Oxygen Adsorption-Induced Morphological Evolution of Hägg Iron Carbide at High Oxygen Chemical Potentials

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1. INTRODUCTION

The carbides have been regarded as admirable candidates in a broad range of fields thanks to their excellent properties. However, the oxidation behavior of these carbides to some extent makes an adverse impact on their applications, which trigger huge interest in the process of oxidation. After investigating the oxidation kinetics of WC-based material, del Campo et al. found that the inversion of oxidation rates changes the activation energy. It was reported by Berkowitz-Mattuck that the oxidation of zirconium and carbon is simultaneous and occurs along grain boundaries preferentially. Also, through studying the reaction of iron carbides with gaseous oxygen, Frei found that the metal and carbon were oxidized at the same time. For iron carbides, Arabczyk et al. proposed that both magnetite and hematite are present in its reaction with water vapor, and their content is related to the oxidizing potential.

The oxidation of carbides has been proved to occur generally in heterogeneous catalysis from oxygen-containing feedstocks. Specifically, Fischer–Tropsch synthesis (FTS), as a sustainable way to generate contaminant-free transportation fuels (sulfur-, nitrogen-, and aromatics-free) and essential chemical building blocks from syngas, has drawn much attention over the past decades. It is the distinguishing feature, such as low cost and wider operation conditions, of iron-based catalysts that makes them attractive in practical industries. In catalytic FTS reactions, iron carbides have been recognized as the active phase and are responsible for observed activity and selectivity. Until now, a great deal of endeavor has been committed to design iron-based catalysts with outstanding performance, together with comprehension of specific reaction mechanisms. Meanwhile, understanding upon the deactivation behavior of iron-based catalysts is rather significant for us to enhance the stability of catalysts and furthermore realize the balance between cost and performance in industrial applications.

Among studies over the loss of activity of iron-based catalysts, deactivation caused by oxidation has been assumed as one of the main reasons. Through scanning electron microscopy, secondary ion mass spectrometry, and X-ray diffraction studies, Duvenhage et al. found that there are two patterns for decreasing activity in different parts of the catalyst bed: the poisoning of the catalyst due to sulfur impurities is dominant in the top, while hydrothermal sintering and oxidation of the active phase result in deactivation in the bottom of the fixed bed. Similarly, Bukur et al. marked out that oxidizing species (magnetite or siderite) were discovered in the basement of the reactor irrespective of pretreatment conditions. In addition, Gormley et al. attributed the greater deactivation rate for the Fischer–Tropsch reaction in heavier starting media to local high partial pressures of water.
Analogously, research conducted by Bartholomew et al.\textsuperscript{49} indicated that the oxidation of Fe\textsubscript{5}C\textsubscript{2} to Fe\textsubscript{3}O\textsubscript{4} is notably sensitive to partial pressure of water, and increasing partial pressures and high temperature result in rapid oxidation. The author also pointed out that increasing the content of silica and potassium is beneficial to inhibit oxidation. In a subsequent study,\textsuperscript{50} after observing the parallel process of deactivation and phase transformation from iron carbide to magnetite, the author ascribed this oxidation to changes of the surface of carbide (formation of the Fe\textsubscript{3}O\textsubscript{4} layer). What is more, according to experimental observations of Zhao et al.\textsuperscript{51} and Thi"{e}ne et al.,\textsuperscript{52} the iron carbides are covered with adsorbed oxygen atoms on the surface in an oxidizing atmosphere. Thi"{e}ne also proposed that the carbides would be reactivated by removing the adsorbed oxygen atoms, meaning that carbons in bulk were not oxidized with the impact of H\textsubscript{2}O, which is different from that of O\textsubscript{2}. Apart from the aforementioned changes of bulk/surface structures and activity, the oxidizing atmosphere may also affect the morphology of nanoparticles at the equilibrium state.\textsuperscript{53,54}

From the research studies mentioned above, it is clear that surface-related knowledge sheds light on the deactivation process of the catalysts caused by oxidation. However, due to the dynamic nature of the iron carbide surface and limitations of the current \textit{in situ} characterization method,\textsuperscript{55,56} it is very challenging to investigate the interactions between the surface and atomic oxygen in detail experimentally since it is the initial stage of oxidation. As a supplement, theoretical calculations provide a feasible means to gain fundamental insights at the atomic level.\textsuperscript{57} To the best of our knowledge, there are rare theoretical studies devoted to the process of oxidation deactivation of iron carbides,\textsuperscript{58,59} and a systemic investigation about facet-dependent adsorption of oxygen on Fe\textsubscript{5}C\textsubscript{2} remains absent.

