

Manganese promoter hinders carbon permeation on iron-based catalyst surfaces: A first-principles study

YANG Tao^{1,2}, MA Huan^{3,4,5,*}, LIU Xingchen^{3,4,*}

¹ Beijing Advanced Innovation Center for Materials Genome Engineering, Beijing Information Science and Technology University, Beijing 102206, China;

² School of Computer Science, Beijing Information Science and Technology University, Beijing 102206, China;

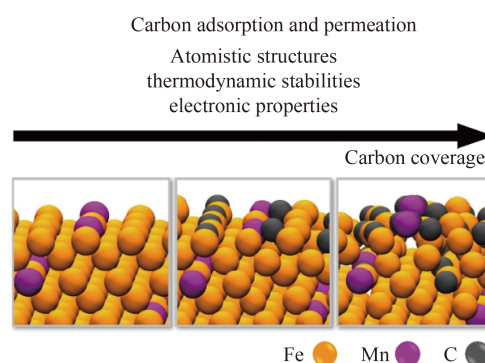
³ State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China;

⁴ University of Chinese Academy of Sciences, Beijing 100049, China;

⁵ National Energy Center for Coal to Liquids, Synfuels China Co., Ltd., Beijing 101400, China

Abstract: Fe-Mn catalysts have garnered considerable attention for industrial applications in the Fischer-Tropsch synthesis (FTS) process. Carbon adsorption and permeation on catalyst surfaces constitute critical elementary steps in the *in situ* formation of active phases in iron-based FTS catalysts. Herein, density functional theory (DFT) calculations are employed to systematically investigate the atomistic structures, thermodynamic stabilities, and electronic properties of carbon-deposited Fe-Mn alloy surfaces at the early stage of carburization. These Fe-Mn alloy surfaces show distinct thermodynamic sensitivity to carbon atoms adsorbed on the surface and permeating into the interstitial sites. By combining DFT with minima-hopping structural searches, we demonstrate that the initial stage of carbon permeation cannot trigger the reconstruction of surface regions to form surface iron carbide phases. The addition of manganese thermodynamically hinders the carbon permeation process. Although deposited C atoms modulate the electronic structure of metals, the presence of manganese retards the shift of *d*-band centers of metals to those of the bulk iron carbide phases. Our study provides an atomic-scale insight into the *in situ* evolution of Fe-Mn catalyst surfaces during the carbon deposition process and indicates that the manganese promoter has a noticeable effect on carbon permeation.

Key words: Fe-Mn catalyst; carbon adsorption and permeation; DFT; thermodynamic stability; electronic structure



Syngas conversion *via* Fischer-Tropsch synthesis (FTS) offers an efficient and economical way to produce environmentally benign liquid fuels and feedstock for chemicals from carbonaceous sources, including coal, natural gas, biomass, and CO₂^[1–5]. The iron-based catalyst system is pivotal in utilizing syngas derived from coal or biomass due to its intrinsic water-gas shift (WGS) activity, broad operating range, and low cost^[6–8]. Iron-based catalysts typically consist of a complex mixture of iron and iron carbide phases, often modified by promoters to optimize catalytic performance^[9–10]. Because the addition of the manganese promoter can effectively manipulate the FTS

product spectrum, Fe-Mn catalysts have attracted significant attention for industrial applications^[11–17]. It is generally accepted that surface iron carbides constitute the catalytically active phases in FTS^[18–19]. Typically, before the catalyst becomes active in the FTS reaction, these carbides form through the *in situ* carburization, with carbon atoms permeating into the interstitial vacancies of α -Fe species obtained by reducing the Fe₂O₃ precursor during the catalyst preparation^[18]. Consequently, the permeation of carbon has a profound effect on primary iron species. Investigating how *in situ* carburization proceeds on Fe-Mn catalyst surfaces is essential for understanding the structure

Received: 2025-10-30; Revised: 2025-12-19

Foundation items: Supported by National Natural Science Foundation of China (22272009), National Key R&D Program of China (2022YFB4101200, 2022YFA1604102).

* Corresponding author. Tel: 0351-4040895, E-mail: mahuan201@mails.ucas.ac.cn, liuxingchen@sxicc.ac.cn.

DOI: 10.1016/S1872-5813(26)60657-3 CSTR: 32157.14.2097-213X.2026.JFCT.0012 Associated Data DOI: 10.57760/sciencedb.j00124.00360

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

and properties of these surfaces, as well as the formation of active phases, which significantly affect the catalyst performance during FTS, including catalytic activity and selectivity.

While the bulk structure of iron carbides has been extensively characterized by techniques such as X-ray diffraction (XRD), Mössbauer spectroscopy (MES) and transmission electron microscopy (TEM)^[6,20–22], determining the atomic-scale structure of iron-based catalyst surfaces under *operando* conditions remains a substantial experimental challenge. Although the formation of a well-defined Fe carbide surface has been examined by using X-ray photoelectron spectroscopy (XPS) and atom-resolved scanning tunneling microscopy (STM)^[23], the atomic-level evolution of the surfaces during the carburization process remains unclear. The air and temperature sensitivity of surface iron carbides causes the complex nature of structural evolution under working conditions. This complexity necessitates higher requirements for the development of *in situ* experimental techniques^[18,24]. Additionally, due to atomic carbon deposition on catalyst surfaces, determining the effect of the addition of carbon on electronic properties such as *d*-band occupation and Fermi level of iron-based catalysts is difficult in experiments, which is closely related to understanding the iron-based catalyst performance from the perspective of electronic structures^[18]. The introduction of the manganese promoter will further complicate both the surface structure and electronic properties in the catalyst system.

First-principles calculations such as those based on density functional theory (DFT) provide an efficient method for characterizing the surface properties of materials, allowing precise control of surface composition and atomistic geometry. The present work aims to investigate diverse C-deposited surfaces of Fe-Mn catalysts at the early stage of carbon adsorption and permeation. Using DFT calculations in conjunction with a global structure searching algorithm—minima hopping method (MHM), we examine the geometric structures and energetics of these surfaces with atomic carbon adsorbed on the surface and permeating into the interstitial sites of the Fe-Mn alloy. The electronic properties of these surfaces are then calculated for representative C-deposited models. This study provides an atomic-scale understanding of the *in situ* evolution of Fe-Mn catalyst surfaces during the carburization process. Compared with carbon permeation on pure iron surfaces, we further reveal the influence of introducing manganese on carbon permeation.

1 Computational details

1.1 Methods

All energy and electronic structure calculations were performed at the DFT level using the Vienna *ab initio* simulation package (VASP)^[25–26]. The electron-ion

interaction was described with the projector-augmented wave (PAW) method^[27–28]. Electron exchange and correlation energies were treated within the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE)^[29]. The cutoff energy was 400 eV and the Brillouin zone was sampled using the Monkhorst-Pack scheme^[30]. Energies and atomic forces were converged to within 10^{-5} eV and 0.05 eV/Å, respectively. The Methfessel-Paxton method^[31] was chosen as the smearing algorithm. To give an exact description of the magnetic properties of iron and manganese, spin polarization was considered.

The MHM^[32–33] was employed to sample the configurational space of the surfaces and their reconstructions in the presence of adsorbate species. The MHM is a structure prediction method that relies on consecutive short molecular dynamics (MD) trajectories to escape from the catchment basin of the corresponding local minima, followed by geometry optimizations. The search aims at exploring low-energy structures by relying on a feedback mechanism based on the kinetic energy of the MD escape trials. The initial MD velocities are preferably aligned along soft mode directions of a local minimum, leading to crossing over low-energy barriers. Hence, the MHM utilizes the Bell-Evans-Polanyi principle^[34], which states that strongly exothermic reactions have overall low activation barriers. Recently, the MHM has been successfully employed for the exploration of low-dimensional systems, including 2D materials^[35] and surface reconstructions^[36–37].

