A quantum-chemical study of the CO dissociation mechanism on low-index Miller planes of θ-Fe₃C

Robin J.P. Broos¹,b, Bart Klumpersa, Bart Zijlstra², Ivo A.W. Filota,b, Emiel J.M. Hensen²,a,*

¹ Laboratory of Inorganic Materials Chemistry, Schuit Institute of Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands
² Netherlands Center for Multiscale Catalytic Energy Conversion, Universiteitsweg 99, 3585 CG, Utrecht, The Netherlands

ABSTRACT

Spin-polarized density functional theory was employed to determine the preferred CO bond dissociation mechanism on low-index Miller surfaces of θ-Fe₃C in the context of Fischer-Tropsch synthesis. Compared to the most reactive (111) surface of bcc-Fe on which CO binds in a 7-fold coordination, CO prefers to locate in 3-fold or 4-fold sites on the carburized surfaces due to the presence of interstitial C atoms at or below the surface. An important finding is that the lowest activation energies for direct CO bond dissociation are associated with the presence of step-like sites, similar to the case of metallic surfaces. We could identify such sites for 3 out of the 9 investigated surfaces, namely the (111), (111), and (010) terminations of θ-Fe₃C. On the other hand, H-assisted CO dissociation is preferred on the (011), (001), and (100) surfaces. The other (011), (110), and (101) surfaces are inert with CO dissociation barriers close to or exceeding the CO adsorption energy. A kinetic analysis shows that the (111) surface (direct CO dissociation) and the (011) surface (H-assisted CO dissociation via HCO) display comparable CO bond dissociation rates, much higher than the rates computed for the other surfaces. Together these two surfaces make up ca. 28% of the surface enclosing a Wulff nanoparticle of θ-Fe₃C. Using an atomic population analysis, we show that the activation barrier for C-O bond dissociation correlates well with the bond order of adsorbed CO. This implies that pre-activation of CO is important for lowering the overall activation barrier. The present work demonstrates that the high-temperature θ-Fe₃C phase is highly active towards CO bond dissociation, which is the essential first step in the Fischer-Tropsch reaction. Several of the exposed surfaces present lower overall CO dissociation barriers than α-Fe (known to be unstable under Fischer-Tropsch conditions) and the χ-carbide of Fe (usually assumed to be the most stable phase of Fe-carbide under Fischer-Tropsch conditions). Notably, the activity of the (111) surface is higher than that of a stepped cobalt surface.

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1. Introduction

The growing trend to diversify the feedstock mix to cover the energy and transportation fuel demand has led to large-scale chemical processes based on the Fischer-Tropsch (FT) synthesis reaction [1]. In FT synthesis, synthesis gas (a mixture of carbon monoxide and hydrogen) obtained from natural gas and coal is converted to transportation fuels [2]. Approaches to use FT chemistry for the conversion of synthesis gas to light olefins are under development [3].

The CO hydrogenation reactions underlying the FT reaction critically depend on the transition metal catalyst. Fe, Co and Ru provide the highest selectivity towards long-chain hydrocarbons [1]. Fe is attractive because of its cost advantage in comparison to Co and Ru, but also for its high activity in the water-gas-shift (WGS) reaction. The latter aspect is an advantage when synthesis gas compositions with low H₂/CO ratios such as derived from coal gasification are to be converted.

In contrast to Ru and Co for which the metallic phase is considered to be the catalytically active phase, different carbides of iron play an important role in the FT reaction. There is an ongoing debate about which of these phases controls the activity and selectivity of Fe-based catalysts [1,4–6]. It is therefore crucial to understand the nature of the different iron carbide phases and the mechanism by which they convert carbon monoxide with hydrogen to hydrocarbons.

Investigations on the stability of different iron carbide phases suggests that under typical FT conditions (i.e., high CO partial pressure and temperatures around 550-600 K) χ-carbide and ϵ-carbide are the most stable forms of iron [4,7]. This can explain the widespread experimental research on these two phases in the open literature [5–13]. The structure of θ-Fe₃C has been a topic of great interest in the previous century, as θ-Fe₃C is the most stable phase in steel at high...
temperatures. Its structure has been determined experimentally through x-ray, electron, and neutron diffraction measurements [14–26].

