009) 14713–14721.
- [7] P.J. Steynberg, J.A.v.d. Berg, W.J.v. Rensburg, Bulk and surface analysis of Hägg Fe carbide (Fe₅C₂): a density functional theory study, *J. Phys.: Condens. Matter* 20 (2008) 064238.
- [8] D.C. Soreescu, Plane-wave density functional theory investigations of the adsorption and activation of CO on Fe₅C₂ surfaces, *J. Phys. Chem. C* 113 (2009) 9256–9274.
- [9] J.W. Niemantsverdriet, A.M. Van der Kraan, W.L. Van Dijk, H.S. Van der Baan, Behavior of metallic iron catalysts during Fischer–Tropsch synthesis studied with Moessbauer spectroscopy, X-ray diffraction, carbon content determination, and reaction kinetic measurements, *J. Phys. Chem.* 84 (1980) 3363–3370.
- [10] J.W. Niemantsverdriet, A.M. van der Kraan, On the time-dependent behavior of iron catalysts in Fischer–Tropsch synthesis, *J. Catal.* 72 (1981) 385–388.
- [11] J. Gracia, F. Prinsloo, J.W. Niemantsverdriet, Mars–van Krevelen-like mechanism of CO hydrogenation on an iron carbide surface, *Catal. Lett.* 133 (2009) 257–261.
- [12] F.J.E. Scheijen, D.C. Ferré, J.W. Niemantsverdriet, Adsorption and dissociation of CO on body-centered cubic transition metals and alloys: effect of coverage and scaling relations, *J. Phys. Chem. C* 113 (2009) 11041–11049.
- [13] E. de Smit, A.M. Beale, S. Nikitenko, B.M. Weckhuysen, Local and long range order in promoted iron-based Fischer–Tropsch catalysts: a combined in situ X-ray absorption spectroscopy/wide angle X-ray scattering study, *J. Catal.* 262 (2009) 244–256.
- [14] T. Riedel, H. Schulz, G. Schaub, K.-W. Jun, J.-S. Hwang, K.-W. Lee, Fischer–Tropsch on iron with H₂/CO and H₂/CO₂ as synthesis gases: the episodes of formation of the Fischer–Tropsch regime and construction of the catalyst, *Top. Catal.* 26 (2003) 41–54.
- [15] K.R.P.M. Rao, F. Huggins, V. Mahajan, G. Huffman, D.B. Bukur, V.U.S. Rao, Mössbauer study of CO-precipitated Fischer–Tropsch iron catalysts, *Hyperfine Interact.* 93 (1994) 1751–1754.
- [16] G.B. Raupp, W.N. Delgass, Mössbauer investigation of supported Fe catalysts: III. In situ kinetics and spectroscopy during Fischer–Tropsch synthesis, *J. Catal.* 58 (1979) 361–369.
- [17] J.A. Amelse, J.B. Butt, L.H. Schwartz, Carburation of supported iron synthesis catalysts, *J. Phys. Chem.* 82 (1978) 558–563.
- [18] M.D. Shroff, D.S. Kalakkad, K.E. Coulter, S.D. Kohler, M.S. Harrington, N.B. Jackson, A.G. Sault, A.K. Datye, Activation of precipitated iron Fischer–Tropsch synthesis catalysts, *J. Catal.* 156 (1995) 185–207.
- [19] Q. Ge, M. Neurock, Adsorption and activation of CO over flat and stepped Co surfaces: a first principles analysis, *J. Phys. Chem. B* 110 (2006) 15368–15380.
- [20] S. Shetty, A.P.J. Jansen, R.A. van Santen, CO dissociation on the Ru(1121) surface, *J. Phys. Chem. C* 112 (2008) 14027–14033.
- [21] M.R. Elahifard, M. Pérez Jigato, J.W. Niemantsverdriet, Ab-initio calculations of the direct and hydrogen-assisted dissociation of CO on Fe(310), *Chem. Phys. Lett.* 534 (2012) 54–57.
- [22] M.R. Elahifard, M. Pérez Jigato, J.W. Niemantsverdriet, Direct versus hydrogen-assisted CO dissociation on the Fe(100) surface: a DFT study, *ChemPhysChem* 13 (2012) 89–91.
