Visiting CH₄ formation and C₁ + C₁ couplings to tune CH₄ selectivity on Fe surfaces

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ABSTRACT

To tune CH₄ selectivity of Fe-based Fischer-Tropsch synthesis (FTS) in the initial stage is of prime scientific and industrial importance to further improve the catalyst performance. Herein, distribution of CH₄ selectivity on the metallic Fe nanoparticle is predicted by DFT calculations and micro-kinetics analysis about the competition between C₁ hydrogenations and C₁ + C₁ couplings on abundant Fe surfaces including Fe(1 0 0), Fe(1 1 0), Fe(1 1 1), Fe(2 1 1), and Fe(3 1 0). The results show that HCO mechanism (HCO → CH + O) is an available source of C₁ species apart from CO direct dissociation. These Fe surfaces exhibit high effective barriers for CH₄ formation, which is linearly correlated to the thermal stability of CH₂ species. However, carbon chain prolongation on the more stable surfaces greatly depends on the coupling of C and CH species. On the less stable Fe(1 1 1) surface, the CO + C coupling is the main route for chain prolongation. Utilizing the effective barrier difference between the CH₄ formation and the most feasible C₁ + C₁ coupling as a descriptor of CH₄ selectivity, it is quantified that CH₄ selectivity decreases in sequence of Fe(1 0 0) > Fe(2 1 1) > Fe(1 1 0) > Fe(3 1 0) > Fe(1 1 1). It is revealed that thermal stability of the CH₂ species and exposition of the Fe facets could play essential roles in tuning CH₄ selectivity. Trying to expand the area of Fe(2 1 1), Fe(3 1 0) and especially Fe(1 1 1) surfaces would greatly suppress CH₄ selectivity without a decrease of activity. This work provides new insights and design principles for the Fe-based FTS catalysts.

1. Introduction

Iron is an attractive heterogeneous catalyst used in industrial-scale chemistry processes, like N₂ hydrogenation and CO hydrogenation [1,2]. A number of studies have demonstrated that Fe (1 1 1) is the active surface for N₂ hydrogenation [3–5]. CO is an isoelectronic species of N₂, and its hydrogenation is an essential process of Fischer-Tropsch synthesis (FTS) for coal liquefaction and abiogenic petroleum formation. However, CO hydrogenation is much more complicated concerning the catalytic activity and selectivity [1,3].

Under syngas (CO + H₂) atmosphere, the compositions of Fe catalysts are complex and dynamically convertible among iron oxides, iron carbides, and metallic iron, depending on instantaneous local environment [6,7]. Iron carbide is acknowledged to be the main active phase, but its surface structure is dynamically evolved and even partly oxidized during FTS. Before FTS reactions, Fe₂O₃ is reduced to bcc metallic iron (α-Fe), making the catalysts exhibit metallic properties at the initial stage of FTS. Existence of metallic Fe was verified by the Mössbauer spectra during FTS over metallic Fe catalyst at 513 K [8], but metallic iron is easy to be carburized and is hardly present in working FT catalysts, in particular when operated at higher temperatures. Generally, a low CH₄ selectivity correlates with high yields of long chain hydrocarbons in FTS, which is an important factor to evaluate the selectivity of a FT catalyst. In this work, distribution of CH₄ selectivity on the metallic Fe nanoparticle is studied by the competition between CH₄ formation and chain prolongation, to understand CH₄ selectivity of Fe-based FTS in the initial stage. The significance lies in that metallic Fe
could directly reflect the initial performance of the Fe-based FTS catalysts. The carbon source to form CH₄ and carbon chains is CO dissociation in FTS. Experimentally, Erley et al. [9] studied FTS reactions on Fe(1 1 0) at 300 °C with a H₂/CO ratio of 10/1 at the atmospheric pressure (atm), and observed the formation of surface C, CH, CH₂, and CH₃ species at a low CO conversion rate. Gonzalez et al. [10] found that the sputtered Fe(1 1 0) with argon ion exhibits a higher CO conversion rate than the annealed Fe(1 1 0), proposing that the higher activity of Fe could originate from surface defects. Theoretically, energy barriers of CO direct dissociation on less stable Fe surfaces except the most stable Fe(1 1 0) surface [11,12] are very close to those on vacancy sites of iron carbides [13–16]. CO dissociation on Fe(1 0 0) [17,18], Fe(1 1 1) [19] and Fe(3 1 0) [16] could be accelerated by the H-assisted mechanism via HCO intermediate \((\text{CO} + \text{H} \rightarrow \text{HCO} \rightarrow \text{CH} + \text{O})\). Hydrogenation of single carbons \((\text{C}_1)\) dictates the rate of CH₄ formation. On Fe(1 0 0), CH species was reported to be abundant [20], but CH₄ formation by hydrogenation of surface C dissociated directly from CO is more favorable than the CO successive hydrogenation [21]. The aforementioned calculations were performed with different modes and methods, and they can't be easily compared. Therefore, it is necessary to perform systematic investigation on the C₁ generation via CO dissociation using the same mode and method to ensure the accuracy and consistence.