All structural searches in this work were performed at the DFT level by coupling the MHM with VASP. The MHM was employed with an adaptive temperature ladder spanning 700–6700 K, allowing the system to overcome high-energy barriers and escape from local minima. The potential energy surface (PES) was initially screened with the MHM using coarse DFT settings with a cutoff energy of 270 eV. The searched low-energy structures were sorted according to DFT energy calculations with a cutoff energy of 300 eV.

To reflect the adsorption intensity and system stability of carbon, the average carbon binding energy ($\text{Fe} + N_{\text{C}} \rightarrow N_{\text{C}}/\text{Fe}$) was calculated according to the following equation:

$$E_{\text{B}}^{\text{ave}} = [E_{\text{Nc/slab}} - E_{\text{slab}}]/N - E_{\text{C}} \quad (1)$$

where $E_{\text{Nc/slab}}$ is the total energy of the slab with N adsorbed C atoms in its equilibrium geometry, E_{slab} is the total energy of the bare slab, and E_{C} is the total energy of a free carbon in the gas phase. The adsorption energy of CO was calculated according to:

$$E_{\text{ads}} = E_{\text{CO/slab}} - E_{\text{slab}} - E_{\text{CO}} \quad (2)$$

where $E_{\text{CO/slab}}$ and E_{CO} are the total energies of the slab with an adsorbed CO molecule and a CO molecule in the gas phase, respectively. The barrier for CO dissociation was calculated according to:

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{IS}} \quad (3)$$

where E_{TS} and E_{IS} are the total energies of the

corresponding transition state and initial state, respectively. Transition states were located using the climbing-image nudged elastic band method^[38]. Zero-point energy corrections were included in the energetic data.

1.2 Models

A $2 \times 2 \times 2$ supercell containing eight body-centered cubic (BCC) Fe unit cells was built. Further, the Fe₁₅Mn₁ bulk was built by replacing one Fe atom with one Mn atom in the supercell (Figure S1), with equilibrium lattice constants of $a = b = c = 5.733$ Å. The bare surfaces were simulated with six-layer $p(U \times V)$ periodic slab models, in which $p(2 \times 2)$ for the (100) facet, $p(2 \times 1)$ for the (110) facet, and $p(1 \times 1)$ for the (111), (211) and (310) facets were adopted. The lattice parameters of the slab models are as follows: $a = b = 11.47$ Å for the (100) facet; $a = 11.47$ Å and $b = 8.11$ Å for the (110) facet; $a = b = 8.11$ Å and $\gamma = 60^\circ$ for the (111) facet; $a = 9.93$ Å and $b = 8.11$ Å for the (211) facet; and $a = 5.73$ Å and $b = 18.13$ Å for the (310) facet. The k -points of $2 \times 2 \times 1$, $2 \times 3 \times 1$, $4 \times 4 \times 1$, $3 \times 3 \times 1$ and $4 \times 1 \times 1$ were set for the (100), (110), (111), (211) and (310) facets, respectively. The top four layers of these models were fully relaxed to explore the potential surface reconstruction caused by carbon deposition. When performing the structural search, considering the computational cost associated with large systems, slab models were constructed by retaining the top three layers of the obtained local minima geometries, and the top two layers were fully relaxed. The adsorption and dissociation of CO were calculated using the (100)-a and (310) surface structures generated through MHM searches, with the top two layers fully relaxed.

During the carbon deposition process on Fe-Mn surfaces, the position of the C atoms adsorbed/permeating on/into the slab model was determined by the respective atomic layers they entered/presented. To address the complexity introduced by the geometrical variety of surface structures, atomic layers are defined throughout the rest of the article. The atoms in the 1st, 2nd, and 3rd layers of each slab model were represented by different colors and denoted as 1L, 2L and 3L, respectively. Given the existence of certain “open” surfaces, there may be more than one sublayer within a defined layer. As carbon permeates into the interstices of the Fe-Mn alloy in atomic form, no particular carbon source is chosen in this work.

2 Results and discussion

2.1 Structures of carbon-deposited surfaces

In accordance with our previous studies^[39–40], three low-index facets, namely (100), (110), and (111), and two facets with higher Miller indices, namely (211) and (310), were chosen to investigate carbon adsorption and permeation for Fe-Mn catalysts. For a comprehensive analysis, the models of the (100), (110) and (111) facets were categorized into

two types, denoted as a and b for Fe-terminated and FeMn-terminated surfaces, respectively, to distinguish whether the Mn atom is a surface termination atom. The models of these surfaces are presented in Figure S2. The energetically stable surface structures and corresponding average carbon binding energies (E_B^{ave}) at various carbon coverages during the carbon deposition process are shown in Figures S3–S10, which illustrate the sequential incorporation of carbon atoms into Fe-Mn surfaces.

Figure 1 illustrates the surface structures with the first C atom adsorbed on the 1L layer and permeating into the 2L and 3L layers on various surfaces. We first focus on the Fe-Mn(100)-a surface to illustrate the detailed mechanism of carbon adsorption and permeation. As shown in Figures 1 and S3, the first C atom adsorbs on the 4-fold hollow site in the 1L layer of the slab model, and additional C atoms adsorbed on the 1L layer continue to enter the 4-fold hollow site, mostly along diagonal directions relative to the first adsorbed C atom. The corresponding bonding geometry and carbon separation tendencies are consistent with both theoretical and experimental observations on the Fe(100) surface^[39,41]. The E_B^{ave} of the 14th C atom (10.6 C/nm²) becomes more stable in the 2L layer than in the 1L layer by approximately 0.03 eV, indicating that the C atom prefers to permeate into the 2L layer at this point. Proceeding in this way, it is found that the 2L layer can accommodate only one C atom before additional C atoms begin to permeate further into the 3L layer. For the Fe-Mn(100)-b surface with the Mn atoms exposed on the surface instead of located in the 2L layer, although it is also the 14th C atom that begins to enter the 2L layer, the 2L layer can accommodate up to 11 C atoms (18.3 C/nm²) before additional C atoms permeate further into the next layer. In contrast, the (111) facet exhibits significant differences. As shown in Figure 1, after introducing 8 C atoms into the first layer (14.1 C/nm²), the subsequent C atom prefers to directly enter the 3L layer instead of the 2L layer. For (110)-a, (110)-b, (211), and (310) surfaces, C atom permeation into the 2L layer occurs at 6.5, 8.6, 12.4 and 12.4 C/nm², respectively, and permeation into the 3L layer occurs at 10.8, 11.8, 14.9 and 16.4 C/nm², respectively. It is found that as the carbon coverage increases, the (211) facet undergoes reconstruction, during which an exposed Mn atom and an adjacent Fe atom migrate to nearby sites (Figure S9). These results demonstrate that crystallographic orientation and surface termination jointly govern the carburization behavior of Fe-Mn alloy surfaces.

It is worth noting that, for these results, each C-deposited surface structure discussed above represents a local minimum. This is achieved by “shooting in” C atoms through specified sequential processes and allowing them to reach the optimum site *via* a single geometry optimization. Surface reconstructions can cause phase transformations and form carbide phases. To determine if there are reconstructed structures with lower energy on the PES that can be achieved by overcoming activation barriers, we conducted minima-hopping structural searches for C-deposited surface structures.