Herein, we conducted a theoretical study on the adsorption of oxygen on nine Fe\textsubscript{5}C\textsubscript{2} surfaces which are predicted to be exposed after pretreatment of practical FTS operation\textsuperscript{60} to reveal the interaction of oxygen with diverse Fe\textsubscript{5}C\textsubscript{2} surfaces. Combining \textit{ab initio} atomistic thermodynamics and Wulff construction, we then explored the surface phase diagram of oxygen-adsorbed Fe\textsubscript{5}C\textsubscript{2} surfaces and finally studied how the equilibrium morphology of theoretically established Fe\textsubscript{5}C\textsubscript{2} model changes under a varied oxygen atmosphere. It is worthy to note that although the other surface species also play a role in morphology reconstruction, our work provides an atomistic insight into the influence on morphology and stability of Fe\textsubscript{5}C\textsubscript{2} caused by environmental oxygen chemical potential and furthermore enriches our understanding of the initial process of the oxidation of carbides under \textit{operando} FTS conditions.

### 2. CALCULATION METHODS AND MODELS

#### 2.1. Computational Methods

All calculations were carried out with plane-wave-based DFT method in the Vienna \textit{Ab initio} Simulation Package (VASP).\textsuperscript{61,62} Projector-augmented wave (PAW)\textsuperscript{63,64} potentials were applied to elaborate the electron–ion interaction, and the Perdew–Burke–Ernzerhof functional of generalized gradient approximation (GGA-PBE)\textsuperscript{65} was adopted to describe exchange and correlation interaction. The plane-wave cutoff energy of 400 eV and the electron smearing of 0.2 eV were used.\textsuperscript{66} Once forces in each degree of freedom and energy difference reach the limitation of 0.02 eV/Å and 10\textsuperscript{\textendash}4 eV, respectively, we assumed that the convergence is reached. Because of the existence of magnetic atoms, spin polarization was applied in all the calculations to accurately describe the electronic properties of \textit{x}-Fe\textsubscript{5}C\textsubscript{2}. A Monkhorst–Pack \textit{k}-point grid was set up to 15×15×15 for the bulk structure. The adsorption energy of the surface oxygen atom is defined as $E_{\text{ads}} = E_{(\theta/\text{slab})} - E_{(\theta/\text{bare})} - (E_{(\text{H}_2\text{O})} - E_{(\text{H}_2)})$, where $E_{(\theta/\text{slab})}$ and $E_{(\theta/bare)}$ represent the total energy of slab with and without atomic oxygen adsorption, respectively. $E_{(\text{H}_2\text{O})} - E_{(\text{H}_2)}$ is the reference state of the atomic oxygen in which the energy of H\textsubscript{2}O and H\textsubscript{2} in the gas phase consists of zero-point energy (ZPE) correction.

The atomistic thermodynamics method\textsuperscript{26,67,68} is widely used to solve problems related to experimental conditions such as temperature and pressure.\textsuperscript{69,70} In the FTS process, the reactions can be simplified as eqs 1 and 2.\textsuperscript{72} Given that iron oxides are the main phases for the WGS reaction,\textsuperscript{67,69} here, the thermodynamic equilibrium with eq 3 was used to explore the oxidative behavior on phase-pure Fe\textsubscript{5}C\textsubscript{2}. The Gibbs free energy of adsorption (Δ$G$) was calculated based on eq 4.