The FTS products follow the so-called Anderson-Schulz-Flory (ASF) distribution [22]. However, it is hard to correlate the CH₄ selectivity with surface structures of the catalysts. CH₄ formation was reported to be more favorable on Fe₃C(C1)/Fe₃C(1 1 0) and Fe₅C₂(1 0 0) than that on Fe₃C(C0)/Fe₃C(1 0 0) [13], only based on the stepped hydrogenations of surface C atoms without considering competition with chain prolongation. The surface features (facet, step, defect, electronic feature) among the iron carbides may play important roles in determining the CH₄ formation. Wezendonk et al. [23,24] reported that Fe₅C₂ is featured with a lower CH₄ selectivity, compared to Fe₅C₂. They ascribed the difference in CH₄ selectivity to the different ratio of the atomic C/Fe numbers, the different active sites and the electron density on the iron carbide surfaces, constructed by the interstitial occupation of the carbon atoms. However, Krebs et al. [25] investigated the CO hydrogenation on polycrystalline Fe surfaces (clean Fe foil) in a CO/H₂ mixture at 1 atm and 460–750 K, finding that CH₄ was the dominant product. Erley et al. [9] also reported that CH₄ was the main product with trace of C₁, C₂ hydrocarbons on Fe(1 1 0) at 300 °C with a H₂/CO ratio of 10/1 at 1 atm, and advanced that FTS proceeds through the surface carbon hydrogenation. Compared to the iron carbides, the high CH₄ selectivity on the Fe surfaces is usually attributed to the higher hydrogen coverage on the Fe surfaces [24]. Cheng et al. [26] have used the effective barrier (\(E_{\text{act},\text{eff}}\)), which is defined as the energy difference between the highest transition state and the most stable species [13], to evaluate CH₄ selectivity, concluding that CH₄ selectivity on Fe(2 1 0) is lower than that on Ru(0 0 1) and Rh(0 0 1) but is higher than that on Co(0 0 1) and Cu(0 0 1). However, CH₄ formation was studied to be observed on other Fe surfaces like Fe(2 1 1) and Fe(3 1 0), both of which account for a big area on the surface of a Fe-Wulff structure. CH₄ formation by the C₁ hydrogenation is in competition with the C₁ + C₁ coupling with double-carbon species (\(C_2^h\)) produced (C₁ + C₁ → C₂). The competition closely depends on the surface structure of iron catalyst. Three kinds of C₂ formation mechanisms have been reported in literatures, as the carbide mechanism [27], the hydroxyxcarbene mechanism [28] and the CO-insertion mechanism [29]. Chain initiation mechanism on iron carbides might be different from one surface to another [30]. That might be also true on Fe surfaces. For example, on Fe(1 0 0), the most favorable C₂ species contain the acetylenic carbon at the \(\alpha\)-position (i.e., C + CH, C + CH₂, and C + CH₃) [31]. On Fe(1 1 1) and Fe(2 1 0) [32,33], the CH + CH and C + CH₂ couplings were regarded as the most likely coupling pathways, respectively. However, on Fe(7 1 0) [34], the C hydrogenation towards CH₃ formation precedes over the formation of CH₂CH₁ and CH₂CO \((i = 0–3)\). All these previous reports are valuable in revealing the C₂ formation mechanisms, but CH₄ selectivity on various Fe surfaces remains elusive.

This work focuses on CH₄ selectivity in the initial stage of Fe-based FTS by systematic calculations of the CH₄ formation and C₁ + C₁ couplings on abundant Fe surfaces. Firstly, generation of C₁ species through breaking C–O bond in CO molecular is studied by three mechanisms, including direct route and H-assisted route via HCO intermediate (HCO mechanism) and via COH intermediate (COH mechanism). Secondly, the stepped hydrogenation of the dissociated C atom is studied to explore the ability to form CH₄ as well as the most stable C₁ species on these Fe surfaces. Subsequently, the most feasible C₁ + C₁ coupling pathways are picked out from both the carbide mechanism (CH₁ + CH₁ → CH₂CH₁, \(i = 0–3\)) and the CO-insertion mechanism (CO + CH₁ → COCH₂, \(j = 0–3\)). Finally, our interest focuses on competition between CH₄ formation and C₁ + C₁ couplings, which shed lights on distribution of the CH₄ selectivity on surface structures of the Fe nanoparticles.