The Θ-Fe3C phase is a meta-stable iron carbide which is seen as an intermediate in the transition from pure α-Fe to the more carbon-rich χ-phase. In addition, it is also identified as the most prevalent phase under high temperatures and low carbon-pressures [7], e.g. at short exposures to FT conditions, indicating that Θ-Fe3C may play an important role in the high-temperature FT reaction. To this date, the catalytic properties of χ-carbide (Θ-Fe3C) have only been studied in a few works [9,13,27,28].

CO dissociation is often reported to be one of the rate-determining steps in FT synthesis [2,5]. It is the principle step that has to be facile for a catalyst to be active in the FT mechanism [29]. Herein, we will study the mechanism and kinetics of CO dissociation over the Θ-iron carbide. Although there is a study on the CO dissociation mechanism on the (100) surface [9] and a study on direct CO dissociation on the (001) surface of Θ-Fe3C [13], a detailed theoretical evaluation of the catalytic nature of the other low Miller-index surfaces of the Θ-Fe3C has to the best of our knowledge not been conducted yet.

In this study, we will start by exploring which terminations of bulk Θ-iron carbide are stable and are expected to occur under FT conditions. Next, we will systematically study CO adsorption and direct C-O bond scission on all unique low Miller-index surfaces. Finally, we will compare the direct CO dissociation mechanism with the H-assisted CO dissociation ones, using simple kinetic models and discuss the feasibility of FT chemistry on these Θ-Fe3C surfaces. Most notably, we identified a direct CO dissociation pathway over the (111) surface, which indicates that this surface termination plays an important role in high-temperature Fe-based synthesis gas conversion.

2. Methods

Density functional theory (DFT) computations were performed using the Vienna Ab Initio Simulation Package (VASP) [30–33] with the Perdew-Burke-Ernzerhof GGA exchange correlation functional [34,35]. For structure optimization, spin-polarized DFT computations were conducted using a plane-wave basis set using the projector-augmented wave method [36,37]. The cut-off energy for the plane-wave basis set was 400 eV. Orbital occupations were set according to the 1st order Methfessel-Paxton method with a smearing coefficient of 0.2 eV.

For computations of gaseous CO and H2, the Γ-point was used. Gas-phase molecules were centered in a $10 \times 10 \times 10 \text{Å}^3$ vacuum for the same reason. For the bulk solid computations, a $5 \times 5 \times 5$ Monkhorst-Pack k-mesh grid was used. It was verified that a larger number of grid points did not yield significantly more accurate results given the required computational expense. In order to assure that the surface model was not influenced by its own images due to plane-wave periodicity along the surface normal, a vacuum layer of 7.5 Å was added on each side of the slab model. To prevent dipole moments over the periodic surfaces, adsorbed species were placed symmetrically on both sides of the surface models. For surface computations, a $5 \times 5 \times 1$ k-mesh grid was used. Structural data for bulk Θ-Fe3C was derived from the work of Fruchart et al [25]. Θ-Fe3C has an orthorhombic unit cell with the space group $Pnma$ (62, Pbnm) and cell dimensions $a = 5.082 \text{Å}$, $b = 6.733 \text{Å}$ and $c = 4.514 \text{Å}$ [14–26]. The orthorhombic unit cell is comprised of 8 octahedral iron atoms in Wyckoff d-positions and 4 tetrahedral iron and carbon atoms in Wyckoff c-positions as can be seen in Figure S1.1 of the supporting information.