\begin{equation}
\text{CO} + (1 + m/2n)\text{H}_2 → 1/n\text{C}_n\text{H}_m + \text{H}_2\text{O} \quad (1)
\end{equation}

\begin{equation}
\text{CO} + \text{H}_2\text{O} ⇄ \text{CO}_2 + \text{H}_2 \quad (2)
\end{equation}

\begin{equation}
\text{Fe}_x\text{C}_y + n\text{H}_2\text{O} → n\text{O}/\text{Fe}_x\text{C}_y + n\text{H}_2 \quad (3)
\end{equation}

\begin{equation}
ΔG = G_{(\theta/\text{slab})} - G_{(\theta/\text{bare})} - n(μ_{\text{H}_2\text{O}} - μ_{\text{H}_2}) \quad (4)
\end{equation}

In eq 4, $G(\text{Fe}_x\text{C}_y)$ and $G(n\text{O}/\text{Fe}_x\text{C}_y)$ are the Gibbs free energies of the bare slab and slab with oxygen adsorption, respectively. $μ_{\text{H}_2\text{O}}$ and $μ_{\text{H}_2}$ represent the chemical potential of H\textsubscript{2}O and H\textsubscript{2}, respectively. $n$ is the number of adsorbed oxygen atoms. Given that the vibrational term of the solid is ignorable compared to that of the gases,\textsuperscript{74} the Gibbs free energies are substituted by the energies from DFT. In addition, the chemical potentials of gaseous H\textsubscript{2}O and H\textsubscript{2} are described as eq 5, where $μ^\theta(T)$ and $E_{\text{ZPE}}$ represent the chemical potential at standard pressure and zero-point energy, respectively. $kT\ln(p/p^\theta)$ represents the contribution of temperature and pressure to total free energy, in which $k$ is the Boltzmann constant and $p^\theta$ is the standard atmospheric pressure. Consequently, eq 4 can also be rewritten as eq 6. In this equation, the two terms on the left side are DFT-calculated energies. $Δ\mu^\theta = μ_{\text{H}_2\text{O}}^\theta - μ_{\text{H}_2}^\theta$ and the $μ^\theta$ of both H\textsubscript{2}O and H\textsubscript{2} is available in the thermodynamic database.\textsuperscript{75} The term $ΔE_{\text{total}}$ is written as $ΔE_{\text{total}} = E_{\text{H}_2\text{O}} - E_{\text{H}_2}$, where the terms on the right side are DFT-calculated energies including zero-point energy corrections. $p_{\text{H}_2\text{O}}$ and $p_{\text{H}_2}$ are the partial pressures of H\textsubscript{2}O and H\textsubscript{2}, respectively. In this way, we get the correlation between $ΔG$ and temperature or partial pressure ratio of H\textsubscript{2}O/H\textsubscript{2}.

\begin{equation}
μ(p, T) = μ^\theta(T) + E_{\text{ZPE}} + kT\ln(p/p^\theta) \quad (5)
\end{equation}

\begin{equation}
ΔG = E_{(\theta/\text{Fe}_x\text{C}_y)} - E_{(\theta/\text{slab})} - n[Δ\mu^\theta + ΔE_{\text{total}} + kT\ln(p_{\text{H}_2\text{O}}/p_{\text{H}_2})] \quad (6)
\end{equation}

And then, surface free energy after oxygen adsorption ($γ_{\text{ads}(\theta)}$) can be evaluated using eq 7, where $γ_{\text{clean}}$ is surface energy without adsorption, which could be obtained according to eq 9 from former work.\textsuperscript{66} $A$ and $S$ stands for the surface area of the substrate. In eq 9, $G_{\text{ads}}$ represents the Gibbs free energy of a slab with two equivalent surfaces, $μ_\text{C}$ is the chemical potentials of the C atom, and $N_{\text{Fe}}$ and $N_{\text{C}}$ are the numbers of Fe and C.
In addition, $g_{\text{bulk}}^{\text{Fe}_5\text{C}_2}$ is Gibbs free energy per formula unit of the $\chi$-$\text{Fe}_5\text{C}_2$ bulk and $A$ is the area of the surface unit cell. Taking the relationship between $\Delta G$ and $\mu_O$ into consideration, finally, eq 7 can be rewritten as eq 8.