2. Methods and models

2.1. Methods

All calculations were performed with the plane wave based pseudo-potential code in Vienna ab initio simulation package (VASP) [35,36]. The electron-ion interaction was described with the projector augmented wave (PAW) method [37,38]. The electron exchange and correlation energy was treated within the generalized gradient approximation in the Perdew-Burke-Ernzerhof formalism (GGA-PBE) [39], which is very well applicable in studying the reactions involved in FTS mechanism on different Fe surfaces [11,15,16]. The Kohn-Sham one-electron states were expanded in a plane wave basis set up to 400 eV and a second-order Methfessel-Paxton [40] electron smearing with \(\sigma = 0.2\) eV was used. Spin-polarization was included for ferromagnetic iron systems. The geometry optimization was done when forces became smaller than 0.02 eV/Å and the energy difference was lower than \(10^{-4}\) eV. Transition states on iron surfaces were located using the nudged elastic band method [41] to evaluate the energy barriers. The vibrational frequencies were analyzed to evaluate whether a stationary point is a minimum state without imaginary frequencies or a transition state with only one imaginary frequency.

2.2. Models

The optimized equilibrium constant for bulk bcc iron has been determined as 2.83 Å with a 15 × 15 × 15 k-point grid generated automatically using the Monkhorst-Pack method (Table S1), which is in good agreement with other calculated values of 2.84 Å [11] and 2.83 Å [12] and experimental value of 2.87 Å [42]. The Wulff structure (Fig. S1) of Fe predicted in the previous work [43] is covered by seven surfaces with the decreasing stability sequence: \((1 1 0) > (1 0 0) > (3 1 0) > (2 1 0) > (2 1 1) > (3 2 1) > (1 1 1)\). We focus on five surfaces of Fe(1 0 0), Fe(1 1 0), Fe(1 1 1), Fe(2 1 1) and Fe(3 1 0). For these Fe surfaces, the super cells of the p \((4 \times 4), (r(4 \times 4), p(3 \times 3), p(3 \times 3)\), and \(p(4 \times 2)\) were used, respectively with four, four, ten and eleven atomic layers. The lowest one layer was fixed for Fe(1 0 0) and Fe(1 1 0), and the lowest two layers were fixed for Fe(1 1 1), Fe(2 1 1) and Fe(3 1 0). The
of H atoms contained in C1 species; \( A_{\text{CH}_2} \) and \( A_{\text{COH}} \) are the pre-exponential factors and the effective barriers for \( \text{CH}_4 \) and \( \text{CH}_3 \) couplings and \( \text{CO} + \text{CH}_4 \) couplings, respectively.

\[
r_{\text{CH}_3+\text{CH}_4} \approx A_{\text{ij}} \exp\left(-E_{\text{eff,ij}}^{\text{CH}_4}/RT\right) \theta_2
\]  

(6)

\[
r_{\text{CO}+\text{CH}_4} \approx A_{\text{ij}} \exp\left(-E_{\text{eff,CO}}^{\text{CH}_4}/RT\right) \theta_3 \theta_0 \theta_c
\]  

(7)

According to the results of Hu and coworkers\,[26,33,45,46], the calculation of effective barriers is based on the potential energy of C atoms. For the \( \text{CH}_4 + \text{CH}_4 \) coupling, it is the happen when the \( \text{CH}_4 \) and \( \text{CH}_3 \) species have been produced by the \( C + i\text{H} \to \text{CH}_4 \) and \( C + i\text{H} \to \text{CH}_3 \) respectively, and thus the effective barrier \( E_{\text{eff,ij}}^{\text{CH}_4} = E_{\text{ij}} + E_p \) where \( E_{\text{ij}} \) is the reaction barrier of the \( \text{CH}_4 + \text{CH}_3 \) coupling, \( E_i \) and \( E_j \) are the reaction energies for the \( C + i\text{H} \to \text{CH}_4 \) and \( C + i\text{H} \to \text{CH}_3 \) respectively. For the \( \text{CO} + \text{CH}_4 \) coupling, the coupled CO is regarded to be from the syngas (CO + H\(_2\)), and the effective barrier \( E_{\text{eff,CO}}^{\text{CH}_4} = E_{\text{CO}} + E_p \) where \( E_{\text{CO}} \) is the reaction barrier of the \( \text{CO} + \text{CH}_4 \) coupling.

The CH\(_4\) selectivity \( (S_{\text{CH}_4}) \) is calculated according to the ratio of \( r_{\text{CH}_4}/r_{\text{C1+C1}} \) in the Eq. (8) for carbide mechanism and the Eq. (9) for CO-inserted mechanism.

\[
S_{\text{CH}_4} \approx A_{\text{key}}/A_{\text{ij}} \exp\left[-(E_{\text{eff,CH}_4} - E_{\text{ij}})\right]/(1/RT) \theta_2
\]  

(8)

\[
S_{\text{CH}_4} \approx A_{\text{key}}/A_{\text{ij}} \exp\left[-(E_{\text{eff,CH}_4} - E_{\text{ij}})\right]/(1/P_{\text{CO}})
\]  

(9)