Energy minimization of the structures was performed using the Kosugi algorithm as implemented in VASP. An energy criterion of $10^{-6} \text{eV/Å}$ and $10^{-5} \text{eV/Å}$ was employed for electronic convergence and structural convergence, respectively. All geometry optimizations were conducted using the conjugate-gradient algorithm. Transition states were determined using the climbing-image nudged elastic band (CI-NEB) method [38]. A frequency analysis was performed to confirm that all transition state geometries correspond to a first-order saddle point on the potential energy surface with an imaginary frequency in the direction of the reaction coordinate. Zero-point energy (ZPE) corrections were applied to all calculations. ZPE-corrections were computed through the energies of the vibrational states based on the eigenvalues of the mass-corrected Hessian matrix. This Hessian matrix was constructed using a finite difference approach with a step size of 0.02 Å for the displacement of individual atoms along each Cartesian coordinate.

In the frequency analysis, we neglected the contribution of Fe by excluding the corresponding terms in the Hessian matrix as the mass of Fe is significantly higher than of C, O or H. We corrected the barriers for the migration of fragments after dissociation by considering the energy difference of the geometry directly after dissociation and their most stable adsorption positions at infinite distance. All surfaces were cleaved with respect to the origin of the bulk unit cell, i.e. at a fractional distance of 0.0.

Surface energies were calculated using

$$E_{\text{surface}} = \left( E_{\text{b}} - n^* E_{\text{bulk}} \right) / 2a^2$$

where $E_b$ refers to the total energy of the slab, containing $n$ times the bulk cell, $E_b$ to the bulk energy, $A$ to the area of the surface, and $E_{\text{surface}}$ to the surface energy of the surface. A Wulff particle was obtained from the different surface free energies using VESTA [39].

To compare the CO dissociation rates on the different surfaces, we formulated several microkinetic models. In these models, we have constructed the chemokinetic network corresponding to the different pathways for CO bond dissociation (i.e. direct or hydrogen-assisted), as depicted in Figure S3.1 in the supporting information. The set of ordinary differential equations that describes a particular chemokinetic network has been constructed using all elementary reaction steps up to and including the C-O bond scission steps, wherein we implicitly assume that the kinetic pathway after the C-O bond scission step that leads to methane does not control the overall rate. The corresponding mechanisms used to formulate the microkinetic models are given in the supporting information. For these calculations we used, unless otherwise specified, temperatures ranging between 100 K and 1000 K and CO pressures between 10–8 Pa and 105 Pa. We have assumed that C-O bond scission is the rate-determining step. For the reaction rate in the hydrogen-assisted mechanisms via HCO or COH, we assumed that HC-O and C-OH scission are the rate-determining steps. To understand the influence of the $H_2$/CO ratio, the ratio between $H_2$ and CO was varied between 1 and 2.

For each elementary reaction step, a rate constant $k$ was computed using an equation based on Eyring’s transition state theory [40]:

$$k = v \exp \left( -\frac{E_{\text{act}}}{kT} \right)$$

where $E_{\text{act}}$ stands for the activation energy, $k_B$ for the Boltzmann constant, $T$ for temperature, and $v$ for the pre-exponential factor. This pre-exponential factor can be calculated for the forward and backward reaction and is defined as follows:

$$v_{\text{forward}} = \frac{k_B T}{\hbar} \left( \frac{q_{\text{TS}}^{\text{FS}}}{q_{\text{TS}}^{\text{FS}}} \right) and v_{\text{backward}} = \frac{k_B T}{\hbar} \left( \frac{q_{\text{TS}}^{\text{FS}}}{q_{\text{TS}}^{\text{FS}}} \right)$$

where $v_{\text{forward}}$ and $v_{\text{backward}}$ refer to the pre-exponential factors for the forward and the backward reaction, respectively, $q_{\text{TS}}$ stands for the vibrational partition function of the initial state (IS) and the transition state (TS), and $h$ for Planck’s constant. Here, we assumed that the adsorption complexes relevant to CO dissociation are immobile on the surface.

In order to understand the underlying chemistry of C-O bond scission on the different surfaces, we also computed the bond orders, using the DDEC6 method developed by Manz and co-workers [41].
3. Results and Discussion

We used DFT to determine the adsorption and reaction energetics of CO dissociation on various θ-carbide surfaces. First, we will present the bulk structure and surface terminations of the θ-carbide and the corresponding energies. Next, we will discuss CO adsorption and direct CO dissociation, followed by an overview of the different H- and C-assisted C-O bond scission pathways for the most stable surfaces. Microkinetic simulations are then used to compare rates of the different CO dissociation pathways. Finally, a bond order analysis is made to rationalize differences in these CO dissociation rates in terms of bonding of CO to the various θ-carbide surfaces.