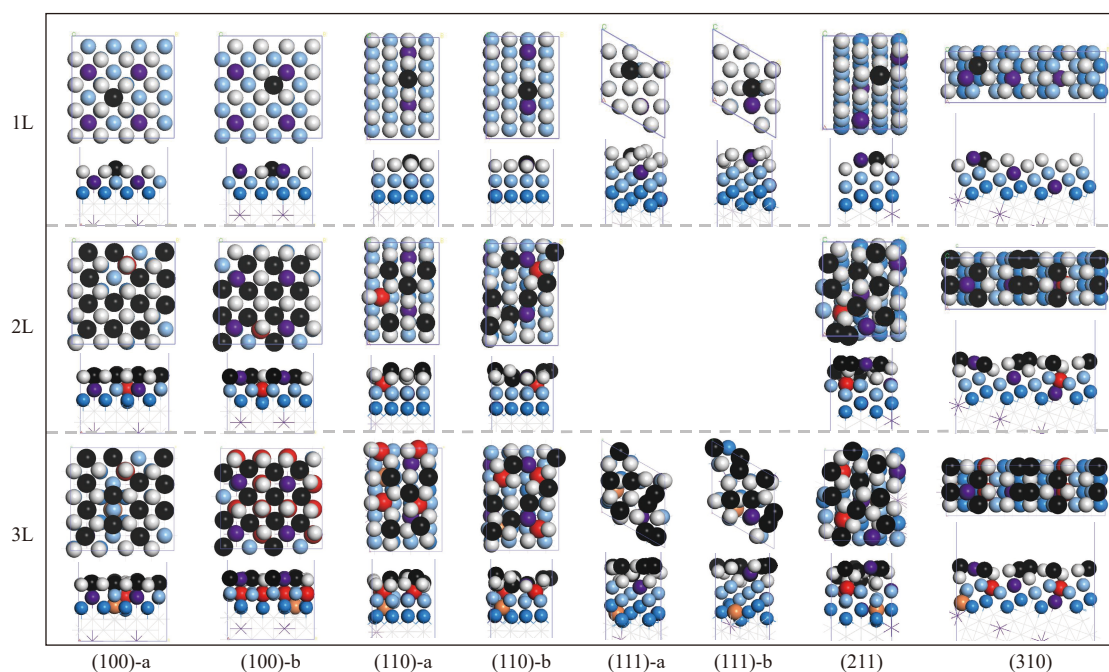


Fig. 1 Top and side views of optimized structures with the first C atom adsorbed on the 1L layer (in black) and permeating into the 2L and 3L layers (in red and orange, respectively) for eight different surfaces
The 1L, 2L and 3L Fe atomic layers are shown in light gray, sky blue, and dodger blue, respectively;
the Mn atoms are shown in dark violet.

Herein, the Fe-Mn(100)-a and (310) surfaces at medium and high carbon coverages were selected to represent the low-index and high-index surfaces, respectively. After removing duplicate configurations, the number of candidate configurations generated by the MHM was 57 and 56 for the (100)-a surface at medium and high carbon coverages, respectively, and 49 and 49 for the (310) surface at medium and high carbon coverages, respectively. Geometry optimizations were then performed on the top ten most stable structures predicted by the MHM for each system to access the global minima. As shown in Figure 2(a), the surface structure of the (100)-a surface at medium carbon coverage (6.1 C/nm^2) remains almost unchanged before and after applying the MHM. At high carbon coverage (11.4 C/nm^2), carbon diffusion occurs after exploring the PES using the MHM. The atom A diffuses from the 4-fold hollow site (1L layer) above the Mn atom to another 4-fold hollow site (1L layer) above the Fe atom. The atom B in the interstitial site diffuses from the 2L layer with Mn atoms to the 3L layer without Mn atoms. These findings suggest that, for the (100) facet at increasing carbon coverages, C atoms may not tend to be located near Mn atoms. For the (310) surface at medium carbon coverage (8.7 C/nm^2), the surface structure searched through the MHM does not undergo the rearrangement of atomic sites (Figure 2(b)). At high carbon coverage (16.4 C/nm^2), for carbon atoms, the atoms A and B in the 2L layer diffuse to the 3L layer, and the atom C diffuses from the 2L layer to the junction of the 1L and 2L layers. This indicates that, for the (310) surface at high carbon coverages, the permeated C atoms are prone to diffuse, forming a structure with lower energy. No

segregation of Mn atoms from the subsurface to the outermost layer was observed for either facet, indicating that Mn atoms doped into the Fe lattice remain in a stably separated state in our models.

To deepen our understanding of the structural differences between local minima and global minima, we investigated the radial pair distribution function (RDF) of these surface structures. The RDF provides the density probability of finding neighboring atoms at a given distance from a reference atom. For (100)-a and (310) surfaces at medium carbon coverages, as shown in Figure 3(a) and Figure 4(a), the shapes and positions of the RDF curves for local minima closely resemble those of the global minima obtained through the MHM. This is consistent with our previous discussion that the surface structure at medium carbon coverages remains nearly unchanged before and after applying the MHM (Figure 2). When a high carbon coverage is reached, the shapes and positions of their RDF curves remain similar, except for the highest peaks of the Fe-C and Fe-Mn curves (Figure 3(b) and Figure 4(b)). This discrepancy can be attributed to the diffusion of carbon atoms and the accompanying geometry relaxations of Fe and Mn atoms (Figure 2). Overall, our local minima, obtained by adding carbon atoms with a specified sequence, closely approximate the global minima geometries obtained from the MHM. For both (100)-a and (310) surfaces, although Fe and Mn atoms in the 1L and 2L layers undergo noticeable relaxations at high carbon coverages, no surface reconstructions occur, which indicates that the initial stage of carbon permeation is insufficient to induce a phase transition.

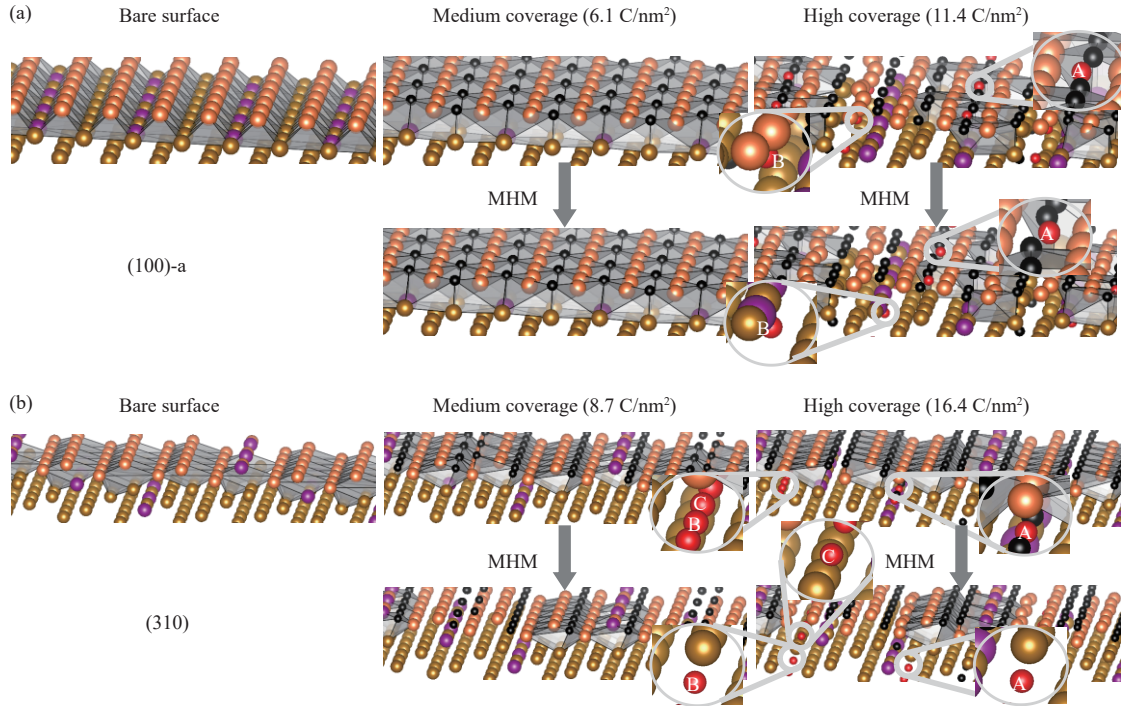


Fig. 2 C-deposited structures of (a) Fe-Mn(100)-a and (b) Fe-Mn(310) surfaces at medium and high carbon coverages before and after performing the minima-hopping structural searches

The Fe atoms in the 1L layer are shown in orange; the Fe atoms in the 2L and 3L layers are shown in brown; the Mn atoms are shown in violet; the C atoms are shown in black; the diffused C atoms are shown in red.