3. Results and discussion

3.1. Surface structures

The top views and possible adsorption sites of the five iron surfaces of \( (1 \ 0 \ 0) \), \( (1 \ 1 \ 0) \), \( (1 \ 1 \ 1) \), \( (2 \ 1 \ 1) \) and \( (3 \ 1 \ 0) \) are shown in Fig. 1. Fe\((1 \ 0 \ 0)\) has top (T), bridge (B) and 4-fold hollow (4F) sites, Fe\((1 \ 1 \ 0)\) has top (T), short-bridge (SB), long-bridge (LB) and 3-fold (3F) sites. Fe\((1 \ 1 \ 1)\) has top (T), bridge (B), shallow-hollow (SH), deep-hollow (DH), 4-fold hollow (4F) and bridge (B) sites. Fe\((2 \ 1 \ 1)\) has top (T), bridge (B), 3-fold (3F, 3F\(_2\)) and 4-fold (4F) sites. Fe\((3 \ 1 \ 0)\) has top (T), bridge site (B), 3-fold (3F, 3F\(_2\)), 4-fold (4F) sites and 5-site constructed by 4F-site and 3F\(_2\)-site.

3.2. Stability of involved species

For C\(_1\) species of C, CO, \( \text{CH}_3 \) and \( \text{C}_2 \) species of \( \text{COCH}_3 \) and \( \text{CH}_3\text{CH}_3 \) \( (i = 0–2, j = 0–3) \), their adsorption on these Fe surfaces was computed. The configurations and corresponding adsorption energies are given in Fig. S2. For \( \text{CH}_4 \), \( (i = 0–3) \) and \( \text{CH}_3\text{CH}_3 \), \( (i = 0–2) \), as shown in Fig. 2(a), \( E_{\text{ads}} \) is decreased with the \( i \) increasing on the same Fe surface. From \( \text{CH}_3 \), \( (i = 0–3) \) to \( \text{CH}_3\text{CH}_3 \), \( (i = 0–2) \), \( E_{\text{ads}} \) is reduced by about 2.0 eV. It’s a common sense that hydrogenation and carbon
chain propagation will weaken the C bonding ability for CH$_i$ species.

However, it's hard to quantitatively measure the adsorption strength only by coordination numbers of the C atoms, when the Fe–C bonds without the same length. The sum of bond valences (SBV) is usually used for the bonds between the adsorbate and the surface (details in SI) [47], to deliver information on the bond length and the bond number. The variation of adsorption energies can be understood partly from the bond order conservation principle, apart from the repulsion of C–H bonds with the surface. The adsorption energy contains three parts: the bonding energy, the deformed energy of the Fe surface and the adsorbate. The adsorption energy becomes more negative with deformed energy of the Fe surface and the adsorbate. The adsorption energy on these Fe surfaces are shown in Figs. S3 to S7.

The reaction barriers (without ZPE corrections) for direct mechanism (CO $\rightarrow$ TS1 $\rightarrow$ C + O) on the studied 4H pre-covered Fe surfaces are in Table S4. On the 4H pre-covered Fe(1 0 0) surface, the barrier is 1.08 eV, which is close to those of 1.03, 1.09 and 0.90 eV on the clean Fe(1 0 0) surface, respectively reported by Wang et al. [11] and Elahifard et al. [15] and Amaya-Roncancio et al. [17]. On the 4H pre-covered Fe(1 1 0), Fe(1 1 1) and Fe(2 1 1) surfaces, the barriers are 1.47, 1.11 and 1.17 eV, respectively, which are in agreement with the literature values of 1.52, 1.17 and 1.06 eV on the clean Fe(1 1 0), Fe(1 1 1) and Fe(2 1 1) surfaces, respectively, reported by Wang et al. [11]. On the 4H pre-covered Fe(3 1 0) surface, the barrier of 0.98 eV is the same with that reported by Wang et al. [11], and is very close to other literature values of 0.91 and 1.01 eV on the clean Fe(3 1 0) surface, respectively reported by Sorescu et al. [12] and Elahifard et al. [16]. Moreover, the 4H pre-covering changes the reaction energy just by 0.1–0.2 eV except that on Fe(3 1 0). On Fe(3 1 0), O atom at 4F-site is more stable by 0.62 eV than 3F1-site, which is responsible for the difference in reaction energy from the literature (~0.97 vs. ~0.35 eV, respectively). Therefore, the 4H pre-covering has no obvious effect on the CO direct dissociation in our work.

3.3. Generation of C$_1$ species

In the process of FTS, C$_1$ species is generated through breaking C–O bond of the adsorbed CO on catalyst surface. It is considered by the CO dissociation routes, including direct mechanism and H-assisted mechanism, as is schemed in Fig. 3. According to the first hydrogenation on C-end or O-end of adsorbed CO, the H-assisted mechanism could proceed via the HCO intermediate (H + CO $\rightarrow$ TS6 $\rightarrow$ HCO $\rightarrow$ TS7 $\rightarrow$ HC + O) and the COH intermediate (H + CO $\rightarrow$ TS8 $\rightarrow$ COH $\rightarrow$ TS9 $\rightarrow$ C + OH). The second hydrogenation is also calculated by considering the H$_2$CO intermediate (HCO + H $\rightarrow$ TS10 $\rightarrow$ H$_2$CO $\rightarrow$ TS11 $\rightarrow$ CH$_2$ + O) and the HCOH intermediate (HCO + H $\rightarrow$ TS12 $\rightarrow$ HCOH $\rightarrow$ TS13 $\rightarrow$ CH + OH). The PESs of CO dissociation on these Fe surfaces are shown in Figs. S3 to S7.