- [23] D.C. Soreescu, Plane-wave DFT investigations of the adsorption, diffusion, and activation of CO on linked Fe(710) and Fe(310) surfaces, *J. Phys. Chem. C* 112 (2008) 10472–10489.
- [24] M.A. Petersen, J.-A. van den Berg, W.J. van Rensburg, Role of step sites and surface vacancies in the adsorption and activation of CO on χ -Fe₅C₂ surfaces, *J. Phys. Chem. C* 114 (2010) 7863–7879.
- [25] F. Fischer, H. Tropsch, *Brennstoff Chem.* 4 (1923).
- [26] F. Fischer, H. Tropsch, *Brennstoff Chem.* 7 (1926).
- [27] A. Govender, D. Curulla Ferré, J.W. Niemantsverdriet, The surface chemistry of water on Fe(100): a density functional theory study, *ChemPhysChem* 13 (2012) 1583–1590.
- [28] A. Govender, D. Curulla-Ferré, M. Pérez-Jigato, H. Niemantsverdriet, First-principles elucidation of the surface chemistry of the C₂H_x (x = 0–6) adsorbate series on Fe(100), *Molecules* 18 (2013) 3806–3824.
- [29] A. Govender, D. Curulla Ferré, J.W. Niemantsverdriet, A density functional theory study on the effect of zero-point energy corrections on the methanation profile on Fe(100), *ChemPhysChem* 13 (2012) 1591–1596.
- [30] F. Fischer, H. Tropsch, Über die direkte Synthese von Erdöl-Kohlenwasserstoffen bei gewöhnlichem Druck (Erste Mitteilung), *Berichte deutschen chem. Gesellschaft (A and B Series)* 59 (1926) 830–831.
- [31] B. Sarup, B.W. Wojciechowski, Studies of the Fischer–Tropsch synthesis on a cobalt catalyst I. Evaluation of product distribution parameters from experimental data, *Can. J. Chem. Eng.* 66 (1988) 831–842.
- [32] B.W. Wojciechowski, The kinetics of the Fischer–Tropsch synthesis, *Catal. Rev.* 30 (1988) 629–702.
- [33] V. Poncet, Some aspects of the mechanism of methanation and Fischer–Tropsch synthesis, *Catal. Rev.* 18 (1978) 151–171.
- [34] D.-B. Cao, S.-G. Wang, Y.-W. Li, J. Wang, H. Jiao, What is the product of ketene hydrogenation on Fe₅C₂(001): oxygenates or hydrocarbons?, *J. Mol. Catal. A: Chem.* 272 (2007) 275–287.

- [35] D.-B. Cao, F.-Q. Zhang, Y.-W. Li, H. Jiao, Density functional theory study of CO adsorption on $\text{Fe}_3\text{C}_2(001)$, $-(100)$, and $-(110)$ surfaces, *J. Phys. Chem. B* 108 (2004) 9094–9104.
- [36] D.-B. Cao, F.-Q. Zhang, Y.-W. Li, J. Wang, H. Jiao, Density functional theory study of hydrogen adsorption on $\text{Fe}_3\text{C}_2(001)$, $\text{Fe}_3\text{C}_2(110)$, and $\text{Fe}_3\text{C}_2(100)$, *J. Phys. Chem. B* 109 (2004) 833–844.
- [37] T.C. Bromfield, D. Curulla Ferré, J.W. Niemantsverdriet, A DFT study of the adsorption and dissociation of CO on $\text{Fe}(100)$: influence of surface coverage on the nature of accessible adsorption states, *ChemPhysChem* 6 (2005) 254–260.
- [38] I.M. Ciobica, R.A. van Santen, Carbon monoxide dissociation on planar and stepped $\text{Ru}(0001)$ surfaces, *J. Phys. Chem. B* 107 (2003) 3808–3812.
- [39] M.O. Ozbek, J.W. Niemantsverdriet, Elementary reactions of CO and H_2 on C-terminated $\chi\text{-Fe}_3\text{C}_2(001)$ surfaces, *J. Catal.* 317 (2014) 158–166.