3.1. Surface θ-carbide models

We focus in this work on low-index Miller surfaces of the θ-carbide of iron. Based on the crystal symmetry, 9 unique surface planes can be distinguished. An overview of these crystallographically different surfaces is given in Table 1. Due to the presence of interstitial carbon in θ-carbide, several surface terminations are possible when the unit cell is cleaved at a fractional distance of 0.0. Table 1 lists the free energies of these surfaces, which are in good agreement with available literature data [28]. The only significant difference is the higher stability of the (101) surface over the (111) surface, which may be due to the use of different GGA functionals. The (011) and (111) surfaces included in Table 1 are studied here for the first time. Figure S1.2 (see the supporting information) shows a Wulff construction of θ-carbide, which is a model for relatively large nanoparticles. The corresponding predicted composition of this Wulff particle is given in Table 1. From Table 1 and Figure S2, it follows that the contribution of different surfaces to the surface enclosing the Wulff particle decreases in the following order (110) > (011) > (101) > (010) > (111). > (001) > (011) > (100) > (111). To determine the importance of these surface terminations for FT synthesis, we investigated C-O bond scission as the important initial step.

3.2. CO adsorption energies and dissociation barriers

We first determined the most stable adsorption site for CO for each of the surfaces. These configurations are shown in Fig. 1. CO adsorption on α-Fe(111) is included for comparison. It is well known that metallic Fe is not stable as an active phase in Fe-catalyzed FT synthesis, as it gets carburized to different carbide phases. This is due to a combination of its high activity for CO dissociation [42,43] and the strong interaction between Fe and C atoms, resulting in formation of iron carbide phases. CO prefers to adsorb in high-coordination sites, unless the surface or subsurface contains C atoms. For example, CO adsorbs in a five-fold configuration on the (111) surface of the θ-carbide. A seven-fold coordination of CO is predicted as the most stable one on α-Fe(111). The adsorption energies on θ-carbide surfaces vary from 155 kJ/mol for the (011) surface to 214 kJ/mol for the (101) surface. A previous investigation of the (100) surface predicted a CO adsorption energy of 177 kJ/mol [9], which agrees with our computed value of 180 kJ/mol.

We considered direct and H-assisted CO dissociation mechanisms. Fig. 2 displays the overall activation barriers for these CO dissociation pathways on all 9 considered surfaces. It follows that direct CO dissociation on the (111) surface has the lowest overall barrier (40 kJ/mol). H-assisted pathways on this surface involve barriers that are higher than 100 kJ/mol. Other reactive surfaces are (011) and (001), which can break the CO bond via a HCO intermediate with overall barriers of 72 kJ/mol and 103 kJ/mol.

3.3. Direct CO dissociation

In the direct CO dissociation mechanism, adsorbed CO dissociates in a single elementary reaction step to C and O. Table 2 presents the computed CO adsorption energies, reaction enthalpies, and the forward and backwards activation energies for direct CO dissociation on the different surfaces. The corresponding geometries are shown in the supporting information (Fig. S2.1-S2.4). Among the different surfaces, C-O bond scission on the (111) surface resembles most the mechanism on the α-Fe(111) surface. The CO dissociation barrier on the (111) surface is only 40 kJ/mol, which is 15 kJ/mol lower than the barrier on α-Fe(111). Both these surfaces are strongly corrugated. CO dissociation on the (111) surface of θ-carbide is for instance more facile than on Ru(112I) (65 kJ/mol) [44] and Co(112I) (103 kJ/mol) [45]. Similar to the latter two surfaces, the (111) surface of θ-carbide exhibits a step-like site involving an ensemble of 5 Fe atoms [46]. It is well known that B2 sites exhibit a favorable geometry for CO dissociation because of the favorable overlap of the metal d orbitals with the 2σ* orbital of CO, the low coordinative saturation of the metal atoms and the absence of sharing of metal atoms with C and O in the transition state [47]. Obviously, the nature of the iron carbide surface gives rise to additional Fe-C bonds and increases the sharing of Fe atoms with C and O. The barrier on the (111) surface is substantially higher (107 kJ/mol) than for the (111) surface.