![Fig. 2.](image_url) (a) Comparisons about the adsorption energy ($E_{ads}$); (b) Variations about $E_{ads}$ ~ SBV (SBV is the sum of bond valences) for the most stable CH$_i$ ($i = 0–3$) and CH$_{2i}$ ($i = 0–2$) species on the five Fe surfaces. The solid line is a line regression.
CH species from HCO → CH + O is alternative choice to produce CH₄. Apparent barriers of 1.40 and 1.74 eV for HCO → CH + O on Fe(1 0 0) and Fe(1 1 1), are close to the values of 1.45 eV on Fe(1 0 0) obtained by Tian et al. [21], 1.69 and 1.74 eV on Fe(1 1 1) obtained by Li et al. [32] and Huo et al. [19], respectively. Meanwhile, apparent barriers for HCO → CH + O on Fe(1 0 0) and Fe(1 1 1) are higher than those of 1.81 and 1.27 eV for CH₄ formation, respectively, and those of 1.59 and 1.26 eV on Fe(1 1 1) and Fe(3 1 0) are lower than those of 1.80 and 1.90 eV for CH₄ formation, respectively. The results indicate that HCO → CH + O could be an alternative CH source for CH₄ formation on Fe(1 1 0), Fe(2 1 1) and Fe(3 1 0), rather than on Fe(1 0 0) and Fe(1 1 1).

CO direct dissociation could be the main C source. Microkinetics analysis on its rate (r_{CO}) by the L-H mechanism assumption is performed under the temperature of T = 500 K and 600 K and low coverage [44] (evaluated by CO pressure of P_{CO} = 3.0 × 10⁻⁵ Pa) conditions (more details in SI). Fig. 4 and Table S5 show that r_{CO} is increased by at least a factor of 10⁴, with T from 500 K to 600 K. The less stable Fe(1 0 0), Fe(1 1 1), Fe(2 1 1) and Fe(3 1 0) surfaces exhibit much higher activity than the most stable Fe(1 1 0) surface. Erley et al. [9] and Gonzalez et al. [10] found that in the absence of H₂ gas, CO conversion is improved on the Fe(1 1 0) with surface defects generated by argon ion sputtering. Those defects could be featured with the surface sites like those for CO dissociation on the less stable Fe surfaces.

### 3.4. CH₄ formation

PES of CH₄ formation by C stepped hydrogenation, as is shown in Fig. 5, are calculated on the five iron surfaces. Detailed structures and energies in PES for IS, TS and FS, are given in Figs. S3 to S7. The reaction barrier and reaction energy for each step are listed in Table S8.

On Fe(1 0 0), each hydrogenation step in the CH₄ formation route is endothermic by 0.46, 0.63, 0.25 and 0.03 eV, respectively. The barrier of 0.84 eV for CH₂ + H → CH₃ is highest, which is a little different from the result by Tian et al. [21] due to different hydrogenation sequence but in agreement with that by Source et al. [48].

On Fe(1 1 0), the C-stepped hydrogenation route occurs with reaction energies of 0.61, 0.60, 0.51 and 0.25 eV, respectively, and hydrogenation barriers are 0.85, 0.72, 0.71 and 1.01 eV, respectively. Thus, CH₃ hydrogenation exhibits the highest barrier and is endothermic least.

On Fe(1 1 1), the C-stepped hydrogenations are endothermic by 0.01, 0.58, 0.39 and 0.30 eV, respectively. CH₂ + H → CH₃ has the highest barrier of 1.08 eV. Because CH + H → CH₂ is nearly neutral in thermo but CH + H → CH is strongly endothermic, CH coverage could be slightly lower than C coverage.

On Fe(2 1 1), the C-stepped hydrogenation steps are endothermic by 0.18, 0.49, 0.25 and 0.50 eV, respectively, and with the barriers of 0.81, 1.06, 0.92 and 1.16 eV, respectively. Thus, The TS energy for CH₃ hydrogenation is highest on the PES. CH + H → CH₂ is strongly endothermic and consequently, atomic C and CH species could be more than CH₂ species.

On Fe(3 1 0), the C-stepped hydrogenations are endothermic by 0.52, 1.01, 0.37 and 0.36 eV, respectively. CH + H → CH₂ is strongly endothermic and its barrier is very close to reaction energy, making CH₂ species unstable. CH₃ hydrogenation has the highest barrier of 1.18 eV.