- [40] F. Fischer, H. Tropsch, *Chem. Ber.* 59 (1926).
- [41] J.T. Kummer, P.H. Emmett, Fischer–Tropsch synthesis mechanism studies. The addition of radioactive alcohols to the synthesis gas, *J. Am. Chem. Soc.* 75 (1953) 5177–5183.
- [42] H. Pichler, H. Schulz, Neuere Erkenntnisse auf dem Gebiet der Synthese von Kohlenwasserstoffen aus CO und H_2 , *Chem. Ing. Tech.* 42 (1970) 1162–1174.
- [43] I. Chorkendorff, J.W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics*, Wiley, 2007, pp. 310.
- [44] P. Mars, D.W. van Krevelen, Oxidations carried out by means of vanadium oxide catalysts, *Chem. Eng. Sci.* 3 (Suppl. 1) (1954) 41–59.
- [45] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1996) 15–50.
- [46] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium, *Phys. Rev. B* 49 (1994) 14251–14269.
- [47] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation, *Phys. Rev. B* 46 (1992) 6671.
- [48] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (1994) 17953–17979.
- [49] B. Hammer, L.B. Hansen, J.K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew–Burke–Ernzerhof functionals, *Phys. Rev. B* 59 (1999) 7413–7421.
- [50] G. Henkelman, B.P. Uberuaga, H. Jónsson, Climbing image nudged elastic band method for finding saddle points and minimum energy paths, *J. Chem. Phys.* 113 (2000) 9901–9904.
- [51] D.C. Sorescu, First-principles calculations of the adsorption and hydrogenation reactions of CH_x ($x = 0, 4$) species on a $\text{Fe}(100)$ surface, *Phys. Rev. B* 73 (2006) 155420.
- [52] A. Alavi, P. Hu, T. Deutsch, P.L. Silvestrelli, J. Hutter, CO oxidation on $\text{Pt}(111)$: an ab initio density functional theory study, *Phys. Rev. Lett.* 80 (1998) 3650–3653.
- [53] J. Cheng, P. Hu, P. Ellis, S. French, G. Kelly, C.M. Lok, Chain growth mechanism in Fischer–Tropsch synthesis: A DFT study of C–C coupling over Ru, Fe, Rh, and Re surfaces, *J. Phys. Chem. C* 112 (2008) 6082–6086.
- [54] J. Cheng, P. Hu, P. Ellis, S. French, G. Kelly, C.M. Lok, A DFT study of the chain growth probability in Fischer–Tropsch synthesis, *J. Catal.* 257 (2008) 221–228.
- [55] J. Cheng, P. Hu, P. Ellis, S. French, G. Kelly, C.M. Lok, Density functional theory study of iron and cobalt carbides for Fischer–Tropsch synthesis, *J. Phys. Chem. C* 114 (2009) 1085–1093.
- [56] J. Cheng, P. Hu, P. Ellis, S. French, G. Kelly, C.M. Lok, Some understanding of Fischer–Tropsch synthesis from density functional theory calculations, *Top. Catal.* 53 (2010) 326–337.
- [57] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, CO activation pathways and the mechanism of Fischer–Tropsch synthesis, *J. Catal.* 272 (2010) 287–297.
- [58] J. Gao, Y. Wang, Y. Ping, D. Hu, G. Xu, F. Gu, F. Su, A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas, *RSC Adv.* 2 (2012) 2358–2368.
- [59] G.P. Van Der Laan, A.A.C.M. Beenackers, Kinetics and selectivity of the Fischer–Tropsch synthesis: a literature review, *Catal. Rev.* 41 (1999) 255–318.
- [60] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Knief, M. Tovar, R.W. Fischer, J.K. Nørskov, R. Schlögl, The active site of methanol synthesis over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ industrial catalysts, *Science* 336 (2012) 893–897.
- [61] S. Lin, J. Ma, X. Ye, D. Xie, H. Guo, CO hydrogenation on $\text{Pd}(111)$: competition between Fischer–Tropsch and oxygenate synthesis pathways, *J. Phys. Chem. C* 117 (2013) 14667–14676.