$$
\gamma = \gamma_{\text{clean}} + \Delta G_{\text{ads}}(T, p, n\text{O})/A \quad (7)
$$

$$
\gamma = \gamma_{\text{clean}} + [E_{n\text{O}}^{\text{Fe}_5\text{C}_2} - E_{\text{Fe}_5\text{C}_2} - n\mu_O]/A \quad (8)
$$

2.2. Calculation Models. Monoclinic $\chi$-$\text{Fe}_5\text{C}_2$ has a hexagonally close-packed structure and a $\text{C}_2/c$ crystallographic

3. RESULTS AND DISCUSSION

3.1. Stable Adsorption of Atomic Oxygen at Different Coverages. 3.1.1. Adsorption at Low Coverage. At low coverage, the adsorption of atomic oxygen on the nine Fe₅C₂ surfaces was systematically studied. The most stable adsorption configurations of oxygen are presented in Figure 1, and the detailed structural parameters are displayed in Table 1. The ratio of exposed C to Fe on the surface was also listed to relate the surface structure to adsorption performance. It is worth mentioning that adsorption of O on (100)₀.₄₀₂ is endothermic due to positive adsorption energy (the adsorption configurations were depicted in Figure S2). Perhaps, it can be attributed to the unique structure of the surface where the number of carbon atoms is as many as iron atoms, and half of the iron atoms are seated in the valley of the surface. On C-rich surfaces (C/Fe = 0.57) such as (111)₀.₅₇₃, atomic oxygen is more likely to be adsorbed on the C-top site (Tᵥ), with an almost heat-neutral adsorption energy of −0.15 eV. Nevertheless, oxygen atoms are highly coordinated with iron atoms (3F site) on Fe-rich surfaces (C/Fe = 0.20–0.30) with adsorption energy ranging from −1.11 to −0.76 eV. The bond length of Fe–O is around 1.90 Å, in accordance with the calculated bond length of O adsorption on Fe₅C₂(010) (1.89 Å). For (110)₀.₆₀₂ with a moderate C/Fe ratio (C/Fe = 0.33), the favorable adsorption site of atomic oxygen is the bridge site with a small adsorption energy of ~0.35 eV. To summarize, the adsorption strength of O at low coverage on the studied Fe₅C₂ surfaces follows the order of (411)₀.₁₈₈ > (510)₀.₀₀ > (010)₀.₂₅ > (111)₀.₆₀₂ > (001)₀.₀₀ > (110)₀.₅₇₃ > (111)₀.₀₀ > (100)₀.₄₀₂.

3.1.2. O Adsorption at High Coverage. The adsorption at different coverages is vital for us to comprehend the state of oxygen atoms under experimental conditions. Stepwise adsorption energy can be expressed as \( \Delta E_{\text{ads}} = E_{\text{O/(n+1)/slab}} - E_{\text{O/slab}} - (E_{\text{H₂O}} - E_{\text{H₂}}) \). Once the stepwise adsorption energy is greater than zero, we assume that the adsorption has reached saturation. Figures S3–S10 show the stable adsorption configurations of surface oxygen atoms from low coverage to saturation. The stepwise adsorption energy and the corresponding structural parameters are displayed in Table 1. As we can see, both stepwise adsorption energy and average adsorption energy (shown in Figure 3) increase as more oxygen atoms bind to the surface, which is a result of lateral interaction, while the average distance between adsorbed oxygen and surface iron (or carbon) varies within a narrow limit of 0.1 Å, indicating negligible structural change.