The coordinate of C + 4H → CH₄ on the studied Fe surfaces shows an increasing tendency in total energies. The tendency mainly depends on the thermo stability of CHᵢ (i = 0–3), among which the C atom is most stable. The tendency is also exhibited on metal surfaces of Ru(0 0 1), Co(0001) and Re(0 0 1) [33], as well as carbide surfaces of Fe₅C₂(5 1 0) [45] and Fe₅C₂(1 0 0) [46]. However, the tendency is not true on the metal surfaces of Rh(2 1 1) [33] and Ni(2 1 1) [49] and the carbide surfaces of CoC(0 0 1) [46], Fe₅C(0 1 1), Fe₅C(0 0 1) and Fe₅C(1 0 0) [13].

CH₃ hydrogenation, with the highest TS energy on each PES, determines the E_{a_{eff},CH₄} with respect to the C atom, which is 2.16, 2.74, 1.81, 2.08 and 3.08 eV on Fe(1 0 0), Fe(1 1 0), Fe(1 1 1),
Fe(2 1 1) and Fe(3 1 0), respectively. The $E_{a\text{,CH4}}$ values on Fe (1 0 0) and Fe(1 1 1) are in agreement with those of 2.16 eV on Fe (1 0 0) reported by Tian et al. [21] and 2.08 eV on Fe(1 1 1) reported by Li et al. [32], respectively. From the micro-kinetics given in Eq. (5), CH$_4$ formation rate ($r_{\text{CH4}}$) is mainly governed by $E_{a\text{,CH4}}$. As is estimated at 600 K, a change of 0.1 eV in $E_{a\text{,CH4}}$ will cause a 10-fold change in $r_{\text{CH4}}$. Seen from Fig. 6, $E_{a\text{,CH4}}$ values on the Fe surfaces are higher than those on Co(0 0 1), Ni(2 1 1), Ru(0 0 1) and Rh(0 0 1) [33,49]. In particular, with the Fe/C ratio increasing from the bulk Fe carbides to the bulk Fe, an increase of $E_{a\text{,CH4}}$ is shown on Fe$_2$C(0 1 1) < Fe$_5$C$_2$(0 0 1) < Fe$_3$C(0 0 1) < Fe$_4$C(1 0 0) < Fe(1 1 0), which are regarded as the most stable surface on the individual crystal [13]. Therefore, it’s promising to further slowdown the CH$_4$ formation rate by reducing the C concentration in Fe carbides.

It has been reported that the $E_{a\text{,CH4}}$ on Fe carbides is linearly correlated to the charge of surface carbon ($q_C$) [13]. In Fe carbides, Fe atoms exhibit positive charge, and C atoms have negative charge. On metallic Fe, the adsorbed C atom is also negatively charged (Table S7). Both the $E_{a\text{,CH4}}$ and $E_{r\text{,CH4}}$ are not directly correlated with the $q_C$ of adsorbed C atom. However, the $E_{a\text{,CH4}}$ is linearly correlated to the $E_{r\text{,CH4}}$ with $R^2 = 0.87$ in Fig. 7(a) and the $E_{r\text{,CH4}}$ with $R^2 = 0.82$ in Fig. 7(b), respectively. The linear correlations are ascribed to the strong endothermic reactions for CH$_4$ and CH$_2$. With these correlations, we could predict the reactivity of CH$_4$ formation on Fe surfaces.

### 3.5. C$_1 + C_1$ couplings

The C$_1 + C_1$ couplings are studied from carbide mechanism (CH$_i$ + CH$_j$ → CH$_i$CH$_j$, $i$ and $j = 0–3$) and CO-insertion mechanism (CO + CH$_j$ → COCH$_j$, $j = 0–3$). The corresponding IS, TS and FS structures are given in Fig. S8 to S12. The reaction barriers ($E_r$) and reaction energies ($E_a$) are listed in Table S8. Comparisons between energy profiles of the C$_1 + C_1$ coupling pathways and the CH$_4$ formation are depicted in Fig. 8(a–e). The details on the energy profiles are illustrated in Fig. S13. The next is to explore the most feasible coupling.

Compared to the CH$_4$ formation on Fe(1 0 0), the carbide mechanisms are difficult to happen due to the higher effective barrier, and the CO-insertion mechanisms are also difficult to proceed due to being strongly endothermic. Relatively, thermo advantage of the C + CH coupling makes it most feasible.

With regards to the competition on Fe(1 1 0), the CH + CH coupling with a lower effective barrier than CH$_4$ formation (2.17 vs. 2.74 eV), and it is least endothermic (0.18 eV) among all the carbide mechanisms. The CO-insertion mechanisms are strongly endothermic and thus infeasible. Therefore, the CH + CH coupling is most feasible.

On Fe(1 1 1), several coupling pathways have lower effective barriers than CH$_4$ formation (1.81 eV). However, the CO-insertion mechanism by the CO + C coupling has the lowest effective barrier of 0.47 eV and is nearly neutral in thermo, which remains true for the less stable iron carbides surfaces like Fe$_3$C(1 0 0) and Fe$_5$C$_2$(0 0 1) [50]. Therefore, the most feasible pathway is the CO + C coupling.