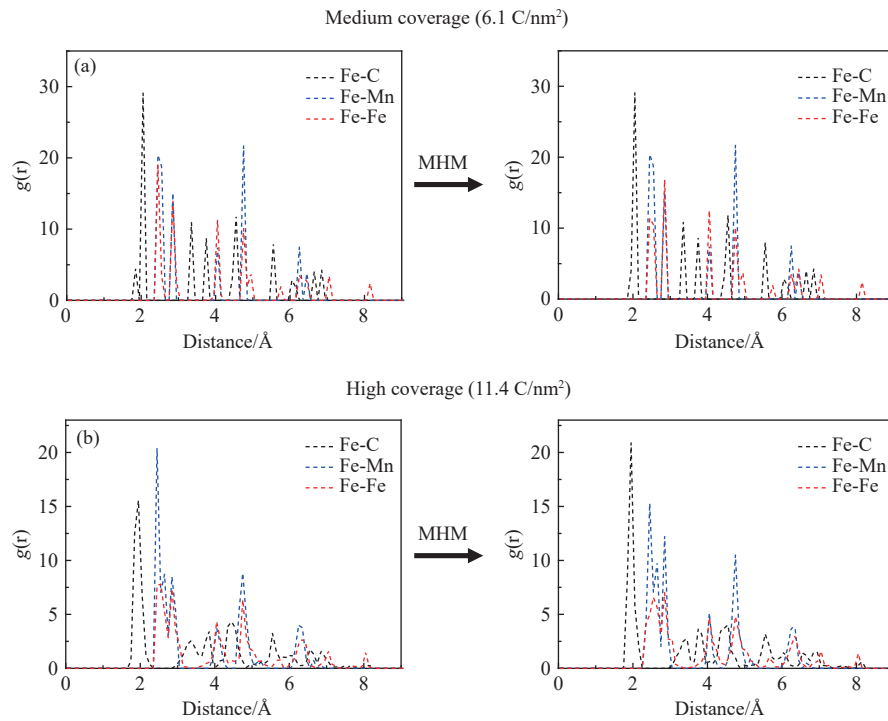


Fig. 3 Radial pair distribution function of C-deposited structures of the Fe-Mn(100)-a surface at (a) medium and (b) high carbon coverages before and after performing the minima-hopping structural searches

2.2 Energetics of carbon-deposited surfaces

The E_B^{ave} represents the thermodynamic stability of C atoms deposited on the Fe-Mn surfaces. The more negative

the value of E_B^{ave} , the more energetically favorable the C-deposited surface structure is. Figure 5 illustrates the E_B^{ave} as a function of the number of introduced C atoms per unit area (N_C/nm^2).

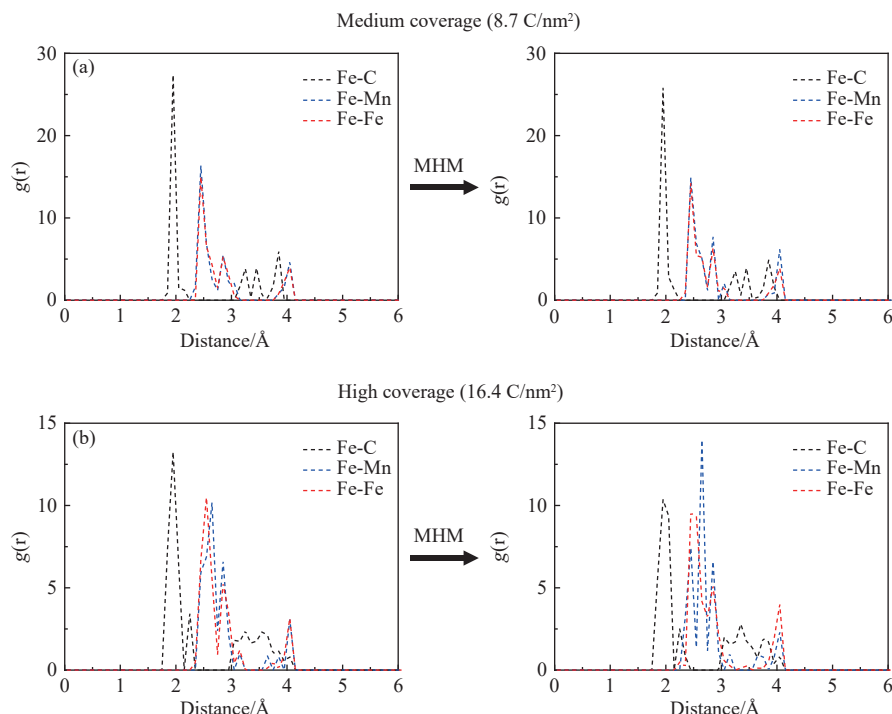


Fig. 4 Radial pair distribution function of C-deposited structures of the Fe-Mn(310) surface at (a) medium and (b) high carbon coverages before and after performing the minima-hopping structural searches

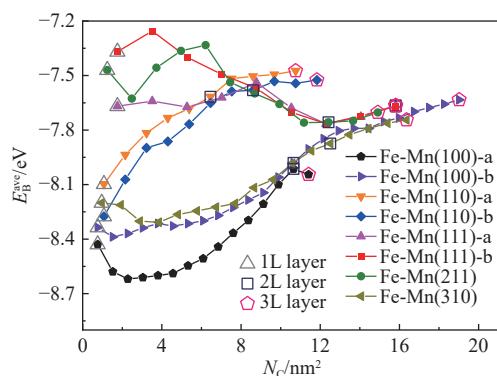


Fig. 5 Average carbon binding energy as a function of the number of introduced C atoms per unit area for different surfaces

Gray triangles, navy squares, and pink pentagons represent the first C atom adsorbed on the 1L layer and permeating into the 2L and 3L layers, respectively.

At the lowest carbon coverage, the E_B^{ave} of different Fe-Mn surfaces follows the sequence (100)-a < (100)-b < (110)-b < (310) < (110)-a < (111)-a < (211) < (111)-b, indicating that carbon adsorption on the (100) facet is initially most favorable compared with other surfaces.