Compared to these corrugated surfaces, CO dissociation is very difficult on the terrace-like (011) surface (316 kJ/mol) on which CO is adsorbed in a top configuration. In general, barriers on terrace-like surfaces like (001), (011) and (101) are comparable to or higher than the adsorption energy of CO. Given the entropy gained during CO desorption, we infer that CO dissociation is not likely on these surfaces. The barrier computed for the (100) surface of 163 kJ/mol compares well with the result obtained by Jiao et al [9].
Our data show that all the studied surfaces of $\theta$-carbide, for which direct CO dissociation is the preferred pathway, involve a B5-like site. This preference seems in contrast to the direct CO dissociation on Hägg carbide ($\chi$-Fe$_5$C$_2$) as computed by Chen et al. [48]. These authors reported a lower barrier on a terrace surface compared to the barrier on the stepped (100) surface of Hägg carbide. However, close inspection of the terrace-like surface shows that it also contains a four-fold site with an adjacent three-fold site, which is similar to a B5 surface topology. We mention that in our earlier work [49] we computed a lower barrier (128 kJ/mol) for direct CO dissociation on the (100) surface of Hägg carbide than the barrier reported by Chen et al. It is also worthwhile to mention that the lowest CO dissociation barrier on Hägg carbide is computed to be 118 kJ/mol for the (111) surface. Based on the lower barriers for $\theta$-carbide determined in the present study, we conclude that this phase is the more active one for CO dissociation in comparison to $\chi$-carbide. The dominant mechanism on the $\theta$-carbide is direct CO dissociation. Out of the 9 low Miller index surfaces investigated, five contain B5-like sites that prefer direct CO dissociation. Only on the (001) surface, where the four-fold site of the B$_5$ site is occupied by a surface carbon atoms, CO dissociation does not proceed via a direct CO dissociation mechanism. On the (111), (110), (010), and (101) surfaces, the direct CO dissociation mechanism over the B$_5$-like sites has the lowest energy barrier for C-O bond scission.

3.4. H- and C-assisted CO dissociation

H-assisted CO dissociation was also considered for all of the surfaces. The computed energy barriers and the $H_2$ adsorption energies are

![Fig. 1. The most stable adsorption configurations and corresponding adsorption energies of CO on all $\theta$-Fe$_3$C surfaces. As a reference, we have also added the $\alpha$-Fe (111) (second row, fifth image). CO adsorb in high-coordination sites unless hampered by surface or interstitial C atoms. The unit cells used for the calculations are indicated by the white rectangles.](image1)

![Fig. 2. Overall activation barriers for direct CO dissociation (red) and for CO dissociation involving H-assistance via HCO (blue) and COH (green). CO desorption energies are depicted in grey. For the H-assisted pathways, the overall activation barriers for CO hydrogenation and C-O bond scission are given. The surfaces are ordered left-to-right by increasing overall barrier.](image2)

![Fig. 3. Stability plot of all surface reaction intermediates. Intermediates located closer to the center are more stable. The energy of each compound is calculated using atomic carbon, oxygen, and/or hydrogen adsorbed on the surface at infinite distance as the reference state (all energies are in kJ/mol). The surfaces are ordered left-to-right by increasing overall activation barrier as in Fig. 2.](image3)
presented in Table 3. H₂ adsorption energies are computed via

\[ E_{\text{ads}}^{\text{H}_2} = 2 \left( E_{\text{ads}}^{\text{H}} - E_{\text{empty}} - \frac{1}{2} E_{\text{H}_2}^{\text{gas}} \right) \]