The stable surface structures with saturated oxygen adsorption for each facet are shown in Figure 2. The adsorption configurations are much different for surfaces with different C/Fe ratios, suggesting that O adsorption is sensitive to the surface structure. For (111)₀.₆₀₂ and (110)₀.₅₇₃, the two C-rich surfaces, O is located at the bridge site, and the distance of Fe–O is almost unchanged from low coverage to saturation, indicating that the adsorption configuration of O is insensitive to coverage on such surfaces. Moreover, the O atom interacts with not only the Fe atom but one C atom on (111)₀.₆₀₂, resulting in lower average adsorption energy. On (001)₀.₀₀, (010)₀.₂₅ and (111)₀.₀₀ O adsorbs at the threefold site with O interacting with three Fe atoms at the lowest coverage, and adsorption configurations on the C site become possible as the coverage increases, which confirms that O adsorbs preferentially on the Fe site. In addition, O adsorbs on Fe sites on (510)₀.₀₀ and (221)₀.₇₈₃ invariably. Among the nine...
surfaces, the stable adsorption configurations of O on (111)$_{0.602}$, (001)$_{0.00}$, and (411)$_{0.188}$ are similar to the previous study by Gao et al.$^{39}$ the slight deviations might be caused by the difference in computational models.

Moreover, the local geometric feature of the surface, especially the C/Fe ratio, largely determines the rising trend of the adsorption energy with increasing O coverage. As Figure 3 shows, although the average adsorption energy is rising with the increase in O coverage, the magnitude of the growth is very small for surfaces with a C/Fe ratio greater than 0.30, such as (110)$_{0.573}$ and (111)$_{0.602}$. This indicates that the lateral interaction between adsorbed oxygens is weak on these two surfaces. Despite diverse structures, the average adsorption energy lies in the range of $-0.5$ to $-0.7$ eV when the saturation coverage is reached, except (111)$_{0.602}$ and (110)$_{0.573}$. The weaker binding strength between oxygen atoms and these two surfaces with a higher C/Fe ratio indicates that C-rich surfaces are resistant to oxidation.

Experimentally, the coverage of O and its adsorption behavior on the Fe$_5$C$_2$ facets are expected to be strongly influenced by external conditions such as temperature and gaseous pressure. Using an atomistic thermodynamics approach, we investigated the effect of external conditions on oxygen coverage by calculating adsorption Gibbs free energy change ($\Delta G$) under varying temperature and gaseous pressure. Positive $\Delta G$ means that the adsorption is unstable. First, we calculated $\Delta G$ under different temperatures in a defined atmosphere ($P_{H_2O}/P_{H_2} = 0.001, 0.01, 0.1, 1$, and $3$), as well as $\Delta G$ with varying $H_2O/H_2$ partial pressure ratios under given temperature ($T = 500, 550, 600, 650$, and $700$ K) for different numbers of deposited oxygen atoms (Figures S11 and S12). As the trends for all facets are similar, (510)$_{0.00}$ was used as a representative surface for further discussion.

As shown in Figure 4a, $\Delta G$ increases as the temperature increases at various O coverages, indicating that the adsorption of surface oxygen atoms is more favorable thermodynamically at lower temperature. Besides temperature, partial pressure ratio of $H_2O/H_2$ ($P_{H_2O}/P_{H_2}$) also has an impact on the O coverage. In Figure 4b, we could see that rising $H_2O/H_2$ ratio leads to more negative $\Delta G$. Therefore, either elevating partial pressure ratio of $H_2O/H_2$ or depressing temperature could stabilize the oxygen-adsorbed system, resulting in oxidation of the surface. This conclusion is in accordance with the previous theoretical$^{38,39}$ and experimental$^{52}$ study. Moreover, the intersections among the lines in the temperature/partial pressure ratio of the $H_2O/H_2$ range illustrate the changing coverage. Taking the terrace-like surface (510)$_{0.00}$ in the range of 100–1000 K as an example, when partial pressure ratio of $H_2O/H_2$ is equal to 0.001 (Figure S11), the adsorption of five oxygen atoms is more preferred compared to that of four oxygens under 400 K, but the situation is reversed when the temperature is elevated to 600 K. In addition, the $\Delta G$ is the most negative when five oxygen atoms bind to the surface under 400 K, whereas adsorption of two oxygen atoms is the most advantageous within the temperature limit of 500–800 K. By examining the sensitivity of O coverage to these two varied parameters within the limit of our consideration, we found that the adjustable range of oxygen coverage by controlling temperature is relatively narrow when the environment is filled with a large amount of water. As a consequence, to prevent the catalyst from oxidation, excess water should be removed in time in the FTS reaction to avoid surface oxidation.