With increasing carbon coverage, the investigated surfaces can be classified into three types according to the evolution in their E_B^{ave} before C atoms permeate into the 2L layer. The E_B^{ave} of (100)-a, (100)-b, and (310) surfaces show an initial gentle and subsequent rapid rise, while the E_B^{ave} of (110)-a and (110)-b surfaces experience a drastic increase. Conversely, the E_B^{ave} of (111)-a, (111)-b, and (211) surfaces gradually decrease with oscillation. We observe a strong

correlation between the diverse trends in the thermodynamic stability of carbon adsorption on the 1L layer of these three types of surfaces and the degree of surface undercoordination (d_{suc}) of these surface structures. This descriptor quantifies the surface undercoordination of arbitrary metal surfaces by measuring the disruption of intermolecular bonds^[40,42]. The (100)-a, (100)-b and (310) surfaces with high d_{suc} values of 0.034, 0.033 and 0.044, respectively, show a higher affinity for C atoms compared with other surfaces. Until the carbon coverage reaches approximately 16 C/nm², C atoms preferentially deposit on (100)-a, (100)-b, and (310) surfaces. The (111)-a, (111)-b and (211) surfaces with low d_{suc} values of 0.013, 0.011 and 0.009, respectively, display poor thermodynamic stability of carbon adsorption due to their high coordination. The decreasing trend in E_B^{ave} as the carbon coverage increases indicates that the binding strength of carbon on these surfaces strengthens with the introduction of more C atoms into the system. The (110)-a and (110)-b surfaces, which exhibit stability between the two types of surfaces mentioned above, are characterized by moderate d_{suc} values of 0.026 and 0.027, respectively, compared with other surfaces.

As C atoms begin to permeate into the 3L layer, the number of introduced C atoms per unit area follows the order (100)-a $\approx$ (110)-a $\approx$ (110)-b < (211) $\approx$ (111)-a $\approx$ (111)-b $\approx$ (310) < (100)-b, and the corresponding E_B^{ave} follows the order (100)-a < (310) $\approx$ (211) $\approx$ (111)-a $\approx$ (111)-b $\approx$ (100)-b < (110)-a $\approx$ (110)-b (Figure 5). Consequently, from the perspective of thermodynamics, the (100)-a surface exhibits the highest stability for C atoms permeating into the 3L layer at lower carbon coverage compared with other

surfaces. Additionally, the (100)-b surface shows the most significant capability to accommodate C atoms in the 1L and 2L layers, while the (110)-a and (110)-b surfaces possess the strongest resistance to the permeation of additional C atoms into the 3L layer.

Several studies have reported that the formation of a solid solution compound over the coprecipitated Fe-Mn catalysts could influence the reduction and carburization behaviors of Fe catalysts^[12–13,43]. Furthermore, the manganese promoter was found to enhance the catalyst's resistance to deactivation induced by carbon deposition^[44]. These studies uncover the significant impact of the manganese promoter on the carburization of iron-based catalysts. To understand the impact of manganese on the initial stage of carbon permeation during the carburization process from an atomic-scale perspective, we compared the calculated results for carbon permeation on Fe-Mn surfaces with those on pure Fe surfaces reported in our earlier study^[39]. As illustrated in Figure 6(a), when the first C atom permeates into 2L and 3L layers, the E_B^{ave} of various Fe-Mn surfaces (except for (100)-a surface with the first C atom permeating into the 3L layer) are higher than those of Fe surfaces with the corresponding Miller indices. This indicates that the thermodynamic stability of carbon permeation on Fe-Mn surfaces is lower than that on Fe surfaces. Additionally, as shown in Figure 6(b), the number of C atoms that can be introduced per unit area on Fe-Mn surfaces (except for (100)-a and (110)-a surfaces with the first C atom permeating into the 3L layer) is similar to or higher than that on Fe surfaces. Thus, in comparison to Fe surfaces, Fe-Mn surfaces may accommodate more C atoms before the C atoms permeate into the bulk region. These results suggest that the addition of manganese is thermodynamically unfavorable for carbon permeation on iron surfaces.

2.3 Electronic structures of carbon-deposited surfaces

The binding strength between metal surfaces and adsorbates essentially depends on the electronic structure of the surface. To elucidate how carbon deposition and permeation regulate the electronic properties of Fe-Mn surfaces, the projected density of states (PDOS) of different C-deposited Fe-Mn surfaces were calculated in this work. The (100) facet is selected as a representative case to illustrate the electronic structure of C-deposited Fe-Mn surfaces. For the bare surface, as shown in Figure 7(a) and 7(d), the spin-up total density of states (TDOS) peaks at energy level around -4.0 to -2.5 eV and -1.5 to -0.9 eV appears clearly. Besides, there are obvious spin-down TDOS peaks at energy level around -2.3 to -0.6 eV and 1.3 to 2.5 eV. These four peaks are contributed by d electrons of Fe and Mn atoms, suggesting that there is considerable overlap between Fe $3d$ and Mn $3d$ orbitals. They collectively constitute the main part of the energy bands near the Fermi level. While there are wide and low-intensity regions at high energy level, which are composed of the overlap between Fe $s-p$ and Mn $s-p$ orbitals, mixing with Fe $3d$ and Mn $3d$ orbitals. Compared with Mn, the increased nuclear charge of Fe will be less effectively screened by the tight-bound $3d$ electrons. Therefore, the $3d$ bands of Fe, feeling more attraction from the nucleus, are slightly lower in energy than the $3d$ bands of Mn, as indicated by the low energy region of approximately -4.5 eV.

The permeation of C atoms into vacancies within the Fe-Mn alloy can be regarded as a perturbation to the alloy DOS. With carbon permeation, the four main peaks mentioned above are weakened to varying degrees but remain prominent, indicating that the electron density is picked up by C atoms from the d bands of metals due to the electronegativity difference between metals and carbon (Figure 7(b) and 7(e)).

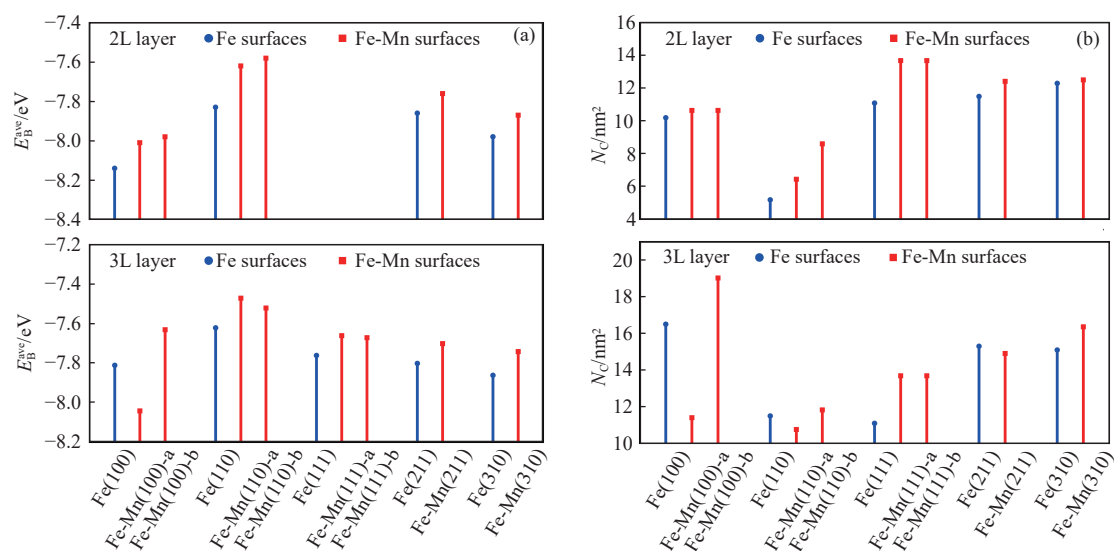


Fig. 6 Comparison of Fe surfaces with Fe-Mn surfaces

(a) average carbon binding energy and (b) the corresponding number of introduced C atoms per unit area of different surface structures with the first C atom permeating into the 2L and 3L layers.