where \( E_{\text{ads}}^{\text{H}_2} \) is the adsorption energy for \( \text{H}_2 \), \( E_{\text{ads}}^{\text{H}} \) is the total energy of a single H atom adsorbed on the surface, \( E_{\text{empty}} \) is the total energy of the empty surface, and \( E_{\text{H}_2}^{\text{gas}} \) is the total energy of the \( \text{H}_2 \) molecule in the gas phase. HCO and COH pathways and, for the surface with the highest barrier for direct CO dissociation, also a CCO pathway were investigated. Table 3 shows that HCO formation is endothermic, while subsequent HCO dissociation is exothermic for all surfaces except for the (010) surface. Thus, in general the HCO intermediate is unstable on \( \Theta \)-carbide surfaces. For the (011), (110) and (101) surfaces, the barriers for HCO formation are in the order of 250 kJ/mol, which is much higher than the barriers determined for direct CO dissociation. For some of the surfaces, the overall barrier for CO dissociation via HCO is lower than the corresponding barrier for the direct CO dissociation mechanism. Important cases are the (011) and the (001) surfaces, with a barrier close to or lower than 100 kJ/mol. On the (111), (110) and (001) surfaces, the CO hydrogenation barrier is relatively high with values between 100 kJ/mol and 150 kJ/mol. H-assisted CO dissociation via the HCO intermediate is favored over direct dissociation on the (001) and (011) surfaces. For the (111) and (110) surfaces, direct CO dissociation is preferred.

Relatively facile CO hydrogenation pathways were determined for the (100), (010), and (001) surfaces with barriers of 60 kJ/mol, 59 kJ/mol, and 72 kJ/mol, respectively. On the (100) surface, CO dissociation is more favorable via a HCO intermediate compared to direct CO dissociation. For the (010) surface, the barrier of CO dissociation via a HCO intermediate is close to the barrier for direct C-O bond scission. For the (010) surface, Jiao et al. [13] also considered a hydrogen-assisted pathway. They reported a HCO formation energy of 94 kJ/mol and an overall activation barrier of 121 kJ/mol. These values are respectively 34 kJ/mol higher and 14 kJ/mol lower than our results. This difference can be attributed to their use of a co-adsorbed initial state, where we have used a migration-corrected initial state. Huo et al. reported a forward activation barrier of 109 kJ/mol for HCO formation on the (001) surface [13]. This agrees reasonably well with the value we determined for H-assisted CO dissociation via the HCO intermediate (100 kJ/mol). Huo et al. did not report a barrier for HCO dissociation.

Hydrogenation of CO to COH on the \( \Theta \)-carbide surfaces involves high barriers (> 200 kJ/mol) for all surfaces, except for the (010) surface. While all COH formation reactions are highly endothermic, COH dissociation reactions are exothermic. This shows that the COH intermediates are typically not very stable. However, the barrier on the (010) surface is relatively low. Accordingly, we may expect that the COH dissociation pathway can compete with direct CO dissociation and HCO dissociation pathways on this particular surface. The reason for the high CO hydrogenation barriers towards COH on the other surfaces is that the coordination of CO in the initial state is unfavorable for hydrogenation of the oxygen atom. On most surfaces, the orientation of the CO molecule is perpendicular to the surface, resulting in a large distance between the oxygen atom and the surface. Hydrogenation then requires bending of the CO molecule towards the surface, which costs energy, because it results in less overlap of the metal d-band orbitals with the molecular orbitals of CO.

Overall, we can conclude that the activation barriers for COH dissociation to C + OH are comparable to those computed for HCO.
dissociation to CH + O and lower than values for direct C-O bond dissociation. This can be attributed to weakening of the C-O bond due to protonation of C or O. However, COH formation is much more difficult than HCO formation. Thus, the overall barrier for the COH pathway can be approximated by the COH formation barrier.