3.1.3. Equilibrium Phase Diagram of Stable O Coverage. According to the analysis mentioned above, the relationship between stable O coverage and temperature/partial pressure ratio of $H_2O/H_2$ has been discussed. These relationships would help us understand the effect of external conditions on O coverage and furthermore provide us with a feasible approach to keep the surface stable. Based on calculated energies of diverse adsorption configurations at different coverages, the phase diagrams of the Fe$_5$C$_2$ surfaces under various external conditions are obtained, as presented in Figure 5.

From the phase diagrams, the stable O coverage on the studied Fe$_5$C$_2$ facets under a selected experimental situation$^{32}$ [500–700 K, $ln(P_{H_2O}/P_{H_2}) = -1–1$], the zoned area in Figure
can be systematically compared. Among the nine surfaces, the adsorption of oxygen atoms on most surfaces under given conditions is thermodynamically feasible except for (111)0.602 and (100)0.402. However, the most favorable adsorption configuration is varied owing to diverse local structural features of the surfaces. For (510)0.00, (001)0.00, and (010)0.25 with a similar surface C/Fe ratio of about 0.20, the highest oxygen coverage occurs on (001)0.00 which originated from the fact that both iron and carbon atoms are evenly distributed on this Fe-rich surface. (111̅)0.00 and (4̅11)0.188 with a similar surface C/Fe ratio of about 0.30 have medium coverage under the same condition. In addition, it is noted that the adsorption of oxygen atoms is thermodynamically infeasible on (111)0.602 and (100)0.402 under given conditions, whereas it is feasible on (110)0.573 only at low O coverage.

Based on the abovementioned data, a relationship between the C/Fe ratio and oxygen coverage under the experimental condition [500−700 K, \( \ln(\frac{p_{H_2O}}{p_{H_2}}) = -1 \)] can be established to correlate this adsorption performance with the surface structure (Figure 6). As expected, the oxygen coverage has a linear relationship with the C/Fe ratio of the surface, resulting from different affinities of atomic oxygen to iron and carbon atoms on Fe₅C₂ surfaces. Consequently, the oxidation degree of different surfaces under the same conditions shows a downward trend: (100)0.402 = (111)0.602 < (110)0.573 < (111)0.00 < (411)0.188 < (010)0.25 < (221)0.785 < (510)0.00 < (001)0.00 following the rule that surfaces with more carbons are more resistant to oxidation. According to Li et al., oxidation of the carbide surface forming a Fe₃O₄ layer that leads to the loss of activity, and our calculations mentioned above indicate that all nine facets hold a different capacity of antioxidation even at a unified environment. Therefore, the resistance of the exposed surfaces to oxygen adsorption reflected by the surface C/Fe ratio should be a good indicator of the stability of the catalyst against oxidation. It has been observed experimentally that unpromoted χ-Fe₅C₂ oxidizes to pure Fe₃O₄ within 450 h of the reaction, whereas K-promoted Fe₂C (Fe₂.2C) maintains its phase after 400 h, although the mechanism (the stability difference or the

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Figure 5. Phase diagrams for the oxygen adsorption state (\( \theta, n_{O}/\text{nm}^2 \), n in parentheses): (a) (510)0.00, (b) (111)0.00, (c) (221)0.785, (d) (010)0.25, (e) (110)0.573, (f) (001)0.00, (g) (411)0.188, (h) (111)0.602, and (i) (100)0.402.