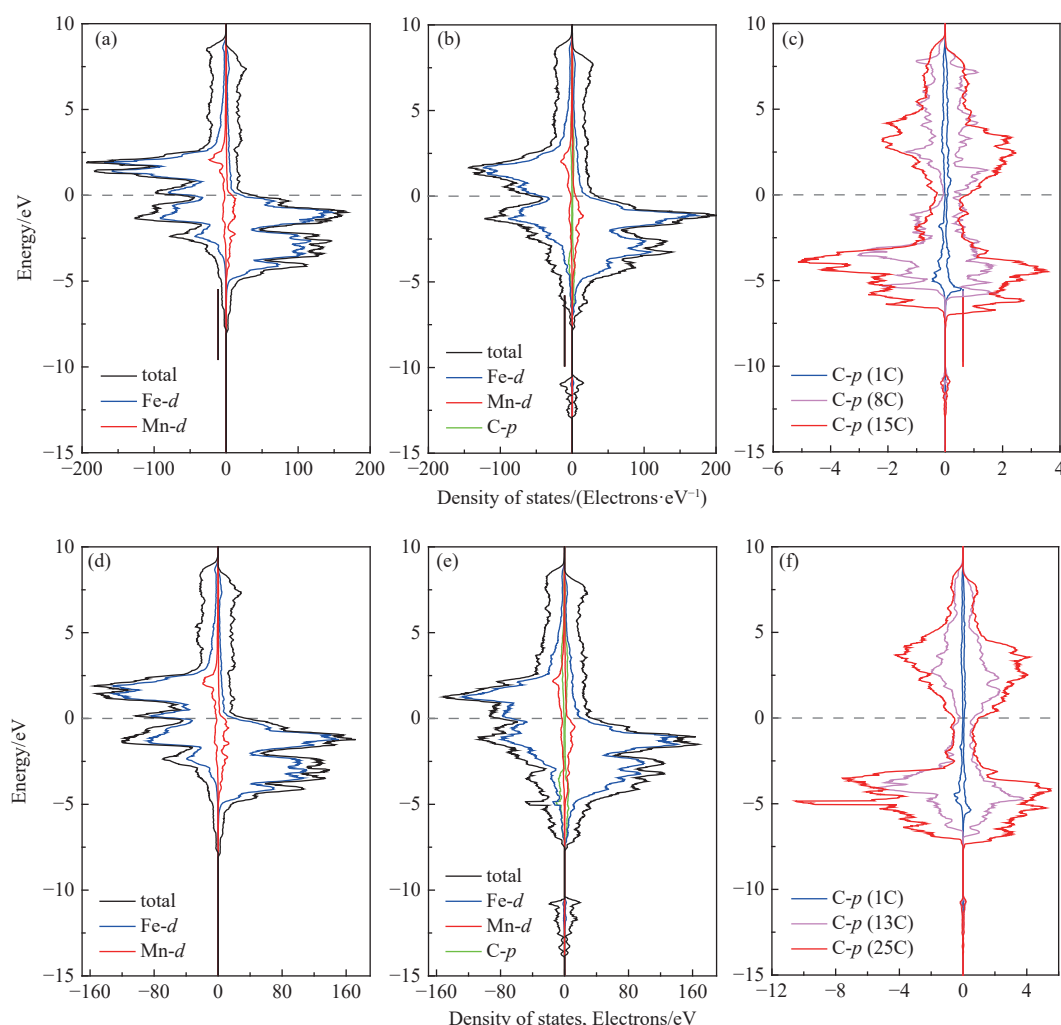


Fig. 7 Projected density of states of (a) bare (100)-a surface, (b) (100)-a surface with 15 C atoms deposited, (c) C-*p* states of (100)-a surface with different numbers of C atoms deposited, (d) bare (100)-b surface, (e) (100)-b surface with 25 C atoms deposited, and (f) C-*p* states of (100)-b surface with different numbers of C atoms deposited

Spin-up and spin-down channels are shown with positive and negative values, respectively. The Fermi level is located at 0 eV.

The PDOS of Fe-*d* and Mn-*d* tend to shift to a lower energy level, indicating the potential downshift of the overall *d* bands. The spin-up TDOS at energy level around -7.5 to -5.0 eV and the spin-down TDOS at energy level around -7.5 to -3.0 eV intensify clearly. As shown in Figure 7(c) and 7(f), we find that these intensified states are mostly the 2*p* states of C, and the density of these states increases with the increase of the number of introduced C atoms. Moreover, there are isolated states of TDOS at energy level around -14.0 to -10.5 eV, which consists mainly of *s* and *p* electrons of C, with little contribution from Fe-*d*. The features of PDOS discussed above are basically the same as all Fe-Mn surfaces we investigated, so we do not elaborate on the other surfaces (Figures S11–S16). The difference in electronic structure between different surfaces is mainly reflected in the *d*-band center, thus we next focus on the *d*-band centers of these surfaces.

The *d*-band center is the average energy of the *d*-band and can serve as an effective descriptor of the ability for electron transfer between metal surfaces and adsorbates^[45–46]. Therefore, the *d*-band centers of the entire

metal on different C-deposited surface structures were calculated to further elucidate the influence of the addition of carbon atoms on the catalytic-activity-related electronic properties. As shown in Figure 8, the *d*-band centers of different C-deposited surfaces move away from the Fermi level with the increase of the number of introduced C atoms (except for Fe-Mn (111)-b), which indicates that there is an interaction between the C *s-p* orbitals and metal 3*d* orbitals to modulate the *d*-band centers of Fe-Mn surfaces. Compared with Fe surfaces^[39], the *d*-band centers of Fe-Mn surfaces are closer to the Fermi level and exhibit a more gentle decline, suggesting that manganese incorporation retards the evolution of surface electronic structures toward those characteristic of bulk iron carbide phases.

To further elucidate how changes in surface geometry and electronic structure induced by varying carbon coverage affect catalytic behavior, we employed CO as a probe molecule and calculated its adsorption and dissociation on the (100)-a and (310) surface structures identified through MHM searches. These processes play a critical role in FTS^[5].

As shown in Figure 9(a) and 9(b), compared with the bare surfaces, CO adsorption energies on the C-deposited surfaces become more positive, indicating weakened adsorption. This behavior is consistent with the downward shift of the *d*-band center away from the Fermi level, which weakens interactions with the antibonding orbitals of the adsorbate and thus leads to reduced adsorption strength^[45–46]. In addition, the activation barriers for CO direct dissociation on C-deposited surfaces are higher than those on the corresponding bare surfaces (Figure 9(c) and 9(d)). These trends are particularly pronounced on the (310) facet, which provides a higher density of active sites; as a result, geometric effects become less dominant, allowing the influence of changes in electronic properties to be more clearly manifested.