- [62] C.T. Au, T.J. Zhou, W.J. Lai, Theoretical studies of CO hydrogenation to methanol over Cu, Pd, and Pt metals, *Catal. Lett.* 62 (1999) 147–151.
- [63] K. Habermehl-Ćwirzeń, J. Lahtinen, P. Hautiojärvi, Methanol on $\text{Co}(0001)$: XPS, TDS, WF and LEED results, *Surf. Sci.* 598 (2005) 128–135.
- [64] C.J. Weststrate, H.J. Gericke, M.W.G.M. Verhoeven, I.M. Ciobica, A.M. Saib, J.W. Niemantsverdriet, Ethanol decomposition on $\text{Co}(0001)$: C–O bond scission on a close-packed cobalt surface, *J. Phys. Chem. Lett.* 1 (2010) 1767–1770.
- [65] M.E. Bridge, C.M. Comrie, R.M. Lambert, Hydrogen chemisorption and the carbon monoxide–hydrogen interaction on cobalt (0001), *J. Catal.* 58 (1979) 28–33.
- [66] M. Zhuo, K.F. Tan, A. Borgna, M. Saeys, Density functional theory study of the CO insertion mechanism for Fischer–Tropsch synthesis over Co catalysts, *J. Phys. Chem. C* 113 (2009) 8357–8365.
- [67] T.H. Pham, X. Duan, G. Qian, X. Zhou, D. Chen, CO activation pathways of Fischer–Tropsch synthesis on $\chi\text{-Fe}_3\text{C}_2(510)$: direct versus hydrogen-assisted CO dissociation, *J. Phys. Chem. C* 118 (2014) 10170–10176.
- [68] T. Wang, X.-X. Tian, Y.-W. Li, J. Wang, M. Beller, H. Jiao, Coverage-dependent CO adsorption and dissociation mechanisms on iron surfaces from DFT computations, *ACS Catal.* 4 (2014) 1991–2005.
- [69] I. Wender, S. Friedman, W.A. Steiner, R.B. Anderson, *Chem. Ind.* (1958) 1694.
- [70] S. Storsæter, D. Chen, A. Holmen, Microkinetic modelling of the formation of C_1 and C_2 products in the Fischer–Tropsch synthesis over cobalt catalysts, *Surf. Sci.* 600 (2006) 2051–2063.
- [71] C.-F. Huo, J. Ren, Y.-W. Li, J. Wang, H. Jiao, CO dissociation on clean and hydrogen precovered $\text{Fe}(111)$ surfaces, *J. Catal.* 249 (2007) 174–184.
- [72] O.R. Inderwildi, S.J. Jenkins, D.A. King, Fischer–Tropsch mechanism revisited: alternative pathways for the production of higher hydrocarbons from synthesis gas, *J. Phys. Chem. C* 112 (2008) 1305–1307.
- [73] C.-F. Huo, Y.-W. Li, J. Wang, H. Jiao, Formation of CH_x species from CO dissociation on double-stepped $\text{Co}(0001)$: exploring Fischer–Tropsch mechanism, *J. Phys. Chem. C* 112 (2008) 14108–14116.
- [74] H.H. Storch, N. Golumbic, R.B. Anderson, *The Fischer–Tropsch and Related Syntheses*, Wiley, New York, 1951.
- [75] D. Gall, E.J. Gibson, C.C. Hall, The distribution of alcohols in the products of the Fischer–Tropsch synthesis, *J. Appl. Chem.* 2 (1952) 371–380.
- [76] W.K. Hall, R.J. Kokes, P.H. Emmett, Mechanism studies of the Fischer–Tropsch synthesis. The addition of radioactive methanol, carbon dioxide and gaseous formaldehyde, *J. Am. Chem. Soc.* 79 (1957) 2983–2989.
- [77] E. Ortelli, J. Weigel, A. Wokaun, Methanol synthesis pathway over Cu/ZrO_2 catalysts: a time-resolved DRIFT ^{13}C -labelling experiment, *Catal. Lett.* 54 (1998) 41–48.