Figure 6. Correlation of the surface C/Fe ratio with oxygen coverage (\( \theta_O, n_{O}/\text{nm}^2 \)) under experimental condition [500−700 K, \( \ln(\frac{p_{H_2O}}{p_{H_2}}) = -1 \)].
presence of potassium) remains unclear. Our findings provide a possible explanation for the observed experimental phenomenon: K+ ions might enhance the resistance of the iron carbide surface against oxidation by stabilizing the surface C atoms of the carbides through an electronic effect. 79

3.1.4. Electronic Properties of Fe₅C₂ Surfaces after Oxygen Adsorption. Additionally, d-band center (\(e_d\)), charge density difference, and Bader charge analyses were conducted to exemplify the effect of surface oxygen adsorption on the electronic structure of Fe₅C₂ surfaces in FTS surroundings. Despite the distinct local structure of each surface, these characteristics appear to have identical trends qualitatively. As a consequent, d-band center and charge density difference plot of (510)₀.₀₀ as a representative case were displayed (Figure 7). It has been reported that metal with a d-band center close to the Fermi level promotes the electron back-donation from metal d-states to the CO 2π* orbital and hence is more active for C=O bond dissociation. 30 Here, in Figure 7a, \(e_d\) has a reduction of 0.18 eV after atomic oxygen adsorption, meaning that surface oxygen impedes the transfer of electrons to the adsorbate from Fe atoms and probably hinders the CO activation. The plotted charge density difference in Figure 7b,c reveals that electron density is mainly concentrated on the surface oxygen (yellow isosurfaces), while the iron atoms bonded to oxygen show decreased electron density (green isosurfaces), implying electron transfer from Fe atoms to adsorbed O atoms. Bader charge analysis also affirms this statement that Fe atoms associated with O atoms lose 0.27 e, and adsorbed O has a negative charge of −0.94 e. Accordingly, deposited oxygen atoms may be responsible for the deteriorated performance of the \(\chi\)-Fe₅C₂ catalyst after oxidation; a detailed study will be covered in our forthcoming work.

3.2. Morphology Modified by O. Generally, both surface energy and orientation determine the contribution of each surface to the total surface area of a particle. 80 Therefore, we first calculate the surface free energies in varied oxygen characteristics appear to have identical trends qualitatively. As a consequent, d-band center and charge density difference plot of (510)₀.₀₀ as a representative case were displayed (Figure 7).

Figure 7. (a) Plot for d-orbital centers of involved Fe atoms for \(\chi\)-Fe₅C₂(510)₀.₀₀ and O/\(\chi\)-Fe₅C₂(510)₀.₀₀ surfaces, in which vertical red dashed lines denote the Fermi level and vertical green lines represent the d-band center. (b) Top view and (c) side view of the charge density difference of the O-adsorbed \(\chi\)-Fe₅C₂(510)₀.₀₀ surface. The green and yellow shaded isosurface indicates electronic charge depletion and charge accumulation, respectively. Purple, gray, and red balls denote Fe, C, and O atoms, respectively.

It is clear that adsorption of surface oxygen minimizes the surface free energy and stabilizes the surfaces, similar to the report that K₂O serves to stabilize the metallic iron and iron carbide surface. 77 Besides, the surface free energy of all eight facets changes from 1.660 to 2.545 J/m² and can be divided into two sets depending on the sensitivity of their surface free energy to oxygen chemical potential. (510)₀.₀₀, (221)₀.₇₈₃, (010)₀.₂₅₃, (110)₀.₆₇₃, (001)₀.₄₆, and (411)₀.₁₈₃ belong to the first set, which are more sensitive to \(\mu_O\). Both (110)₀.₅₇₃ and (111)₀.₆₀₃ in the second set show little change in surface free energy within the limit of \(\mu_O\) up to −7.50 eV, which is due to the fact that the adsorption of oxygen atoms is thermodynamically unfavorable on (110)₀.₅₇₃ and (111)₀.₆₀₃ unless the oxygen chemical potential is very high. Additionally, since the adsorption of oxygen atoms on (100)₀.₄₀₂ is not facile in the selected range, its surface energy is maintained in the studied \(\mu_O\) range.