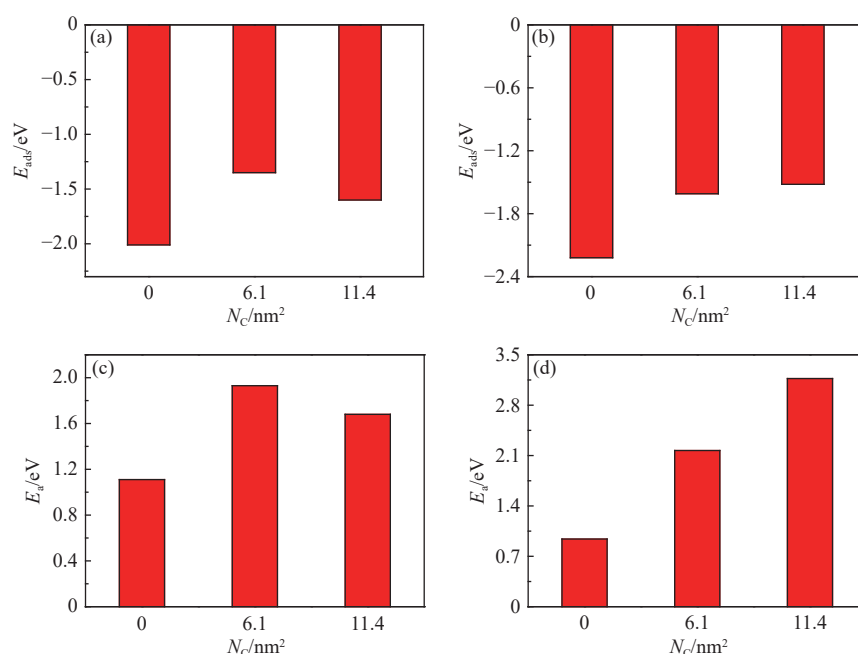


Fig. 9 Adsorption energies of CO on the (a) (100)-a and (b) (310) facets, and activation barriers for CO direct dissociation on the (c) (100)-a and (d) (310) facets

3 Conclusions

In summary, to gain an atomic-scale understanding of the early stages of carbon adsorption and permeation for Fe-Mn FTS catalysts, we perform a first-principles study to investigate the atomistic structures, thermodynamic stabilities, and electronic properties of different C-deposited surfaces of a Fe-rich Fe-Mn alloy. By sequentially introducing C atoms onto surface and subsurface sites, we provide *in situ* surface structures and the corresponding thermodynamic stabilities at various carbon coverages during the carburization process, demonstrating that different Fe-Mn surfaces exhibit different carburization behaviors. Using DFT in conjunction with the MHM, we find that no surface reconstructions leading to the formation of iron carbide phases occur within the considered carbon coverage range. The introduction of manganese makes

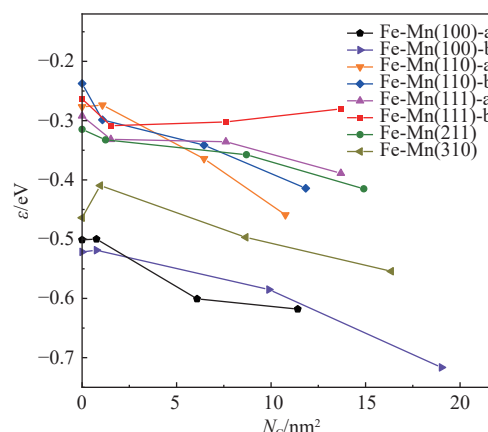


Fig. 8 *d*-Band centers as a function of the number of introduced C atoms per unit area for different surfaces

carbon permeation thermodynamically less favorable compared with pure iron. Consistent with our electronic structure analysis, although carbon deposition significantly modulates the electronic states of the metal surfaces, the presence of manganese suppresses the evolution of *d*-band centers from those characteristic of iron surfaces toward bulk iron carbide phases.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] DRY M E. Fischer-Tropsch reactions and the environment[J]. Appl Catal A: Gen, 1999, 189(2): 185–190.

- [2] CHU S, MAJUMDAR A. Opportunities and challenges for a sustainable energy future[J]. *Nature*, 2012, 488(7411): 294–303.
- [3] JIAO F, LI J, PAN X, et al. Selective conversion of syngas to light olefins[J]. *Science*, 2016, 351(6277): 1065–1068.
- [4] ZHANG R, WANG Y, GASPARD P, et al. The oscillating Fischer-Tropsch reaction[J]. *Science*, 2023, 382(6666): 99–103.
- [5] ROMMENS K T, SAEYS M. Molecular views on Fischer-Tropsch synthesis[J]. *Chem Rev*, 2023, 123(9): 5798–5858.
- [6] DE SMIT E, CINQUINI F, BEALE A M, et al. Stability and reactivity of ϵ - χ - θ iron carbide catalyst phases in fischer-tropsch synthesis: Controlling μ_c [J]. *J Am Chem Soc*, 2010, 132(42): 14928–14941.
- [7] CHANG Q, ZHANG C, LIU C, et al. Relationship between iron carbide phases (ϵ -Fe₂C, Fe₃C₃, and χ -Fe₅C₂) and catalytic performances of Fe/SiO₂ Fischer-Tropsch catalysts[J]. *ACS Catal*, 2018, 8(4): 3304–3316.
- [8] WEZENDONK T A, SUN X, DUGULAN A I, et al. Controlled formation of iron carbides and their performance in Fischer-Tropsch synthesis[J]. *J Catal*, 2018, 362: 106–117.
- [9] HERRANZ T, ROJAS S, PÉREZ-ALONSO F J, et al. Genesis of iron carbides and their role in the synthesis of hydrocarbons from synthesis gas[J]. *J Catal*, 2006, 243(1): 199–211.
- [10] DE SMIT E, BEALE A M, NIKITENKO S, et al. 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]. *J Catal*, 2009, 262(2): 244–256.
- [11] YANG Y, XIANG H, ZHANG R, et al. A highly active and stable Fe-Mn catalyst for slurry Fischer-Tropsch synthesis[J]. *Catal Today*, 2005, 106(1): 170–175.
- [12] Li T, YANG Y, ZHANG C, et al. Effect of manganese on an iron-based Fischer-Tropsch synthesis catalyst prepared from ferrous sulfate[J]. *Fuel*, 2007, 86(7): 921–928.
- [13] Li T, WANG H, YANG Y, et al. Effect of manganese on the catalytic performance of an iron-manganese bimetallic catalyst for light olefin synthesis[J]. *J Energy Chem*, 2013, 22(4): 624–632.
- [14] XU J-D, ZHU K-T, WENG X-F, et al. Carbon nanotube-supported Fe-Mn nanoparticles: A model catalyst for direct conversion of syngas to lower olefins[J]. *Catal Today*, 2013, 215: 86–94.
- [15] LIU Y, CHEN J-F, BAO J, et al. Manganese-modified Fe₃O₄ microsphere catalyst with effective active phase of forming light olefins from syngas[J]. *ACS Catal*, 2015, 5(6): 3905–3909.
- [16] ZHANG Y, MA L, WANG T, et al. MnO₂ coated Fe₂O₃ spindles designed for production of C₅₊ hydrocarbons in Fischer-Tropsch synthesis[J]. *Fuel*, 2016, 177: 197–205.
- [17] Li J, WU L, ZHANG S, et al. The promotional effect of Mn on Fe-based Fischer-Tropsch catalysts for the synthesis of C₅₊ hydrocarbons[J]. *Sustainable Energy Fuels*, 2019, 3(1): 219–226.
- [18] DE SMIT E, WECKHUYSSEN B M. The renaissance of iron-based Fischer-Tropsch synthesis: On the multifaceted catalyst deactivation behaviour[J]. *Chem Soc Rev*, 2008, 37(12): 2758–2781.
- [19] PAALANEN P P, WECKHUYSSEN B M. Carbon pathways, sodium-sulphur promotion and identification of iron carbides in iron-based Fischer-Tropsch synthesis[J]. *ChemCatChem*, 2020, 12(17): 4202–4223.
- [20] PARK E, OSTROVSKI O, ZHANG J, et al. Characterization of phases formed in the iron carbide process by X-ray diffraction, mossbauer, X-ray photoelectron spectroscopy, and raman spectroscopy analyses[J]. *Metall Mater Trans B*, 2001, 32(5): 839–845.
- [21] SANTOS V P, WEZENDONK T A, JAÉN J J D, et al. Metal organic framework-mediated synthesis of highly active and stable Fischer-Tropsch catalysts[J]. *Nat Commun*, 2015, 6(1): 6451.
- [22] LIU X-W, CAO Z, ZHAO S, et al. Iron carbides in Fischer-Tropsch synthesis: Theoretical and experimental understanding in epsilon-iron carbide phase assignment[J]. *J Phys Chem C*, 2017, 121(39): 21390–21396.
- [23] LI Y, LI Z, AHSEN A, et al. Atomically defined iron carbide surface for Fischer-Tropsch synthesis catalysis[J]. *ACS Catal*, 2019, 9(2): 1264–1273.
- [24] FISCHER N, CLAEYS M. In situ characterization of Fischer-Tropsch catalysts: A review[J]. *J Phys D: Appl Phys*, 2020, 53(29): 293001.
- [25] KRESSE G, FURTHMÜLLER J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set[J]. *Phys Rev B*, 1996, 54(16): 11169–11186.
- [26] KRESSE G, FURTHMÜLLER J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set[J]. *Comput Mater Sci*, 1996, 6(1): 15–50.
- [27] BLÖCHL P E. Projector augmented-wave method[J]. *Phys Rev B*, 1994, 50(24): 17953–17979.
- [28] KRESSE G, JOUBERT D. From ultrasoft pseudopotentials to the projector augmented-wave method[J]. *Phys Rev B*, 1999, 59(3): 1758–1775.
- [29] PERDEW J P, BURKE K, ERNZERHOF M. Generalized gradient approximation made simple[J]. *Phys Rev Lett*, 1996, 77: 3865–3868.
- [30] MONKHORST H J, PACK J D. Special points for Brillouin-zone integrations[J]. *Phys Rev B*, 1976, 13(12): 5188–5192.
- [31] METHFESSEL M, PAXTON A. High-precision sampling for Brillouin-zone integration in metals[J]. *Phys Rev B*, 1989, 40: 3616–3621.
- [32] GOEDECKER S. Minima hopping: An efficient search method for the global minimum of the potential energy surface of complex molecular systems[J]. *J Chem Phys*, 2004, 120(21): 9911–9917.
- [33] AMSLER M, GOEDECKER S. Crystal structure prediction using the minima hopping method[J]. *J Chem Phys*, 2010, 133(22): 224104.
- [34] ROY S, GOEDECKER S, HELLMANN V. Bell-Evans-Polanyi principle for molecular dynamics trajectories and its implications for global optimization[J]. *Phys Rev E*, 2008, 77(5): 056707.
- [35] EIVARI H A, GHASEMI S A, TAHMASBI H, et al. Two-dimensional hexagonal sheet of TiO₂[J]. *Chem Mater*, 2017, 29(20): 8594–8603.
- [36] AMSLER M, BOTTI S, MARQUES M A L, et al. Conducting boron sheets formed by the reconstruction of the α -boron (111) surface[J]. *Phys Rev Lett*, 2013, 111(13): 136101.