On Fe(2 1 1), the C + CH coupling has a lower effective barrier than CH$_4$ formation (1.47 vs. 2.08 eV), is just endothermic by 0.07 eV and the reactants has an energetic advantage, among all the carbide pathways. The CO-insertion mechanisms are strongly endothermic and thus infeasible. Therefore, the C + CH coupling is more feasible.

For the competition on Fe(3 1 0), the C + CH coupling has a lower effective barrier than CH$_4$ formation (2.45 vs 3.08 eV), and it is less endothermic than other carbide pathways. Meanwhile, the CO-insertion mechanisms are inaccessible in thermo. Therefore, the C + CH coupling is most feasible.

From the micro-kinetics analysis based on the Eqs.(6) and (7), the rate of C$_1 + C_1$ couplings is mainly dominated by effective barriers in kinetic. Beside the lower effective barrier, coupling feasibility is also influenced by product stability in thermo. Taking the carbide pathways on Fe(1 1 0) as an example, the C + C coupling exhibits the fastest rate (Fig. S14 and Table S6). Compared to the C + C coupling, the effective barrier of CH + CH coupling is just higher by 0.29 eV (1.88 vs. 2.17 eV), but its reaction energy is much lower by 1.04 eV (0.18 vs. 1.22 eV), indicating the great thermo advantage of the formed CHCH species over the CC product. Therefore, the CH + CH coupling is more feasible.
Fig. 8. Energy profiles of the carbide mechanism, the CO-inserted mechanism and the CH₄ formation: (a–e) are for Fe(100), Fe(110), Fe(111), Fe(211) and Fe(310), respectively.
3.6. CH₄ selectivity

According to Eqs. (8) and (9), CH₄ selectivity mainly depends on the effective barriers difference between the CH₄ formation and the most feasible C₁ + C₁ coupling \((\Delta E_{a,\text{eff}} = E_{a,\text{CH4}} - E_{a,\text{C1+C1}})\). Herein, \(\Delta E_{a,\text{eff}}\) is used to evaluate CH₄ selectivity. The increase of \(\Delta E_{a,\text{eff}}\) value suggests a decrease of CH₄ selectivity. The most feasible C₁ + C₁ coupling and the corresponding energies are listed in Table 1, on these Fe surfaces and other reported surfaces.

As is illustrated in Fig. 9, among the five Fe surfaces, the Fe(1 0 0) and Fe(1 1 1) surfaces have the smallest and biggest values of \(\Delta E_{a,\text{eff}}\) (−0.08 and 1.34 eV, respectively), and thus could be featured with the highest and the lowest CH₄ selectivity, respectively. The Fe(1 0 0), Fe(2 1 1) and Fe(3 1 0) surfaces have the middle CH₄ selectivity. It implies that exposition of the Fe facets could play an essential role in tuning CH₄ selectivity. Trying to expand the area of Fe(2 1 1), Fe(3 1 0) and especially Fe(1 1 1) surfaces would suppress CH₄ selectivity.

For the most stable surface of Fe, Ru and Co, the Fe(1 1 0) surface has a higher \(\Delta E_{a,\text{eff}}\) than the Ru(0 0 1) and Co(0001) surfaces (0.54, 0.10 and −0.24 eV, respectively) [33]. It could provide an understanding for the lower CH₄ selectivity on Fe-based catalysts than those on Ru-based and Co-based catalysts. The Fe(1 1 1) surface has a higher \(\Delta E_{a,\text{eff}}\) than the Fe₅C₂(5 1 0) surface (1.34 vs. 0.73 eV), and the latter was reported to suppress CH₄ selectivity [45]. Therefore, Fe is promising for getting a lower CH₄ selectivity in FTS.

4. Conclusion

Spin-polarized DFT method is utilized to investigate CH₄ formation and C₁ + C₁ couplings on iron surfaces of (1 0 0), (1 1 0), (1 1 1), (2 1 1) and (3 1 0), to reveal the distribution of CH₄ selectivity on Fe catalysts in the initial stage of Fe-based FTS. We find that CH₄ selectivity is tunable from CH₂ species stability and Fe facets exposed.

Generation of C₁ species is considered at first. It is found that the atomic C produced by direct CO dissociation is a main carbon source. Fe(1 1 0) is obviously less active than the other studied surfaces. Meanwhile, on Fe(1 1 0), Fe(2 1 1) and Fe(3 1 0), route H by means of HCO → CH + O could be an alternative CH source.

The study on CH₄ formation by the stepwise hydrogenation of C shows that the total energies gradually increase along the coordinate of C + 4H → CH₄. The effective barriers increase in sequence of Fe(1 1 1) < Fe(1 0 0) < Fe(2 1 1) < Fe(1 1 0) < Fe(3 1 0), showing a positive linear correlation to the thermal stability of CH₂ species.