We also investigated a C-assisted mechanism for the (011) surface, because other C-O bond scission pathways were found to be unfavorable on this particular surface. We started from an adsorption state where CO forms a bond with a surface carbon atom. The resulting adsorption energy is lower than typical bonds of CO to Fe sites. The CO adsorption energy that results in the CCO species is 121 kJ/mol higher than the most stable CO adsorption configuration on a Fe site on this surface. Thus, we need to take the formation of the CCO species into account as well. The overall forward activation barrier for CO dissociation from CCO is 198 kJ/mol, which is comparable to the adsorption energy (205 kJ/mol). Thus, CO desorption and dissociation in this way will compete. The moderate reaction barrier can be rationalized by the favorable bridged coordination of the oxygen atom of the CCO-intermediate with the surface Fe atoms. The backward activation energy is somewhat higher due to the relaxation of the surface in the final state, resulting in a lower energy.

3.5. Microkinetic analysis

We have developed microkinetic models for the different CO dissociation pathways, including C- and H-assisted CO dissociation pathways, based on transition state theory [40]. Typically, such microkinetic models are constructed within the Langmuir-Hinshelwood-Hougen-Watson framework, wherein the C-O bond scission step is assumed to be the rate-determining step and all other steps prior to this step are assumed to be in pre-equilibrium [45]. Then, it is possible to derive an analytical expression for the overall activity. However, as the barrier for C-O bond scission was found to be relatively low, such a pre-equilibrium could not be readily assumed here. Accordingly, we developed a set of ordinary differential equations corresponding to all steps up to and including the C-O bond scission step that were time-integrated to obtain the steady-state solution. In other words, we assume that the adsorption and dissociation of CO are controlling the overall rate but we do not assume a pre-equilibrium. The simulations correspond to initial rate measurements (no re-adsorption), relevant to the case of zero conversion. The resulting reaction rates were compared to the rate of CO conversion over a stepped Co(112) surface at a CO partial pressure of 10^5 Pa and a temperature of 500 K. In our models, we varied the CO partial pressure between 10^-5 Pa and 10^5 Pa as depicted in Fig. 4. We also include data for stepped α-Fe(111) and terrace Co (0001) surfaces. Relevant kinetic data for Co(112) and Co(0001) were taken from the literature [45]. The direct CO dissociation mechanism exhibits the highest relative rates for the following 5 surfaces: (111), (111), (010), (110). At low CO pressure, the (101) surface also displays high activity. The other surfaces, i.e. (100), (011), (001) and, at higher pressure, the (101) surface are more active for H-assisted CO dissociation via HCO. The (011) surface preferentially dissociates CO via a C-assisted mechanism. The (010) and (111) surfaces show a comparable rate to the stepped Co(112), whereas the (111) surface exhibits a rate comparable to the α-Fe(111), which is nearly 5 orders of magnitude higher compared to the direct CO dissociation rate on the stepped cobalt surface. The higher reactivity (towards CO dissociation) of the α-Fe (111) in comparison to Co(112) is expected based on the higher binding energies of C and O on iron [50]. Carburing of iron to θ-carbide lowers the activity for most surfaces, except for the (111) surface. Notably, the relative rates do not strongly depend on the CO pressure, except for direct CO dissociation on the (111) surface and C-assisted CO dissociation on the (011) surface. In these calculations, we kept the H_2/O ratio constant and lateral interactions were neglected. The influence of the H_2/O ratio on these results was minor as can be appreciated from Table S8.1.

3.6. The nature of CO activation

In an attempt to identify the underlying electronic factors determining the CO dissociation barrier, we correlated typical reactivity descriptors such as reaction energies, adsorption energies and atomic charges to the activation energy of CO dissociation. None of these descriptors however showed a strong correlation with the activation barriers. The absence of a correlation between reaction barrier and adsorption thermodynamics has also been noted for CO activation on ruthenium surfaces [51]. We did not include a detailed analysis of H-assisted CO activation, because the lower C-O bond dissociation barriers are mostly related to protonation of CO which destabilizes the C-O bond and decreases the C-O bond order. Especially due to stability differences of H atoms on different surfaces, the correlation of the activation energy and the bond order is weak (Figure S9.1).