- [37] FISICARO G, SICHER M, AMSLER M, et al. Surface reconstruction of fluorites in vacuum and aqueous environment[J]. Phys Rev Mater, 2017, 1(3): 033609.
- [38] HENKELMAN G, UBERUAGA B P, JÓNSSON H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths[J]. J Chem Phys, 2000, 113(22): 9901–9904.
- [39] GAO R, LIU X, CAO Z, et al. Carbon permeation: The prerequisite elementary step in iron-catalyzed Fischer-Tropsch synthesis[J]. Catal Lett, 2019, 149(3): 645–664.
- [40] MA H, JIAO Y, GUO W, et al. Predicting crystal morphology using a geometric descriptor: A comparative study of elemental crystals with high-throughput DFT calculations[J]. J Phys Chem C, 2020, 124(29): 15920–15927.
- [41] PANACCIONE G, FUJII J, VOBORNIK I, et al. Local and long-range order of carbon impurities on Fe(100): Analysis of self-organization at a nanometer scale[J]. Phys Rev B, 2006, 73(3): 035431.
- [42] MA H, JIAO Y, GUO W, et al. Machine learning predicts atomistic structures of multielement solid surfaces for heterogeneous catalysts in variable environments[J]. Innovation, 2024, 5(2): 100571.
- [43] ZHANG J-L, MA L-H, FAN S-B, et al. Synthesis of light olefins from CO hydrogenation over Fe–Mn catalysts: Effect of carburization pretreatment[J]. Fuel, 2013, 109: 116–123.
- [44] CAMPOS A, LOHITHARN N, ROY A, et al. An activity and xanes study of Mn-promoted, Fe-based Fischer-Tropsch catalysts[J]. Appl Catal A: Gen, 2010, 375(1): 12–16.
- [45] HAMMER B, NORSKOV J K. Why gold is the noblest of all the metals[J]. Nature, 1995, 376(6537): 238–240.
- [46] STAMENKOVIC V R, MUN B S, ARENZ M, et al. Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces[J]. Nat Mater, 2007, 6(3): 241–247.

锰助剂阻碍铁基催化剂表面渗碳的第一性原理研究

杨 涛^{1,2}, 马 欢^{3,4,5,*}, 刘星辰^{3,4,*}

(1. 北京信息科技大学 北京材料基因工程高精尖创新中心, 北京 102206; 2. 北京信息科技大学 计算机学院, 北京 102206;
3. 中国科学院山西煤炭化学研究所 煤炭高效低碳利用全国重点实验室, 山西 太原 030001; 4. 中国科学院大学, 北京 100049;
5. 中科合成油技术股份有限公司 国家能源煤基液体燃料研发中心, 北京 101400)

摘 要: Fe-Mn 催化剂因其在费托合成 (Fischer-Tropsch Synthesis, FTS) 过程中的工业应用而受到广泛关注。碳的表面吸附与渗入过程在铁基 FTS 催化剂的原位形成中起着关键作用。为深入理解这一过程, 本研究基于密度泛函理论 (Density Functional Theory, DFT) 探索了渗碳早期阶段不同碳沉积 Fe-Mn 合金表面的原子结构、热力学稳定性及电子性质。结果表明, Fe-Mn 合金表面对表面吸附和间隙渗入的碳原子表现出不同的热力学敏感性。结合 DFT 计算与极小值跳跃结构搜索, 研究表明, 渗碳的初始阶段不足以触发表面区域的重构从而难以直接生成表面碳化铁物相。锰的引入在热力学上对渗碳过程具有抑制作用。尽管沉积的碳原子会调控金属的电子结构, 但锰的存在延缓了金属 d 带中心向碳化铁物相的迁移。本研究从原子尺度揭示了 Fe-Mn 催化剂表面在碳沉积过程中的原位演化, 并明确了锰助剂对渗碳行为具有显著影响。

关键词: Fe-Mn 催化剂; 碳吸附与渗碳; 密度泛函理论; 热力学稳定性; 电子结构

中图分类号: O643

文献标识码: A

作者简介:



杨涛(1980), 博士, 助理研究员, 主要从事数据驱动的铁基催化材料体系、能源转化材料体系的基础研究工作, ytyangmei@bistu.edu.cn。



刘星辰(1984), 博士, 研究员, 研究方向为碳基小分子催化转化的多尺度模拟, 基于数据驱动研究范式和人工智能的催化剂设计, liuxingchen@sxicc.ac.cn。



马欢(1994), 博士, 研究方向为基于理论模拟和数据驱动的能源转化催化材料体系基础研究, mahuan201@mails.ucas.ac.cn。