The C₁ + C₁ couplings pathways are explored from carbide mechanism and CO-insertion mechanism. The most feasible pathway is through the CO + C coupling on Fe(1 1 1), the CH + CH coupling on Fe(1 1 0) and the C + CH coupling on Fe(1 0 0), Fe(2 1 1) and Fe(3 1 0).

CH₄ selectivity is described by the effective barrier difference between the CH₄ formation and the most feasible C₁ + C₁ coupling. The Fe(1 0 0) and Fe(1 1 1) surfaces exhibit the highest and the lowest CH₄ selectivity, respectively. The Fe(1 1 0), Fe(2 1 1) and Fe(3 1 0) surfaces have a middle CH₄ selectivity.

The results imply that thermal stability of the CH₂ species and exposition of the Fe facets could play essential roles in tuning CH₄ selectivity. It is possible to suppress CH₄ selectivity without a decrease of activity, by making CH₂ species stable and expanding the exposed area of Fe(2 1 1), Fe(3 1 0) and especially Fe(1 1 1) surfaces. Fe metal is predicted to have a lower CH₂ selectivity than Fe carbides, and could exhibit a lower CH₄ selectivity in FTS. It should further be pointed out that metallic Fe is hardly present in current operando FTS. These insights might be helpful to design Fe-based FTS catalysts.

Appendix A. Supplementary material

Details of bond valence concept and micro-kinetics analysis; Influence of k-points on the bcc-Fe lattice parameters and total energy (Table S1); Influence of slab thickness and k-points on adsorption and reaction (Table S2 and Table S3); Structure and energy parameters about CO direct dissociation (Table S4); Kinetic parameters about CO direct dissociation (Table S5) and C₁ + C₁ couplings (Table S6); Effective Barrier, reaction energy (Er_CH4 and Er_CH2) and Bader Charge (qc) of adsorbed C on the Fe surfaces (Table S7); reaction barriers and reaction energies for C₁ hydrogenation and C₁ + C₁ coupling on the Fe surfaces (Table S8); Wulff structure of iron nanoparticle (Fig. S1); Configurations and adsorption energy of involved species (Fig. S2); Structures of stationary points and reaction barriers \((E_r, eV)\) for CH₄ formation and C₁ species generation (Figs. S3 to S7); energy barrier, reaction energy and structures about IS, TS and FS for C₁ + C₁ couplings (Figs. S8–S12); Illustration of the energy profiles for C₁ + C₁ coupling pathways and CH₄ formation (Figures S13); CH₁ + CH₁ coupling rate on the Fe surfaces (Fig. S14). Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.03.007.

Acknowledgments

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Table 1

<table>
<thead>
<tr>
<th>Surface</th>
<th>(E_{a,\text{eff}}/C0)</th>
<th>(C_1 + C_1)</th>
<th>(E_{a,\text{eff}}/C0)</th>
<th>(\Delta E_{a,\text{eff}})</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1 0 0)</td>
<td>2.16</td>
<td>C + CH</td>
<td>2.28</td>
<td>−0.08</td>
<td>This work</td>
</tr>
<tr>
<td>Fe(1 1 0)</td>
<td>2.74</td>
<td>CH + CH</td>
<td>2.17</td>
<td>0.54</td>
<td>This work</td>
</tr>
<tr>
<td>Fe(1 1 1)</td>
<td>1.81</td>
<td>CO + C</td>
<td>0.47</td>
<td>1.34</td>
<td>This work</td>
</tr>
<tr>
<td>Fe(2 1 1)</td>
<td>2.08</td>
<td>C + CH</td>
<td>1.47</td>
<td>0.41</td>
<td>This work</td>
</tr>
<tr>
<td>Fe(3 1 0)</td>
<td>3.08</td>
<td>C + CH</td>
<td>2.45</td>
<td>0.63</td>
<td>This work</td>
</tr>
<tr>
<td>Fe(2 1 1)</td>
<td>2.13</td>
<td>C + CH</td>
<td>2.19</td>
<td>−0.06</td>
<td>33</td>
</tr>
<tr>
<td>Fe₅C₂(5 1 0)</td>
<td>2.39</td>
<td>C + C</td>
<td>1.66</td>
<td>0.73</td>
<td>45</td>
</tr>
<tr>
<td>Fe₅C₂(1 0 0)</td>
<td>1.89</td>
<td>C + CH</td>
<td>1.94</td>
<td>−0.05</td>
<td>46</td>
</tr>
<tr>
<td>Ru(0 0 1)</td>
<td>1.23</td>
<td>CH + CH</td>
<td>1.68</td>
<td>−0.45</td>
<td>33</td>
</tr>
<tr>
<td>Co(0001)</td>
<td>1.44</td>
<td>C + CH</td>
<td>1.34</td>
<td>0.10</td>
<td>33</td>
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</tbody>
</table>

Fig. 9. Distribution of CH₄ selectivity predicted on the Fe nanoparticle.