Based on the calculated surface energies, the equilibrium shape of \(\chi\)-Fe₅C₂ crystallites upon varied oxygen chemical potential is depicted (shown in Figure 9a) on account of Wulff theory. 81 The corresponding proportions of each surface to the area of the entire particle are illustrated in Figure 9b. Within the oxygen chemical potential range we considered, (510)₀.₀₀, (221)₀.₇₈₃, and (111)₀.₀₀ expose more areas with increasing O potential, while the contribution of surfaces with strong antioxidation capability such as (110)₀.₅₇₃, (111)₀.₆₀₂, and (100)₀.₄₀₂ declines in the equilibrium morphology as \(\mu_O\) goes up. In particular, (510) has the highest exposure at high oxygen chemical potential. The experiment conducted by Ma et al. 23 shows that the synthesized Fe₅C₂ nanoparticles of 20 nm in size also has a very high exposure ratio of (510), which is, according to our calculations, probably because of the partial oxidation of the nanoparticle under the synthetic conditions. Moreover, (110)₀.₅₇₃ even diminishes completely when \(\mu_O\) rises to −7.42 eV. Decreasing proportion of the antioxidation surface would reduce the overall stability of the particle. Additionally, the contribution of (411)₀.₁₈₃ reaches the maximum (12%) at a \(\mu_O\) of −7.64 eV, and the contribution of (001)₀.₀₀ is the minimum (6%) at −7.91 eV. According to the DFT studies by Yin et al., 40 the effective free energy barrier for the overall CH₄ formation on (510)₀.₀₀, (411)₀.₁₈₃, (010)₀.₂₅₃, and (111)₀.₀₀ is relatively higher than surface (111)₀.₆₀₂, (110)₀.₅₇₃, and (100)₀.₄₀₂. Experimentally, Ma et
realize the balance between activity and selectivity of the Fe5C2 possibility of modulating the oxygen chemical potential to these structure promising in elevating the selectivity of ole adsorption of O is unfeasible on (100). The adsorption of adsorption on C sites is possible at low O coverage, and the lower the coverage on Fe5C2 surfaces, which is bene temperature and reducing partial pressure ratio of H2O/H2 will of addition, electronic structure analysis suggests that the activity carbon atoms are more resistant to surface oxidation. In related to the C/Fe ratio of the surface: a higher C/Fe ratio protect the surface from oxidation. The O coverage is linearly by atomic oxygen adsorption. Besides, morphology evolution equilibrium shape.

We have comparatively analyzed the interaction between the surface oxygen atom and nine facets of the Hågg carbide and revealed the morphology evolution at varied O chemical potential under FTS-related conditions by combining DFT, ab initio atomistic thermodynamics, and Wulff construction. It was found that surface oxygen binds to surface Fe sites preferentially and then turns to the C sites with increasing O coverage. For a carbon-rich surface such as (111)0.602, adsorption on C sites is possible at low O coverage, and the adsorption of O is unfeasible on (100)0.402. The adsorption of oxygen is also correlated with the working environment: raising temperature and reducing partial pressure ratio of H2O/H2 will lower the coverage on Fe5C2 surfaces, which is beneficial to protect the surface from oxidation. The O coverage is linearly related to the C/Fe ratio of the surface: a higher C/Fe ratio leads to lower O coverage, indicating that surfaces with rich carbon atoms are more resistant to surface oxidation. In addition, electronic structure analysis suggests that the activity of χ-Fe5C2 may decline due to impeded CO activation caused by atomic oxygen adsorption. Besides, morphology evolution upon O adsorption at different oxygen chemical potentials through analysis of surface free energy and Wulff construction is examined. Surfaces with strong resistance to oxidation such as (110)0.852, (111)0.602, and (100)0.402 expose less surface areas in the equilibrium morphology as the oxygen chemical potential goes up, while the proportion of the other surfaces rises with increasing O potential. This work provides an atomic level understanding of the thermodynamics of the interaction between oxygen and Fe5C2 surfaces and shows how oxygen adsorption under different external conditions tunes the structure, electronic structure, and particle morphology of Fe5C2. Our atomistic insights also shed light on the initial stage of deactivation of the iron carbide catalyst caused by surface oxidation.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c10822.

Fe5C2 surface models, stable configurations of surface oxygen on nine facets, and relationship between Gibbs free energy change and experimental conditions (temperature, partial pressure ratio of H2O/H2, and oxygen chemical potential) (PDF)

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Notes

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