In our system, the lattice C atoms interact with the dissociating CO molecule in two ways: (i) the C atoms coordinate to the Fe surface atoms by which the interaction between the Fe atoms and CO becomes weaker and (ii) there is an electronic repulsion between carbide C and the dissociating CO molecule. These interactions strongly influence the reaction pathway in a non-systematic fashion, explaining why we cannot find a strong correlation between the activation barriers and the reaction energies, adsorption energies or atomic charges.

Accordingly, we investigated the CO bond order using the DDEC6 atomic population analysis [41]. This methodology allows for accurate determination of the CO bond order (BO), a direct descriptor of the strength of the C-O bond. The results are provided in the supporting information in Tables S9.1-S9.3. Herein, it can be seen that the BO for gaseous CO is 2.5. Upon adsorption of CO, the BO decreases to values in the 1.5-2.3 range (depending on the surface) and after CO dissociation
the bond order is zero. In Fig. 5a, the activation energy as a function of the BO of CO in the initial state is shown. A linear regression of the data only showed a weak correlation as evident from a regression coefficient (R^2) of only 0.67. Based on the confidence intervals and the mode of CO adsorption (i.e., bridged), we identified the data point corresponding to the (011) surface as an outlier. Linear regression on the subset without this data point shows a much higher regression coefficient of 0.80, as shown in Fig. 5b. Using the concept of BO based on the DDEC6 analysis, it is clear that the activation energy correlates with the BO of CO in the initial state. This correlation can be understood by using the Blyholder model [52]. This model, which is strongly inspired by frontier molecular orbital (MO) theory, describes the interaction of CO with a metal surface as the result of electron donation from the 5σ MO and simultaneous back-donation into the 2π* MO. The latter causes the C-O bond to weaken, leading to activation of the CO adsorbate and is thus considered favorable for CO dissociation. The low CO dissociation barrier of 40 kJ/mol over the (111) surface is thus caused by its unique topology allowing for a favorable overlap of the molecular orbitals with the metallic d-band, significantly destabilizing the CO bond in the initial state. This conclusion is further supported by considering the data for the (111), (010), and (111) surfaces in Fig. 5. The surface structures of these three surfaces with a low activation barrier for CO dissociation all exhibit a stepped topology, which are highlighted in Fig. 5c. An important finding in this work is that, similar to metallic surfaces, such step-like sites are important to low barrier direct CO dissociation on θ-Fe(C).

4. Conclusion

All 9 θ-carbide surfaces of iron (θ-FeC) were investigated for their reactivity towards CO dissociation by DFT. Compared to the most reactive (111) surface of bcc-Fe on which CO binds in 7-fold coordination, CO binds in 3-fold or 4-fold sites on the carburized surfaces. This is a direct consequence of the interstitial C atoms present at or below the surface. Adsorption of O and H is less affected by the presence of C atoms. The surfaces that exhibit a step-edge like geometry (B5-like site)
favor direct CO dissociation. Surfaces containing such step-like sites are the (111), (110), and (010) terminations. For the (111) surface a very low activation energy of 40 kJ/mol is computed. When we also consider H-assisted mechanisms, the (011), (001), and (100) surfaces are also predicted to be active in CO dissociation. On the other hand, the (011), (110), and (101) surfaces are inert with CO dissociation barriers close to or exceeding the CO adsorption energy. Based on surface free energies, we find that the three most active surfaces, i.e. (111), (110), and (011), make up ca. 31% of a Wulff nanoparticle surface, while the moderately active surfaces contribute ca. 14% to the total surface. The remainder of such a Wulff model particle consists of relatively inert surfaces. Using microkinetic simulations, we show that the (111) surface (direct CO dissociation) and the (011) surface (H-assisted CO dissociation via HCO) display comparable CO bond dissociation rates, much higher than computed for the other surfaces. Using an atomic population analysis, we find that the activation barrier for C-O bond dissociation correlates well with the bond order of adsorbed CO. This finding of this work that is direct CO dissociation on Θ-Fe3C preferentially follows a similar mechanism as on metallic surfaces involving stepped surface sites.

Conflict of interest

The authors declare no competing financial interest.

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